Quality Assurance Project Plan for the Hudson River PCBs Site

Baseline Monitoring Program

Book 2 of 2

Prepared for:
General Electric Company
Corporate Environmental Programs
Albany, NY

Prepared by:
Quantitative Environmental Analysis, LLC
Montvale, NJ

In Conjunction with:
Environmental Standards, Inc.
Valley Forge, PA

May 28, 2004

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APPENDICES

Appendix 22 SOP for the Tissue Reduction/Grinding for Whole Body and Filleted Fish (NE132_04).

Appendix 23 SOP for the Extraction and Cleanup of PCBs from Fish and Biota Material (NE17_07).

Appendix 24 SOP for the Extraction of Lipids from Fish and Biota Material (NE158_03).

Appendix 25 SOP for the Analysis of Aroclor PCBs by SW-846 8082 (NE148_04).

Appendix 26 SOP for the Analysis of PCB Congeners by NEA013_07.

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Appendix 28 SOP for Data Validation of Congener PCB Data Low-Level Calibration Method (DVNE207_03).

Appendix 29 SOP for Data Validation of ICP Metals Data (DV200.8).

Appendix 30 SOP for Data Validation of CVAA Mercury Data (DV245.1/7470A/7471A).

Appendix 31 *This Appendix is no longer necessary. It has been left for convenience for potential future use.*

Appendix 32 SOP for Data Validation of Wet Chemistry Data (DVWETCHEM).

Appendix 33 SOP for Data Validation of Congener PCB Data (DVNE013_07).

Appendix 34 SOP for Data Validation of Aroclor PCB Data (DV8082).

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Appendix 36 SOP for Data Validation of Organochlorine Pesticide Data (DV8081A).

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APPENDIX 1

STANDARD OPERATING PROCEDURE FOR THE COLLECTION OF WATER COLUMN SAMPLES

PROCEDURES

1.0. Scope & Application

This Standard Operating Procedure (SOP) is applicable to the collection of water column samples for the Hudson River Baseline Monitoring Program.

2.0. Summary of Method

This method involves the use of a multiple aliquot depth integrating sampler (Figure 1) to collect water column samples. Depending on the station (defined in Section 7 below) the water column samples will either be a depth-integrated composite collected from a centroid location (defined as the approximate center of the channel; consistent with historical sampling locations at Bakers Falls and Rogers Island), a depth-integrated and flow-proportioned composite from two centroid locations on either side of an island, or will be a composite sample formed from depth-integrated aliquots collected from multiple substations across the river in a manner that is similar to the Equal Discharge Increment (EDI) method developed by the USGS.

The locations of the EDI sampling substations will be selected by dividing the cross-sectional area of the river into either 5 or 6 (depending on the station) areas of equal flow. EDI locations initially will be based on historical bathymetry data (i.e., increments of equal cross-sectional area); EDI locations will be refined based on the results of a series of velocity profile surveys (Appendix 3) performed under varying flow rates to be conducted in 2004. Depth-integrated, equal volume aliquots will be collected from the center of each EDI. These equal volume aliquots will be combined to form a composite sample for each parameter or set of related parameters. Field parameters, including temperature, specific conductivity, pH, dissolved oxygen, and turbidity will also be collected at mid-depth at each center channel or transect substation using portable field instrumentation.

3.0. Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; BBL, 2003).

4.0. Interferences

Cross contamination
Variable river flow rates
Inclement weather conditions

5.0. Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

6.0. Equipment and Supplies

Equipment needed for water sample collection includes:

- Multiple aliquot depth-integrating sampler (Figure 1)
- Portable hand winch (Rogers Island)
- Boat and motor equipped w/anchors or spuds
- Safety equipment for boat as required to meet USCG regulations
- Portable electric winch w/two-directional line speed and distance control (all other locations)
- Global Positioning System (GPS; WAAS enabled)
- Sample containers
- Disposable gloves
- Laboratory supplied organic free water
- Lap top computer and printer
- Field parameter testing meter
- Field log
- Chain of custody forms
- Cooler with temperature blank and ice
- Labels for containers
- Reflective safety vests
- Resealable food storage bags
- Trash bags

7.0. Collection of Water Samples

Sampling Locations

Sample locations are defined in Section B1.1 of the main text of the QAPP. Samples will be collected from the centroid (center of the channel) at the following locations:

- Bakers Falls Bridge
- Rogers Island (Rt. 197 Bridge; east/west channel composite)
- Waterford (Rt. 4 Bridge; high flow only)
- Albany (near RM 145; boat access)
- Poughkeepsie (near RM 76; boat access)

Samples will be collected along transects using the EDI sampling method at the following locations:

- Thompson Island (boat access)
- Schuylerville (Rt. 29 Bridge, east/west channel composite)
- Stillwater (Bridge)
- Above Lock 1 (boat access)
- Waterford (Rt. 4 Bridge)
- Mohawk River at Cohoes (Rt. 32 Bridge)

Sampling Procedures (Bridge Access)

1. Locate the desired sampling station. The locations of sampling stations and substations on bridges will be predetermined based on historical center channel sampling locations or bathymetric and flow velocity surveys conducted in accordance with the SOP for measuring velocity profiles included as Appendix 3 of this QAPP. If these surveys indicate that significant changes in the proportion of discharge assigned to each sub-area under various river flows at EDI stations occurs, the locations of the sampling substations may be shifted based on river flow. Stations on the Bakers Falls and Rt. 197 Bridges will be consistent with historical sampling locations.
2. Upon arrival at each station (or substation at EDI stations), obtain measurements for temperature, dissolved oxygen (DO), pH, conductivity and turbidity using a YSI 6920 (or equivalent) probe as described in the SOP for probe measurements included as Appendix 2 of this QAPP.
3. Depending on location, either rig a hand winch or maneuver a portable electric winch into position above the sampling location.
4. Put on a new pair of disposable gloves.
5. Place a set of 12, pre-cleaned sample collection vessels in the depth integrating sampler. The sample collection vessels will consist of a 500 ml glass container equipped with a teflon lined cap. The cap will contain a ¼ in. ID teflon inlet nozzle for water and a 1/32 in. ID teflon/stainless steel outlet nozzle for air to escape as the vessel fills (Figure 2). A clean set of sample collection vessels will be used at each station; however, the same vessels will be used at all EDI sub-stations used to collect aliquots for the station composite. The glass collection vessels will be cleaned by the laboratory between sampling events. The caps and nozzles will be dedicated to each site. After each use the caps and nozzles will be rinsed with DI water in the field and placed in a re-sealable plastic bag labeled with the station name.

6. Tighten the caps on the sample collection vessels and use a squeeze bulb to pressurize the vessels to clear any residual water from the air escape nozzle. Proper filling of the vessels may not occur due to surface tension of residual water in the nozzle.
7. Determine the amount of sample that will be required from each station or sub-station to fill all sample containers, including any duplicate or split samples. The volume of sample will be adjusted so that an approximately equal volume of sample will be collected at each sub-station, and that little or no sample is collected that is not needed to fill sample containers (i.e., collection of excess sample will be avoided and, to the extent possible, all of the sample collected will be put into containers.
8. Prior to actual sample collection, the sampler must be calibrated to water depth and river flow conditions in a manner that will produce the desired sample volume following Steps 9 – 11 below.
9. Lower the sampler using either a manual winch (Rogers Island) equipped with a marked tagline or using an electric winch equipped with line speed and distance control through the water column until approximately 75% of the water depth is reached. Distance from the bridge to 75% water depth will be determined during prior surveying.
10. As soon as the 75% water depth is reached, retrieve the sampler using the same approximate line speed used to deploy the sampler.
11. When the sampler is retrieved, remove the sample collection vessels and inspect to confirm that the vessel is filled to the desired level. If the target sample volume is not collected, the winch line speed will either be increased (to reduce sample volume) or decreased (to increase sample volume). Discard the sample and adjust sampling procedures accordingly. Repeat as necessary to obtain an appropriate sample volume. Experience gained as the program progresses will reduce the amount of time required to calibrate the sampler.
12. Once the sampler is calibrated so that an acceptable sample volume is collected, the sample containers will be filled. A single sampler deployment should be sufficient to obtain the sample volume necessary for all parameters, including QA/QC samples. Each time the sampler is retrieved, the contents of one sample collection vessel will be poured into one of the sample containers, including duplicate or split samples. Depending on the analytical program being followed for a sampling event, the contents of one or more of the sample collection vessels may not be needed. When this occurs, the unused sample will be poured out prior to using the sampler at the next EDI. Samples collected at Rogers Island will be composited using a volume ratio that is consistent with the approximate flow ratio in the east and the west channel; the flow ratio will be determined for a range of flows through hydrologic surveys (see Appendix 3). Sample container specifications and volumes are presented in Section B3 and Table B-5 of the main text.
13. Label sample containers appropriately, in accordance with Section B3 of the main text.
14. Place one of the sample collection vessels used at each station in a re-sealable plastic bag, and label with date, time, and station. At Bakers Falls and Rogers Island, multiple sample collection vessels will be used to form the large volume (8

L) composite for PCB analysis required for these sites. At these locations, all sample collection vessels used to obtain aliquots for the 8L composite will be placed in a re-sealable plastic bag and labeled. This container(s) will be submitted to the laboratory for a hexane rinse, which will be combined with the composite sample submitted for PCB analysis.

15. The remaining sample collection vessels will be placed in a container and delivered to the laboratory for cleaning. Enough sample collection vessels will be available to allow sampling at all stations during a single sampling event. Two full sets of vessels will be maintained to allow the laboratory sufficient time to clean the vessels. Decontamination using organic solvents (acetone, hexane) will only be performed under controlled conditions in the laboratory due to waste management issues in the field and concerns related to residual solvent biasing organic carbon analyses.
16. Rinse the sample collection vessel caps and nozzles thoroughly with DI water in the field and place in a re-sealable plastic bag labeled with the station name.

Sampling Procedures (Boat Access)

1. Sampling stations (or substations at EDI stations) will be predetermined by bathymetric and flow velocity surveys conducted in accordance with the SOP for measuring velocity profiles included as Appendix 3 of this QAPP. If these surveys indicate that significant changes in the proportion of discharge assigned to each sub-area under various river flows at EDI stations occurs, the locations of the sampling substations may be shifted based on river flow. The locations of sub-stations that lie outside of the navigational channel will be marked with surface buoys. Buoys will be set using GPS (WAAS enabled).
2. Where buoys are available, navigate the sampling boat to the buoy and tie the vessel up to the buoy. The buoys will be set in a manner that will hold the boat within approximately 10 ft. of the substation. Where buoys cannot be deployed, navigate the sampling boat to the coordinates of the sampling station or sub-station using GPS (WAAS enabled) and anchor the boat (or use spuds, if so equipped) in a manner that will hold the boat within approximately 10 ft. of the target coordinates. Field conditions may be such that anchoring (or using spuds) is not practical (rocky bottom, high flow velocity, etc.). At these locations, the boat engine will be used to hold the boat in position as close as possible to the sampling location.
3. If anchors or spuds are used, allow a minimum of 5 minutes to elapse before starting sampling to allow any suspended sediment to settle or pass downstream.
4. Collect field data as specified in Step 2 (Bridge Access) above.
5. Set up a portable winch with line speed control on the sampling boat.
6. Calibrate the sampler and collect samples in the same manner specified in Steps 4 through 16 above.

8.0. Sample Handling and Preservation

Sample containers will be labeled prior to sample collection in accordance with labeling requirements specified in Section B3 and Figure B-5. Once water samples have been collected at a sampling location, transfer the aliquot of water to the appropriate sample containers (specified in Section B3 and Table B-5 of this QAPP). Place each container in a re-sealable plastic bag, and place in a cooler with ice to chill the samples to approximately 4° C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be hand delivered to the laboratory at the end of each day (unless requested otherwise by the laboratory). Chain of custody procedures will be followed, as specified in Section B3 of this QAPP.

9.0. Data and Records Management

All data from water sample collection will be recorded in the field database (Microsoft Access®) provided by QEA using a laptop computer. Upon completion of sampling at one location, all data from the location will be entered into the database and the field log for that location printed and the hard copy stored in the field notebook. This will limit the risk of losing sample information due to computer failure. Blank field log sheets can also be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

10.0. Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in Section B5 of this QAPP, and include the collection of field QA/QC samples. Field QA/QC samples to be collected are blind duplicate samples, equipment blank samples, and matrix spike samples. One set of field QA/QC samples will be collected for each sampling event. Blind duplicate samples and matrix spike samples will be prepared by filling additional appropriately marked containers at pre-selected sampling stations (both samples will not be collected at the same station). The station where these samples are collected will be rotated randomly for each sampling event. Equipment blank samples will be prepared as follows:

1. Put on new disposable gloves.
2. Place a set of clean sample collection vessel in the depth integrating sampler.
3. Slowly pour laboratory supplied organic free water into the nozzles and fill enough of the sample collection vessels to provide sufficient sample volume to fill the sample containers.
4. When nearly full, remove the sample collection vessels and distribute to appropriately labeled sample containers.
5. After collection, handle equipment blank samples in a manner that is consistent with all other environmental samples.
6. After preparation of equipment blank samples, the sample collection vessels may be reused to collect river water samples without cleaning.

11.0. References

Appendix 2 - SOP for Probe Measurements of Surface Water Quality Measurements

Appendix 3 - SOP for Determining Equal Discharge Increments (Hydrologic Surveys)

BBL. 2003. Revised Health and Safety Plan.

USGS. 1999. Techniques of Water-Resources Investigations of the United States Geological Survey. Book 9. Chapter 4.1.1.A. Isokinetic, Depth-Integrated Sampling Methods. September, 1999.

12.0 Figures

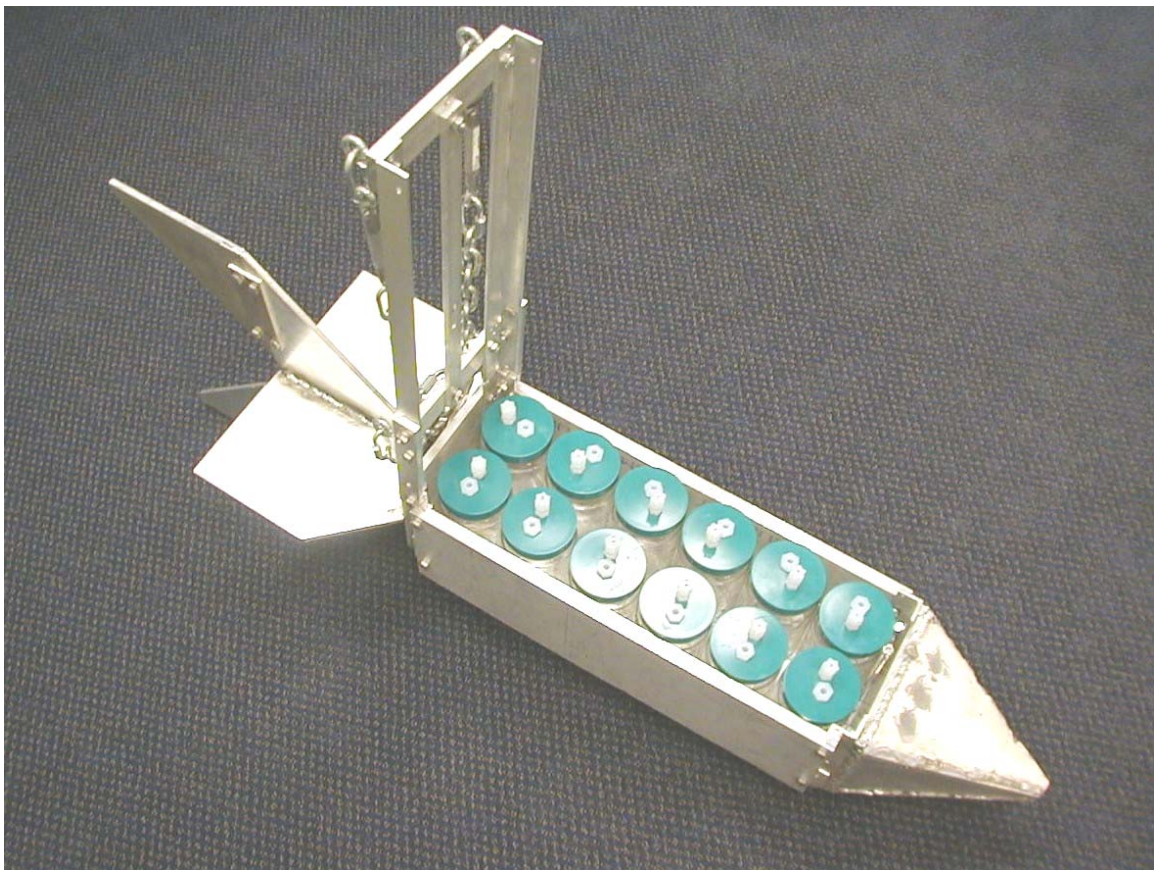

Figure 1. Multiple aliquot depth-integrating sampler (QEA, LLC)

Figure 2. Sample collection vessels with caps and teflon nozzles.

APPENDIX 2

STANDARD OPERATING PROCEDURE FOR PROBE MEASUREMENTS OF WATER QUALITY PARAMETERS

PROCEDURES

1.0. Scope & Application

This Standard Operating Procedure (SOP) is applicable to the measurement of water quality (WQ) parameters including temperature, conductivity, pH, dissolved oxygen, and turbidity using a multi-parameter probe.

2.0. Summary of Method

At each sampling location, WQ measurements are taken at mid-depth in the water column. These measurements will be made for temperature, specific-conductivity, pH, DO, and turbidity using a probe. A YSI 6920 (or equivalent) multi-parameter probe will be calibrated at the beginning of each sampling day following the manufacturer's calibration procedure.

3.0. Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; BBL, 2003).

4.0. Interferences

Improper calibration.

5.0. Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

6.0. Equipment and Supplies

Equipment needed for the measurement of WQ parameter include:

- Disposable gloves.

- YSI 6920 (or equivalent) multi-parameter probe with100 ft of cable.
- Data logger.
- Data transfer cable.
- Calibration fluids.
- Deionized water.
- Field log.
- Health and Safety equipment (consistent with Water Sample Collection SOP – Appendix 1)

7.0. WQ Parameter Measurement

Measurement Locations

Water sample locations are defined in Section B1.1 of the main text of the QAPP. WQ parameter measurements will be taken at the same locations as surface water samples. Samples will be collected from the center of the channel at the following locations:

- Bakers Falls Bridge
- Rogers Island (Rt. 197 Bridge; east/west channel composite)
- Waterford (Rt. 4 Bridge; spring high flow only)
- Albany (near RM 145; boat access)
- Poughkeepsie (near RM 76; boat access)

Samples will be collected along transects using the EDI sampling method at the following locations:

- Thompson Island (boat access)
- Schuylerville (Rt. 29 Bridge, east/west channel composite)
- Stillwater (Bridge)
- Above Lock 1 (boat access)
- Waterford (Rt. 4 Bridge)
- Mohawk River at Cohoes (Rt. 32 Bridge)

Measurement Procedures

1. At the beginning of each sampling day, calibrate the multi-parameter probe using a multi-parameter calibration fluid per the instrument manufacturer's instructions. Rinse the probe with deionized water and store per the manufacturer's recommendations.

2. Verify that the time and date on the data logger is accurate and that sufficient memory and battery power exist for the day's sampling events.

3. Occupy each sampling location per the SOP for the Collection of Water Samples; Appendix 1.

4. At bridge locations, probe measurements should not be taken within 5 minutes of a vessel traversing near the sampling location. At EDI locations accessed by boat, probe measurements should not be taken with 5 minutes of setting spuds or other anchoring device.

5. At each sampling location, lower the probe to mid-depth in the water column. Wait at least 30 seconds for the readings to stabilize and then log the readings with the data logger.

6. Upon completion of sampling at each station, download the WQ parameter measurements for each sampling station in the field log form on a laptop computer. The field log form will be printed for each sampling station (see Appendix 1, Section 9).

7. Repeat steps 3 to 6 at each sampling location.

8.0. Sample Handling and Preservation

Probe measurements of WQ parameters are made directly in the river, no sample is taken.

9.0. Data and Records Management

All data from probe measurements will be recorded by the instrument data logger. At the end of each sampling day, the probe measurement data will be downloaded to the laptop computer, transformed (if necessary), and added to field database (Microsoft Access ®) using a laptop computer. Hard copies of the measurements will maintained by printing out the field log which will include the results of WQ parameter measurements associated with each sampling location. This will limit the risk of losing sample information due to computer or data logger failure. Blank field log sheets can also be used to record information manually in case of difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

10.0. Quality Control and Quality Assurance

The primary QA/QC procedure for WQ parameter measurement with a multi-parameter probe is proper calibration of the instrument at the start of each sampling day. The instrument will be calibrated following the manufacturer's instructions using a multi-parameter calibration fluid.

Once per day at a random EDI location, consecutive measurements will be taken to verify probe stability. These measurements will be taken by leaving the probe at mid-depth at the EDI location and logging two readings at least one minute apart. If the consecutive

readings appear to be off by 20% or more, the probe will be recalibrated and the consecutive readings will be repeated.

At the end of each day, the probe(s) will be immersed in the calibration fluid to assess instrument drift or loss of calibration.

11.0. References

Appendix 1 - SOP for Water Column Sampling
BBL. 2003. Revised Health and Safety Plan.

APPENDIX 3

STANDARD OPERATING PROCEDURE FOR DETERMINING EQUAL DISCHARGE INCREMENTS (HYDROLOGIC SURVEYS)

PROCEDURES

1.0. Scope & Application

This Standard Operating Procedure (SOP) is applicable to the collection of representative data (stream dimensions and water velocity) for the determination of Equal Discharge Increments (EDI) to support selection of sampling substations along transects across the Hudson River for the Baseline Monitoring Program.

2.0. Summary of Method

This method involves: 1) the collection of water velocity and stream depth, data across transects at select water monitoring locations in the Hudson River; 2) the calculation of cross-sectional area and flow discharge in order to divide each transect into equal discharge increments; and 3) the evaluation of EDI centroid location dependency on river stage and flow.

Water velocity and stream depth data will be acquired via standard current meter survey procedures (Section 7.0 below). If schedule and logistics permit, Acoustic Doppler Current Profile (ADCP) surveys may be substituted for standard current meter surveys. These surveys may be performed in conjunction with the velocity profile data collected under the Supplemental Engineering Data Collection (SEDC) Work Plan (see BBL, 2003a). Velocity profile surveys will be repeated under varying flow conditions over a period of several months until it can be determined that the EDIs can be accurately defined. Once sufficient data have been collected, these surveys will result in the production of approximate flow rating tables for each station for use in EDI sampling (see Appendix 1 – SOP for the Collection of Water Column Samples). If significant changes in the EDIs occur as a result of changes in flow, the EDIs and associated sampling substations will be adjusted accordingly prior to each sampling event based on the flow conditions at that time. If it is determined as the program progresses that significant variability does not occur in the EDIs at a sampling station (i.e., if sampling sub-stations need to be moved 10 ft. or less in either direction due to changes in EDI as a result of changes in flow), the substation locations will be standardized, and will not be adjusted between sampling events.

3.0. Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; BBL, 2003b).

4.0. Interferences

Variable river flow rates
Inclement weather conditions
Boat traffic

5.0. Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for conducting bathymetric and water flow velocity surveys.

6.0. Equipment and Supplies

Equipment needed for conducting hydrologic surveys includes:

- Staff gage.
- Marsh-McBirney Flowmate Model 2000 flow velocity meter or equivalent.
- Calibrated rods.
- Boat and motor equipped w/ spuds.
- Safety equipment for boat as required to meet USCG regulations.
- Global Positioning System (GPS; WAAS enabled).
- Surveying rod.
- Laptop computer.
- Field log.
- Waders
- Personal floatation devices

7.0. Methods

Survey Locations

Surveys will be conducted at the following sampling stations, that are designated to be sampled using USGS' EDI techniques and as identified in Section B1.1 of the main text:

- Thompson Island (boat access)
- Schuylerville (Rt. 29 Bridge)
- Stillwater (Bridge)
- Above Lock 1 (boat access)

- Waterford (Rt. 4 Bridge)
- Mohawk River at Cohoes (Rt. 32 Bridge)

Current Meter Survey Procedures

The following procedures are adapted, in part, from standard USGS procedures for discharge measurements (USGS, 1976).

1. Current meter surveys will be conducted during favorable weather conditions. Data collection under windy or stormy conditions will be avoided.
2. Establish horizontal control. Unless field conditions permit data collection from a bridge, set up a RTK GPS base station on a nearby control point established for the SSAP. If data can be collected from a bridge, conventional surveying techniques will be used to establish horizontal control.
3. Establish vertical control by reading and recording water level on a staff gage (to be installed) or by measuring the distance from a fixed point on a bridge down to the water's surface. Record data on a laptop computer and manually in a field log book.
4. Position the survey vessel appropriately to allow collection of data within 3 ft. of the target data collection point. Coordinates for data collection points will be predetermined using GIS. At stations where sampling will be conducted from bridges, the coordinates for data collection points will be placed far enough upstream or downstream (depending on which side of the bridge the sampling will be conducted) so that the bridge will not interfere with the GPS signal. If data are collected from a bridge, the locations of the data collection points will be marked on the bridge. Each survey will begin at the east shore, and progress westward, with the exception of the Mohawk River station, where the surveys will progress from north to south. The beginning and end point of each transect (at each shoreline) will be determined using GPS.
5. Secure the vessel in position using spuds. Where water depths are too shallow to allow boat access, the data collection point will be reached by wading.
6. Once in position, obtain a water depth (nearest 0.1 ft.) using a conventional survey rod. Record data on a laptop computer and manually in a field log book.
7. Calibrate the water velocity meter (Marsh-McBirney Flowmate Model 2000 or equivalent) in accordance with the manufacturer's specifications.
8. Adjust calibrated rods for velocity meter appropriately for water depth (i.e., so that they are long enough to reach the river bed).
9. Secure flow meter probe at 20% of the water depth (measured from water surface).
10. With probe facing upstream, place calibrated rod in river and allow bottom of rod to rest on river bed. Turn on meter and watch velocity output. Adjust range as appropriate. Rotate rod and probe slightly clockwise until velocity readings begin to decrease, then rotate counterclockwise. Velocity should increase as the probe becomes directly parallel with the flow, then a decrease should be noted as the probe is rotated further. Rotate the probe back to the point where maximum

velocity was noted, hold the probe as steady as possible, and begin data collection. Velocity will be an average value calculated by the meter after holding the probe steady for approximately 1 minute. Record data on a laptop computer and manually in a field log book.

11. Remove calibrated rod and probe, and move probe down to a point on the rod that represents 80% of the water depth. Repeat Step 10 above.
12. Repeat the data collection procedure at the remaining data collection points.
13. Upon completion of the data collection, obtain a reading from the staff gage and record.

Equal Discharge Increment Calculations

Initial EDI locations will be calculated based on simple cross-sectional area calculations using the nearest upstream bathymetry data. This approach will allow the water sampling program to commence in the spring of 2004; seasonal lock closures, as well as adverse flow and weather conditions will likely prevent the first current meter or ADCP velocity profile study to be conducted prior to mid-May 2004.

Subsequent to velocity data collection, the USGS-preferred midpoint method will be used to calculate discharges using the partial cross-sectional areas of adjacent segments and the average velocity at each current meter measurement station. Individual discharge calculations will then be used to develop a cumulative discharge relationship (i.e., total discharge versus the distance from a reference point on shore) for each transect for a particular flow rate / stage height. Centroid locations for each EDI are then determined based on the number of increments required and the percentage of cumulative discharge (e.g., if 20 % discharge intervals are required, the corresponding EDI centroid locations will be at the transect distances corresponding to 10, 30, 50, 70, and 90 % of the cumulative flow).

With reference to Figure 1, midpoint method discharges are calculated as follows:

1. Calculate the horizontal distance (D in ft) along each transect for each velocity measurement station (1, 2, 3 ...) from the GPS coordinates using the initial “to shore” measurement as a reference point (0).
2. Divide the cross-sectional area of the river into sub-areas that correspond to each velocity measuring station (Figure 1).
3. Calculate the average velocity (V) at each measurement station (n). The average velocity (V_n) is the average of the velocities at the 0.2 and 0.8 depths (d).
4. Calculate the cross-sectional area of each sub-area using bathymetry and river stage at the time of the survey with a computer-aided drafting (CAD) system.
5. Determine flow (Q) by multiplying average velocity (V) determined at the mid-point of each sub-area by the cross-sectional area (A) of that sub-area.

For velocity data obtained through ADCP studies, cumulative discharge versus transect length relationships will be obtained from the ADCP contractor along with the reference location and flow rate/stage height; this data is commonly generated during post-processing. EDI centroid locations will be determined as described previously. The SOP for ADCP studies is presented in the SEDC work plan (BBL, 2003a).

Cumulative discharge and EDI centroid locations will be determined for a range of flow rates/stage heights. An assessment will then be made as to the variability of each location with flow. If a location is found to vary by more than 10' across the expected range of flows, the station location will be adjusted prior to water column sampling based the station flow using a linear interpolation of the established percent discharge versus distance curves.

8.0. Data and Records Management

All data from the bathymetric and flow velocity surveys will be recorded in a database provided by QEA using a laptop computer. Each water level (staff gage reading), water depth, and flow velocity measurement will be entered into the database and recorded manually in a field log. This will limit the risk of losing sample information due to computer failure.

9.0. Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in Section B6 and B7 of this QAPP, and include requirements for instrument testing, inspection, maintenance, and calibration.

10.0. References

BBL, 2003a. Supplemental Engineering Data Collection Work Plan.

BBL, 2003b. Revised Health and Safety Plan.

USGS, 1976. Techniques in Water Resources Investigations, Book 3, Chapter 8: Discharge Measurements at Gaging Stations.

11.0. Figures

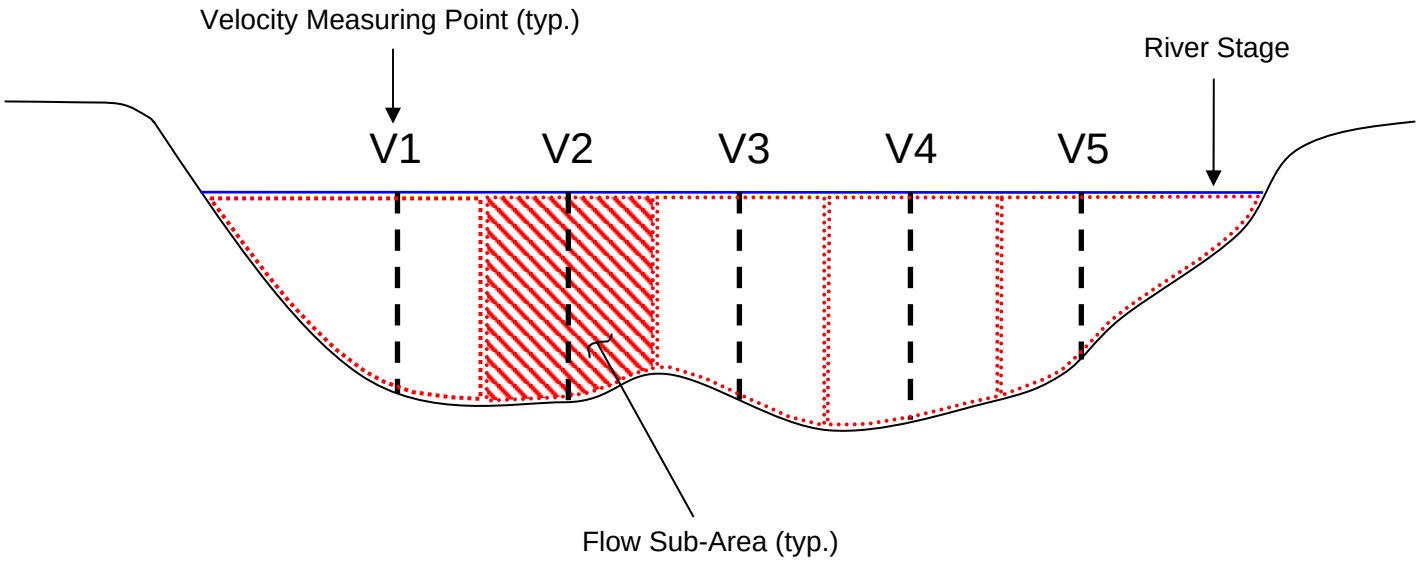

Figure 1. Variable definitions for discharge calculations at each current meter velocity profile station. Note that actual number of velocity measuring points will vary with actual width of river.

APPENDIX 4

STANDARD OPERATING PROCEDURE FOR FIELD-FILTRATION OF SURFACE WATER SAMPLES (DISSOLVED/PARTICULATE PHASE SAMPLING)

PROCEDURES

1.0. Scope & Application

This Standard Operating Procedure (SOP) is applicable to the field-filtration of aqueous samples.

2.0. Summary of Method

This method will be used to perform field filtrations as a preparatory step in the measurement of dissolved and particulate PCBs in Hudson River water. Water will be collected at 5 equal discharge interval (EDI) locations in accordance with the procedures defined in Appendix 1. At each station, samples will be collected at these 5 EDI points across the river and combined to form a composite sample to account for cross-section heterogeneity in the PCB levels. A total of 8 liters (L) will be collected for each transect (i.e., 1.6 L at each of the five EDI locations). To separate the water samples into solid and aqueous phases, field filtration of approximately 8 L of water will be performed using a 142 mm stainless steel pressure filter holder. The sample will be filtered in the field as soon as possible after collection but no more than four hours after collection. Nitrogen gas will be used as a medium to pressurize the filtration apparatus. Filters will be 0.7 micron glass fiber filters, pre-cleaned by heating at ~450° C. Following filtration, the filter and the filtrate will be submitted for congener specific PCB analysis. Analysis of the solids on the filter will determine particulate phase PCBs; analysis of the filtrate will measure dissolved phase PCBs.

3.0. Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; BBL, 2003).

4.0. Interferences

Cross contamination
Improper sample collection
Filter rupturing

5.0. Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring

program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

6.0. Equipment and Supplies

Equipment needed for field-filtration of surface water samples includes:

- Stainless steel pressure filtration apparatus.
- Tubing.
- 4 L amber glass pre-cleaned containers.
- 142 mm, 0.7 µm glass fiber filters (cleaned) in Petri dish.
- Forceps.
- Decontamination supplies.
- Nitrogen tank and pressure regulator.
- Lap top computer.
- Field note book.
- Printer.
- Sample labels.
- Cooler.
- Ice.
- Temperature blank.

7.0. Collection and Field Filtration of Water Samples

1. Collect water samples in accordance with the water sample collection SOP presented in Appendix 1. The multiple aliquot depth integrating sampler will be equipped with twelve 0.5 L sample collection vessels. The sampler will be deployed at each EDI location as required to obtain approximately 1.6 L of sample (approximately 8 L total). After each sampler deployment, sample will be transferred from the 0.5 L sample collection vessels to 4 L amber glass sample containers.
2. Set up a decontaminated stainless steel pressure filtration apparatus either on site or in a near-by field laboratory facility. The filtration unit will be capable of accepting 142 mm diameter filters.
3. Prior to installing a filter, add approximately 0.5 L of river water to the reservoir of the filtration unit. Rinse the filtration unit by gently swirling the water, and discard the rinsate.
4. Carefully place a clean, pre-weighed filter onto the filtration unit using forceps in a manner that will not deform or perforate the filter. The filters (142 mm Wattman GF/F 0.7 micron glass fiber filter or equivalent) will be obtained from the analytical laboratory prior to each sampling event. The laboratory will prepare the filters by heating in the laboratory at 450 ^{o}C for 24 hours. Once the filters are cool, they will be weighed and placed in a new Petri dish. The tare weight of each filter will be written on the Petri dish.
5. Fill the reservoir of the filtration unit with sample.

6. Using nitrogen gas, increase the pressure gradually to a maximum of 15 psi to push the sample through the filter. Collect the filtrate in a clean 4 L amber glass container (two required).
7. Continue to add additional sample to the filtration unit until the entire 8 L sample has been sampled or it appears that it will be necessary to change the filter due to reduced filtration rate. If required, allow all sample in the reservoir to pass through the filter, then release the pressure, disassemble the filtration unit, and put in a new filter.
8. Continue the filtration until the entire sample has been filtered. Rinse the sample bottle(s) with filtrate to recover any additional suspended matter remaining in the bottle and add rinsate to the filtration unit. Cap the empty sample bottles and deliver them to the laboratory along with the filtrate and filter samples. The laboratory will hexane-rinse the sample bottles and add the solvent rinse to the sample solvent extract for the filtrate sample.
9. Disassemble the filtration unit. Remove the filter with forceps and place back in the Petri dish that was supplied with the filter. Label the Petri dish with pertinent information, as described in Section B3 of this QAPP.

8.0. Sample Handling and Preservation

Sample containers will be labeled prior to sample collection in accordance with labeling requirements specified in Section B3 and Figure B6. The filtrate will be collected directly in 4 L amber glass containers, which will be submitted directly to the laboratory. Filters will be contained in Petri dishes supplied with the filters from the laboratory. After labeling, place each container in a re-sealable food storage bag, and place in a cooler with ice to chill the samples to approximately 4° C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be hand delivered to the laboratory at the end of each day (unless requested otherwise by the laboratory). Chain of custody procedures will be followed, as specified in Section B3 of this QAPP.

9.0. Data and Records Management

All data from water sample collection will be recorded in the field database (Microsoft Access) provided by QEA using a laptop computer. Upon completion of sampling at one location, all data from the location will be entered into the database and the field log for that location printed and the hard copy stored in the field notebook. This will limit the risk of losing sample information due to computer failure. Blank field log sheets can also be used to record information manually in case of difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

10.0. Quality Control and Quality Assurance

Field QA/QC samples (blind duplicate and matrix spike samples) will be collected as part of the routine monitoring program at the same time that the samples for field filtration are

collected. Therefore, these samples will provide adequate QA/QC for the program; no additional field QA/QC samples will be collected during dissolved/particulate phase sampling events.

11.0. References

BBL. 2003. Revised Health and Safety Plan.
SOP for Water Column Sampling (Appendix 1)

APPENDIX 5

STANDARD OPERATING PROCEDURE FOR TIME OF TRAVEL STUDY IN UPPER HUDSON RIVER

PROCEDURES

1.0. Scope & Application

This Standard Operating Procedure (SOP) describes the procedure that will be followed to attempt to collect a single parcel of water as it traverses the Upper Hudson River.

2.0. Summary of Method

This sampling program involves timing the collection of samples at the routine BMP sampling stations in a manner that will characterize a parcel of water as it flows past each station. This study is termed a "pseudo-time of travel (TOT)" study because true TOT sampling is impractical due to continual changes in river flow and the need to avoid health and safety risks that would be associated with attempts to sample at night. Sampling will be restricted to Monday through Friday during daylight hours to alleviate worker scheduling and safety logistics. The sampling schedule will be developed to come as close as possible to sampling a single water parcel without violating the sampling time constraints. Samples will be collected in accordance with the procedures specified in the SOP for the Collection of Water Samples (Appendix 1).

3.0. Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; BBL, 2003).

4.0. Interferences

Cross contamination
Variable river flow rates
Inclement weather conditions

5.0. Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

6.0. Equipment and Supplies

Equipment needed for pseudo-TOT water sample collection is included in the SOP for the Collection of Water Samples (Appendix 1). Access to the Internet is required on a daily basis to obtain real-time and average daily flow conditions at the USGS gage station at Fort Edward:

http://waterdata.usgs.gov/ny/nwis/uv?01327750

7.0. Timing the Collection of Water Samples

The collection of water samples during pseudo-TOT sampling events will be timed such that each station is sampled at approximately the time that the centroid of the parcel of water is expected to be at a station. The time of travel for the parcel will be based on the average daily flow at Fort Edward. The pseudo-TOT event will be restricted to daylight hours between Monday through Friday, thus, "approximately the correct time" may equate to +/- several hours depending on the average daily flow. Reasonable effort will be made to try to collect the sample as close to the predicted time as possible.. The following table presents the results of a 1-D model flow run (QEA 1999) that predicts the approximate number of hours from Rogers Island to the next monitoring location versus average daily flow as measured at the USGS gage station at Fort Edward.

	Travel Time from Rogers Island to Downstream Station (hr)			
Flow (cfs)	TI	Schuylerville	Stillwater	Waterford
1500	27	80	148	186
2000	21	62	115	144
3500	13	38	71	89
5500	9	26	49	62
6000	9	24	46	58
7500	7	20	39	49
9500	6	17	33	41
11500	5	15	29	36
13500	5	13	26	32

Samples will be collected at Bakers Falls and Rogers Island on the first day of sampling and the observed stage height at Fort Edward will be recorded. Decisions for the timing of sampling at the next downstream station will be based on the real-time flow at Fort Edward when the Fort Edward station is sampled, a review of the hydrograph for the previous 48 hrs, and real-time tracking of flow at Fort Edward after sample collection to estimate the appropriate time for sampling at Thompson Island. Real time tracking will be used to continually update the estimated mean flow after sampling at Fort Edward. The actual time of sampling at downstream stations will be adjusted so that the field activities can be completed during daylight. Subsequent stations will be sampled based on a similar estimation of the mean daily flow and the differential time of travel between stations.

8.0. Sample Handling and Preservation

Sample handling and preservation procedures will be consistent with those presented in the SOP for the Collection of Water Samples (Appendix 1).

9.0. Data and Records Management

Sample handling and preservation procedures will be consistent with those presented in the SOP for the Collection of Water Samples (Appendix 1).

10.0. Quality Assurance and Quality Control (QA/QC)

QA/QC procedures will be consistent with those presented in the SOP for the Collection of Water Samples (Appendix 1). While pseudo-TOT samples are collected over multiple days, each pseudo-TOT sampling week will be considered a single sampling event in terms of the number of QA/QC samples collected.

11.0. References

Appendix 1 - SOP for the Collection of Water Column Samples

BBL. 2003. Revised Health and Safety Plan.

Quantitative Environmental Analysis, LLC, 1999. *PCBs in the Upper Hudson River. Volume 2. A Model of PCB Fate, Transport, and Bioaccumulation.* Prepared for General Electric Company. May 1999.

APPENDIX 6

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE178_02.DOC

REVISION NUMBER: 02

STANDARD OPERATING PROCEDURE FOR THE EXTRACTION AND CLEANUP OF AQUEOUS SAMPLES FOR POLYCHLORINATED BIPHENYLS (PCBs) USING US-EPA SW-846 METHOD 3535, SOLID PHASE EXTRACTION

March 9, 2004

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STANDARD OPERATING PROCEDURE

Author: Robert E. Wagner

Reviewed by:

Mike Bergmann, Laboratory Manager

Approved by:

William A. Kotas-Quality Assurance Officer

Northeast Analytical, Inc.
Issuing Section: Organics
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Revision: 02

STANDARD OPERATING PROCEDURE FOR THE EXTRACTION AND CLEANUP OF AQUEOUS SAMPLES FOR POLYCHLORINATED BIPHENYLS (PCBs) USING US-EPA SW-846 METHOD 3535, SOLID PHASE EXTRACTION

1.0 Scope:

1.1 The purpose of this standard operating procedure (SOP) is to provide procedures required for both the extraction and subsequent extract cleanup of PCBs in aqueous samples using the solid phase extraction method USEPA SW-846 Method 3535.

1.2 This method was developed to utilize an automated extraction system, and provides details for the extraction of 1-liter water samples. The SPE-DEX 4790 extractor (or equivalent) from Horizon Technologies will be used for automated sample extraction.

1.3 A disk extraction filter will be used for sample extraction. The disk chosen is a 50mm Bakerbond Speedisk™ styrene divinyl benzene filter (Baker or equivalent).

2.0 Summary of Method:

2.1 This SOP provides detailed procedures for the automated extraction of 1-liter water samples and also provides instruction for sample clean-up procedures for sample extracts prior to gas chromatographic analysis for PCBs.

2.2 The sample extraction is initiated by adding sulfuric acid to the 1-liter water sample as a matrix modifier. The appropriate surrogate is added to all samples and quality control samples. A method blank and laboratory control spike is performed with the extraction batch from laboratory organic free water. The laboratory control spike is fortified with the PCB spiking solution. Other quality control samples, such as matrix spike, matrix spike duplicate, blind duplicate, are initiated along with the samples and receive surrogates and, if required, fortified with PCB spiking solution. The SPE-DEX 4790

extraction unit is programmed from the control station and the extraction method is initialized. The sample bottle is placed onto the SPE-DEX 4790 extractor and sample extraction is initiated by placing the extractor into start mode. The SPE-DEX 4790 passes the 1-liter water sample through the solid-phase disk with the aid of vacuum. Once the 1-liter sample completely passes through the solid-phase disk, the SPE-DEX 4790 automatically dries the solid-phase disk, rinses the sample container with solvent that is directed to the disk and extraction of analyte is initiated. Several additional solvent rinses are performed which are collected into the extract receiver glassware. The extract is transferred and further processed through specified clean-up procedures. The extract is set to a final volume of 5mL and is ready for analysis.

2.3 This method is applicable to trace analysis of PCB. All glassware, solid-phase extractor components, solvents, and reagents used during clean-up procedures must be kept scrupulously clean.

3.0 Definitions:

3.1 Surrogate Analyte: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are added to all laboratory method blanks, laboratory QC reference samples (Laboratory Control Spikes), laboratory duplicates, calibration and continuing check standards, field samples, field duplicate samples, field matrix spike samples, field matrix spike duplicate samples prior to extraction and/or analysis. Percent recovery is calculated for each surrogate to assess extraction efficiency.

3.2 Laboratory Method Blank: A laboratory derived sample consisting of reagent water or other blank matrix that consists of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The laboratory method blank is used to define the level of laboratory analyte background or other interferences that exist in the laboratory environment, the reagents, or the apparatus.

3.3 Laboratory Control Sample (LCS): Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

3.4 Sample Matrix Spike/Sample Matrix Spike Duplicate (MS/MSD): An aliquot of a field sample that is fortified with known quantities of the method analytes and subjected to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring recovery.

4.0 Interferences:

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment (such as the SPE-DEX 4790 extractor) that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials and equipment must be routinely verified to be free from interferences by running laboratory method blanks.

4.1.1 All glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by first rinsing with acetone, followed by detergent washing with hot water. Glassware should then be thoroughly rinsed with tap water, followed by a distilled water rinse. Place the washed glassware in a drying oven at 100°C for at least 30 minutes. After the glassware is dried and allowed to cool store in a clean environment to prevent any exposure to dust or other contaminates. Prior to use, rinse all glassware and other components with high purity hexane.

4.1.2 The use of high purity solvent and reagents will minimize interference problems. Purification of reagents by washing with solvent will also help to reduce interference problems.

4.2 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

4.3 The sample matrix itself is also a potential source for method analyte interference. The clean-up procedures provided in this SOP can be used to overcome many of these interferences.

5.0 Safety:

5.1 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets (MSDS) to familiarize themselves with the hazards of handling the compounds used for standards and samples.

5.2 Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, all solvents and standards should be manipulated in a chemical fume hood. All sample extracts should be manipulated in a chemical fume hood.

6.0 Equipment and Supplies:

6.1 Sample Containers – 1-liter clear glass bottle fitted with polypropylene screw cap. Bottles used for sample collection are purchased pre-cleaned (Eagle-Picher, level 1 cleaned, part number 112-01C or equivalent). Protect collected sample from light.

6.2 Automated Solid-Phase Extractor - SPE-DEX 4790 extractor system including the SPE-DEX 4700 Series Controller unit, Horizon Technology. All necessary accessories required for operation including glassware, gas regulators and compressed nitrogen source, Teflon tubing for solvent delivery, solvent delivery bottles, solvent waste recovery bottle, water recovery carboy, solvent exhaust hose, low-pressure flexible gas tubing, bottle adapters, and vacuum system.

6.3 Bakerbond Speedisk DVB – Styrene divinylbenzene 50mm disk for sample extraction. Part number 8059-06 or equivalent.

6.4 2-liter graduated cylinder – Used for measuring volume of water sample. Scienceware or equivalent.

6.5 Disposable Pasture 9" pipettes – Krackeler 67-450-900-CS or equivalent.

6.6 TurboVap Evaporator – Zymark ZW640-3.

6.7 TurboVap Evaporator concentrator tubes – Zymark 250mL.

6.8 Turbovap LV Evaporator – Zymark ZW700.

6.9 Disposable 1mL pipettes – Kimble part number 72120-1110 or equivalent.

6.10 pH Indicator Strips – EM Science part number 9590 or equivalent.

6.11 Disposal Vials, 15mL and 30mL – Disposal glass vials with polyseal caps, Industrial Glassware or equivalent.

6.12 Vial Rack – plastic rack used to hold vials during processing of extracts. Scienceware.

6.13 Beakers – Pyrex, assorted sizes – 100mL, 250mL, and 600mL.

6.14 Centrifuge – Model CL or equivalent. International Equipment Company.

6.15 Wrist-action shaker – Burrel model 75 and 88 or equivalent.

6.16 GC autosampler vials – Scientific Resource Inc. part number 99468-A or equivalent.

6.17 Analytical Balance – Capable of weighing 0.0001g. Mettler AG204 or equivalent.

6.18 VOA Vials – 40mL and 60mL, Environmental Sampling Supply.

7.0 Reagents and Standards:

7.1 Reagent Water – 18-megaohm water obtained from the laboratory's water purification system. Used for solid-phase disk preparation, laboratory method blanks, laboratory control spikes, MDL studies, and P&A studies.

7.2 Sulfuric Acid, concentrated – Mallinckrodt part number 2468. Sulfuric acid is cleaned by washing with hexane prior to use. See SOP NE174 for details on procedure.

7.3 1:1 Sulfuric acid – Prepared from solvent washed concentrated sulfuric acid. Preparation – To a beaker containing 500mL cold reagent water slowly add 500mL concentrated sulfuric acid. Transfer to a pre-cleaned 1-liter bottle for storage.

7.4 Hexane – Pesticide residue quality. Burdick&Jackson part number 216-4 or equivalent.

7.5 Acetone - Pesticide residue quality. Burdick&Jackson part number 010-4 or equivalent.

7.6 Methanol – Pesticide residue quality. EM Science OmniSolv part number MX0488P-1 or equivalent.

7.7 Florisil – J.T. Baker part number M368-08. Florisil is solvent washed and dried before use. See SOP NE094 for details on cleaning procedures. After the Florisil is purified, it is deactivated with reagent water to a specified % water content to adjust the activity level of the Florisil currently in use. The amount of water added to the Florisil is determined for each lot and tested by exposing PCB standards (Aroclors 1232, 1248, and 1262) to the Florisil and determining that no pattern change has occurred. The deactivated Florisil is stored in amber glass containers and stored in a desiccator.

7.8 Mercury – Triple distilled, Mercury Waste Solutions Inc. Mercury is solvent washed prior to use. See SOP NE175 for details on cleaning procedures.

7.9 Standard Solutions – The following standards are used during extraction and preparation of sample extracts:

7.9.1 Surrogate Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 100ug/mL in Hexane: The surrogate stock standard is prepared from a solid standard obtained from AccuStandard, Inc. (part number C-207N). Weigh 5.0mg of the solid surrogate standard into a solvent rinsed 10mL vial. Quantitatively transfer the surrogate standard using six successive 2-mL washings of hexane to a 50mL volumetric flask. Be sure to rinse the 10mL vial walls carefully so that the entire surrogate standard is completely transferred to the 50mL volumetric flask. Make to volume with hexane and mix the surrogate standard solution by shaking the flask several times. This will give a concentration of surrogate standard of 100ug/mL. Carefully transfer the surrogate standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. The surrogate standard must be replaced after one year.

7.9.2 Surrogate Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 0.200ug/mL in Acetone: The Surrogate Standard is prepared from the 100ug/mL Surrogate Stock Standard. Into a 100mL volumetric flask, using a 500-microliter syringe, transfer 200uL of the Surrogate Stock Standard at 100ug/mL. Make to volume with acetone and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Surrogate Standard of 0.200ug/mL. The Surrogate Standard must be replaced after six months. To every water sample and QC sample, 0.5mL of Surrogate Standard is added before extraction is initiated.

7.9.3 Aroclor 1242 Stock Standard at 990ug/mL in Hexane: The Aroclor 1242 stock standard is prepared from a neat Aroclor formulation (obtained from Monsanto directly) by weighing approximately 0.0990g and dissolving and diluting to volume in a 100mL volumetric flask with hexane. This will give a stock concentration of 990ug/mL. The stock standard is transferred into a screw cap 120mL boston bottle and stored in a refrigerator, protected from light. Stock standards should be checked at frequent intervals for signs of evaporation, especially just prior to preparing calibration standards. The stock standard must be replaced after one year.

7.9.4 Aroclor 1242 Spiking Standard at 0.990ug/mL in Acetone: The Aroclor 1242 Spiking Standard is prepared from the 990ug/mL Aroclor 1242 Stock Standard. Into a 100mL volumetric flask, using a 100-microliter syringe, transfer 100uL of the Aroclor 1242 Stock Standard at 990ug/mL. Make to volume with acetone and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a

refrigerator. This will give a concentration of Aroclor 1242 Spiking Standard of 0.990ug/mL. The A1242 Spiking Standard must be replaced after six months. To every laboratory control spike, matrix spike, and matrix spike duplicate 0.2mL of Aroclor 1242 spiking standard is added before extraction is initiated.

7.9.5 Internal Standard Solution at 202ug/mL: The internal standard used for capillary gas chromatography of PCBs will be octachloronaphthalene (OCN). This is obtained as a solid from Ultra Scientific, part number RCN-012. Weigh 10.1mg of solid octachloronaphthalene (OCN) into a 5mL vial. Quantitatively transfer the OCN using six successive 2-mL washings of toluene to a 50mL volumetric flask. Be sure to rinse the 5mL vial walls carefully so that all OCN is completely transferred to the 50mL volumetric flask. Make the solution to volume using toluene and mix the internal standard solution by shaking the flask several times. This will give a concentration of OCN of 202ug/mL. Carefully transfer the internal standard solution to 25mL vials, tightly cap, and store in a refrigerator. OCN internal standard must be replaced after one year. This internal standard is added to every sample and QC extract once the final volume has been accomplished. T he internal standard is added at a volume of 4.5uL per 5mL of extract.

8.0 Sample Collection, Preservation, Shipment and Storage:

8.1 Sample Collection and Preservation:

8.1.1 Routine 1-liter water samples should be collected in 1-liter clear glass narrow-mouth bottles. The bottles should be pre-cleaned to EPA specification protocol A - recommended for extractable organic, semivolatile and pesticide analysis. Protect samples from light. The specific requirements for sample collection at the site is outlined and detailed by the client.

8.1.2 All samples must be placed on ice or refrigerated at 4°C (±2°C) from the time they are collected until delivery to the lab.

8.2 Sample Shipment:

8.2.1 Sample shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

8.3 Sample Storage:

8.3.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from time of receipt until they are removed from storage for extraction. Typically the entire water sample grab will be consumed at time of extraction and no sample is left for log-term storage.

8.3.2 Low-level water samples are stored in a refrigerator dedicated for this type of sample to further minimize exposure to potential contaminants.

8.3.3 All samples must be extracted within 7 days of collection.

8.4 Sample Extract Storage:

8.4.1 Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C) during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements. The auto-sampler vial to be used for frozen storage will be filled to the neck of the vial. If the vial cannot be filled to the neck due to multiple analyses being performed, whatever remains will be placed in the vial and the volume marked. The volume level will be marked on all vials.

8.4.2 Field samples, sample extracts, and calibration standards must be stored separately.

8.4.3 All extracts must be analyzed within 40 days from date of extraction.

9.0 Quality Control:

9.1 The following table lists the Quality Control samples required for analysis of PCBs.

Quality Control Requirements

QC Sample	Frequency
Lab Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Duplicate Analysis	Field generated sample – analyzed at discretion of client
Matrix Spike	One matrix spike per 20 field samples or designated sample batch may be performed as specified in the client site plan.
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples or designated sample batch may be performed as specified in the client site plan.

9.1.1 Laboratory Blank: The laboratory blank will monitor and assess whether contamination or excessive interference is occurring from laboratory solvents, reagents, and glassware used in processing samples for analysis. The laboratory blank is taken through the sample extraction and clean-up procedures to include all manipulations exposed to actual samples (required volume of solvents, concentration steps, clean-up procedures, *etc.)* If the laboratory blank is positive for PCB above the reporting limit (based on Total PCB concentration), the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis. The laboratory blank will consist of organic free water for water samples.

9.1.1.1 Samples associated with a positive laboratory blank should be flagged when the data is reported. If a laboratory blank is positive for PCBs, the source of contamination must be located and eliminated. If the contamination occurred during the extraction procedure and more sample is available the samples will require re-extraction and re-analysis. If the contamination occurred after this step, then re-extraction may not be required and the existing extracts will be reanalyzed. Any aliquots of the extracts (*i.e.*, injection vials), which could have become contaminated, will be discarded.

9.1.2 Laboratory Control Spike: A Laboratory Control Spike sample is analyzed with each extraction batch. An Aroclor is spiked into organic free water. This Control Spike must achieve a percent recovery of 70 to 130 percent for SOP NE013 or 60 to 140 percent for SOP NE207 based on Total PCB concentration. If the Control Spike recovery is not within limits, the cause must be identified and corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no more sample is available, the data must be flagged to indicate low or high Control Spike recovery.

9.1.3 Duplicate Analysis: Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike / matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

RPD = (DUP1 – DUP2)/AVG x 100

Where: RPD = Relative Percent Difference.
DUP1 = The greater of the measured values.
DUP2 = The lesser of the measured values.
AVG = Average of the two analysis.

9.1.3.1 The relative percent difference must be less than or equal to 30%.

9.1.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD): Spiked sample matrix data are analyzed to assess analytical accuracy and recovery of analytes of interest. Thus the sample is spiked and carried through sample analytical procedures including extraction, clean up, and GC analysis. Depending on the specific project plans and at the discretion of the client a matrix spike or matrix spike and matrix spike duplicate can be analyzed.

9.1.4.1 There must be sufficient sample for analysis of matrix spike/matrix spike duplicate samples and the sample must be homogeneous in PCB distribution for valid data to be produced. Spike MS and/or MSD samples with the Aroclor matrix spike standard at a concentration approximately two to five times the sample concentration. Extract and analyze the two spiked samples following procedures used for actual

sample analysis. Calculate the percent recovery of the matrix spike/matrix spike duplicate by the following equation:

P = A-B/T x 100

Where: P = Percent recovery, %.
A = concentration of analyte in the spike sample aliquot
T = Known true value of the spike concentration
B = Background concentration of PCB in the unspiked sample aliquot

9.1.4.2 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 70% and less than or equal to 130% for SOP NE013 and greater than or equal to 60% and less than or equal to 140% for SOP NE207 based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

9.1.5 Surrogates: Surrogate-spiking compounds monitor the exaction efficiency and sample processing procedures for each sample. Surrogate compounds are chosen which do not chromatographically interfere with the PCB target congeners and which behave similarly to the target PCB congeners during extraction and sample processing.

9.1.5.1 Surrogate spike additions are made to each field sample, method blank, and extracted QC check sample prior to extraction. Congener IUPAC 207 (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) is used as the surrogate spike compound.

9.1.5.2 Calculate the surrogate percent recovery as follows:

% Recovery = (Surr. Amount spiked / Theoretical Spike conc.) * 100

9.1.5.3 The percent recovery limits for the surrogate:

IUPAC 207 70% - 130% for SOP NE013 and 60% - 140% for SOP NE207

10.0 Calibration and Standardization:

10.1 The gas chromatographic system calibration and standardization procedures are detailed in the determinative method for the analysis of PCBs. Refer to method SOP NE207 or NE013 for operating conditions to analyze PCBs by congener-specific methodology.

11.0 Procedure:

11.1 Initial Sample Preparation:

11.1.1 Remove the samples to be extracted from cold storage and allow to warm up to room temperature for at least 30 minutes. This can be done first while the extraction equipment is prepared to do the sample extraction.

11.1.2 Prepare a 1-liter method blank and a 1-liter laboratory control spike sample using reagent water. Use the same bottles that were used to collect field samples.

11.1.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume.

11.2 Initialization and Purge Cycle of Extractor System:

11.2.1 Turn the power on to the SPE-DEX 4700 Controller. The Controller provides power to the SPE-DEX 4790 Extractor units. The Controller also contains the programming logic to download to the extractor unit that specifies which extraction method to perform.

11.2.2 Make sure to check the solvent reservoir bottles used for the pre-wet and rinse steps and fill if necessary. Also empty the solvent recovery bottle and the large carboy used to collect extracted water.

11.2.3 Turn on the nitrogen gas supply and set the regulator to 60 to 80 PSI.

11.2.4 Turn on the power to the vacuum pump and adjust the main vacuum to 20-26" Hg.

11.2.5 Adjust the left regulator on the Pressure Bracket Assembly to 25-35 PSI. Adjust the right regulator on the Pressure Bracket Assembly to 10-15 PSI.

11.2.6 Adjust the non-venting vacuum regulator on the Solvent Recovery Manifold Assembly to 15" Hg. Do not adjust the regulator greater than 15" Hg or the higher levels could cause the solid-phase disk to go dry during the pre-wet steps.

11.2.7 Attach a cap adapter onto an empty clean 1-liter bottle, invert the bottle and place onto the bottle holder of the SPE-DEX 4790 Extractor unit.

11.2.8 Place a pre-rinsed disk holder base onto the disk holder assembly of the SPE-DEX 4790 Extractor unit.

11.2.9 Place a collection vessel (40mL VOA vial and adapter) onto the bottom tapered joint of the disk holder assembly. Attach a Keck clamp to the receiver vessel to secure it to the tapered joint.

11.2.10 On the SPE-DEX 4700 Controller press the select key and the LCD display will show extractor number. Enter the extractor number to be programmed and press the enter key (example: enter 1 if SPE-DEX 4790 Extractor unit number 1 is to be programmed). The LCD display will show method number. Enter the method number (for this SOP enter 8082.3) and press the enter key. This will download the extractor method to the selected SPE-DEX 4790 Extractor unit.

11.2.11 Press the purge key on the SPE-DEX 4790 Extractor unit. This will initiate the purge cycle sequence. The purge cycle will clean the extractor unit by dispensing the pre-wet solvents and directing them to the solvent recovery bottle. Next the rinse solvents will be sprayed into the empty sample bottle and directed to the collection vessel.

11.2.12 During the purge cycle, carefully observe the operation of the SPE-DEX 4790 Extractor unit. Make sure that it is functioning properly and that the check valve located in the disk holder assembly is operating correctly and solvents are being delivered to the correct locations.

11.2.13 Once the purge cycle is complete the SPE-DEX 4790 Extractor unit is ready to process samples.

11.3 Final Sample Preparation and Sample Extraction:

11.3.1 Using a 1.0mL disposable pipette, add 1.0mL of 1:1 sulfuric acid to every sample and QC sample. Invert the sample container several times to mix.

11.3.2 Using a disposable pasture pipette remove a small volume of sample (approximately 0.1mL) and wet a pH indicator strip. Determine that the pH of the sample is less than 2. If not, then add 0.5mL more of 1:1 sulfuric acid and test pH again. Continue to add 1:1 sulfuric acid in 0.5mL aliquots until the pH is less than 2.

11.3.3 Using a 1.0mL micro-liter syringe, add 0.5mL of surrogate standard solution to every sample and QC sample. Invert the sample container several times to mix.

11.3.4 To the laboratory control sample, matrix spike, and matrix spike duplicate samples add 0.2mL of the matrix spike standard solution using a 0.5mL micro-liter syringe. Invert these sample containers several times to mix.

11.3.5 Install a new 50mm Bakerbond Speedisk DVB onto the disk holder platform by using the luer adapter for correct connection. Note that the manual Speedisk must be used on the SPE-DEX 4790 Extractor unit for proper operation.

11.3.6 Re-attach a pre-rinsed collection vessel (40mL VOA vial and adapter) onto the disk holder taper joint. Attach a Keck clamp to the receiver vessel to secure it to the tapered joint.

11.3.7 Select the first sample to be extracted. Remove the bottle cap and place a 2" X 2" piece of aluminum over the mouth of the bottle. Gently screw the 33 X 400 adapter over the foil onto the screw threads of the bottle. When done properly the aluminum foil will be taut and no rips will be evident in the foil. If a tear is detected, the adapter must be removed and a new piece of aluminum foil must be installed.

11.3.8 Invert the sample bottle and inspect for bubbles rising from the seal of the bottle and the adapter. If no bubbles are detected then a good seal has been made and the sample container can be installed into the bottle holder assembly. If bubbles are observed, turn the bottle right way up and tighten the adapter. Try inverting the bottle again and look for bubbles. If they have stopped then a good seal has been made. If the bottle continues to bubble, remove the bottle adapter and install a new piece of aluminum foil and test again until a good seal is made.

11.3.9 With the bottle inverted, place the bottle onto the bottle holder assembly making sure that the solvent rinse stem is inside the bottle adapter. Gently lower and then firmly push the sample bottle into the bottle holder assembly. Turn the

bottle clockwise three quarters around to break an opening in the foil to allow the sample to flow freely.

11.3.10 Once the sample bottle has been installed the SPE-DEX 4790 Extractor unit can be started by pressing the start key. The method selected during the purge cycle (8082.3) is the method used to process the sample.

11.3.11 The SPE-DEX 4790 Extractor will automatically pre-wet the solid-phase disk, extract the sample, air dry the disk post extraction, and extract the disk to recover the analytes of interest.

11.3.12 Once the process is complete the collection vessel is removed. The collection adapter is removed from the 40mL VOA vial and the Teflon lined cap is placed back onto the VOA vial. At this point, the sample is either placed into cold storage or taken through the required clean-up steps before the extract is analyzed.

11.3.13 Take the original sample bottle and fill with tap water to the mark made at the water meniscus. Measure the volume of water using a 2-liter graduated cylinder to the nearest 10mLs. Record this value in the extraction logbook.

11.3.14 The following table outlines the 8082.3 extraction method that the SPE-DEX 4790 Extractor unit uses to process and extract a water sample:

Extraction Method 8082.3

Step Number	Procedure
Pre-wet Step 1	Solvent: Hexane Soak Time: 1:00 minute Air Dry Time: 0:30 minutes
Pre-wet Step 2	Solvent: Acetone Soak Time: 1:00 minute Air Dry Time: 0:30 minutes
Pre-wet Step 3	Solvent: Methanol Soak Time: 1:30 minutes Air Dry Time: 0:00 minutes
Pre-wet Step 4	Solvent: Reagent Water Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Pre-wet Step 5	Solvent: Reagent Water Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Sample extraction Step 6	Time depends on particulates and sample flow through solid-phase filter
Air Dry Disk Step 7	Air Dry Time: 5:00 minutes
Rinse Step 8	Solvent: Acetone Soak Time: 1:30 minute Air Dry Time: 1:00 minute
Rinse Step 9	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute

Rinse Step 10	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute
Rinse Step 11	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute

11.4 Sample Extract Concentration and Clean-up Procedures:

11.4.1 Extract Solvent Reduction, Florisil Clean-up Procedure and Internal Standard Addition:

11.4.1.1 The sample extract will have two phases, the top layer will be composed of the hexane used to elute components from the solid-phase disk and the bottom layer will be composed of residual water and acetone from the extraction process. Carefully transfer the top layer of solvent to either a 250mL turbo-tube or a 60mL VOA vial. Glassware selection depends on which solvent evaporator will be used (TurboVap concentrator uses the 250mL glassware and the TurboVap LV uses standard 60mL VOA vials.).

11.4.1.2 Backwash the residual water/acetone in the 40mL VOA collection vial three successive times with hexane (approximately 5mL) and add these rinses to either a 250mL turbo-tube or a 60mL VOA vial.

11.4.1.3 Take the volume of the extract to 50mL with hexane so that the evaporation rate will be equal for all the samples being concentrated.

11.4.1.4 Whether the sample extract is concentrated in the TurboVap or the TurboVap LV, the procedure is the same.

11.4.1.5 The TurboVap evaporator system is used to reduce the sample volume. The TurboVap uses a heated water bath and positive pressure nitrogen flow with vortex action. The unit maintains a slight equilibrium imbalance between the liquid and the gaseous phase of the solvent extract, which allows fractional reduction of the solvent without loss of higher boiling point analytes.

11.4.1.6 Turn the unit on and allow to heat up to 40°C $\pm$ 2°C.

11.4.1.7 As a precaution the TurboVap system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and therefore cause cross contamination of samples or loss of sample extract. To bleed the system of residual gas pressure, place an empty turbo-tube into the water bath and close lid. Make sure that the nitrogen gas pressure regulator is closed. Remove turbo-tube.

11.4.1.8 Wipe down the inside of TurboVap with a Hexane wetted paper towel including top lid and gas pins. Place turbo-tubes containing the sample extract into TurboVap and close lid. Slowly open the pressure regulator. Keep the gas pressure very low to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the volume reduction.

11.4.1.9 **DO NOT** leave the unit unattended as extracts may be blown to dryness and PCB loss may occur.

11.4.1.10 Concentrate the extract to approximately 5.0mL. Remove the turbo-tube or 60mL VOA vial from the evaporator unit. Carefully transfer the extract to a 15mL vial.

11.4.1.11 Rinse the turbo-tube or 60mL VOA vial three successive times with hexane (approximately 2mL) and add these rinses to the 15mL vial. Keep this turbo-tube or 60mLVOA vial to be used during the second concentration step.

11.4.1.12 To the extract add approximately 1.0g of deactivated Florisil and shake the sample by hand for approximately 15 seconds. Allow the Florisil to settle and transfer the extract to the 250mL turbo-tube or 60mL VOA vial used for the first concentration of the extract.

11.4.1.13 Backwash the Florisil three successive times with 2mL hexane and transfer these rinses to the 250mL turbo-tube or 60mL VOA vial.

11.4.1.14 Following procedures detailed above, concentrate the extract to approximately 2.0mL. Remove the turbo-tube or 60mL VOA vial from the evaporator unit. Carefully transfer the extract to a 5mL volumetric flask.

11.4.1.15 Rinse the turbo-tube or 60mL VOA vial with approximately 1.0mL of hexane and add this to the 5mL volumetric flask. Repeat this process two more times, adding the rinses to the 5mL volumetric flask. Make the extract to volume with hexane.

11.4.1.16 At this point the internal standard is added to the extract. Using a 10 micro-liter syringe, add 4.5 micro-liters of internal standard to the extract. Mix the extract by capping and inverting the volumetric several times. Transfer the extract to a 15mL vial.

11.4.2 Sulfuric Acid Clean-up:

11.4.2.1 Add approximately 2mL of the solvent washed concentrated sulfuric acid (NE174.doc) to each extract vial and shake by hand for 30 seconds. Place the vial in a bench top centrifuge and centrifuge on speed setting 5 for at least 1 minute. Transfer the extract (upper) layer to a correctly labeled, pre-rinsed 15mL vial.

11.4.3 Mercury Clean-up for sulfur Removal:

11.4.3.1 ***NOTE:*** Mercury is a highly toxic metal, all operations involving mercury should be performed within a fume hood. Prior to using mercury, the chemist should become aquatinted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the Material Safety Data Sheet (MSDS).

11.4.3.2 Using a disposable pasture pipette, add 3 drops of solvent washed Mercury (NE175.doc) to the sample extracts, cap and place on the wrist shaker for 30 minutes. The sulfur is converted to Mercuric Sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental Sulfur.

11.4.3.3 Transfer the extracts to pre-rinsed and labeled 15mL vials. Submit the sample extract vials, along with the Job Tracking Folder containing the GC Queue Lab Sheet to the GC department supervisor.

12.0 Calculations:

12.1 All calculations pertaining to data analysis and reporting can be found in the determinative method SOP NE207 or NE013.

13.0 Method Performance:

13.1 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at a reasonable concentration above the low-level calibration standard and below the high-level calibration standard. The analyte will be added to a laboratory organic free water sample and taken through all extraction and analytical procedures. Aroclor 1242 is used as the analyte and recovery on a total basis is used to calculate percent recovery. To be valid, Aroclor 1242 will be recovered between the limits of 70 to 130 percent. Also, a percent relative standard deviation will be calculated for the replicates will be less than or equal to 20% to be valid.

13.2 Method Detection Limit: A method detection limit will be determined for this method. A minimum of seven laboratory organic free water samples will be prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

$$MDL = S * t_{(n-1,\ 1\text{-}alpha=0.99)}$$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1\text{-}alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)}$ = 2.998

13.2.1 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

14.0 Pollution Prevention:

14.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols.

14.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload.

14.3 For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

15.0 Data Assessment and Acceptance Criteria for Quality Control Measures and Corrective Actions for Out-of-Control Data:

15.1 The gas chromatographic (GC) department will interface with the extraction department about any problems or issues that arise once the sample extracts are analyzed and assessed for method compliance with quality control parameters or limits that are out of control. This interaction is on a case by case basis and both departments will need to work together to resolve problems with samples that require re-extraction if sample is available.

15.2 In general, most water samples collected in the field are completely consumed during the extraction process (the whole 1-liter water sample is extracted and the bottle rinsed with solvent and considered part of the sample extract) and therefore more sample is normally not available and re-extraction is not possible. Some field sampling programs require the collection of an additional 1-liter water sample (an archived sample) for each sampling site. For these instances, the archived water sample can be extracted (usually out of the 7 day hold time) and analyzed. A sample case narrative would accompany the data report to explain the re-extraction. Typically the original data and the re-extract data would be provided to the client.

15.3 The GC analyst and the extraction chemist may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. A Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed with the data and is also useful for production of case narratives that are issued with final data reports.

15.4 For a complete outline of data assessment, acceptance criteria, and corrective action procedures for out-of-control criteria refer to SOP NE207 or NE013.

16.0 Contingencies for Handling Out-of-Control or Unacceptable Data:

16.1 Data that is detected to be out-of-control during sample analysis, when compared to method acceptance criteria, will be addressed in the following manner:

16.1.1 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out-of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

16.2 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

17.0 Waste Management:

17.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

17.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

18.0 References:

18.1 US EPA 40 CFR Part 136, “Guidelines Establishing Test Procedures for the Analysis of Pollutants,” July, 1988.

18.2 US EPA SW-846, “Test Methods for Evaluating Solid Waste Physical/Chemical Methods,” Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

APPENDIX 7

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE208_02.DOC

REVISION NUMBER: 02

STANDARD OPERATING PROCEDURE FOR THE EXTRACTION AND CLEANUP OF LARGE VOLUME AQUEOUS SAMPLES FOR POLYCHLORINATED BIPHENYLS (PCBs) USING US-EPA SW-846 METHOD 3535, SOLID PHASE EXTRACTION

March 9, 2004

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STANDARD OPERATING PROCEDURE

Author: Robert E. Wagner

Reviewed by:

Mike Bergmann, Laboratory Manager

Approved by:

William A. Kotas-Quality Assurance Officer

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STANDARD OPERATING PROCEDURE FOR THE EXTRACTION AND CLEANUP OF LARGE VOLUME AQUEOUS SAMPLES FOR POLYCHLORINATED BIPHENYLS (PCBs) USING US-EPA SW-846 METHOD 3535, SOLID PHASE EXTRACTION

1.0 Scope:

1.1 This standard operating procedure (SOP) is applicable to the extraction of large volume (4 to 8 liters) aqueous samples.

1.2 The purpose of this SOP is to provide procedures required for both the extraction and subsequent extract cleanup of PCBs in aqueous samples using the solid phase extraction method USEPA SW-846 Method 3535.

1.3 This method was developed to utilize an automated extraction system, and provides details for the extraction of large volume water samples in the 4 to 8 liter range. The SPE-DEX 4790 extractor (or equivalent) from Horizon Technologies will be used for automated sample extraction.

1.4 A disk extraction filter will be used for sample extraction. The disk chosen is a 50mm Bakerbond Speedisk™ styrene divinyl benzene filter (Baker or equivalent).

2.0 Summary of Method:

2.1 This SOP provides detailed procedures for the automated extraction of 4 to 8 liter water samples and also provides instruction for sample clean-up procedures for sample extracts prior to gas chromatographic analysis for PCBs.

2.2 The sample extraction is initiated by adding sulfuric acid to the 4 to 8 liter water sample as a matrix modifier. The appropriate surrogate is added to all samples and quality control samples. A method blank and laboratory control spike is performed with the extraction batch from laboratory organic free water. The laboratory control spike is fortified with the PCB spiking solution. Other quality control samples, such as matrix spike, matrix spike duplicate, blind duplicate, are initiated along with the samples and receive surrogates and, if required, fortified with PCB spiking solution. The SPE-DEX 4790 extraction unit is programmed from the control station and the extraction method is initialized. The sample bottle is placed onto the SPE-DEX 4790 extractor and sample extraction is initiated by placing the extractor into start mode. The SPE-DEX 4790 passes the large volume water sample through the solid-phase disk with the aid of vacuum. Once the large volume sample completely passes through the solid-phase disk, the SPE-DEX 4790 automatically dries the solid-phase disk, rinses the sample container with solvent that is directed to the disk and extraction of analyte is initiated. Several additional solvent rinses are performed which are collected into the extract receiver glassware. The extract is transferred and further processed through specified clean-up procedures. The extract is set to a final volume of 5mL and is ready for analysis.

2.3 This method is applicable to trace analysis of PCB. All glassware, solid-phase extractor components, solvents, and reagents used during clean-up procedures must be kept scrupulously clean.

3.0 Definitions:

3.1 Surrogate Analyte: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are added to all laboratory method blanks, laboratory QC reference samples (Laboratory Control Spikes), laboratory duplicates, calibration and continuing check standards, field samples, field duplicate samples, field matrix spike samples, field matrix spike duplicate samples prior to extraction and/or analysis. Percent recovery is calculated for each surrogate to assess extraction efficiency.

3.2 Laboratory Method Blank: A laboratory derived sample consisting of reagent water or other blank matrix that consists of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The laboratory method blank is used to define the level of laboratory analyte background or other interferences that exist in the laboratory environment, the reagents, or the apparatus.

3.3 Laboratory Control Sample (LCS): Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

3.4 Sample Matrix Spike/Sample Matrix Spike Duplicate (MS/MSD): An aliquot of a field sample that is fortified with known quantities of the method analytes and subjected to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring recovery.

4.0 Interferences:

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing equipment (such as the SPE-DEX 4790 extractor) that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials and equipment must be routinely verified to be free from interferences by running laboratory method blanks.

4.1.1 All glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by first rinsing with acetone, followed by detergent washing with hot water. Glassware should then be thoroughly rinsed with tap water, followed by a distilled water rinse. Place the washed glassware in a drying oven at 100°C for at least 30 minutes. After the glassware is dried and allowed to cool store in a clean environment to prevent any exposure to dust or other contaminates. Prior to use, rinse all glassware and other components with high purity hexane.

4.1.2 The use of high purity solvent and reagents will minimize interference problems. Purification of reagents by washing with solvent will also help to reduce interference problems.

4.2 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

4.3 The sample matrix itself is also a potential source for method analyte interference. The clean-up procedures provided in this SOP can be used to overcome many of these interferences.

5.0 Safety:

5.1 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets (MSDS) to familiarize themselves with the hazards of handling the compounds used for standards and samples.

5.2 Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, all solvents and standards should be manipulated in a chemical fume hood. All sample extracts should be manipulated in a chemical fume hood.

6.0 Equipment and Supplies:

6.1 Sample Containers – 4-liter amber glass bottle fitted with polypropylene screw cap. Bottles used for sample collection are purchased pre-cleaned (Industrial Glassware, part number #4000BA-PC or equivalent). Protect collected sample from light.

6.2 Automated Solid-Phase Extractor - SPE-DEX 4790 extractor system including the SPE-DEX 4700 Series Controller unit, Horizon Technology. All necessary accessories required for operation including glassware, gas regulators and compressed nitrogen source, Teflon tubing for solvent delivery, solvent delivery bottles, solvent waste recovery bottle, water recovery carboy, solvent exhaust hose, low-pressure flexible gas tubing, bottle adapters, and vacuum system.

6.3 Bakerbond Speedisk DVB – Styrene divinylbenzene 50mm disk for sample extraction. Part number 8059-06 or equivalent.

6.4 2-liter graduated cylinder – Used for measuring volume of water sample. Scienceware or equivalent.

6.5 Disposable Pasture 9” pipettes – Krackeler 67-450-900-CS or equivalent.

6.6 TurboVap Evaporator – Zymark ZW640-3.

6.7 TurboVap Evaporator concentrator tubes – Zymark 250mL.

6.8 Turbovap LV Evaporator – Zymark ZW700.

6.9 Disposable 1mL pipettes – Kimble part number 72120-1110 or equivalent.

6.10 pH Indicator Strips – EM Science part number 9590 or equivalent.

6.11 Disposal Vials, 15mL and 30mL – Disposal glass vials with polyseal caps, Industrial Glassware or equivalent.

6.12 Vial Rack – plastic rack used to hold vials during processing of extracts. Scienceware.

6.13 Beakers – Pyrex, assorted sizes – 100mL, 250mL, and 600mL.

6.14 Centrifuge – Model CL or equivalent. International Equipment Company.

6.15 Wrist-action shaker – Burrel model 75 and 88 or equivalent.

6.16 GC autosampler vials – Scientific Resource Inc. part number 99468-A or equivalent.

6.17 Analytical Balance – Capable of weighing 0.0001g. Mettler AG204 or equivalent.

6.18 VOA Vials – 40mL and 60mL, Environmental Sampling Supply.

6.19 Speedisk 185mL Reservior, J.T. Baker part number 8097-06.

7.0 Reagents and Standards:

7.1 Reagent Water – 18-megaohm water obtained from the laboratory's water purification system. Used for solid-phase disk preparation, laboratory method blanks, laboratory control spikes, MDL studies, and P&A studies.

7.2 Sulfuric Acid, concentrated – Mallinckrodt part number 2468. Sulfuric acid is cleaned by washing with hexane prior to use. See SOP NE174 for details on procedure.

7.3 1:1 Sulfuric acid – Prepared from solvent washed concentrated sulfuric acid. Preparation – To a beaker containing 500mL cold reagent water slowly add 500mL concentrated sulfuric acid. Transfer to a pre-cleaned 1-liter bottle for storage.

7.4 Hexane – Pesticide residue quality. Burdick&Jackson part number 216-4 or equivalent.

7.5 Acetone - Pesticide residue quality. Burdick&Jackson part number 010-4 or equivalent.

7.6 Methanol – Pesticide residue quality. EM Science OmniSolv part number MX0488P-1 or equivalent.

7.7 Florisil – J.T. Baker part number M368-08. Florisil is solvent washed and dried before use. See SOP NE094 for details on cleaning procedures. After the Florisil is purified, it is deactivated with reagent water to a specified % water content to adjust the activity level of the Florisil currently in use. The amount of water added to the Florisil is determined for each lot and tested by exposing PCB standards (Aroclors 1232, 1248, and 1262) to the Florisil and determining that no pattern change has occurred. The deactivated Florisil is stored in amber glass containers and stored in a desiccator.

7.8 Mercury – Triple distilled, Mercury Waste Solutions Inc. Mercury is solvent washed prior to use. See SOP NE175 for details on cleaning procedures.

7.9 Standard Solutions – The following standards are used during extraction and preparation of sample extracts:

7.9.1 Surrogate Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 100ug/mL in Hexane: The surrogate stock standard is prepared from a solid standard obtained from AccuStandard, Inc. (part number C-207N). Weigh 5.0mg of the solid surrogate standard into a solvent rinsed 10mL vial. Quantitatively transfer the surrogate standard using six successive 2-mL washings of hexane to a 50mL volumetric flask. Be sure to rinse the 10mL vial walls carefully so that the entire surrogate standard is completely transferred to the 50mL volumetric flask. Make to volume with hexane and mix the surrogate standard solution by shaking the flask several times. This will give a concentration of surrogate standard of 100ug/mL. Carefully transfer the surrogate

standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. The surrogate standard must be replaced after one year.

7.9.2 Surrogate Secondary Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 0.200ug/mL in Acetone: The Surrogate Secondary Stock Standard is prepared from the 100ug/mL Surrogate Stock Standard. Into a 100mL volumetric flask, using a 500-microliter syringe, transfer 200uL of the Surrogate Stock Standard at 100ug/mL. Make to volume with acetone and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Surrogate Secondary Stock Standard of 0.200ug/mL. The Surrogate Secondary Stock Standard must be replaced after six months.

7.9.3 Surrogate Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 0.0200ug/mL in Acetone: The Surrogate Standard is prepared from the 0.200ug/mL Surrogate Secondary Stock Standard. Into a 100mL volumetric flask, using a 10mL class A pipette, transfer 10.0mL of the Surrogate Secondary Stock Standard at 0.200ug/mL. Make to volume with acetone and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Surrogate Standard of 0.0200ug/mL. The Surrogate Standard must be replaced after six months. To every water sample and QC sample, 0.5mL of Surrogate Standard is added before extraction is initiated.

7.9.4 Aroclor 1242 Stock Standard at 990ug/mL in Hexane: The Aroclor 1242 stock standard is prepared from a neat Aroclor formulation (obtained from Monsanto directly) by weighing approximately 0.0990g and dissolving and diluting to volume in a 100mL volumetric flask with hexane. This will give a stock concentration of 990ug/mL. The stock standard is transferred into a screw cap 120mL boston bottle and stored in a refrigerator, protected from light. Stock standards should be checked at frequent intervals for signs of evaporation, especially just prior to preparing calibration standards. The stock standard must be replaced after one year.

7.9.5 Aroclor 1242 Secondary Stock Standard at 0.495ug/mL in Acetone: The Aroclor 1242 Secondary Stock Standard is prepared from the 990ug/mL Aroclor 1242 Stock Standard. Into a 100mL volumetric flask, using a 100-microliter syringe, transfer 50uL of the Aroclor 1242 Stock Standard at 990ug/mL. Make to volume with acetone and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Aroclor 1242 Secondary Stock Standard of 0.495ug/mL. The A1242 Spiking Standard must be replaced after six months.

7.9.6 Aroclor 1242 Spiking Standard at 0.0495ug/mL in Acetone: The Aroclor 1242 Spiking Standard is prepared from the 0.495ug/mL Aroclor 1242 Secondary Stock Standard. Into a 100mL volumetric flask, using a 10mL class A pipette, transfer 10.0mL of the Aroclor 1242 Secondary Stock Standard at 0.495ug/mL. Make to volume with acetone and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Aroclor 1242 Spiking Standard of 0.0495ug/mL. The A1242 Spiking Standard must be replaced after six months. To every laboratory control spike, matrix spike, and matrix spike duplicate 1.0mL of Aroclor 1242 spiking standard is added before extraction is initiated.

7.9.7 Internal Standard Stock Solution at 202ug/mL: The internal standard used for capillary gas chromatography of PCBs will be octachloronaphthalene (OCN). This is obtained as a solid from Ultra Scientific, part number RCN-012. Weigh 10.1mg of solid

octachloronaphthalene (OCN) into a 5mL vial. Quantitatively transfer the OCN using six successive 2-mL washings of toluene to a 50mL volumetric flask. Be sure to rinse the 5mL vial walls carefully so that all OCN is completely transferred to the 50mL volumetric flask. Make the solution to volume using toluene and mix the internal standard solution by shaking the flask several times. This will give a concentration of OCN of 202ug/mL. Carefully transfer the internal standard solution to 25mL vials, tightly cap, and store in a refrigerator. OCN internal standard must be replaced after one year.

7.9.8 Internal Standard Solution at 20.2ug/mL: The internal standard is prepared from the 202ug/mL Internal Standard Stock Solution. Into a 10mL volumetric flask, using a 1000 microliter syringe, transfer 1.0mL of the Internal Standard Stock Solution at 202ug/mL. Make to volume with toluene and transfer the standard to a 15mL vial, tightly cap, and store in a refrigerator. This will give a concentration of OCN of 20.2ug/mL. OCN internal standard must be replaced after six months. This internal standard is added to every sample and QC extract once the final volume has been accomplished. The internal standard is added at a volume of 4.5uL per 5mL of extract.

8.0 Sample Collection, Preservation, Shipment and Storage:

8.1 Sample Collection and Preservation:

8.1.1 Large volume (4 to 8 liters) water samples should be collected in 4-liter amber glass bottles. The bottles should be pre-cleaned to EPA specification protocol A - recommended for extractable organic, semivolatile and pesticide analysis. Protect samples from light. The specific requirements for sample collection at the site is outlined and detailed by the client.

8.1.2 All samples must be placed on ice or refrigerated at 4°C (±2°C) from the time they are collected until delivery to the lab.

8.2 Sample Shipment:

8.2.1 Sample shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

8.3 Sample Storage:

8.3.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from time of receipt until they are removed from storage for extraction. Typically the entire water sample grab will be consumed at time of extraction and no sample is left for log-term storage.

8.3.2 Low-level water samples are stored in a refrigerator dedicated for this type of sample to further minimize exposure to potential contaminants.

8.3.3 All samples must be extracted within 7 days of collection.

8.4 Sample Extract Storage:

8.4.1 Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C) during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements. The auto-sampler vial to be used for frozen storage will be filled to the neck of the vial. If the vial cannot be filled to the neck due to multiple analyses being performed, whatever remains will be placed in the vial and the volume marked. The volume level will be marked on all vials.

8.4.2 Field samples, sample extracts, and calibration standards must be stored separately.

8.4.3 All extracts must be analyzed within 40 days from date of extraction.

9.0 Quality Control:

9.1 The following table lists the Quality Control samples required for analysis of PCBs.

Quality Control Requirements

QC Sample	Frequency
Lab Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Duplicate Analysis	Field generated sample – analyzed at discretion of client
Matrix Spike	One matrix spike per 20 field samples or designated sample batch may be performed as specified in the client site plan.
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples or designated sample batch may be performed as specified in the client site plan.

9.1.1 Laboratory Blank: The laboratory blank will monitor and assess whether contamination or excessive interference is occurring from laboratory solvents, reagents, and glassware used in processing samples for analysis. The laboratory blank is taken through the sample extraction and clean-up procedures to include all manipulations exposed to actual samples (required volume of solvents, concentration steps, clean-up procedures, etc.) If the laboratory blank is positive for PCB above the reporting limit (based on Total PCB concentration), the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis. The laboratory blank will consist of organic free water for water samples.

9.1.1.1 Samples associated with a positive laboratory blank should be flagged when the data is reported. If a laboratory blank is positive for PCBs, the source of contamination must be located and eliminated. If the contamination occurred during the extraction procedure and more sample is available the

samples will require re-extraction and re-analysis. If the contamination occurred after this step, then re-extraction may not be required and the existing extracts will be reanalyzed. Any aliquots of the extracts (i.e., injection vials), which could have become contaminated, will be discarded.

9.1.2 Laboratory Control Spike: A Laboratory Control Spike sample is analyzed with each extraction batch. An Aroclor is spiked into organic free water. This Control Spike must achieve a percent recovery of 60 to 140 percent based on Total PCB concentration. If the Control Spike recovery is not within limits, the cause must be identified and corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no more sample is available, the data must be flagged to indicate low or high Control Spike recovery.

9.1.3 Duplicate Analysis: Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike / matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

RPD = (DUP1 – DUP2)/AVG x 100

Where: RPD = Relative Percent Difference.
DUP1 = The greater of the measured values.
DUP2 = The lesser of the measured values.
AVG = Average of the two analysis.

9.1.3.1 The relative percent difference must be less than or equal to 30%.

9.1.4 Matrix Spike and Matrix Spike Duplicate (MS/MSD): Spiked sample matrix data are analyzed to assess analytical accuracy and recovery of analytes of interest. Thus the sample is spiked and carried through sample analytical procedures including extraction, clean up, and GC analysis. Depending on the specific project plans and at the discretion of the client a matrix spike or matrix spike and matrix spike duplicate can be analyzed.

9.1.4.1 There must be sufficient sample for analysis of matrix spike/matrix spike duplicate samples and the sample must be homogeneous in PCB distribution for valid data to be produced. Spike MS and/or MSD samples with the Aroclor matrix spike standard at a concentration approximately two to five times the sample concentration. Extract and analyze the two spiked samples following procedures used for actual sample analysis. Calculate the percent recovery of the matrix spike/matrix spike duplicate by the following equation:

P = A-B/T x 100

Where: P = Percent recovery, %.
A = concentration of analyte in the spike sample aliquot
T = Known true value of the spike concentration
B = Background concentration of PCB in the unspiked sample aliquot

9.1.4.2 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 60% and less than or equal to 140% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

9.1.5 Surrogates: Surrogate-spiking compounds monitor the exaction efficiency and sample processing procedures for each sample. Surrogate compounds are chosen which do not chromatographically interfere with the PCB target congeners and which behave similarly to the target PCB congeners during extraction and sample processing.

9.1.5.1 Surrogate spike additions are made to each field sample, method blank, and extracted QC check sample prior to extraction. Congener IUPAC 207 (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) is used as the surrogate spike compound.

9.1.5.2 Calculate the surrogate percent recovery as follows:

% Recovery = (Surr. Amount spiked / Theoretical Spike conc.) * 100

9.1.5.3 The percent recovery limits for the surrogate:

IUPAC 207 60% - 140%

10.0 Calibration and Standardization:

10.1 The gas chromatographic system calibration and standardization procedures are detailed in the determinative method for the analysis of PCBs. Refer to method NE207 for operating conditions to analyze PCBs by congener-specific methodology.

11.0 Procedure:

11.1 Initial Sample Preparation:

11.1.1 Remove the samples to be extracted from cold storage and allow to warm up to room temperature for at least 30 minutes. This can be done first while the extraction equipment is prepared to do the sample extraction.

11.1.2 Prepare a 4 to 8 liter method blank and a 4 to 8 liter laboratory control spike sample using reagent water. Use the same bottles that were used to collect field samples. The volume used will depend on the sample volume collected for field samples.

11.1.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume.

11.2 Initialization and Purge Cycle of Extractor System:

11.2.1 Turn the power on to the SPE-DEX 4700 Controller. The Controller provides power to the SPE-DEX 4790 Extractor units. The Controller also contains the programming logic to download to the extractor unit that specifies which extraction method to perform.

11.2.2 Make sure to check the solvent reservoir bottles used for the pre-wet and rinse steps and fill if necessary. Also empty the solvent recovery bottle and the large carboy used to collect extracted water.

11.2.3 Turn on the nitrogen gas supply and set the regulator to 60 to 80 PSI.

11.2.4 Turn on the power to the vacuum pump and adjust the main vacuum to 20-26" Hg.

11.2.5 Adjust the left regulator on the Pressure Bracket Assembly to 25-35 PSI. Adjust the right regulator on the Pressure Bracket Assembly to 10-15 PSI.

11.2.6 Adjust the non-venting vacuum regulator on the Solvent Recovery Manifold Assembly to 15" Hg. Do not adjust the regulator greater than 15" Hg or the higher levels could cause the solid-phase disk to go dry during the pre-wet steps.

11.2.7 Attach a cap adapter onto an empty clean 1-liter bottle, invert the bottle and place onto the bottle holder of the SPE-DEX 4790 Extractor unit.

11.2.8 Place a pre-rinsed disk holder base onto the disk holder assembly of the SPE-DEX 4790 Extractor unit.

11.2.9 Place a collection vessel (40mL VOA vial and adapter) onto the bottom tapered joint of the disk holder assembly. Attach a Keck clamp to the receiver vessel to secure it to the tapered joint.

11.2.10 On the SPE-DEX 4700 Controller press the select key and the LCD display will show extractor number. Enter the extractor number to be programmed and press the enter key (example: enter 1 if SPE-DEX 4790 Extractor unit number 1 is to be programmed). The LCD display will show method number. Enter the method number (for this SOP enter 8082.3) and press the enter key. This will download the extractor method to the selected SPE-DEX 4790 Extractor unit.

11.2.11 Press the purge key on the SPE-DEX 4790 Extractor unit. This will initiate the purge cycle sequence. The purge cycle will clean the extractor unit by dispensing the pre-wet solvents and directing them to the solvent recovery bottle. Next the rinse solvents will be sprayed into the empty sample bottle and directed to the collection vessel.

11.2.12 During the purge cycle, carefully observe the operation of the SPE-DEX 4790 Extractor unit. Make sure that it is functioning properly and that the check valve located in the disk holder assembly is operating correctly and solvents are being delivered to the correct locations.

11.2.13 Once the purge cycle is complete the SPE-DEX 4790 Extractor unit is ready to process samples.

11.3 Final Sample Preparation and Sample Extraction:

11.3.1 Using a 10.0mL disposable pipette, add 4.0mL to 8.0mL (1.0mL/1-liter of water) of 1:1 sulfuric acid to every sample and QC sample. Invert the sample container several times to mix.

11.3.2 Using a disposable pasture pipette remove a small volume of sample (approximately 0.1mL) and wet a pH indicator strip. Determine that the pH of the sample is less than 2. If not, then add 0.5mL more of 1:1 sulfuric acid and test pH again. Continue to add 1:1 sulfuric acid in 0.5mL aliquots until the pH is less than 2.

11.3.3 Using a 1.0mL micro-liter syringe, add 0.5mL of surrogate standard solution to every sample and QC sample. Invert the sample container several times to mix.

11.3.4 To the laboratory control sample, matrix spike, and matrix spike duplicate samples add 1.0mL of the matrix spike standard solution using a 1.0mL micro-liter syringe. Invert these sample containers several times to mix.

11.3.5 Install a new 50mm Bakerbond Speedisk DVB onto the disk holder platform by using the luer adapter for correct connection. Before installing the disk, attach a Speedisk 185mL reservoir to the disk. The reservoir is necessary for large volume samples so that water will not overflow the disk during extraction. Note that the manual Speedisk must be used on the SPE-DEX 4790 Extractor unit for proper operation.

11.3.6 Attach a pre-rinsed collection vessel (60mL VOA vial and adapter) onto the disk holder taper joint. Attach a Keck clamp to the receiver vessel to secure it to the tapered joint.

11.3.7 Select the first sample to be extracted. Remove the bottle cap and screw the 38 X 400 4-liter bottle adapter onto the screw threads of the bottle. Place a 2” X 2” piece of aluminum over the mouth of the bottle adapter. Gently screw the 33 X 400 1-liter bottle adapter onto the screw threads of the 38 X 400 bottle adapter. When done properly the aluminum foil will be taut and no rips will be evident in the foil. If a tear is detected, the adapter must be removed and a new piece of aluminum foil must be installed.

11.3.8 Invert the sample bottle and inspect for bubbles rising from the seal of the bottle and the two adapters. If no bubbles are detected then a good seal has been made and the sample container can be installed into the bottle holder assembly. If bubbles are observed, turn the bottle right way up and tighten the adapters. Try inverting the bottle again and look for bubbles. If they have stopped then a good seal has been made. If the bottle continues to bubble, remove the bottle adapters and install a new piece of aluminum foil and test again until a good seal is made.

11.3.9 With the bottle inverted, place the bottle onto the bottle holder assembly making sure that the solvent rinse stem is inside the bottle adapter. Gently lower and then firmly push the sample bottle into the bottle holder assembly. Turn the bottle clockwise three quarters around to break an opening in the foil to allow the sample to flow freely.

11.3.10 Once the sample bottle has been installed the SPE-DEX 4790 Extractor unit can be started by pressing the start key. The method selected during the purge cycle (8082.3) is the method used to process the sample.

11.3.11 The SPE-DEX 4790 Extractor will automatically pre-wet the solid-phase disk, extract the sample, air dry the disk post extraction, and extract the disk to recover the analytes of interest.

11.3.12 Once the process is complete the collection vessel is removed. The collection adapter is removed from the 60mL VOA vial and the Teflon lined cap is placed back onto the VOA vial. At this point, the sample is either placed into cold storage or taken through the required clean-up steps before the extract is analyzed.

11.3.13 If a second 4-liter sample is to be processed (two 4-liter bottles comprising one 8-liter sample), then the extraction process must be manually stopped prior to the disk going dry and prior to the elution (rinse steps) occurring. The first 4-liter bottle (empty of water sample at this point) is removed and the second 4-liter bottle is installed onto the bottle holder assembly. From the 4700 controller download method 8082.8 to the SPE-DEX 4790 Extractor unit. This method skips the pre-wet steps and continues with extraction of the water sample and subsequent rinse (elution of analytes from solid-phase disk) steps. When this procedure is followed, the first 4-liter sample container must be rinsed with acetone (once) and then hexane (once) and added to the final extract collected during the second 4-liter bottle processing.

11.3.14 Take the original sample bottle and fill with tap water to the mark made at the water meniscus. Measure the volume of water using a 2-liter graduated cylinder to the nearest 10mLs. Record this value in the extraction logbook.

11.3.15 The following table outlines the 8082.3 and 8082.8 extraction methods that the SPE-DEX 4790 Extractor unit uses to process and extract a water sample:

Extraction Method 8082.3

Step Number	Procedure
Pre-wet Step 1	Solvent: Hexane Soak Time: 1:00 minute Air Dry Time: 0:30 minutes
Pre-wet Step 2	Solvent: Acetone Soak Time: 1:00 minute Air Dry Time: 0:30 minutes
Pre-wet Step 3	Solvent: Methanol Soak Time: 1:30 minutes Air Dry Time: 0:00 minutes
Pre-wet Step 4	Solvent: Reagent Water Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Pre-wet Step 5	Solvent: Reagent Water Soak Time: 1:00 minute Air Dry Time: 0:00 minutes
Sample extraction Step 6	Time depends on particulates and sample flow through solid-phase filter
Air Dry Disk Step 7	Air Dry Time: 5:00 minutes
Rinse Step 8	Solvent: Acetone Soak Time: 1:30 minute Air Dry Time: 1:00 minute

Rinse Step 9	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute
Rinse Step 10	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute
Rinse Step 11	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute

Extraction Method 8082.8

Step Number	Procedure
Continue water extraction Step 1	Pressing Start key on SPE-DEX 4790 Extractor will continue to process second 4-liter bottle.
Air Dry Disk Step 2	Air Dry Time: 5:00 minutes
Rinse Step 3	Solvent: Acetone Soak Time: 1:30 minute Air Dry Time: 1:00 minute
Rinse Step 4	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute
Rinse Step 5	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute
Rinse Step 6	Solvent: Hexane Soak Time: 1:30 minute Air Dry Time: 1:00 minute

11.4 Sample Extract Concentration and Clean-up Procedures:

11.4.1 Extract Solvent Reduction, Florisil Clean-up Procedure and Internal Standard Addition:

11.4.1.1 The sample extract will have two phases, the top layer will be composed of the hexane used to elute components from the solid-phase disk and the bottom layer will be composed of residual water and acetone from the extraction process. Carefully transfer the top layer of solvent to either a 250mL turbo-tube or a 60mL VOA vial. Glassware selection depends on which solvent evaporator will be used (TurboVap concentrator uses the 250mL glassware and the TurboVap LV uses standard 60mL VOA vials.).

11.4.1.2 Backwash the residual water/acetone in the 60mL VOA collection vial three successive times with hexane (approximately 5mL) and add these rinses to either a 250mL turbo-tube or a 60mL VOA vial.

11.4.1.3 Take the volume of the extract to 50mL with hexane so that the evaporation rate will be equal for all the samples being concentrated.

11.4.1.4 Whether the sample extract is concentrated in the TurboVap or the TurboVap LV, the procedure is the same.

11.4.1.5 The TurboVap evaporator system is used to reduce the sample volume. The TurboVap uses a heated water bath and positive pressure nitrogen flow with vortex action. The unit maintains a slight equilibrium imbalance between the liquid and the gaseous phase of the solvent extract, which allows fractional reduction of the solvent without loss of higher boiling point analytes.

11.4.1.6 Turn the unit on and allow to heat up to 40°C $\pm$ 2°C.

11.4.1.7 As a precaution the TurboVap system regulators should be checked to assure that there is no residual gas pressure within the system and that the gas pressure regulator is off before placing samples in the apparatus. Residual gas pressure may cause splashing and therefore cause cross contamination of samples or loss of sample extract. To bleed the system of residual gas pressure, place an empty turbo-tube into the water bath and close lid. Make sure that the nitrogen gas pressure regulator is closed. Remove turbo-tube.

11.4.1.8 Wipe down the inside of TurboVap with a Hexane wetted paper towel including top lid and gas pins. Place turbo-tubes containing the sample extract into TurboVap and close lid. Slowly open the pressure regulator. Keep the gas pressure very low to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the volume reduction.

11.4.1.9 **DO NOT** leave the unit unattended as extracts may be blown to dryness and PCB loss may occur.

11.4.1.10 Concentrate the extract to approximately 5.0mL. Remove the turbo-tube or 60mL VOA vial from the evaporator unit. Carefully transfer the extract to a 15mL vial.

11.4.1.11 Rinse the turbo-tube or 60mL VOA vial three successive times with hexane (approximately 2mL) and add these rinses to the 15mL vial. Keep this turbo-tube or 60mLVOA vial to be used during the second concentration step.

11.4.1.12 To the extract add approximately 1.0g of deactivated Florisil and shake the sample by hand for approximately 15 seconds. Allow the Florisil to settle and transfer the extract to the 250mL turbo-tube or 60mL VOA vial used for the first concentration of the extract.

11.4.1.13 Backwash the Florisil three successive times with 2mL hexane and transfer these rinses to the 250mL turbo-tube or 60mL VOA vial.

11.4.1.14 Following procedures detailed above, concentrate the extract to approximately 2.0mL. Remove the turbo-tube or 60mL VOA vial from the evaporator unit. Carefully transfer the extract to a 5mL volumetric flask.

11.4.1.15 Rinse the turbo-tube or 60mL VOA vial with approximately 1.0mL of hexane and add this to the 5mL volumetric flask. Repeat this process two more times, adding the rinses to the 5mL volumetric flask. Make the extract to volume with hexane.

11.4.1.16 At this point the internal standard is added to the extract. Using a 10 micro-liter syringe, add 4.5 micro-liters of internal standard to the extract. Mix the extract by capping and inverting the volumetric several times. Transfer the extract to a 15mL vial.

11.4.2 Sulfuric Acid Clean-up:

11.4.2.1 Add approximately 2mL of the solvent washed concentrated sulfuric acid (NE174.doc) to each extract vial and shake by hand for 30 seconds. Place the vial in a bench top centrifuge and centrifuge on speed setting 5 for at least 1 minute. Transfer the extract (upper) layer to a correctly labeled, pre-rinsed 15mL vial.

11.4.3 Mercury Clean-up for sulfur Removal:

11.4.3.1 ***NOTE:*** Mercury is a highly toxic metal, all operations involving mercury should be performed within a fume hood. Prior to using mercury, the chemist should become aquatinted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the Material Safety Data Sheet (MSDS).

11.4.3.2 Using a disposable pasture pipette, add 3 drops of solvent washed Mercury (NE175.doc) to the sample extracts, cap and place on the wrist shaker for 30 minutes. The sulfur is converted to Mercuric Sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental Sulfur.

11.4.3.3 Transfer the extracts to pre-rinsed and labeled 15mL vials. Submit the sample extract vials, along with the Job Tracking Folder containing the GC Queue Lab Sheet to the GC department supervisor.

12.0 Calculations:

12.1 All calculations pertaining to data analysis and reporting can be found in the determinative method SOP NE207.

13.0 Method Performance:

13.1 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at a reasonable concentration above the low-level calibration standard and below the high-level calibration standard. The analyte will be added to a laboratory organic free water sample and taken through all extraction and analytical procedures. Aroclor 1242 is used as the analyte and recovery on a total basis is used to calculate percent recovery. To be valid, Aroclor 1242 will be recovered between the limits of 70 to 130 percent. Also, a percent relative standard deviation will be calculated for the replicates will be less than or equal to 20% to be valid.

13.2 Method Detection Limit: A method detection limit will be determined for this method. A minimum of seven laboratory organic free water samples will be prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

$$MDL = S * t_{(n-1,\ 1\text{-}alpha=0.99)}$$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1\text{-}alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)}$ = 2.998

13.2.1 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

14.0 Pollution Prevention:

14.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols.

14.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload.

14.3 For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

15.0 Data Assessment and Acceptance Criteria for Quality Control Measures and Corrective Actions for Out-of-Control Data:

15.1 The gas chromatographic (GC) department will interface with the extraction department about any problems or issues that arise once the sample extracts are analyzed and assessed for method compliance with quality control parameters or limits that are out of control. This interaction is on a case by case basis and both departments will need to work together to resolve problems with samples that require re-extraction if sample is available.

15.2 In general, most water samples collected in the field are completely consumed during the extraction process (the whole 1-liter water sample is extracted and the bottle rinsed with solvent and considered part of the sample extract) and therefore more sample is normally not available and re-extraction is not possible. Some field sampling programs require the collection of an additional 1-liter water sample (an archived sample) for each sampling site. For these instances, the archived water sample can be extracted (usually out of the 7 day hold time) and analyzed. A

sample case narrative would accompany the data report to explain the re-extraction. Typically the original data and the re-extract data would be provided to the client.

15.3 The GC analyst and the extraction chemist may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. A Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed with the data and is also useful for production of case narratives that are issued with final data reports.

15.4 For a complete outline of data assessment, acceptance criteria, and corrective action procedures for out-of-control refer to SOP NE207.

16.0 Contingencies for Handling Out-of-Control or Unacceptable Data:

16.1 Data that is detected to be out-of-control during sample analysis, when compared to method acceptance criteria, will be addressed in the following manner:

16.1.1 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out-of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

16.2 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

17.0 Waste Management:

17.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

17.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

18.0 References:

18.1 US EPA 40 CFR Part 136, “Guidelines Establishing Test Procedures for the Analysis of Pollutants,” July, 1988.

18.2 US EPA SW-846, “Test Methods for Evaluating Solid Waste Physical/Chemical Methods,” Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

APPENDIX 8

STANDARD OPERATING PROCEDURE

Author: Chad Biski
Reviewed by:

William A. Kotas

Approved by:

James D. Daly
Assistant Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Organics
SOP Name: NE005_05.SOP
Date:10-March-04
Revision: 05

1.0 TITLE Standard Operating Procedure for the extraction and cleanup of soil, sediment, and solid samples for Polychlorinated Biphenyl (PCB) analysis using the Soxhlet extraction technique by SW-846 Method 3540C for subsequent Analysis by SW-846 Method 8082.

2.0 PURPOSE The purpose of this SOP is to provide to the chemist the procedures required to perform extractions of PCBs, in soil/sediment/solid sample, using the soxhlet extraction technique and to perform the subsequent extract volume reduction and cleanup.

3.0 SCOPE The following procedure is utilized by Northeast Analytical, Inc. for the extraction and cleanup of PCBs from soil/sediment/solid samples using the soxhlet extraction method for analysis by SW-846 Method 8082.

4.0 COMMENTS Other extraction methods such as the sonication technique and automated solvent extraction may be used in place of the soxhlet extraction at the discretion of the supervising chemist. Time restraints (i.e. requested turn around time) may render this method inapplicable, as it requires 18 +/-2 hours of extraction reflux time. Extract cleanup steps employed may vary from sample to sample matrix to matrix.

5.0 SAFETY The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples.

Polychlorinated biphenyls have been tentatively classified as known or suspected carcinogens. The chemist must review the Material Safety Data Sheets (MSDS) for PCBs and all reagents used in the procedure before handling them. All equipment and solvents should be handled within a lab fume hood.

6.0 REQUIREMENTS The chemist must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3540, 3500, 2500A. An approved instructor must also certify the chemist to perform the procedure.

7.0 EQUIPMENT:

7.1 **Water Cooled Condenser:** Pyrex 45/50 #3840-MCO.

7.2 **250mL Round Bottom Flask:** Pyrex #4100.

7.3 **Soxhlet Repetitive Flushing (reflux) Unit:** 45/50 Pyrex #3740-M.

7.4 **Heating Mantle**: Type "VF" laboratory heating mantle #HM0250VF1. (or equivalent)

7.5 **Heating Mantle Controller:** Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

7.6 **Analytical Balance**: Mettler AG-245 used to determine sample mass.

7.7 **Cellulose Extraction Thimble:** Contains sample during soxhlet extraction.

7.8 **Sodium Sulfate:** Anhydrous (12-60 Mesh), washed with Hexane and baked overnight. Used for the laboratory method blank.

7.9 **Boiling Chips:** Chemware PTFE Boiling Stones P#0919120(or equivalent)

7.10 **Chiller:** Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

7.11 **Hexane:** High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

7.12 **Acetone:** High Purity Solvent Baxter (Burdick/Jackson) #UN1090. (or equivalent)

7.13 **TurboVap Evaporator:** Zymark #ZW640-3.

7.14 **TurboVap Evaporator concentrator tubes:** Zymark 250mL, 0.5mL endpoint.

7.15 **Beakers:** Assorted Pyrex: 250mL, 600mL, and 1000mL, used for liquid containment and pipette storage.

7.16 **1:1 Hexane/Acetone:** 50%/50% by volume solvent mixture prepared in the lab.

7.17 **Vials:** glass, 8 dram & 4 dram (with Polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

7.18 **Vial Rack:** Plastic rack used to hold vials, during all phases of the extract processing.

7.19 **Centrifuge:** International Equipment Co., Model CL. (or equivalent)

7.20 **Wrist Shaker:** Burrell wrist action shaker, Model 75 and 88. (or equivalent)

7.21 **Florisil:** deactivated, see NE094-05.doc, **SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.**

7.22 **TBA Reagent:** Tetrabutylammonium Hydrogen-Sulfite Reagent. (prepared in the laboratory)

7.23 **Mercury:** Triple distilled Mercury Waste Solutions, Inc, (or equivalent)

7.24 **Sulfuric Acid:** Na_2SO_4 (concentrated) Mallinkrodt #2468 #UN1830. (or equivalent)

7.25 **Pipettes:** S/P Disposable Serological Borosilicate Pipettes.
1. **1mL** X 1/10
2. **5mL** X 1/10
3. **10mL** X 1/10

Fisher Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

7.26 **4oz. Jars:** Industrial Glassware

8.0 PROCEDURES:

8.1 Sample Preparation

8.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should **STOP!** Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

8.1.2 Before any steps are taken, the chemist should first review the sample job folder and fill in the appropriate spaces on the internal sample tracking form and initial.

8.1.3 If the sample is sediment and contains a water layer, decant and discard the layer as aqueous PCB waste. Remove sample from container, using a metal spatula, into a mixing tray. Mix the sample thoroughly and discard any foreign objects such as sticks, rocks or leaves. **Note** however that the sample may be composed entirely of rock, concrete or some other solid material in which case the entire sample is treated as the solid.

8.2 Sample Extraction

8.2.1 Fill a Pyrex pan with ice cubes and cold water about 1/2 inch deep. As the samples are weighed out, place the beakers or 4oz. jars in the Pyrex pan to chill for at least 15 minutes prior to the drying step.

8.2.2 Rinse all extraction thimbles with Hexane to remove extraneous material. Place thimble into a 100 mL beaker and allow to dry.

8.2.3 Setup one 250 mL glass beaker or 4oz. jar for each sample. Using the first sample, label a beaker with the sample number, and tare the beaker. Using a metal spatula, add 10 g to 11 g of the wet sample to the beaker. Record the weight in the PCB solid extraction logbook. At this point, a sample for percent total solids may also be taken (see 8.2.4). Place the beaker in the ice bath to chill.

8.2.4 If the PCB concentration is to be determined on a dry weight basis the percent total solid must be determined. Weigh approximately 5 grams of the previously homogenized sample in a previously weighed, aluminum weighing pan. Record the weight of the pan and the weight of the (pan and sample) in the percent total solids log. Place the sample in a drying oven at 100 to 110°C for at least 8 hours. Record the time placed in the oven and the oven temperature in the percent total solids log. Remove the samples from the drying oven and allow to cool in a desiccator. Weigh the pan and sample.

Calculate the percent solids by:

$$\frac{\{(\text{wt. of pan + dried sample}) - (\text{wt.of pan})\}}{(\text{wt. of wet sample})} \times 100$$

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIDGERATOR. FOR ALL EMPTY SAMPLE CONTAINERS, SEE THE CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

8.2.5 After the sample has been sufficiently chilled, add approximately 10g of a 1:1 mix of Magnesium Sulfate/Sodium Sulfate to the sample and mix well with a metal spatula. If the sample has not dried after a few minutes, another 10g may be added. Once the sample is well-dried and free flowing, transfer the sample to a pre-rinsed extraction thimble. Repeat with remaining samples. Set empty mixing beaker and stirring utensil aside for later rinsing into soxhlet extractor to complete sample transfer. **Be careful not to add too much drying agent to the sample, if too much is added, the sample may not fit completely in the thimble. In this case the sample will have to be split into two different soxhlets.**

8.2.6 Add 200 mL of a 1:1 mixture of Hexane/Acetone to a 250 mL round bottom flask. Add several boiling chips. Place a soxhlet extractor on top of the round bottom flask. Label the round bottom with the sample number. Place the corresponding thimble into the soxhlet extractor. Rinse corresponding beaker & metal spatula with a few pipettes of

Hexane. Transfer into thimble. Repeat this step twice more with the same sample, and then repeat all preceding steps with remaining samples. After all samples have been processed, add the specified surrogate and matrix spikes required directly into thimble.

8.2.7 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the soxhlet extraction of the sample. Turn on chiller to cool the condensers.

8.2.8 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 5. At this time double check soxhlets for any cracks or chips which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

8.2.9 The samples should be extracted overnight for a minimum of 16 hours. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Once cool, rinse the inside of the condenser with several pipette volumes of Hexane. Disengage the soxhlet and condenser unit and rinse the joint off as well into the soxhlet.

8.2.10 Move soxhlet units into a chemical fume hood and flush the remaining solvent from the soxhlet extractor by tipping the soxhlet. Using a pair of long-handled tweezers, pull the thimbles out of the soxhlets one at a time and allow them to drip dry by balancing the thimbles on the tops of the soxhlets. Once dry; remove the thimbles to a Pyrex drying pan for total solvent evaporation.

8.2.11 Rinse the soxhlet with several pipettefull of Hexane and tip again to drain into the round bottom. Set the soxhlet aside at this time. Procure the same number of TurboTubes as there are samples. Using an individual TurboTube stand, label a TurboTube with the corresponding sample ID number and place in the holder. Pour the contents of the round bottom into the TurboTube, using a pipette and Hexane to rinse the last drops out of the mouth of the round bottom. Rinse the round bottom with several pipettefull of Hexane, swirl gently, and decant into same TurboTube. Repeat this step twice for same sample then repeat all preceding steps for all other samples.

8.2.12 All glassware must be rinsed with technical grade (tech)-Acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

8.3 Solvent Reduction: TurboVap Evaporator System

8.3.1 The TurboVap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The TurboVap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

8.3.2 Turn the unit on (switch is located on the back side of the unit) and allow to heat up to the specified temperature for individual solvent use. This is indicated by the "Heating" display light, located above the temperate control knob on the right side of the unit. The system is at the proper temperature when the "At Temperature" light is lit. This is located above the "Heating" display light.

8.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that gas pressure regulators is off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty TurboTube into the water bath and close the lid. Make sure that the nitrogen gas pressure regulator is turned off. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4. Make sure to wipe down all surfaces with Hexane before concentrating samples.

8.3.4 Place the TurboTube containing the samples into the TurboVap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

8.3.5 The process for solvent (Hexane/Acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

8.3.6 Concentrate the solvent to approximately 5.0 mL. Remove the samples from the TurboVap and place in the rack. **NOTE:** Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 5.0 mL point is achieved Samples, which stop reducing, should be removed as soon as possible.

8.3.7 Quantitatively transfer the sample extract with a Pasteur pipette into an appropriate volumetric flask (25ML for soil extracts). Rinse the TurboTube with 3 Pasteur pipettes of Hexane, and then transfer the Hexane rinse to the volumetric. Repeat the Hexane rinse two more times for a total of three Hexane rinses of the TurboTube. After the sample has been transferred, rinse the Pasteur pipette with 0.5mL of Hexane into the volumetric flask. Add Hexane to the volumetric meniscus mark. Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 8 dram vial.

8.3.8 All dirty glassware must be rinsed with tech-Acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

8.4 Sample Extract Cleanup

Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed. Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the analyst combined with the sampling site history should guide the selection of which clean-up procedures are necessary. The sample preparation chemist in the extraction logbook records the sequence and number of repeats of cleanup steps performed.

Sample extract cleanups are performed on set volume extracts. The set volume is 25 mL for soil/sediment/solid samples.

8.4.1 Sulfuric Acid Wash

8.4.2 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds that are co-extracted with the PCB residues.

8.4.3 Chill the sample to approximately 0□C. Add 5.0 mL concentrated H_2S0_4 and shake for 30 seconds by hand, centrifuge for approximately 1 minute, transfer approximately 20mLs of the Hexane upper layer to an 8 dram vial.

8.4.4 Repeat 8.4.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. **Note:** it is entirely possible that all colored material will not be removed from the extract.

8.5 Elemental Sulfur Clean-up

8.5.1 Elemental sulfur is soluble in the extract solvents used for sediment and soil samples. It is commonly found sediment/soil samples, decaying organic material and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

8.5.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

8.6 Removal of Sulfur Using Mercury

Note: Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.

8.6.1 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 minutes. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

8.6.2 Remove the sample extracts from the wrist shaker and place in the centrifuge for 2 minutes on speed setting on #4.

8.6.3 Transfer the sample extract to a new 8 dram vial.

8.6.4 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or Florisil slurry (discussed in 8.8.0).

8.7 Removal of Sulfur using TBA Sulfite

8.7.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water soluble.

8.7.2 Add 2.0mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 1 scoop (using the dedicated dispenser) of sodium sulfite crystals to the extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more scoops to the extract and observe.

8.7.3 Place the samples on the wrist shaker for 45 minutes observing at 15 minute intervals to make sure that the sodium sulfite is not consumed. Add 5mL organic free water and shake for ten minutes.

8.7.4 Place the samples into the centrifuge and spin for approximately 2 minutes on setting #4.

8.7.5 Transfer the Hexane layer to a new 8 dram vial and cap.

8.8 Florisil Adsorption (Slurry)

8.8.1 The Florisil slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

8.8.2 Add approximately 3 grams of tested and approved deactivated Florisil to each vial containing the sample extract. **SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.**

8.8.3 Vigorously shake the vial for approximately 1 min by hand or on the wrist shaker.

8.8.4 Place the vial(s) into the centrifuge for 2 minutes on setting #4.

8.8.5 Transfer the extract to a clean 8 dram vial.

8.9 Extract Screening and Dilution:

8.9.1 PCB extracts are generally screened by GC to determine the approximate concentration before final analysis. Prior site history and client supplied estimates of sample concentration may be used to determine what, if any, extract dilution is necessary. Extracts of unknown concentration are generally screened at a 10 to 100 fold dilution.

8.9.3 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of Hexane. For example, adding 1.0 mL of the extract to 9.0 Ml Hexane performs a 1 to 10 dilution. The vial containing the diluted extract is labeled denoting the equivalent extract volume after the dilution; e.g. a 25Ml extract diluted 1 to 10 is labeled “250X”, an undiluted 25Ml extract is labeled “25X”. When high dilutions are prepared, secondary (serial) dilutions of the initial diluent are prepared; e.g. a 100 fold dilution is prepared by a 1 to 10 dilution of the initial extract, then a 1 to 10 dilution of the resulting diluent.

8.9.3 Perform the dilution using appropriate class “A” disposable volumetric pipettes to transfer the extract and to add the make-up volume of Hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

8.9.4 Transfer 1 mL of the extract to a labeled 1.5 mL GC autosampler vial. Record the screening dilution on the GC Queue Lab Sheet (LIMS spreadsheet) along with the extract volume, the sample mass, and the percent total solids. Submit the GC Queue Lab Sheet with the sample extracts to the GC analyst.

8.10 Sample Extract Storage

Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C) during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements. The auto-sampler vial to be used for frozen storage will be filled to the neck of the vial. If the vial cannot be filled to the neck due to multiple analyses being performed, whatever remains will be placed in the vial and the volume marked. The volume level will be marked on all vials.

9.0 Pollution Prevention and Waste Management

9.1 Pollution Prevention: see NEA168.SOP

9.2 Waste Management: see NEA054.SOP, NEA083.SOP, NEA089.SOP

10.0 References

1. U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

2. "Guide to Environmental Analytical Methods", Third Edition, Genium Publishing Corporation, 1996.

11.0 Attachments

1. Method Outline

PCBs IN SOIL/SEDIMENT
OUTLINE FOR SOXHLET EXTRACTION

1. **PREPARE SAMPLE FOR PREPARATION**
2. **RINSE EXTRACTION THIMBLES**
3. **WEIGH SAMPLE AND RECORD WEIGHT**
4. **DRY SAMPLES**
5. **ADD SAMPLE TO THIMBLES**
6. **SET UP SOXHLET EXTRACTOR APPARATUS**
7. **ADD SURROGATES AND/OR MATRIX SPIKE**
8. **EXTRACT SAMPLE FOR APPROXIMATELY 16 HOURS**
9. **BREAKDOWN SOXHLET EXTRACTOR APPARATUS**
10. **TRANSFER SOLVENT TO TURBOTUBE**
11. **SOLVENT REDUCTION, USING THE ZYMARK TURBOVAP EVAPORATION SYSTEM**
12. **TRANSFER AND SET VOLUME**
13. **EXTRACT CLEANUP (ACID, MERCURY OR TBA, FLORISIL)**
14. **EXTRACT DILUTION**
15. **GC SCREENING/ ANALYSIS**

APPENDIX 9

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE207_03.DOC

REVISION NUMBER: 03

STANDARD OPERATING PROCEDURE FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) ANALYSIS

(Low-level Calibration Method)

METHOD FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) QUANTIFICATION AND IDENTIFICATION BY CAPILLARY COLUMN/GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

March 8, 2004

COPY #_____

NORTHEAST ANALYTICAL, INC.
2190 TECHNOLOGY DRIVE
SCHENECTADY, NEW YORK 12308
(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY METHOD NE207_03.DOC

REVISION 3 (3/8/2004)

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Author: Robert E. Wagner

Reviewed by:

William A. Kotas/Quality Assurance Officer

Approved by:

Robert E. Wagner/Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Organics Laboratory
SOP Name: NE207_03.DOC
Date: 3/8/2004
Revision: 03

Lab Method NE207_03.SOP

Congener-Specific Polychlorinated Biphenyl (PCB) Analysis

(Low-level Calibration Method)

Method for Congener-Specific Polychlorinated Biphenyl (PCB) Quantification and Identification by Capillary Column/Gas Chromatography with Electron Capture Detection

1.0 Scope:

1.1 This method is applicable in the determination and quantification of Polychlorinated Biphenyls (PCB) in water. This method is a congener-specific determination, employing a high resolution fused-silica capillary chromatographic column. The method has been, in part, developed from the following documents:

1.) "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office", prepared by Deborah L. Swackhamer, Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987. This document outlines quality assurance and quality control procedures to be followed by laboratories participating in the Green Bay Mass Balance Study. Where applicable, Northeast Analytical, Inc., will incorporate and utilize this information in quality control of data generated. Instrumental analysis and conditions (Mullin, M.D., 1985, PCB Workshop, US EPA Large Lakes Research Station, Gross Ile, MI, June.) cited in the Green Bay Mass Balance Study document will be refined to be applicable to an in-house data management software package.

2.) "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns", George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996. This journal publication provides complete assignment of all 209 PCB congeners to the GC peaks separable on a DB-1 capillary column. It also provides weight percent information for PCB congeners in Aroclor formulations used in labeling protocols for reporting purposes.

3.) "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", USEPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2. This USEPA SOP summarizes M. Mullin's congener composition of the mixed Aroclor standard used for calibration.

4.) "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10. This LLRS SOP written by M. Mullin summarizes the calibration composition of the mixed Aroclor standard reported in "Mullin, M.D., PCB Workshop, U.S. EPA Large Lakes Research Station, Grosse Ile, MI, June 1985.

1.2 This gas chromatographic capillary column method, utilizing an electron capture detector, will effectively separate 112 or more peaks representing 209 PCB congeners.

2.0 Summary of Method:

2.1 This method provides detailed instructions for gas chromatographic conditions for analysis of PCBs by capillary gas chromatography.

2.2 This method utilizes a mixed Aroclor standard (Aroclor 1232/1248/1262 in the ratio of 25:18:18) for calibration. A three- or four-point internal standard calibration will be performed for quantification. Method detection limit and practical quantitation limit will be established experimentally using the procedure in USEPA 40 CFR, Part 136, App. B.

2.3 In general, samples are first extracted with a pesticide-grade solvent. The extracts are further processed through a series of clean-up techniques. The sample is then analyzed by direct liquid injection onto the gas chromatographic column and detected by an electron capture detector. This method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

2.4 A key component of this method is the importance placed on the chromatographic separation that must be achieved for this congener specific technique. A total of 112 chromatographic peaks are detected, containing 209 PCB congeners in various ratios. This allows an almost complete profile of environmentally occurring PCBs.

3.0 Definitions:

3.1 Surrogate Analyte: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are added to all laboratory method blanks, laboratory QC reference samples (Laboratory Control Spikes), laboratory duplicates, calibration and continuing check standards, field samples, field duplicate samples, field matrix spike samples, field matrix spike duplicate samples prior to extraction and/or analysis. Percent recovery is calculated for each surrogate to assess extraction efficiency.

3.2 Stock Standard Solution: A concentrated standard solution containing the method analytes. This stock standard can be used to prepare other more dilute standards.

3.3 Primary Standard Solution: A solution of several analytes prepared from stock solutions that can be diluted as needed to prepare calibration solutions and to prepare other standard solutions.

3.4 Calibration Standard: A series of known standard solutions used by the analyst for instrument calibration. Calibration standards are prepared are prepared from primary standard and/or stock standard solutions.

3.5 Continuing Calibration Check Standard: An analytical standard that is prepared from an alternate source than the one used to prepare the calibration standards. The continuing calibration check standard contains all the target analytes found in the calibration standards and is used to verify that the initial calibration is prepared correctly and that the instrument system is correctly calibrated as defined by the method calibration criteria.

3.6 Laboratory Method Blank: A laboratory derived sample consisting of reagent water or other blank matrix that consists of all reagents, internal standards and surrogate standards, that is carried through the entire analytical procedure. The laboratory method blank is used to define the level of laboratory analyte background or other interferences that exist in the laboratory environment, the reagents, or the apparatus.

3.7 Laboratory Control Sample (LCS): Also known as the Quality Control (QC) Check Standard or Quality Control (QC) Check Sample. The LCS consists of an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added. The LCS is extracted and analyzed exactly like a field sample, and its purpose is to determine whether the analysis is in control and whether the laboratory is capable of making accurate and precise measurements.

3.8 Sample Matrix Spike/Sample Matrix Spike Duplicate (MS/MSD): An aliquot of a field sample that is fortified with known quantities of the method analytes and subjected to the entire analytical procedure. Its purpose is to assess the appropriateness of the method for the matrix by measuring recovery.

4.0 Interference:

4.1 One of the major sources of interference in the analysis of PCBs is from organochlorine pesticides that are co-extracted from the samples. Several of these ECD responding pesticides can be separated cleanly from the PCB profile by the resolving characteristics of the capillary column. Several of the commonly found pesticides and degradation products (DDT, DDE, DDD) overlap the PCB profile envelope and co-elute with several of the PCB congeners found in environmental samples. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in total PCB values generated.

4.2 The sample matrix itself is also a potential source for method analyte interference. Sample preparation, extraction procedures, and extract clean-up protocols are covered in separate SOPs that deal exclusively with sample extraction and clean-up procedures.

4.3 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters exhibit response on

electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

5.0 Safety:

5.1 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets (MSDS) to familiarize themselves with the hazards of handling the compounds used for standards and samples.

5.2 Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, all solvents and standards should be manipulated in a chemical fume hood. All sample extracts should be manipulated in a chemical fume hood.

6.0 Equipment and Apparatus:

6.1 Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Northeast Analytical, Inc. will use an Agilent Model 6890 gas chromatograph (or equivalent), equipped with a capillary split/splitless injector (or equivalent), temperature programmable oven, Model 7683 automatic sampler (or equivalent), and Micro-ECD electron capture detector (or equivalent). A data system (Waters Associates, Millennium_32 Workstation or equivalent) for chromatographic operations and integration of detector signal is interfaced to the gas chromatograph.

6.1.1 GC Column: The gas chromatograph column to be used for analysis will be a DB-1 (J&W Company), bonded polydimethylsilicone, 30 meter fused silica capillary column with an internal diameter of 0.25mm and phase coating thickness of 0.25 microns. This column is capable of resolving 112 chromatographic peaks from the full spectrum of all PCB congeners that could be expected in an environmental sample. Refer to Appendix A and Appendix B for a complete description of PCB congeners identified in each GC chromatographic peak and achievable chromatographic separations.

6.2 Chromatograph Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates), will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

6.3 Volumetric Flasks: 10, 50 and 100mL, ground-glass stopper. For standard preparation.

6.4 Microsyringe: 10, 100, 500 and 1000uL for standard preparation.

6.5 Pipettes: Class A volumetric, 1mL, 5mL, and 10mL.

6.6 Vials: Glass, 10 and 20mL capacity for sample extracts.

6.7 Bottles: Glass, 120mL capacity for standard storage.

7.0 Reagents and Standards:

7.1 Solvents: Pesticide grade quality. Hexane, acetone, toluene, methylene chloride.

7.2 Octachloronaphthalene: Obtained from Ultra Scientific (Hope, RI) with a purity greater than 95%.

7.3 Polychlorinated Biphenyls: Neat commercial material or solutions for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as transformers and capacitors. Monsanto was the largest producer of PCB formulations and sold them under the tradename Aroclor.

7.4 PCB Congeners: A complete set of all 209 PCB congeners to individually verify the exact elution on the chosen chromatographic system. A subset of congeners is also used as a secondary supplemental calibration standard for those congeners that do not exist at a high enough level in the Aroclor based calibration standard. Obtained from AccuStandard or Ultra Scientific.

7.5 Stock Standard Solutions:

7.5.1 Stock standards are prepared from individual neat Aroclor formulations by weighing approximately 0.1000g to the nearest 0.2 mg and dissolving and diluting to volume in a 100mL volumetric flask with hexane. This will give a stock concentration of 1,000ug/mL.

7.5.2 The stock standard is transferred into screw-cap 120mL boston bottles and stored in a refrigerator, protected from light. Stock standards should be checked at frequent intervals for signs of evaporation, especially just prior to preparing calibration standards.

7.5.3 Stock PCB standards must be replaced after one year, or sooner if comparison with continuing calibration check standards indicate a problem.

7.5.4 Stock standards for the following are prepared by the above procedure:

Aroclor 1232
Aroclor 1248

Aroclor 1262

7.6 Mixed Aroclor Stock Standard at 62.7ug/mL: A primary standard is prepared at 62.7ug/mL that is used for preparing secondary stock standards and calibration standards. This stock standard is prepared by combining Aroclor 1232, Aroclor 1248, and Aroclor 1262 in a 25:18:18 ratio with a final mixture concentration of 25.7ug/mL, 18.6ug/mL, and 18.4ug/mL respectively (total=62.7ug/mL). These ratios are strictly maintained so that the percent composition data remains applicable, since it was developed for use under these fixed mixture parameters. The final concentration of the mixed standard may vary to accommodate instrument sensitivity or more closely represent sample concentrations, but the same ratio values must be maintained. Using a 5.0mL Class A pipette, accurately add 2.49mL of stock Aroclor 1232 standard (1,033ug/mL) to a 100mL volumetric flask. Using a 2.0mL Class A pipette, accurately add 1.82mL of stock Aroclor 1248 standard (1,019ug/mL) and 1.80mL of stock Aroclor 1262 standard (1,024ug/mL) to the same 100mL volumetric flask. Make volume to the 100mL mark with hexane.

7.6.1 Store the Mixed Aroclor Stock Standard at 62.7ug/mL in a refrigerator in a tightly capped bottle. This standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

7.7 Mixed Aroclor Secondary Stock Standard at 6.27ug/mL: The secondary stock standard is prepared from the 62.7ug/mL mixed Aroclor stock standard. Using a 10.0mL Class A pipette, accurately add 10.0mL of the 62.7 stock standard into a 100mL volumetric flask. Make to volume with hexane. Transfer the standard solution to a 120-ml boston bottle and store in a refrigerator.

7.7.1 The 6.27ug/mL Secondary Stock Standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

7.8 Mixed Aroclor Calibration Standard 1 at 313.5ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 1 at 313.5ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 5.0mL Class A pipette, accurately transfer 2.5mL of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 1 of 313.5ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 1 at 313.5ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months.

7.9 Mixed Aroclor Calibration Standard 2 at 125ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 2 at 125ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 1.0mL Class A pipette, accurately transfer 1.0mL of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 2 of 125ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 2 at 125ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months.

7.10 Mixed Aroclor Calibration Standard 3 at 12.5ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 3 at 12.5ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 100-microliter syringe, accurately transfer 100 microliters of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 3 of 12.5ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 3 at 12.5ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months.

7.11 Mixed Aroclor Secondary Stock Standard at 125ng/mL: The Mixed Aroclor Secondary Stock Standard at 125ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL. Using a 1.0mL Class A pipette, accurately transfer 1.0mL of the Mixed Aroclor Secondary Stock Standard at 6.27ug/mL into a 50mL volumetric flask. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Secondary Stock Standard of 125ng/mL. The Mixed Aroclor Secondary Stock Standard at 125ng/mL must be replaced after six months.

7.12 Mixed Aroclor Calibration Standard 4 at 6.25ng/mL with Internal Standard (OCN) at 18.18ng/mL: The Calibration Standard 4 at 6.25ng/mL with Internal Standard (OCN) at 18.18ng/mL is prepared from the Mixed Aroclor Secondary Stock Standard at 125ng/mL and the Internal Standard Calibration Standard at 20.2ug/mL. Using a 5.0mL Class A pipette, accurately transfer 2.50mL of the Mixed Aroclor Secondary Stock Standard at 125ng/mL into a 50mL volumetric flask. Into the same 50mL volumetric flask transfer, using a 100-microliter

syringe, 45 microliters of the 20.2ug/mL Internal Standard Calibration Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Mixed Aroclor Calibration Standard 4 of 6.25ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Mixed Aroclor Calibration Standard 4 at 6.25ng/mL with Internal Standard at 18.18ng/mL must be replaced after six months. This calibration standard will be analyzed to produce a four-point calibration curve for the majority of the DB-1 peaks/congeners. There are, however, 22 DB-1 peaks that cannot be measured in Calibration Standard 4 and only a three-point calibration curve will be generated for the following peaks: DB-1 peaks 10, 13, 20, 44, 52, 55, 56, 67, 72, 79, 84, 87, 89, 91, 98, 101, 104, 108, 111, 113, 114, and 118.

7.13 Supplemental Congener Standard: A Supplemental Congener Standard is analyzed along with the four calibration standards. This standard contains congeners that exist at low levels in the mixed Aroclor standard and comprises congeners that are not typically found in Aroclor formulations, but could become important in by-product PCB analysis or the study of model experiments that use unusual PCB congeners. This standard is analyzed to supply accurate retention time information and response factors for quantification.

7.13.1 Supplemental Congener Stock Standard at 2.00ug/mL: All stock standards are purchased as solutions at 100ug/mL from Ultra Scientific. All supplemental congeners are diluted together (except 3-Chlorobiphenyl) to 2.00ug/mL. Using a 1000uL syringe, pipette 2.0mL of the 100ug/mL stock standard into the same 100mL volumetric flask and make to volume with hexane. The 3-Chlorobiphenyl, due to its low ECD response, will be added to the secondary stock standard. Transfer the standard solution to a 120mL boston bottle and store in a refrigerator. This stock standard must be replaced after one year.

7.13.2 Supplemental Congener Secondary Stock Standard at 0.0500ug/mL: Into a 50mL volumetric flask pipette, using a 1000uL syringe, 1.25mL of the Supplemental Congener Stock Standard. To the same 50mL volumetric flask pipette, using a 1000uL syringe, 1.0mL of the 3-Chlorobiphenyl purchased stock standard at 100ug/mL. To the same 50mL volumetric flask pipette, using a 100uL syringe, 45uL of the Octachloronaphthalene Stock Standard at 202ug/mL. Make to volume with hexane and transfer the standard solution to a 120mL boston bottle and store in a refrigerator. The octachloronaphthalene is used as an internal standard for instrument calibration and is at a concentration of 0.1818ug/mL in the standard. The standard concentration is 2.00ug/mL for 3-Chlorobiphneyl and 0.050ug/mL for all other congeners in the standard.

7.13.3 Supplemental Congener Calibration Standard at 0.00500ug/mL: The Supplemental Congener Calibration Standard is prepared by a 10-fold dilution of the Supplemental Congener Secondary Stock Standard at

0.0500ug/mL. Into a 50mL volumetric flask, using a 5mL Class A pipette, transfer 5.0mL of the Supplemental Congener Secondary Stock Standard at 0.0500ug/mL. Make to volume with hexane and transfer the standard solution to a 120mL boston bottle and store in a refrigerator. The standard concentration is 0.200ug/mL for 3-Chlorobiphneyl and 0.00500ug/mL for all other congeners in the standard. The octachloronaphthalene is used as an internal standard for instrument calibration and is at a concentration of 0.01818ug/mL in the standard. The following table lists the congeners included in this standard and the DB-1 peaks where they elute and also lists the other non-Aroclor congeners that co-elute with these 14 congeners. The Supplemental Congener Calibration Standard must be replaced after one year.

Supplemental Congener Standard Calibration Standard

DB-1 Peak Number	IUPAC Congener Number	(IUPAC #) PCB Congener Analyzed		Conc ug/mL
3	2	(2)	3-Chlorobiphenyl	0.200
9	14	(14)	3,5-Dichlorobiphenyl	0.00500
11	30	(30)	2,4,6-Trichlorobiphenyl	0.00500
12	11	(11)	3,3'-Dichlorobiphenyl	0.00500
19	23,34,54	(34)	2',3,5-Trichlorobiphenyl	0.00500
28	36	(36)	3,3',5-Trichlorobiphenyl	0.00500
30	39	(39)	3,4',5-Trichlorobiphenyl	0.00500
35	62,65	(65)	2,3,5,6-Tetrachlorobiphenyl	0.00500
36	35	(35)	3,3',4-Trichlorobiphenyl	0.00500
41	68,96	(96)	2,2',3,6,6'-Pentachlorobiphenyl	0.00500
43	57,103	(103)	2,2',4,5',6-Pentachlorobiphenyl	0.00500
62	154	(154)	2,2'4,4',5,6'-Hexachlorobiphenyl	0.00500
68	123	(123)	2',3,4,4',5-Pentachlorobiphenyl	0.00500
70	140	(140)	2,2',3,4,4',6'-Hexachlorobiphenyl	0.00500
76	127,168,184	(127)	3,3',4,5,5'-Pentachlorobiphenyl	0.00500

7.14 Internal Standard Stock Standard at 202ug/mL: The internal standard used for capillary gas chromatography of PCBs will be octachloronaphthalene (OCN). Weigh 10.1mg of solid octachloronaphthalene (OCN) into a 5mL vial. Quantitatively transfer the OCN using six successive 2-mL washings of toluene to a 50mL volumetric flask. Be sure to rinse the 5mL vial walls carefully so that all OCN is completely transferred to the 50mL volumetric flask. Make the solution to volume using toluene and mix the internal standard solution by shaking the flask several times. This will give a concentration of OCN of 202ug/mL. Carefully transfer the internal standard solution to 25mL vials, tightly cap, and store in a refrigerator. OCN internal standard must be replaced after one year.

7.15 Internal Standard Calibration Standard at 20.2ug/mL: The Internal Standard Calibration Standard is prepared from the Internal Standard Stock Standard. Into a 10mL volumetric flask, using a 1mL Class A pipette, transfer 1.0mL of the Internal Standard Stock Standard at 202ug/mL. Make to volume with toluene and transfer the standard solution to a 5mL reacti-vial with a Teflon syringe-valve cap and store in a refrigerator. This will give a concentration of OCN of 20.2ug/mL. The react-vial minimizes evaporation since the cap does not have to be removed.

7.15.1 The OCN internal standard is added to all calibration standards, continuing check standards, blanks, samples, and QC samples at the same amount. In most cases this will be achieved by spiking 4.5uL of OCN internal standard solution at 20.2ug/mL to 5mL of standard or sample extract to give a concentration of 0.01818ug/mL.

7.15.2 The internal standard will be added to calibration standards, sample extracts, blanks, and QC samples prior to gas chromatographic analysis. Thus, the internal standard is used as a quantification spiking standard and will eliminate sample injection volume variations, but will not correct for analytical losses during sample preparation.

7.15.3 OCN internal standard must be replaced after one year.

7.16 Surrogate Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 100ug/mL: The surrogate stock standard is prepared from a solid standard. Weigh 5.0mg of the solid surrogate standard into a solvent rinsed 10mL vial. Quantitatively transfer the surrogate standard using six successive 2-mL washings of hexane to a 50mL volumetric flask. Be sure to rinse the 10mL vial walls carefully so that the entire surrogate standard is completely transferred to the 50mL volumetric flask. Make to volume with hexane and mix the surrogate standard solution by shaking the flask several times. This will give a concentration of surrogate standard of 100ug/mL. Carefully transfer the surrogate standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. The surrogate standard must be replaced after one year.

7.17 Surrogate Secondary Stock Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 20.0ng/mL with Internal Standard at 181.8ng/mL: The Surrogate Secondary Stock Standard is prepared from the 100ug/mL Surrogate Stock Standard and the 202ug/mL Internal Standard Stock Standard. Into a 100mL volumetric flask, using a 50-microliter syringe, transfer 20uL of the Surrogate Stock Standard at 100ug/mL. Into the same 100mL volumetric flask transfer, using a 100-microliter syringe, 90 microliters of the 202ug/mL Internal Standard Stock Standard. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Surrogate Secondary Stock Standard of 20ng/mL and Internal Standard (OCN) of 181.8ng/mL. The Surrogate Secondary Stock Standard with Internal Standard must be replaced after six months.

7.18 Surrogate Standard (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) at 2.00ng/mL with Internal Standard at 18.18ng/mL: The Surrogate Standard is prepared from the 20.0ng/mL Surrogate Secondary Stock Standard with Internal Standard at 181.8ng/mL Into a 50mL volumetric flask, using a Class A 5mL pipette, transfer 5.0mL of the Surrogate Secondary Stock Standard at 20.0ng/mL with Internal Standard at 181.8ng/mL. Make to volume with hexane and transfer the standard solution to a 125mL boston bottle, tightly cap, and store in a refrigerator. This will give a concentration of Surrogate Standard of 2.00ng/mL and Internal Standard (OCN) of 18.18ng/mL. The Surrogate Stock Standard with Internal Standard must be replaced after six months. This standard is used to calibrate the gas chromatograph to measure surrogate recoveries in field samples and QC samples.

7.19 Continuing Calibration Check Standard: A continuing calibration check standard at 0.122ug/mL is prepared from Aroclor solutions obtained from a different source (ULTRA Scientific) than the calibration standard. The continuing calibration check standard is a mixed Aroclor 1232, 1248, and 1262 in the fixed ratio used to prepare the calibration standard and must be strictly adhered to.

7.19.1 50.0ug/mL Continuing Calibration Check Stock Standards: Aroclor 1232, Aroclor 1248, and Aroclor 1262 are obtained from ULTRA Scientific at 1000ug/mL in isooctane. Using a 500uL syringe transfer 0.5mL of 1000ug/mL Aroclor 1232 to a 10.0mL volumetric flask and make to volume with hexane. This procedure is repeated for Aroclor 1248 and Aroclor 1262. The 50ug/mL stock standards are transferred to a 10mL vial, tightly capped and stored in a refrigerator. These stock standards must be replaced after one year.

7.19.2 1.22ug/mL Continuing Calibration Check Standard without OCN: Using a 1000uL syringe transfer 1.0mL of 50.0ug/mL Aroclor 1232, 0.72mL of 50.0ug/mL Aroclor 1248, and 0.72mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 1.22ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

7.19.2.1 Transfer the 1.22ug/mL Continuing Calibration Check Standard without OCN to a 120mL boston bottle, cap tightly, and store in a refrigerator. A new continuing calibration check standard must be prepared every six months. This continuing calibration check standard without OCN is used to prepare the 0.122ug/mL Continuing Calibration Check Standard with OCN.

7.19.3 0.122ug/mL Continuing Calibration Check Standard with OCN: Using a 10.0mL Class A pipette transfer 10.0mL of 1.22ug/mL Continuing Calibration Check Standard without OCN to a 100mL volumetric flask. Using a 100uL syringe, add 90.0uL of 20.2ug/mL OCN internal standard (final concentration of 0.01818ug/mL). Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 0.122ug/mL PCB (0.050ug/mL Aroclor 1232, 0.036ug/mL Aroclor 1248, and 0.036ug/mL Aroclor 1262).

7.19.3.1 Transfer the 0.122ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a refrigerator. A new continuing calibration check standard must be prepared every six months.

8.0 Sample Collection, Preservation, Shipment and Storage:

8.1 Sample Collection and Preservation:

8.1.1 Routine 1-liter water samples should be collected in 1-liter clear glass narrow-mouth bottles, fitted with a Teflon-lined cap. The bottles should be pre-cleaned to EPA specification protocol A - recommended for extractable organic, semivolatile and pesticide analysis. Protect samples from light. Low-level water samples should be collected in 4-liter amber jugs, fitted with a Teflon-lined cap. Two 4-liter jugs should be collected for each sample, providing an 8-liter sample for processing. The specific requirements for sample collection at the site is outlined and detailed by the client.

8.1.2 All samples must be placed on ice or refrigerated at 4°C (±2°C) from the time they are collected until delivery to the lab.

8.2 Sample Shipment:

8.2.1 Sample shipment is accomplished through a carrier such as Federal Express or United Postal Service for overnight 1-day delivery to the lab. Shipment is normally handled by the field personnel collecting the samples and coordinated with sample receiving department at the lab. Samples can also be picked up by the lab courier service if samples are collected within driving distance to the lab.

8.3 Sample Storage:

8.3.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from time of receipt until they are removed from storage for extraction. Typically the entire water sample grab will be consumed at time of extraction and no sample is left for log-term storage.

8.3.2 Low-level water samples are stored in a refrigerator dedicated for this type of sample to further minimize exposure to potential contaminants.

8.4 Sample Extract Storage:

8.4.1 Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C) during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements.

8.4.2 Field samples, sample extracts, and calibration standards must be stored separately.

8.5 Required Holding Times:

8.5.1 Extraction of water samples by appropriate technique must be completed within seven days from sample collection.

8.5.2 Sample extracts must be analyzed within forty days of sample extraction.

9.0 Quality Control:

9.1 The following table lists the Quality Control samples required for capillary gas chromatography analysis of PCBs.

Quality Control Requirements

QC Sample	Frequency
Lab Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Cont Cal Check Std	Analyzed prior to each sample batch and at a frequency of one per ten injections. Each analytical sequence must close with a Continuing Calibration Check Standard.
Duplicate Analysis	Field generated sample – analyzed at discretion of client
Matrix Spike	One matrix spike per 20 field samples or designated sample batch may be performed as specified in the client site plan.
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples or designated sample batch may be performed as specified in the client site plan.

9.1.1 Laboratory Blank: The laboratory blank will monitor and assess whether contamination or excessive interference is occurring from laboratory solvents, reagents, and glassware used in processing samples for analysis. The laboratory blank is taken through the sample extraction and clean-up procedures to include all manipulations exposed to actual samples (required volume of solvents, concentration steps, clean-up procedures, *etc*.) If the laboratory blank is positive for PCB above the reporting limit (based on Total PCB concentration), the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis. The laboratory blank will consist of organic free water for water samples.

9.1.1.1 Samples associated with a positive laboratory blank should be flagged when the data is reported. If a laboratory blank is positive for PCBs, the source of contamination must be located and eliminated. If the contamination occurred during the extraction procedure and more sample is available the samples will require re-extraction and re-analysis. If the contamination occurred after this step, then re-extraction may not be required and the existing extracts will be reanalyzed. Any aliquots of the extracts (*i.e.,* injection vials), which could have become contaminated, will be discarded.

9.1.2 Laboratory Control Spike: A Laboratory Control Spike sample is analyzed with each extraction batch. An Aroclor is spiked into organic free water. This Control Spike must achieve a percent recovery of 60 to 140 percent based on Total PCB concentration. If the Control Spike recovery is not within limits, the cause must be tracked down and corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no more sample is available, the data must be flagged to indicate low or high Control Spike recovery.

9.1.3 Continuing Calibration Check Standard: As outlined in Section 9.1.8, a Continuing Calibration Check Standard will be analyzed on each working day prior to sample analysis and at an interval of one Continuing Calibration Check Standard per 10 samples. The Continuing Calibration Check Standard must meet the acceptance criteria established in Section 10.3.2.1. If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the following guidance must be followed.

9.1.3.1 If samples are being run using an autoanalyzer (*i.e.,* the instrument is unattended) and a Continuing Calibration Check Standard that fails to meet the acceptance criteria is

present in the analytical sequence but acceptable Continuing Calibration Check Standards are observed later in the analytical sequence, samples bracketed by acceptable Continuing Calibration Check Standards will be reported.

9.1.3.2 If the reason for the failure of the Continuing Calibration Check Standard appears to be a poor injection (or a degraded standard solution), the Continuing Calibration Check Standard will be re-injected (or reprepared and re-injected) immediately following the failed Continuing Calibration Check Standard. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the Continuing Calibration Check Standard meets all the acceptance criteria established in Section 10.3.2.1 and there is no apparent impact on the sample data (*i.e.,* acceptable internal standard areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported.

9.1.3.3 If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the initial calibration standards must be re-analyzed and new response factors generated. After re-calibration, the Continuing Calibration Check Standard must be analyzed again and compared to the acceptance criteria. If the Continuing Calibration Check Standard fails to meet the acceptance criteria after re-calibration, sample analysis must not proceed until the problem is corrected.

9.1.3.4 All samples that were analyzed directly before or after the Continuing Calibration Check Standard exceeded established criteria must be re-analyzed.

9.1.4 Duplicate Analysis: Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, so that identification with original sample is withheld. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike / matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

$$RPD = (DUP1 - DUP2)/AVG \times 100$$

Where: RPD = Relative Percent Difference.
DUP1 = The greater of the measured values.

DUP2 = The lesser of the measured values.
AVG = Average of the two analysis.

9.1.4.1 The relative percent difference must be less than or equal to 30%.

9.1.5 Matrix Spike and Matrix Spike Duplicate (MS/MSD): Spiked sample matrix data are analyzed to assess analytical accuracy and recovery of analytes of interest. Thus the sample is spiked and carried through sample analytical procedures including extraction, clean up, and GC analysis. Depending on the specific project plans and at the discretion of the client a matrix spike or matrix spike and matrix spike duplicate can be analyzed.

9.1.5.1 There must be sufficient sample for analysis of matrix spike/matrix spike duplicate samples and the sample must be homogeneous in PCB distribution for valid data to be produced. Spike MS and/or MSD samples with the Aroclor matrix spike standard at a concentration approximately two to five times the sample concentration. Extract and analyze the two spiked samples following procedures used for actual sample analysis. Calculate the percent recovery of the matrix spike/matrix spike duplicate by the following equation:

$$P = A-B/T \times 100$$

Where: P = Percent recovery, %.
A = concentration of analyte in the spike sample aliquot
T = Known true value of the spike concentration
B = Background concentration of PCB in the unspiked sample aliquot

9.1.5.2 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 60% and less than or equal to 140% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

9.1.6 Surrogates: Surrogate-spiking compounds monitor the exaction efficiency and sample processing procedures for each sample. Surrogate compounds are chosen which do not chromatographically interfere with the PCB target congeners and which behave similarly to the target PCB congeners during extraction and sample processing.

9.1.6.1 Surrogate spike additions are made to each field sample, method blank, and extracted QC check sample prior to extraction. Congener IUPAC 207 (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) is used as the surrogate spike compound.

9.1.6.2 Calculate the surrogate percent recovery as follows:

% Recovery = (Surr. Amount spiked / Theoretical Spike conc.) * 100

9.1.6.3 The percent recovery limits for the surrogate:

IUPAC 207 60% - 140%

9.1.7 Retention Time Windows:

9.1.7.1 Refer to the table entitled "Quality Control Acceptance Criteria and Corrective Action Plan" in Section 15.4 for retention time window and retention time shift acceptance criteria and corrective action.

9.1.7.2 The Initial Continuing Calibration Check Standard of each analytical sequence is used to establish the retention time window for each analyte. The retention time window equals the absolute retention time of the Initial Continuing Calibration Check Standard for a given batch of samples ±0.07 minutes.

9.1.7.3 Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-response sample analysis.

9.1.8 Analytical Sequence Queue:

A typical analytical sequence is as follows:

1)	Initial Continuing Calibration Check Standard
2)	Method Blank
3)	Lab Control Spike
4 to 10)	Samples (including Duplicates, MS/MSD)
11)	Continuing Calibration Check Standard
12 to 20)	Samples (including Duplicates, MS/MSD)
21)	Continuing Calibration Check Standard; repeat 12 to 20

10.0 Calibration and Standardization:

10.1 Calibration:

10.1.1 Gas chromatographic Operation Parameters:

Establish the gas chromatographic operation parameters as follows:

GC Column: DB-1 (J&W, bonded polydimethylsilicone), 30 meters, 0.25 mm internal diameter, 0.25 micron phase coating.

Oven Temperature Program: 50°C for 2.5 min hold time, 50°C to 150°C at 15.0°C/min hold at 150°C for 0.01 min., 150°C to 220°C at 4.3°C/min hold at 220°C for 35.1 min.

GC Column Velocity: Pressure approximately 23.6 PSI (adjusted to elute OCN Internal Standard between 42.0 and 48.0 minutes).

Detector: Electron Capture Detector (micro-ECD), attenuation 0, range 4 (adjusted for sensitivity).

Detector Temperature: 300°C.

Injector Temperature: Splitless injection, 250°C, purge time 0.75 min., purge flow 15.0 mL/min.

Detector Make-up Gas: Approximately 70.0mL/min Nitrogen. Adjusted for signal sensitivity.

Autosampler: 0.5uL sample volume (adjustable based on signal sensitivity). Sample pumps 4, viscosity delay 3, sample wash 2, solvent A 2 washes, solvent B 2 washes, slow plunger OFF, sampling offset OFF, solvent A pre-wash 1, solvent B pre-wash 1.

10.2 Initial GC Calibration:

Prior to running samples the system must be calibrated and the Initial Continuing Calibration Check Standard must be verified.

10.2.1 Establish the gas chromatographic operation parameters outlined in Section 11.1.1 and prepare the appropriate calibration standards composed of a mixture of Aroclors 1232, 1248, and 1262 as outlined in Sections 7.6 through 7.11.

10.2.2 Prior to sample analysis, a four-point or three-point calibration for each separable (single PCB congener or congener mixture) chromatographic peak is performed. There are 22 DB-1 peaks that cannot be measured in Calibration Standard 4 (low-calibration standard) and only a three-point calibration curve will be generated for the following peaks: DB-1 peaks 10, 13, 20, 44, 52, 55, 56, 67, 72, 79, 84, 87, 89, 91, 98, 101, 104, 108, 111, 113, 114, and 118.

10.2.3 The initial calibration sequence is analyzed as follows:

Injection	Calibration Standard ID
1	Hexane Instrument Blank
2	Hexane Instrument Blank
3	0.00625ug/mL Calibration Std 4
4	0.0125ug/mL Calibration Std 3
5	0.125ug/mL Calibration Std 2
6	0.3135ug/mL Calibration Std 1
7	Hexane Instrument Blank
8	Supplemental Congener Calibration Std
9	Surrogate Calibration Std
10	Hexane Instrument Blank
11	0.122ug/mL Initial Continuing Cal Check Std

10.2.4 Calibration Curve Criteria: The correlation coefficient of the three-or four-point calibration curve must be greater than or equal to 0.995 for each quantified peak using a linear equation with 1/X weighting. The three- or four-point calibration curve must also meet a percent relative standard deviation of less than or equal to 20% for each quantified peak.

10.2.5 Chromatographic Resolution Criteria: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis. This measurement is performed on the Initial Continuing Calibration Check Standard and all other subsequent Continuing Calibration Check Standards. This measurement is performed with a millimeter ruler on the chromatogram displayed on the computer terminal.

10.2.6 Retention Time Window: The ±0.07 minutes retention time window is the default window used in Contract Laboratory Program, Statement of Work for Organic Analysis for PCB/Pesticide analysis. The retention times for compounds in the Continuing Calibration Check Standards

must fall within the established retention time windows from the Initial Continuing Calibration Check Standard.

10.2.7 Our laboratory will use a computer based data acquisition workstation (Waters Associates, Millennium_32 workstation software or equivalent), interfaced to the gas chromatograph. The workstation processes the detector signal, performs an analog to digital conversion, and stores the digitized chromatograms on the computer hard disk. All data analysis will be done on the specialized software package including peak integration, calculating calibration curves/response factors, report generation, chromatogram hardcopies, and archival of data. Calculate the response factor for each separated and identified peak.

10.2.8 After the above criteria are met system calibration for sample analysis can be performed. Appendix A identifies which congener and or congeners compose each resolvable GC peak in the calibration standard, along with the amount that each congener or co-eluting group of congeners are represented in the calibration standard. Throughout this document the IUPAC PCB numbering system will be used for congener identification. Appendix B is an example of an acceptable chromatogram of the calibration standard, along with peak congener labels for cross-reference to data in Appendix A. Analyze the four initial calibration standards to initiate calibration of the GC system. Also analyze the Supplemental Congener Standard to calculate relative response factors for congeners that do not exist in the four initial calibration standards. Response factors are calculated relative to the internal standard by the following equation:

$$RRF = (A_x/A_{is})*(C_{is}/C_x)$$

Where:
- RRF = Relative response factor of congener(s)
- A_x = Area of peak for the congener(s).
- A_{is} = Area of peak for the internal standard.
- C_x = Concentration of the congener(s).
- C_{is} = Concentration of the internal standard.

The calibration curve is based on 1/X weighted linear regression, not forced through zero.

10.3 Continuing Calibration

10.3.1 Chromatographic Resolution: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

10.3.2 Response Factor Verification:

10.3.2.1 The relative response factors calculated from the initial calibration curve will be verified on each working day by analyzing a Continuing Calibration Check Standard, calculating the selected congener concentrations and comparing to their known concentration. A subset of six congeners and Total PCBs will be used to verify the relative response factors before samples are processed. The Percent Difference for Total PCBs must be ±15%. The six congeners include:

DB-1 Peak Number	IUPAC Congener Number	Relative Peak Level in Calibration Standard	Peak Concentration 0.122ug/mL Continuing Calibration Std (ng/mL)	Percent Difference Limits
7	6	Low level peak in standard	1.35	±30
116	205	Low level peak in standard	0.0788	±30
47	70	Medium level peak in standard	2.42	±15
93	174,181	Medium level peak in standard	2.28	±15
37	104,44	High level peak in standard	3.06	±15
102	180	High level peak in standard	4.35	±15

10.3.2.2 After the Continuing Calibration Check Standard is analyzed calculate the amount for these six congeners and Total PCBs and compare those values to the known concentrations by the following equation:

Percent Difference = [Amt(1)-Amt(2)]/Amt(2) x 100

Where: Amt(1) = Amount calculated for congener or Total PCBs.
Amt(2) = Known amount for congener or Total PCBs.

10.3.2.3 A percent difference greater than ±30% for the two low-level peaks (7 and 116) indicates an instrument problem or unacceptable relative response factors. A percent difference greater than ±15% for the medium level (47 and 93) and high-level (37 and 102) peaks also indicates an instrument problem or unacceptable relative response factors. If any of the evaluation congeners or Total PCBs fail to meet the percent difference acceptance criteria, the guidance provided in Section 9.1.3 must be followed.

10.3.2.4 The percent recovery for the internal standard octachloronaphthalene (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the average OCN area among the associated initial calibration standards. If the OCN area fails to meet the acceptance

criteria, the guidance provided in Section 9.1.3 must be followed.

10.3.2.5 If re-calibration is performed, the Continuing Calibration Check Standard must be analyzed again and values calculated using the new relative response factors. If the Continuing Calibration Check Standard fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (*i.e.,* GC gas leak, autosampler syringe plugged, broken injector liner).

11.0 Procedure

11.1 Sample Extraction and Preparation:

11.1.1 This low-level analytical procedure is specifically performed for analysis of water samples. The following SOPs detail sample extraction procedures that may be utilized in preparing samples for analysis by this analytical method:

SOP NAME	TITLE
NE006	Separatory Funnel PCB Extraction
NE124	CLLE PCB Extraction
NE178	Solid Phase PCB Extraction

11.2 Gas Chromatograph Procedures:

11.2.1 Sample extracts are set to a volume of 5mLs at which time the internal standard is added. Approximately 1.0mL of the extract is transferred to an autosampler vial.

11.2.3 The sequence for the analytical queue is set up in the chromatography software in the sample set file and given a unique sample set name. This file contains the exact order in which standards, instrument blanks, and samples will run. Once the sample set is in place the GC autosampler tray can be loaded with the autosampler vials and verified to printed sample set for correct position.

11.2.4 The following labeling will be used on the autosampler vial and for the sample set file created for the analytical queue:

11.2.4.1 The Initial Calibration Standards will be labeled as CS0731A, CS0731B, and CS0731C. Substitute the actual date of analysis in the file name.

11.2.4.2 The Supplemental Congener Standard will be labeled SCS0731. Substitute the actual date of analysis in the file name.

11.2.4.3 The Surrogate Standard will be labeled SS0731. Substitute the actual date of analysis in the file name.

11.2.4.4 The Instrument blanks will be labeled 030731B1, B2, B3, *etc*. Substitute the actual date of analysis in the file name.

11.2.4.5 The Continuing Calibration Check Standards will be labeled CCCS0731A, CCCS0731B, *etc*. Substitute the actual date of analysis in the file name.

11.2.4.6 Samples are labeled with the laboratory identification number on the autosampler vial. In the sample set file the laboratory identification number along with the client identification are entered.

11.2.5 At this point the chromatography software can be initiated to start data collection. The gas chromatograph is placed into run mode and sample analysis is performed until the analytical queue is complete.

11.3 Peak Integration and Analyte Identification:

11.3.1 Due to the complex nature of the PCB patterns encountered and the range of peak intensities that can occur in the sample chromatograms, manual peak integration is performed to accurately integrate the samples. Manual peak integration is also performed on standards to best address the changing signal intensities. Manual integration provides for better peak start and peak end positioning, better control of peak baselines and more accurate data.

11.3.2 Analytes are identified by matching retention time to the calibrated peak in the initial calibration standard that are within the retention time window of ±0.07 minutes. The analyst must also use judgment in pattern recognition.

11.3.3 The PCB congener composition of DB-1 peaks is identified in Appendix A. DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. With exception of congeners IUPAC 77 and 122, the resolved peaks are found at trace levels in Aroclors (and, therefore, not present in the calibration standards) and are addressed in this method in the event they are detected. If these

congeners are detected in a sample, the retention time window of the assigned DB-1 peak is set to ensure the congener is quantitated. A standard comment is included on the Congener Weight and Mole Report (see Appendix B) identifying this issue. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indicating that the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak[1]	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76*, *98*, *80*, *93*, **95**, **102**, *88*)	*80*, *88*, *93*
56 (*78*, **83**, *112*, *108*)	*108*
61 (**77**, **110**, 148)	**77**
72 (**122**, 131, 133, 142)	**122**
89 (**128**, *162*)	*162*
105 (**200**, *169*)	*169*

1 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

12.0 Calculations:

12.1 Internal Standard Calibration:

12.1.1 The capillary column GC analysis will be done by the internal standard calibration technique. Calibration and sample quantification will be performed by a commercial GC software package. The capillary GC will be standardized by using an Aroclor mixture that encompasses all the possible PCB congeners present in environmental samples.

12.1.2 Response factors for each separated and identified peak in the standard will be calculated using the following formula:

$RRF = (A_x/A_{is}) \times (C_{is}/C_x)$

Where: RRF = Relative response factor of congener(s).
A_x = Area of peak for the congener(s).
A_{is} = Area of peak for the internal standard.
C_x = Concentration of the congener(s) (ng/mL).
C_{is} = Concentration of the internal standard (ng/mL).

12.2 Sample Calculations:

12.2.1 The sample PCB concentration of each standardized PCB peak is calculated as follows:

$$\text{Concentration (ng/L)} = \frac{[(A_x)(C_{is})(V)(D)]}{[(A_{is})(RRF)(L_s)]}$$

Where: A_x = Peak area for congener(s) being measured.
C_{is} = Amount of internal standard added to sample extract (ng/mL).
D = Dilution factor, if sample was diluted prior to analysis.
V = Extract volume (mL).
A_{is} = Peak area of added internal standard.
RRF = Relative response factor for congener(s) being measured from initial calibration curve.
L_s = Volume of sample extracted (L).

12.2.2.1 The calculated PCB concentration for each PCB peak will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results for peaks with concentrations at or above the MDL but below the RL will be reported as detects and flagged as estimated ("J"). The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

12.2.2.2 The Total PCB concentration will be calculated and reported as follows:

12.2.3.1 All peak results above their respective MDL (both "J" flagged and unqualified results) will be summed and compared to the sample-specific Total PCB MDL and RL.

12.2.3.2 If no peaks are detected above their respective MDL, the Total PCB results will be reported as not detected at or above the sample-specific Total PCB MDL.

12.2.3.3 If the summed peaks from Section 12.2.3.1 are below the Total PCB MDL the result would be reported as less than ("<") the sample-specific Total PCB MDL.

12.2.3.4 If the summed peaks from Section 12.2.3.1 are at or above the Total PCB MDL but below the Total PCB RL, the summed result will be flagged as estimated ("J").

12.2.3.5 If the summed peaks from Section 12.2.3.1 are at or above the Total PCB RL, the Total PCB result will be reported as the unqualified numeric value.

12.3 Data Output and Reporting Format:

12.3.1 Reporting limit: The reporting limit for the method is established on a Total PCB basis. The reporting limit is generated from the 6.25ng/mL Calibration Standard 4 (low-level calibration standard) plus the 22 peaks from the 12.5ng/mL Calibration Standard 3 that cannot be measured in the low-level calibration standard. The concentration from the summing of the two calibration standards is 6.36ng/mL. There also exist several instances where the method detection limit (MDL) for several peaks exceeded the reporting limit (RL) for the one-liter and eight-liter water MDL studies. For these instances, where the MDL was higher than the RL, the RL has been raised to be equal to the MDL value. This will establish a reporting limit of 32.3ng/L for a one-liter water sample and 4.00ng/L for an eight-liter water sample. Data reported below the reporting limit but above the current compliant method detection limit will be flagged estimated as "J".

12.3.2 Several specialized software routines have been developed for high resolution PCB analysis to aid the data user in understanding and organizing the complex data generated from this extremely detailed analysis. Appendix C contains examples of the sample hard copy format that will be used in reporting sample information. This data is also available in electronic format as an Excel™ file or other electronic formats as required by the client.

12.4 Data adjustments for Hudson River water samples:

12.4.1 In 1997 a report was issued by General Electric to EPA (HydroQual, 1997. Development of Corrections for Analytical Biases in the 1991 – 1997 GE Hudson River PCB Database. Prepared for General Electric Company Corporate Environmental Programs, Albany, NY.) that outlined concentration corrections required for several DB-1 GC peaks containing more than one PCB congener. These PCB congeners were present in different proportions in Hudson River water samples compared to the method calibration standards. The technical details

and research that support the following data conversion can be found in the above referenced document.

12.4.2 The EPA 1993 Reassessment Remedial Investigation and Feasibility Study (RRI/FS) Phase II Hudson River water column data were used as a qualitative benchmark for data comparison to the GE weekly Hudson River water column study. This 1993 data set was chosen because EPA collected a significant number of samples to compare to the GE weekly sampling events.

12.4.3 Significant concentration differences were detected in Green Bay method GC peaks 5, 8, and 14 (which are comprised of congeners IUPAC 4 and 10; IUPAC 5 and 8; and IUPAC 15 and 18, respectively) when compared to the EPA database, which determined concentrations of these congeners as individual eluting GC peaks. These congeners differ in gas chromatographic response between each other when analyzed individually. It was determined that when these congeners were measured in Hudson River water samples as co-elutions their composition did not match the calibration standard congener composition in peaks 5, 8, and 14 and measurement was not as precise as when these congeners were determined by the EPA analytical method.

12.4.4 To address this measurement bias for the above peaks, a correction ratio was determined and applied to the concentration values obtained by the initial quantification. The correction ratio was derived by analysis of Hudson River water column extracts on a chromatographic system that was calibrated using individual congeners as standards and that could baseline resolve the co-elution congeners found in Green Bay method GC peaks 5, 8, and 14. These results were utilized to report a more accurate concentration value for the congeners comprising Green Bay method peaks 5, 8, and 14. The correction factors historically used were 0.65, 0.45, 1.44 for DB-1 peaks 5, 8, and 14, respectively. The correction ratios were confirmed and verified in March 2004 by conducting confirmatory analyses utilizing the gas chromatographic system that baseline resolved the six PCB congeners that required the correction ratio. GE confirmed and updated the correction factors for DB-1 peaks 5, 8 and 14 in a manner consistent with the approach described in the above report. The results of the evaluation of the correction factors for DB-1 peaks, 5, 8, and 14 were delivered to EPA via email on March 31, 2004 in a technical memorandum. Based on the findings summarized in the technical memorandum, upon initiation of the BMP, the correction factors developed based on the 2003 data set (0.61, 0.36 and 1.26) will be used to adjust DB-1 peaks 5, 8 and 14, respectively, for the bias identified in HydroQual 1997.

12.4.5 After the concentration values are corrected for Green Bay method peaks 5, 8, and 14 several other parameters require re-calculation prior to data reporting. These include the following: total PCB concentration, Homolog distribution, weight percent per peak, chlorination levels (ortho-Cl per biphenyl, meta+para-Cl per biphenyl, and total Cl per biphenyl), total micromoles, and average molecular weight.

13.0 Method Performance:

13.1 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at a reasonable concentration above the calibration standard 4 and below the calibration standard 1. The analyte will be added to a laboratory organic free water sample and taken through all extraction and analytical procedures. Aroclor 1242 is used as the analyte and recovery on a total basis is used to calculate percent recovery. To be valid, Aroclor 1242 will be recovered between the limits of 70 to 130 percent. Also, a percent relative standard deviation will be calculated for the replicates will be less than or equal to 20% to be valid.

13.2 Method Detection Limit: A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures are made or at a minimum frequency of every 2 years. A minimum of seven laboratory organic free water samples will be prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

$$MDL = S * t_{(n-1,\ 1-alpha=0.99)}$$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1-alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)} = 2.998$

13.2.1 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

14.0 Pollution Prevention:

14.1 Pollution prevention is practiced in the laboratory by minimizing usage of solvents and chemicals, so that disposal of waste generated is held to the smallest amount possible. This is directly linked to the types of extraction procedures in place at the laboratory to reduce the volumes of solvents used for semi-volatile extraction procedures. Northeast Analytical employs extraction procedures such as continuous liquid/liquid and solid phase extraction methods to reduce solvent requirements for water extraction protocols.

14.2 Pollution prevention also relies on minimizing to the best extent the chemicals and solvents required to perform extraction and analysis procedures. The laboratory personnel strive to purchase chemicals and standards that will be consumed based on anticipated workload.

14.3 For additional information about laboratory pollution prevention, please refer to laboratory SOP NE168.

15.0 Data Assessment and Acceptance Criteria for Quality Control Measures and Corrective Actions for Out-of-Control Data:

15.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration compliance.

15.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing check standards.

15.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. A Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed with the data and is also useful for production of case narratives that are issued with final data reports.

15.4 The Table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration	• Establish initially and when Continuing check standard fails criteria. • Calibration curve at 3 or 4 concentration levels. The surrogate calibration is a single point at 2ng/mL.	• %RSD≤20% for each relative response factor and a correlation coefficient ≥0.995 for each calibrated peak. • Calibration factors are to be calculated using area for each quantifiable peak with internal standard method and 1/X linear weighting, not forced through zero.	• Re-analyze the initial calibration curve and/or evaluate/correct instrument malfunction to obtain initial calibration that meets criteria. • Sample results above highest standard concentration require dilution and re-analysis.
Continuing Calibration Check Standard (CCC)	• Initially analyze a CCC immediately following a calibration curve. • After the initial CCC of the sequence, a CCC must be analyzed after every 10 samples. • Analytical sequence must end with analysis of a CCC.	• ≤ 30% difference based on "true" concentration for peaks 7, 116. • ≤ 15% difference based on "true" concentration for peaks 37, 47, 93, 102 and Total PCBs • Retention time of all quantitated peaks must be within RT window (reset with each initial CCC of a sequence) • The percent recovery for the internal standard (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the average OCN area among the associated initial calibration standards. • All samples must be bracketed by CCCs that meet all criteria stated above	• If the reason for the failure of the CCC appears to be a poor injection (or a degraded standard solution), the CCC will be re-injected (or reprepared and re-injected) immediately following the failed CCC. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCC meets all the acceptance criteria and there is no apparent impact on the sample data (*i.e.,* acceptable OCN areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. • If CCC failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCC failure, correct system, if necessary, and recalibrate. Initial calibration and CCC criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCs must be re-analyzed. • If acceptable CCCs are observed later in the sequence, samples bracketed by acceptable CCCs will be reported. Samples between the failed CCC and prior/ subsequent complaint CCC will be re-analyzed.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Retention Time (RT) Windows	• Default RT window is ±0.07 minutes • RT windows are re-centered based on the initial CCC analyzed after calibration curve or if using the first CCC of the day to start a new sequence.	• RT of CCC peaks must be within established windows in the CCs analyzed for a sequence. • Re-centering windows is allowed only once per 24 hours.	• Adjust system, re-establish RT windows, and re-calibrate if necessary.
Retention Time (RT) shift	• Each CCC analysis: RT of all quantitated peaks in the CCC is evaluated against the initial CCC following the initial calibration curve. • Each sample analysis: Rely on RT windows to identify PCB congeners to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because congener composition may shift RT for GC peaks.	• Each quantitated peak and surrogate peak should be with established windows.	• Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	• One per extraction batch of ≤20 samples of the same matrix per day. • Must be analyzed on each instrument used to analyze associated samples. • Must undergo all sample preparative procedures.	• Concentration does not exceed the total PCB method reporting limit (typically the MDL for aqueous samples). • Must meet surrogate criteria of 60 to 140 % recovery.	• Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. • If method blank is found to contain PCB contamination above total PCB reporting limit. Then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate method blank contamination or have client re-sample if possible.
Laboratory Control Spike (LCS)	• One per extraction batch of ≤20 samples per matrix per day. The LCS is typically Aroclor 1242 at approximately 20.0ng/L	• Percent recovery of Aroclor 1242 on a total PCB basis must be within method limits of 60 to 140% • Must meet surrogate criteria of 60 to 140% recovery.	• Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. • If LCS recovery is still out of limits, then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate LCS failed recovery or have client re-sample if possible.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	• For aqueous samples, normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. The MS is typically Aroclor 1242 at approximately 20.0ng/L. • If requested, an MSD can be extracted an analyzed. The MSD would follow the above criteria as for the MS.	• Percent recovery for MS on a total PCB basis should be 60 to 140% • If MS/MSD is analyzed, relative percent difference (RPD) should be within 30%. • Must meet surrogate criteria of 60 to 140%(unless original unspiked sample is also outside of criteria).	• Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. • Check for errors such as calculations and spike preparation. • Check original unspiked sample results and surrogate recovery for indications of matrix effects. • If no errors are found, and the associated LCS is within 60 to 140 %, then sample matrix effects are likely the cause. Note exceedence in case narrative.
Surrogates	• 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl is added to all samples and QC samples at a concentration of approximately 10ng/L.	• Percent recovery for the surrogate should be 60 to 140%	• Re-analyze the affected sample or QC sample to determine if instrument was the cause. If surrogate passes, then report samples. • Check for errors in surrogate calculations and surrogate solutions. • If no problem is found, then re-extract and re-analyze the sample. • If re-analysis is within limits and sample extract holding time, then report only the re-analysis. • If the re-analysis is within limits, but out of extraction holding time, then report both sets of data. • If the re-extraction produces surrogate recovery still out of limits, then report both sets of data. • If no sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have client re-sample if possible.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Internal Standard	• Octachloronaphthalene (OCN) is added to all sample extracts, QC samples and calibration standards. For sample extracts, 4.5uL of 20.2ug/mL OCN is added to 5mL final extract volume. See text for OCN amounts in calibration standards.	• The internal standard area for samples and QC samples should be 50 to 150% of the average internal standard area among the associated initial calibration standards. • The internal standard area for CCCs must be 50 to 150% of the average internal standard area among the initial calibration standards.	• Re-analyze the affected sample or standard to determine if instrument was the cause. If internal standard passes, then report samples. • For Standards – If no problem is found, prepare new standards and re-test. If problem still exists, prepare new internal standard and then prepare new standard solutions and re-test. • For Sample Extracts – If no problem is found, then follow procedures outlined above for surrogate corrective action steps for re-extraction and re-analysis.

16.0 Contingencies for Handling Out-of-Control or Unacceptable Data:

16.1 Data that is detected to be out-of-control for any reason, when compared to method acceptance criteria, will addressed in the following manner:

16.1.1 If the problem exists with the gas chromatographic instrumentation, appropriate action will be taken to repair and perform maintenance to bring the instrument back to operating condition. Once the instrumentation is determined to be correctly operating analysis can begin again.

16.1.2 If the problem exists with calibration standard solutions, the analyst will prepare new standards and discard the standard solutions that are suspect. Instrument calibration can be performed and analysis can begin once system is in control.

16.1.3 If the problem exists with sample extraction and extract preparation, the extraction step that is producing the out-of-control situation will be diagnosed and rectified. Once the troubleshooting procedures correct the problem extraction can once again occur and analysis can continue.

16.2 In situations where data is reported under out-of-control conditions, the data will be annotated with data qualifiers and/or appropriate descriptive comments defining the nature of the excursion in the sample case narrative. If warranted, a corrective action report (CAR) will be issued to define the problem, steps to correct the problem, and final resolution.

17.0 Waste Management:

17.1 All applicable federal and state rules and regulations governing hazardous waste will be followed when disposing of laboratory waste generated during the execution of this method.

17.2 Please refer to standard operating procedures NE089 and NE054 regarding how hazardous waste is handled and disposed of by the laboratory.

18.0 References:

18.1 US EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants," July, 1988.

18.2 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Published by: American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1995.

18.3 US EPA SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

18.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual," Wadsworth Center for Laboratories and Research, 1988.

18.5 Mullin, M.D. 1985. PCB Workshop, US EPA Large Lakes Research Station, Grosse Ile, MI, June.

18.6 M. Zell, K. Ballschmiter, Baseline Studies of the Global Pollution, III. Trace Analysis of Polychlorinated Biphenyls (PCB) by ECD Glass Capillary Gas Chromatography in Environmental Samples of Different Trophic Levels, Fresenius Z. Anal. Chem., 304, 337-349, 1980.

18.7 M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Save, "High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of All 209 PCB Congeners," Environ. Sci. Technol., Vol 18, No. 6, pp 468-476, 1984.

18.8 D.L. Swackhamer, "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office" Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987.

18.9 George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB

Congener Assignments on DB-1 Capillary GC Columns ", Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996.

18.10 "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", USEPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2

18.11 "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10.

18.12 Contract Laboratory Program – Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration. Document OLM3.2, 1996.

APPENDIX A

Congener Composition of Mixed Aroclor Calibration Standard 1 (313.5ng/mL)

Congener Composition of Mixed Aroclor Calibration Standard 1(313.5ng/mL) (Aroclors 1232, 1248, 1262 in a ratio of 25:18:18)

file: S:/TEXT/SOP/ne207_appendix_A_Gbcalstd_313.5_ng_ml.DOC

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
2	**001**	21.93
3	**002**	-
4	**003**	12.79
5	**004 010**	6.21
6	**007 009**	2.19
7	**006**	3.47
8	**005 008**	25.58
9	*014*	-
10	**019**	0.51
11	*030*	-
12	**011**	-
13	**012 013**	0.49
14	**015 018**	6.76
15	**017**	6.76
16	**024 027**	0.48
17	**016 032**	7.13
19	*023* **034** *054*	-
20	**029**	0.10
21	**026**	1.32
22	**025**	0.58
23	**031**	7.53
24	**028** *050*	9.64
25	**020** *021* **033 053**	7.26
26	**022 051**	5.30
27	**045**	1.63
28	*036*	-
29	**046**	0.73
30	*039*	-
31	**052** *069 073*	8.72
32	**043 049**	4.20
33	*038* **047**	1.83
34	**048** *075*	1.83
35	*062 065*	-
36	**035**	-
37	*104* **044**	7.86
38	**037 042 059**	4.75
39	**041 064 071** *072*	7.49
41	*068* **096**	-
42	**040**	1.72
43	**057** *103*	-
44	*058* **067** *100*	0.20
45	**063**	0.38
46	**074** *094 061*	3.47
47	**070**	6.21
48	**066** *076 098 080 093* **095 102** *088*	13.16

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
49	*055* **091** *121*	0.93
50	**056 060**	6.40
51	**084 092** *155*	3.29
52	**089**	0.18
53	**090 101**	3.29
54	*079* **099** *113*	1.35
55	**119** *150*	0.05
56	*078* **083** *112 108*	0.27
57	**097** *152 086*	1.02
58	*081* **087** *117 125* **115** *145*	2.12
59	*111 116* **085**	1.28
60	*120* **136**	1.37
61	**077 110** *148*	3.89
62	*154*	-
63	**082**	0.80
64	**151**	3.11
65	**124 135**	0.53
66	**144**	1.10
67	*107* **109** *147*	0.24
68	*123*	-
69	*106* **118** *139* **149**	7.31
70	*140*	-
71	**114 134** *143*	0.37
72	**122 131 133** *142*	0.05
73	**146** *165 188*	0.71
74	**105 132** *161*	2.48
75	**153**	5.38
76	*127 168 184*	-
77	**141**	3.11
78	**179**	2.67
79	**137**	0.14
80	**130 176**	0.48
82	**138 163 164**	4.93
83	**158** *160 186*	0.46
84	*126* **129**	0.02
85	*166* **178**	2.01
87	**175** *159*	0.37
88	*182* **187**	6.58
89	**128** *162*	0.18
90	**183**	3.11
91	**167**	0.09
92	**185**	0.86
93	**174** *181*	5.85
94	**177**	3.11
95	**156 171**	1.44
96	**157 202**	0.12
98	**173**	0.07
99	**201**	0.71
100	**172** *204*	1.02
101	*192* **197**	0.20

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
102	**180**	11.15
103	**193**	0.77
104	**191**	0.22
105	**200** *169*	0.79
106	**170**	2.34
107	**190**	0.77
108	**198**	0.22
109	**199**	7.68
110	**196 203**	7.86
111	**189**	0.07
112	**195**	1.01
113	**208**	0.45
114	*207*	0.17
115	**194**	3.29
116	**205**	0.20
117	**206**	1.24
118	*209*	0.02

1 - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low-level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.
PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 81 (176) now elutes in PK 80 (130,176)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

2 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

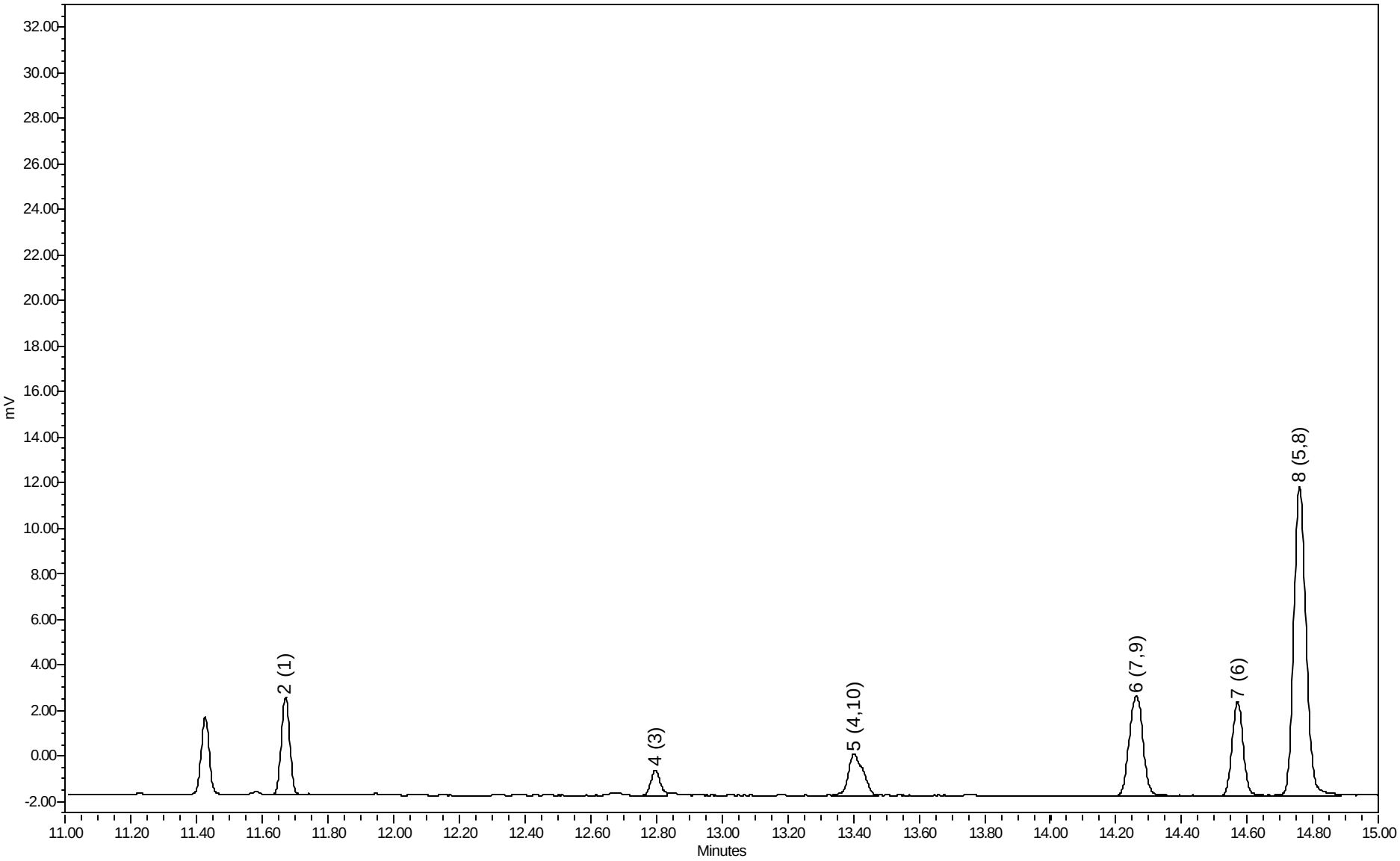
APPENDIX B

DB-1 Capillary GC/ECD Chromatograms:

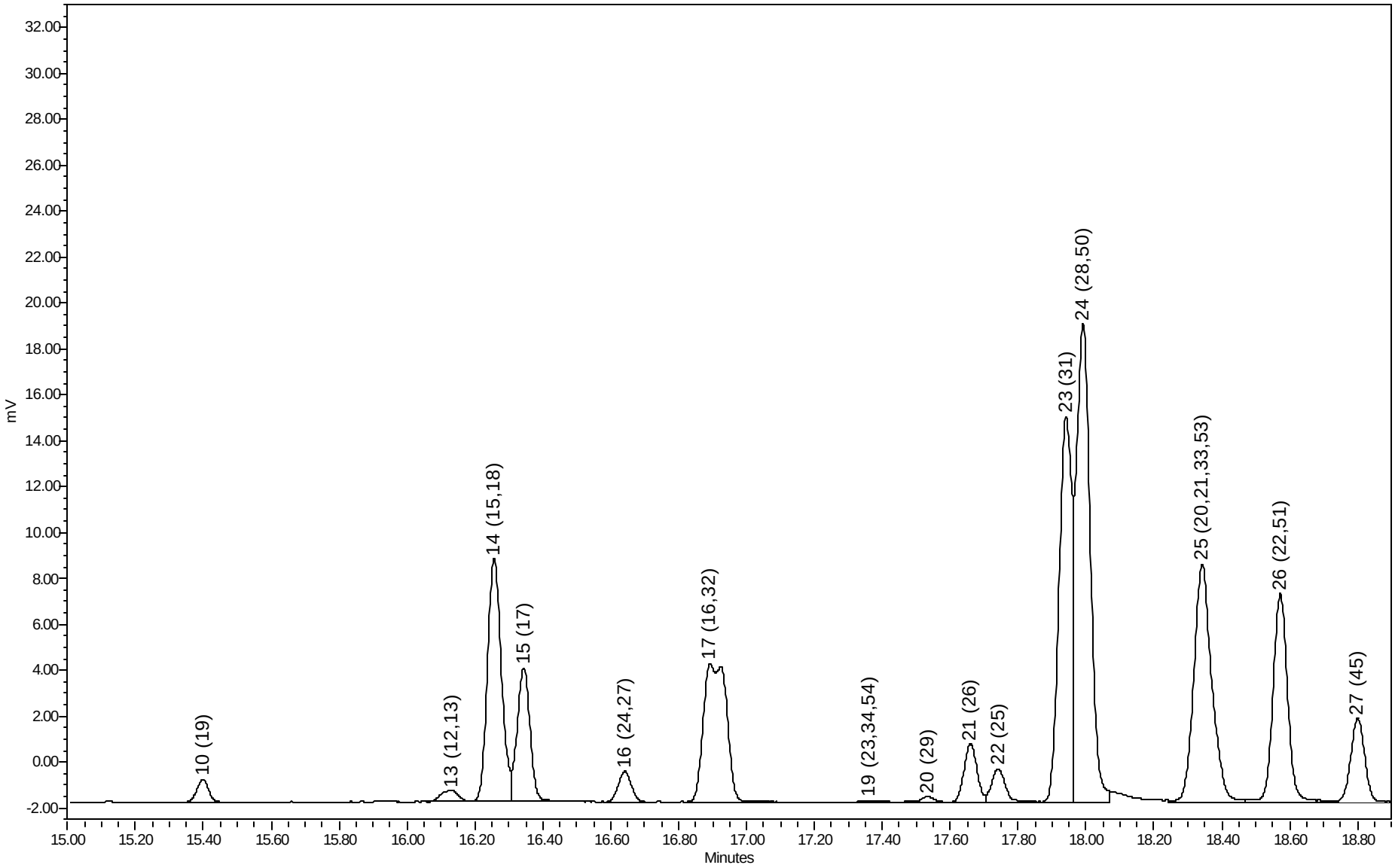
1 Initial Calibration Standard 1 (313.5ng/mL)

2 Supplemental Congener Standard: 3-chlorobiphenyl at 200ng/mL
All other PCB congeners at 5.00ng/mL

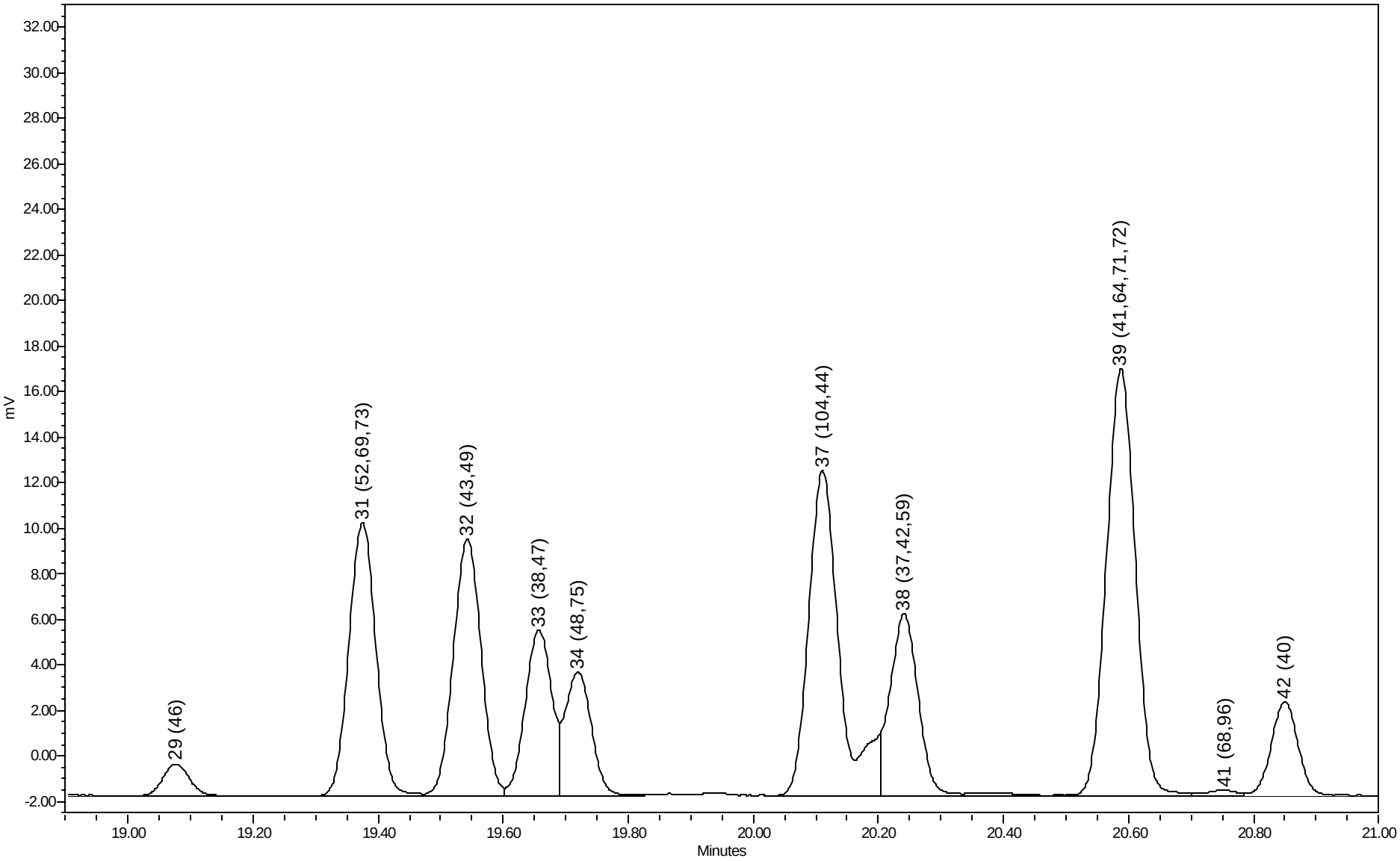
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



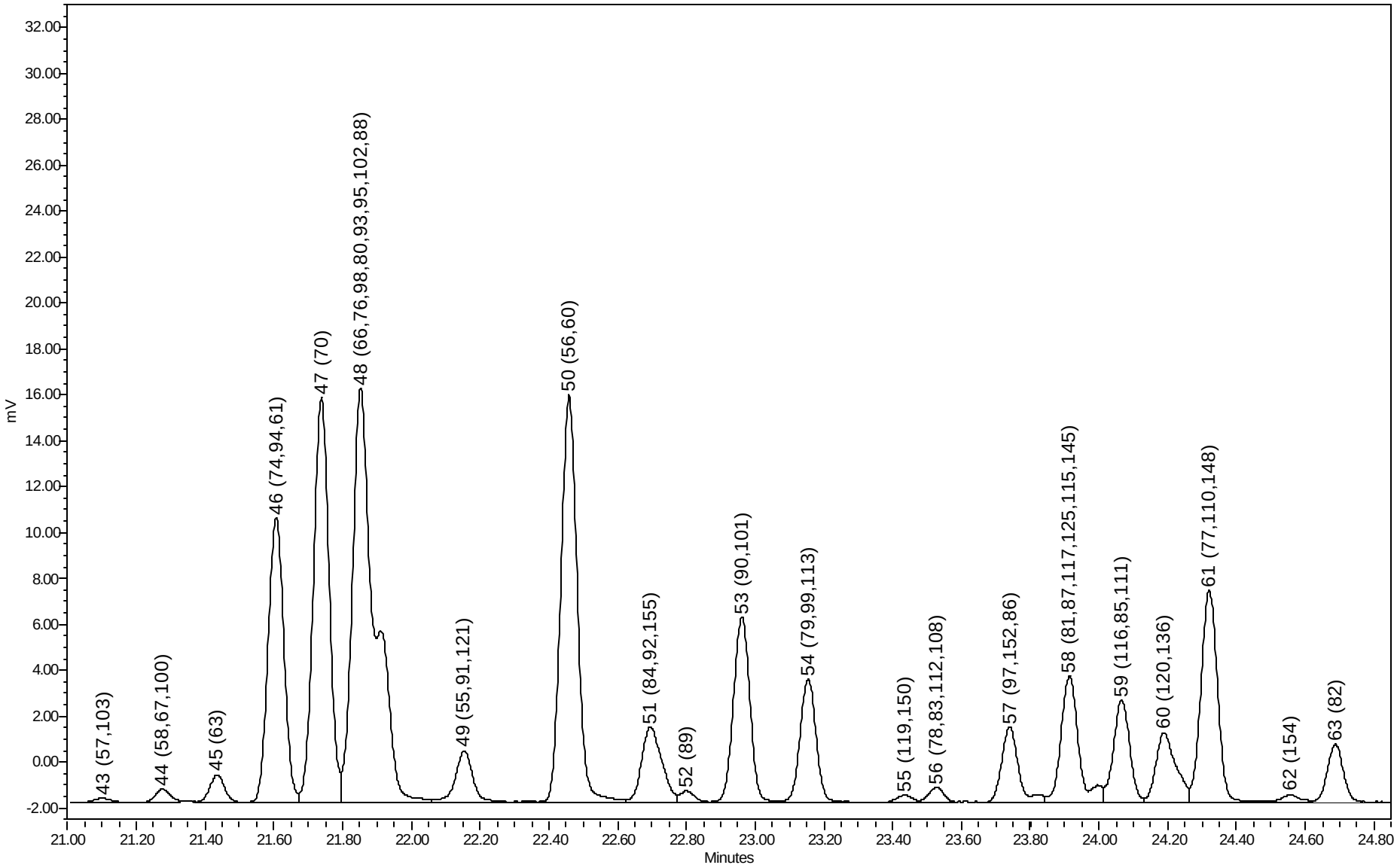
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



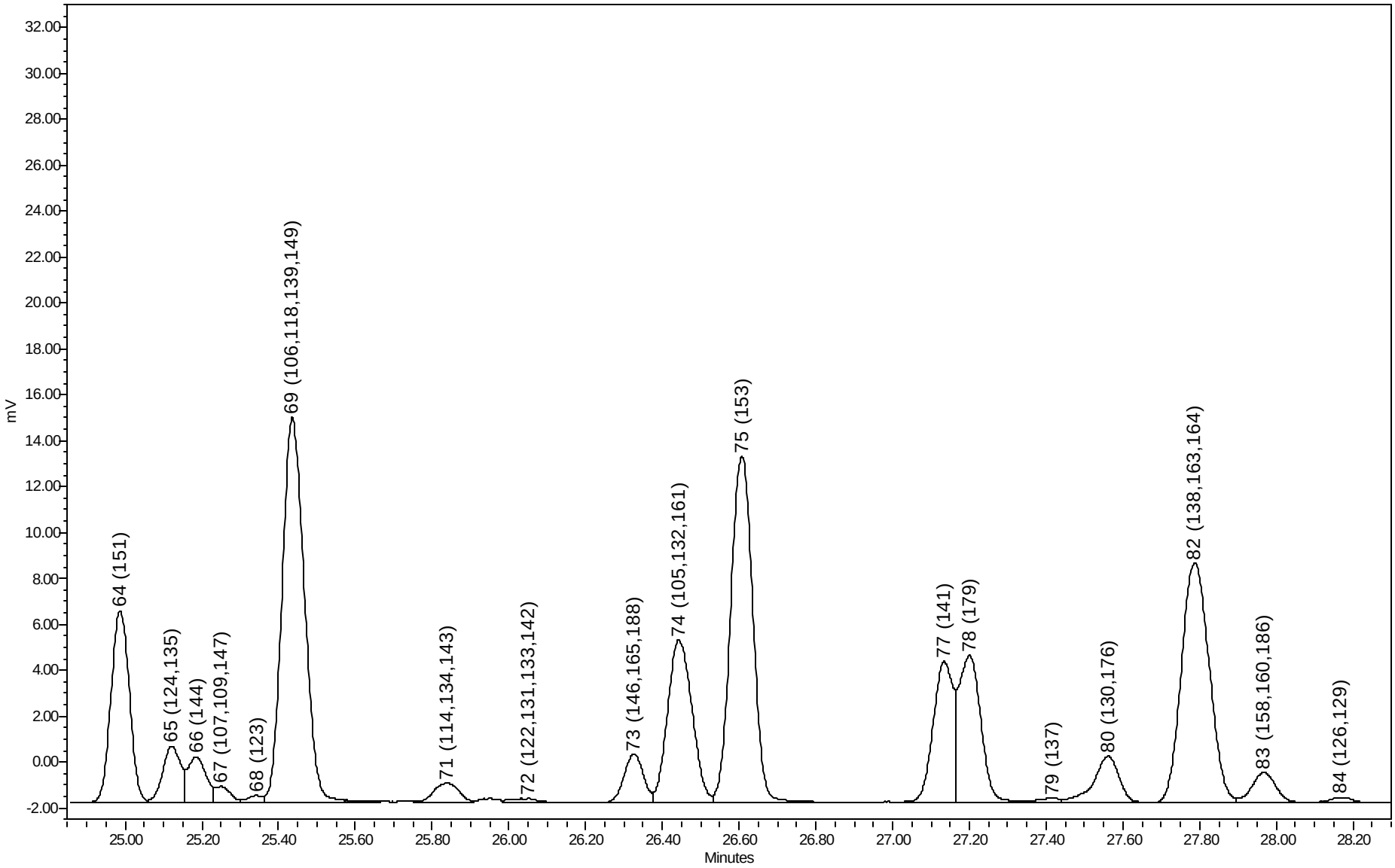
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



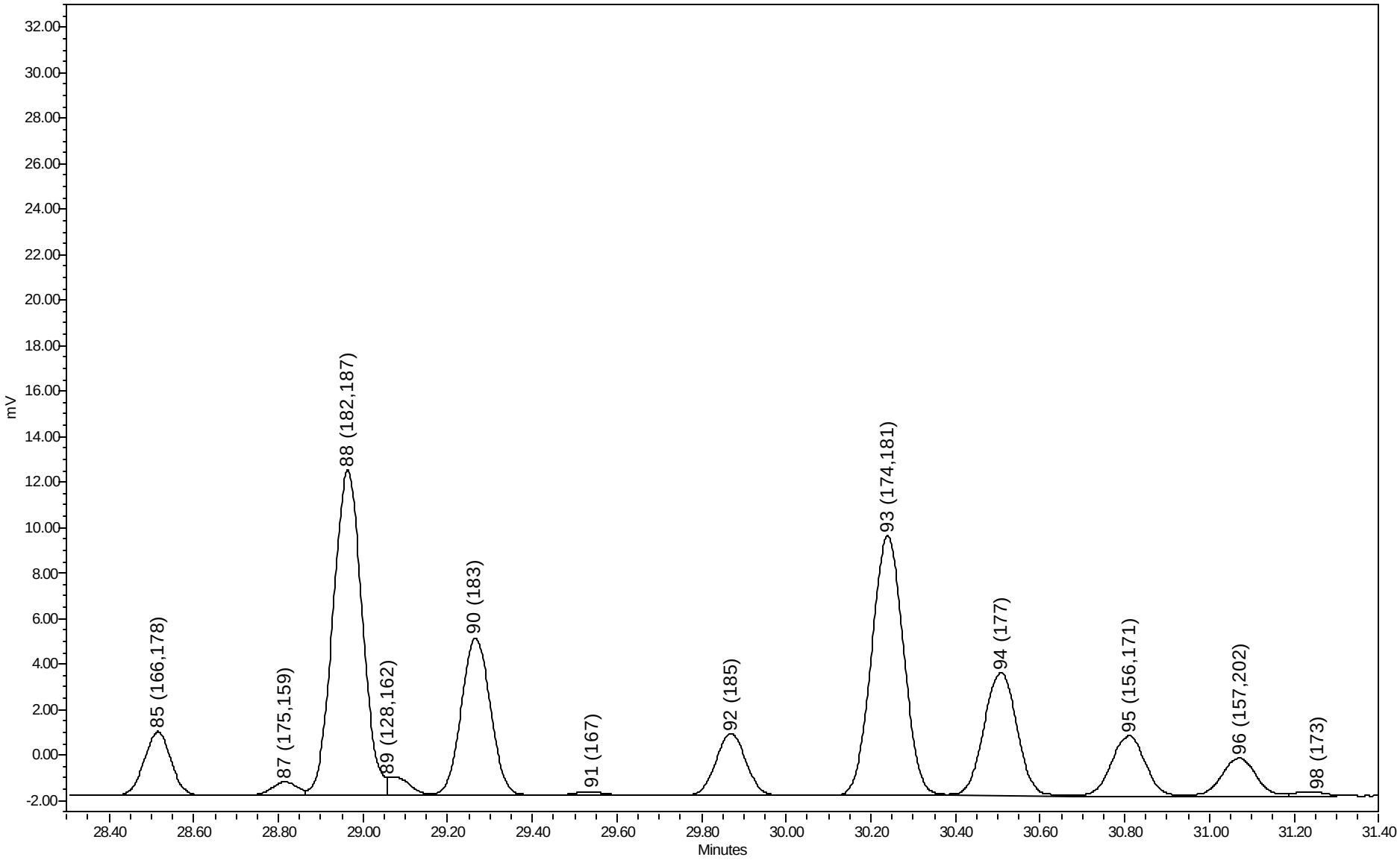
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng / mL)



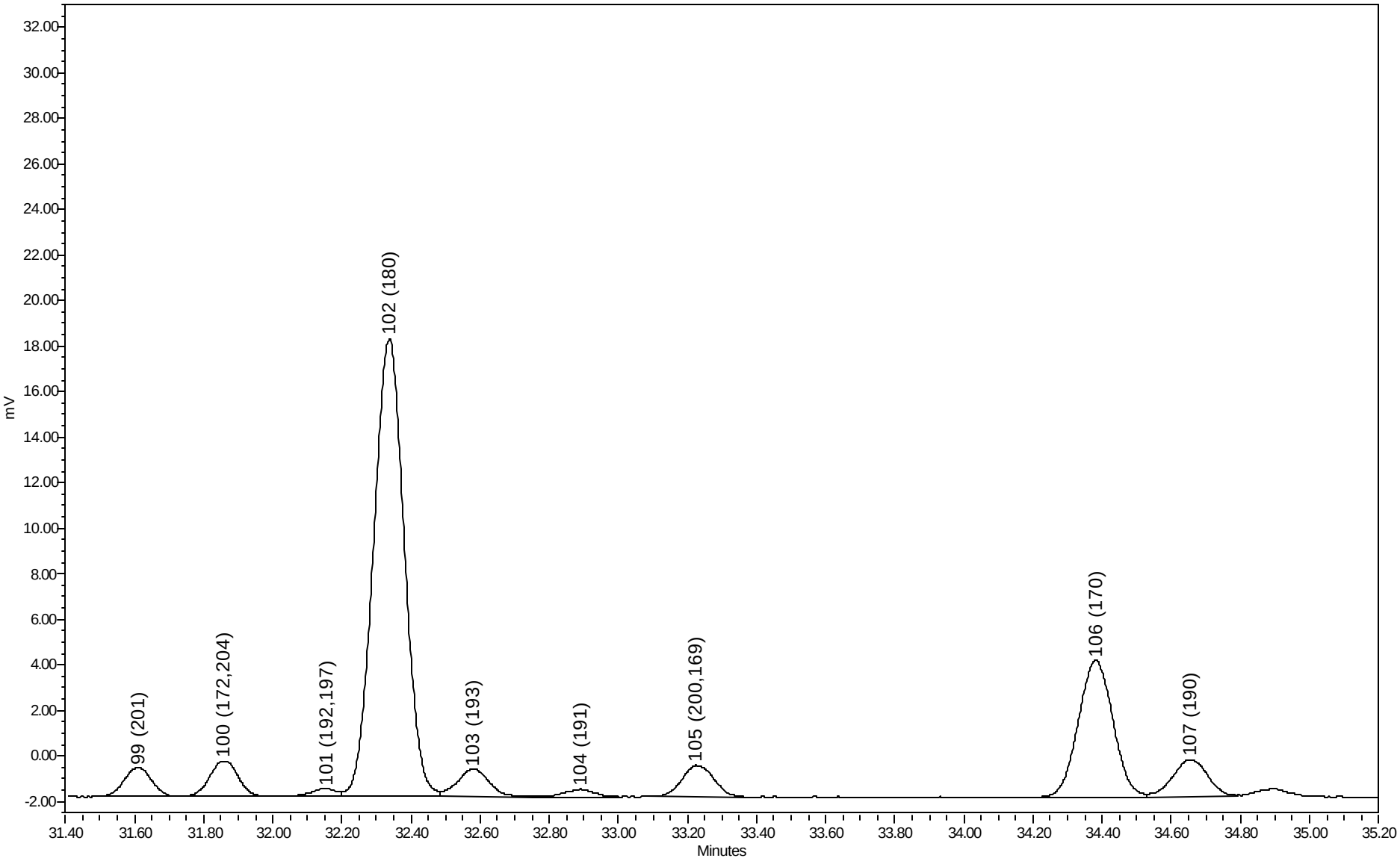
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



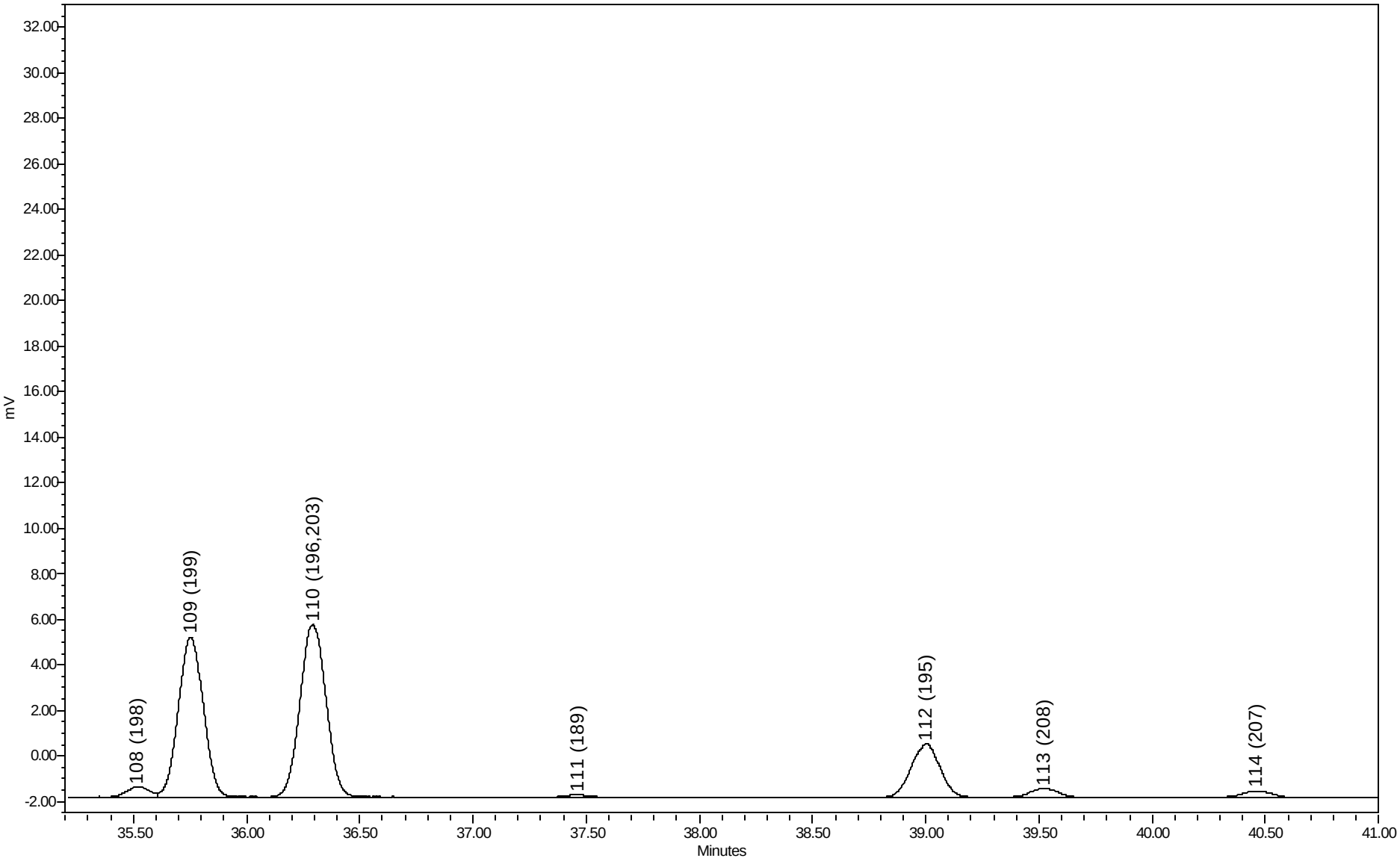
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



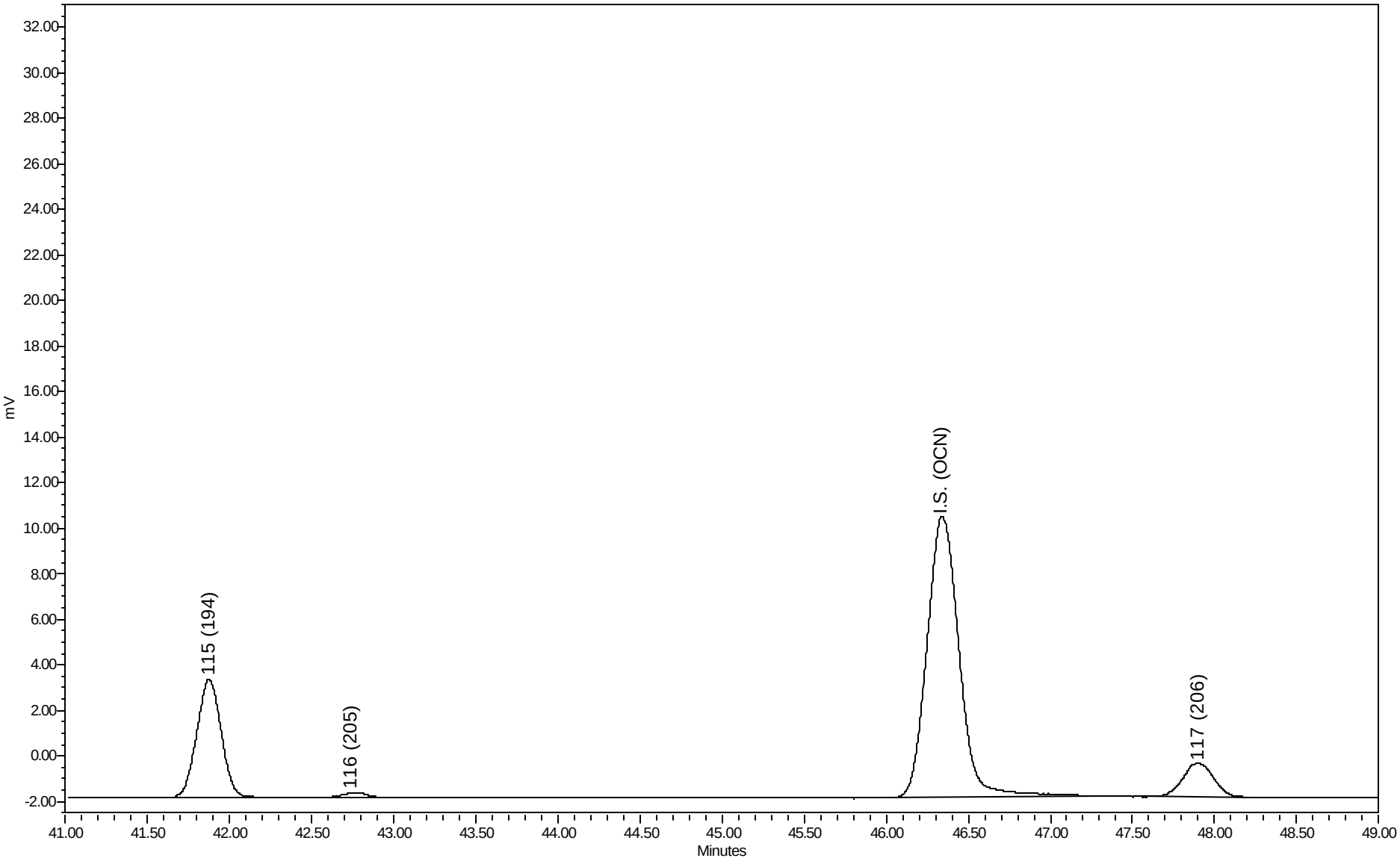
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



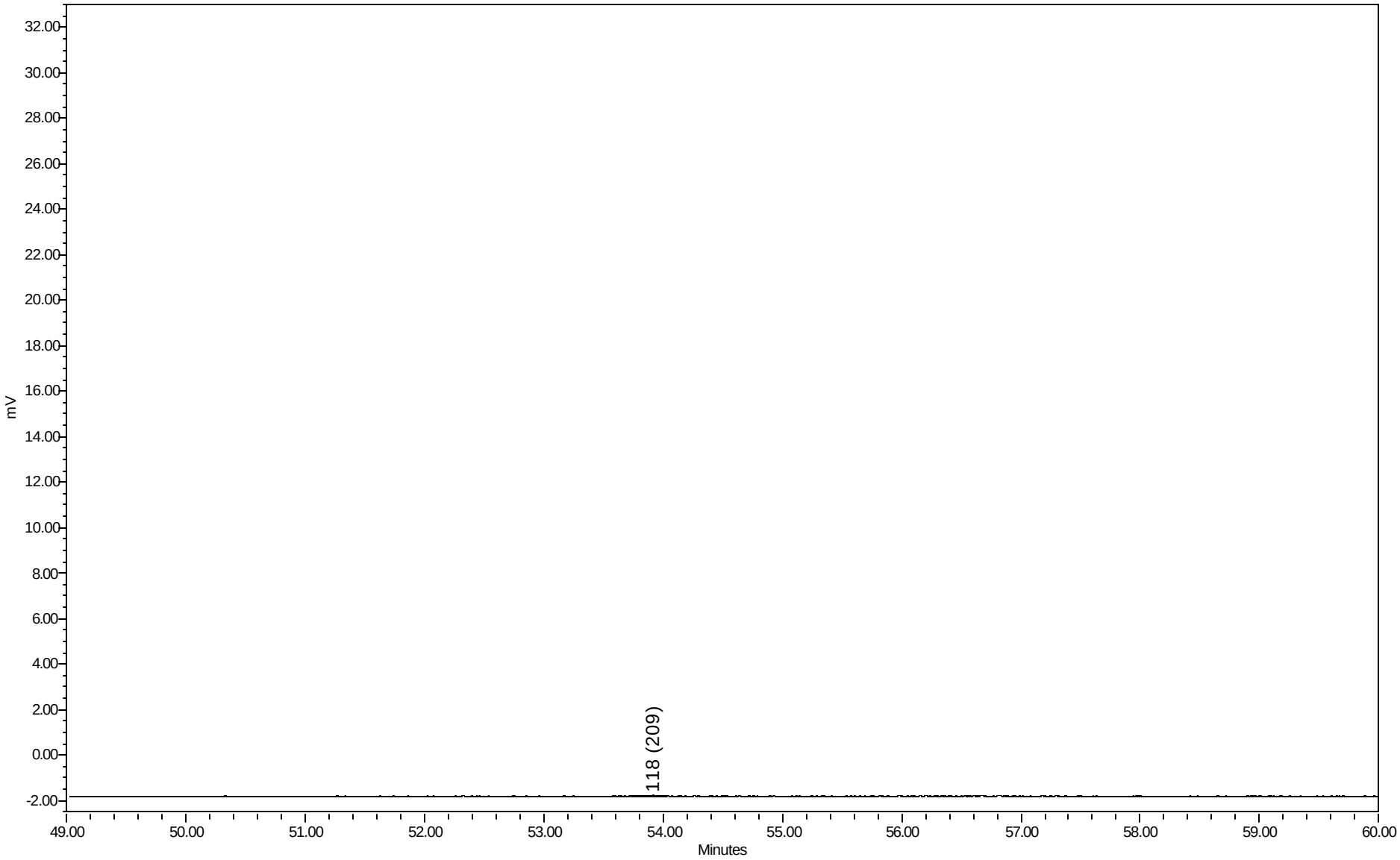
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



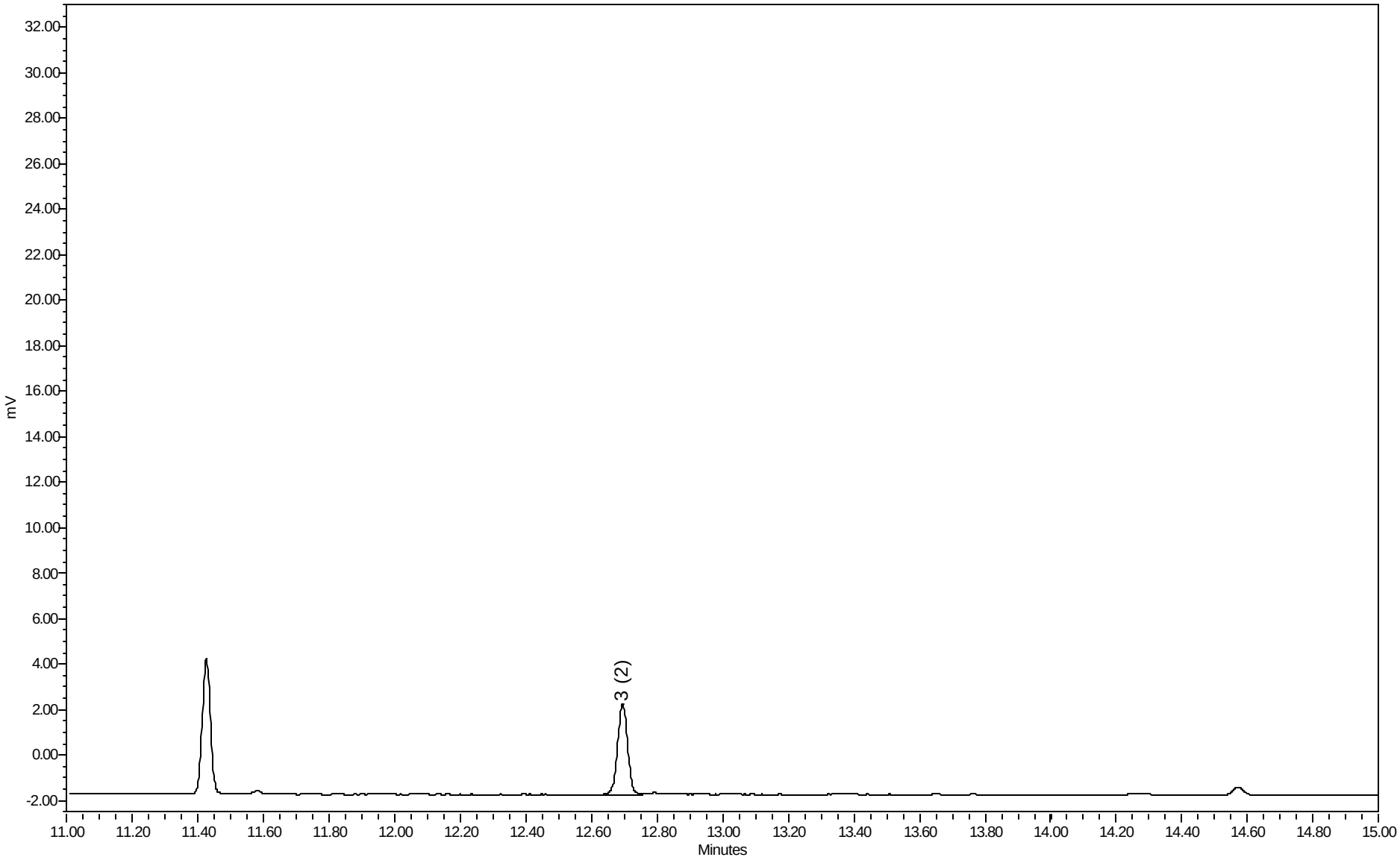
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



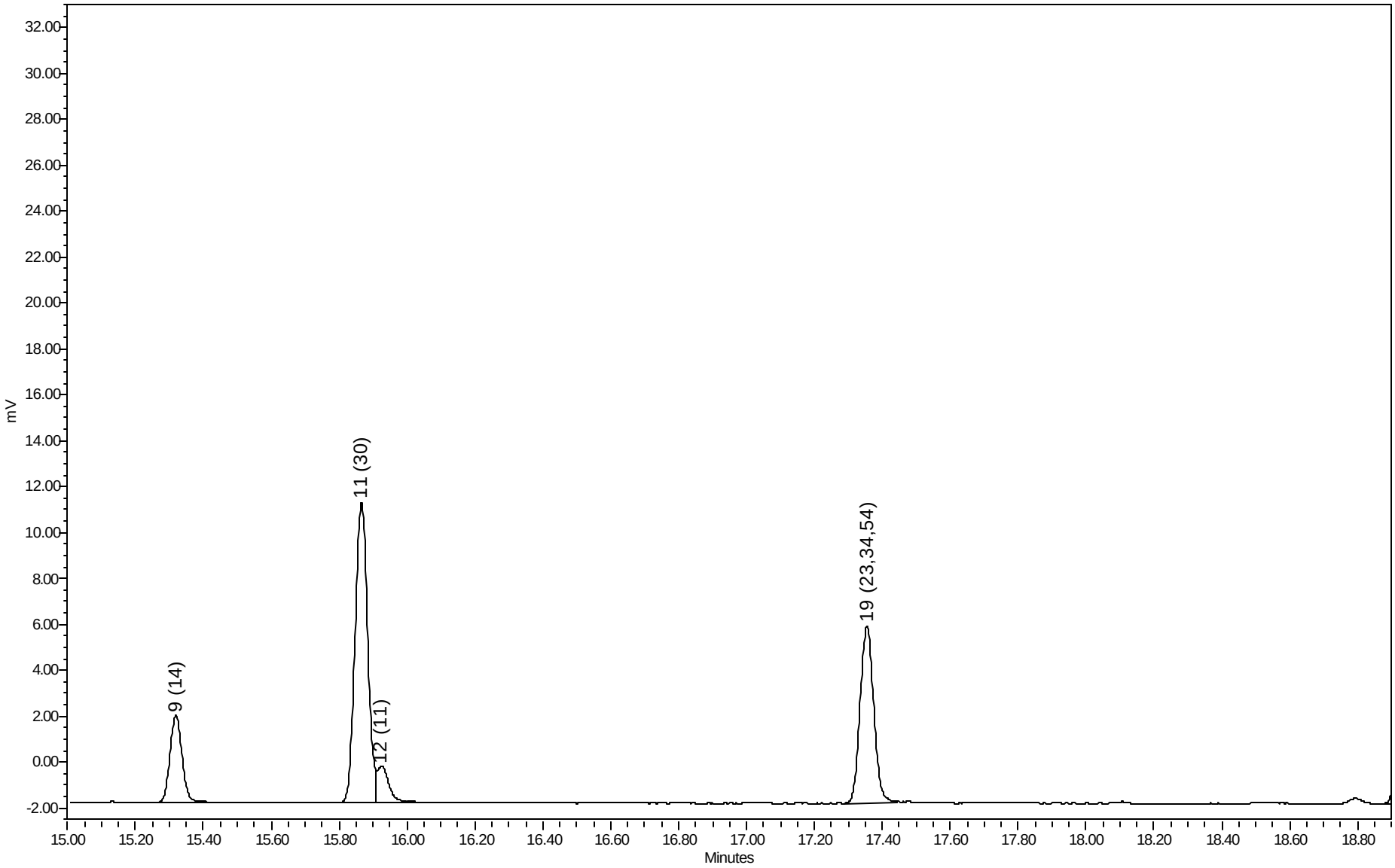
Congener Composition Chromatogram of Aroclor Calibration Mixture (314 ng/mL)



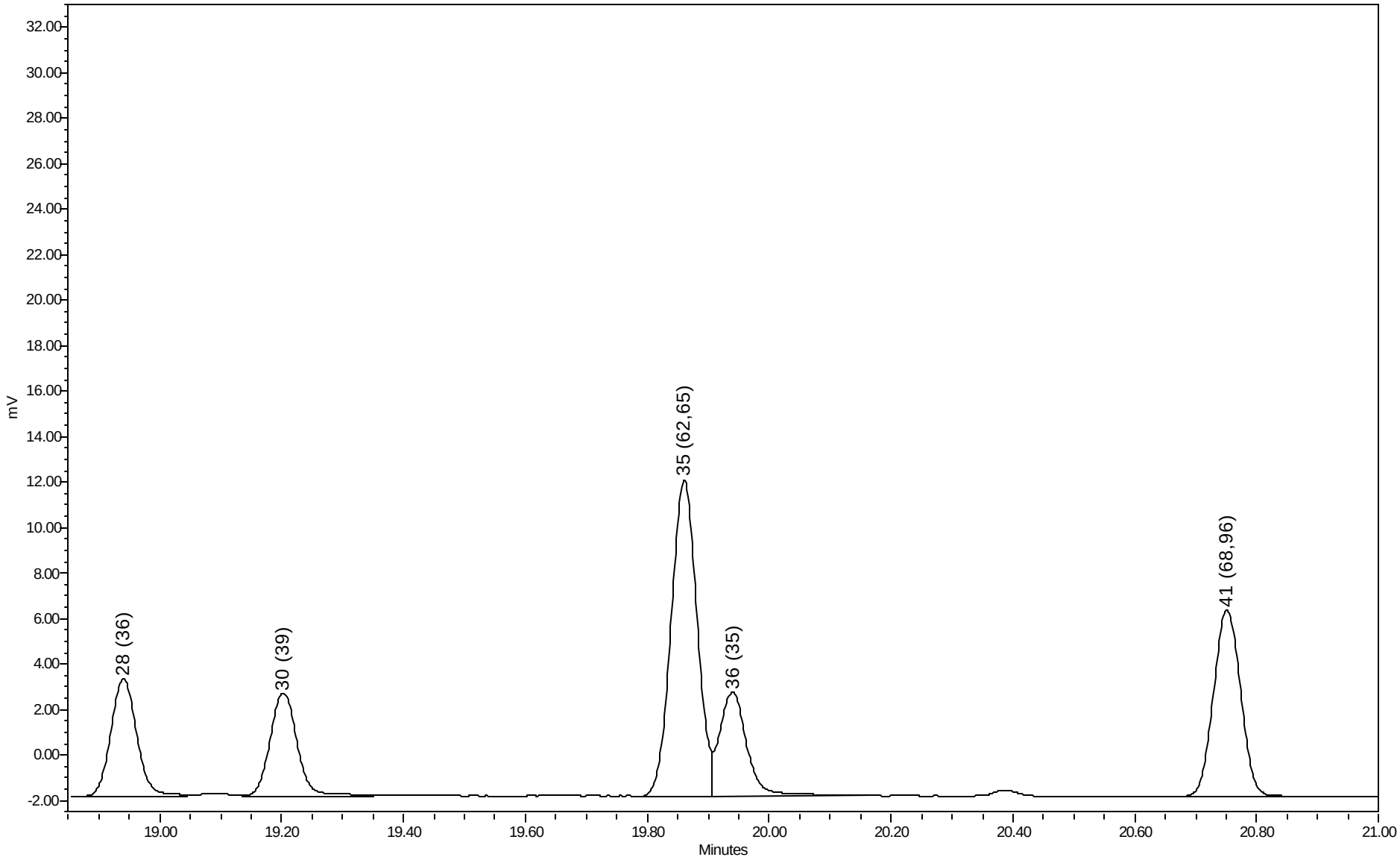
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



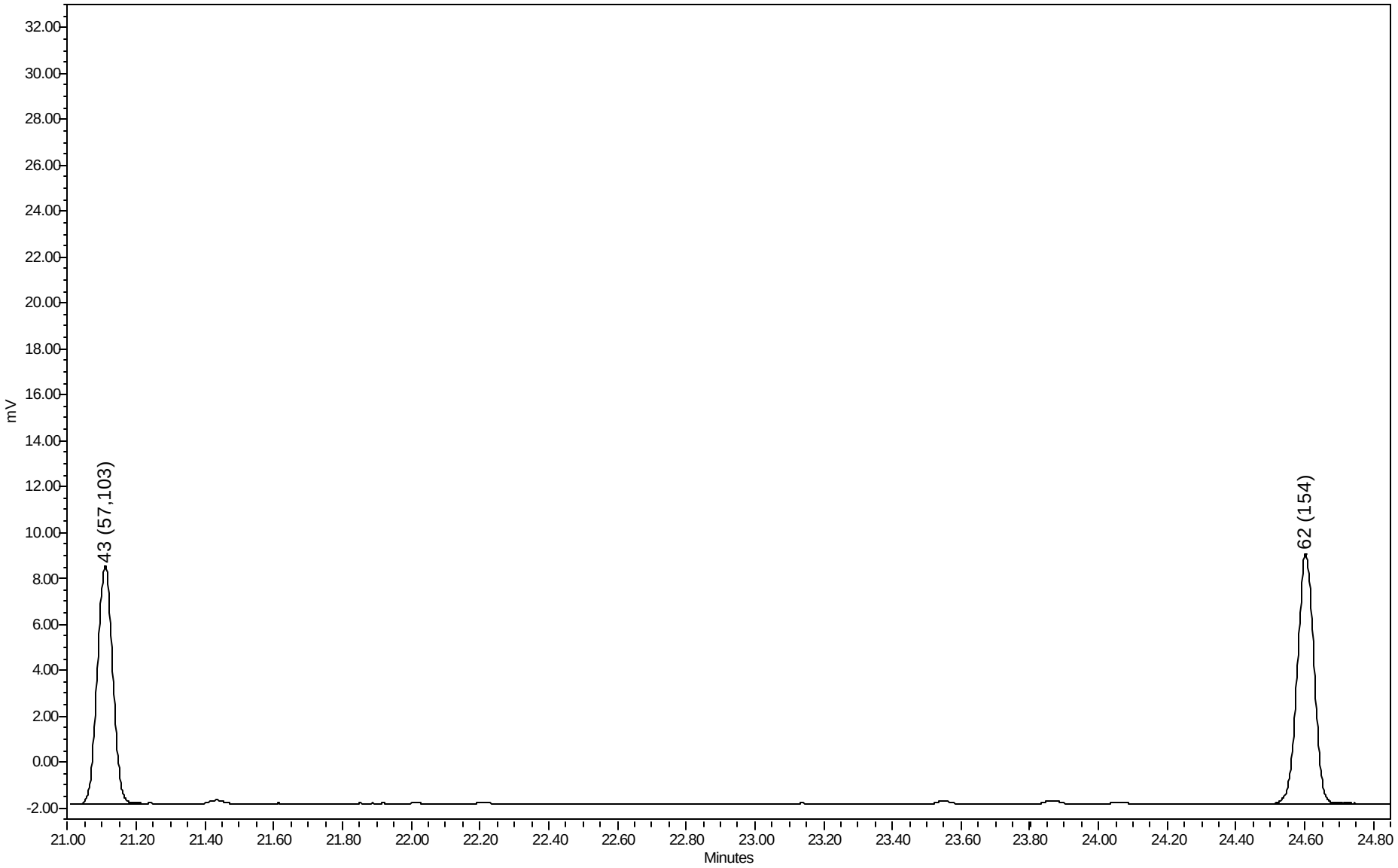
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



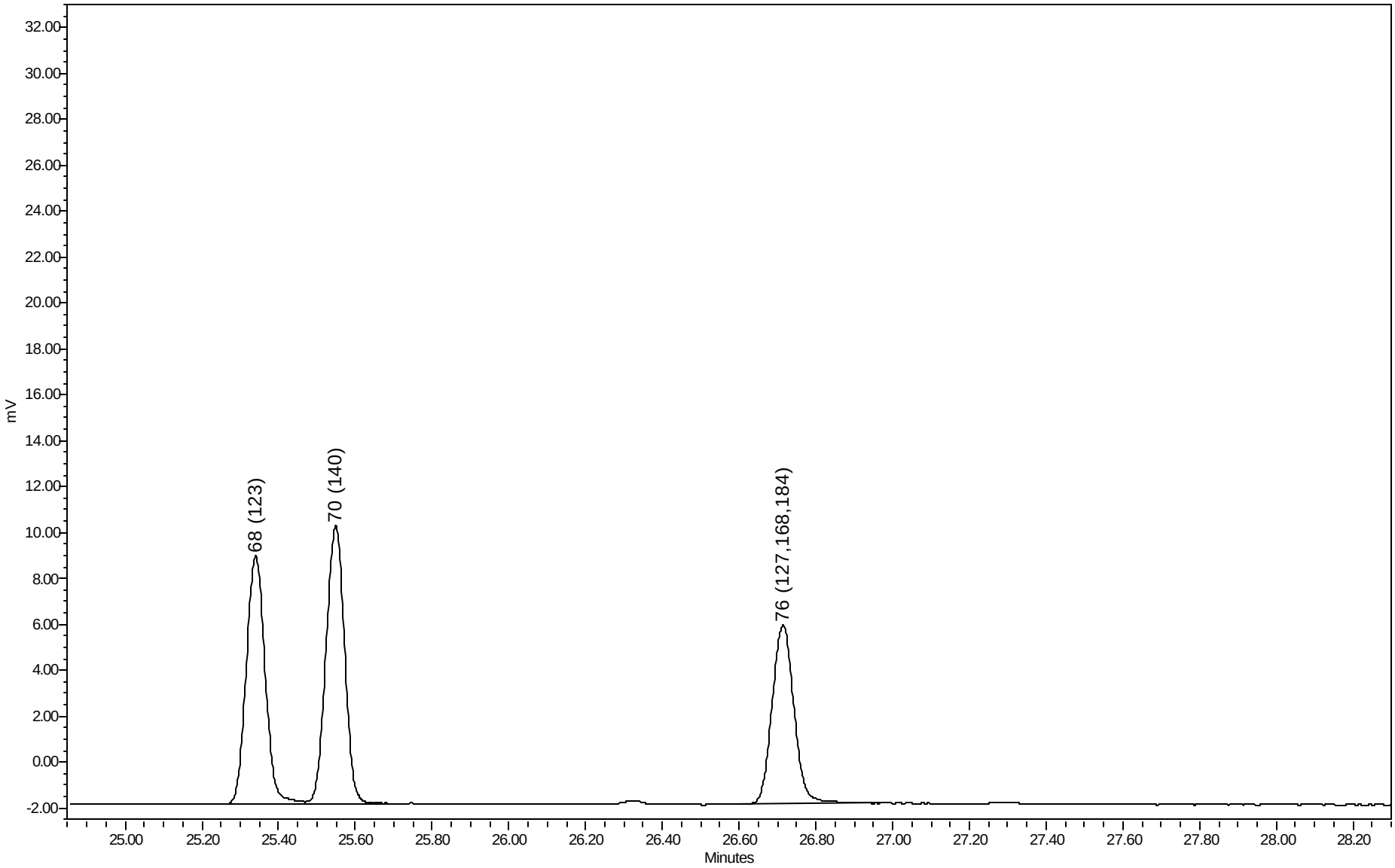
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



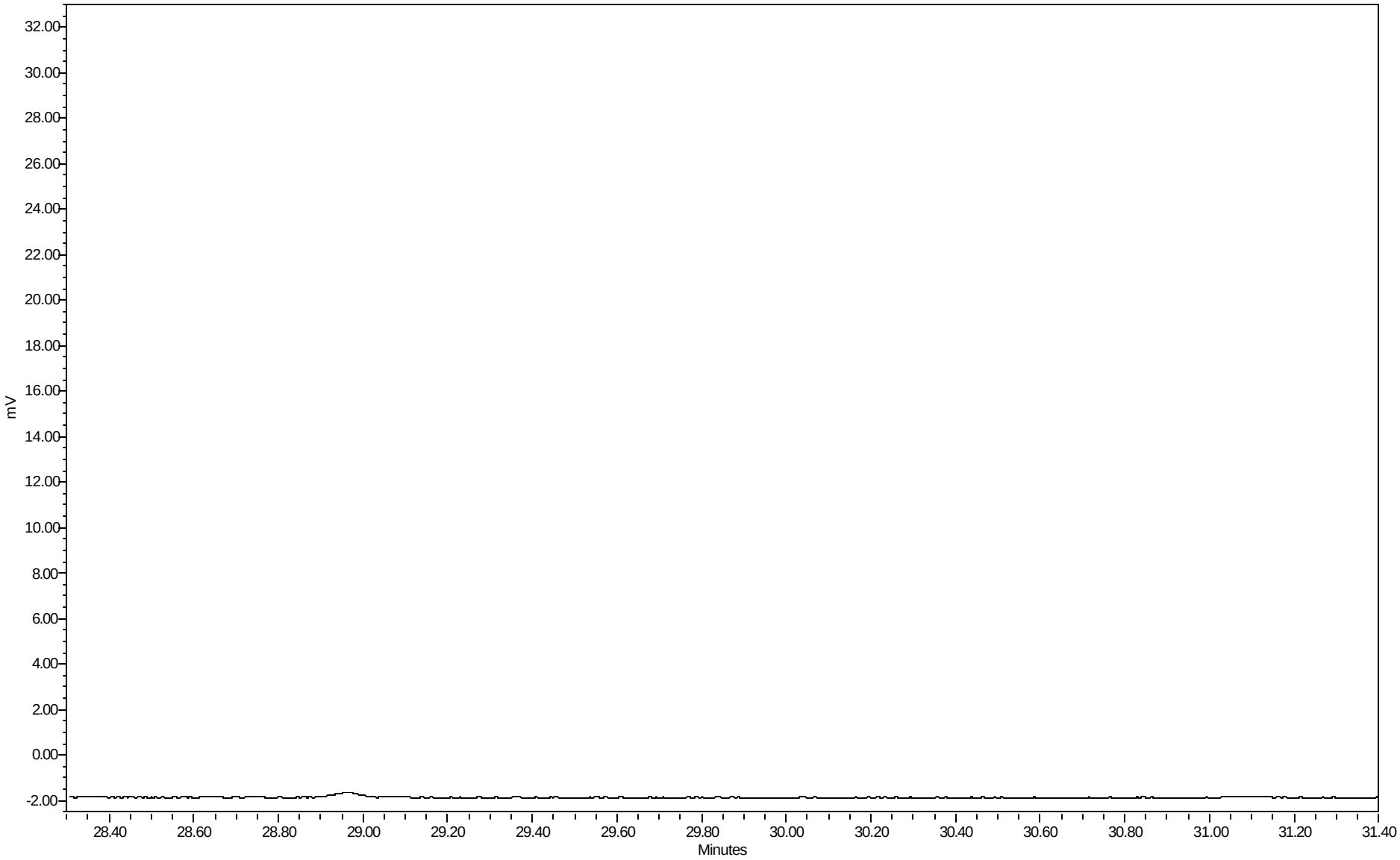
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



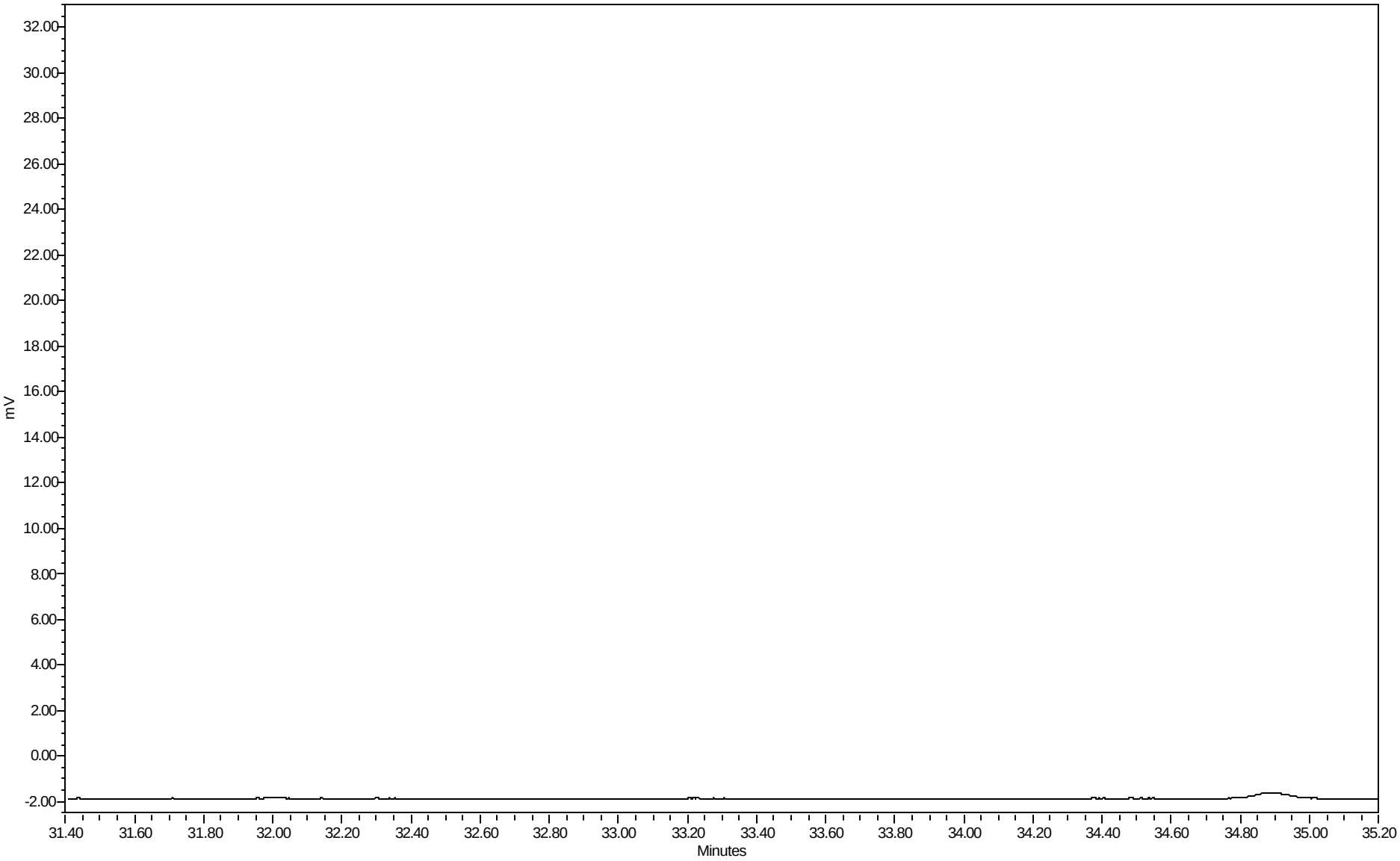
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



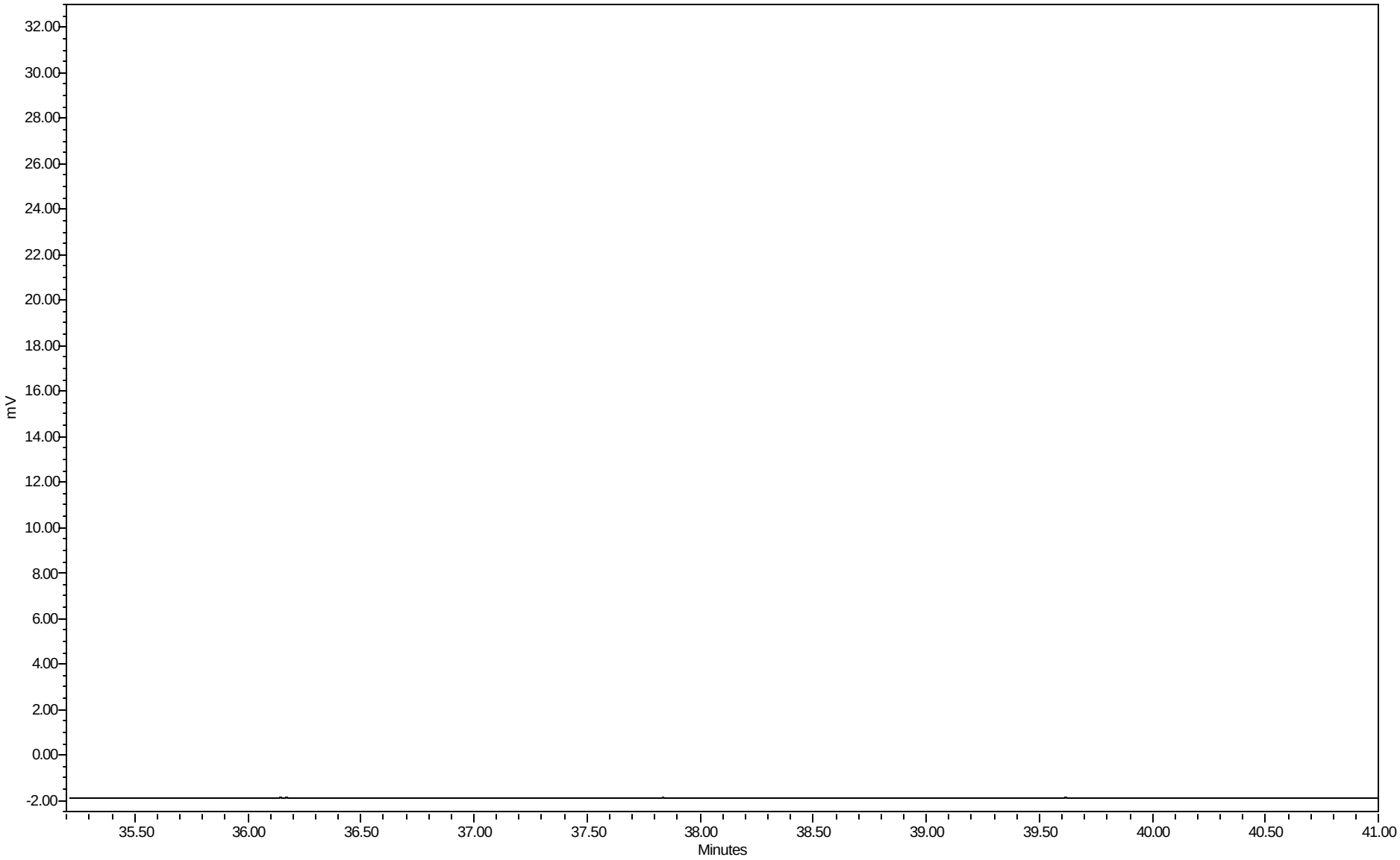
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



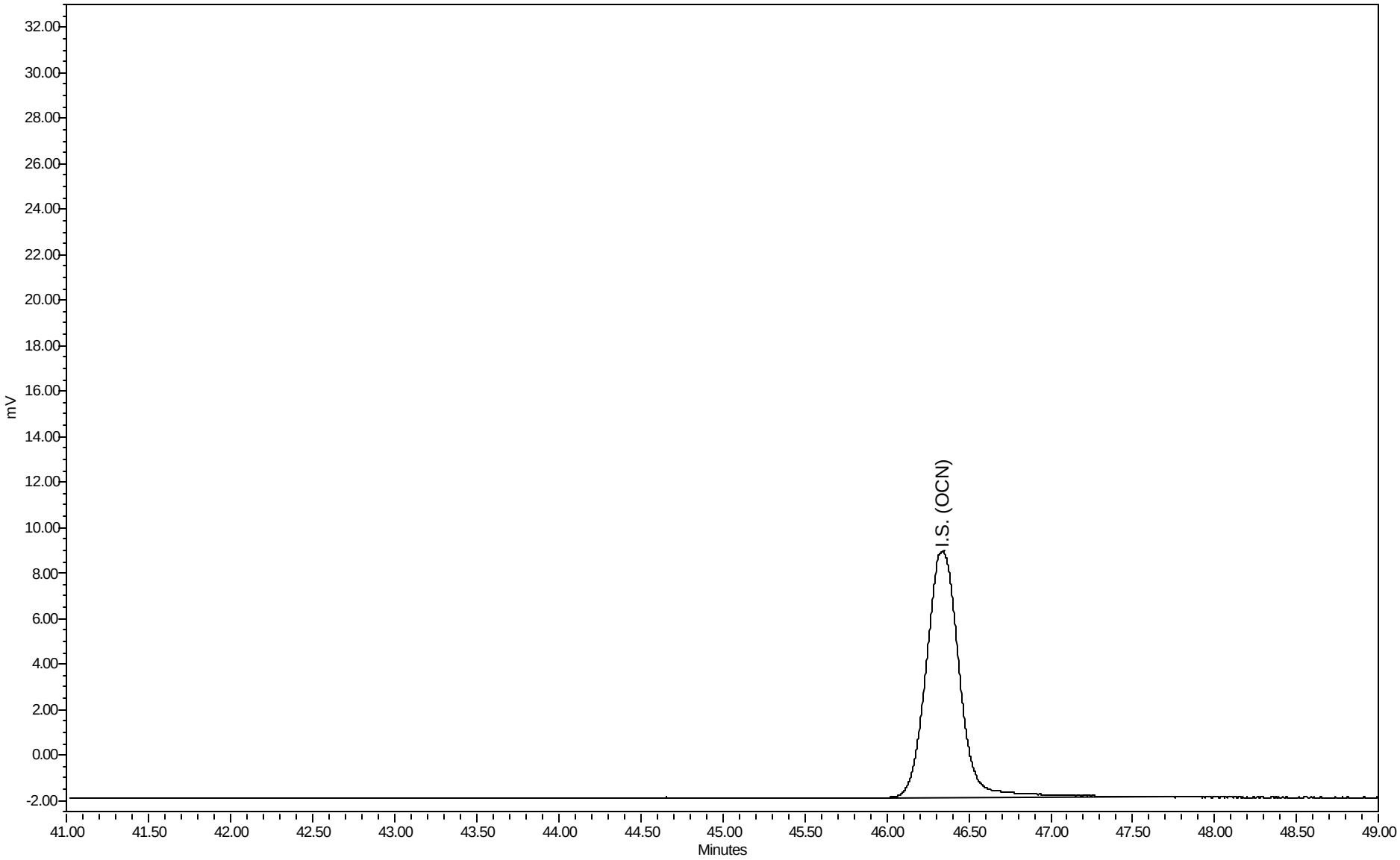
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



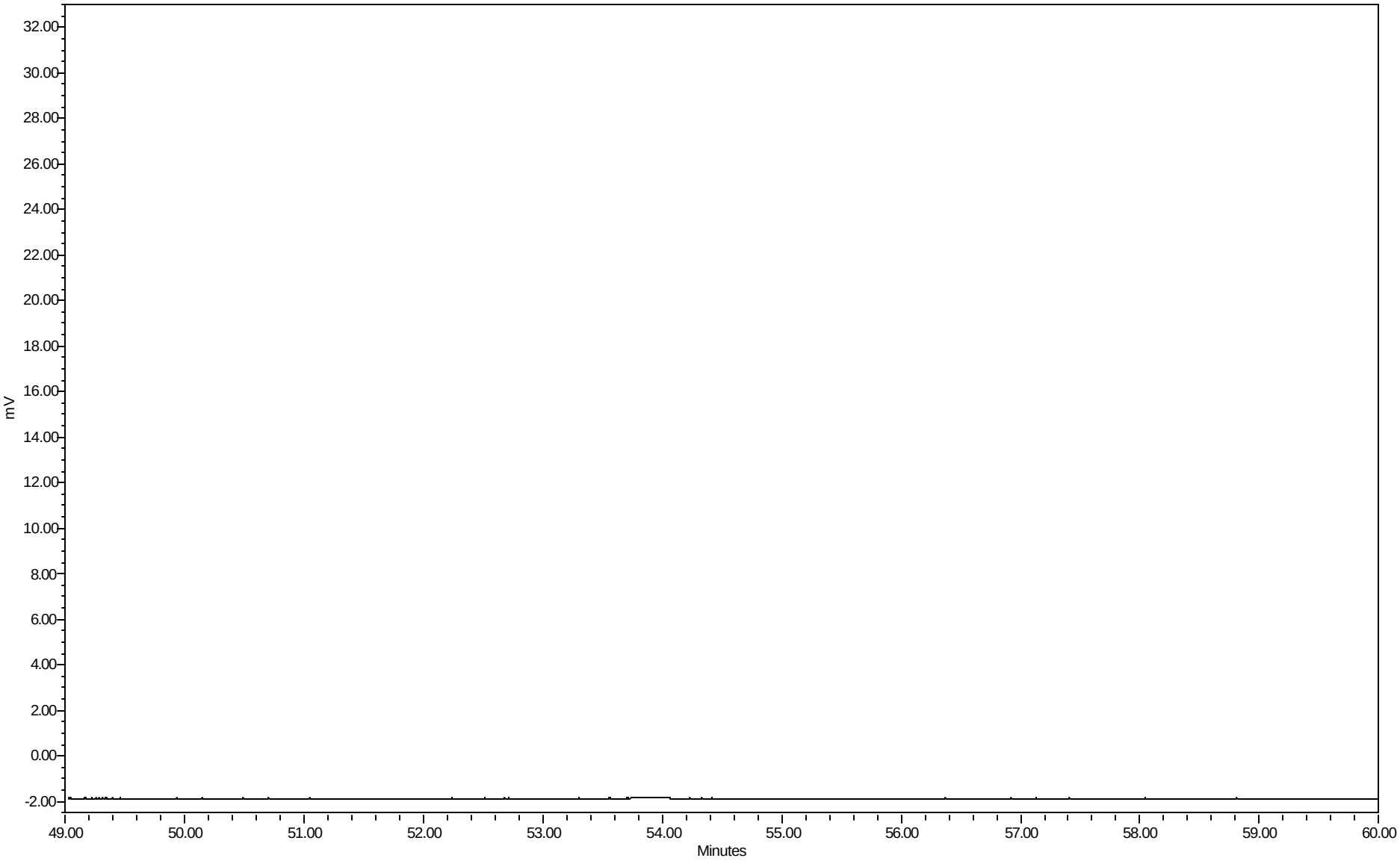
Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



Composition Chromatogram of Supplemental Congener Standard (200 / 5.0 ng/mL)



APPENDIX C

Example of reporting format

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

NEA File Name : M:\MIL2004\LIMSGC16\AH03735L.ARS

Customer : Client ID
Sample Description : Lab Control Spike

Comment : This is a comment line
Date Acquired : 04/26/2004 16:38:14

Total PCBs in sample = 175 ng/L

PCB Homolog Distribution

Homologs	Weight %	Mole %
Mono	0.00	0.00
Di	16.75	19.61
Tri	46.56	47.67
Tetra	31.07	28.19
Penta	4.95	4.03
Hexa	0.67	0.51
Hepta	0.00	0.00
Octa	0.00	0.00
Nona	0.00	0.00
Deca	0.00	0.00

Nominal 'Aroclor' Distribution

Aroclor	Indicator Peak (PK # / IUPAC #)	Amount ng/L	Percent Sediment	Percent Biota
A1221	2/001		0.0	0.0
A1242	23+24/31+28	22.7675	93.6	96.0
A1254SED	61/110	1.5444	6.4	
A1254BIO	***/###	0.9387		4.0
A1260	102/180		0.0	0.0
A1268	115/194		0.0	0.0

***/### : 69+75+82/149+153+138

Ortho Cl / biphenyl Residue = 1.44

Meta + Para Cl / biphenyl Residue = 1.74

TOTAL Cl / biphenyl Residue = 3.18

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

PCB Congener Amount Report

NEA File Name : M:\MIL2004\LIMSGC16\AH03735L.ARS

Customer : Client ID
Sample Description : Lab Control Spike

Comment : This is a comment line
Date Acquired : 04/26/2004 16:38:14
Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount ng/L	Picomoles/L Sample	MDL ng/L	RL ng/L	Qual
2	11.67	188.7				0.582	2.19	
3	12.70	188.7				25.1	1000	
4	12.80	188.7				0.318	1.28	
5	13.40	223.1	559	3.12	14.0	0.363	0.621	
6	14.26	223.1	816	0.685	3.07	0.0894	0.219	
7	14.57	223.1	1053	1.84	8.26	0.188	0.347	
8	14.76	223.1	5543	20.9	93.7	0.528	2.56	
9	15.32	223.1				0.845	25.0	
10	15.40	257.5	729	0.850	3.30	0.0660	0.102	
11	15.87	257.5				0.247	25.0	
12	15.93	223.1				0.347	25.0	
13	16.13	223.1				0.0617	0.0975	
14	16.25	249.0	9335	10.9	44.0	0.0978	0.676	
15	16.34	257.5	4867	11.1	43.2	0.142	0.676	
16	16.64	257.5	1192	0.858	3.33	0.0762	0.0762	
17	16.89	257.5	9035	12.0	46.7	0.165	0.713	
19	17.36	267.9				0.212	25.0	
20	17.53	257.5	185	0.124	0.480	0.0190	0.0194	
21	17.66	257.5	2242	2.30	8.94	0.0674	0.132	
22	17.74	257.5	1781	1.29	5.01	0.101	0.101	
23	17.94	257.5	11669	10.3	40.1	0.144	0.753	
24	17.99	257.5	15202	12.5	48.4	0.184	0.964	
25	18.34	259.5	11267	11.2	43.1	0.121	0.726	
26	18.57	258.7	7974	8.04	31.1	0.197	0.530	
27	18.80	292.0	2512	1.95	6.70	0.105	0.163	
28	18.94	257.5				0.181	25.0	
29	19.08	292.0	1154	1.03	3.51	0.117	0.117	
30	19.20	257.5				0.481	25.0	
31	19.37	292.0	5883	7.32	25.1	0.180	0.872	
32	19.54	292.0	5586	3.48	11.9	0.0508	0.420	
33	19.66	292.0	2196	0.983	3.37	0.0671	0.183	
34	19.72	292.0	2517	1.51	5.17	0.0562	0.183	
35	19.86	292.0				0.167	25.0	
36	19.94	257.5				0.200	25.0	

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount ng/L	Picomoles/L Sample	MDL ng/L	RL ng/L	Qual
37	20.11	292.0	8183	6.71	23.0	0.122	0.786	
38	20.24	272.4	6080	6.04	22.2	0.126	0.475	
39	20.58	292.0	9758	6.21	21.3	0.148	0.749	
41	20.75	326.4	83			0.209	25.0	
42	20.84	292.0	2099	1.56	5.35	0.0990	0.172	
43	21.11	298.9	91			0.221	25.0	
44	21.28	298.9	448	0.270	0.905	0.0232	0.0402	
45	21.43	292.0	440	0.260	0.892	0.115	0.115	
46	21.60	292.0	4507	1.97	6.74	0.0478	0.347	
47	21.74	292.0	8334	4.69	16.1	0.108	0.621	
48	21.85	293.5	10065	8.25	28.1	0.267	1.32	
49	22.16	324.7	741	0.464	1.43	0.0278	0.0932	
50	22.45	292.0	8631	4.85	16.6	0.0865	0.640	
51	22.69	326.4	1097	1.40	4.29	0.209	0.329	
52	22.82	326.4	287	0.190	0.581	0.0328	0.0366	
53	22.95	326.4	1541	0.997	3.06	0.0548	0.329	
54	23.15	326.4	1042	0.444	1.36	0.0573	0.135	
55	23.42	326.4	62	0.0171	0.0525	0.0150	0.0150	
56	23.52	326.4	196	0.139	0.426	0.0373	0.0548	
57	23.74	326.4	922	0.434	1.33	0.0426	0.102	
58	23.91	326.4	1781	1.03	3.15	0.0799	0.212	
59	24.07	326.4	882	0.428	1.31	0.0525	0.128	
60	24.23	360.9	456	0.297	0.822	0.0511	0.137	
61	24.32	315.8	2330	1.54	4.89	0.0768	0.389	
62	24.56	360.9				0.373	25.0	
63	24.68	326.4	871	0.449	1.37	0.0978	0.0978	
64	24.99	360.9	118	0.0644	0.178	0.0502	0.311	J
65	25.13	350.5	70	0.0231	0.0659	0.0150	0.0530	J
66	25.15	360.9	58			0.0591	0.110	
67	25.25	336.8	132	0.0924	0.274	0.0396	0.0475	
68	25.34	326.4				0.135	25.0	
69	25.45	337.5	1662	0.819	2.43	0.106	0.731	
70	25.55	360.9				0.156	25.0	
71	25.84	347.8				0.0750	0.0750	
72	26.04	336.8				0.0129	0.0129	
73	26.32	360.9				0.0260	0.0713	
74	26.43	347.8	1362	0.630	1.81	0.0802	0.248	
75	26.60	360.9				0.126	0.538	
76	26.71	360.9				0.147	25.0	
77	27.13	360.9				0.0767	0.311	
78	27.20	395.3				0.0351	0.267	
79	27.40	360.9				0.0249	0.0274	
80	27.56	360.9				0.0169	0.0475	
82	27.77	360.9	269	0.120	0.331	0.118	0.493	J
83	27.96	360.9				0.0611	0.0611	
84	28.17	360.9				0.00672	0.00672	
85	28.51	395.3				0.0903	0.201	
87	28.81	395.3				0.0165	0.0731	
88	28.96	395.3				0.0926	0.658	
89	29.08	360.9				0.0335	0.0366	
90	29.26	395.3				0.0768	0.311	

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount ng/L	Picomoles/L Sample	MDL ng/L	RL ng/L	Qual
91	29.53	360.9				0.0143	0.0179	
92	29.86	394.3				0.0265	0.0859	
93	30.24	394.3				0.130	0.585	
94	30.50	394.3				0.125	0.311	
95	30.80	382.2				0.0934	0.144	
96	31.07	429.8				0.00417	0.0121	
98	31.23	395.3				0.0799	0.0799	
99	31.61	429.8				0.0547	0.0713	
100	31.85	395.3				0.0563	0.102	
101	32.15	429.8				0.110	0.110	
102	32.33	395.3				0.163	1.11	
103	32.58	395.3				0.0731	0.0768	
104	32.88	395.3				0.0395	0.0438	
105	33.23	429.8				0.0247	0.0786	
106	34.38	395.3				0.0576	0.234	
107	34.65	395.3				0.0426	0.0768	
108	35.52	429.8				0.0443	0.0443	
109	35.75	429.8				0.244	0.768	
110	36.28	429.8				0.185	0.786	
111	37.45	395.3				0.0340	0.0340	
112	38.99	429.8				0.0492	0.101	
113	39.51	464.2				0.0532	0.0902	
114	40.45	464.2				0.0236	0.0340	
115	41.87	429.8				0.108	0.329	
116	42.76	429.8				0.0623	0.0623	
117	47.90	464.2				0.118	0.124	
118	53.86	498.6				0.0236	0.0236	

Concentration = 175 ng/L

Total Nanomoles = 0.662

Average Molecular Weight = 263.7

Number of Calibrated Peaks Found = 54

Internal Standard Retention Time = 46.33 Minutes

Internal Standard Peak Area = 158798.0

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

Congener Weight and Mole Report

NEA File Name : M:\MIL2004\LIMSGC16\AH03735L.ARS

Customer : Client ID
Sample Description : Lab Control Spike

Comment : This is a comment line
Date Acquired : 04/26/2004 16:38:14

Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
2	11.67	1:1	**001**	0.3567	2	-	-	2
3	12.70	1:0	**002**	0.3853	3	-	-	3
4	12.80	1:0	**003**	0.3880	4	-	-	4
5	13.40	2:2	**004 010**	0.4039	2-2 ; 26	1.785	2.111	5
6	14.26	2:1	**007 009**	0.4236	24 ; 25	0.392	0.463	6
7	14.57	2:1	**006**	0.4304	2-3	1.055	1.247	7
8	14.76	2:1	**005 008**	0.4346	23 ; 2-4	11.960	14.139	8
9	15.32	2:0	*014*	0.4462	35	-	-	9
10	15.40	3:3	**019**	0.4474	26-2	0.487	0.498	10
11	15.87	3:2	*030*	0.4572	246	-	-	11
12	15.93	2:0	**011**	0.4584	3-3	-	-	12
13	16.13	2:0	**012 013**	0.4622	34 ; 3-4	-	-	13
14	16.25	2:0 3:2	**015 018**	0.4650	4-4 ; 25-2	6.265	6.636	14
15	16.34	3:2	**017**	0.4668	24-2	6.370	6.524	15
16	16.64	3:2	**024 027**	0.4721	236 ; 26-3	0.491	0.503	16
17	16.89	3:2	**016 032**	0.4783	23-2 ; 26-4	6.878	7.045	17
19	17.36	3:1 4:4	*023* **034** *054*	0.4856	235 ; 35-2 ; 26-26	-	-	19
20	17.53	3:1	**029**	0.4889	245	0.071	0.072	20
21	17.66	3:1	**026**	0.4912	25-3	1.318	1.349	21
22	17.74	3:1	**025**	0.4926	24-3	0.738	0.756	22
23	17.94	3:1	**031**	0.4965	25-4	5.903	6.046	23
24	17.99	3:1 4:3	**028** *050*	0.4969	24-4 ; 246-2	7.128	7.301	24
25	18.34	3:1 4:3	**020** *021* **033 053**	0.5031	23-3 ; 234 ; 34-2 ; 25-26	6.403	6.508	25
26	18.57	3:1 4:3	**022 051**	0.5074	23-4 ; 24-26	4.602	4.692	26
27	18.80	4:3	**045**	0.5109	236-2	1.119	1.011	27
28	18.94	3:0	*036*	0.5135	35-3	-	-	28
29	19.08	4:3	**046**	0.5157	23-26	0.587	0.530	29
30	19.20	3:0	*039*	0.5172	35-4	-	-	30
31	19.37	4:2	**052** *069 073*	0.5209	25-25 ; 246-3 ; 26-35	4.188	3.783	31
32	19.54	4:2	**043 049**	0.5236	235-2 ; 24-25	1.992	1.800	32
33	19.66	4:2	*038* **047**	0.5262	345 ; 24-24	0.563	0.508	33
34	19.72	4:2	**048** *075*	0.5267	245-2 ; 246-4	0.865	0.781	34
35	19.86	4:2	*062 065*	0.5289	2346 ; 2356	-	-	35
36	19.94	3:0	**035**	0.5302	34-3	-	-	36
37	20.11	5:4 4:2	*104* **044**	0.5333	246-26 ; 23-25	3.838	3.467	37
38	20.24	3:0 4:2	**037 042 059**	0.5352	34-4 ; 23-24 ; 236-3	3.458	3.348	38
39	20.58	4:2	**041 064 071** *072*	0.5406	234-2 ; 236-4 ; 26-34 ; 25-35	3.555	3.211	39
41	20.75	5:4	*068* **096**	0.5435	24-35 ; 236-26	-	-	41
42	20.84	4:2	**040**	0.5446	23-23	0.894	0.807	42
43	21.11	4:1 5:3	**057** *103*	0.5489	235-3 ; 246-25	-	-	43
44	21.28	4:1 5:3	*058* **067** *100*	0.5517	23-35 ; 245-3 ; 246-24	0.155	0.137	44
45	21.43	4:1	**063**	0.5534	235-4	0.149	0.135	45
46	21.60	4:1 5:3	**074** *094 061*	0.5570	245-4 ; 235-26 ; 2345	1.127	1.018	46

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
47	21.74	4:1	**070**	0.5595	25-34	2.684	2.424	47
48	21.85	4:1 5:3	**066** *076 098 080 093* **095 102** *088*	0.5609	24-34 ; 345-2 ; 246-23 ; 35-35 ; 2356-2 ; 236-25 ; 245-26 ; 2346-2	4.722	4.243	48
49	22.16	4:1 5:3	*055* **091** *121*	0.5658	234-3 ; 236-24 ; 246-35	0.266	0.216	49
50	22.45	4:1	**056 060**	0.5701	23-34 ; 234-4	2.776	2.507	50
51	22.69	5:3 6:4	**084 092** *155*	0.5739	236-23 ; 235-25 ; 246-246	0.802	0.648	51
52	22.82	5:3	**089**	0.5761	234-26	0.108	0.088	52
53	22.95	5:2	**090 101**	0.5788	235-24 ; 245-25	0.571	0.461	53
54	23.15	5:2	*079* **099** *113*	0.5814	34-35 ; 245-24 ; 236-35	0.254	0.205	54
55	23.42	5:2 6:4	**119** *150*	0.5860	246-34 ; 236-246	0.010	0.008	55
56	23.52	5:2	*078* **083** *112 108*	0.5874	345-3 ; 235-23 ; 2356-3 ; 2346-3	0.080	0.064	56
57	23.74	5:2 6:4	**097** *152 086*	0.5903	245-23 ; 2356-26 ; 2345-2	0.248	0.201	57
58	23.91	5:2	*081* **087** *117 125* **115** *145*	0.5929	345-4 ; 234-25 ; 2356-4 ; 345-26 ; 2346-4 ; 2346-26	0.589	0.476	58
59	24.07	5:2	*116* **085** *111*	0.5953	23456 ; 234-24 ; 235-35	0.245	0.198	59
60	24.23	6:4	*120* **136**	0.5971	245-35 ; 236-236	0.170	0.124	60
61	24.32	4:0 5:2	**077 110** *148*	0.5998	34-34 ; 236-34 ; 235-246	0.884	0.738	61
62	24.56	6:3	*154*	0.6039	245-246	-	-	62
63	24.68	5:2	**082**	0.6055	234-23	0.257	0.207	63
64	24.99	6:3	**151**	0.6101	2356-25	0.037	0.027	64
65	25.13	5:1 6:3	**124 135**	0.6129	345-25 ; 235-236	0.013	0.010	65
66	25.15	6:3	**144**	0.6139	2346-25	-	-	66
67	25.25	5:1 6:3	*107* **109** *147*	0.6152	234-35 ; 235-34 ; 2356-24	0.053	0.041	67
68	25.34	5:1	*123*	0.6166	345-24	-	-	68
69	25.45	5:1 6:3	*106* **118** *139* **149**	0.6186	2345-3 ; 245-34 ; 2346-24 ; 236-245	0.469	0.366	69
70	25.55	6:3	*140*	0.6202	234-246	-	-	70
71	25.84	5:1 6:3	**114 134** *143*	0.6256	2345-4 ; 2356-23 ; 2345-26	-	-	71
72	26.04	5:1 6:3	**122 131 133** *142*	0.6289	345-23 ; 2346-23 ; 235-235 ; 23456-2	-	-	72
73	26.32	6:2	**146** *165 188*	0.6342	235-245 ; 2356-35 ; 2356-246	-	-	73
74	26.43	5:1 6:3	**105 132** *161*	0.6364	234-34 ; 234-236 ; 2346-35	0.361	0.274	74
75	26.60	6:2	**153**	0.6393	245-245	-	-	75
76	26.71	6:2	*127 168 184*	0.6412	345-35 ; 246-345 ; 2346-246	-	-	76
77	27.13	6:2	**141**	0.6488	2345-25	-	-	77
78	27.20	7:4	**179**	0.6499	2356-236	-	-	78
79	27.40	6:2	**137**	0.6537	2345-24	-	-	79
80	27.56	6:2 7:4	**130 176**	0.6565	234-235 ; 2346-236	-	-	80
82	27.77	6:2	**138 163 164**	0.6605	234-245 ; 2356-34 ; 236-345	0.068	0.050	82
83	27.96	6:2	**158** *160 186*	0.6639	2346-34 ; 23456-3 ; 23456-26	-	-	83
84	28.17	6:2	*126* **129**	0.6674	345-34 ; 2345-23	-	-	84
85	28.51	7:3	*166* **178**	0.6735	23456-4 ; 2356-235	-	-	85
87	28.81	7:3	**175** *159*	0.6790	2346-235 ; 2345-35	-	-	87
88	28.96	7:3	*182* **187**	0.6816	2345-246 ; 2356-245	-	-	88
89	29.08	6:2	**128** *162*	0.6838	234-234 ; 235-345	-	-	89
90	29.26	7:3	**183**	0.6871	2346-245	-	-	90
91	29.53	6:1	**167**	0.6919	245-345	-	-	91
92	29.86	7:3	**185**	0.6980	23456-25	-	-	92
93	30.24	7:3	**174** *181*	0.7046	2345-236 ; 23456-24	-	-	93
94	30.50	7:3	**177**	0.7094	2356-234	-	-	94
95	30.80	6:1 7:3	**156 171**	0.7149	2345-34 ; 2346-234	-	-	95
96	31.07	8:4	**157 202**	0.7195	234-345 ; 2356-2356	-	-	96
98	31.23	7:3	**173**	0.7226	23456-23	-	-	98
99	31.61	8:4	**201**	0.7294	2346-2356	-	-	99
100	31.85	7:2	**172** *204*	0.7339	2345-235 ; 23456-246	-	-	100
101	32.15	8:4	*192* **197**	0.7392	23456-35 ; 2346-2346	-	-	101
102	32.33	7:2	**180**	0.7427	2345-245	-	-	102
103	32.58	7:2	**193**	0.7471	2356-345	-	-	103
104	32.88	7:2	**191**	0.7527	2346-345	-	-	104
105	33.23	8:4	**200** *169*	0.7588	23456-236 ; 345-345	-	-	105
106	34.38	7:2	**170**	0.7799	2345-234	-	-	106
107	34.65	7:2	**190**	0.7850	23456-34	-	-	107
108	35.52	8:3	**198**	0.8007	23456-235	-	-	108

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
109	35.75	8:3	**199**	0.8050	2345-2356	-	-	109
110	36.28	8:3	**196 203**	0.8149	2345-2346 ; 23456-245	-	-	110
111	37.45	7:1	**189**	0.8365	2345-345	-	-	111
112	38.99	8:3	**195**	0.8647	23456-234	-	-	112
113	39.51	9:4	**208**	0.8743	23456-2356	-	-	113
114	40.45	9:4	*207*	0.8909	23456-2346	-	-	114
115	41.87	8:2	**194**	0.9177	2345-2345	-	-	115
116	42.76	8:2	**205**	0.9342	23456-345	-	-	116
117	47.90	9:3	**206**	1.0294	23456-2345	-	-	117
118	53.86	10:4	*209*	1.1406	23456-23456	-	-	118

Concentration = 175 ng/L

Total Nanomoles = 0.662

Average Molecular Weight = 263.7

Number of Calibrated Peaks Found = 54

[1] - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)

PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

[2] - IUPAC congener numbers listed in **boldface** font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in *italic* font were absent or present below 0.05 weight percent.

[3] - PCB congener identification is denoted by position of the chlorine atoms on each ring of the biphenyl molecule. Designation used in this report has unprimed chlorines separated from prime chlorines by a hyphen that represents separation of the biphenyl rings.

[4] - DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indication the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76, 98, 80, 93*, **95**, **102**, *88*)	*80, 88, 93*
56 (*78,* **83**, *112, 108)*	*108*
61 (**77, 110**, *148*)	**77**
72 (**122**, *131, 133, 142*)	**122**
89 (**128**, *162*)	*162*
105 (**200**,*169*)	*169*

APPENDIX 10

NITROGEN, NITRATE-NITRITE

Method 353.3 (Spectrophotometric, Cadmium Reduction)

STORET NO. Total 00630

1. Scope and Application

1.1 This method is applicable to the determination of nitrite singly, or nitrite and nitrate combined in drinking, surface and saline waters, domestic and industrial wastes. The applicable range of this method is 0.01 to 1.0 mg/l nitrate-nitrite nitrogen. The range may be extended with sample dilution.

2. Summary of Method

2.1 A filtered sample is passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite (that originally present plus reduced nitrate) is determined by diazotizing with sulfanilamide and coupling with N-(I-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye which is measured spectrophotometrically. Separate, rather than combined nitrate-nitrite, values are readily obtained by carrying out the procedure first with, and then without, the Cu-Cd reduction step.

3. Sample Handling and Preservation

3.1 Analysis should be made as soon as possible. If analysis can be made within 24 hours, the sample should be preserved by refrigeration at 4oC. When samples must be stored for more than 24 hours, they should be preserved with sulfuric acid (2 ml H2S04 per liter) and refrigeration.

Caution: Samples for reduction column must not be preserved with mercuric chloride.

4. Interferences

4.1 Build up of suspended matter in the reduction column will restrict sample flow. Since nitrate-nitrogen is found in a soluble state, the sample may be pre-filtered through a glass fiber filter or a 0.45u membrane filter. Highly turbid samples may be pretreated with zinc sulfate before filtration to remove the bulk of particulate matter present in the sample.

4.2 Low results might be obtained for samples that contain high concentrations of iron, copper or other metals. EDTA is added to the samples to eliminate this interference.

4.3 Samples that contain large concentrations of oil and grease will coat the surface of the cadmium. This interference is eliminated by pre-extracting the sample with an organic solvent.

4.4 This procedure determines both nitrate and nitrite. If only nitrate is desired, a separate determination must be made for nitrite and subsequent corrections made. The nitrite may be determined by the procedure below without the reduction step.

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Issued 1974

Method SOP
Analyte NITRATE- NITRITE
Doc. No. 353.3 Rev. No. 1
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John Wilson
Laboratory Supervisor

5. Apparatus

5.1 Reduction column: The column in Figure I was constructed from a 100 ml pipet by removing the top portion. This column may also be constructed from two pieces of tubing joined end to end. A 10 mm length of 3 cm I. D. tubing is joined to a 2 5 cm. length of 3.5 mm I.D. tubing.

5.2 Spectrophotometer for use at 540 rim, providing a light path of 1 cm or longer.

6. Reagents

6.1 Granulated cadmium: 40-60 mesh (MCB Reagents).

6.2 Copper-Cadmium: The cadmium granules (new or used) are cleaned with dilute HCl and copperized with 2% solution of copper sulfate in the following manner: 6.2.1 Wash the cadmium with dilute HCl (6. 10) and rinse with distilled water. The color *of* the cadmium should be silver.

6.12

6.2.2 Swirl 25 g cadmium in 100 ml portions of a 2% solution of copper sulfate (6.11) for 5 minutes -or until blue color partially fades, decant and repeat with fresh copper sulfate until a brown colloidal precipitate forms.

6.2.3 Wash the copper-cadmium with distilled water (at least 10 times) to remove all the precipitated copper. The color of the cadmium so treated should be black.

6.3 Preparation of reaction column: Insert a glass wool plug into the bottom of the reduction column and fill with distilled water. Add sufficient-copper-cadmium granules to produce a column 18.5 cm in length. Maintain a level of distilled water above the copper cadmium granules to eliminate entrapment of air. Wash the column with 200 ml of dilute ammonium chloride solution (6.5). The column is then activated by passing through the column 100 ml of a solution composed of 25 ml of a 1.0 mg/l $N0_3$-N standard and 75 ml *of* ammonium chloride - EDTA solution (6.4). Use a flow rate between 7 and 10 ml per minute.

6.4 Ammonium chloride - EDTA solution: Dissolve 13 g ammonium chloride and 1.7 g disodium ethylenediamine tetracetate in 900 ml of distilled water. Adjust the pH to 8.5 with conc. ammonium hydroxide (6.9) and dilute to I liter.

6.5 Dilute ammonium chloride-EDTA solution: Dilute 300 ml of ammonium chloride EDTA solution (6.4) to 500 ml with distilled water.

6.6 Color reagent: Dissolve 10 g sulfanilamide and I g N(1-naphthyl)-ethylene-diamine dihydrochloride in a mixture of 100 ml conc. phosphoric acid and 800 ml of distilled water and dilute to I liter with distilled water.

6.7 Zinc sulfate solution: Dissolve 100 g $ZnSO_4 \cdot 7H_20$ in distilled water and dilute to 1 liter.

6.8 Sodium hydroxide solution, 6N: Dissolve 240 g NaOH in 500 ml distilled water, cool and dilute to I liter.

6.9 Ammonium hydroxide, conc.

6.10 Dilute hydrochloric acid, 6N: Dilute 50 ml of conc. HCI to 100 ml with distilled water.

6.11 Copper sulfate solution, 2%: Dissolve 20 g of $CuSO_4.5H_2O$ in 500 ml of distilled water and dilute to I liter.

Stock nitrate solution: Dissolve 7.218 g $KN0_3$ in distilled water and dilute to 1000 ml. Preserve with 2 ml of chloroform per liter. This solution is stable for at least 6 months. 1.0 ml = 1.00 mg $N0_3$-N.

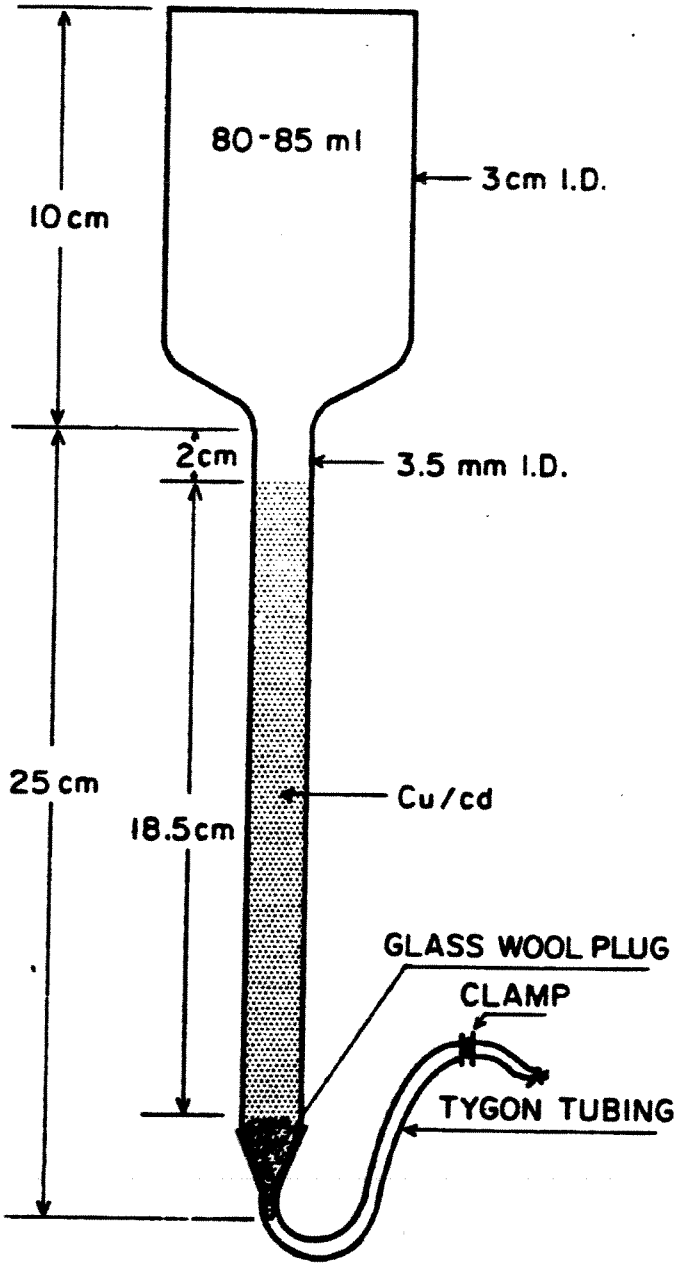

FIGURE 1. REDUCTION COLUMN

6.13 Standard nitrate solution: Dilute 10.0 ml of nitrate stock solution (6.12) to 1000 ml with distilled water. 1.0 ml = 0.0 1 mg $N0_3$-N.

6.14 Stock nitrite solution: Dissolve 6.072 g KNO_2 in 500 ml of distilled water and dilute to 1000 ml. Preserve with 2 in] of chloroform and keep under refrigeration. Stable for approximately 3 months. 1.0 ml = 1.00 mg $N0_2$-N.

6.15 Standard nitrite solution: Dilute 10.0 ml of stock nitrite solution (6.14) to 1000 ml with distilled water. 1.0 ml = 0.01 mg $N0_2$-N.

6.16 Using standard nitrate solution (6.13) prepare the following standards in 100 in] volumetric flasks:

Conc., mg-$N0_3$-N/l	ml of Standard Solution/100.0 ml
0.00	0.0
0.05	0.5
0.10	1.0
0.20	2.0
0.50	5.0
1.00	10.0

7. Procedure

7.1 Turbidity removal: One of the following methods may be used to remove suspended matter.

7.1.1 Filter sample through a glass fiber filter or a 0.45u membrane filter.

7.1.2 Add 1 ml zinc sulfate solution (6.7) to 100 ml of sample and mix thoroughly. Add 0.4-0.5 ml sodium hydroxide solution (6.8) to obtain a pH of 10.5 as determined with a pH meter. Let the treated sample stand a few minutes to allow the heavy flocculent precipitate to settle. Clarify by filtering through a glass fiber filter or a 0.45u membrane filter.

7.2 Oil and grease removal: Adjust the pH of 100 ml of filtered sample to 2 by addition of conc. HCl. Extract the oil and grease from the aqueous solution with two 25 ml portions of a non- polar solvent (freon, chloroform or equivalent).

7.3 If the pH of the sample is below 5 or above 9, adjust to between 5 and 9 with either conc. HC1 or conc. NH_40H. This is done to insure a sample pH of 8.5 after step 7.4.

7.4 To 25.0 ml of sample or an aliquot diluted to 25.0 ml, add 75 ml of ammonium chloride EDTA solution (6.4) and mix.

7.5 Pour sample into column and collect sample at a rate of 7-10 ml per minute.

7.6 Discard the first 25 ml, collect the rest of the sample (approximately 70 ml) in the original sample flask. Reduced samples should not be allowed to stand longer than 15 minutes before addition of color reagent, step 7.7.

7.7 Add 2.0 ml of color reagent (6.6) to 50.0 ml of sample. Allow 10 minutes for color development. Within 2 hours measure the absorbance at 540 nm against a reagent blank. **NOTE:** If the concentration of sample exceeds 1.0 mg $N0_3$-N/l, the remainder of the reduced sample may be used to make an appropriate dilution before proceeding with step 7.7.

7.8 Standards: Carry out the reduction of standards exactly as described for the samples. At least one nitrite standard should be compared to a reduced nitrate standard at the same concentration to verify the efficiency of the reduction column.

8. Calculation

8.1 Obtain a standard curve by plotting the absorbance of standards run by the above procedure against N03-N mg/l. Compute concentration of samples by comparing sample absorbance with standard curve.

8.2 If less than 25 ml of sample is used for the analysis the following equation should be used:

$$\text{mgNO2 + NO, - N/l} = \frac{\text{A x 25}}{\text{ml sample used}}$$

where:

A = Concentration of nitrate from standard curve.

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using sewage samples at concentrations of 0.04, 0.24, 0.55 and 1.04 mg $N0_3$ + $N0_2$-N/l, the standard deviations were ±0.005, ±0.004, ±0.005 and -±0.01, respectively.

9.2 In a single laboratory (EMSL), using sewage samples at concentrations of 0.24, 0.55, and 1.05 mg $N0_3$+ $N0_2$-N/1, the recoveries were 100%, 102% and 100%, respectively.

Bibliography

1 Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 423, Method 419C (19 7 5).

2. Henrikson, A., and Selmer-Olsen, "Automatic Methods for Determining Nitrate and Nitrite in Water and Soil Extracts". Analyst, May 1970, Vol. 95, p 514-518.

3. Grasshoff, K., "A Simultaneous Multiple Channel System for Nutrient Analysis in Sea Water with Analog and Digital Data Record", "Advances in Automated Analysis", Technicon International Congress, 1969, Vol. 11, p 133-145.

4. Brewer, P. G., Riley, J. P., "The Automatic Determination of Nitrate in Sea Water", Deep Sea Research, 1965, Vol. 12, p 765-772.

APPENDIX 11

NITROGEN, NITRITE

Method 354.1 (Spectrophotometric)

STORET NO. Total 00615

1. Scope and Application
   - 1.1 This method is applicable to the determination of nitrite in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The method is applicable in the range from 0.01 to 1.0 mg NO_2–N/1.
2. Summary of Method
   - 2.1 The diazonium compound formed by diazotation of sulfanilamide by nitrite in water under acid conditions is coupled with N–(1-naphthyl)–ethylenediamine dihydrochloride to produce a reddish-purple color which is read in a spectrophotometer at 540 nm.
3. Sample Handling and Preservation
   - 3.1 Samples should be analyzed as soon as possible. They may be stored for 24 to 48 hours at 4°C.
4. Interferences
   - 4.1 There are very few known interferences at concentrations less than 1,000 times that of the nitrite; however, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity (> 600 mg/1) will give low results due to a shift in pH.
5. Apparatus
   - 5.1 Spectrophotometer equipped with 1 cm or larger cells for use at 540 nm.
   - 5.2 Nessler tubes, 50 ml or volumetric flasks, 50 ml.
6. Reagents
   - 6.1 Distilled water free of nitrite and nitrate is to be used in preparation of all reagents and standards.
   - 6.2 Buffer-color reagent: To 250 ml of distilled water, add 105 ml conc. hydrochloric acid, 5.0 g sulfanilamide and 0.5 g N–(1-naphthyl) ethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate ($CH_3COONa \cdot 3H_2O$) and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.
   - 6.3 Nitrite stock solution: 1.0 ml = 0.10 mg NO_2–N. Dissolve 0.1493 g of dried anhydrous sodium nitrite (24 hours in desiccator) in distilled water and dilute to 1000 ml. Preserve with 2 ml chloroform per liter.
   - 6.4 Nitrite standard solution: 1.0 ml = 0.001 mg NO_2–N. Dilute 10.0 ml of the stock solution (6.3) to 1000 ml.
7. Procedure
   - 7.1 If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg/1, adjust to approximately pH 6 with 1:3 HCl.

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Method SOP
Analyte NITRITE
Doc. No. 354.1 Rev. No. 1
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John Wilson
Laboratory Supervisor

7.2 If necessary, filter the sample through a 0.45 *u* pore size filter using the first portion of filtrate to rinse the filter flask.

7.3 Place 50 ml of sample, or an aliquot diluted to 50 ml, in a 50 ml Nessler tube; hold until preparation of standards is completed.

7.4 At the same time prepare a series of standards in 50 ml Nessler tubes as follows:

ml of Standard Solution 1.0 ml = 0.001 mg NO_2-N	Conc., When Diluted to 50 ml, mg/l of NO_2–N
0.0	(Blank)
0.5	0.01
1.0	0.02
1.5	0.03
2.0	0.04
3.0	0.06
4.0	0.08
5.0	0.10
10.0	0.20

7.5 Add 2 ml of buffer-color reagent (6.2) to each standard and sample, mix and allow color to develop for at least 15 minutes. The color reaction medium should be between pH 1.5 and 2.0.

7.6 Read the color in the spectrophotometer at 540 nm against the blank and plot concentration of NO_2–N against absorbance.

8. Calculation

8.1 Read the concentration of NO_2–N directly from the curve.

8.2 If less than 50.0 ml of sample is taken, calculate mg/l as follows:

$$NO_2 - N, \text{ mg/l} = \frac{\text{mg/l from std. curve} \times 50}{\text{ml sample used}}$$

9. Precision and Accuracy

9.1 Precision and Accuracy data are not available at this time.

Bibliography

1. Standard Methods for the Examination for Water and Wastewater, 14th Edition, p 434, Method 420, (1975).

APPENDIX 12

NITROGEN, KJELDAHL, TOTAL

Method 351.3 (Colorimetric; Titrimetric; Potentiometric)

STORETNO.00625

1. Scope and Application

1.1 This method covers the determination of total Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes. The procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, but may not convert the nitrogenous compounds of some industrial wastes such as amines, nitro compounds, hydrazones, oximes, semicarbazones and some refractory tertiary amines.

1.2 Three alternatives are listed for the determination of ammonia after distillation: the titrimetric method which is applicable to concentrations above 1 mg N/liter; the Nesslerization method which is applicable to concentrations below 1 mg N/liter; and the potentiometric method applicable to the range 0.05 to 1400 mg/L

1.3 This method is described for macro and micro glassware systems.

2. Definitions

2.1 Total Kjeldahl nitrogen is defined as the sum of free-ammonia and organic nitrogen compounds which are converted to ammonium sulfate $(NH_4)_2SO_4$, under the conditions of digestion described below.

2.2 Organic Kjeldahl nitrogen is defined as the difference obtained by subtracting the free ammonia value (Method 350.2, Nitrogen, Ammonia, this manual) from the total Kjeldahl nitrogen value. This may be determined directly by removal of ammonia before digestion.

3. Summary of Method

3.1 The sample is heated in the presence of conc. sulfuric acid, K_2SO_4 and $HgSO_4$ and evaporated until $S0_3$ fumes are obtained and the solution becomes colorless or pale yellow. The residue is cooled, diluted, and is treated and made alkaline with a hydroxide-thiosulfate solution. The ammonia is distilled and determined after distillation by Nesslerization, titration or potentiometry.

4. Sample Handling and Preservation

4.1 Samples may be preserved by addition of 2 ml of conc. H_2SO_4 per liter and stored at 4oC. Even when preserved in this manner, conversion of organic nitrogen to ammonia may occur. Preserved samples should be analyzed as soon as possible.

5. Interference

5.1 High nitrate concentrations (10X or more than the TKN level) result in low TKN values. The reaction between nitrate and ammonia can be prevented by the use of an anion exchange resin (chloride form) to remove the nitrate prior to the TKN analysis.

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Method SOP
Analyte TKN
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Laboratory Supervisor

6. Apparatus

6.1 Digestion apparatus: A Kjeldahl digestion apparatus with 800 or 100 ml flasks and suction takeoff to remove SO_3 fumes and water.

6.2 Distillation apparatus: The macro Kjeldahl flask is connected to a condenser and an adaptor so that the distillate can be collected. Micro Kjeldahl steam distillation apparatus is commercially available.

6.3 Spectrophotometer for use at 400 to 425 nm with a light path of 1 cm or longer.

7. Reagents

7.1 Distilled water should be free of ammonia. Such water is best prepared by the passage of distilled water through an ion exchange column containing a strongly acidic cation exchange resin mixed with a strongly basic anion exchange resin. Regeneration of the column should be carried out according to the manufacturer's instructions.
NOTE 1: All solutions must be made with ammonia-free water.

7.2 Mercuric sulfate solution: Dissolve 8 g red mercuric oxide (HgO) in 50 ml of 1:4 sulfuric acid (10.0 ml conc. H_2SO_4 : 40 ml distilled water) and dilute to 100 ml with distilled water.

7.3 Sulfuric acid-mercuric sulfate-potassium sulfate solution: Dissolve 267 g K_2SO_4 in 1300 ml distilled water and 400 ml conc. H_2SO_4. Add 50 ml mercuric sulfate solution (7.2) and dilute to 2 liters with distilled water.

7.4 Sodium hydroxide-sodium thiosulfate solution: Dissolve 500 g NaOH and 25 g $Na_2S_2O_3 \cdot 5H_20$ in distilled water and dilute to 1 liter.

7.5 Mixed indicator: Mix 2 volumes of 0.2% methyl red in 95% ethanol with I volume of 0.2% methylene blue in ethanol. Prepare fresh every 30 days.

7.6 Boric acid solution: Dissolve 20 g boric acid, H_3BO_3, in water and dilute to I liter with distilled water.

7.7 Sulfuric acid, standard solution: (0.02 N) I ml = 0.28 mg NH_3-N. Prepare a stock solution of approximately 0.1 N acid by diluting 3 ml of conc. H_2SO_4 (sp. gr. 1.84) to I liter with $C0_2$-free distilled water. Dilute 200 ml of this solution to I liter with C02-free distilled water. Standardize the approximately 0.02 N acid so prepared against 0.0200 N Na2CO3 solution. This last solution is prepared by dissolving 1.060 g anhydrous Na_2CO_3, oven-dried at 140°C, and diluting to 1 liter with $C0_2$-free distilled water.
NOTE 2: An alternate and perhaps preferable method is to standardize the approximately 0. 1 N H_2SO_4 solution against a 0. 100 N Na_2C0_3 solution. By proper dilution the 0.02 N acid can the be prepared.

7.8 Ammonium chloride, stock solution: 1.0 ml = 1.0 mg NH_3-N. Dissolve 3.819 g NH_4CI in water and make up to I liter in a volumetric flask with distilled water.

7.9 Ammonium chloride, standard solution: 1.0 ml = 0.01 mg NH_3-N. Dilute 10.0 ml of the stock solution (7.8) with distilled water to I liter in a volumetric flask.

7.10 Nessler reagent: Dissolve 100 g of mercuric iodide and 70 g potassium iodide in a small volume of distilled water. Add this mixture slowly, with stirring, to a cooled solution of 160 g of NaOH in 500 ml of distilled water. Dilute the mixture to I liter. The solution is stable for at least one year if stored in a pyrex bottle out of direct sunlight.

NOTE 3: Reagents 7.7, 7.8, 7.9, and 7. 10 are identical to reagents 6.8, 6.2, 6.3, and 6.6 described under Nitrogen, Ammonia (Colorimetric; Titrimetric; Potentiometric Distillation Procedure, Method 350.2).

8. Procedure

8.1 The distillation apparatus should be pre-steamed before use by distilling a 1: 1 mixture of distilled water and sodium hydroxide-sodium thiosulfate solution (7.4) until the distillate is ammonia-free. This operation should be repeated each time the apparatus is out of service long enough to accumulate ammonia (usually 4 hours or more).

8.2 Macro Kjeldahl system

8.2.1 Place a measured sample or the residue from the distillation in the ammonia determination (for Organic Kjeldahl only) into an 800 ml Kjeldahl flask. The sample size can be determined from the following table:

Kjeldahl Nitrogen in Sample, mg/l	Sample Size ml
0-5	500
5-10	250
10-20	100
20-50	50.0
50-500	25.0

Dilute the sample, if required, to 500 ml with distilled water, and add 100 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Continue heating for 30 additional minutes. Cool the residue and add 300 ml distilled water.

8.2.2 Make the digestate alkaline by careful addition of 100 ml of sodium hydroxide - thiosulfate solution (7.4) without mixing.

NOTE 5: Slow addition of the heavy caustic solution down the tilted neck of the digestion flask will cause heavier solution to underlay the aqueous sulfuric acid solution without loss of free-ammonia. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.2.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an ,extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask.

8.2.4 Distill 300 ml at the rate of 6-10 ml/min., into 50 ml of 2% boric acid (7.6) contained in a 500 ml Erlenmeyer flask.

8.2.5 Dilute the distillate to 500 ml in the flask. These flasks should be marked at the 350 and the 500 ml volumes. With such marking, it is not necessary to transfer the distillate to volumetric flasks. For concentrations above I mg/l, the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

8.3 Micro Kjeldahl system

8.3.1 Place 50.0 ml of sample or an aliquot diluted to 50 ml in a 100 ml Kjeldahl flask and add 10 ml sulfuric acid-mercuric sulfate-potassium sulfate solution (7.3). Evaporate the mixture in the Kjeldahl apparatus until SO_3 fumes are given off and the solution turns colorless or pale yellow. Then digest for an additional 30 minutes. Cool the residue and add 30 ml distilled water.

8.3.2 Make the digestate alkaline by careful addition of 10 ml of sodium hydroxidethiosulfate solution (7.4) without mixing. Do not mix until the digestion flask has been connected to the distillation apparatus.

8.3.3 Connect the Kjeldahl flask to the condenser with the tip of condenser or an extension of the condenser tip below the level of the boric acid solution (7.6) in the receiving flask or 50 ml short-form Nessler tube.

8.3.4 Steam distill 30ml at the rate of 6-10 ml/min., into 5 ml of 2% boric acid (7.6).

8.3.5 Dilute the distillate to 50 ml. For concentrations above I mg/l the ammonia can be determined titrimetrically. For concentrations below this value, it is determined colorimetrically. The potentiometric method is applicable to the range 0.05 to 1400 mg/l.

8.4 Determination of ammonia in distillate: Determine the ammonia content of the distillate

titrimetrically, colorimetrically, or potentiometrically, as described below.

8.4.1 Titrimetric determination: Add 3 drops of the mixed indicator (7.5) to the distillate andtitrate the ammonia with the 0.02 N H_2SO_4 (7.7), matching the endpoint against a blank containing the same volume of distilled water and H_3BO_3 (7.6) solution.

8.4.2 Colorimetric determination: Prepare a series of Nessler tube standards as follows:

ml of Standard 1.0 ml = 0.01 mg NH_3-N	mg NH_3-N/50.0 ml
0.0	0.0
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
5.0	0.050
8.0	0.080
10.0	0.10

Dilute each tube to 50 ml with ammonia free water, add 1 ml ofNessler Reagent (7. 10) and mix. After 20 minutes read the absorbance at 425 nm against the blank. From the values obtained for the standards plot absorbance vs. mg NH_3-N for the standard curve. Develop color in the 50 ml diluted distillate in exactly the same manner and read mg NH_3-N from the standard curve.

8.4.3 Potentiometric determination: Consult the method entitled Nitrogen, Ammonia:Potentiometric, Ion Selective Electrode Method, (Method 350.3) in this manual.

8.4.4 It is not imperative that all standards be treated in the same manner as the samples. It is recommended that at least 2 standards (a high and low) be digested, distilled,

and compared to similar values on the curve to insure that the digestion-distillation technique is reliable. If treated standards do not agree with untreated standards the operator should find the cause of the apparent error before proceeding.

9. Calculation

9.1 If the titrimetric procedure is used, calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{(A - B)N \times F \times 1{,}000}{S}$$

where:
A = milliliters of standard 0.020 N H_2SO_4 solution used in titrating sample.
B = milliliters of standard 0.020 N H_2SO_4 solution used in titrating blank.
N = normality of sulfuric acid solution.
F = milliequivalent weight of nitrogen (14 mg).
S = milliliters of sample digested.

If the sulfuric acid is exactly 0.02 N the formula is shortened to:

$$\text{TKN, mg/l} = \frac{(A - B) \times 280}{S}$$

9.2 If the Nessler procedure is used, calculate the Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{A \times 1{,}000}{D} \times \frac{B}{C}$$

where:
A = mg NH_3-N read from curve.
B = ml total distillate collected including the H_3BO_3.
C = ml distillate taken for Nesslerization.
D = ml of original sample taken.

9.3 Calculate Organic Kjeldahl Nitrogen in mg/l, as follows: Organic Kjeldahl Nitrogen = TKN - (NH_3-N.)

9.4 Potentiometric determination: Calculate Total Kjeldahl Nitrogen, in mg/l, in the original sample as follows:

$$\text{TKN, mg/l} = \frac{B}{D} \times A$$

where:
A = mg NH3-N/ I from electrode method standard curve.
B = volume of diluted distillate in ml.
D = ml of original sample taken.

10. Precision

10. 1 Thirty-one analysts in twenty laboratories analyzed natural water samples containing exact increments of organic nitrogen, with the following results:

Increment as Nitrogen, Kjeldahl mg N/liter	Precision as Standard Deviation mg N/liter	Accuracy as Bias %	Bias mg N/liter
0.20	0.197	+15.54	+0.03
0.31	0.247	+ 5.45	+0.02
4.10	1.056	+1.03	+0.04
4.61	1.19	-1.67	-0.08

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 437, Method 421 (1975).

2. Schlueter, Albert, "Nitrate Interference In Total KjeIdahl Nitrogen Determinations and Its Removal by Anion Exchange Resins", EPA Report 600/7-77-017.

APPENDIX 13

PHOSPHORUS, ALL FORMS

Method 365.2 (Colorimetric, Ascorbic Acid, Single Reagent)

STORET NO. See Section 4

1. Scope and Application
   - 1.1 These methods cover the determination of specified forms of phosphorus in drinking, surface and saline waters, domestic and industrial wastes.
   - 1.2 The methods are based on reactions that are specific for the orthophosphate ion. Thus, depending on the prescribed pre-treatment of the sample, the various forms of phosphorus given in Figure 1 may be determined. These forms are defined in Section 4.
     - 1.2.1 Except for in-depth and detailed studies, the most commonly measured forms are phosphorus and dissolved phosphorus, and orthophosphate and dissolved orthophosphate. Hydrolyzable phosphorus is normally found only in sewage-type samples and insoluble forms of phosphorus are determined by calculation.
   - 1.3 The methods are usable in the 0.01 to 0.5 mg P/1 range.
2. Summary of Method
   - 2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.
   - 2.2 Only orthophosphate forms a blue color in this test. Polyphosphates (and some organic phosphorus compounds) may be converted to the orthophosphate form by sulfuric acid hydrolysis. Organic phosphorus compounds may be converted to the orthophosphate form by persulfate digestion[2].
3. Sample Handling and Preservation
   - 3.1 If benthic deposits are present in the area being sampled, great care should be taken not to include these deposits.
   - 3.2 Sample containers may be of plastic material, such as cubitainers, or of Pyrex glass.
   - 3.3 If the analysis cannot be performed the day of collection, the sample should be preserved by the addition of 2 ml conc. H_2SO_4 per liter and refrigeration at 4°C.
4. Definitions and Storet Numbers
   - 4.1 Total Phosphorus (P) — all of the phosphorus present in the sample, regardless of form, as measured by the persulfate digestion procedure. (00665)
     - 4.1.1 Total Orthophosphate (P, ortho) — inorganic phosphorus $[(PO_4)^{-3}]$ in the sample as measured by the direct colorimetric analysis procedure. (70507)
     - 4.1.2 Total Hydrolyzable Phosphorus (P, hydro) - phosphorus in the sample as measured by the sulfuric acid hydrolysis procedure, and minus pre-determined orthophosphates. This hydrolyzable phosphorus includes polyphosphorus. $[(P_2O_7)^{-4}, (P_3O_{10})^{-5}$, etc.] plus some organic phosphorus. (00669)

Approved for NPDES
Issued 1971

Method SOP
Analyte PHOSPHORUS
Doc. No. 365.2 Rev. No. 1
Date: 11-3-03
John Wilson
Laboratory Supervisor

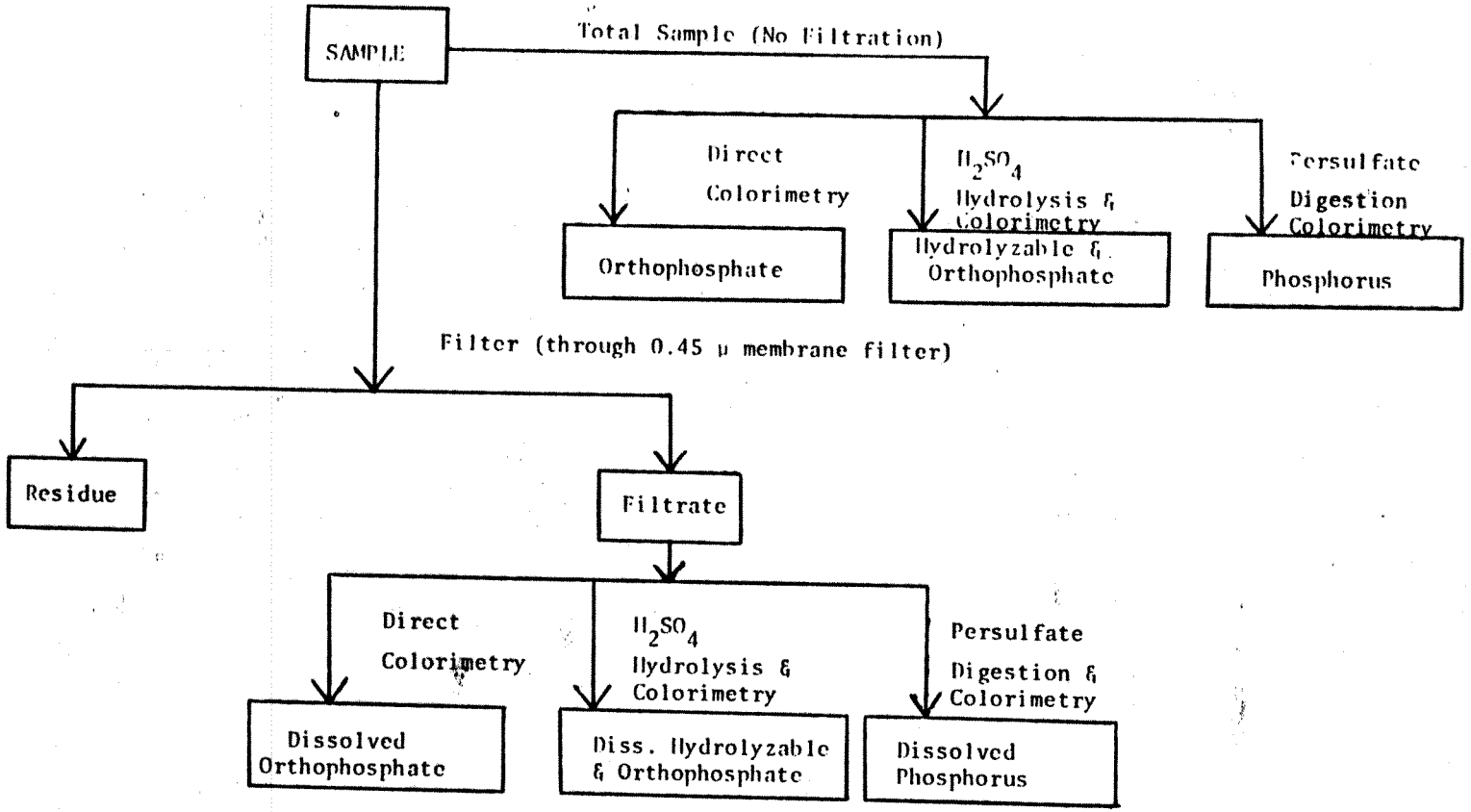


FIGURE 1. ANALYTICAL SCHEME FOR DIFFERENTIATION OF PHOSPHORUS FORMS

4.1.3 Total Organic Phosphorus (P, org) — phosphorus (inorganic plus oxidizable organic) in the sample measured by the persulfate digestion procedure, and minus hydrolyzable phosphorus and orthophosphate. (00670)

4.2 Dissolved Phosphorus (P–D) — all of the phosphorus present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 micron pore size and measured by the persulfate digestion procedure. (00666)

4.2.1 Dissolved Orthophosphate (P–D, ortho) — as measured by the direct colorimetric analysis procedure. (00671)

4.2.2 Dissolved Hydrolyzable Phosphorus (P–D, hydro) — as measured by the sulfuric acid hydrolysis procedure and minus pre-determined dissolved orthophosphates. (00672)

4.2.3 Dissolved Organic Phosphorus (P–D, org) — as measured by the persulfate digestion procedure, and minus dissolved hydrolyzable phosphorus and orthophosphate. (00673)

4.3 The following forms, when sufficient amounts of phosphorus are present in the sample to warrant such consideration, may be calculated:

4.3.1 Insoluble Phosphorus (P-I)=(P)-(P-D). (00667)

4.3.1.1 Insoluble orthophosphate (P-I, ortho)=(P, ortho)-(P-D, ortho). (00674)

4.3.1.2 Insoluble Hydrolyzable Phosphorus (P-I, hydro)=(P, hydro)-(P-D, hydro). (00675)

4.3.1.3 Insoluble Organic Phosphorus (P-I, org)=(P, org) – (P-D, org). (00676)

4.4 All phosphorus forms shall be reported as P, mg/1, to the third place.

5. Interferences

5.1 No interference is caused by copper, iron, or silicate at concentrations many times greater than their reported concentration in sea water. However, high iron concentrations can cause precipitation of and subsequent loss of phosphorus.

5.2 The salt error for samples ranging from 5 to 20% salt content was found to be less than 1%.

5.3 Arsenate is determined similarly to phosphorus and should be considered when present in concentrations higher than phosphorus. However, at concentrations found in sea water, it does not interfere.

6. Apparatus

6.1 Photometer – A spectrophotometer or filter photometer suitable for measurements at 650 or 880 nm with a light path of 1 cm or longer.

6.2 Acid-washed glassware: All glassware used should be washed with hot 1:1 HCl and rinsed with distilled water. The acid-washed glassware should be filled with distilled water and treated with all the reagents to remove the last traces of phosphorus that might be adsorbed on the glassware. Preferably, this glassware should be used only for the determination of phosphorus and after use it should be rinsed with distilled water and

kept covered until needed again. If this is done, the treatment with 1:1 HCl and reagents is only required occasionally. Commercial detergents should never be used.

7. Reagents

7.1 Sulfuric acid solution, 5N: Dilute 70 ml of conc. H_2SO_4 with distilled water to 500 ml.

7.2 Antimony potassium tartrate solution: Weigh 1.3715 g $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$, dissolve in 400 ml distilled water in 500 ml volumetric flask, dilute to volume. Store at 4°C in a dark, glass-stoppered bottle.

7.3 Ammonium molybdate solution: Dissolve 20 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 500 ml of distilled water. Store in a plastic bottle at 4°C.

7.4 Ascorbic acid, 0.1M: Dissolve 1.76 g of ascorbic acid in 100 ml of distilled water. The solution is stable for about a week if stored at 4°C.

7.5 Combined reagent: Mix the above reagents in the following proportions for 100 ml of the mixed reagent: 50 ml of 5N H_2SO_4, (7.1), 5 ml of antimony potassium tartrate solution (7.2), 15 ml of ammonium molybdate solution (7.3), and 30 ml of ascorbic acid solution (7.4). Mix after addition of each reagent. All reagents must reach room temperature before they are mixed and must be mixed in the order given. If turbidity forms in the combined reagent, shake and let stand for a few minutes until the turbidity disappears before proceeding. Since the stability of this solution is limited, it must be freshly prepared for each run.

7.6 Sulfuric acid solution, 11 N: Slowly add 310 ml conc. H_2SO_4 to 600 ml distilled water. When cool, dilute to 1 liter.

7.7 Ammonium persulfate.

7.8 Stock phosphorus solution: Dissolve in distilled water 0.2197 g of potassium dihydrogen phosphate, KH_2PO_4, which has been dried in an oven at 105°C. Dilute the solution to 1000 ml; 1.0 ml = 0.05 mg P.

7.9 Standard phosphorus solution: Dilute 10.0 ml of stock phosphorus solution (7.8) to 1000 ml with distilled water; 1.0 ml = 0.5 ug P.

7.9.1 Using standard solution, prepare the following standards in 50.0 ml volumetric flasks:

ml of Standard Phosphorus Solution (7.9)	Conc., mg/l
0	0.00
1.0	0.01
3.0	0.03
5.0	0.05
10.0	0.10
20.0	0.20
30.0	0.30
40.0	0.40
50.0	0.50

7.10 Sodium hydroxide, 1 N: Dissolve 40 g NaOH in 600 ml distilled water. Cool and dilute to 1 liter.

8. Procedure

8.1 Phosphorus

8.1.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.1.2 Add 0.4 g of ammonium persulfate.

8.1.3 Boil gently on a pre-heated hot plate for approximately 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.1.4 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with 1 N NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1.**

8.1.5 Determine phosphorus as outlined in 8.3.2 Orthophosphate.

8.2 Hydrolyzable Phosphorus

8.2.1 Add 1 ml of H_2SO_4 solution (7.6) to a 50 ml sample in a 125 ml Erlenmeyer flask.

8.2.2 Boil gently on a pre-heated hot plate for 30–40 minutes or until a final volume of about 10 ml is reached. Do not allow sample to go to dryness. Alternatively, heat for 30 minutes in an autoclave at 121°C (15–20 psi).

8.2.3 Cool and dilute the sample to about 30 ml and adjust the pH of the sample to 7.0 ±0.2 with NaOH (7.10) using a pH meter. If sample is not clear at this point, add 2–3 drops of acid (7.6) and filter. Dilute to 50 ml.
Alternatively, if autoclaved see **NOTE 1.**

8.2.4 The sample is now ready for determination of phosphorus as outlined in 8.3.2 Orthophosphate.

8.3 Orthophosphate

8.3.1 The pH of the sample must be adjusted to 7±0.2 using a pH meter.

8.3.2 Add 8.0 ml of combined reagent (7.5) to sample and mix thoroughly. After a minimum of ten minutes, but no longer than thirty minutes, measure the color absorbance of each sample at 650 or 880 nm with a spectrophotometer, using the reagent blank as the reference solution.

NOTE 1: If the same volume of sodium hydroxide solution is not used to adjust the pH of the standards and samples, a volume correction has to be employed.

9. Calculation

9.1 Prepare a standard curve by plotting the absorbance values of standards versus the corresponding phosphorus concentrations.

9.1.1 Process standards and blank exactly as the samples. Run at least a blank and two standards with each series of samples. If the standards do not agree within ±2% of the true value, prepare a new calibration curve.

9.2 Obtain concentration value of sample directly from prepared standard curve. Report results as P, mg/1. SEE **NOTE 1.**

10. Precision and Accuracy

10.1 Thirty-three analysts in nineteen laboratories analyzed natural water samples containing exact increments of organic phosphate, with the following results:

Increment as Total Phosphorus mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as Bias, %	Accuracy as Bias mg P/liter
0.110	0.033	+3.09	+0.003
0.132	0.051	+11.99	+0.016
0.772	0.130	+2.96	+0.023
0.882	0.128	–0.92	–0.008

(FWPCA Method Study 2, Nutrient Analyses)

10.2 Twenty-six analysts in sixteen laboratories analyzed natural water samples containing exact increments of orthophosphate, with the following results:

Increment as Orthophosphate mg P/liter	Precision as Standard Deviation mg P/liter	Accuracy as Bias, %	Accuracy as Bias, mg P/liter
0.029	0.010	–4.95	–0.001
0.038	0.008	–6.00	–0.002
0.335	0.018	–2.75	–0.009
0.383	0.023	–1.76	–0.007

(FWPCA Method Study 2, Nutrient Analyses)

Bibliography

1. Murphy, J., and Riley, J., "A modified Single Solution for the Determination of Phosphate in Natural Waters", Anal. Chim. Acta., 27, 31 (1962).
2. Gales, M., Jr., Julian, E., and Kroner, R., "Method for Quantitative Determination of Total Phosphorus in Water", Jour. AWWA, 58, No. 10, 1363 (1966).
3. Annual Book of ASTM Standards, Part 31, "Water", Standard D515–72, Method A, p 389 (1976).
4. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 476 and 481, (1975).

APPENDIX 14

STL PITTSBURGH LAB SPECIFIC SOP

TITLE: ACID DIGESTION OF AQUEOUS SAMPLES BY SW846 METHODS 3005A, 3010A, AND MCAWW METHOD 200.7

(SUPERSEDES: REVISION 2)

Prepared by: _____

Reviewed by: _____
Technical Review

Approved by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Lab Director

TABLE OF CONTENTS

LIST OF APPENDICES:

1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation of aqueous samples for the analysis of certain metals by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) using the MCAWW Method 200.7 (NPDES) and SW846 Methods 3005A and 3010A (RCRA).

1.2. The applicability of each of these preparation protocols to specific analytes is detailed in Tables I and II (Appendix A). Additional elements may be analyzed following digestion by these protocols provided that the method performance criteria specified in Section 13.0 of this SOP are met.

1.3. This SOP provides procedures applicable to the preparation of dissolved, total recoverable and total elements in surface water, ground water, aqueous samples, leachates/extracts.

1.4. SW-846 Method 3005A is used to prepare surface and groundwater samples for total recoverable and dissolved metals determination by ICP.

1.5. MCAWW Method 200.7 is used to prepare surface water, domestic and industrial waste samples for total recoverable and dissolved metals determination by ICP.

1.6. SW-846 Method 3010A is used to prepare aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for total metals analysis by ICP.

1.7. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators do require digestion of dissolved samples and this must be clarified before project initiation.

2. SUMMARY OF METHOD

2.1. Method 3005A / Method 200.7 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP Spectroscopy

A representative aliquot of sample is heated with nitric and hydrochloric acids (concentrations and volumes differ between methods) and substantially reduced in volume. The digestate is filtered (if necessary) and diluted to volume.

2.2. Method 3010A - Preparation for Total Metals Analysis by ICP Spectroscopy

A representative aliquot of sample is refluxed with nitric acid. This step is repeated until the digestate is light in color or until its color has stabilized. After the digestate has been reduced to a low volume, it is refluxed with hydrochloric acid, filtered (if necessary) and brought up to volume.

2.3. Digestion Procedures

The laboratory performs all the digestion procedures listed in the SOP, depending on the project requirements.

3. DEFINITIONS

Additional definitions of terms used in this SOP may be found in the glossary of the QAMP.

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination include: metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, impure reagents, dirty glassware, improper sample transfers, dirty work areas, atmospheric inputs such as dirt and dust, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

4.2. The entire work area, including the bench top and fume hood, should be thoroughly cleaned on a routine schedule in order to minimize the potential for environmental contamination. Refer to Appendix C for additional contamination control guidelines.

4.3. Boron and silica from the glassware will migrate into the sample solution during and following sample processing. For critical low level determinations of boron and silica, only quartz and/or plastic labware should be used.

4.4. Physical interference effects may contribute to inaccuracies in the determinations of trace elements. Oils, solvents and other matrices may not be digested using these methods if they are not soluble with acids. If physical interferences are present, they should be documented.

4.5. Visual interferences or anomalies (such as foaming, emulsions, precipitates, etc.) must be documented.

4.6. Allowing samples to boil or go dry during digestion may result in the loss of volatile metals . If this occurs the sample must be reprepared. Antimony is easily lost by volatilization from hydrochloric acid media.

4.7. Precipitation of silver chloride (AgCl) may occur when chloride ions and high concentrations of silver (i.e., greater than 1 mg/L) are present in the sample.

4.8. Specific analytical interferences are discussed in each of the determinative methods.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid and nitric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid and hydrogen peroxide.

5.3.3. All sample digestions, including cooling of digestates, must be carried out in a fume hood.

5.4. The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood. The analyst should also be aware of the potential for a vigorous reaction.

5.5. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.6. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit or under other means of mechanical ventilation.

5.7. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.8. Always carry bulk concentrated acid bottles in appropriate impact proof containers.

5.9. Acid/peroxide spills must be neutralized immediately, flushed with water and cleaned up using appropriate spill kits.

5.10. Discard chipped or broken beakers to prevent injury. Chipped glassware may be fire polished as an alternative to disposal.

5.11. Any and all accidents and spills must be reported to the lab supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot plate, hot block, or other adjustable heating source capable of maintaining a temperature of 90 - 95?C.

6.2. Thermometer that covers a temperature range of 0-200?C.

6.3. Hot Block Disposable Digestion Cups (from Environmental Express).

6.4. Watch glasses, ribbed or equivalent.

6.5. Whatman No. 41 filter paper or equivalent.

6.6. Funnels or equivalent filtration apparatus.

6.7. Centrifugation equipment (if desired method of removing particulates is centrifugation).

6.8. Graduated cylinder or equivalent capable of measuring 50 mL within 3% accuracy.

6.9. Analytical balance capable of accurately weighing to the nearest 0.01 grams.

6.10. Repipetors or suitable reagent dispensers.

6.11. Calibrated automatic pipettes with corresponding pipet tips or Class A glass volumetric pipettes.

6.12. Class A volumetric flasks.

6.13. pH indicator strips (pH range 0 - 6).

6.14. Plastic digestate storage bottles.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks as defined in the determinative SOPs.

7.2. Laboratory Control Sample (LCS) and matrix spike (MS) solutions are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Working ICP LCS/MS spike solution: The ICP LCS/MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.4. The TCLP MS working spike solution is provided directly by the vendor, no further standard preparation is necessary.

7.5. The LCS and MS samples must contain all the elements designated for analysis in each batch of samples. If a non-routine element is required that is not contained in the custom STL solution, a solution must be purchased from the designated vendor that will cover the additional analyte(s) of interest and provide for a final spike concentration that is appropriate to the determinative method.

7.6. Aqueous laboratory control samples (LCSW) and matrix spike samples are prepared as described in Sections 9.5 and 9.6. Refer to Tables III and IV (Appendix A) for details regarding the stock, working standard and final digestate spike concentrations for ICP LCS and matrix spike preparations.

7.7. Nitric acid (HNO_3), concentrated, trace metal grade or better.

7.8. Nitric acid, 1:1 - dilute concentrated HNO_3 with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

7.9. Hydrochloric acid (HCl), concentrated, trace metal grade or better.

7.10. Hydrochloric acid, 1:1 - dilute concentrated HCl with an equal volume of reagent water.

Note: When preparing diluted acids always add acid to water. If the water is added to the acid a violent reaction may occur.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for metals included under the scope of this SOP is 180 days from the date of collection to the date of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. For dissolved metals analysis, the samples should be filtered through a 0.45 um filter prior to preservation. Filtration must be done in the field or within 24 hours of collection.

Note: If a sample being analyzed for dissolved metals is found to contain sediment the analyst should contact their supervisor or group leader. The client should be notified of the problem to decide how to treat the sample.

9. QUALITY CONTROL

Table V (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to analysis of any analyte using any method contained within this SOP the following requirements must be met:

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDL's must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements as detailed in STL QA Policy QA-005. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance, which should contain all the analytes of interest. The results of the initial demonstration study must be acceptable before analysis of samples may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.1.2.2. Calculations and acceptance criteria for QC check samples are given in the determinative SOP (C-MT-0001).

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate (SW-846 Methods) or a matrix spike for every 10 or fewer sample (200.7). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS, MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. Criteria for the acceptance of blanks are contained within the individual analytical method SOP's. If the method blank does not meet the criteria contained within

the analytical method SOPs, the blank and all associated samples in the batch must be redigested.

9.4.1. Aqueous method blanks are prepared by taking 50 mL or 50 g of reagent water through the appropriate procedure as described in Section 11.

9.4.2. TCLP method blanks are prepared by taking 50 mL or 50 g of leachate fluid through the appropriate procedure as described in Section 11.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in 200.7) must be processed with each preparation batch. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. Criteria for the acceptance of LCS results are contained within the individual analytical method SOP's. Corrective action when LCS results fail to meet control limits will be repreparation and reanalysis of the batch. Refer to Section 7.3 for instructions on preparation of the aqueous LCS spike solution.

9.5.1. The aqueous LCS is prepared by spiking a 50 mL aliquot of reagent water with 0.5 mL of the working LCS/MS spike solution (7.3). The LCS is then processed through the appropriate procedure as described in Section 11.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples (SW-846 Methods) or one matrix spike is processed for every 10 or fewer samples (200.7). A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 200.7). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Samples identified as field blanks cannot be used for MS/MSD analysis. If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. Corrective action when MS results fail to meet control limits does not include repreparation of samples unless the results indicate that a spiking error may have occurred.

9.6.1. The aqueous matrix spike sample is prepared by spiking a 50 mL aliquot of a sample with 0.5 mL of the working LCS/MS spike solution (7.3). The matrix spike sample is then processed as described in Section 11.

9.6.2. The TCLP matrix spike sample is prepared by spiking a 50 mL aliquot of a leachate with 0.5 mL of the working TCLP spike solution (7.4). The matrix spike sample is then processed as described in Section 11.

NOTE: The TCLP matrix spike must be added prior to preservation of the leachate.

9.6.3. If insufficient sample is available to process a MS/MSD, then a second LCS must be processed. The LCS pair is then evaluated according to the MS/MSD criteria.

9.7. Quality Assurance Summaries - Certain clients may require specific project or program QC, which may supersede the SOP requirements. Quality Assurance Summaries (QAS) should be developed to address these requirements.

10. CALIBRATION AND STANDARDIZATION

10.1 Hotplate/hotblock temperature must be verified daily for each hotplate/hotblock used and must be recorded on either the metals preparation log or in a hotplate/hotblock temperature logbook. The hotplate/hotblock temperature should be verified by measuring the temperature of a beaker or an equivalent digestion sample container of reagent water placed on each hotplate/hotblock.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. All preparation procedures must be carried out in a properly functioning hood.

11.4. All samples are to be checked out of sample control with the chain of custody documentation filled out completely.

11.5. Proper sample identification is extremely important in any preparation procedure. Labeling of beakers and bottles must be done in a manner to ensure connection with the proper sample.

11.6. Samples are typically logged in as either waters or wastes. Wastes such as organic liquids or sludges and tissues (animal/vegetable) are usually logged in with solid test codes. When initiating prep examine the sample to see if the sample matches the matrix designation. If the sample is logged in as aqueous but it appears more like a waste (biphasic, sludge like, organic liquid, lots of sediment etc.) contact the lab supervisor or project manager for further instructions. In some cases it may be more appropriate to process these samples as solids.

11.7. If possible prepare all the samples of a project at the same time to minimize the QC required and streamline the flow of the project through the lab and reporting group.

11.8. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards.

11.9. The following procedure must be followed for all aqueous sample preparations:

11.9.1. Measure and record sample pH with pH paper on a separate aliquot of sample. This is typically verified and documented at sample receipt.

Note: If the sample pH is > 2 pH units, the client must be notified of the anomaly.

11.9.2. Mix sample by shaking the container.

11.9.3. Measure and transfer 50 mL or 50 g of the sample into a beaker.

Note: This SOP allows for samples to be weighed instead of measured volumetrically (See Section 17.1.1.2).

11.9.4. Measure extra aliquots of sample(s) selected for the MS or MS/MSD analysis. Spike each aliquot with 0.5 mL of spiking solution (7.3 or 7.4).

11.9.5. Measure and transfer 50 mL of reagent water into a beaker for the method blank.

11.9.6. Measure and transfer 50 mL of reagent water into a beaker for the LCS and add 0.5 mL of spiking solution (7.3)

11.10. Proceed to the appropriate Section for the desired method as follows:

Method 3005A	11.11
Method 3010A	11.12
Method 200.7	11.13

11.11. **Method 3005A - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP (See Figures 1)**

11.11.1. To the sample beaker, add 1 mL of concentrated HNO_3 and 2.5 mL of concentrated HCl.

11.11.2. Cover with ribbed watch glass.

11.11.3. Heat at 90 - 95?C until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.11.4. Cool the beaker in a fume hood.

11.11.5. Add 1.5 mL of concentrated HNO_3.

11.11.6. Wash down beaker walls and watch glass with reagent water.

11.11.7. Filter sample, if insoluble materials are present, though a prewashed (1% nitric acid) Whatman 41 filter paper or plunger filter into a disposable sample container.

Note: If any samples in a preparation batch are filtered, the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.11.8. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.11.9. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis

11.12. **Method 3010A - Preparation for Total Metals Analysis by ICP Spectroscopy (See Figures 2)**

11.12.1. To the sample beaker, add 1.5 mL of concentrated HNO_3.

11.12.2. Cover with ribbed watch glass.

11.12.3. Place beaker on hotplate or hotblock (90-95 ?C) and evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.12.4. Cool the beaker in a fume hood.

11.12.5. Add another 1.5 mL portion of concentrated HNO_3 and re-cover the beaker.

11.12.6. Continue refluxing until the digestion is complete.

Note: Digestion is complete when the digestate is light in color or does not change in appearance. For most samples the addition of two nitric acid aliquots is sufficient, additional aliquots of nitric acid may be added if necessary.

11.12.7. Evaporate to low volume of 5 - 10 mL while ensuring that no portion of the bottom of the beaker is allowed to go dry.

11.12.8. Cool the beaker in a fume hood.

11.12.9. Add 5 mL of 1:1 HCl.

11.12.10. Cover and reflux for an additional 15 minutes to dissolve precipitate or residue.

11.12.11. Wash down beaker walls and watch glass with reagent water.

11.12.12. Filter sample, if insoluble materials are present, though a prewashed (1% nitric acid) Whatman 41 filter paper or plunger filter into a disposable sample container.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.12.13. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.12.14. Adjust final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

11.13. **Method 200.7 - Preparation for Total Recoverable or Dissolved Metals Analysis by ICP (See Figures 1)**

11.13.1. To the sample beaker, add 1 mL of 1:1 HNO_3 and 2.5 mL of 1:1 HCl.

11.13.2. Cover with ribbed watch glass.

11.13.3. Heat at 80-85 ?C until volume is reduced to between 15 and 20 mL.

NOTE: DO NOT ALLOW SAMPLE TO BOIL OR GO DRY. Doing so will result in the loss of analyte and the sample must be reprepared.

11.13.4. Gently reflux for 30 minutes.

11.13.5. Cool the beaker in the fume hood.

11.13.6. Add 2 mL of concentrated HNO_3 and 2.25 mL concentrated HCl.

11.13.7. Wash down beaker walls and watch glass with reagent water.

11.13.8. Filter sample, if insoluble materials are present, though a prewashed (1% nitric acid) Whatman 41 filter paper or plunger filter into a disposable sample container.

Note: If any samples in the QC batch are filtered the method blank and LCS associated with that batch must also be filtered.

Note: In place of filtering, the samples, after dilution and mixing , may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

11.13.9. Rinse beaker and filter paper with reagent water to ensure complete sample transfer.

11.13.10. Adjust the final volume/mass to 50 mL or 50 g with reagent water. The sample is now ready for analysis.

12. DATA ANALYSIS AND CALCULATIONS

Not Applicable.

13. METHOD PERFORMANCE

13.1. Method performance is determined by the analysis of matrix spike and matrix spike duplicate samples as well as method blanks and laboratory control samples. In general, the matrix spike recovery should fall within +/- 25 % (SW-846 Methods) or +/- 30% (200.7) and the matrix spike duplicates should compare within 20% RPD. Method blanks must meet the criteria specified in determinative SOPs. The laboratory control samples should recover within 20% (SW-846 Methods) or 15% (200.7) of the true value until in house control limits are established. Acceptance criteria are given in the determinative SOPs.

13.2. The initial demonstration study as detailed in Section 9.1.2 must be acceptable before the analysis of field samples under this SOP may begin. The results of the initial demonstration study may be used to extend a method for the analysis of other elements provided all acceptance criteria are met.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The facility EH & S coordinator should be contacted if additional information is required.

15.2. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update I, Revision 1, July 1992. Methods 3005A and 3010A.

16.2. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Method 200.7, Revision 4.4, May 1994.

16.3. C-MT-0001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analysis of Water and Wastes, Method 6010A and Method 200.7.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference methods.

17.1.1. Modifications applicable to SW-846 reference methods.

17.1.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client.

17.1.1.2. This SOP allows for aqueous samples to be weighed instead of measured volumetrically. This assumes the density of the sample is close to 1.0 g/mL. Samples with large amounts of sediment or suspended solids, sludges, non-aqueous liquids must be processed volumetrically. Weighing samples directly into the digestion vessel minimizes the potential for cross contamination, offers improved accuracy over the use of graduated cylinders (comparable to volumetric flask accuracy), uses less glassware and is more efficient.

17.1.1.3. The referenced methods as well as Table 3-1 of SW-846 refer to the use of a 100 mL aliquot for digestion. This SOP requires the use of a 50 mL sample size to reduce waste generation. The use of reduced sample volumes are supported in EPA's document "Response to Public Comments Background Document, Promulgation of the Second Update to SW-846, Third Edition" dated November 3, 1994. This document stated "..flexibility to alter digestion volumes is addressed and "allowed" by the table (3-1) and is also inherently allowed by specific digestion methods. Table 3-1 is only to be used as guidance when collecting samples..." EMSL-Ci has also taken the stance that "reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology." Additionally, in written correspondence from the Office of Solid Waste, Olliver Fordham stated " As a "representative sample" can be assured, scaling causes no loss of precision and accuracy in the analysis."

17.1.2. Modifications Specific to Method 3005A

17.1.2.1. In order to matrix match the digestate to the ICP calibration standards, Section 11.11.8 requires the addition of 1.5 mL of concentrated nitric acid to the digestate prior to dilution to final volume. This step ensures that bias due to differences in acid matrix will not be a factor in the analytical determination. Since this step is performed post-digestion it does not impact the digestion recoveries. This approach to matrix matching was discussed with Olliver Fordham of OSW who indicated that it was an acceptable practice.

17.1.3. Modifications Specific to Method 3010A

17.1.3.1. Section 11.12.7 of this SOP requires the sample be reduced to a volume of 5 - 10 mL. Section 7.2 of Method 3010A states the volume should be reduced to 3 mL but also states that no portion of the bottom of the beaker should go dry. The SOP required volume is a closer approximation of the volume required to provide an adequate covering of the beaker so as to prevent the loss of critical analytes through volatilization.

17.1.3.2. The scope of 3010A has been expanded to include silver based on comparison studies with 7760A. Method 3010A consistently demonstrated improved accuracy and precision over Method 7760A in the matrices tested (reagent water, surface water and TCLP leachate) up to a concentration of 1 ppm silver.

17.1.4. Modifications Specific to Method 200.7

17.1.4.1. In order to matrix match the digestate to the ICP calibration standards, Section 11.13.9 requires the addition of 2 mL of concentrated nitric acid and 2.25 mL of concentrated HCl to the digestate prior to dilution to final volume. This step ensures that bias due to differences in acid matrix will not be a factor in the analytical determination. Since this step is performed post-digestion it does not impact the digestion recoveries. This approach to matrix matching was discussed with Olliver Fordham of OSW who indicated that it was an acceptable practice.

17.2. Documentation and Record Management

The preparation benchsheet should, at a minimum, include the following information:

? Preparation date, analyst name, matrix, prep type), SOP reference.

? Sample ID, initial weight/volume and final weight/volume.

? Standards Documentation (source, lot, prep date, volume added).

? Analyst Signature.

? Reviewer's Signature and date.

Figure 1. **Method 3005A**

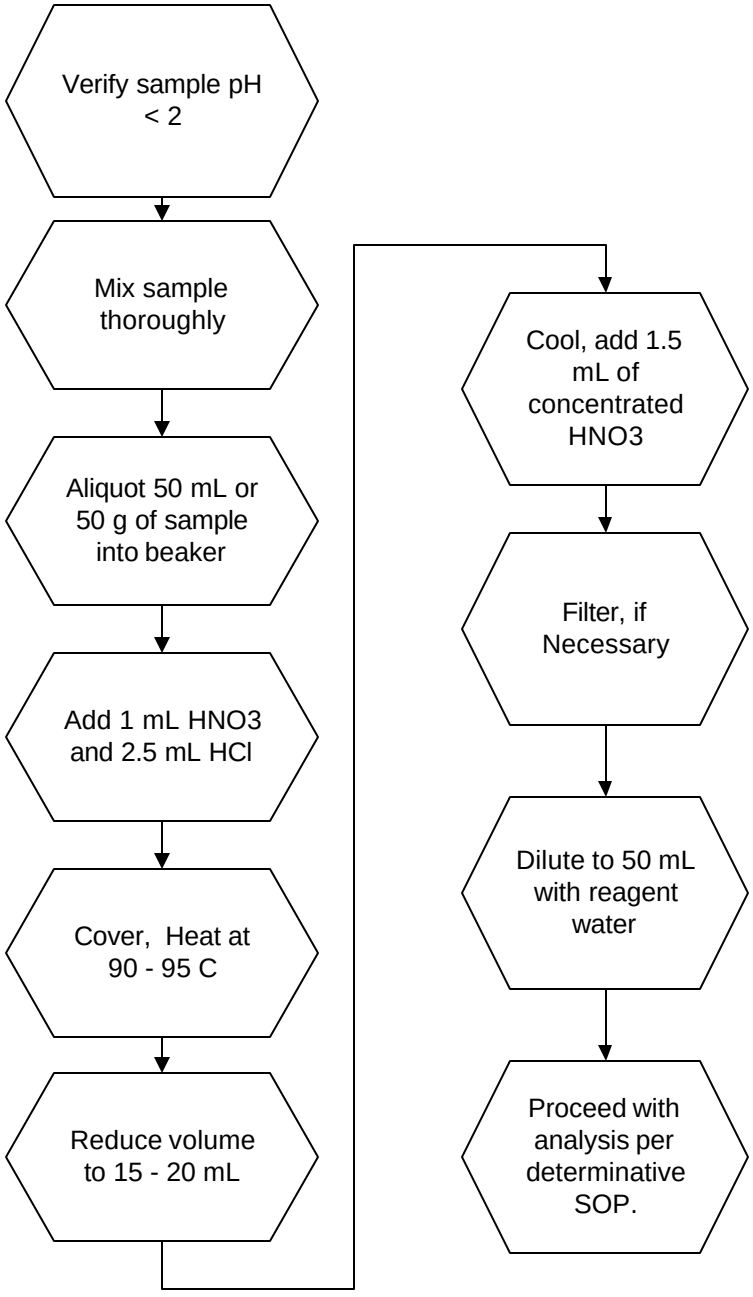


Figure 2. Method 3010A

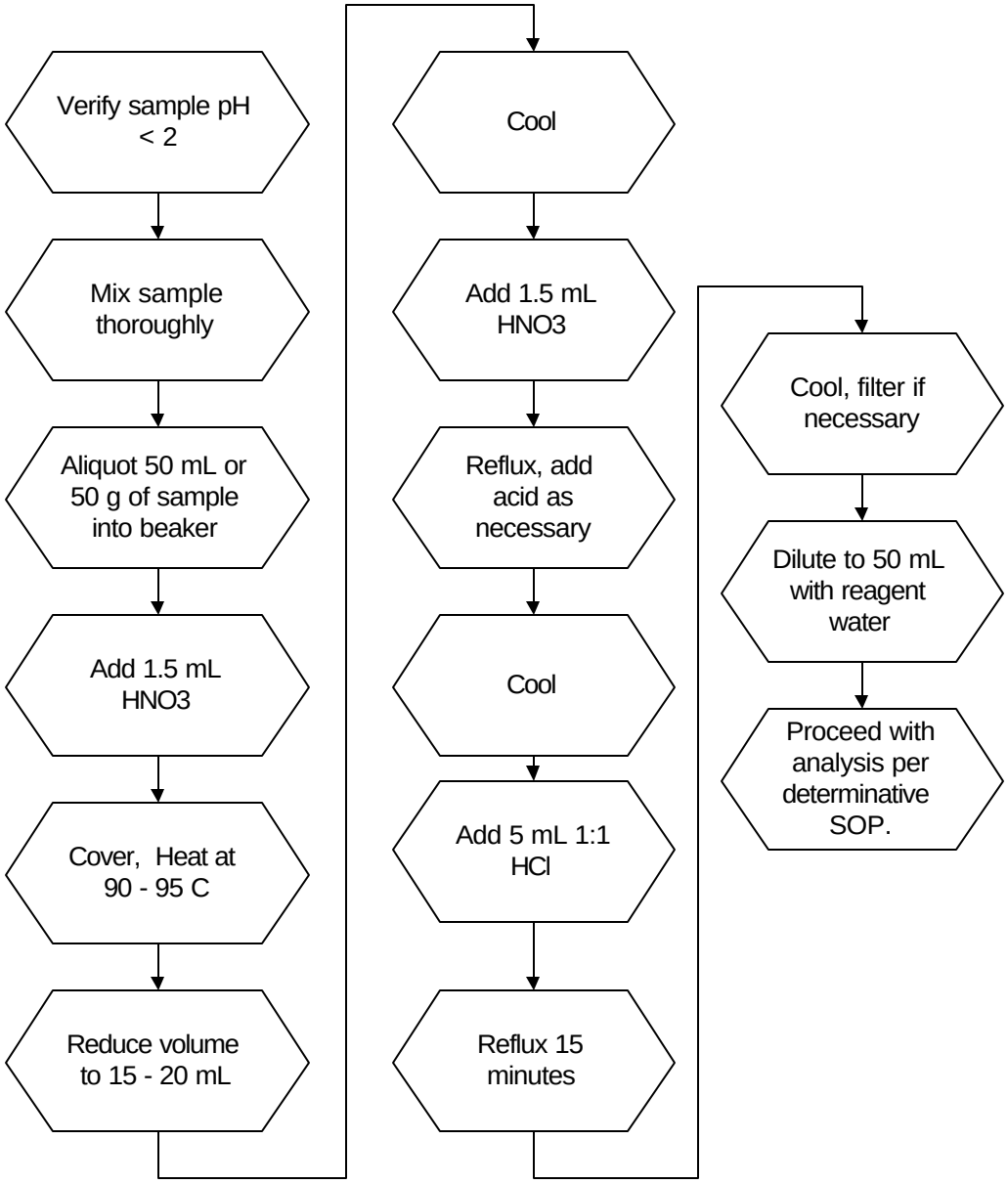
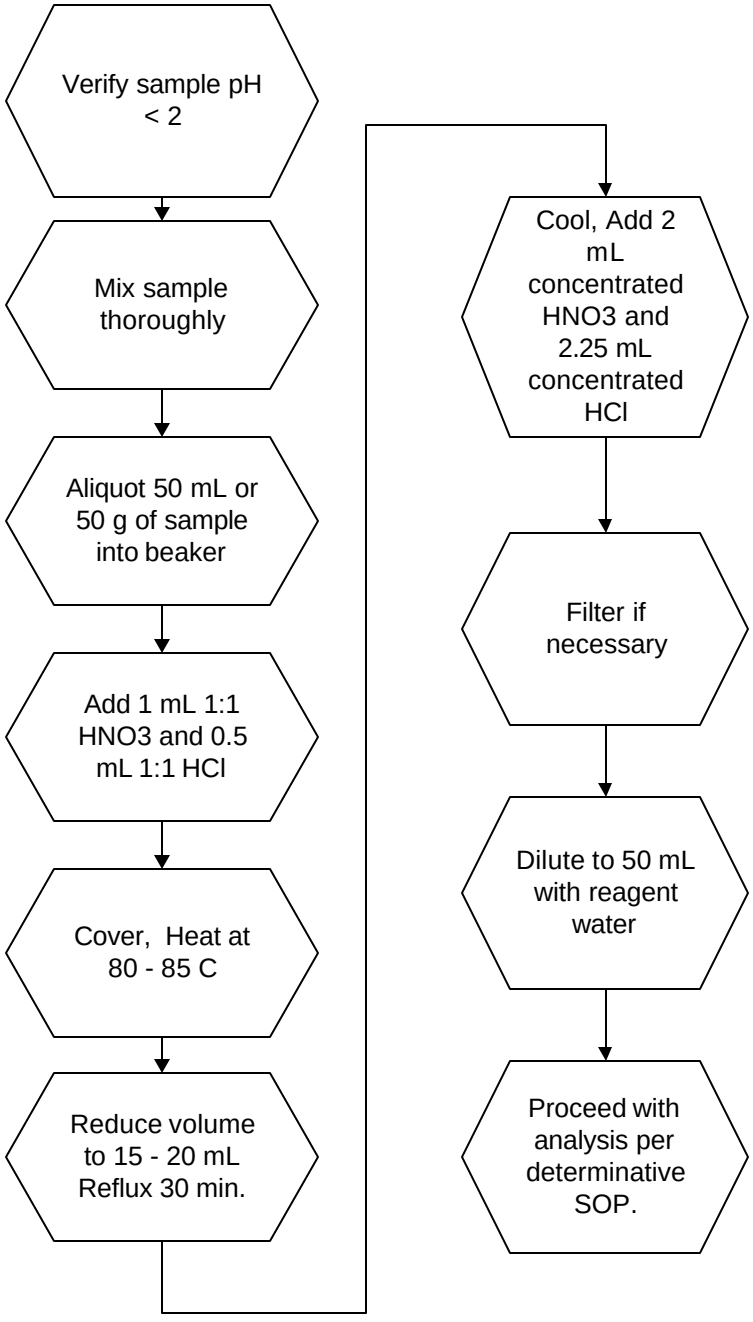


Figure 3. Method 200.7



APPENDIX A

TABLES

TABLE I. Approved Preparation Method Analytes - SW846

ELEMENT	Symbol	CAS Number	3005A	3010A
Aluminum	Al	7429-90-5	X	X
Antimony	Sb	7440-36-0	X	X
Arsenic	As	7440-38-2	X	X
Barium	Ba	7440-39-3	X	X
Beryllium	Be	7440-41-7	X	X
Cadmium	Cd	7440-43-9	X	X
Calcium	Ca	7440-70-2	X	X
Chromium	Cr	7440-47-3	X	X
Cobalt	Co	7440-48-4	X	X
Copper	Cu	7440-50-8	X	X
Iron	Fe	7439-89-6	X	X
Lead	Pb	7439-92-1	X	X
Magnesium	Mg	7439-95-4	X	X
Manganese	Mn	7439-96-5	X	X
Molybdenum	Mo	7439-98-7	X	X
Nickel	Ni	7440-02-0	X	X
Potassium	K	7440-09-7	X	X
Selenium	Se	7782-49-2	X	X
Silver	Ag	7440-22-4	X	X
Sodium	Na	7440-23-5	X	X
Thallium	Tl	7440-28-0	X	X
Vanadium	V	7440-62-2	X	X
Zinc	Zn	7440-66-6	X	X

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE II. Approved Preparation Method Analytes - NPDES

ELEMENT	Symbol	CAS Number	200.7
Aluminum	Al	7429-90-5	X
Antimony	Sb	7440-36-0	X
Arsenic	As	7440-38-2	X
Boron	B	7440-42-8	X
Barium	Ba	7440-39-3	X
Beryllium	Be	7440-41-7	X
Cadmium	Cd	7440-43-9	X
Calcium	Ca	7440-70-2	X
Chromium	Cr	7440-47-3	X
Cobalt	Co	7440-48-4	X
Copper	Cu	7440-50-8	X
Iron	Fe	7439-89-6	X
Lead	Pb	7439-92-1	X
Magnesium	Mg	7439-95-4	X
Manganese	Mn	7439-96-5	X
Molybdenum	Mo	7439-98-7	X
Nickel	Ni	7440-02-0	X
Potassium	K	7440-09-7	X
Selenium	Se	7782-49-2	X
Silicon	Si	7631-86-9	X
Silver	Ag	7440-22-4	X
Sodium	Na	7440-23-5	X
Thallium	Tl	7440-28-0	X
Vanadium	V	7440-62-2	X
Zinc	Zn	7440-66-6	X

X - Designates that the preparation method is approved for an element

Note: Additional elements may be analyzed following digestion by these protocols provided the method performance criteria specified in Section 13.0 of the SOP are met.

TABLE III. ICP Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	Working LCS/MS Standard (mg/L)	Aqueous LCS/ MS Level * (ug/l)
Aluminum	200	2000
Antimony	50	500
Arsenic	200	2000
Barium	200	2000
Beryllium	5	50
Cadmium	5	50
Calcium	5000	50000
Chromium	20	200
Cobalt	50	500
Copper	25	250
Iron	100	1000
Lead	50	500
Lithium	100	1000
Magnesium	5000	50000
Manganese	50	500
Molybdenum	100	1000
Nickel	50	500
Potassium	5000	50000
Selenium	200	2000
Silver	5	50
Sodium	5000	50000
Strontium	100	1000
Thallium	200	2000
Vanadium	50	500
Zinc	50	500
Boron	100	1000
Silica	1000	10000
Tin	200	2000
Titanium	100	1000

* Levels shown indicate the spike concentration in the final digestate of the aqueous LCS or matrix spike based on the addition of 0.5 mL working spike (7.3) to 50 mL of sample.

TABLE IV. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

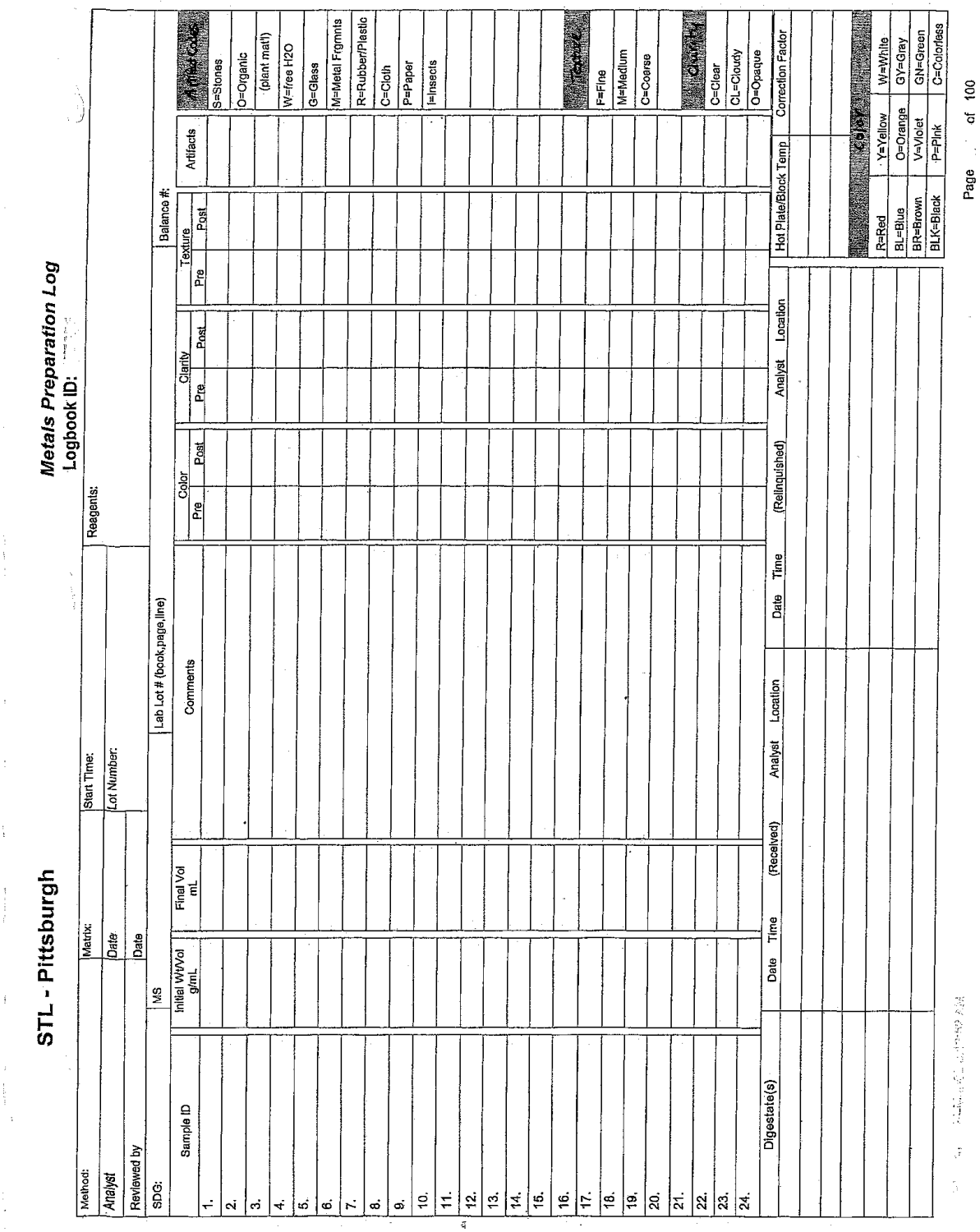
ELEMENT	RL (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE V. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method Blank	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: C-MT-0001	Redigest and reanalyze samples associated with the method blank.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Refer to determinative SOPs: C-MT-0001	Redigest and reanalyze all samples associated with the LCS.
Matrix Spike	One per sample preparation batch of up to 20 samples (SW-846 Methods) or one per every 10 or fewer samples (200.7).	Refer to determinative SOPs: C-MT-0001	Reprep not required unless preparation error suspected.
Matrix Spike Duplicate	See Matrix Spike	Refer to determinative SOPs: C-MT-0001	See Corrective Action for Matrix Spike.

APPENDIX B

STL METALS PREP BENCHSHEET



STL - Pittsburgh

Metals Preparation Log

Logbook ID:

Method: | Matrix: | Start Time: | Reagents:

Analyst | Date | Lot Number:

Reviewed by | Date

SDG: | MS | Lab Lot # (book,page,line) | Balance #:

Sample ID	Initial Wt/Vol g/mL	Final Vol mL	Comments	Color Pre	Color Post	Clarity Pre	Clarity Post	Texture Pre	Texture Post	Artifacts
1.										
2.										
3.										
4.										
5.										
6.										
7.										
8.										
9.										
10.										
11.										
12.										
13.										
14.										
15.										
16.										
17.										
18.										
19.										
20.										
21.										
22.										
23.										
24.										

Digestate(s)	Date	Time	(Received)	Analyst	Location	Date	Time	(Relinquished)	Analyst	Location

Artifact Codes
S=Stones
O=Organic (plant matl)
W=free H2O
G=Glass
M=Metal Frgmnts
R=Rubber/Plastic
C=Cloth
P=Paper
I=Insects

Texture
F=Fine
M=Medium
C=Coarse

Clarity
C=Clear
CL=Cloudy
O=Opaque

Hot Plate/Block Temp | Correction Factor

Color

R=Red	Y=Yellow	W=White	
BL=Blue	O=Orange	GY=Gray	
BR=Brown	V=Violet	GN=Green	
BLK=Black	P=Pink	C=Colorless	

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APPENDIX C

CONTAMINATION CONTROL GUIDELINES

APPENDIX C. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with nitric acid prior to routine cleaning.

APPENDIX 15

STL PITTSBURGH STANDARD OPERATING PROCEDURE

TITLE: ANALYSIS OF METALS BY INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY (ICPMS) FOR METHODS 200.8, 6020 & ILM05.2

(SUPERSEDES: NONE)

Prepared by: _____

Reviewed by: _____
Technical Reviewer

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental Health and Safety Coordinator

Approved by: _____
Lab Director

Table of Contents

1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of metals by inductively coupled plasma mass spectrometry (ICP-MS) by EPA Method 6020 and EPA Method 200.8.

1.2. This method is applicable to drinking, surface, and saline waters; soil and waste samples.

1.3. Reporting Limits

The standard reporting limits for metals analyzed by ICP-MS are listed in Table 1. Upon client request, results below the standard reporting limit but above the current method detection limit (MDL) may be reported and qualified as “estimated”.

1.4. Methods are based on the requirements of the US EPA Contract Laboratory Program (CLP) method ILM05.2D, and SW-846 methods 6020 and 6020. Instructions within this document that are general are given in BLACK, whilst those that apply only to 6020 are in BLUE and those that apply only to ILM05.2D are in RED.

1.5. Elements that may be determined using this procedure include: Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Si, Ag, Sr, Tl, Sn, Ti, V, Zn, Ca, Mg, K, and Na.

Note: successful Ag analysis may require all solutions to be prepared as described, but with the addition of hydrochloric acid to 1% (v/v). This may degrade performance for As, Se and V.

2. SUMMARY OF METHOD

2.1. The sample solution is introduced into a pneumatic nebulizer via a peristaltic pump. The nebulizer generates a fine aerosol by bringing the solution into contact with a high velocity flow of argon gas at its tip. The nebulized sample is sorted by droplet size in the spray chamber. Large droplets are rejected, whilst smaller particles are transported with the gas stream into the plasma.

2.2. The argon plasma operates with a continuously applied radio frequency (RF) field to give a high-energy discharge consisting of argon atoms, ions and electrons. The hottest part of the plasma can attain 6000-8000 K. In the plasma, aerosol droplets undergo evaporation, atomization and ionization. Ions are sampled through an aperture in a metal cone (sampler) at atmospheric pressure, into the expansion region at about 2 mbar and subsequently through an aperture in a second metal cone (skimmer) into the intermediate chamber.

2.3. An electrostatic ion lens system focuses the ion beam through a differential aperture into the analyser chamber, at about 10-7 mbar. The ions are filtered by mass-to-charge ratio in microsecond timescales by the quadrupole. The selected mass is detected by a discrete dynode electron multiplier. The multiplier has two simultaneous modes of operation: pulse count and analogue. The combination of these two modes allows seamless detection spanning 8 - 9 orders of magnitude. A detector “cross-calibration” is required for the analogue counts to be converted to equivalent pulse counts. The output from the detector is proportional to the concentration of the element in the aspirated solution, hence the concentration of unknown samples may be calculated when the instrument response is calibrated with standards of known concentration.

2.4. The linear range may vary from instrument to instrument and is dependant upon the sensitivity determined by the optimization parameters. This should be determined by the individual laboratory. In the test study at STL Pittsburgh, the linear ranges listed in Table 1 were obtained:

2.4.1. Table 1. Test study linear ranges for the X5 ICP-MS

Analytes	Linear Range (mg/L)
Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, Zn	0.20 – 20.0
Ca, Mg, K Na, Fe	100 - 1500

2.5. Calibration standard concentrations are listed in Table 2.

2.5.1. Table 2. Calibration standard concentrations for analysis of water and waste

Analytes	Calibration Range (mg/L)
Al,	1.0
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, Zn	0.20
Ca, Mg, K Na, Fe	100
Fe	50
B, Mo, Sn, Sr, Ti	0.20
Si	10

3. DEFINITIONS

3.1. See the LQM for definitions of general terms

3.2. See appendix for Glossary of Abbreviations

4. INTERFERENCES

4.1. Isobaric Isobaric interferences. Elemental isobaric interferences occur when different elements have isotopes at the same nominal mass, e.g. ^{114}Cd and ^{114}Sn. Problematic elemental isobaric interferences for these methods are listed in Table 3. The correction factors given in Table 3 are based on theoretical isotopic abundance ratios and may require adjustment.

Table 3 Isobaric Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
58	Ni	Fe	58Ni=58M-0.0040*56Fe
64	Zn	Ni	64Zn=64M-0.0440*60Ni
82	Se	Kr	82Se=82M-1.0010*83Kr
114	Cd	Sn	114Cd=114M-0.0270*118Sn
115	In	Sn	115In=115M-0.0140*118Sn
123	Sb	Te	123Sb=123M-0.1240*125Te
138	Ba	Ce	138Ba=138M-0.0030*140Ce

4.2. Abundance Sensitivity - Abundance sensitivity is the ability of the quadrupole to separate a low intensity peak from an adjacent high intensity peak. An example of the requirement of this is the detection of low concentrations of manganese (m/z 55) in the presence of high concentrations of iron (m/z 56). Quadrupole resolution and bias can be adjusted during set-up to resolve these signals.

4.3. Isobaric Polyatomic Ion Interferences - Polyatomic ions are produced by chemical reaction in the plasma and the interface region. If these polyatomic ions have the same nominal mass to charge (m/z) ratio as an analyte a polyatomic interference is observed. The principle polyatomic species for this method are listed in Table 4. Some of the correction factors given in Table 4 are based on theoretical isotopic abundance ratios and may require adjustment. Other factors were derived empirically. The stability of the empirical factors was determined during the test study at Thermo Electron. It was found that the factors require little or no adjustment and can be transferred between similarly configured X5 instruments.

Table 4. Isobaric Polyatomic Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
51	V	ClO	51V = 51M-3.0460*53ClO 53ClO = M53-0.114*52Cr
52	Cr	ArC, ClOH	52Cr = 52M-0.0050*13C
56	Fe	CaO	56Fe = 56M-0.1500*43Ca
56	Co	CaO, CaOH	59Co = 59M-0.0046*43Ca
60	Ni	CaO	60Ni = 60M-0.0020*43Ca
75	As	ArCl	75As = 75M-3.000*77ArCl 77ArCl = 77M-0.8000*82Se 82Se = 82M-1.0010*83Kr
111	Cd	MoO	111Cd = 111M-0.9820*108MoO 108MoO = 108M-0.712*106Cd

4.4. Physical Interferences - Physical interferences include transport effects, ionization effects and deposition effects in the sample introduction system, plasma and interface, which result in signal suppression and signal drift. Transport effects arise from variations in solution properties, e.g. viscosity or surface tension, which affect nebulization efficiency and aerosol droplet size. The concentration of dissolved matter will affect the ionization efficiency of the analytes in the plasma and will cause a mass-dependant suppression effect and contribute to space-charge effects. Dissolved matter may also condense on the cones, altering the ion beam profile. This normally manifests itself as a time-dependant downward signal drift. To reduce the severity of these effects it is advised that the total dissolved solids concentration of solutions aspirated should be limited to <0.05%. Samples known to contain higher dissolved solids concentrations should be diluted. Signal suppression and drift can be corrected, to a degree, with the use of internal standardization techniques. Since these effects can be mass-dependant and may be related to the ionization potential of the element, a multiple-element internal standard approach should be used.

4.5. Memory Effects - Memory effects occur when the signal for an analyte from a sample

contributes to the signal of a subsequent sample. This effect can be severe for certain elements due to their physico-chemical properties, e.g. mercury. This effect is minimised by aspirating a wash solution between samples. A monitored wash can be used in order to ensure that analyte signals recover to the background level.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all associates.

5.2. Eye protection that satisfied ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.2.1. Neoprene, NDex (nitrile), and TRIonic® Cleanroom gloves provide varying degrees of protection against those chemicals listed. Refer to permeation/degradation charts for the actual data.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.3.1. The following materials are known to be corrosive: sulfuric acid; hydrochloric acid; and nitric acid.

5.3.2. The following materials are known to be oxidizing agents: nitric acid; hydrogen peroxide.

5.3.3. The waste pumped from the spray chamber is corrosive and must be handled with care, especially if large volume containers are used, as these may be heavy and awkward to carry. Empty the waste vessel daily to reduce the quantity that must be disposed each time and to keep weight to a minimum. Protective clothing, including hand and eye protection must be worn when handling this waste.

5.3.4. The wash solution is corrosive and must be handled with care. This solution must be prepared and stored in a vessel made of a robust acid-resistant material with a tight fitting lid that it is resistant to breakage if dropped. Large volumes of this solution will be heavy and may be awkward to carry. Ensure adequate provision for transporting the vessel, i.e. suitable handles on the vessel, minimum distance between the preparation area and the instrument. Use a cart to transport the vessel where necessary or ask for assistance in carrying.

5.3.5. Many of the concentrated metal standard solutions are toxic and must be handled with care. Skin and eye protection should be worn when handling and inhalation of vapours must be prevented.

5.3.6. Fumes generated by the plasma can be hazardous and must be removed from the laboratory with an extraction system as detailed in the X Series site planning guide. If the extraction system is faulty do not attempt to use the instrument. The extraction system should be inspected on a regular basis.

5.3.7. The plasma emits strong UV light and is harmful to vision.

5.3.8. *WARNING:* AVOID looking directly at the plasma.

5.3.9. The plasma is a source of radio frequency (RF) radiation and intense, ultra-violet radiation that can damage the eyes. This radiation is normally contained by the system, but operators must be aware of the dangers. The instrument must be

properly maintained by qualified service personnel. Never attempt to defeat hardware interlocks – they are there for your safety.

5.3.10. WARNING: People with pacemakers should not go near the instrument while in operation. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free from etches, cracks, chips, and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90?C. Diazomethane must be generated and handled in a fume hood.
Note: Diazomethane has not been classified as a carcinogen under the current OSHA definition.

5.3.11. Should the plasma need to be extinguished in an emergency, open the torch box door. This will immediately cut-off the power to the plasma RF generator, extinguishing the plasma. After extinguishing the plasma, the torch, torch box, cones and cone housing may remain very hot for some time. Operators must be aware of this fact and allow cooling time prior to handling these components.

5.3.12. There are high voltage components inside the instrument. Routine maintenance does not require access to any of the electronic components. If an electronic fault is suspected, a qualified service engineer must be called. Do not attempt to tamper with electronic components yourself.

5.4. Exposure to chemicals must be maintained as low as reasonably achievable, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported immediately to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Top pan balance, 2 kg capacity and minimum accuracy ±10mg.

6.2. Analytical balance, 300 g capacity and minimum accuracy ±0.1mg.

6.3. X Series ICP-MS fitted with Xi interface and Y-connector for on-line internal standard addition (supplied with this package).

6.4. Cetac ASX-510 autosampler.

6.5. Ultrapure water system capable of delivering de-ionized, polished water of at least 18 M? cm

6.6. Yellow/orange tab peristaltic pump tubes (~0.5 mm ID)

6.7. White/white tab peristaltic pump tubes (~1 mm ID)

6.8. A range of adjustable pipettes, such as Rainin pipettes. Adjustable pipettes with a capacity of 0.1 mL, 1 mL, and 10 mL are recommended. These must be calibrated regularly to ensure accurate volumes are delivered.

7. REAGENTS AND STANDARDS

7.1. General Reagents

7.1.1. **Laboratory Water** - All laboratory water used in these procedures must be of very high quality, purified with a reverse osmosis system and polished with an ion exchange system to give a final product of resistivity >18 MO cm.

7.1.2. **Hydrochloric Acid** (sp. gr. 1.18) - Hydrochloric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/ Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – corrosive, causes severe burns.

7.1.3. **Nitric Acid** (sp. gr. 1.42) - Nitric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/ Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – oxidising and corrosive, causes severe burns.

7.1.4. **2 % (m/v) Nitric Acid** - This reagent is used for the calibration blank, ICB, CCB, sample dilution and solution preparation. Add 5 mL of Conc of HNO3 to DI water and dilute to 250 mL

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Samples are to be collected in plastic or glass containers.

8.2. All soils must be refrigerated to $4^{o}C \pm 2^{o}C$.

8.3. The analytical holding time for metals by ICP-MS is 6 months.

8.4. Aqueous samples for total metals must be digested before analysis using an appropriate digestion procedure. Method 3005A is used for total metals by 200.8 or total recoverable metals by 6020 and method 3010A is used for total metals by 6020. These are covered in the SOP C-IP-003. Upon consultation with the client dissolved samples can forego digestion to help prevent contamination when very low detection limits are required.

8.5. Soil or waste samples should be digested before analysis using an appropriate digestion procedure. Method 3050B of SW846 is the appropriate digestion procedure. The SOP for 3050B is C-IP-0002.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration IDC and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.1.2. For new analytes an MDL study should be performed and calibration curve generated before analyzing any samples.

9.2. Control Limits

9.2.1. Control limits are utilized for matrix spikes and laboratory control samples (LCS). These limits must be reviewed at least annually against current data.

QC Type	200.8	6020	ILM05.2
LCS	85 – 115	80 – 120	80 – 120
MS	70 – 130	75 – 125	75 – 125
RPD	? 20	? 20	? 20

9.2.2. All LCS and MS recoveries must be entered into QuantIMS or other database so that accurate historical control charts can be generated. For tests without a separate extraction, matrix spikes will be reported for all dilutions.

9.2.3. Refer to the QC program document (QA-003) for further details regarding control limits.

9.3. Quality Control Batch

The batch is a set of up to 20 field samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike/matrix spike duplicate. (In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD). If clients specify particular samples for MS/MSD, the batch may contain multiple MS/MSDs. See policy QA-003 for further definition of the batch.

9.4. Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS may be processed, if precision data is required by the client. The LCS pair is then evaluated according to the MS/MSD RPD criteria. Use of a LCS pair in place of a MS/MSD must be documented using Clouseau.

9.5. Method Blank

One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher. Certain programs, such as USACE, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.

? If the analyte is a common laboratory contaminant (copper, iron, zinc), the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than five times the RL. Such action must be documented in the NCM program.

? Re-preparation and reanalysis of any samples with reportable concentrations of analytes less that 10 times the value found in the method blank is required unless other actions are agreed with the client.

? If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported. This must be documented in the NCM program.

? If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all positive results in associated samples are flagged with a "J", and appropriate comments may be made in a narrative to provide further documentation.

9.5.1. Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.5.2. For dissolved metals samples which have not been digested or matrix matched, a CCB result is reported as the method blank. The CCB analyzed immediately prior

to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.5.3. Methodologies for MDL assessment are detailed in SW-846 Chapter 1, method 6020 and in 40 CFR Part 136 Appendix B.

9.6. Laboratory Control Sample (LCS)

9.6.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of samples. All analytes must be within established control limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless otherwise requested by the client.

9.6.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur:

- Check calculations,
- Check instrument performance,
- Reanalyze the LCS, and if still outside of control limits,
- Evaluate the data, and/or
- Re-prepare and reanalyze all samples in the QC batch.

9.6.3. Data may be reported with an anomaly in the following cases:

- The LCS recoveries are high and the analyte of concern is not detected in field samples,
- All target requested analytes are within control, but other LCS compounds are out of control,
- If no sample preparation is performed (eg, dissolved metals), the LCS may be reprepared and reanalyzed within the same sequence.

9.6.4. The analyst should evaluate the anomalous analyte recovery for possible trends.

9.6.5. If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.

9.6.6. If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.6.7. For dissolved metals samples which have not been digested or matrix matched, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of samples. The MS/MSD is spiked with the same analytes as the LCS (See Tables 9 and 10). Compare the percent recovery and relative percent difference (RPD) to that in the historically generated limits.

Note: Some programs require an Matrix Spike and Matrix Replicate in lieu of an MS/MSD. When a matrix spike/matrix replicate is performed the matrix spike is evaluated for accuracy (% recovery) and the matrix replicate is evaluated for precision (RPD).

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis may proceed. The reasons for accepting the batch must be documented.
- If the recovery for any component is outside QC limits for both the matrix spike/spike duplicate and the LCS, the process is out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.
- If a MS/MSD or MS/Dup is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.
- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.7.1. If the amount of an analyte found in the unspiked sample is greater than 4 times the amount of spiked analyte added, then routine control limits do not apply and recoveries are not evaluated. Other analytes in the MS and MSD must still be reported. File an NCM stating that the 4X rule was applied, and report the recovery in the LIMS as "ND MSB". This NCM must be included in the final report.

9.7.2. For dissolved metals samples which have not been digested or matrix matched, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample.

9.8. Linear Range Verification (LR) - The linear range is determined semi-annually (2x/year) for each element on the standard list. See section 13 for details of the linear range verification. The Linear Range study must be performed quarterly if doing ILM05.2.

9.9. The internal standard intensities in samples must be within 70 to 130% of the IS intensities for the Calibration Blank. If this criterion is not met, the sample will be diluted and reanalyzed until the IS recoveries are within the limits. If the upper control limit is exceeded, the analyst should review the data for the presence possible contribution from the native sample. Narrate any findings.

9.9.1. The internal standard intensity in the ICV, ICB, CCV and CCB should be within 20% of the IS intensity in the calibration blank of the initial calibration. If not, the analyst should check for any instrument anomalies and continue if none are noted.

9.10. Interference Check Solutions (ICSAs) - The results of ICSA must be within ±3CRQL of the analytes "true" value or ±20% of the analytes "true" value, whichever is the greater. The "true" value will be taken as zero, unless otherwise indicated in the solution manufacturer's literature. The software automatically checks for compliance with the above, based on a "true" value of zero. If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed.

9.11. Interference Check Solution Spike Recoveries (ICSABs) - Results of ICSAB must be within ±20% of the analytes "true" value. The software automatically checks for compliance with the above, based on the values indicated in (6.5.2 or 6.5.4). If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed.

9.12. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV must fall within ? 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy

and system cleanliness. The ICB result must fall within ? the reporting limit (RL) from zero. (Certain programs, may require a more stringent evaluation of ICB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.) If either the ICV or ICB fail to meet criteria, the analytical sequence should be terminated, the problem corrected, the instrument recalibrated and the calibration re-verified.

9.13. CRQL Check Standard (CRI)

THE RESULTS OF THE CRI MUST BE WITHIN THE RANGE 70-130% RECOVERY FOR ALL ANALYTES, EXCEPT CO, MN AND ZN, WHICH MUST BE IN THE RANGE 50-150% RECOVERY. THIS IS CHECKED BY THE SOFTWARE, BASED ON THE VALUES GIVEN IN (6.6.3). IF ANY ANALYTE IS OUTSIDE THE RANGE INDICATED, THE SAMPLE MAY BE RE-RUN ONCE. IF THE RESULTS FALL WITHIN THE REQUIRED VALUES UPON RE-RUN, NO FURTHER CORRECTIVE ACTION NEED BE TAKEN. IF STILL OUTSIDE THE ACCEPTABLE RANGE, THE ANALYSIS SHALL BE TERMINATED, THE PROBLEM CORRECTED AND THE SAMPLES REANALYZED.

9.14. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. Results for the CCV must be within the range 90-110% recovery. This is checked by the software, based on the values in (6.6.2). If outside this range, the analysis must be terminated, the problem corrected and the samples since the last valid CCV must be re-analyzed.. The CCB result must fall within ? RL from zero. (Certain programs, may require a more stringent evaluation of the CCB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit. The analyst should refer to the project notes provided by the PM to identify when this is an issue and if so what the corrective actions to take for exceedances) Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the CCV or CCB may be reanalyzed once and accepted if there is a reason for the initial out-of-control event such as carryover from a high concentration sample. Otherwise, if the CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 11.9 for an illustration of the appropriate rerun sequence).

9.15. Post-Digestion Spike Samples (PDS) A post digestion spike will be run on a sample if the MS/MSD for the sample falls outside of % recovery criteria. A post digestion spike is a matrix spike on a sample, which is added after the sample preparation is completed. For 6020 the default matrix spike protocol is a “post digestion spike”. However, STL Pittsburgh will perform a conventional matrix spike and spike duplicated as the default matrix QC. We will perform the “PDS” only where the conventional matrix spike fails. We believe that this approach will provide more complete matrix information than the default requirements. The spike recovery from the post digestion spiked sample must be within the range 75-125% where the spike value is greater than 25% of the indigenous analyte concentration. The software calculates this based on the following equation:

%Repeatability = 100 * (Spk-Orig)/Tru

where, Spk is the spiked sample result and Orig is the original sample result and Tru is the True spiked concentration value.If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis.

When doing method 6020 the PM needs to advise the analytical group when a client requires an MS/MSD in lieu of a post digestion spike.

9.16. Serial Dilution Samples (SER) - Some regulatory programs such as require a dilution test be performed for each matrix within an analytical batch determination. The results of the serial

dilution sample(s) (SER) after dilution correction must be within the range 90-110% of the original sample, if the result for the original sample is greater than 50*IDL for CLP or greater than 50*MDL for 200.8 or 6020.

9.17. The software calculates this based on the following equation:

9.18. %Repeatability = 100 * Ser/Orig

9.19. where, Ser is the dilution corrected serial diluted sample result and Orig is the original sample result. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis.

9.20. Duplicate Samples (DUP); %RPD = ?20% : Results of the duplicate sample(s) (DUP) must be within ?20% of the results of the original sample, where the result is greater than or equal to 5*CRQL for CLP or greater than 5*RL for 200.8 or 6020. The software calculates this based on the following equation:

%RPD = (S-D) / [(S+D)/2] * 100%

where, D is the duplicate sample result and S is the original sample result.

If a result is outside the required range, the data should be assessed carefully and samples affected may need to be reanalyzed where the project requires it.

9.21. Nonconformance and Corrective Action

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.22. Quality Assurance Summaries

Certain clients may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.23. QC Program

Further details of QC and corrective action guidelines are presented in the QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

10.1. Instrument start-up

10.1.1. Follow the instrument start-up procedure outlined in the Thermo X-Series ICP-MS Operator's Manual.

10.2. Instrument Tuning

10.2.1. Aspirate a 20 ppb tuning solution containing all of the tuning elements. The 6020 tuning elements are Li, Co, In, and Tl. The instrument manufacturer monitors Mg, Ce, Be & Pb for instrument performance.

10.2.2. Mass calibration and resolution checks must be documented and included as part of the raw data package.

10.2.3. Resolution must be < 0.75 amu at 10% peak height for the 6 tuning (Be, Ce, Co, In, Mg , & Pb) for 6020. Resolution must be ? 0.75 amu at 5% of the peak height for EPA 200.8 and ILM05.2. And the resolution must be ? 0.9 amu at 5% of the peak height for Method 200.8.

10.2.4. Mass calibration must be within ± 0.1 amu from the actual value for the 6 tuning elements (Be, Ce, Co, In, Mg, & Pb) or the mass calibration must be adjusted.

10.2.5. A “daily” performance check must be performed. This uses the same tuning solution as above. The 6 tuning elements must have RSDs below 5%. The oxides must be below 3.5%. If any of these conditions are not met repairs or optimization procedures must be performed until these specifications are met.

10.3. Initial Calibration

10.3.1. Calibration consists of a blank and the following calibration standards (STD, STD 2X, and STD 3X see Table 2 for concentrations) in accordance with the manufacturer’s procedure. Use the average of three integrations for both calibration and sample analyses.

10.3.2. Following the STD, STD2X & STD3X, an ICV/ICB pair is analyzed. The ICV must be within ? 10% of the true value to be acceptable.

10.3.3. For 6020 and ILM05.2, following the ICV/ICB pair, the CRI/RLV is run then the ICSA is analyzed.

10.3.4. For 6020 and ILM05.2, following the ICSA, analyze the ICSAB. The ICSAB must be within ? 20% of the true value.

10.3.5. Internal standards are added to all standards and samples by the instrument prior to analysis.

10.4. Continuing Calibration:

10.4.1. Following every 10 samples (including lab QC), analyze a CCV/CCB pair. These must be within ? 10% of the true value for analysis to continue. For methods 6020 and ILM05.2, a CCV/CCB pair should also be analyzed immediately after the ICSAB.

10.4.2. All samples must be bracketed by an acceptable CCV/CCB pair. Where a CCV/CCB fails the samples preceding it back to the last acceptable CCV/CCB must be reanalyzed.

11. PROCEDURE

11.1. Instrument Set-up

11.1.1. Configure the X Series with the standard sample introduction equipment, i.e. a glass concentric nebulizer, glass impact bead spray chamber and a one-piece torch with 1.5mm ID injector tube. A Peltier spray chamber cooling unit is optional. Ensure that the Xi interface cones are fitted. These are standard with the X5 instrument and an option for the X7. They can be identified as follows:

Xi Sampler - 1.1 mm orifice, no nipple, no holes around the flat circumference

Xi Skimmer - Small pointed skimmer mounted in a copper adapter with two screws

Yellow/orange tab peristaltic pump tubes (5.2.6) should be used for sample and internal standard uptake. Connect the liquid output end of the peristaltic pump tubes to the 1.0 mm (OD) barbed fitting screwed into the Y connector. Note that the barbed fitting may require tightening with a pair of grips to ensure a good fluid-tight seal. The mixed output flow should be connected to the nebulizer. See diagram in Appendix 6 for plumbing schematic. A white/white tab peristaltic pump tube (5.2.7) should be connected to the spray chamber drain outlet at one end and to a tube running into a waste vessel at the other and wound on the pump to draw the waste liquid away from the spray chamber.

11.1.2. Perform the daily maintenance as outlined in Appendix 3.

11.1.3. Switch the instrument into the *Operate* state by clicking the *ON* button at the top of the screen. During the automated ignition sequence, the following processes occur:

i. Torch purge with argon gas

ii. RF power match

iii. Plasma ignition

iv. Slide valve open

v. Electronics on

This process takes about two minutes. Upon successful ignition, the software will display *Operate* in the *Instrument State* bar. If the event of unsuccessful ignition, the software will display an error message and/or place a message in the *Technician Event Log*. Upon unsuccessful ignition, inspect the sample introduction equipment and torch, ensuring a good gas-seal at each connection and ensuring the torch is not misaligned or damaged. If all appears satisfactory, the ignition may be attempted again. If the ignition process consistently fails, contact your local Thermo service agent for advice.

11.1.4. Once the instrument is in the *Operate* state, it should be left for 30 minutes to reach thermal equilibrium prior to starting analytical measurements. The optimization (tuning), performance testing and instrument set-up calibrations may be performed after 15 minutes. Ensure that the peristaltic pump is operated at a default analytical speed of 15%. This is done by clicking on *Instrument*, *Configurations*, *Configuration Editor*, *View Selected Accessories* (network icon), *Peristaltic Pump*, *Connect* (chain icon). Set pump speed to 15% using the slider bar and adjust the *Settle Time* to 10 seconds and click on *Apply*. Click *OK* to close the dialogue box.

11.1.5. During the initial 15 minutes, the system can be “conditioned” by aspirating the system thoroughly with 2% nitric acid + 1% HCL solution (6.1.4) prior to continuing.

11.1.6. Instrument tuning (optimization) is performed using a 20 µg/L Tune Solution (6.4.1), aspirated through the sample uptake tube. Optimization may not be necessary from day to day if the sample introduction system and cones have not been adjusted in any way and if the instrument fulfils the performance requirements given below. If the instrument gives performance exceeding the requirements shown below, proceed to 8.1.7. Otherwise, tune the instrument manually or using *Autotune* while aspirating 20 µg/L Tune Solution (6.4.1) through both the sample and internal standard uptake tubes. *Autotune*, using an appropriately defined sequence is advised (see Appendix 4).

The final conditions must give the following:

^{9}Be	>5000cps
^{115}In	>50000cps
^{208}Pb	>25000cps
$^{156}CeO/^{140}Ce$	<0.02

If the above criteria are met, proceed to 8.1.7. If the above criteria are not met, do not proceed. Check that the tune solution was prepared as per instructions in (6.4.1) and remake if necessary. If the sensitivity is below the minimum requirement, a new detector plateau may be required (see Appendix 6), the cones may require cleaning (see Appendix 8), or the nebuliser or sample uptake lines may have become blocked or may not be properly clamped on the peristaltic pump. If the CeO/Ce ratio is >0.02, the nebulizer gas flow can be reduced and/or the sampling depth increased, obtaining a corresponding reduction in oxide formation. Recheck the above parameters after taking any remedial action.

11.1.7. Save the satisfactory instrument settings by clicking on the disk icon on the Tune page. Note that this is not necessary if Autotune has been used, as the instrument settings are saved automatically (unless manual adjustments have been made after autotuning).

11.1.8. Set-up the resolution as described in Appendix 5.

11.1.9. Perform a cross-calibration (and mass-calibration and detector voltage setup if required) as explained in Appendix 6. Note that retuning may be necessary after performing this routine.

11.1.10. Aspirate Tune solution (6.4.1) and run a *Performance Report* (see Appendix 4) to confirm the mass-calibration, resolution, minimum sensitivity and maximum cerium oxide requirement given in (8.1.6) and to verify instrument stability. The performance report acquires five consecutive one minute runs and calculates the percentage relative standard deviation (RSD) of the five measurements for each isotope. The RSD of the elemental analytes in the performance report must be <5%. If the performance report passes, proceed to (8.1.11). If the performance report fails, check:

a. Liquid uptake tubes for kinks or other damage

b. Condition and position of the peristaltic pump tubing

c. Tightness of the peristaltic pump clamp screws (these should be just tight enough to draw liquid through the tube smoothly)

d. Joints of all sample introduction components, ensuring a good seal

e. Nebulizer for blockage

f. Salt deposition on cones

Remedy the above as necessary and repeat the test. Note that retuning may be required if any sample introduction components are adjusted or replaced.

Note: Resolution set-up may require adjustment if the resolution check fails (see Appendix 5). Note that the quadrupole and hexapole bias strongly influence abundance sensitivity (Pole Bias should be kept >+4V and Hexapole Bias <-3V).

If the measured mass position for each mass in the performance report is not within ±0.1 amu of the nominal mass position, a new mass-calibration must be performed (see Appendix 6).

11.1.11. Place the both probes into 2% nitric acid solution (6.1.4) to rinse the system well for at least five minutes prior to commencing analysis.

11.2. Sample Analysis

11.2.1. Open the method template by clicking on *Templates* and then *EPA 6020 ILM*

Temp Full Sample List. The method template will be opened. This contains all the saved analytical parameters and only the sample list need be amended.

11.2.2. Go to *Sample List*. This grid contains all the information about calibration, QC and samples to be run. The calibration and QC concentration information is already stored. Enter all unknown samples into the list in the appropriate order below the existing calibration and QC samples by overwriting the sample label fields. Delete any QC samples that do not apply to the required method. (If sample list changes are to be made permanent to the method, save the method as a *Template*, by going to *File*, *Save as Template*. Enter a new name to create an amended method, or use the same name to overwrite the current one.)

11.2.3. Ensure that a sample is analyzed in duplicate (given the suffix "X") at a frequency of once every 20 samples per matrix. Define the "X" sample as a *QC Sample* in the *Type* column. Set the *QC Type* to *DUP* and ensure that the entry in the *Reference Sample* column is set to the name of the original sample.

11.2.4. Ensure that the same sample as in 8.2.3 is analyzed after dilution (1+4) (given the suffix "P") at a frequency of once every 20 samples per matrix. Enter the dilution factor as 5 for the "P" sample. Define the "P" sample as a *QC Sample* in the *Type* column. Set the *QC Type* to SER and ensure that the entry in the *Reference Sample* column is set to the name of the original sample in (8.2.3).

11.2.5. Ensure that the same sample is analyzed after spike addition (given the suffix "A") at a frequency of once every 20 samples per matrix (see 8.3.4 for spike addition instructions). Define the "A" sample as a *QC Sample* in the *Type* column. Set the *QC Type* to *PDS* and ensure that the entry in the *Reference Sample* column is set to the name of the original sample in (8.2.3).

11.2.6. Once all the sample information is added, check the required autosampler positions have been correctly entered. Amend as necessary. To sequentially renumber positions, add the correct position required for the initiation of the sequence and right mouse click on the first correctly numbered cell. A pop-up menu will appear. Select *Renumber autosampler positions* from this. Ensure that all samples have one survey run and 3 main runs and a probe depth of 155mm.

11.2.7. Delete any rows that are not required. This can be done by selecting the rows for deletion by clicking and dragging on the grey boxes to the left of the grid. Then right mouse click and select delete from the pop-up menu.

11.2.8. Save the experiment run by clicking on the *File* menu, then *Save as*. Enter the required file name, e.g. *enviro090902* and click *Save*.

11.2.9. To print the sample list, go to *Reports* and check the *Sample List* box. Click the refresh icon. The sample list will be displayed in a printable format. Press the print icon. Note that this can only be done with PlasmaLab version 2.3 and above.

11.3. Loading the Autosampler

11.3.1. Pour the required samples into pre-cleaned 15ml polypropylene test tubes (5.1.4). To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination.

11.3.2. Pour blanks, standards and QCs (positioned in rack 0) into pre-cleaned 50ml polypropylene tubes (5.1.5). To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will

rinse out any residual contamination. Note that **2% nitric acid** (6.1.4) is used as the calibration blank, IBC, and CCB.

11.3.3. For the **serial dilution** ("P") sample(s), dispense 2.00±0.02 mL of the original sample into a pre-cleaned 15 mL polypropylene test-tube (5.1.4) and add 8.00±0.08 mL of 2% nitric acid (6.1.4). Mix well. This is a 5-fold dilution.

11.3.4. Place the tubes for each sample into the appropriate position in the rack according to the sample list. Note that the autosampler works on a two-dimensional grid position system by rack number (0-4). See Appendix 9 for autosampler position map.

11.4. Initiating Analysis

11.4.1. Place the sample probe into the autosampler arm and the internal standard probe into the internal standard solution (6.4.6).

11.4.2. Go to *Instrument*, *Tune* and click on the accessories dialog icon. Click on *Autosampler* and then on the chain icon to connect. The autosampler should initialize. Ensure that the probe is at the correct height by positioning it so that its tip just protrudes through the hole in the bottom of the arm. Click on the *Go to Wash* icon (faucet) to send the probe to the wash station. Ensure that the wash solution is being correctly delivered to the wash station via the peristaltic pump at the rear of the autosampler. Allow at least 2 minutes for the liquid to be delivered to the sample introduction system.

11.4.3. Click on the experiment to be run. Click the *Queue* icon and then *Append* and *OK*. The analysis has now been initiated.

11.4.4. To monitor the progress of the analysis, right-mouse click on the *MS* icon at the bottom-right of the screen and select *Open Service Window* from the pop-up menu. The Service Window hovers over the current application window until moved or closed and displays the current instrument activity. This window is also used **to stop an analysis** if required. This is done by clicking on the ***^{x}Q* icon**.

11.4.5. To view results as they are generated, click on the experiment icon and go to the *Results* tab. Click on the *Refresh* button or the refresh icon (green circular arrows on a page) to calculate the results from the data obtained.

11.4.6. To view calibration plots, click on the *Calibration Data* tab. The calibration for each analyte can be viewed by clicking on the required isotope in the *Analyte* box. Each subsequent set of calibrations (calibration block) can be displayed by selecting the required calibration block from the drop-down combo box, e.g. *FQ Block 1*, *FQ Block 2*, etc. FQ denotes a Fully-Quantitative calibration and SQ denotes a Semi-Quantitative calibration, i.e. a response curve generated from the *FQ* calibrations. The SQ response curve is used to calculate semi-quantitative concentrations if required.

11.4.7. To view data, click on the *Numerical Results* tab. The *Analyte Dilution Conc.* tab is a tabular display of the calculated corrected concentrations for each analyte. These values have been corrected for internal standardization, external drift correction (if used), and dilution (where entered). The *Mass Uncorrected ICPS* tab shows the uncorrected raw data for each measured mass in units of integrated counts per second (ICPS). The *Analyte ICPS* tab shows integrated counts per second data that has been mathematically corrected for blank deduction, internal standardization, drift correction (if used), and dilution (as appropriate). The *Survey* tabs show the data integrated from the survey scan for each sample. Any

concentrations displayed in the survey page will be semi-quantitative only.

11.4.8. To edit the amount of data on screen (filter the results display), click on the filter icon (funnel and lightening). Alter the numerical values or the check boxes to select the required data to display and click on *OK*. To jump directly to a particular sample of interest, find the sample in the drop-down combo box at the top of the data display and click on it.

11.4.9. To display mass-spectra, click on the *Spectra* tab. Display the spectrum for a particular sample by double-clicking on the sample name in the selection box on the left of the screen. Note that several spectra may be overlaid by double-clicking on each sample to be displayed. To zoom into a particular area, click the zoom icon (magnifying glass) and click and drag on the spectral display to zoom into the required area. The dashed-lines represent data acquired in the analogue mode of the detector whilst the solid-lines represent pulse-count data. To remove the noise associated with analogue detection at low signal levels, point at the display and right-mouse click to bring up a menu. Go to *View Options* and then click on *Eliminate Analogue Noise*. To identify a peak, click on it and wait for the options for that mass to be displayed in the box above the spectral display. To fingerprint a spectrum, double click on the species to fingerprint in the options box. This will overlay the isotopic pattern for the selected species, based on the lowest relative intensity signal for the pattern masses. The spectra may be navigated by using the arrow buttons above the display. Allow the arrow cursor to hover over each button for an on-screen explanation of its function.

11.5. Post-Analysis Data Processing

11.5.1. Internal Standards

11.5.1.1. Check the internal standard recovery percentage for each internal standard isotope used for every sample. The percentage for each isotope must be within the range 70-130%.

11.5.1.2. If above 130%, check that the other internal standard isotopes show similar deviation. If not, this may be due to the presence of the internal standard element in the sample. This is particularly common with the isotopes of Li, Sc and Y in environmental materials. If this is the case, the affected internal standard isotope may be excluded for the sample affected, as follows. Go to the *Sample List*.

Find the sample affected and select it in the list by clicking on the box in the left-hand column. Click *Show Advanced* and go to *Internal Standards*. Click on *New Internal Standard Set*. Select the affected isotope(s) in the *Internal Standards* box on the right. Remove the affected isotope from the *Internal Standards* box by using the left hand arrow button (<<). Recalculate the results for this sample by going back to *Results* and clicking on *Refresh*.

11.5.1.3. If any internal standard isotope is outside the range 70-130% and all other internal standard isotopes show similar values for that sample, the instrument may have drifted, or the sample may be producing a suppression or enhancement effect. Find the nearest blank following the sample in question and check its internal standard results. If these are similarly reduced or elevated, the instrument has drifted and the samples must be reanalyzed from the last compliant blank. If the blank does not exhibit similar drift, the sample must be producing a suppression or

enhancement effect due to its matrix. In this case the sample must be re-analyzed after a five-fold (1+4) or a two-fold (1+1) dilution to reduce the matrix effect.

11.6. General protocols

11.6.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.6.3. An analytical run will consist of all customer samples and quality control samples analyzed under a daily initial calibration. Each new initial calibration will begin a new analytical run.

11.6.4. Type in the QC and sample information into the autosampler table.

11.6.5. In order to use the ICP-MS data upload program into LIMS, the following naming conventions must be followed:

- Samples are identified by the 5 character work order number
- Matrix spikes, duplicates, and matrix spike duplicates are identified by the 5-character work order number followed by S (matrix spike), D (matrix spike duplicate) or X (sample duplicate).
- Prep Blanks are identified by the 5 character work order number followed by B.
- LCSs are identified by the 5 character work order number followed by C (LCS) or L (LCS Duplicate).

11.7. Initial Calibration

11.7.1. Open a new dataset using the date and instrument in the title. For instance the first run (A) on instrument 2 on JAN 1, 2003 would be A30101A.

11.7.2. Open the appropriate method if one already exists or create a new one for the analytes to be quantitated in the run. Solicit the assistance of a senior ICP-MS operator in creating a new method.

11.7.3. See Tables 7, 8, and 9 for recommended isotopes and interference equations for commonly analyzed elements.

11.7.4. If no recommended isotopes are given for the element to be analyzed, consult a senior ICP-MS operator or appropriate reference (see Section 13.2).

11.7.5. See Table 10 for commonly used internal standards.

11.7.6. All masses which could affect data quality should be monitored to determine potential interferences either simultaneously during an analytical run or in a separate scan.

11.7.7. Internal standards are added to all standards and samples by the instrument prior to analysis.

11.7.8. Use of an existing autosampler table is suggested. A read delay of 45 to 60 seconds is used between all analyses.

11.7.9. Calibration consists of a blank and a single calibration standard (STD1, see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

11.8. The order of analysis for the initial QC samples and calibration should be:

1. Rinse
2. Performance Report (Tune Check)
3. STD1 (Calibration Standard)
4. STD2 (2x Calibration Standard)
5. STD3 (3X Calibration Standard)
6. ICV (Second source, must be ? 10% of true value)
7. ICB
8. CRI / RLV (Reporting Limit Verification Standard)
9. ICSA (Interference check solution.)
10. ICSAB (Interference check solution, ? 20% of true value)
11. CCV
12. CCB
13. Prep QC such as LCS or MB, followed by samples (up to 10 runs)

11.8.1. To continue the analytical run, add an additional 10 runs followed by CCV/CCB, and repeat for up to 24 hours.

11.8.2. Analysis sequence when out-of-control QC is observed: Recalibrate and rerun all affected samples (including initial QC)

12. DATA ANALYSIS AND CALCULATIONS

12.1. All pertinent calculations are performed by the ELAN software.

12.2. Reporting Requirements

12.2.1. Units are ug/L for aqueous samples and mg/kg for soil samples.

12.2.2. If dilutions were required due to insufficient sample, interferences, or other problems, the laboratory reporting limits are multiplied by the dilution factor.

12.2.3. For results less than 10 mg/L, two significant figures will be reported. For results greater than or equal to 10 mg/L, three significant figures will be reported. Refer to Policy QA-004 for additional information on significant figures and rounding.

12.2.4. Document any non-standard procedures or anomalies by using the anomaly program (Clouseau).

12.3. Data Package Requirements

12.3.1. A complete data package consists of: the daily tuning package, the method

printout, run log, internal standard summary, standards documentation, level 1 checklist, and all raw data.

12.3.2. Level I review will be completed by the analyst.

12.3.3. Level II review will be completed by a senior level laboratory analyst familiar with the technical aspects of ICP-MS and in accordance with the ICP-MS DATA REVIEW checklists. The instrument operator of an analytical run may not perform the Level II review for that run.

12.4. Disk Back-Up

12.4.1. Datasets must be backed up monthly onto CD disks. All the datasets for each calendar month are copied onto a disk. Note that the dataset names do not change. The Optimization ("optimization") Reprocess files for that month are also copied onto the disk. The disks are stored in a storage cabinet in the laboratory for 5 years from the last day of the month saved.

12.4.2. Laboratory instrument data archival will be performed entirely on network servers as new hardware is available. Full implementation is expected by the end of calendar year 2002.

13. METHOD PERFORMANCE

13.1. Initial Demonstration of Capacity

Prior to analysis of any analyte using Method 6020, the following requirements must be met.

13.2. Instrumentation Detection Limit (IDL) – IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined quarterly for the standard analytes listed in Appendix A. All other elements will be determined annually. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined.

13.2.1. IDLs shall be determined by multiplying by three the average of the standard deviations obtained on three non-consecutive days from the analysis of a blank solution with seven consecutive measurements per day.

13.2.2. Each measurement must be performed as though it were a separate analytical sample.

13.2.3. Each measurement must be followed by a rinse and/or any other procedure normally performed between the analyses of separate samples.

13.2.4. The IDL measurement must consist of the same number of replicates used for analytical samples with the average result used for reporting.

13.3. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. MDL's must be redetermined on an annual basis as detailed in Policy S-Q-003 and further defined in QA-005.

13.3.1. On occasion, a non-routine analyte is requested by the client. In lieu of a full MDL study, a standard containing the non-routine analyte must be analyzed. The concentration of the standard must correspond to the reporting limit or ½ the reporting limit. This is to verify that the method can satisfactorily quantify the element near the chosen reporting limit. The recovery of the standard must be between 50% and 150% of the expected value. The standard analysis should be kept with the analytical data.

13.4. Linear Range Verification (LR) - The linear range is determined semi annually (2x/year) for each element on the standard list. Some regulatory programs, such as AFCEE, may require more frequent determinations.

13.4.1. To determine the linear range, analyze 3 standards at increasing concentration up to 90% of the last concentration where the element was within 10 % of true value is considered the upper linear range.

13.4.2. An alternative is to prepare a higher concentration standard and run this in the analytical run. If this standard is within 10% of the expected value this value can be used as the upper linear range. If this option is chosen, then note the action in an anomaly.

13.5. Training Qualification

13.5.1. The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. Standards or solutions are not approved for disposal to the sink.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed in accordance with the STL Corporate Safety Manual and facility hazardous waste procedures. Contact the Environmental Health and Safety Coordinator or the Hazardous Material Technician with questions regarding disposal.

15.2. Samples and other solutions containing high concentrations of toxic materials must be segregated and disposed in accordance with the STL Corporate Safety Manual and facility hazardous waste procedures. Contact the Environmental Health and Safety Coordinator or the Hazardous Material Technician with questions regarding disposal.

15.3. Standards should be purchased and prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

15.4. Expired standards must be rotated out of the laboratory to the Hazardous Waste disposal area.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, Method 6020, Inductively Coupled Plasma – Mass Spectrometry, Revision 0, September, 1994.

16.2. Thermo Electron X Series Users Manual

16.3. EPA Method 6020 CLP M, Version 8.

16.4. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111) , Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994

16.5. EPA Method 200.8 EMSL office of Research & Development, Cincinnati, OH (Draft Method, Revision 4.3, August 1990).

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

Appendices

17.1. Tables

TABLE 1

STANDARD ANALYTE LIST AND REPORTING LIMITS*

Element	Symbol	CAS #	Aqueous RL mg/L	Aqueous QC SPIKE Mg/L	Soil RL mg/Kg	Soil QC SPIKE Mg/kg
Aluminum	Al	7429-90-5	0.03	2.0	3.0	200
Antimony	Sb	7440-36-0	0.002	0.10	0.2	10
Arsenic	As	7440-38-2	0.002	0.04	0.2	4
Barium	Ba	7440-39-3	0.010	2.0	1.0	200
Beryllium	Be	7440-41-7	0.001	0.05	0.1	5
Boron	B	7440-42-8	0.005	1.0	0.5	100
Cadmium	Cd	7440-43-9	0.001	0.05	0.1	5
Calcium	Ca	7440-70-2	0.10	50	10.0	5000
Chromium	Cr	7440-47-3	0.002	0.2	0.2	20
Cobalt	Co	7440-48-4	0.0005	0.5	0.05	50
Copper	Cu	7440-50-8	0.002	0.25	0.2	25
Iron	Fe	7439-89-6	0.05	1.0	5.0	100
Lead	Pb	7439-92-1	0.001	0.02	0.1	2
Magnesium	Mg	7439-95-4	0.10	50	10.0	5000
Manganese	Mn	7439-96-5	0.0005	0.5	0.05	50
Molybdenum	Mo	7439-98-7	0.005	1.0	0.5	100
Nickel	Ni	7440-02-0	0.002	0.5	0.2	50
Potassium	K	7440-09-7	0.100	50	10.0	5000
Selenium	Se	7782-49-2	0.005	0.01	0.5	1
Silver	Ag	7440-22-4	0.001	0.05	0.1	5
Sodium	Na	7440-23-5	0.10	50	10.0	5000
Strontium	Sr	7440-24-6	0.005	1.0	0.5	100
Tin	Sn	7440-31-5	0.005	2.0	0.5	200
Titanium	Ti	7440-03-26	0.005	1.0	0.5	100
Thallium	Tl	7440-28-0	0.001	0.05	0.1	5
Vanadium	V	7440-62-2	0.001	0.5	0.1	50
Zinc	Zn	7440-66-6	0.001	0.5	0.1	50

***** *Note: These are the routine reporting limits for most sample types. Lower reporting limits may be achievable for special projects. Difficult sample matrices may cause reporting limits to be raised.*

TABLE 2

Composition of the CAL Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.200	Mn	0.200
Al	1.00	Mo	0.200
As	0.200	Na	100
B	0.200	Ni	0.200
Ba	0.200	Pb	0.200
Be	0.200	Sb	0.200
Ca	100	Se	0.200
Cd	0.200	Si	10
Co	0.200	Sn	0.200
Cr	0.200	Sr	0.200
Cu	0.200	Ti	0.200
Fe	50	Tl	0.200
K	100	V	0.200
Mg	100	Zn	0.200

TABLE 3
Composition of the ICV Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.08	Mn	0.08
Al	0.4	Mo	0.08
As	0.08	Na	40
B	0.08	Ni	0.08
Ba	0.08	Pb	0.08
Be	0.08	Sb	0.08
Ca	40	Se	0.08
Cd	0.08	Si	4.0
Co	0.08	Sn	0.08
Cr	0.08	Sr	0.08
Cu	0.08	Ti	0.08
Fe	20	Tl	0.08
K	40	V	0.08
Mg	40	Zn	0.08

TABLE 4
Composition of the ICSA Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Al	100	P	100
Ca	100	S	100
Fe	100	C	200
K	100	Cl^-	1000
Mg	100	Mo	2.0
Na	100	Ti	2.0

TABLE 5
Composition of the ICSAB Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.02	Na	100
Al	100	Ni	0.02
As	0.02	Pb	0.02
B	0.05	Sb	0.02
Ba	0.02	Se	0.05
Be	0.02	Si	0.50
Ca	100	Sn	0.10
Cd	0.02	Sr	0.02
Co	0.02	Ti	2.0
Cr	0.02	Tl	0.02
Cu	0.02	V	0.02
Fe	100	Zn	0.025
K	100	P	100
Mg	100.0	S	100
Mn	0.0225	C	200
Mo	2.00	Cl-	720

TABLE 6[1]

COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

Molecular Ion	Mass	Element Interferences[2]	Molecular Ion	Mass	Element Interferences[2]
BACKGROUND MOLECULAR IONS					
NH^+	15		$^{38}ArH^+$	39	
OH^+	17		$^{40}ArH^+$	41	
OH_2^+	18		CO_2^+	44	
C_2^+	24		CO_2H^+	45	Sc
CN^+	26		ArC^+, ArO^+	52	Cr
CO^+	28		ArN^+	54	Cr
N_2^+	28		$ArNH^+$	55	Mn
N_2H^+	29		ArO^+	56	
NO^+	30		$ArOH^+$	57	
NOH^+	31		$^{40}Ar^{36}Ar^+$	76	Se
O_2^+	32		$^{40}Ar^{38}Ar^+$	78	Se
O_2H_+	33		$^{40}Ar_2^+$	80	Se
$^{36}ArH^+$	37				
MATRIX MOLECULAR IONS – Chloride					
$^{35}Cl0^+$	51	V	$^{37}Cl0H^+$	54	Cr
$^{35}Cl0H^+$	52	Cr	$^{35}Cl0^+$	51	V
$^{37}Cl0^+$	53	Cr	$^{35}Cl0H^+$	52	Cr
$Ar^{35}Cl^+$	75	As	$Ar^{37}Cl^+$	77	Se
MATRIX MOLECULAR IONS – Sulfate					
$^{32}SO^+$	48		$^{34}SOH^+$	51	V
$^{32}SOH^+$	49		SO_2^+, S_2^+	64	Zn
$^{34}SO^+$	50	V, Cr			
$Ar^{32}S^+$	72		$Ar^{34}S^+$	74	
MATRIX MOLECULAR IONS – Phosphate					
PO^+	47		PO_2^+	63	Cu
POH^+	48				
ArP^+	71				
MATRIX MOLECULAR IONS – Group I, II Metals					
$ArNa^+$	63	Cu	$ArCa^+$	80	
ArK^+	79				
MATRIX OXIDES[3]					
TiO	62-66	Ni, Cu, Zn	MoO	108-116	Cd
ZrO	106-112	Ag, Cd			

[1] From Method 200.8, Section 13.2.6

[2] Method elements or internal standards affected by the molecular ions.

[3] Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 7

RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES WHICH MAY BE MONITORED [1]

Isotope	Element of Interest	Isotope	Element of Interest
27	Aluminum [2]	80,**78**,**82**,**76**,**77**,74	Selenium
121,123	Antimony [2]	**107**,**109**	Silver [2]
75	Arsenic [2]	**23**	Sodium [2]
138,137,136,**135**,134,132,130	Barium [2]	203, **205**	Thallium [2]
9	Beryllium [2]	**51**,**50**	Vanadium [2]
114,112,**111**,110,113,116,106,**108**	Cadmium [2]	**66**, **68**	Zinc [2]
42,**43**,**44**,46,48	Calcium [2]	83	Krypton
52,**53**,**50**,54	Chromium [2]	72	Germanium
59	Cobalt [2]	139	Lanthanum
63,**65**	Copper [2]	140	Cerium
56,**54**,**57**,58	Iron [2]	129	Xenon
206,**207**,**208**	Lead [2]	**118**	Tin
24,**25**,**26**	Magnesium [2]	105	Palladium
55	Manganese [2]	47,**49**	Titanium
98,96,92,**97**,94	Molybdenum	125	Tellurium
58,**60**,62,**61**,64	Nickel [2]	69	Gallium
39	Potassium [2]	35,37	Chlorine

[1] *From Method 6020 CLP-M, Table 9*

[2] *Element approved for ICP-MS determination by SW846 Method 6020 CLP-M*

NOTE: Isotopes recommended for analytical determination are **bolded**.

TABLE 8

RECOMMENDED ISOTOPES AND ADDITIONAL MASSES WHICH MAY BE MONITORED

Rare Earth Elements	ICPMS Preferred Mass	Elemental Equations	Additional Masses
Lanthanum	138.906		
Cerium	139.905		
Praseodymium	140.907		
Neodymium	141.908	-0.125266 * ^{140}Ce	142.910, 144.912
Samarium	151.920	-0.012780 * ^{157}Gd	144.912
Europium	152.929		
Gadolinium	157.924	-0.004016 * ^{163}Dy	156.934
Terbium	158.925		
Dysprosium	163.929	-0.047917 * ^{166}Er	
Holmium	164.930		
Erbium	165.930		
Thulium	168.934		
Ytterbium	173.939	-0.005935 * ^{178}Hf	171.937
Lutetium	174.941		

TABLE 8			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES WHICH MAY BE MONITORED			
Rare Earth Elements			
Other Elements			
Boron	11.009		
Calcium	43.956		
Cesium	132.905		
Galium	68.926		
Germanium	71.922		
Gold	196.967		
Hafnium	177.944		176.944
Holmium	164.930		
Iridium	192.963		
Lithium	7.016		
Tungsten	183.951	-0001242* ^{189}Os	
Uranium	238.050		
Yttrium	88.905		
Zirconium	238.050		
Niobium	92.906		
Palladium	104.905		
Phosphorus	30.994		
Platinum	194.965		
Rhenium	186.965	-0.099379 * ^{189}Os	
Rhodium	102.905		
Rubidium	84.912		
Ruthenium	101.904	-0.045678 * ^{105}Pd	
Scandium	44.956		
Strontium	87.906		
Tantalum	180.948		
Tellurium	127.905	-0.072348 * ^{129}Xe	
Thorium	232.03		

TABLE 9

ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS

Element	Elemental Equation	Note
Al	(1.000) (^{27}C)	
Sb	(1.000) (^{121}C)	
As	(1.000) (^{75}C) - (3.1278)[^{77}C) - (1.0177)(^{78}C)]	Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
Ba	(1.000) (^{137}C)	
Be	(1.000) (^{9}C)	
Cd	(1.000) (^{111}C) - (1.073) [(^{108}C) - (0.712) (^{106}C)]	Correction of MoO interference. An additional isobaric elemental correction should be made if palladium is present.
Cr	(1.000) (^{52}C)	In 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
Co	(1.000) (^{59}C)	
Cu	(1.000) (^{63}C)	
Pb	(1.000) (^{206}C) + (1.000) (^{207}C) + (1.000) (^{208}C)	Allowance for isotopic variability of lead isotopes.
Mn	(1.000) (^{55}C)	
Mo	(1.000) (^{98}C) - (0.146) (^{99}C)	Isobaric elemental correction for ruthenium.
Ni	(1.000) (^{60}C)	
Se	(1.000) (^{82}C)	Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
Ag	(1.000) (^{107}C)	
Tl	(1.000) (^{205}C)	
Th	(1.000) (^{232}C)	
U	(1.000) (^{238}C)	
V	(1.000) (^{51}C) - (3.127) [(^{53}C) - (0.113) (^{52}C)]	Correction of chloride inference with adjustment for Cr53. Cl0 51/53 ratio may be determined from the reagent blank.
Zn	(1.000) (^{66}C)	
Internal Standards		
Bi	(1.000) (^{209}C)	
In	(1.000) (^{115}C) -(0.0149) (^{118}C)	Isobaric elemental correction for tin.
Ge	(1.000) (^{72}C)	
Sc	(1.000) (^{45}C)	
Tb	(1.000) (^{159}C)	
Tm	(1.000) (^{169}C)	
Y	(1.000) (^{89}C)	

* Method elements or internal standards affected by the molecular ions.

C = Calibration blank subtracted counts at specified mass.

TABLE 10

INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal Standard	Mass	Possible Limitation
Lithium	6	a
Scandium	45	Polyatomic Ion Interference
Germanium	72	
Yttrium	89	a, b
Rhodium	103	
Indium	115	Isobaric Interference by Sn
Terbium	159	
Holmium	165	
Thulium	169	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

b In some instruments Yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Appendices

Appendix 1

Cleaning Procedure for Glass- and Plastic-ware

All glassware and plastic-ware coming into contact with samples, reagents and standards must be cleaned in the following manner. Plastic pipette tips may be cleaned in the same manner by soaking them in a suitable plastic container.

1) Completely fill the container to be leached with 10% nitric acid solution (6.1.5) and fit the lid.
2) Leave soaking for at least 12 hours.
3) Empty the container of acid and rinse thoroughly with laboratory water (6.1.1). Note that the acid may be collected and re-used until it becomes too contaminated.
4) Allow the vessel to air-dry in a clean area (preferably Class-1000 or better). If no such clean area is available, the container should be allowed to dry in the cleanest possible environment, or may be emptied of residual water as much as is possible and re-capped.
5) Containers should be capped ready for use and stored in the cleanest area available.
6) If pre-cleaned containers are to be stored for long periods (weeks to months) prior to use, it is most effective to store them full of laboratory water (6.1.1). This must be discarded and the containers rinsed thoroughly with laboratory water (6.1.1) and dried before use.

Appendix 2

Wash Solution Preparation Instructions (2% Nitric Acid (v/v))

A large volume of this solution is required for supply to the autosampler rinse station in order to wash the probe between samples. These instructions detail the preparation procedure for 2.5 L of this solution which is normally sufficient for one day of analytical use. The procedure may be scaled up or down as required.

1) Into a 2.5 L container (pre-cleaned as per Appendix 1), add 500±450 mL of laboratory water (6.1.1)
2) Add 50±10 mL of concentrated nitric acid (6.1.3)
3) Make to 2.50±0.25 L with laboratory water (6.1.1)
4) Mix well

Notes:

If preparing larger quantities simply scale-up quantities proportionally.

If analyzing Ag, add hydrochloric acid at 1% by adding 50±10 mL of concentrated hydrochloric acid (6.1.2) after step 2.

Appendix 3
Daily Instrument Maintenance

1) Wipe all instrument, autosampler and surrounding bench surfaces with a damp wipe – continual cleanliness is important for the minimization of contamination
2) Check Wash Solution volume and remake if necessary (see Appendix 2)
3) Empty Waste Vessel according to laboratory disposal policy
4) Check the condition of all peristaltic pump tubes and replace if required (it is recommended to replace these daily although this may not be necessary with lower sample loads)
5) Check condition of sample introduction system and cones and clean and/or replace as necessary (see Appendix 8)
6) Ensure instrument fume-extraction system is operational

Appendix 4
Autotune and Performance Reports

Description

Autotune is a *PlasmaLab* software tool that allows the X Series to be optimized in a consistent, routine manner, giving reproducible levels of performance and saving the operator time and effort. It works by following a pre-defined sequence, optimizing individual instrument parameters in turn. Default sequences are provided with the software upon installation and a further customized sequence is provided on the CD accompanying this productivity pack.

Performance Reports are a *PlasmaLab* software tool that allows the X Series performance to be checked on a daily basis. The *Performance Report* can be set-up to give information about instrument sensitivity, stability, background, oxide species, doubly charged species, mass-calibration validity and peak resolution. Like *Autotune*, the *Performance Report* is user definable but defaults are provided with the software. Customized *Performance Reports* are provided on the CD accompanying this package.

The philosophy of use of these tools is as follows. After the sample introduction system or the cones have been removed and replaced or upon using the instrument for the first time or following major adjustments, the full *Autotune* sequence should be used to properly optimize the system. This takes about 15 minutes. From this, an *Autotune Update* sequence can be automatically created. This is a shortened version of the optimization sequence and will take about 5 minutes to run. The performance of the X Series is, in general, very stable from day-to-day, meaning that large amounts of optimization are not normally needed on a daily basis. To check whether optimization is needed, a *Performance Report* can be run initially. The results of this tell the operator if the system requires resolution adjustment, re-mass-calibration, or re-optimization. If the required sensitivity, background, stability or oxide performance is not satisfied, an *Autotune* should be run (the faster *Autotune Update* is normally sufficient). The *Performance Report* should then be repeated to ensure that the problem has been resolved.

Installing the EPA Autotune Sequence

To install the custom Autotune sequence, follow the instructions below:

1) Insert the CD in the CD ROM drive of the instrument operating PC. Wait for it to autorun and install the Productivity Pack by following the prompts after clicking on *Install*.
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed

3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Autotune* icon (musical note).
4) Point to *Tools* in the menu and then select *Import Autotune Sequences*
5) Click *Next* in the Autotune Wizard
6) Click on *Browse* and find the path

C:/Program Files/ThermoElemental/PlasmaLab/Data

7) Select *EPA Autotune Sequence* and click on *Open*
8) Click on *Next*
9) Select *EPA – Xi Interface* and click on *Next*
10) Click on *Finish*

Installing the EPA Performance Reports

To install the custom Performance Reports, follow the instructions below:

1) Ensure the Pack is installed from the CD as described above
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Performance Report* icon (musical note on page).
4) Point to *Tools* in the menu and then select *Import Performance Report*
5) Click *Next* in the Performance Report Wizard
6) Click on *Browse* and find the path for the CD ROM drive

   C:/Program Files/ThermoElemental/PlasmaLab/Data
7) Select *EPA 6020 Report* and click on *Open*
8) Click on *Next*
9) Select *EPA 6020 2.1* and click on *Next*
10) Click on *Finish*

To install the second Performance Report, follow instructions 1) to 10) above, selecting the alternative Performance Report name, i.e. *EPA ILM05_2D Report*.

Running Autotune from the Tune Page

To run an Autotune Sequence follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Autotune* icon (musical note)

2) Select *Run an Existing Autotune Sequence* and click on *Next*

3) Select the required sequence, e.g. *EPA Xi Interface*, or *EPA Xi Interface – Update* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebuliser

5) Click on *Finish*

The selected Autotune sequence will now be run. To monitor its progress, observe the processes indicated at the bottom left of the PlasmaLab screen and open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Autotune Report* is generated at the end of the sequence. To continue, this report must be closed. To access this report upon closure, go to *Instrument*, *Configurations*, *Configuration Editor* and point to the appropriate *Instrument Settings* line. Open a pop-up menu by right-clicking and use the *View Tune Report* selection.

Running a Performance Report from the Tune Page

To run a Performance Report follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Performance Report* icon (musical note on a page)

2) Select *Run an Existing Performance Report* and click on *Next*

3) Select the required sequence, e.g. *EPA ILM05 / 6020*, or *EPA 6020* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

   The selected *Performance Report* will now be run. To monitor its progress, open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Performance Report* is generated at the end of the sequence. To access this report upon closure, go to *Instrument*, *Tune*, and click on the down arrow to the right of the Performance Report icon. Point at *Tools* and then select *View Performance Report Results*. Select the required Performance Report to view and click *OK*.

Running Performance Reports and Autotune in an Experiment

It is also possible to automate the running of these procedures using an instrument setup sample within an experiment. To do this, insert an *Instrument Setup Sample* at the beginning of the Sample List by selecting the first sample and using a right-mouse-click menu to *Insert New Before*. Define the *Sample Type* for this new sample as *Instrument Setup* and click on *Show Advanced*. Click on the *Instrument Performance Tests* tab and setup the Performance Report and Autotune functions following the logic and using the drop-down combo boxes to select the next action. An example would be as follows:

Acquire Performance Report	*EPA ILM05.2 / 6020*
If mass calibration verification fails then	*Abort the Queue*
If the Performance Report fails then	*Autotune using EPA – Xi Interface*
If the Autotune fails then	*Abort the experiment*
If the Autotune passes then	*re-run the Performance Report*
If the Performance Report fails again then	*Abort the Queue*

When Performance Reports and Autotunes are acquired in this way, the results are stored as part of the experiment report. Note that since this method of acquiring the report is done using the autosampler, the solution concentration should be adjusted if on-line internal standard addition is to be used, e.g. if the addition dilutes the samples 1:1, the solution concentration should be doubled to get an accurate measure of sensitivity.

Appendix 5
Resolution Set up

With the instrument in *Operate* mode, aspirate 10 µg/L Tune solution (6.4.1) (through both probes if using on-line internal standard addition). Go to *Instrument*, *Tune* and stop the real time display (RTD) using the square stop icon. Change the display mode from *Time vs ICPS* to *ICPS on the full mass range*. Insert Be as the mass to monitor and change the spacing to 10, the dwell to 1 ms and the channels to 200. Disable all other masses in the grid. Restart the RTD by clicking on the triangular play icon. The software will display the scanned peak for mass 9, Be. To adjust the resolution, go to the *Global* tab and use the slider bar marked *Standard resolution*. This must be set up to give a peak width of less than 0.75 amu at 5% peak height. This is typically reached at a setting of between 100 and 200. If high resolution mode is to be used, this can be setup by changing the resolution setting on the RTD to *High*. The High Resolution peak width is typically set at about 0.4 amu at 5% peak height, again with values typically between 100 and 200. Note that this method does not use High resolution mode. Each resolution mode should be checked with several other masses across the mass range, typically 55Mn, 115In, 203Tl and 238U are used. Special attention should be paid to the resolution setup for Mn. This is measured at m/z 55, which is adjacent to both iron and argon oxide at mass 56. These high signals must be properly resolved from the low Mn signal in standard resolution mode. When the correct resolution settings are achieved, save the setting using the disk icon. **Note that a new mass-calibration must always be performed after adjustment of the resolution.**

17.2. Appendix 6

17.3. Instrument Calibrations

There are three instrument calibrations that are fundamental for obtaining good quality data on the X Series. These are:

1) Mass-calibration
2) Detector Plateau and Analogue voltage set routines
3) Detector cross-calibration.

Mass calibration sets the quadrupole scan parameters to give the correct measured mass positions. The detector plateau sets the optimum voltage on the ion or pulse counting section of the discrete dynode detector. The analogue voltage set routine applies an appropriate voltage on the analogue part of the detector to obtain a cross-calibration factor of approximately 20,000 for a mid-mass isotope. The detector calibration, or cross-calibration, calculates the correction factor, for each measured mass, between the two detector modes, pulse counting and analogue. All three calibrations may be performed in a single routine, or may be performed separately.

Mass Calibration

A mass-calibration must be performed whenever the resolution settings are adjusted as this will affect the apparent mass position. Mass-calibration must be performed when the Performance Report shows that measured peak positions are >0.1 amu from their nominal position. Mass-calibrations are best performed using a solution containing as many elements as possible or with every analyte required for analysis at the very least. The solution should contain Li and U as these are used as low and high mass datum points. An appropriate concentration solution be used (one that gives between **100,000-1,500,000 cps** for each mass to be calibrated is appropriate). To perform a mass calibration, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Mass-Calibration* box

12) There is an option to *Update current mass-calibration* or form a *New mass-calibration*. Unless a major hardware change has been performed, the *Update current mass-calibration* option should be selected.

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *masscal 090902* and click *Save*

15) Click *Append*

16) Click *OK*

Mass-calibration will now be performed.

To view the mass-calibration results, go to *Instrument*, *Calibrations*, *Mass-Calibration*. A mass-calibration for each of the two resolution modes is displayed in the graph of Peak Width and Error (y) versus Mass (x). The current mass-calibration is indicated by the row(s) displayed in green. To display alternative mass-calibrations, click on the appropriate date/time-stamped line in the top grid. The Performance Report function can be used to check mass-calibration accuracy (see Appendix 4).

Detector Plateau and Analogue Voltage Set

These routines can be performed separately, but it is advised to run them simultaneously as described here. The necessary frequency of these calibrations depends upon the amount of signal the detector is exposed to, i.e. how many samples are analyzed, which analytes and what concentrations. For most laboratories running a moderate sample load, this procedure may be run weekly. Up to three masses may be used in this procedure, however here, the use of a single mass is described. A solution that gives a countrate of between **100,000-1,500,000 cps** is appropriate. The default mass used here is indium (m/z 115), so this must be present in the solution for the routine to work. For an X5 instrument, an appropriate concentration would typically be between 10 and 100 µg/L, depending upon the sensitivity of the system. To perform this routine, follow the instructions below.

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check *the Set analogue voltage* box

12) Set the *Number of iterations* to *2*

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *plateau 090902* and click *Save*

15) Click *Append*

16) Click *OK*

The voltage setup will now be performed. To view the plateau, go to *Instrument*, *Calibrations*, *Detector Plateau*. A graph of signal intensity (y) versus voltage (x) is displayed. The “knee” inflexion on this plot corresponds to the plateau voltage. This is automatically selected and applied to the detector by the software.

Detector Calibration (Cross-Calibration)

This routine must be performed whenever the detector voltages are altered and daily prior to analysis of samples. The solution used must contain all the analytes to be measured as an absolute minimum. The more analytes present, the better. All analytes should ideally be set at a concentration that gives between **500,000 and 1,500,000cps**. To perform the detector calibration, follow the instructions below:

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click in the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button
10) Click on the *Instrument Calibrations* tab
11) Check the *Detector Calibrate* box
12) Click *Queue*
13) Save the experiment with an appropriate name, e.g. *xcal 090902* and click *Save*
14) Click *Append*
15) Click *OK*

The detector calibration will now be performed. To view the cross-calibration grap, go to *Instrument*, *Calibrations*, *Detector Cross-Calibration*. A graph of cross-calibration factor (y) versus mass (x) is displayed. **Use the data table to check that all analytical masses of interest have been used in the cross-calibration**. If not, the cross-calibration factor will be estimated from the equation of the graph. This may result in error.

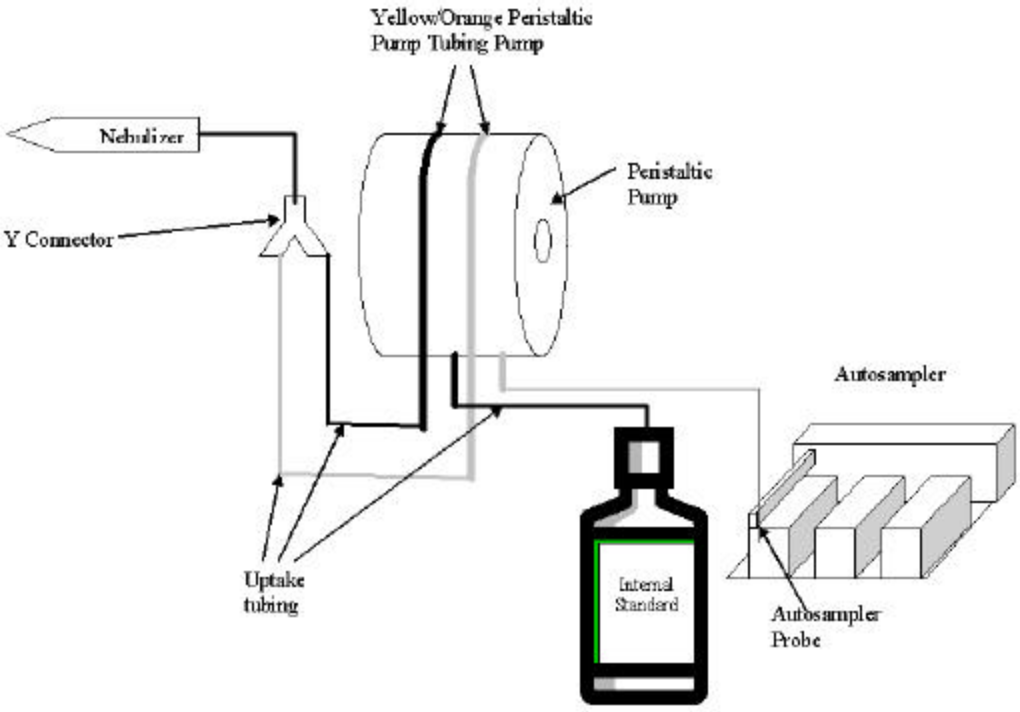
All Routines in One

It is possible to run all three of the above routines on a single run if the solution used conforms to all of the criteria spelt out above. To do this, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click in the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button
10) Click on the *Instrument Calibrations* tab
11) Check the *Mass calibration*, *Detector Calibrate* and *Set analogue voltage* boxes
12) Set the *Number of iterations* to *2*
13) Click *Queue*
14) Save the experiment with an appropriate name, e.g. *instr cal 090902* and click *Save*
15) Click *Append*
16) Click *OK*

The instrument calibrations will now be performed. Each parameter can be viewed as described above.

Appendix 7
Sample Introduction Plumbing Diagram



Appendix 8

Procedure for Cleaning Sample Introduction Equipment and Cones

1) Ensure that the instrument is in the *vacuum* or *shutdown* state (i.e. the plasma is OFF and the slide valve is SHUT)
2) Dismantle the sample introduction system as follows:

a) Remove the gas connection from the nebulizer

b) Remove the sample input plug from the nebulizer

c) Remove the metal clip on the spray chamber to elbow joint

d) Remove the drain plug from the spray chamber

e) Slide the spray chamber and nebulizer away from the elbow

f) Carefully slide the nebulizer out of the spray chamber and set both pieces aside in a safe place

g) Open the torch box and the internal Faraday cage

h) Pull the gas connections away from the torch

i) Undo the torch catch

j) Remove the metal clip on the elbow to torch joint

k) Carefully remove the torch from the load coil and set aside in a safe place

l) Remove the elbow by sliding it out of the torch box bulkhead toward spray chamber end

m) Slide the torch box away from the mass spectrometer to reveal the interface

n) Use the flat metal cone tool to undo the locking ring over the sample cone

o) Carefully remove the sample cone and set aside in a safe place

p) Carefully unscrew and remove the skimmer cone from the interface using the cylindrical aluminium tool and set aside in a safe place

3) Clean the cones as follows.

a) Carefully place the cones into a large beaker and fill with sufficient 0.05% nitric acid to cover – CAUTION: Stronger acids will corrode the cone material and reduce lifetime

b) Place the beaker in an ultrasonic bath for about 10 minutes or until surface deposition has been removed

c) Carefully remove the cones from the solution and rinse thoroughly with deionised water

d) Allow the cones to air-dry prior to refitting

4) Clean the sample introduction equipment as follows.

e) Carefully place the glass sample introduction components into a large beaker and fill with sufficient 10% nitric acid to cover all components

f) Place in an ultrasonic bath for between 20 minutes and 1 hour

g) Carefully remove the glass components and rinse thoroughly with deionised water

h) Allow to air-dry prior to refitting

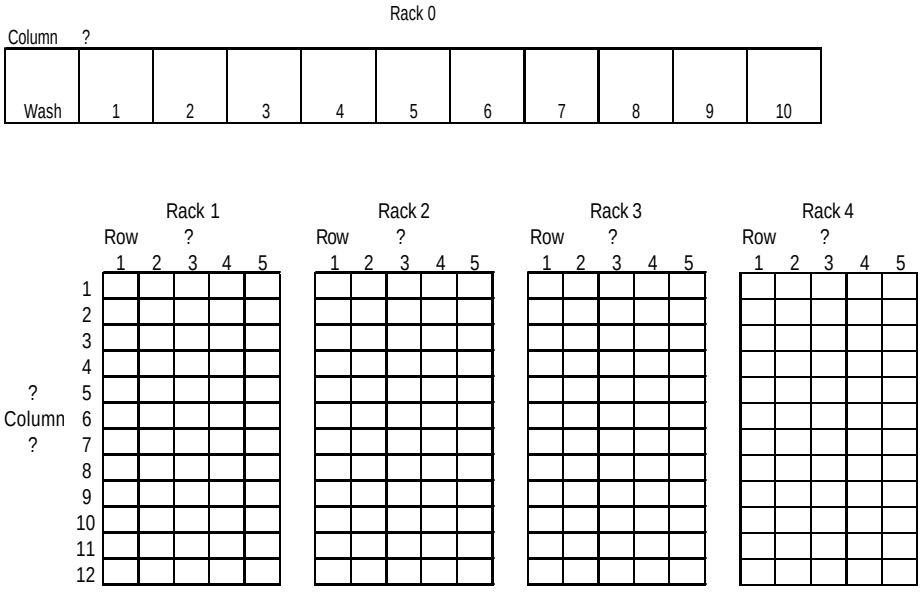
5) Reassemble the components in the reverse order to disassembly

Note: Occasionally, glass sample introduction components crack when the ultrasonic cleaning procedure is used. To avoid this, the components may be soaked in acid, as above, for 12 hours, without ultrasonic treatment.

Thermo Electron can not take any responsibility for any breakage that occurs during cleaning.

Appendix 9

Autosampler Position Map



NB: This map is only applicable for CETAC ASX-500/510 autosamplers fitted with 60 position racks.

Appendix 10
ILM05.2D Contract Required Quantitation Limits (CRQLs)

Analyte	CRQL (µg/L)
Al	30
Sb	2
As	1
Ba	10
Be	1
Cd	1
Ca	(100)
Cr	2
Co	0.5
Cu	2
Fe	(50)
Pb	1
Mg	(100)
Mn	0.5
Ni	1
K	(100)
Se	5
Ag	1
Na	(100)
Tl	1
V	1
Zn	1

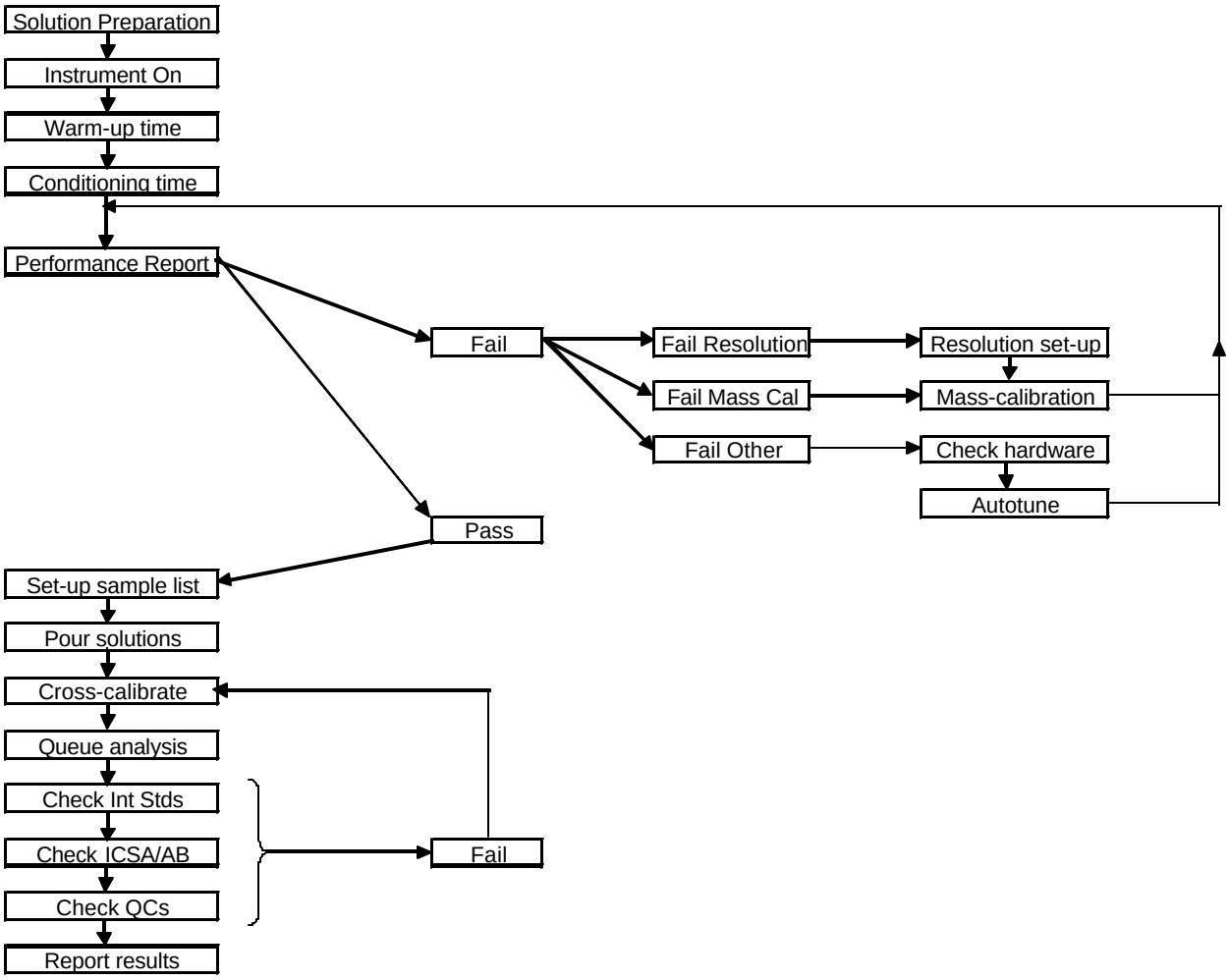
CRQLs given in parentheses are not specified for ICP-MS in EPA document ILM05.2 and are for ICP-AES. This is for information only.

Appendix 11
Spiking Levels

(Concentration in Final Solution Based on Instructions Within this Document)

Analyte	Spike Value (µg/L)
Al	2000
Sb	100
As	40
Ba	2000
Be	50
Cd	50
Cr	200
Co	500
Cu	250
Pb	20
Mn	500
Ni	500
Se	10
Ag	50
Tl	50
V	500
Zn	500

Appendix 12
Work Flow-Chart



Appendix 13
Glossary of Abbreviations

QC Code	QC Name	Purpose	Frequency	Limits
ICV	Initial Calibration Verification	checks the calibration against a second calibration source	After initial calibration	90-110%
ICB	Initial Calibration Blank	initial check of read-back at blank level	After initial calibration	<CRQL
CRI	Contract Required Quantitation Limit Check	checks accuracy at the required limit of quantitation	After each calibration and every 20 samples	70-130% 50-150% for Co, Mn, Zn
ICSA	Interference Check Solution A	checks for freedom from interference	After initial calibration	±3CRQL or ±20% of the true value (whichever is the greater)
ICSAB	Interference Check Solution AB	checks that analytes are accurately measured in an interference-producing matrix	After initial calibration	80-120% of true value
CCV	Continuing Calibration Verification	a continuing periodic check on accuracy and drift	After each calibration and every 10 samples	90-110%
CCB	Continuing Calibration Blank	a continuing periodic check on the read-back at blank levels	After each calibration and every 10 samples	<CRQL
PDS	Post Digestion Spike	checks the recovery of	Once every 20 samples per	75-125%

QC Code	QC Name	Purpose	Frequency	Limits
		analytes spiked into an unknown sample after preparation (digestion)	matrix	
DUP	Duplicate	checks the reproducibility of results by analyzing an unknown sample in duplicate	Once every 20 samples per matrix	±20% Relative Percentage Difference (RPD)
SER	Serial Dilution	checks for matrix effects by assessing the variation of results for an unknown sample before and after dilution	Once every 20 samples per matrix	±10% of the original undiluted result after dilution correction
LCS	Laboratory Control Sample	checks the accuracy of the entire analytical process	Once every 20 samples per matrix	80-120%

APPENDIX 16

STANDARD OPERATING PROCEDURE

Author: John Nicpon
Reviewed by:

_____

Approved by:

_____

Northeast Analytical, Inc.
Issuing section: Inorganics laboratory
NE025_04.DOC
Date: : 6/12/03
Revision Number: 4

1. TITLE

1.1. Standard operating procedures for the preparation and analysis of mercury in samples according to *EPA 1994 Methods for the Chemical Analysis of Water and Wastes 245.1, Test methods for Evaluating Solid Waste SW-846 7471*, and NYSDOH ELAP requirements

2. PURPOSE

2.1. The purpose of this SOP is to provide procedures for measuring mercury by Cold vapor atomic absorption.

3. SCOPE/APPLICABLE MATRICES

3.1. Methods in this procedure are used for analyzing soils, sediments, bottom deposits, and drinking, surface, ground, sea, brackish waters, industrial and domestic wastewater.

3.2. All matrices require digestion before analysis.

4. COMMENTS

4.1. Atomic absorbance spectroscopy is a process in which the light absorbed by atoms or ions is measured. The wavelengths of light absorbed are specific to the element, which are present in the sample. The absorption occurs when sufficient thermal or electrical energy is available to excite a free atom or ion to an unstable energy state. Light is emitted when the atom or ion returns to a more stable configuration or the ground state.

4.2. There are two types of mercury: simple inorganic mercury, and organic mercury. During the digestion HNO_3, H_2SO_4, potassium permanganate, and potassium persulfate are used to release the organically bound mercury. This is a very vigorous and extensive digestion, and allows the total amount of mercury present in the sample to be analyzed.

4.3. The cold vapor technique uses a 5 channel peristaltic pump that pushes the reducing agent ($SnCl_2$), and the sample through a reaction coil to a gas liquid separator. Mercury compounds in an acid solution are reduced to the free element in $SnCl_2$ and a continuous stream of argon sweeps the mercury vapor into the 30 cm cell. Mercury atoms in the sample absorb radiation emitted by a mercury specific lamp at 254 nm using a dual beam detection system.

4.4. For each batch of samples, analysts need to determine the analytical procedures required for preparation and analysis. Each program varies in the type of QC samples, the concentration of the elements in the QC samples, and the frequency that they are determined.

5. Summary of method:

5.1. A known portion of a sample is transferred to a container. It is digested in diluted potassium permanganate-potassium persulfate solutions and digested for 2 hours at 95^{o} C to form mercury in the +2 state.

5.2. The liquid sample with mercury present enters the system and is mixed with a reducing agent (Stannous chloride) to form elemental mercury vapor. The mixture flows into a liquid-gas mixer where agron is introduced to carry the mercury vapor. The gaseous-liquid mixture enters the liquid-gas separator where the liquid is drained away and the mercury bearing gas continues to the drying tube. The drying tube dehumidifies the gaseous mixture.

5.3. The dry vapor enters the dual beam optical cell. Absorbance by the mercury cold vapor is measured using a solid state detector with a wide dynamic range.

5.4. The detector signal is constantly monitored to determine when the system is free of mercury. Once the system has returned to baseline the analysis of the next sample proceeds.

6. Sample storage and handling:

6.1. Samples are stored in the walk-in cooler.

6.2. Solid samples require no preservation prior to analysis other than storage at 4 ^{o}C.

6.3. For the determination of the dissolved elements, the sample must be filtered through a 0.45- µm pore diameter membrane filter at the time of collection or as soon as thereafter as practically possible. Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH<2 and document the analyst, date of filtration and acidification.

6.4. For the determination of total recoverable elements in aqueous sample, samples are not filtered, but acidified with (1+1) nitric acid to pH<2 (normally, 3 ml of (1+1) nitric acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the sample be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH<2. If for some reason such as high alkalinity the sample is verified to be >2, contact the client, and add more acid to the sample and hold the sample for sixteen hours until verified to be pH<2. Document the date the sample pH was verified and if the addition of acid was necessary. Aqueous samples for total metals must be acidified to a pH of < 2 with nitric acid. The preserved sample should be analyzed with 28 days of collection.

7. Interferences

7.1. Interferences have been reported for waters containing sulfide, chloride, copper and tellurium. Organic compounds that have broadband UV absorbance (254 nm) are confirmed interferences. The concentration levels for interferants are difficult to define. This suggests that quality control procedures must be strictly followed.

7.2. Volatile materials, which at 254 nm will cause positive interferences. In order to remove any interfering volatile materials, the dead air space in the digestion vessel should be purged before the addition of stannous chloride solution.

7.3. Low-level mercury preparation, digestion, and analysis may be subject to environmental contamination if performed in areas with high ambient backgrounds where mercury was previously employed as an analytical reagent.

8. Documentation

8.1. The following information is documented in logbooks:

8.1.1. Document maintenance or replacement of parts in the online Scheduled Maintenance page.

8.1.2. Document the following information during the preparation and analysis of samples:

8.1.2.1. The method, the analyses file name, elements (mercury) in the method, and the date of analysis.

8.1.2.2. Analyst's initials.

8.1.2.3. The standard codes of solutions used during the course of analysis.

8.1.2.4. The NEA sample identification numbers, post digestion dilution factors, and any relevant comments.

9. SAFETY

9.1. Safety glasses, lab coat or lab apron, and disposable gloves must be worn when handling chemicals and samples.

9.2. Personnel should familiarize themselves with the necessary safety precautions by reading MSDS information covering any chemicals used to perform SOP.

9.3. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Specifically, concentrated nitric, sulfuric, and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood and if skin contact occurs, flush with large volumes of water.

9.4. Mercury compounds are highly toxic if swallowed, inhaled, or absorbed through the skin. Analysts should wear chemical resistant gloves when handling mercury standards.

10. EQUIPMENT

10.1. **Instrumentation**

10.1.1. Leeman Labs Hydra AA Mercury Analyzer

10.1.2. Argon (gaseous). Located in the Inorganics laboratory.

10.2. **Apparatus and Equipment**

10.2.1. Inorganics department mercury sample and standard preparation logbook. Located in the Inorganics laboratory

10.2.2. Class A volumetric flasks at volumes of 10, 25, 50, 100, and 200 ml.

10.2.3. 250 and 1000 µL Rainin autopipets. Rainin (P/N EP-250 and EP-1000).

10.2.4. 250 and 1000 µL pipette tips. Rainin (P/N RT-96 and RT-200).

10.2.5. Inorganics department standard preparation logbook. Located in the Inorganics laboratory.

10.2.6. AAS run logbook. Located in the Inorganics laboratory.

10.2.7. Leeman Labs autosampler with rinse solution reservoir and waste container. Located in the Inorganics laboratory.

10.2.8. Drain pump tubing (blue/blue) Leeman (p/n 120-00412-1). Located in the Inorganics laboratory.

10.2.9. Pump tubing (blue) Leeman (p/n 309-00104-1). Located in the Inorganics laboratory.

10.2.10. Pump tubing (black) Leeman (p/n 309-00088-3). Located in the Inorganics laboratory.

10.2.11. Waste tubing aasembly. Leeman (p/n 120-00284-1). Located in the Inorganics laboratory.

10.2.12. Reductant pump tubing(red). Leeman (p/n 309-00088-4). Located in the Inorganics laboratory.

10.2.13. Rinse pump tubing(black). Leeman (p/n 309-00088-6). Located in the Inorganics laboratory.

10.2.14. Gas-Liquid separator Leeman (p/n 120-00416-1). Located in the Inorganics laboratory.

10.2.15. Graduated cylinders. Located in the Inorganics laboratory.

10.2.16. Laboratory beakers. Located in the Inorganics laboratory.

10.2.17. 1-5 ml Eppendorf pipette with pipette tips. Located in the Inorganics laboratory.

10.2.18. Glass powder funnels. Located in the Inorganics laboratory.

10.2.19. Plastic bottles with Polyseal caps. Located in the bottle storage room.

10.2.20. Varian mercury hollow cathode lamp Leeman (p/n 217-00003). Located in the Inorganics laboratory.

10.2.21. Drying tube (p/n12000281-1). Located in the Inorganics laboratory.

10.2.22. 50 ml cups. Leeman (p/n 116-2102). Located in the Inorganics laboratory.

10.2.23. 15 ml Test tubes. Leeman (P/N 116-2107-1). Located in the Inorganics laboratory.

10.2.24. Fisher Scientific Water Bath.

10.2.25. Analytical balance. Located in Inorganics laboratory.

10.3. **Reagents**

10.3.1. Sulfuric Acid, Mallinckrodt (p/n 2468). Located in the Inorganics laboratory.

10.3.2. 5% potassium permanganate, Labchem (p/n LC19940-4). Located in the Inorganics laboratory.

10.3.3. 5% potassium persulfate: Aldrich (p/n 3239-01). Dissolve 100 grams to a final volume of 2000 ml. Located in the Inorganics laboratory.

10.3.4. NaCl-hydroxylamine sulfate. NaCl, Aldrich (p/n 22,351-4) and Hydroxylamine sulfate, Aldrich (p/n 21,025-0). Dissolve 120 grams of each reagent together to a final volume of 1000 ml. Located in the Inorganics laboratory.

10.3.5. $SnCl_2$ in 20% HCl: Place 200 ml of HCl in a 1000-ml beaker and heat on a hotplate. Add 250 grams of $SnCl_2$ to the HCl. Stir until dissolved. Turn off hotplate and bring to volume by slowly add RO water.

10.3.5.1. $SnCl_2$: Aldrich (p/n 20,825-6).

10.3.5.2. Hydrochloric acid: Fisher certified ACS plus grade or equivalent (p/n A144SI-212). Located in the Inorganics laboratory and storage room.

10.3.6. Nitric acid: Fisher certified ACS plus grade or equivalent (p/n A200SI-212). Located in the Inorganics laboratory and storage room.

10.3.7. LGR water: Metal free water obtained from NEA's water system. Laboratory research grade water system from U.S. Filter Water Systems Corporation.

10.3.8. Stock standard solutions. Located in the Inorganics laboratory.

10.3.9. Alconox. Located in all laboratories.

11. METHOD PERFORMANCE

11.1. Statistics for method performance are maintained by the Quality Assurance unit and are available for review.

12. PROCEDURE

12.1. There are ten general procedures that are employed for the successful completion of data analysis.

12.1.1. **General Startup**
12.1.2. **Preparation and Digestion of samples, calibration and verification standards.**
12.1.3. **Preparation of Aqueous Samples.**
12.1.4. **Preparation of Oil/Soil/Solid samples.**
12.1.5. **Instrument start-up.**
12.1.6. **Generation of Report.**
12.1.7. **Method of Standard additions (MSA).**
12.1.8. **Transfer of data to LIMs.**

12.2. **General Startup**

12.2.1. Before starting an analytical run, review the general quality control requirements.
12.2.2. The procedures in the Leeman Hydraa AA Automated Mercury Analyser Manual describes the Leeman software and commands. These commands are used to construct methods and to operate the instrument.
12.2.3. Fill out the run logbook using attachment **A** as an example.

12.3. **Preparation and Digestion of samples, calibration and verification standards.**

12.3.1. Refer to the quality control requirements and determine the concentration of mercury required for the Laboratory fortified blank (LFB), Laboratory fortified matrix (LFM), Instrument Performance check solution (IPC), and the Quality control sample (QCS).
12.3.2. Prepare 100-ppb standard solutions from stock standards and prepare the calibration standards and the fortifying solution with these solutions.
12.3.3. Prepare five standards at concentrations of 0.2, 0.5, 1.5, 3.0 and 7.5 ppb with the 100 ppb W.S. Prepare two blanks, a QCS, an IPC, and a LFB. These solutions must be prepared daily with each batch of samples digested.
12.3.4. Prepare the QCS by diluting 2.5 ml of the fortifying solution to 50 ml with DI water. A minimum of one QCS per digestion batch is required.
12.3.5. Prepare the IPC by diluting 1.5 ml of the 100 ppb W.S. to 50 ml with LGR water. A minimum of one IPC per digestion batch is required.
12.3.6. Prepare the two blanks using 50 ml of DI water for each. A minimum of one blank per sample digestion batch is required.
12.3.7. Transfer the blanks and solutions to labeled and properly numbered 250-ml plastic bottles. Record this data in the mercury preparation logbook.
12.3.8. For each 50 ml of sample, add 1.25 ml HNO_3, 2.4 ml H_2SO_4 and 8.0 ml of potassium permanganate (wait 15 minutes, if $KMnO_4$ has been reduced, add more $KMnO_4$.) Add 4.0-ml potassium Persulfate.
12.3.9. Swirl well, and gently cap the bottles.
Optional: Place in the Water bath for 2 hours at 95^{o}C. Record the temperature of the steam bath and the start and end time of the digestion in the digestion logbook.
12.3.10. Remove the bottles from the steam bath, cool, and add 5.0 ml of NaCl-Hydroxylamine sulfate solution. Cap and shake vigorously until samples are clear.

12.4. **Preparation of Aqueous Samples.**

12.4.1. Measure out the sample and make the required dilutions based on the matrix of the sample. The final volume of the sample must be 50 ml before the addition of reagents.
12.4.1.1. For Drinking water, measure 50 ml of sample.
12.4.1.2. For TCLP extracts, dilute 5 ml of extract with 45 ml of LGR water.
12.4.1.3. For unknown liquids, dilute according to expected mercury concentration or organic content.
12.4.2. Transfer the samples to labeled 125-ml plastic bottles.
12.4.3. Fortify samples according to analytical program with fortifying solution.
12.4.4. For each 50 ml of sample, add 1.25 ml HNO_3, 2.4 ml H_2SO_4 and 8.0 ml of potassium permanganate (wait 15 minutes, if $KMnO_4$ has been reduced, add more $KMnO_4$.) Add 4.0-ml potassium Persulfate.
12.4.5. Swirl well, and gently cap the bottles.
12.4.6. Place in the Water bath for 2 hours at 95^{o}C. Record the temperature of the steam bath and the start and end time of the digestion in the digestion logbook.

12.4.7. Remove the bottles from the steam bath, cool, and add 5.0 ml of NaCl-Hydroxylamine sulfate solution. Cap and shake vigorously until samples are clear.

12.5. **Preparation of Oil/Soil/Solid samples.**

12.5.1. Weigh out approximately 0.60 grams of sample into a 125-ml plastic. Add 5.0 ml of Aqua Regia and 5.0 ml of LGR water.
12.5.2. Fortify samples according to analytical program with fortifying solution.
12.5.3. Swirl sample and place in a 95°C water bath for two minutes. Remove the samples and let cool.
12.5.4. Add 45.0 ml of DI water and 8.0 ml of potassium permanganate (purple color must persist for 15 minutes). Add 4.0 ml of potassium persulfate.
12.5.5. Swirl well, and gently cap plastic bottles. Place in the Water bath for 30 minutes at 95°C. Record the temperature of the steam bath and the start and end time of the digestion in the digestion logbook.
12.5.6. Remove from bath, cool, and add 5.0 ml of NaCl-Hydroxylamine Sulfate solution. Cap and shake vigorously until samples are clear (no permanganate can be allowed to persist).
12.5.7. If necessary, filter samples with Whatman #41 filter paper.

12.6. **Instrument start-up.**

12.6.1. Turn on the argon. Pressure should be between 75-90 psi.
12.6.2. Turn on Hg analyzer. The switch is located on the rear of the instrument.
12.6.3. On the computer open Win Hg. Create a new data set by clicking file, then New Data Set. Use the date as the name (i.e. 1-22-02 would be 012202hg. Use extensions if more than one analysis is run for each day).
12.6.4. Fill the 20% Stannous Chloride bottle and connect the smaller line to stannous chloride bottle.
12.6.5. Fill the 2 liter bottle rinse with 2% HCl and conntect the line with black tape to HCL bottle.
12.6.6. Connect and tighten lines on peristaltic pump.
12.6.7. Make sure wash tubes are in appropriate carboy.
12.6.8. In Win Hg:

a. Click the control tab and turn on Hg lamp, gas and pump. Let the Hg lamp warm up for approximately 30 minutes.
b. Open rack editor and enter in sample identifications and save as “date”.
c. On sample tab select rack that you just created and enter sample start cup and end cup.
d. Open “database” and check line information to make sure calibration standards are correct.
e. Prepare new standards daily.
f. After the Hg lamp has warmed up go to the control tab and adjust the Hg lamp by clicking button.
g. Go to the standards tab and click off all standards that you are using.(up to ten standards are allowed)
h. Click on the number of replicates that are needed.(3)
i. Load the required standards into the rack. Load the samples into the rack.
j. Click the standard auto button to start the instrument calibration. In the “Database” calculation curve tab you can watch the calibration. The calibration should be linear. If the calibration is acceptable, click accept on the bottom of the screen and then go th the sample tab in Win Hg and click “Run Auto” to start analysis. You can watch the sample in the output tab or the report tab.
k. After analysis is completed and the data is satisfactory clean the pump lines by running 2% HCL through the stannous chloride pump lines for approximately ten minutes and then run pump lines dry.
l. Generate a report. See section 12.7.
m. If finished for the day close Win Hg.
n. Turn off Hg analyzer . Switch is located in rear.
o. Empty sample and standard cups in the waste carboy and dispose of the wast carboy to the proper waste container.

12.7. **Generation of Report.**

12.7.1 After the analysis is completed click the Database icon in the WinHg Runner 1.3 program.
12.7.2 In WinHg Database 1.3 click the Report tab.
12.7.3 Click on the In column for the batches you want to report.
12.7.4 In the record list on the right click off any samples that you don’t want to report.
12.7.5 Click the Generate Report button and change the format to WKS file type.
12.7.6 Change the output file name path to M:\aas0#\”date of run” (#is the last number of the current year)
12.7.7 Click on Generate. Close out Report Generation Window.
12.7.8 On the main screen on the computer “Open My Computer”, go to the M directory, then go to aas0#.

12.7.9 Double click on the file you just created, when the "open with" window pops up click off the always use this program to open this file' then click on Excel.
12.7.10 When it opens click on the first sample ID then go to the Data column.
12.7.11 Under Data go to Sort. A window will pop up, from there do Sort By Column D and click OK.
12.7.12 Do a File, Save As and change the file type to Microsoft excel workbook, then click Save. Exit all programs.

12.8. **Method of Standard additions (MSA)**

12.8.1. MSA is required for analyzing TCLP extracts when the sample result is within 20% of the regulatory level (0.2 mg/L).

12.9. **Transfer of Data to LIMs**

12.9.1. Each method has tests for the required QC parameters.
12.9.2. Add QC parameters to the assigned samples by QC batching.
12.9.3. QC samples are added as individual tests to predetermined samples in LIMs. Access LIMs and go to 'QC Batching'.
12.9.4. See the following table as an example for information for samples and QC parameters that can be entered into LIMs.
12.9.5. Select 'CHRMET' template. Type the required LIMs sample numbers if necessary.
12.9.5.1. Select 'OK' until the results database appears.
12.9.5.2. Enter the required information into the database (see LIMs table).
12.9.5.3. Enter the mercury raw data into the appropriate input cells.

LIMS TABLE-MERCURY

CHRMET template for mercury	
LIMS code	**Name**
B_HGDF	Blank DF
L_HGFVOL	LCS final vol.
D_HGDF	Dup. DF*
D_HGDRYA	Dup. Dry amt.*
D_HGFVOL	Dup. Final vol.
D_HGAMT	Dup. Sample amt.
D_HGDFI	Dup. Raw DF
S_HGDF	Spk. Sample DF*
S_HGAMAT	Spk. Sample amt.
S_HGDFI	Spk. Sample raw DF
S_HGDRYA	Spk. Sample dry wt.*
S_HGFVOL	Spk. Sample final vol.

Water samples fields	
LIMS code	**Name**
HGWA	Mercury water*

Common fields	
LIMS code	**LIMS code**
HGI	Mercury raw data
HGDF	Mercury DF*

#QC Solids*	
LIMS code	**Name**
P_HGSD	Dup. Precision
B_HGSD	Blank result
D_HGSD	Dup. Result
L_HGSD	LCS solid result
R_HGSD	MS rec. solid
A_HGSS	True value:LCSS

Solids fields	
LIMS code	**Name**
%METSOL	%total solids (metal)*
HGSD	Metals results*
DRYSAWT	%TS dry sample wt.**
WETSAWT	%TS sample wt.**
%SOLIDS	%total solids*
BOATWT	%TS boat wt.**
HGMETAMT	Sample amt.
HGMETDFI	Raw dil. Factor
HGDRYAM	Dry sample amt.*
HGMETVOL	Sample final vol.

#QC Water samples*	
LIMS code	**Name**
P_HGWA	Dup. Precision
B_HGWA	Blank result
D_HGWA	Dup. Result
R_HGWA	MS rec. solid

QC common fields	
LIMS code	**Name**
A_HG	Amount spiked
L_HG	LCS R.D.
D_HG	Dup. R.D.
ITA_HG	ICV true amt.
I_HG	ICV R.D.
IR_HG	ICV rec.*
S_HG	MS R.D.
B_HG	Blank R.D.
CR_HG	CCV rec.*
C_HG	CCV R.D.
CTA_HG	CCV true amt.

R.D. = Raw data, .GRF files can be entered into raw data fields.
***Calculation or entry field**
****Result imported from balance.**

13. Calculation of data.

13.1. Data for aqueous samples are reported in "mg/L" and solids are reported in "mg/kg" units.

13.2. For aqueous samples that were digested, multiply the concentration of the digestate by the final volume of the digestate and divide by the original sample volume. Multiply the result by any dilution factors that were used.

13.3. For soil and oil samples, multiply the concentration of the digestate by the final volume of the digestate and divide by the sample weight and the percent total solids. Multiply the result by any dilution factors that were used.

13.4. Calculation for sample preparation dilution factor: DF= [Digestate final volume (ml)] / [{Initial volume (ml)}*{%solids}]

13.5. Calculation for post dilution factor: Post DF= DF*{final volume(ml)} / [initial volume (ml)]

13.6. Matrix spike recovery for each element: %REC.= [{M.S. sample}-{sample}]*100 / {Spike Added}

13.7. Relative Percent Difference for each element: %RPD= Abs.[{Sample}-{Dup.sample}]*200 / {sample}+{dup.sample}

13.8. %Recovery for IPC,PRDL,ICSAB and QCS solutions:%REC.= {Found value} *100 / {True value}

13.9. %Recovery for LCSW/LFB solutions: %REC.= [{found value}*{final volume}]*100 / {Amount spiked}

13.10. %Recovery for LCSS samples: %REC.= [{found value}*{METDF}]*100 / {True Value}

Example of LIMs CALCULATIONS

ANALYTE		ANALYTE	
%SOLIDS=	100*(DRYSAWT- BOATWT) / (WETSAWT- BOATWT)	D_HGDRYA=	(D_HGAMT* %METSOL) / 100
R_HGSD=	{((S_HG*S_HGDF)/1000}- (HGSD))*S_HGDRYA*100 / (A_HG)	S_HGDF=	(S_HGFVOL* S_HGDFI) / S_HGDRYA
L_HGS=	100*(L_HG) * L_HGFVO / (A_LCSS *LCSSWT)	CR_HG=	100*(C_HG)/ (CTA_HG)
HGDRYAM=	(HGMETAMT * %METSOL) / 100	D_HGDF=	(D_HGFVOL* D_HGDFI) / (D_HGDRYA)
P_HGSD=	200*Abs.(HGSD- D_HGSD) / (HGSD+ D_HGSD)	IR_HG=	100*(I_HG)/ (ITA_HG)
P_HGWA=	200*Abs.(HGWA- D_HGWA) / (HGWA+ D_HGWA)	B_HGSD=	(B_HG* * B_HGDF)
D_HG(SD/DW)=	(D_HGI* D_HGDF)	B_HGWA=	(B_HG* * B_HGDF)
HG(SD/DW)=	(HGI* HGDF)	S_HGDRYA=	(S_HGAMT* %METSOL) / 100
HGDF=	(HGMETVOL *HGMETDFI) / HGDRYAM	R_HGWA=	5*{[(S_HG)] -HGI} / (A_HG)

14. Data submission

14.1. The information that is required on the client's certificate is the NEA identification number, client identification, method code, sample results, detection limits, concentration units, and analysis dates.

14.2. Method codes depend on the matrix of the sample or the methods that the client has requested.

14.2.1. Solid samples, oils, and TCLP extracts require SW-846 method codes.

14.2.2. Water samples require EPA method codes.

14.3. The units used for reporting solid samples are mg/kg, and for water, the units are mg/L. Results are rounded to three significant figures.

15. Equipment maintenance.

15.1. The software offers a simple to use online Scheduled Maintenance page. To View the dialog box go to Perform Maintenance in the Utility pull down menu of the Runner application. A page displaying all items necessary to keep the instrument well maintained will be shown..

15.2. An X will appear next to the item requiring maintenance on the Scheduled Maintenance dialog window. To clear the message click the clear button in the information bar or replace, clean, or replenish the item using the maintenance wizard. Once the directions are followed to completion (click Finish button), the usage counter and timed usage gets updated.

16. QUALITY CONTROL

16.1. **Initial Demonstration of Performance**

16.1.1. **Perform Method detection limit studies for water and solid matrices**.

16.1.1.1. MDLs should be determined annually or when in the judgment of the analyst, a change in instrument hardware or operating conditions would dictate they need to be redetermined.

16.1.2. **Linear dynamic range must be established for each wavelength utilized.**

16.1.2.1. The LDR should be determined by analyzing a minimum of three succeeding higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. The LDRs should be verified at least every six months or whenever, in the judgment of the analyst, a change in analytical performance caused by a change in instrument hardware or operating conditions would indicate they be redetermined.

16.2. **Certification for analysts.**

16.2.1. Analysts must read, understand, and use the latest version of the laboratory's SOPs that relate to their job responsibilities. The SOPs must be read during their initial training, annually, and when the SOPs are revised.

16.2.2. When possible, analysts should attend training courses related to their job responsibilities.

16.2.3. For each matrix processed with this method, the analyst must be capable to perform the following tasks:

16.2.3.1. Prepare and analyze four consecutive laboratory control samples within method quality control limits or within the limits supplied with the purchased material.

16.2.4. For each matrix processed with this method, the analyst must be capable of analyzing a blind sample successfully.

16.2.4.1. The blind sample must be analyzed during their initial training and annually thereafter.

16.3. **Sample preparation quality control.**

16.3.1. **Laboratory reagent Blank/Preparation blank**: Prepare and analyze at least one LRB with batch of 20 or fewer samples of the same matrix or batch.

16.3.2. **Laboratory fortified blank/Laboratory control sample**: Prepare and analyze at least one LFB with each batch of samples of the same matrix.

16.3.2.1. For aqueous samples, fortify an aliquot of laboratory grade water with the same solution used to prepare the QCS/ICV solution.

16.3.2.2. For solid samples, prepare and analyze a premade QC solid sample.

16.3.3. **Laboratory fortified matrix/matrix spike**: Prepare and analyze a LFM with a minimum of 10% of the samples prepared per matrix per SDG.

16.3.3.1. For aqueous samples, take a separate aliquot from a designated sample and fortify with the same solution and at the same concentration used to fortify the LRB.

16.3.3.2. For solid samples, take a separate aliquot from a designated sample and fortify with the same solution used to prepare the QCS/ICV solutions.

16.3.4. **Laboratory Duplicates (LD1 and LD2):** Prepare and analyze one duplicate sample a minimum of 10% of the samples prepared per matrix per SDG.

16.3.4.1. Prepare and analyze a separate aliquot of a designated sample.

16.3.5. **Method of Standard Additions**: Employed for metallic contaminants for TCLP extracts if:

16.3.5.1. Spike recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and

16.3.5.2. The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

16.3.5.3. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample.

16.3.6. **Instrument and analysis quality control.**

16.3.6.1. **QCS/ICV**: Analyze immediately after calibrating the instrument. The source of the standards must be different than the source for the calibration standards.

16.3.6.2. **IPC/CCV**: Analyze every ten samples and at the beginning and the end of the analytical run.

16.3.6.2.1. Prepare the solution from the same source as the calibration standards.

16.3.6.3. **Blanks**-Four types of blanks are required for the analysis.

16.3.6.3.1. The rinse blank: Prepared by acidifying reagent water to the same concentration of acids as used in the calibration blank.

16.3.6.3.2. The calibration blank: Prepared by acidifying reagent water to the same concentration of the acids as used for the calibration standard.

16.3.6.3.3. ICB-Initial calibration blank. Prepared similar to the calibration blank.

16.3.6.3.3.a. Analyzed immediately after the QCS/ICV solution.

16.3.6.3.4. CCB-Continuing calibration blank. Prepared similar to the calibration blank.

16.3.6.3.4.a. Analyzed immediately after the IPC/CCV solution.

16.3.6.4. **PRDL/CRA solutions.**

16.3.6.4.1. Prepare a solution at the analytical contract detection limits or the PQL for the element required.

16.3.6.4.2. Analyze the solution at the beginning and the end of each analysis run, or a minimum of twice per 8-hour working shift, whichever is more frequent.

16.3.6.4.3. Do not analyze the solution before the CCV.

17. DATA ASSESSMENT AND ACCEPTANCE CRITERIA FOR QC MEASURES

17.1. **Initial review of documentation**

17.1.1. After the completion of the analysis run, the analyst reviews the logbook(s) and analytical data for completion and completes the required documentation.

17.1.2. The supervisor reviews the logbook(s) and data and records their initials and review dates on the appropriate documents.

17.1.3. Each QC measurement is reviewed and compared to the appropriate acceptance criteria.

17.1.4. The following section supplies the corrective action and or contingencies if the criteria for the QC measure are unacceptable.

17.2. **Calibration curves:**

17.2.1. Acceptance criteria: Correlation coefficient must be $\geq$0.997.

17.3. **Coefficient of variation**: For programs that specify limits for C.V.

17.3.1. Acceptance criteria: The C.V. must be $\leq \pm$20 for multiple injections/integrations for measurements for elements above the PRDL or PQL.

17.4. **Linear dynamic range for samples:**

17.4.1. Acceptance criteria: Determined sample analytes concentrations that are greater than 90% of the determined upper LDR must be diluted and reanalyzed. Report the results for the affected elements from the diluted sample.

17.5. **Laboratory reagent Blank/Preparation blank:**

17.5.1. Acceptance criteria: The absolute value of the concentration must not exceed the PQL/PRDL of the analyte.

17.5.1.1. Not applicable if the sample concentration is > 10X blank level,

17.5.1.2. Or if positive result is reported for the blank but the analyte is not in the sample.

17.6. **Laboratory fortified blank/Laboratory control sample**

17.6.1. Acceptance criteria:

17.6.1.1. For aqueous samples, the %recovery limits are between 80-120%.

17.6.1.2. For solid samples, refer to the vendor supplied acceptance limits.

17.7. **Laboratory fortified matrix/matrix spike.**

17.7.1. Acceptance criteria: The spikes recovery limits are between 75-125%.

17.7.2. Not applicable if sample concentration is >4X spike added.

17.8. **Laboratory Duplicates (LD1 and LD2)**

17.8.1. Acceptance criteria: A %RPD limit of $\pm$20% is used for analytes > 5X PQL or $\pm$PQL limit is used if the analyte concentration in the sample or duplicate is <5X PQL.

17.9. **Method of Standard Additions.**

17.9.1. Acceptance criteria: The calculated correlation coefficient >0.995.

17.9.1.1. The sample and three spikes must be within the LDR for the analyte. Dilute the sample and spiked samples if necessary.

17.10. **QCS/ICV**

17.10.1. Acceptance criteria: A %recovery limit of 90-110% is used.

17.11. **IPC/CCV**

17.11.1. Acceptance criteria: A %recovery limit of 95-105% is used for the initial analysis of the standard.

17.11.2. Acceptance criteria: A %recovery limit of 90-110% is used for subsequent analysis of the standard.

17.12. **Blanks**

17.12.1. Acceptance criteria: Absolute value of ICB and CCB <PQL.

17.13. **PRDL/CRA solutions.**

17.13.1. Acceptance criteria: A recovery limit of 80-120% is used for the analytes in the solutions.

18. CORRECTIVE ACTION FOR OUT OF CONTROL

18.1. **Calibration curves:**

18.1.1. Corrective action: If QC measure not within acceptance criteria, determine source of problem, correct problem and recalibrate instrument.

18.2. **Coefficient of variation:**

18.2.1. Corrective action: If C.V. > 20% and the results for elements above PQL, rerun sample once. Report the results for the elements that have the lowest C.V.

18.3. **Laboratory reagent Blank/Preparation blank:**

18.3.1. Corrective action: Redigest and reanalyze all samples associated with the LRB for the noncompliant elements.

18.4. **Laboratory fortified blank/Laboratory control sample:**

18.4.1. Corrective action: If QC measure not within acceptance criteria, determine source of problem, correct problem and redigest and reanalyze all samples associated with the LFB for the noncompliant elements.

18.5. **Laboratory fortified matrix/matrix spike**

18.5.1. Corrective action: No corrective action required.

18.6. **Laboratory Duplicates (LD1 and LD2).**

18.6.1. Corrective action: No corrective action required.

18.7. **Method of Standard Additions.**

18.7.1. Corrective action: If QC measure not within acceptance criteria, reanalyze sample and three spiked samples.

18.7.1.1. Report the results from the series of analysis that has the greatest correlation coefficient.

18.8. **QCS/ICV.**

18.8.1. Corrective action: If QC measures not within acceptance criteria stop the analysis, determine source of problem, correct problem and verify calibration.

18.9. **IPC/CCV**

18.9.1. Corrective action: If QC measure not within acceptance criteria, stop the analysis, determine source of problem, correct problem, recalibrate instrument, verify calibration and reanalyze all samples since last compliant QC measurement.

18.10. **Blanks**

18.10.1. Corrective action: If QC measure not within acceptance criteria, stop the analysis, determine source of problem, correct problem, recalibrate instrument, verify calibration and reanalyze all samples since last compliant QC measurement.

18.11. **PRDL/CRA solutions**

18.11.1. Corrective action: No corrective action required.

19. Contingencies for handling out of control or unacceptable data.

19.1. If the acceptance criteria for QC measures has been exceeded for requested analytes and the data is to be reported, the following procedures must be implemented:

19.1.1. The Quality assurance officer must be notified.

19.1.2. The data must be flagged with the appropriate qualifiers and case narrative.

19.1.3. The client must be notified about the data.

19.1.4.

20. DEFINITIONS

20.1. **Analytical Batch** – The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples that are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. groundwater, sludge, ash, etc.)

20.2. **Analytical Spike** – The post-digestion spike. The addition of a known amount of standard after digestion.

20.3. **Calibration** – The establishment of an analytical curve based on the absorbance, emission intensity, or other measured characteristic of known standards. The calibration standards must be prepared using the same type of acid and reagents or concentration of acids as used in the sample preparation.

20.4. **Calibration Blank**-A volume of reagent water acidified with the acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the instrument.

20.5. **Calibration Standard (CAL) -** A solution prepared from the dilution of stock standards solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

20.6. **Calibration curve**: If the correlation coefficient is < 0.997 or if the calculated recoveries for any of the calibration standards are not within 10% of the true value (except for the lowest standard), repeat analysis of the outlying standards until curve is within acceptance criteria.

20.7. **Correlation Coefficient** – The correlation coefficient for the calibration curve must be greater than or equal to 0.997 according to NYSDOH requirements.

20.8. **Continuing Check blank (CCB)**: Analyze the CCB solution after each ICV/CCV solution. If the absolute value of the CCB is $\geq$ the PQL, stop the analysis, correct problem, recalibrate the instrument and reanalyze all samples since the last compliant CCB.

20.9. **Dissolved Analyte** – The concentration of analyte in an aqueous sample that pass through a 0.45-µm membrane filter assembly prior to sample acidification.

20.10. **Instrument Detection Limit (IDL)** – The concentration equivalent to the analyte signal that is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the same wavelength.

20.11. **Instrument Performance Check (IPC) Solution** – Also known as **CCV**. A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

20.12. **Laboratory Duplicates (LD1 and LD2)** – Two aliquots of the same sample taken in the laboratory and analyzed with identical procedures. An analysis of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

20.13. **Laboratory Fortified Blank (LFB)** – Also known as a LCSW or LCSS. An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

20.14. **Laboratory Fortified Sample Matrix (LFM)** – An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

20.15. **Laboratory Reagent Blank (LRB)** – An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus.

20.16. **Linear Dynamic Range (LDR)** – The concentration range where the instrument response to an analyte is linear.
20.17. **Matrix** – The predominant material of which the sample to be analyzed is composed.
20.18. **Matrix Spike** – An aliquot of the sample is spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given matrix.
20.19. **Method Detection Limit (MDL)** – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero.
20.20. **Method of Standard Additions (MSA)** – The addition of 3 increments of a standard solution (spikes) to sample aliquots of the same size. Measurements are made on the original and after each addition. The slope is determined by least-square analysis. The analyte concentration is determined by the absolute value of the x-intercept. Ideally, the spike volume is low relative to the sample volume (approximately 10% of the volume). Standard addition may counteract matrix effects; it will not counteract spectral effects. Also referred to as Standard Addition.
20.21. **MSDS** – Material safety data sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication.
20.22. **PQL** – The Practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.
20.23. **PRDL** standard-Also known as CRI and CRA standard. A project–required detection limit standard is analyzed in order to verify linearity near the PRDL for ICP and AA analyses. Analyzed at a concentration at two times the required detection limits for ICP analytes, at the required detection limit for AA or at PQL for either method, whichever is greater.
20.24. **Quality Control Sample (QCS)** – Also known as **ICV:** A solution of method analytes of known concentrations, which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance.
20.25. **Relative Percent Difference (RPD)** – To compare two values, the relative percent difference is based on the mean of the two values, and is reported as an absolute value, i.e., always expressed as a positive number or zero.
20.26. **Replicate** – Repeated operation occurring within an analytical procedure. Two or more analyses for the same constituent in an extract of a single sample constitute replicate extract analyses.
20.27. **RCRA** – Resource Conservation and Recovery Act, PL 94-580. Found at 40 CFR 240-271. EPA has jurisdiction. Enacted November 21, 1976, and amended since. RCRA's major emphasis is the control of hazardous waste disposal. It controls all soil-waste disposal and encourages recycling and alternative energy sources.
20.28. **RCRA Hazardous Waste** – A material designated by RCRA as hazardous waste and assigned a number to be used in record keeping and reporting compliance.
20.29. **Reagent Water** – Water in which an interferent is not observed at or above the minimum quantitation limit of the parameters of interest.
20.30. **Rounding Rules** – If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by:
    20.30.1. If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number.
    20.30.2. If a series of multiple operations is to be performed (add, subtract, divide, multiply), all figures are carried through the calculations. Then the final answer is rounded to the proper number of significant figures.
20.31. **Sample Delivery Group (SDG)** – Unit within a single case that is used to identify a group of samples for delivery. An SDG is a group of 20 or fewer field samples within a case, received over a period of up to 14 calendar days (7 calendar days for 14-day data turnaround contracts). Data from all samples in an SDG are due concurrently.
20.32. **Standard Addition** – The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration.
20.33. **Stock Standard solution-**A concentrated solution containing one or more method analytes prepared in the laboratory or purchased form a reputable commercial source.
20.34. **Total Recoverable Analyte** – The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of < 1 NTU, or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method.
20.35. **Water Sample** – For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

21. POLLUTION REVENTION/WASTE MANAGEMENT

21.1. Refer to NEA168.SOP for instructions for pollution prevention.

21.2. Refer to NEA089.SOP and NEA054.SOP for instructions for the disposal of waste generated during the procedures previously mentioned.

22. DETECTION LIMIT

22.1. The most recent MDL studies and PQLs are maintained by the Quality Assurance unit and are available for review.

23. REFERENCES

23.1. *Methods 245.1 for the determination of Metals in Environmental samples,* Supplement I, EPA/600/R-94/111, May 1994.

23.2. NYSDOH Environmental Laboratory Approval Program Manual item # 233.

23.3. USEPA Contact Laboratory Program Statement of Work for Inorganics analysis Document number ILM03.0

23.4. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods,* SW-846, 3rd Edition, U.S. Environmental Protection Agency, Sept. 1986. Vol. IA method 7471A.

23.5. *General Electric Minimum Standards,* Environmental Standards, Inc.

24. ATTACHMENTS

24.1. **Attachment A:** Example of a run log for CLP.

24.2. **Attachment B:** General method parameters.

24.3. **Attachment C:** Notes page.

ATTACHMENT A

Example of a run log for CLP.

ICP run log	Sample name
QCS	Quality control sample
ICB	Calibration blank
IPC-1	Instrument performance check solution
CCB-1	Calibration blank
PRDL/CRA	PRDL standard
AE01000_PB	Preparation blank
AE01000_LCS	Laboratory fortified blank (LFB).
AE01000	Sample
AE01000_SPK	Laboratory fortified sample matrix (LFSM)
AE01000_DUP	Sample duplicate
PRDL/CRA	PRDL standard
IPC-2	Instrument performance check solution
CCB-2	Calibration blank

ATTACHMENT B
Operating conditions for mercury by CVA

Element	Mercury
EPA 1979 Ref.	245.1
SW-846 Ref.	7471A
Lamp voltage	8.7
Integration	10.00 sec.
Gas	0.60 l/min
Pump Rinse	40 sec.
Pump Uptake	18 sec.
Replicates of standards	3
Wavelength (nm)	254
Sample replicates	1
Full Scale	20
Chemical additive	-
Chemical additive to sample (ml : ml)	-
PQL (mg/L)	0.0002
Working Std. (mg/L)	1.0
Cal. std. #1 (mg/L)	0.0002
Cal. std. #2 (mg/L)	0.0005
Cal. std. #3 (mg/L)	0.0010
Cal. std. #4 (mg/L)	0.0030
Cal. std. #5 (mg/L)	0.0075
ICV Stock conc. (mg/L)	1000
Working std. (mg/L)	1.0
ICV std. (mg/L)	0.0050

ATTACHMENT C
NOTES

APPENDIX 17

Control Copy No._____
Implementation Date: _____

SOP No. C-MT-0005
Revision No. 3.0
Revision Date: 04-01-03
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LABORATORY-SPECIFIC

STL STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND MCAWW 245.1

(SUPERSEDES: C-MT-0005, REVISION 2)

Prepared by: _____ 4/10/03

Reviewed by: _____ 4/11/03
Technical Specialist

Approved by: _____ 4/11/03
Quality Assurance Manager

Approved by: _____ 4/25/03
Environmental, Health and Safety Coordinator

Approved by: _____ 4/12/03
Laboratory Director

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1. Both the water bath digestion and the autoclave digestion are available at the STL Pittsburgh facility, however the default practice is the autoclave digestion for 7470A. The water bath procedure is always used for 245.1. Both procedures are described in this SOP.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A (see C-MT-0007) is usually the method of choice. All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. The STL reporting limit for mercury in aqueous matrices is 0.0002 mg/L except for TCLP, SPLP or EPTOX leachates for which the reporting limit is 0.002 mg/L.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate and the mercury reduced to its elemental state with stannous chloride and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury

concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified after filtration).

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

4. INTERFERENCES

Chemical and physical interferences may be encountered when analyzing samples using this method.

4.1. Potassium permanganate which is used to breakdown organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.2. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.3. Chlorides can cause a positive interference. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample head space before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

Note: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury

concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.5. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.6. The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all STL associates.

5.2. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.3. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory. The following specific hazards are known:

5.3.1. The following materials are known to be **corrosive:**

hydrochloric acid, nitric acid and sulfuric acid.

5.3.2. The following materials are known to be **oxidizing agents**:

nitric acid, potassium permanganate, potassium persulfate and magnesium perchlorate.

5.3.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as:

5.3.3.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.3.3.2. Iodine, 0.25%, in a 3% KI solution.

5.3.4. Magnesium sulfate is known to be a reproductive toxin (mutagen).

5.4. Exposure to chemicals must be maintained **as low as reasonably achievable.** Therefore, unless they are known to be non-hazardous, all samples should be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.5. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.6. All work must be stopped in the event of a known or potential compromise to the health and safety of a STL associate. The situation must be reported **immediately** to a laboratory supervisor.

5.7. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.8. Cylinders of compressed gas must be handled with caution, in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.9. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 ?C) or autoclave that is able to obtain conditions of 15 lbs., 120 ?C for 15 minutes.

6.2. LEEMAN Labs AP200II Mercury Analyzer:

6.2.1. LEEMAN Mercury Lamp P.N. 317-00048.

6.2.2. Peristaltic Pump.

6.2.3. Flow Meter.

6.2.4. Printer.

6.2.5. Dehydrator tube.

6.3. Disposable Sealable Sample Containers (Corning).

6.4. Argon gas supply (ultrahigh purity-grade).

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.6. Class A volumetric flasks.

6.7. Thermometer (capable of accurate readings at 95 ?C).

6.8. Disposable cups or tubes.

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom STL solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the stock mercury standard (7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3. This acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the intermediate mercury standard (7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. A second source working standard is prepared at 0.1 ppm for preparation of the ICV.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water. The 0, .5, 1.0, 5.0 and 10 standards are recommended by Thermo Electron. The 0.2 standard level was selected to include a standard at the RL. See Table 1 (Appendix A) for the preparation of the ICV, CCV and RLV standards.

Note: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (ICV) must be made from a different stock solution than that of the calibration standards.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better.

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous sulfate solution: Add 25 g of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

Note: Stannous chloride may be used in place of stannous sulfate. Prepare the stannous chloride solution according to the recommendations provided by the instrument manufacturer.

7.11. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

Note: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.12. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.13. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis. For TCLP leachates, the holding time is 28 days from the time of TCLP extraction to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to analysis.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

9.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be redetermined on an annual basis in accordance with 40 CFR Part 136 Appendix B requirements. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the STL reporting limit.

9.1.2. Initial Demonstration Study - This requires the analysis of four QC check samples. The QC check sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin.

9.1.2.1. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate for 7470A or a matrix spike (one per 10 or fewer samples) for 245.1. In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS, MS, MSD) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any analyte of interest at or above the reporting limit, or above 10% of either the measured concentration of that analyte in associated samples or the regulatory limit. See QA-003 for more detail on criteria and corrective actions. In addition, blank contamination should always be evaluated against project specific requirements.

? Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

? If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the project narrative.

? If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. This anomaly must be addressed in the project narrative and the client must be notified.

9.5. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in 245.1) must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure. The CCV results can be reported as LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- ? If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied for 7470A (85 – 115% for 245.1).

- ? In the instance where the LCS recovery is > 120% (7470A) or > 115% (245.1) and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- ? In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- ? Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples for 7470A or a MS must be processed for every 10 or fewer samples for 245.1. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 245.1). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MS/MSD's. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I (Appendix A).

- ? If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % (7470A) or 70 – 130% (245.1) recovery and 20% RPD

must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.

? If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

? If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% (7470A) or 5% (245.1) of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples. The ICV is equivalent to the Quality Control Sample (QCS) and the first Initial Performance Check (IPC) specified in 245.1.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% (7470A) or 10% (245.1) of the true value for that solution. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.9. Reporting Limit Verification Standard (RLV) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB. Until in-house control limits are established, a control limit of 50 – 150% recovery will be applied.

9.10. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. Refer to Section 11.2.13 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to CVAA instrument manual for detailed setup and operation protocols.

10.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the STL reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.6. The calibration curve must have a correlation coefficient of ?0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

10.7. Refer to Section 9.0 and Table II for calibration verification procedures, acceptance criteria and corrective actions. The NELAC requirement for verification of the initial calibration at

varied concentrations is met daily since the ICVs, CCVs, and RLVs are all at different concentrations.

11. PROCEDURE

11.1. Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB, RLV) are processed through the digestion procedure as well as the field samples. *An exception to this is for Method 245.1 samples. The calibration curve samples are **not** heated.*

11.1.2. Transfer 100 mL of well mixed sample or standard to a clean sample digestion bottle.

Note: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

11.1.3. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking (LCS, MS, MSD) should be done after the initial addition of acids (see Appendix A, Table 1).

11.1.4. Add 15 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 25 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all associated samples, standards, *and QC samples (e.g. LCS and blank)* in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

11.1.5. Add 8 mL of potassium persulfate solution and heat for two hours in a water bath at 90 - 95 ?C.

NOTE: Alternatively, for analyses using 7470A, samples may be digested using an autoclave for 15 minutes at 120 ?C and 15 lbs (default).

11.1.6. Cool samples.

11.2. Sample Analysis:

11.2.1. Refer to the SOP PITT-MT-0028 and the instrument manual for detailed setup and operation protocols for the LEEMAN AP200II.

11.2.2. Refer to CVAA instrument manual for detailed setup and operation protocols.

11.2.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride "clearing solution" to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6 mL increments until the permanganate is completely reduced i.e. colorless.

11.2.4. Manual determination:

11.2.4.1. Treating each sample individually, purge the headspace of the sample bottle for at least one minute.

11.2.4.2. Add 5 mL of stannous chloride solution and immediately attach the bottle to the aeration apparatus.

11.2.4.3. Allow the sample to stand quietly without manual agitation while the sample is aerated (1 L/min flow). Monitor the sample absorbance during aeration. When the absorbance reaches a maximum and the signal levels off, open the bypass valve and continue aeration until the absorbance returns to its baseline level. Close the bypass valve and remove the aeration device.

11.2.4.4. Place the aeration device into 100 mL of 1% HNO_3 and allow to bubble rinse until the next sample is analyzed.

11.2.5. Automated determination: Follow instructions provided by instrument manufacturer.

11.2.6. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable.

11.2.7. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples for analytes that exceed the highest calibration standard.

11.2.8. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.9. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.10. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

11.2.11. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration
ICV
ICB
RLV
Maximum 10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run
CCV
CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

11.2.12. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 11.2.11. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration
ICV
ICB
RLV or CRA*
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

Refer to the appropriate CLP SOPs (CORP-MT-0006) for quality control requirements for QC samples.

* Refer to the CLP SOPs for information on the CRA.

11.2.13. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

11.3. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

11.4. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and and parts maintenance. For instrument troubleshooting, use the autodiagnostics software. If a the problem cannot be determined using the software, place a call to service personnel.

11.5. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.6. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(ICV)}{True(ICV)}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{Found(CCV)}{True(CCV)}\right)$$

12.3. RLV percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV in the above equations).

12.4. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:

SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.5. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left(\frac{|MSD - MS|}{\frac{MSD + MS}{2}}\right)$$

Where:

MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left(\frac{|DU1 - DU2|}{\frac{DU1 + DU2}{2}}\right)$$

Where:

DU1 = Sample result
DU2 = Sample duplicate result

12.6. The final concentration for an aqueous sample is calculated as follows:

$$mg/L = C \times D$$

Where:

C = Concentration (mg/L) from instrument readout
D = Instrument dilution factor

12.7. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.8. Appropriate factors must be applied to sample values if dilutions are performed.

12.9. Sample results should be reported with up to three significant figures in accordance with the STL significant figure policy.

13. METHOD PERFORMANCE

13.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 9.0.

13.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % (7470A) or +/- 30% (245.1) and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.4. The laboratory control sample should recover within 20% (7470A) or 15% (245.1) of the true value until in house limits are established.

13.3. Training Qualification:

The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. Waste generated in the procedure must be segregated and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Director should be contacted if additional information is required.

16. REFERENCES

16.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

16.2. "Methods for the Chemical Analysis of Water and Wastes", EPA-600/4-79-020, U.S.EPA, 1994, Method 245.1, Revision 3.0.

16.3. U.S.EPA Statement of Work for Inorganics Analysis, ILMO4.1.

16.4. QA-003, STL QC Program.

16.5. QA-004, Rounding and Significant Figures.

16.6. QA-005, Method Detection Limits.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC. . .)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, "Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology."

17.1.1.3. The alternate run sequence presented in Section 11.2.12 is consistent with method requirements.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above the reporting limit.

17.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Olliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 ?C and 15 lbs.).

17.1.3. Modifications from 245.1

17.1.3.1. Method 245.1, Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. STL reports all Hg results under this SOP to two significant figures.

17.2. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

? Raw data (direct instrument printout)

? Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).

? Data review checklist - See Appendix B

? Standards Documentation (source, lot, date).

? Copy of digestion log.

? Non-conformance summary (if applicable).

Figure 1. Aqueous Sample Preparation - Mercury

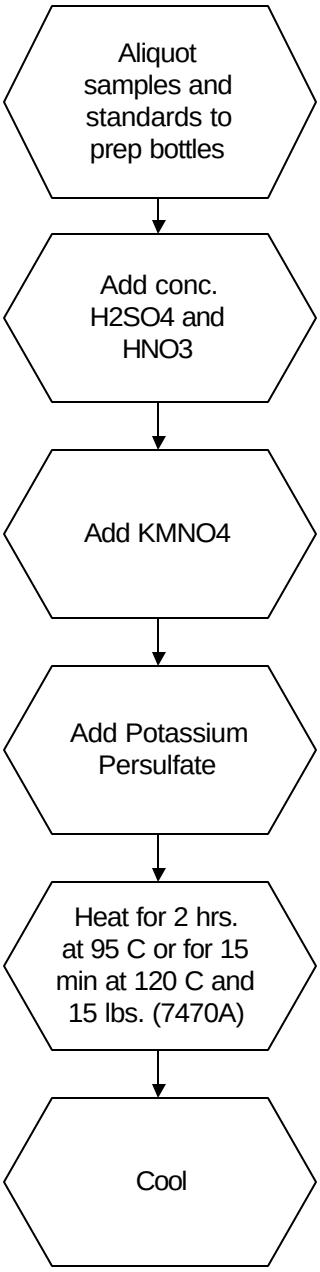
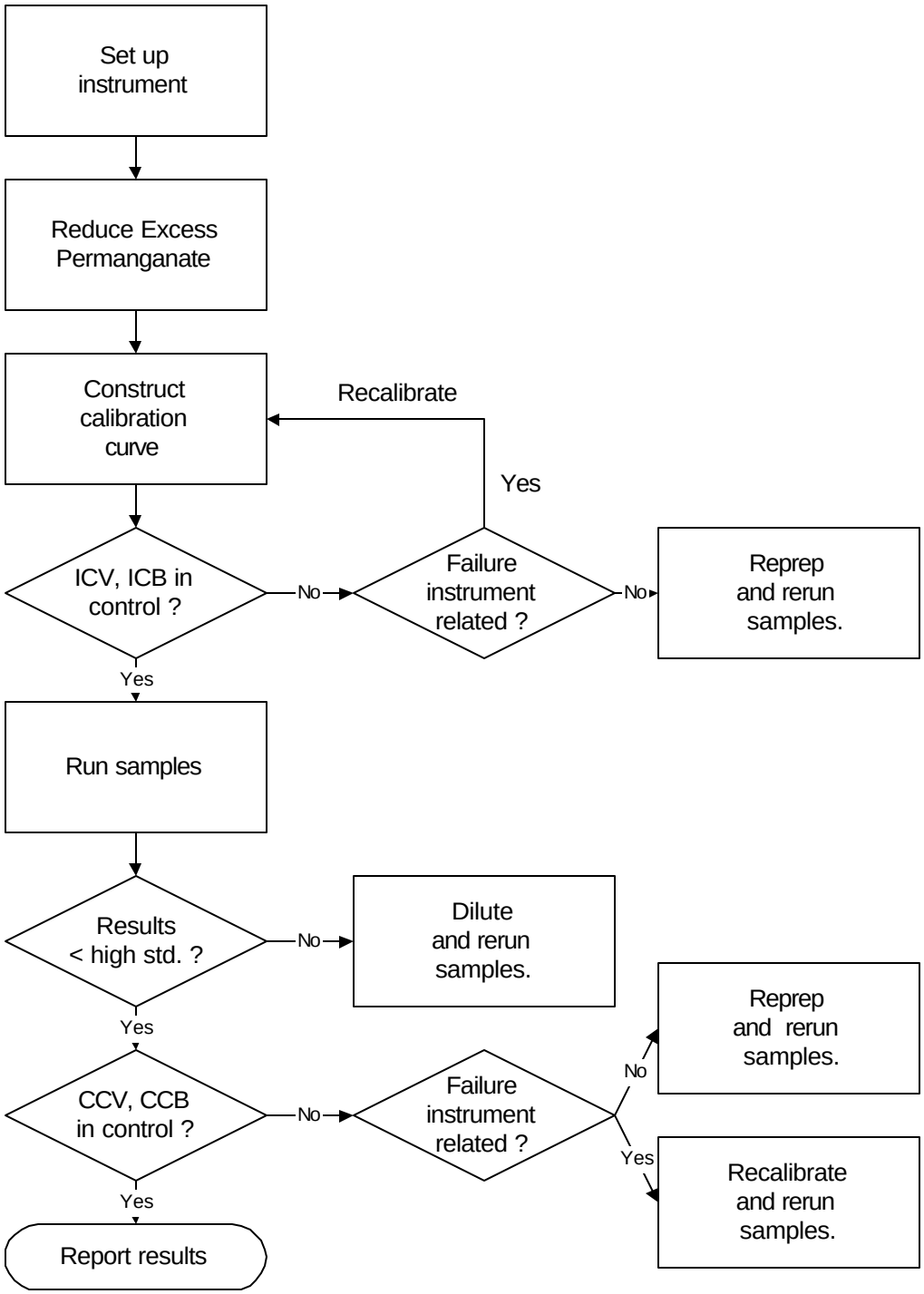


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Method	**Reporting Limit**	
SW846 7470A	0.0002 mg/L	
SW846 7470A (TCLP)	0.002 mg/L	
MCAWW 245.1	0.0002 mg/L	
Standard or QC sample	**mLs of 0.1 ppm Working Standard**	**Concentration (mg/L) *** **
Std 0	0	0
Std 1	0.2	0.0002
Std 2	0.5	0.0005
Std 3	1.0	0.001
Std 4	5.0	0.005
Std 5	10.0	0.010
ICV	2.5 **	0.0025
CCV	5.0	0.005
RLV	0.2	0.0002
LCS	2.5	0.0025
Aqueous MS	1.0	0.001
TCLP MS	5.0	0.005

*** SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements.**

**** Prepared from a second source 0.1 ppm working standard.**

***** When brought to a 100 mL final volume.**

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	7470A: 90 - 110 %. 245.1: 95 – 105%	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
RLV	Beginning of every analytical run, immediately following the ICB.	50 – 150% recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Every 10 samples and at the end of the run.	7470A: 80 - 120 %. 245.1: 90 – 110%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).

Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

TABLE II. Summary of Quality Control Requirements (Continued)

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% (7470A) or 85 – 115% (245.1) recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples (7470A) or one for every 10 or fewer samples (245.1).	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits. If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 11.2.13
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits; RPD ? 20%. (See MS)	See Corrective Action for Matrix Spike.

APPENDIX B
STL Hg DATA REVIEW CHECKLIST

STL- Pittsburgh
Data Review Checklist - Mercury

Run Date	Analyst	Instrument	Prep Batches Run	Method Used

Review Item	Yes (✓)	No (✓)	N/A (✓)	2nd Level Review (✓)	Comments
A. Calibration/Instrument Run QC					
1 Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2 ICV/CCV analyzed at appropriate frequency and within control limits?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA run? (CLP only)					
B. Sample Results					
1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3 Sample analyses done within holding time?					
C. Preparation/Matrix QC					
1 LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3 MS run at required frequency and within limits?					
4. MSD or DU run at required frequency and RPD within SOP limits?					
D. Other					
1. Are all nonconformances documented appropriately?					
2 Current IDL/MDL data on file?					
3. Calculations and transcriptions checked for error?					
4. All client/project specific requirements met?					
5 Date/Time of analysis verified as correct?					

General Comments: _____

Analyst & Date: _____ Second-Level Review & Date: _____

APPENDIX C

MSA GUIDANCE

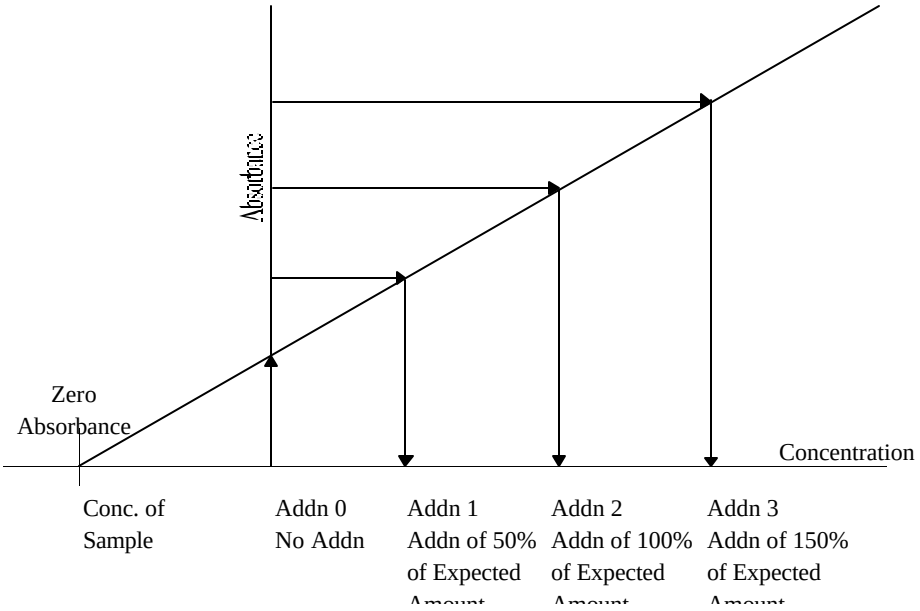
APPENDIX C. MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



? For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.

? The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.

? The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

APPENDIX D

PARTS MAINTENANCE GUIDE

APPENDIX D. PARTS MAINTENANCE GUIDE

Maintenance Schedule

The software offers a simple to use online Scheduled Maintenance page. To view the page go to Instrument:Scheduled Maintenance (F1 Menu, I, S). A page displaying all items necessary to keep the instrument well maintained is shown (see figure 6.1A).

```
RunProt:
RunFold:          Seq: 0    Batch:
                  Prnt: R/T Off
                  Rev: 3.390  15:40:47 14 Jan 1996 Xmit: Off  Gas:        LPM
 None                                              User:            A/S: On
INSTRUMENT:  Scheduled Maintenance
                                    Uses left     Last service    Next service
 replace: Pump tubing                   200        14-Jan-96       24-Jan-96
          Waste drain tubing           2500        14-Jan-96       29-Dec-96
          Liquid/gas separator         5000        14-Jan-96       14-Mar-96
          pump head                   10000          N/A             N/A
          Hg lamp                       N/A        14-Jan-96       12-Jun-96
          Reductant bottle              400        14-Jan-96       12-Jul-96
          prOcess tubing               5000          N/A             N/A
 Clean optical cell                     300          N/A             N/A
 clean External optics                  N/A        14-Jan-96       12-Jul-96

* - needs maintenance

For help on <hotkey> press Shift <hotkey>
```

Figure 6.1a. Scheduled maintenance screen

Each scheduled maintenance item has a usage counter, timed usage, or both (N/A indicates that the usage counter or the timed usage is not applicable for that item). If either condition expires for a given item a maintenance message will alert the user at the top of the status box.

Maintenance Procedures

An asterisk(*) will appear next to the item requiring maintenance on the Scheduled Maintenance screen. To clear the message hit <Tab> or replace, clean, or replenish the item using the hot key for the item on the Scheduled Maintenance page. To perform the maintenance on a given item simply type the hot key (e.g. Type <P> for Pump tubing) and follow the directions. Once the directions are followed to completion, the usage counter and timed usage gets updated.

APPENDIX E

CONTAMINATION CONTROL GUIDELINES

APPENDIX E. CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All glassware should be washed with detergent and tap water and rinsed with 1:1 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

APPENDIX F

PREVENTIVE MAINTENANCE

APPENDIX F. PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, time and instrument number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Cold Vapor Atomic Absorption (Leeman PS 200)

Daily	Semi-annually	Annually
Clean lens windows with methanol.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture.		Check liquid/gas separator.
Check argon flow.		
Check tubing and replace, if needed.		
Check drain.		
Replace drying tube.		

APPENDIX 18

STANDARD OPERATING PROCEDURE

Author: John Nicpon

Reviewed by:

Northeast Analytical, Inc.
Issuing section: Inorganics laboratory
NE117_02.SOP
Date: February 25, 2002
Revision Number: 2

William A Kotas
Quality Assurance Officer

Robert E. Wagner
Laboratory Director

1.0 TITLE

Standard operating procedure for the determination of non-filterable residue (or total suspended solids) according to EPA 1979 method 160.2.

2.0 PURPOSE

The purpose of this SOP is to provide procedures analyzing water samples for suspended solids.

3.0 SCOPE

This method is applicable to waste water and ground water.

4.0 COMMENT

Residue , non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103 - 105 ^{o} C. A measured volume of sample is passed through a preweighed crucible that contains a glass fiber filter. The crucible is dried in a oven and the change in weight is determined. The concentration of non filterable solids is calculated by dividing the difference in the crucible weight by the volume of sample filtered.

The holding time for analyzing samples is seven days from the date that the sample was collected. The detection limit for samples is dependent on the amount of sample filtered. If a client requires the lowest detection limit possible, the entire sample bottle is to be used.

Because the method is based on gravimetric measurements, handle the crucibles with tweezers or with vinyl gloves.

5.0 SAFETY

All safety precautions associated with the preparation and analysis of samples must be followed. Gloves and protective eyeware are required.

6.0 REQUIREMENTS

6.1 Method detection limit study

6.1.1 Analyze eight samples (use ERA control samples or other vendor) and a blank according to the procedures set forth in this document. Calculate the MDL by multiplying the standard deviation of eight MDL measurements by 2.998. For the MDL to be valid, it must be greater than 1/10 the amount spiked but not greater than the amount spiked.

6.2 Precision and accuracy studies

6.2.1. Each analyst must demonstrate the ability to generate acceptable results with this method using the following procedure.

6.2.2 Spike four precision and accuracy samples for the analytes of interest at a level at least ten times the PQL level.

6.3 Knowledge on the operation and calibration of the analytical balance is required.

6.4 Knowledge on the operation of the drying oven located in the Inorganics laboratory.

6.5 Knowledge on the maintenance of the portable desiccator box.

6.6 Knowledge on the operation and maintenance of the vacuum pump.

7.0 EQUIPMENT

7.1 Equipment

7.1.1 Small vacuum pump. Located in the Inorganics laboratory.

7.1.2 Large vacuum pump. Located in the Inorganics laboratory.

7.1.3 One liter Erlenmeyer vacuum flasks with crucible holder and glass insert. (Baxter p/n F4375-1L or equivalent). Located in the Inorganics laboratory.

7.1.4 Glass fiber filters. (Baxter p/n F2835-24 or equivalent). Located in the Inorganics laboratory.

7.1.5 Tweezers. Located in the Inorganics laboratory.

7.1.6 Drying oven. Set at a temperature of 103 -105 ^{o}C. Located in the Inorganics laboratory.

7.1.7 Rinse bottle. Filled with laboratory grade water. Located in the Inorganics laboratory.

7.1.8 500 and 250 ml graduated cylinders. Located in the Inorganics laboratory.

7.1.9 Total suspended solids logbook. Located in the Inorganics laboratory.

7.1.10 Crucibles. (VWR p/n 23835-113 or equivalent)

7.2 Reagents and Standards

7.2.1 Laboratory grade water. Located in the cooler room.

7.2.2 Laboratory control sample. Talc. (Fisher p/n T2-500 or equivalent) Located in the Inorganics chemical shelf. Prepare a 100 mg/L solution for the Laboratory control sample.

8.0 PROCEDURE

8.1 Operation and maintenance of vacuum pumps.

8.1.1 Before using vacuum pumps, check that the minimum volume of pump oil is in the pump oil reservoir. For both pumps, empty the collection flasks frequently to prevent water from entering the pump. For the large vacuum pump, a water trap is used to prevent water from entering the pump. Empty the water trap when necessary.

8.1.2 To operate the large vacuum pump, connect the collect flasks to the vacuum hoses. Before operating the pump the vacuum hoses should be in the closed position. Place the crucibles on the flasks, turn on the pump, turn the desired vacuum hose to the open position and proceed to filter samples as described in **8.5**.

8.1.3 To operate the small vacuum pump, connect the vacuum hose to the pump to the hose connection on the pump. Place the crucible on the flask, turn the pump on, and proceed to filter the sample as describe in **8.5.**

8.2 Oven operation.

8.2.1 Before placing crucibles in the oven, the temperature of the oven must be between 103 and 105 ^{O}C. Check the calibrated thermometer in the glass bottle inside the oven for the oven temperature. Adjust the temperature of the oven if necessary, by slightly turning the control knob. Wait five minutes, check the temperature, repeat the adjustment process until the temperature is within the required temperature range.

8.3 Operation and maintenance of portable desiccator box.

8.3.1 After the crucibles are removed from the oven, they must be placed in the portable desiccator box before they are weighed. The purpose of the desiccator box is to prevent the crucibles from absorbing moisture while they are cooling.

8.3.2 The desiccant material must be dried in the drying oven when the color of the material is a pale blue. Pour the material into a drying pan and placed in the drying oven for a minimum of one hour. Transfer the material to the portable desiccator box, and wait a minimum of one hour for the material to cool to room temperature before placing crucibles in the desiccator box.

8.4 Total suspended solids logbook and preparation of crucibles.

8.4.1 For each day of analysis, a new page of the logbook must be used. Write the date, analyst initials and the 'TSS' at the top of the page. Set up columns with the labels of 'Crucible #'', 'Initial wt. (g)', 'Final wt. (g)', 'NEA #', 'Sample volume (ml)', 'mg/L', and 'D.L. (mg/L)'.

8.4.2 The crucibles must be labeled with identification numbers that allows the analyst to identify the crucibles. Place the desired number of crucibles in a glass drying pan. Place filters into the crucibles with tweezers. The rough side of the filter should be facing up. Using the tweezers, place the crucibles on the collection flasks that are connected to the vacuum pump. Turn the pump on and wet the filter with an aliquot of water from the squirt bottle. **Note:** The filter must cover all the holes of the crucible. Turn off the pump and repeat the process with the next crucible. If a hole appears in the filter, replace the filter and repeat the process. Place the crucibles into the drying pan and place the pan in the drying oven for a minimum of three hour. Prepare extra crucibles with each batch.

8.4.3 Remove the crucibles from the oven and place in the portable desiccator box. Wait one hour, and weigh the crucibles on the analytical balance. Record the crucible number and the initial weight (grams) in the logbook. Using Lims record the intial weight in the appropriate location.

8.5 Sample analysis

8.5.1 Remove the samples from the cooler or refrigerator.

8.5.2 If the entire container of sample is to be filtered, mark the volume level with a marker.

8.5.3 The weight of captured residue on the filter must be greater than 1.0 mg. Generally, a sufficient volume of sample is filtered so that a sufficient amount of solid material covers the filter without clogging the filter. If a client requires the lowest detection limit possible, the entire sample bottle is to be used.

8.5.4 Place the crucible on the collection flask, and record the sample number in the logbook. Turn the pump on and squirt RO water onto the filter. Shake the sample bottle and pour into a 100 ml graduated cylinder. Record the volume (ml), and pour the sample onto the filter.

8.5.5 If the additional sample is required for filtering, repeat **8.5.4**. For samples that require the filtration of the complete sample bottle, pour directly from the bottle into the crucible

8.5.6 Do not overfill the crucible. If the filter clogs, repeat the analysis with a different crucible and use less sample.

8.5.7 After the sample has passed through the filter, rinse the graduated cylinder with aliquots of RO water and pour onto the filter. Rinse filter with several aliquots of RO water from rinse bottle. Turn off the pump and place the crucible into the drying oven. If the entire sample bottle was used, fill the bottle to the mark with water, pour into a graduated cylinder and record the volume.

8.5.8 The crucibles must be in the drying oven a minimum of one hour. Take the crucibles out of the drying oven and follow **8.4.3** and record the final weight (grams) in the logbook.

8.6 Calculations

8.6.1 To calculate the non filterable residue weight (grams), divide the difference of the initial weight and the final weight of the crucible by the total sample volume (ml), and multiply by 1,000,000. Report the result to two significant figures (mg/L).

8.6.2 To calculate the detection limit for the sample, divide 1000 by the sample volume (ml), and report the result to two significant figures (mg/L).

8.7 Quality control

8.7.1 A sample blank is analyzed on each day of analysis. Filter 1000 ml of RO water through one of the crucibles. The calculated value for the blank must be less than 1.00 mg/L. If the result is unacceptable, repeat **8.5.8** for all the samples associated with the blank. If the result is still unacceptable, repeat **8.4** through **8.6** for all samples associated with the blank.

8.7.2 A laboratory control is analyzed on each day of analysis. From the certified value given, filter enough sample for accurate determination. If the result is outside the recovery limits supplied with the control, repeat **8.5.8** for all the samples associated with the control. If the result is still unacceptable, repeat **8.4** through **8.6** for all samples associated with the control. Record the percent recovery on the logbook page.
% recovery = (calculated value/certified value) X 100

8.7.3 A sample duplicate is analyzed on each day of analysis or every ten samples, which ever is more frequent. If additional sample is unavailable for duplicate analysis, analyze the laboratory control a second time. Calculate the relative percent difference (RPD). The limit for RPD is 20 %. If the result is unacceptable, repeat **8.5.8** for all the samples associated with the duplicate. If the result is still unacceptable, repeat the analysis of the samples associated with the duplicate. Record the RPD on the notebook page.
RPD = Abs. {(S1 - S2)/(S1 + S2)} X 200

8.7.4 Sample results, detection limits, NEA numbers and the date of analysis are entered into LIMS.

LIMS RESULT TEMPLATE "TSS" COLUM HEADINGS AND DESCRIPTIONS

Column	Description	Column	Description	Column	Description
INTWGT	Initial wt.: sample	**FINWGT**	Final wt. :sample	**TOTVOL**	Total vol.: sample
TSSI	TSS intermediate cal.	**TSS**	Sample result	**TSS_LIW**	Initial wt.: LCS
B_TSS	Blank result	**D_TSS**	Duplicate sample result	**P_TSS**	Precision calculation
L_TSS	LCS % recovery	**TSS-BFW**	Final wt.: blank	**TSS_BIN**	Blank intermediate cal.
TSS_BV	Total vol.: blank	**TSS_DF**	Final wt.: Duplicate	**TSS_DIN**	Dup. Intermediate cal.
TSS-DV	Total vol. Duplicate	**TSS-LFW**	Final wt.: LCS	**TSS_LIN**	LCS intermediate cal.
A_TSS	True value: LCS	**LITSS**	LCS result	**TSS_DIW**	Initial wt.: Duplicate
TSS_LV	Total vol.: LCS	**TSS_BIW**	Initial wt.: Blank		

8.7.5 Analyst must read, understand, and use the latest version of the laboratory's SOPs that relate to their job responsibilities. The SOPs must be read during their initial training, annually, and when the SOPs are revised.

8.7.6 After the completion of the analysis run, the analyst reviews the logbook(s) and the analytical data for

completion.

8.7.8 The supervisor/designee reviews the logbook(s) and data and records their initials and revew dates on the appropriate documents.

8.7.9 Each QC measurement is reviewed and compared to the appropriate acceptance criteria.

8.7.10 If the acceptance criteria for QC measures has been exceeded for requested analytes and the data is to be reported, the following procedures must be implemented:
8.7.10.1 The quality assurance officer must be notified.
8.7.10.2 The data must be flagged with the appropriate qualifiers and case narrative.
8.7.10.3 The client must be notified about the data.

9.0 REFERENCES

9.1 "Methods of Chemical Analysis of Water and Wastes'," EPA-60/4-79-020, revised March 1983. method # 160.2

9.2 NYSDOH Environmental Laboratory Approval Program Manual item # 271.

10.0 ATTACHMENTS

10.1 **Attachment A**: Summary of procedure for TSS.

ATTACHMENT A

Summary of procedure for TSS

1. Prepare crucibles and place in oven for a minimum of one hour.

2. Remove crucibles from oven and place in desiccator for one hour, weigh crucibles.

3. If client requires entire sample for analysis, mark bottle, else pour portion of sample into 500 ml graduated cylinder.

4. Record volume, place crucible on flask, turn on pump, and pour sample into crucible.

5. Pour additional sample into crucible until sufficient material has collected on top of filter.

6. Place crucibles in oven for a minimum of one hour, place crucibles in desiccator for one hour.

7. Weigh crucibles and calculate results (mg/L) and detection limits (mg/L) to two significant figures.

8. Q.C.: A blank and control for each day of analysis. A sample duplicate on each day of analysis, or every 10 samples.

9. Q.C. sheets for clients requesting documentation: Control and duplicate calculations.

10. Client certificates for clients requesting documentation: Analyst generates certificates using LIMS.

11. Client folders: A copy of notebook page and data result sheet.

11.0 GLOSSARY

11.1 **Residue , non-filterable:** those solids that which are retained by a glass fiber filter and dried to constant weight at 103 -105 ^{o} C.

11.2 **Laboratory control.:** A standard of known concentration that is independent of the standards used for the quantifying samples. It is analyzed at a frequency of once a day.

APPENDIX 19

STANDARD OPERATING PROCEDURE

Author: Chris Hynes
Reviewed by:

Approved by:

Northeast Analytical, Inc.
Issuing section: Inorganics Department
NE128_03.SOP
Date: 10-February-2000
Revision Number: 3

1.0 TITLE

Standard operating procedure for the determination of total and particulate organic carbon according to Tekmar-Dohrmann application note TOC-011.

2.0 PURPOSE

The purpose of this SOP is to provide procedures for particulate organic carbon (POC) and total organic carbon (TOC).

3.0 SCOPE

This method is applicable to waste water and ground water for POC and TOC, and sediments and filters for TOC.

4.0 COMMENTS

Organic carbon is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous material in the sample.

The fractions of total carbon (TC) are defined as:
1) inorganic carbon (IC)-the carbonate, bicarbonate, and dissolved CO_2;
2) total organic carbon (TOC)-all carbon atoms covalently bonded in organic molecules;
3) dissolved organic carbon (DOC)-the fraction of TOC that passes through a 0.45-µm-pore-diameter filter,
4) particulate organic carbon (POC)-also referred to as non dissolved organic carbon, the fraction of TOC retained by a 0.45-µm filter.

IC interference can be eliminated by acidifying samples to pH 2 or less to convert IC species to CO_2. Subsequently, purging the sample with a purified gas removes the CO_2.

Principle: Depending upon the configuration, TOC can be measured by ultra-violet promoted persulfate oxidation or high-temperature combustion, followed by infrared detection.

1) TOC and POC in solid and sludge can be measured by utilizing the combustion-infrared method. The sample is homogenized and treated with acid and then heated to remove IC. The treated sample is placed into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The organic carbon is oxidized to CO_2

and H_2O. The sludge and sediment sampler combusts samples at 800^oC in an oxygen atmosphere so that solids as well as liquids can be analyzed.
The sampler consists of a magnetically coupled boat inlet system which delivers the sample to the high temperature furnace. Two ports are provided for sample introduction, a septum port for liquid injections, and a flip-top port for solid samples. The CO_2 from the oxidation of organic carbon is transported in the carrier-gas stream and is measured by means of a nondispersive infrared analyzer (NDIR).

2) TOC in aqueous samples can be measured by UV promoted persulfate infrared method. External sparging is used to remove inorganic carbon. The acidified persulfate reagent is continuously pumped from the external reservoir to the injection port and then into the bottom of the UV reactor. The reactor is a constant volume design; the excess liquid is pumped to waste from the drain port. The reactor liquid is continuously sparged and this sparge/carrier gas flows out at the top of the reactor to the NDIR. When a sample containing combined carbon is injected, it is carried into the reactor by the reagent flow. The oxidation of organics occurs rapidly, and the resultant carbon dioxide is sparged from the liquid and carried to the NDIR.

The detection limit for samples is dependent on the amount of sample analyzed.

Note: If the determination of TOC, TC and IC is required for a water sample, an unfixed portion of the sample must be supplied and analyzed for TC. The inorganic carbon fraction of the sample is removed from an aliquot of the preserved sample which is then analyzed for TOC. The IC fraction of the sample is determined by taking the difference between the TOC and TC values.

Sampling and storage: The holding time for analyzing soil samples for TOC is 14 days from the date that the samples are collected. Samples are to be stored at 4^oC until the time of analysis.

The holding time for analyzing water samples for TOC is 28 days from the date that the sample was collected. Collect samples in 40 ml VOA vials with silicone rubber-backed TFE septa with open ring caps. Preserve the samples with 1+1 H_2SO_4 or 1+1 H_3PO_4. Samples are to be stored at 4^oC until the time of analysis.

The holding time for analyzing water samples for POC is 14 days from the date that the sample was collected. Collect samples in one liter containers with Polyseal caps. Do not add any preservative to the bottles or samples. Samples are to be stored at 4^oC until the time of analysis.

5.0 SAFETY

5.1 Safety glasses and disposable gloves must be worn when handling chemicals and samples.

5.2 Personnel should familiarize themselves with the necessary safety precautions by reading MSDS information covering any chemicals used to perform SOP.

5.3 Ultra-violet radiation can cause damage to the eyes. Do not open the door to the UV persulfate module without turning the lamp off.

6.0 REQUIREMENTS

6.1 Method detection limit study.

6.1.1 Seven MDLs samples (spike seven aliquots of laboratory water with the TOC standard) should be determined annually at a concentration of two to three times the estimated instrument detection limit for the analytes of interest.

Analyze the samples according to the procedures set forth in this document. Calculate the MDL by multiplying the standard deviation of seven MDL measurements by 3.14. For the MDL to be valid, it must be greater than 1/10 the amount spiked but not greater than the amount spiked.

6.1.2 Knowledge on the operation and maintenance of the Dohrmann DC-80 series IR-I NDIR detector, UV-persulfate Reaction and sludge/sediment sampler modules.

6.1.3 Trainees are required to read the Instrument manual and take notes on subject matter not covered in SOP. Information about maintenance and replacement on specific parts not covered in SOP should be recorded on the "Notes" page of the SOP for future reference.

7.0 EQUIPMENT

7.1 Equipment.

7.1.1 Dohrmann IR-I NDIR detector module. Located in the main laboratory.

7.1.2 Dohrmann sludge/sediment sampler. Dohrmann (p/n 832-222). Located in the main laboratory.

7.1.3 250 and 1000 µL Rainin autopipets. Rainin (p/n EP-250 and EP-1000).

7.1.4 250 and 1000 µL pipet tips. Rainin (p/n RT-96 and RT-200).

7.1.5 1-5 ml Finn digital pipette with pipet tips. Baxter (p/n P5055-14).

7.1.6 Quartz boats. Dohrmann (p/n 899-624). Located in the main laboratory.

7.1.7 Quartz wool. Dohrmann (p/n 511-735). Located in the main laboratory.

7.1.8 GC oven. Set at 75 ^{o}C. Located in the main laboratory.

7.1.9 Propane tank with torch assembly. Located in the main laboratory.

7.1.10 Tweezers and steel spatula. Located in the main laboratory.

7.1.11 Analytical balance. Located in the main laboratory.

7.1.12 Centrifuge. Located in the main laboratory.

7.1.13 40 ml VOA vials. Located in the bottle storage room.

7.1.14 50, 100 and 250 µl syringe. Located in the main laboratory.

7.1.15 High purity oxygen tank with regulator. Located in the main laboratory.

7.1.16 Aluminum weighing boats. Located in the main laboratory.

7.1.17 Gray septum. Dohrmann (p/n 517-807). Located in the main laboratory.

7.1.18 Pasteur Pipets. Located in all laboratories.

7.1.19 UV-Persulfate Reaction Module. Located in the main laboratory.

7.1.20 Blue injection septum. Dohrmann (p/n 517-811). Located in the main laboratory.

7.1.21 Teflon sleeve reactor, taper joint. Dohrmann (p/n 070-627). Located in the main laboratory.

7.1.22 Lamp, Ultra-violet. Dohrmann (p/n 512-092). Located in the main laboratory.

7.1.23 Peristaltic pump tubing.
a) PVC Black/Black (p/n 899-641).
b) PVC Green/Green (p/n 899-645).
c) Viton A Purple/Purple (p/n 899-651).

7.1.24 High purity nitrogen tank with regulator. Attach plastic tubing to the regulator. Located in the main laboratory.

7.1.25 20-mesh tin. Dohrmann (p/n 511-876). Located in the main laboratory and used for tin/copper scrubber.

7.1.26 Copper. Dohrmann (p/n 511-895). Located in the main laboratory and used for tin/copper scrubber.

7.1.27 Pyrex wool. Dohrmann (p/n 511-895). Located in the main laboratory and used for tin/copper scrubber.

7.2 Reagents.

7.2.1 Laboratory grade water. Located in the cooler room.

7.2.2 ~2500 mg/L TOC stock standard. Mallinkrodt (p/n 6704-1). Dry potassium hydrogen phthalate crystals (primary standard grade) in 104 ^{o}C oven for 2 hours and weigh out approximately 2.65675 grams. Record the weight in the Inorganic standard logbook and dissolve in approximately 400 ml of laboratory grade water, add 2 ml of phosphoric acid and bring to a final volume of 500 ml. Calculate the exact concentration of the solution:
(weight of potassium hydrogen phthalate) X 941 = TOC stock standard {mg/L}

7.2.3 TOCS and POC calibration standards:
Prepare 4 calibration standards of different concentrations ranging from ~120.7 - ~1207 mg/L. Record the date and information related to the preparation of the calibration standards in the Inorganic standard logbook.

7.2.4 TOC in water calibration standards (low level):
Prepare 5 calibration standards of different concentrations ranging from ~1.2 - ~24.10 mg/L. Record the date and information related to the preparation of the calibration standards in the Inorganic standard logbook.

7.2.5 7.9N (1+1) nitric acid. Dilute 50 ml of concentrated nitric acid to a final volume of 100 ml. Located in the Inorganics laboratory.

7.2.6 ICV/CCV: TOCS and POC 1000 mg/L TOC control. Ricca (p/n 1847-16). Located in the Inorganics laboratory.

7.2.7 ICV/CCV: TOC in water 10 mg/L TOC control. Ricca (p/n 1847-16). Dilute 1000 mg/L ICV/CCV standard 100x. Located in the Inorganics laboratory.

7.2.8 Concentrated phosphoric acid (H_3PO_4). J.T. Baker. 'Baker analyzed', (Baxter p/n 0260-01*BC). Located in the Inorganics laboratory.

7.2.9 2.0 % potassium persulfate. Add approximately 700 ml of laboratory water to a one liter volumetric flask and add 20 grams of $K_2S_2O_8$ (J.T. Baker 'Baker Instra-analyzed' (Baxter p/n 3239-01*BC)) to the flask with a stir-bar. Add 1 ml of concentrated phosphoric acid to the flask and stir until the $K_2S_2O_8$ has dissolved. Remove the stir-bar and bring to volume.

7.3 Glassware and apparatus.

7.3.1 10, 25, 50, 100 ml Class A volumetric flasks. Located in the Inorganics laboratory.

7.3.2 100 ml graduated cylinder. Located in the Inorganics laboratory.

7.3.3 Rinse bottle. Filled with laboratory grade water. Located in the Inorganics laboratory.

7.3.4 TOC logbook. Located next to TOC instrument.

8.0 PROCEDURE

8.1 Operation and maintenance of the Dohrmann IR-I NDIR detector module.

8.1.1 Refer to the instrument manual for specific instructions and part numbers for all components.

8.1.2 To prepare the tin/copper scrubber, fit one end of the Pyrex scrubber tube with a cored gray septum. Insert a tuft of Pyrex wool and then about 2 inches of tin in the other end. Secure the tin with another tuft of Pyrex wool. Then, fill the remaining half of the scrubber tube with an equal amount of copper. Secure the copper with a third tuft of Pyrex wool. Insert a cored gray septum. Inspect the tin/copper scrubber and change the contents of the tube when one-half of the tin is discolored.

8.1.3 The detector must be on for several hours in order to achieve equilibrium. It is recommended that the detector is turned on the day before the analysis is to be performed. Power up the detector and the main unit.

8.1.4 Verify that the printer has sufficient amount of paper before starting the analysis. Reset the printer so that the number "1" will be printed for the first analysis performed for that day.

8.1.5 Select the "TOC" and the "DET" positions. For the detector, select position "3" for high concentrations, "2" for medium concentrations, and "1" for low concentrations of TOC.

8.1.6 The module will not light the green "ready" light if the baseline is above 0.05. Adjust the "zero" control until the baseline is less than 0.02. The "CALIB" light must be off during analysis.

8.2 Operation and maintenance of the Dohrmann sludge/sediment sampler.

8.2.1 Refer to the instrument manual for specific instructions and part numbers for all components.

8.2.2 A portion of sample is weighed into a quartz boat where it is acidified and dried. The boat is placed in the boat carriage of the sampler and it is moved into the combustion chamber. Gas from the combustion tube flows into the flask to the right where it passes through acidified water.
The gas travels to the flask to the left where excess water is removed before traveling to the detector module. The gas passes through the tin and copper scrubber and into the detector.

8.2.3 Before turning on the solid sampler, carefully examine individual components for sign of wear. Adjust the flow of oxygen to 30 psi. The level of acidified water in the right flask must be above the fritted sparging finger. A vigorous flow of gas emitting from the sparging finger should be easily observed, if not, check the gas lines and connections for leaks. The water collection flask should be emptied on a daily basis.

8.2.4 Turn on the furnace unit. When using the module for the first time or after a long period of inactivity, the furnace should be monitored with a voltmeter to verify that the temperature is at 800^{O}C. Place the black (ground) probe in the "com" port. Place the red (positive) probe in the "monitor", set the voltmeter to "volts". The voltage reading should read "0.80", if not, place the red probe in the "adj" port. The voltage reading should read "0.80", if not, adjust the voltage by turning the set screw until the correct voltage is achieved.

8.2.5 If the gray septum (p/n 517-807) at either end of the combustion tube have corroded and require replacement, the furnace must be turned off before replacing the septum.

8.3 Calibration of Dohrmann sludge/sediment sampler and IR-I NDIR detector module.

8.3.1 Determine the approximate concentration of the samples by analyzing one sample in each of the detector modes. Select the mode where the sample area readout is closest to the middle of the scale.

8.3.2 A new calibration curve must be generated if either the ICV or CCV (see **8.11 Quality Control**) are unacceptable. The calibration curve is based on 'µg of carbon' versus 'area'. Different volumes of the stock standard are injected onto a quartz boat that is lined with quartz wool. The calibration standards require duplicate injections.

8.3.3 A fresh tuft of quartz wool must be inserted into the boat before calibrating the instrument. The boat is placed inside the sediment sampler module. Hook the loop of the boat with the end of the magnetic boat carriage.

8.3.4 Remove contaminates from the boat by placing it in the furnace until the baseline has started to decrease. Pull the boat out of the furnace.

8.3.5 After the boat has cooled (approximately 30 seconds), place the boat underneath the injection port. Remove septum and inject calibration standard onto the boat. Replace septum.

8.3.6 After the baseline has stabilized, place the boat in the furnace. Press the "Start" button. After the signal has started to decrease, pull the boat out of the furnace.

8.3.7 Repeat injection of the standard until consecutive measurements are obtained that are reproducible to within $\pm$ 10%.

8.3.8 Repeat **8.3.5-.7** for the remaining calibration standards.

8.3.9 The calibration and continuing check blank consists of 50 ml of laboratory water and one ml of 1+1 nitric acid. Inject 70 µl of the blank solution for the calibration and continuing check blanks.

8.3.10 For TOC solids and POC, inject 70 µl of each calibration standard and the stock standard. If the needle in the IR meter goes past '95' or if the red error light has lit after injecting the stock standard, inject a smaller volume of the standard. Every standard must be within the scale of the detector.

8.3.11 Enter the injection number, standard label, date analyzed, injection volume, and the area printed by the printer in the TOC logbook. See the **Glossary** for information about the correlation coefficient.

8.4 Preparation of solid samples.

8.4.1 Between 1.0 and 20 mg of material can placed in a boat depending on the percent of carbon in the sample. Solid samples are analyzed in duplicate.

8.4.2 The concentration of the samples must be within the range of the calibration curve. If the sample concentration of the sample is outside the range of the calibration curve, repeat the analysis of the sample. If the µg of carbon of the sample was too low, use more sample up to 20 mg. If the sample concentration was too high, use less sample down to 1.0 mg.

8.4.3 Place each boat in a numbered aluminum weigh boat.

8.4.4 Homogenize a portion of the sample.

8.4.5 Place one boat on the analytical balance and tare the balance. Transfer an aliquot of the sample to the boat and record the NEA #, weight and the boat number in the TOC logbook. Place the boat in the numbered aluminum weigh boat.

8.4.6 Repeat **8.4.5** for the replicate sample analysis.

8.4.7 Add 2 to 3 drops of 1+1 nitric acid to each sample. Turn off the GC oven. Place the aluminum weigh boats in the GC oven. Place a 60 ml beaker over each quartz boat. Turn on the GC oven. Remove samples when dried (minimum of 10 minutes).

8.4.8 Place the boat in the raceway. After the baseline has stabilized, place the boat in the furnace and press the 'Start' button.

8.4.9 Copy the TOC area from the printer into the TOC logbook.

8.4.10 After each sample analysis, scrape any remaining material from the boat and place the boat in the flame of the propane torch to remove any contaminates.

8.4.11 Repeat **8.4.3-.9** for the remaining samples.

8.5 Percent total solids determination

8.5.1 Determine the percent total solids for each sample as described in NE090.

8.6 The determination of Particulate organic carbon (POC)in water.

8.6.1 The purpose of this procedure is to separate the non dissolved TC compounds from the dissolved TC compounds by centrifuging the water sample. The IC fraction of the sample is removed by the addition of 1+1 nitric acid to the particulate matter.

8.6.2 Shake the samp le bottle and measure a maximum of 80 ml aliquot of the sample with a graduated cylinder. Pour the sample into two labeled volatile (VOA) vials. Verify that sample levels in each vial are equal to each other.

8.6.3 Centrifuge the VOA vials at a setting of '7' for 5 minutes.

8.6.4 Remove all of the water from each vial until approximately 10 ml remain in each vial.

8.6.5 Transfer all the material (water and particulates) from the two vials to one vial.

8.6.6 Centrifuge the vial with the water and particulates at a setting of '7' for 5 minutes.

8.6.7 Remove all the water from the vial. Set the 1000 µl Rainin pipet to 650 µl and transfer the particulates to a quartz boat.

Note: If all the material from the VOA vial will not fit inside the boat, transfer a portion of the material from the vial to the boat and dry the boat and the material inside the GC oven. Repeat the process of transferring the sample from the vial to the boat and drying the material until all the sample extract has been transferred to the boat.

8.6.8 Place the boat in the numbered aluminum weigh boat. Record the NEA #, volume of sample centrifuged and the boat number into the TOC logbook.

8.6.9 Add 2 to 3 drops of 1+1 nitric acid to each sample. Turn off the GC oven.. Place the aluminum weigh boats in the GC oven. Place a 60 ml beaker over each quartz boat. Turn on the GC oven. Remove samples when dried (minimum of 10 minutes).

8.6.10 Follow the instructions in **8.3.6** for analyzing samples.

8.6.11 The concentration of the samples must be within the range of the calibration curve. If the sample concentration was too high, extract less than 80 ml of the sample.

8.7 Set up and maintenance of the UV-Persulfate reaction module.

8.7.1 Refer to the instrument manual for specific instructions and part numbers for all components.

8.7.2 Connect the tubing from the oxygen tank to the 'Carrier in' port. Connect the tubing from the 'Carrier out' port to the 'In' port of the NDIR detector module.

8.7.3 For the UV lamp, a thin film of Teflon fabricated in a conical shape is placed over the taper joint. Any excess is trimmed back from the top and bottom ends of the joint with a razor blade.

8.7.4 The position of the lamp should be adjusted so that the reactor coils just clears the fritted glass gas dispenser. Carefully insert the cap and lamp assembly into the reactor and check the clearance to the fritted gas dispenser. The lamp is held together by two springs.

8.7.5 Install the lamp so that the carrier gas exit tube is pointing to the front. The reactor is held in place by a three prong grip utility clamp.

8.7.6 **Reactor Liquid Plumbing.** Connections are made between the ports on the inside of the right side of the module to the reactor and other ports inside the reactor with Teflon lines and red/white septums. The ports on the inside of the module are counted one through six starting with one near the top of the case.

8.7.7 Connect the Teflon line from port 1 to the waste drain port of the reactor (the top of the "U" tube on the right side of the reactor). The 1/16" line should be pushed down through the septum about one inch and later adjusted up or down in the side arm so that the liquid level is about 1/4" above the inlet of the recycle arm.

8.7.8 Connect the line from port 2 to the recycle arm of the reactor. This port is located near the upper-center and points upward. Plug the horizontal port of this side arm with a red/white septum without a hole.

8.7.9 Connect the free line from the injection port to the sample inlet port at he bottom-left of the reactor body. Insert the Teflon tubing almost all the way through the glass capillary section of the inlet port.

8.7.10 **Reactor Gas Plumbing and Liquid Trap Plumbing.**

8.7.11 Connect 1/8" Teflon line from port 4 to the gas inlet at base of reactor with a red/white septum.

8.7.12 Mount liquid trap "U"" tube to the left of the reactor and run drain line to a beaker under the reactor.

8.7.13 Connect 1/8" Teflon line from outlet port of reactor cap to top inlet port of liquid trap with a red/white septum at reactor end and a gray perforated septum at the "U" tube end. Push line at the "U" tube inlet through septum hole until it is just below top of bulb.

8.7.14 Connect 1/8" Teflon line from permeation drier (top left of the interior of the module to the angled port of the "U" tube) with a gray perforated septum.

8.7.15 **Reaction Module Pump Tube Installation and Pump Adjustment**.

8.7.16 Release the pump tube pressure fingers by pressing on the upper part of the while plastic plate located toward the front of the pump assembly. This will release the pressure plate and allow the pressure fingers to rotate downward.

8.7.17 Install a green/green bridged tube at the inner most position. Install a black/black bridged tube in the second position. Install a black Viton purple/purple bridged tube in the third position.

Note: The pump pressure plate and fingers should be left in their operating position overnight to insure that reagent does not siphon out of the reactor.

8.7.18 Raise all four pressure fingers and raise the pressure plate so that the screws press up on the fingers. Push up on the bottom of the pressure plate and push in on the bottom of the white plastic locking block until it locks the pressure plate in place.

8.7.19 Connect a piece of plastic tubing to the back end of the green/green tubing. Place the free end of the plastic tubing into a container of laboratory water. Turn on the pump. Slowly adjust the screw for the green/green tube inward until the water just starts to rise in the tube. Advance the screw one-half turn more.

8.7.20 Repeat the procedure for the black/black and purple/purple tubes.

8.7.21 **Reactor External Plumbing.** The pump tube inlets are to the rear, outlets to the front. Connections between the pump tubing and module tubing are made on the ports outside the module.

8.7.22 Connect the inlet of the green/green pump tube to port 1 with 1/8" Teflon line. Connect a 1/8" Teflon line to the outlet of the green/green pump tube and place the end of the line in a waste container on the bench top.

8.7.23 Connect a 1/16" Teflon line to the inlet of the black/black pump tube and place the end of the line in the 2.0% $K_2S_2O_8$ solution.

8.7.24 Connect a 1/16" Teflon line between port 3 and the exit side (left) of the mixing tee. Connect a 1/16" Teflon line between the outlet of the black/black pump tube and the top of the mixing tee. Connect a 1/8" Teflon line between the outlet of the purple/purple pump tube and the mixing tee.

8.7.25 Connect a 1/8" Teflon line between port 2 and the outlet of the purple/purple pump tube.

8.8 Operation and calibration of the UV-persulfate and IR-I NDIR detector modules.

8.8.1 The blue injection septum must be replaced after approximately 100 injections have been made. Replace the blue septum in the injection port before starting the flow of reagent through the module.

8.8.2 Because there is a low flow of reagent(s) to the reactor, gently remove the top of the reactor and pour 2.0% $K_2S_2O_8$ so that the time required to fill the reactor with reagent is decreased. The reactor should be approximately 2/3 full. Connect the top of the reactor.

8.8.3 Place the pressure plate on the pump tubes. Turn on the pump and lamp by pressing the three white power buttons.
Caution: Do not open the module door while lamp is on.

8.8.4 Turn on the NDIR detector. The level of reagent in the reactor recycle arm must be at the top of the arm before starting analysis. The baseline on the detector must also be stable before starting analysis.

8.8.5 Inject the calibration standards one at a time. Wait 15 seconds and Press the "Start" button. The instrument will 'beep' to indicate that the analysis is completed and is ready for the next injection. Repeat injection of the sample until consecutive measurements are obtained that are reproducible to within $\pm$ 10%.

8.8.6 For low level analysis, the amount of carbon inject into the instrument for the calibration standards should range from ~0.10 to 24 µg. This can be achieved by injecting different volumes of the calibration standards.

8.8.7 Enter the injection number, standard label, date analyzed, injection volume, and the area printed by the printer in the TOC logbook. See the **Glossary** for information about the correlation coefficient.

8.8.8 After the analysis is completed, flush the reactor system by placing the tubing for the 2.0 % $K_2S_2O_8$ in a container of RO water and turn the pump on for one hour.

8.9 The determination of TOC in water.

8.9.1 Remove the IC fraction of the sample by acidifying and sparging the preserved sample with nitrogen gas for 10 minutes.

8.9.2 Transfer a portion of the sample to a VOA vial and place in a test tube rack. Attach a Pasteur pipet to plastic tubing that is connected to a nitrogen tank.
Add three drops of concentrated H_3PO_4 to the sample and place the tip of the Pasteur pipet in the sample. Slowly turn on the gas flow to produce gentle bubbling inside the vial for 10 minutes. The sample is now ready for analysis.

8.9.3 Inject 0.100 ml of sample into the UV-persulfate module. Wait 15 seconds and Press the "Start" button. The instrument will 'beep' to indicate that the analysis is completed and is ready for the next injection. Repeat injection of the sample until consecutive measurements are obtained that are reproducible to within $\pm$ 10%.

8.9.4 The concentration of the samples must be within the range of the calibration curve. If the original concentration of the sample was too low, inject a larger volume of sample up to 0.25 ml. If the sample concentration was too high, inject a smaller volume down to 0.010 ml. If the sample concentration is still too high, dilute a portion of the unsparged sample and repeat **8.7.2** and re analyze the diluted sample.

8.9.5 Repeat **8.9.2-4** for the remaining samples.

8.9.6 Enter the injection number, standard label, date analyzed, injection volume, and the area printed by the printer in the TOC logbook.

8.10 Sample calculations utilizing Lotus spreadsheets.

8.10.1 After the instrument is calibrated, a Lotus spreadsheet is used to construct a calibration curve and the linear regression. Generate a spreadsheet each time that the instrument is calibrated for either water samples or solids.

8.10.2 Log into the network and access "Lotus 1-2-3". Recall a previous spreadsheet, see the following table for an example of the directories and examples of files saved on November 11, 1996.

Analyte (matrix)	Lotus directory	Example
TOC (solids)	S:\DATA\TOCS*.*	S:\DATA\TOCS\1118.WK6
TOC (water)	S:\DATA\TOC*.*	S:\DATA\TOC\1118.WK6
POC (water)	S:\DATA\POC*.*	S:\DATA\POC\1118.WK6

8.10.3 Enter the average area (subtract the average blank area) for the calibration standards in the box used for constructing the calibration curve. Update the linear regression. For the calibration curve, enter the date of analysis.
Note: Except for the lowest calibration standard, the percent recoveries for the calibration standards must be between 90 and 110%.

8.11 Quality control (see attachment B for corrective actions)

8.11.1 A calibration blank is required for each day of analysis. Check blanks are analyzed after every initial and continuing check standard. The concentration of the blank must be less than the MDL for that method.

8.11.3 **Sample duplicate:** A duplicate analysis is performed every 10 samples.
RPD = Abs. {(S1 - S2)/(S1 + S2)} X 200

8.11.4 **Independent and continuing calibration verification standard (ICV) and (CCV)**: A purchased TOC solution of known concentration is analyzed after each calibration curve is generated, after every 10 samples and at the beginning and end of the analysis.
The ICV/CCV is analyzed in replicate.
% recovery = (calculated value/certified value) x 100.

8.11.5 For soil samples, if the sample analyses was off scale and the minimum sample weight of 1.0 mg was used, calculate the maximum concentration of TOC based on the µg of carbon of the highest calibration standard, average sample weight, and the percent total solids. Report the results as greater than the calculated maximum sample concentration , the detection limit and the standard deviation

8.11.6 **Laboratory fortified sample matrix**. Perform a spike on every 20th soil or water sample. For water samples, spike 10 ml of the sample with an aliquot of the ICV/CCV standard and proceed as in **8.9.2-.4**. For soil samples, weigh the sample and proceed as in **8.4.1-.10**. Place the sample and boat in the boat sampler and spike the sample through the injection port with the ICV/CCV standard. The final concentration of the spiked sample must be within the calibration curve.
% recovery = {(spike sample conc.) - (sample conc.)}/(spike added) X 100

8.12 Entry of data into LIMs.

8.12.1 After the calibration curve has been completed, give the LIMs manager a copy of the Lotus spreadsheet for the calibration curve with the area for blank and area for the lowest standard used in the calibration curve.

8.12.2 Log into LIMS. Click "Win Results" or "Results" from LIMS toolbar. Select the appropriate samples by either typing in the sample ID's or selecting the Login Record File.

8.12.3 Choose the result entry template "TOCSOL", then click "OK". A result entry spreadsheet will then be created with the following columns: TOCSO, TOCI_A, TOCI_1, TOCI_2, TOC_1SW, TOC_2SW, %SOLIDS. To find out what should go into these QC data columns, right click on the column heading in gray at the top of the spreadsheet.

8.12.4 The data for samples should be entered into the columns as follows:

TOCI_1 = Area Counts for Sample

TOCI_2 = Area Counts for Sample Replicate

TOC_1SW = Sample weight in grams

TOC_2SW = Sample Replicate weight in grams

%SOLIDS = % Total Solids for Sample (Enter as a percentage, not a decimal)

TOCI_A = Average Area Counts for Sample (Fills in automatically)

TOCSO = Final result for TOC in Solids (Fills in automatically)

8.12.5 Once the field TOCSO has been filled in by the computer, right click on that field and select "detailed edit" from the pull down menu. Confirm that the MDL and the date analyzed for the sample are correct. Proceed to the next sample.

8.12.6 Once the data has been entered for all samples, go the QC section of the spreadsheet. If batching was performed correctly there should be some of these fields displayed in white. Right click on the dark gray fields in that same row so that all appropriate QC tests have been added.

(For example, if the sample has a duplicate be sure all the raw data fields for the duplicate have been turned white.) Enter in all appropriate QA/QC data.

9.0 REFERENCES

9.1 "Determination of Total Organic carbon in sediment," Lloyd Kahn, U.S.E.P.A. Region II, Edison NJ.

9.2 Application Note: TOC-011 "Analysis of sludges and solids for carbon," Tekmar-Dohrmann, Cincinnati, OH 10/95.

9.3 NYSDOH ELAP manual item #271, 4/15/94.

9.4 *Standard Methods for the Examination of Water and Wastes*, method #5310B, 17th edition. 1989.

10 ATTACHMENTS

10.1 **Attachment A**: Note pages for analyst.

10.2 **Attachment B**: Quality assurance and corrective action for problems associated with sample preparation and analysis.

10.3 Attachment C: Disposal of samples and waste.

ATTACHMENT A
NOTES

ATTACHMENT A CONTINUED
NOTES

ATTACHMENT B
QUALITY ASSURANCE AND CORRECTIVE ACTIONS.

Calibration curve: If the correlation coefficient is < 0.997 or if the recoveries for any of the calibration standards are not within 10% of the true value (except for the lowest standard), repeat injections of the outlying standards until curve is within acceptance criteria.

Independent calibration verification (ICV/QCS): Must be within 85 –115% of true value. If the Percent recovery is not within the limits specified, recalibrate the instrument and reanalyze all samples since the last compliant continuing calibration verification standard.

Check standard (CCV/IPC): Use ICV solution as mentioned previously. Must be within 85 –115% of true value. If the Percent recovery is not within the limits specified, recalibrate the instrument and reanalyze all samples since the last compliant continuing calibration verification standard.

Preparation blank: For TOC in water, prepare one blank consisting of laboratory grade water for each batch of samples sparged daily. Prepare blank as described in 8.91-3. If he average area of the blank is greater than the half the value of the lowest standard used to construct the calibration curve, prepare a new blank solution.

Check blank (CCB): For TOC in water**, see Preparation blank**. For TOC in solids, analyze 70 ul of laboratory grade water. Analyze the CCB solution after each ICV/CCV solution. If the average area of the blank is greater than the half the value of the lowest standard used to construct the calibration curve, determine the source of the problem, fix the problem and reanalyze all samples since the last compliant CCB.

Laboratory control sample: Not applicable

Sample duplicate: Prepare and analyze one sample duplicate for every 10^{th} sample. For water samples, a control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to 5x the RDL. A control of +/- the RDL shall be used if either the sample or its duplicate is less than 5x the RDL. For soil samples, refer to the latest control limit for duplicates. If the the results for the sample and duplicate are unacceptable, a case narrative explaining why the RPD for a sample and its duplicate was outside the control limits must be written and approved by the quality assurance officer. A copy of the case narrative must be sent with the report to the client.

Matrix spike: Prepare and analyze one matrix spike for every 20^{th} sample. **TOC**: For water and soil samples, refer to the latest control limit for matrix spikes. Spile with an aliquot of the ICV/CCV solution. If the results for the matrix spike is unacceptable, prepare and analyze another matrix spike. If the results for the matrix spike is still unacceptable, a case narrative explaining why the percent recovery for the matrix spike was outside the control limits must be written and approved by the quality assurance officer. A copy of the case narrative must be sent with the report to the client

Serial dilution: Not applicable

Analytical spike: Not applicable

Method of standard additions: Not applicable

Overrange samples: Dilute or redigest samples that are greater than the value of the highest standard used to prepare the calibration curve so that the results are within the calibration curve.

ATTACHMENT C:
DISPOSAL OF SAMPLES AND WASTE

1. Refer to SOP NE054 for procedures for disposing of laboratory waste.

2. Acidified aqueous samples and extracts that do not contain metals or organic compounds above 0.050 mg/L, can be neutralized to a pH above 4.0 before disposal.

3. All client sample containers must be defaced with a permanent marker before disposal.

11 GLOSSARY

11.1 **Laboratory control.:** A standard of known concentration that is independent of the standards used for quantifying samples.

11.2 **Continuing calibration standard (CCV):** Used to assure calibration accuracy during each analysis run. It must be run at a frequency of 10% during the run. It must also be analyzed at the beginning and the end of the run. Its concentration must be at or near the mid-range level of the calibration curve.

11.3 **Correlation coefficient:** The correlation coefficient for the calibration curve must be greater than or equal to 0.997 according to NYSDOH requirements.

APPENDIX 20

Section 4: 1613 Data Analysis & Reporting

Paradigm Analytical Labs - Standard Operating Procedure

Last Revised By:	Asst. Lab Director:	QA Officer:
W.M. Larkins	C.K. Cornwell	Greg Dickinson

Purpose

To describe the processes used in operating the HRGC/HRMS system, as well as the procedures followed in the generation, interpretation and review of laboratory data for Method 1613.

Summary

This SOP details how to analyze and report samples by EPA Method 1613. HRGC/HRMS is used to detect and quantitate PCDD/Fs. Samples arrive at the MS lab having been extracted and fractionated using procedures in Section 3. Analyses are grouped into 12-hour sequences that include analyses of samples and standards mixtures. Upon completion of the sequence, the analyst reviews the data associated with both standards and samples in order to confirm the validity of the sequence and to determine any potential need for re-analysis or re-extraction. The analyst generates quantitation reports and chromatograms using sophisticated software. These reports are used to generate forms that summarize the results of the analysis.

4.1 Operation of HRGC/HRMS

4.1.1 Equipment

- HP6890 GC, Micromass Autospec Ultima high resolution mass spectrometer, vortex mixer, 10-100 uL pipette

4.1.2 Procedure

- Recall the GC temperature/pressure/flow program.
- Recall the MS experiment (see Table 1).
- Perform any necessary maintenance.
- Tune the MS resolution to 100 ppm at 5% height.
- Acquire location data to calibrate the MS and print a copy of function one MS resolution.
- Inject the window defining/GC resolution/continuing calibration mix (RETCON). Evaluate descriptor-switching times for accuracy. If any window defining peaks have shifted outside the descriptor windows, adjust the switching times before injecting any samples. This injection is also used to verify that there is less than or equal to 25% peak to valley for the two close eluters of 2,3,7,8-TCDD. Print a copy of the GC resolution check. If the valleys are within specifications, proceed to calibrate or verify a previous calibration. If not, further investigation and/or maintenance may be required. Re-inject this solution after maintenance to check for improvement.
- Now that the GC/MS resolution and descriptor switching times have been verified, a series of five initial calibration standards may be injected and reviewed for method requirements. If an initial calibration already exists, a RETCON may be analyzed to verify continuing calibration. If the curve or the RETCON passes method requirements, sample analysis may begin.
- Reconstitution of a sample is accomplished by adding nonane containing the injection standards, capping the vial, and mixing well with a vortex mixer.
- Samples are injected under conditions identical to those used to establish calibration.
- A “back-end” print out of the MS resolution must be performed.
- The calibration data from a sequence is filed in a folder cabinet under the day it was analyzed and includes the all GC/MS resolution checks, window verification, valley verification, front end Retcons, run logs and window defining mix (WDM) retention time sheets.
- Each sample hardcopy should include the quant report, totals pages, deviations, chromatograms, and report forms.
- Columns: DB-225, 30 m, id 0.25 mm, 0.25 µm; DB-5MS, 60 m, id 0.25 mm, 0.25 µm.

Table 1: Mass Descriptors used for Selected Ion Recording HRMS

Function (#)	Channel (#)	Mass (amu)	Dwell Time (ms)	I.C. Delay (ms)
1	1	303.9016	100	20
1	2	305.8987	100	10
1	3	315.9419	40	10
1	4	316.9824	20	10
1	5	316.9824	(Lock)	50
1	6	317.9389	40	10
1	7	319.8965	100	10
1	8	321.8936	100	10
1	9	327.8847	40	10
1	10	331.9368	40	10
1	11	333.9339	40	10
1	12	375.8364	30	20
2	1	339.8597	100	20
2	2	341.8568	100	10
2	3	351.9000	40	10
2	4	353.8970	40	10
2	5	355.8546	100	10
2	6	357.8517	100	10
2	7	366.9792	20	10
2	8	366.9792	(Lock)	50
2	9	367.8949	40	10
2	10	369.8919	40	10
2	11	409.7974	30	20
3	1	373.8207	100	20
3	2	375.8178	100	10
3	3	380.9760	20	10
3	4	380.9760	(Lock)	50
3	5	383.8639	40	10
3	6	385.8610	40	10
3	7	389.8156	100	10
3	8	391.8127	100	10
3	9	401.8559	40	10
3	10	403.8530	40	10
3	11	445.7555	30	20
4	1	407.7818	100	20
4	2	409.7788	100	10
4	3	417.8253	40	10
4	4	419.8220	40	10
4	5	423.7767	100	10
4	6	425.7737	100	10
4	7	430.9728	20	10
4	8	430.9728	(Lock)	50
4	9	435.8169	40	10
4	10	437.8140	40	10
4	11	479.7165	30	20
5	1	441.7427	100	20
5	2	443.7398	100	10
5	3	454.9728	20	10
5	4	454.9728	(Lock)	50
5	5	457.7377	100	10
5	6	459.7348	100	10
5	7	469.7780	40	10
5	8	471.7750	40	10
5	9	513.6775	30	20

4.2 Data Generation, Interpretation and Review

Paradigm Analytical Labs defines a batch of samples as no more than 20 samples processed within a 12-hour shift. One LMB and one OPR are processed per analytical batch, following the same procedures as the field samples. Generally, soil is replaced by salt (Na_2SO_4), effluent by deionized water and biological tissues by vegetable oil. An invalid LMB or OPR requires a re-extraction of the affected samples.

4.2.1 Quality Assurance/Quality control

On an annual schedule, the laboratory shall perform Method Detection Limit studies (MDLs) for each matrix analyzed, as well as for each extraction method utilized per matrix. All MDL studies will be conducted following the guidelines set forth in 40 CFR, Part 136, appendix B and must be lower than one-third the regulatory compliance level or one third the Minimum Levels (ML) set forth in Table 2 of the reference method. In addition, at the time of the MDL a continuing calibration will be analyzed at a concentration other than the regularly utilized CS3, to further demonstrate instrument performance.

4.2.2 Initial Calibrations

The percent relative standard deviations for the mean response factors from the seventeen unlabeled standards must not exceed +/- 20%. The percent relative standard deviations from the labeled standards (i. e. extraction standards, cleanup standards and sampling standards) must not exceed +/- 35%. The signal to noise ratio for all signals present must be $\geq$ 10. The ion abundance ratios must be within specified control limits (see Table 2). Paradigm uses the concentrations in Table 3 to construct the initial calibration.

Table 2. Theoretical Ion Abundance Ratios and Their Control Limits

Level of Chlorination	Theoretical Ratio	Control Limits	
		Lower	Upper
4	0.77	0.65	0.89
5	1.55	1.32	1.78
6	1.24	1.05	1.43
6[a]	0.51	0.43	0.59
7	1.04	0.88	1.20
7[b]	0.44	0.37	0.51
8	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF
[b] Used only for ^{13}C-HpCDF

A new initial calibration is required when the continuing calibration criteria below are not met. Routine maintenance may be performed to correct any failures. Any major maintenance to the analytical system such as slit cleaning, analyzer lens cleaning, magnet shifts, and detector disk changes warrant a new ICAL. At a minimum, a new initial calibration must be performed annually.

Table 3. Initial Calibration Concentrations

Analyte	CS-1	CS-2	CS-3	CS-4	CS-5
	Concentration (pg/µL)				
Unlabeled					
2378-TCDD	0.25	2	10	40	200
2378-TCDF	0.25	2	10	40	200
12378-PeCDD	1.25	10	50	200	1000
12378-PeCDF	1.25	10	50	200	1000
23478-PeCDF	1.25	10	50	200	1000
123478-HxCDD	1.25	10	50	200	1000
123678-HxCDD	1.25	10	50	200	1000
123789-HxCDD	1.25	10	50	200	1000
123478-HxCDF	1.25	10	50	200	1000
123678-HxCDF	1.25	10	50	200	1000
123789-HxCDF	1.25	10	50	200	1000
234678-HxCDF	1.25	10	50	200	1000
1234678-HpCDD	1.25	10	50	200	1000
1234678-HpCDF	1.25	10	50	200	1000
1234789-HpCDF	1.25	10	50	200	1000
OCDD	2.5	20	100	400	2000
OCDF	2.5	20	100	400	2000
Extraction Standards					
^{13}C-2378-TCDD	100	100	100	100	100
^{13}C-2378-TCDF	100	100	100	100	100
^{13}C-12378-PeCDD	100	100	100	100	100
^{13}C-12378-PeCDF	100	100	100	100	100
^{13}C-23478-PeCDF	100	100	100	100	100
^{13}C-123678-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDD	100	100	100	100	100
^{13}C-123478-HxCDF	100	100	100	100	100
^{13}C-123478-HxCDF	100	100	100	100	100
^{13}C-1234678-HpCDD	100	100	100	100	100
^{13}C-1234678-HpCDF	100	100	100	100	100
^{13}C-1234789-HpCDF	100	100	100	100	100
^{13}C-OCDD	200	200	200	200	200
Cleanup Standards					
^{37}Cl-2378-TCDD	0.25	2	10	40	200
Injection Standards					
^{13}C-1234-TCDD	100	100	100	100	100
^{13}C-123789-HxCDD	100	100	100	100	100

4.2.3 Continuing Calibrations

Check that all paperwork is present. A CCal package should contain the documentation listed below.

- Pass: Run log. HRMS Resolution Checks. WDM retention time sheet. WDM chromatograms. GC performance for 2,3,7,8-TCDD. CCal quantitation page. CCal chromatograms. Injection preparation log.
- Fail: The analyst listed on the run log can provide any missing paperwork.

Review the Run log.

- Pass: Check that the 12 hour windows have not been exceeded between the front end Ccal and the last sample of the sequence.
- Fail: Re-analysis of affected samples.

Review the HRMS Resolution checks.

- Pass: Verify 100ppm width at 5% height for PFK mass 318 or higher. Compare the resolution check times to those on the run log to be sure they bracket each sequence.
- Fail: If instrument resolution drops below 10,000 at any point during a 12 hour sequence, the samples from the sequence should be reanalyzed.

Review the Window Defining Mix and GC Performance Documentation.

- Pass: Check that the sample numbers on the WDM sheets match those on the run log. Check that the retention times are correct for the WDM chromatograms.
- Check that the valley between 2,3,7,8-TCDD and its close eluters does not exceed 25%.
- Fail: Any missing peaks in the window-defining sample should be re-identified with a survey scan. Determine proper switching times. These must be entered into the HRMS ion function descriptors before analysis may resume. If the GC performance valley is greater than 25% instrument maintenance may be required. When a valley fails all samples must be reinjected.

Review the CCal Quantitation and Chromatograms.

- Pass: Check that all ion ratios are in specification. Verify that all compounds are within the concentration limits set by the method (see Table 4) for all front end CCals
- Fail: Routine instrument maintenance such as installing new injection port hardware, inner source cleaning, retuning, column clipping etc. will usually correct a calibration failure. If these measures do not work, a new ICal is needed.

Compound Name	CCAL (pg/µL)	Limits (pg/µL)	Compound Name	CCAL (pg/µL)	Limits (pg/µL)
2,3,7,8-TCDD	10	7.8 - 12.9	$^{13}C_{12}$-2,3,7,8-TCDD	100	82 - 121
1,2,3,7,8-PeCDD	50	39 - 65	$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62 - 160
1,2,3,4,7,8-HxCDD	50	39 - 64	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85 - 117
1,2,3,6,7,8-HxCDD	50	39 - 64	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85 - 118
1,2,3,7,8,9-HxCDD	50	41 - 61	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72 - 138
1,2,3,4,6,7,8-HpCDD	50	43 - 58	$^{13}C_{12}$-OCDD	200	96 - 415
OCDD	100	79 - 126	$^{13}C_{12}$-2,3,7,8-TCDF	100	71 - 140
2,3,7,8-TCDF	10	8.4 - 12	$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76 - 130
1,2,3,7,8-PeCDF	50	41 - 60	$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77 - 130
2,3,4,7,8-PeCDF	50	41 - 61	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76 - 131
1,2,3,4,7,8-HxCDF	50	45 - 56	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70 - 143
1,2,3,6,7,8-HxCDF	50	44 - 57	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	74 - 135
2,3,4,6,7,8-HxCDF	50	45 - 56	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	73 - 137
1,2,3,7,8,9-HxCDF	50	44 - 57	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78 - 129
1,2,3,4,6,7,8-HpCDF	50	45 - 55	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77 - 129
1,2,3,4,7,8,9-HpCDF	50	43 - 58	$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9 - 12.7
OCDF	100	63 - 159			

Table 4. Continuing Calibration Limits

Review the Injection Prep log sheet.

- Pass: Check that all samples have been spiked with 2 ng injection standard. Verify that final volume is 20 uL. Be sure that any dilutions or other comments are noted.
- Fail: Calculations of sample concentrations should reflect any deviations from normal injection prep parameters.

4.2.4 Quality Control Work Groups

The following elements should be present in a complete work group file:

- LMB topsheets
- LMB totals sheets
- LMB chromatograms (11 pages)

- OPR topsheets
- OPR chromatograms
- Extraction log sheet
- Cleanup log sheet
- ASE/Cleanup observation forms
- Dry weight sheet (where applicable)
- Any additional information (ex. re-extract request sheet)

The following procedure should be used for reviewing a work group:

- Review the header information on the LMB topsheets. Verify that the method and client sample ID (LMB or OPR) are correct.
- Review the footer information on the LMB and OPR topsheets. Verify that the following information is correct: Paradigm sample ID or OPR project number, extraction date, analysis date, method, matrix, sample weight/volume, percent solids/lipids, pH, work group number, sample datafile, retcheck datafile, beginning cal datafile and ICal datafile.
- Verify that no target analytes are present in the LMB above Method 1613's Minimum Levels. If target analytes are above this limit, the associated samples must have concentrations that exceed 10 times the LMB concentration for the specified analyte. Otherwise, samples must be re-extracted.
- Review the totals data for the LMB. Be sure that any ghosting peaks are removed from the totals concentrations and the associated detection limits are elevated to reflect the subtracted peaks.
- Verify that extraction and cleanup standard recoveries are within method specifications (see Table 5) for the LMB and OPR. These recoveries are found on the topsheets. Validate any failures based upon signal to noise and acceptable detection limits. If the lab validation fails a corrective action is required. Corrective actions may include re-extraction, re-cleanup, lower sample volume, extract dilution, etc.
- Verify that the recoveries in the OPR meet Paradigm's recovery limits, found in Table 6.

Compound Name	Amount Spiked (pg/µL)	Limits %
$^{13}C_{12}$-2,3,7,8-TCDD	100	25 - 164
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25 - 181
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32 - 141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28 - 130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23 - 140
$^{13}C_{12}$-OCDD	200	17 - 157
$^{13}C_{12}$-2,3,7,8-TCDF	100	24 - 169
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24 - 185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21 - 178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26 - 152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26 - 123
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	29 - 147
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	28 - 136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28 - 143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26 - 138
$^{37}Cl_4$-2,3,7,8-TCDD	10	35 - 197

Table 5. Labeled Standard Recovery Limits

Analyte	Amount Spiked (pg/µL)	Limit (pg/µL)
2378-TCDD	10	6.7-15.8
12378-PeCDD	50	35-71
123478-HxCDD	50	35-82
123678-HxCDD	50	38-67
123789-HxCDD	50	32-81
1234678-HpCDD	50	35-70
OCDD	100	78-144
2378-TCDF	10	7.5-15.8
12378-PeCDF	50	40-67
23478-PeCDF	50	34-80
123478-HxCDF	50	36-67
123678-HxCDF	50	42-65
123789-HxCDF	50	39-65
234678-HxCDF	50	35-78
1234678-HpCDF	50	41-61
1234789-HpCDF	50	39-69
OCDF	100	63-170
^{13}C-2378-TCDD	100	20-175
^{13}C-12378-PeCDD	100	21-227
^{13}C-123478-HxCDD	100	21-193
^{13}C-123678-HxCDD	100	25-163
^{13}C-1234678-HpCDD	100	26-166
^{13}C-OCDD	200	26-397
^{13}C-2378-TCDF	100	22-152
^{13}C-12378-PeCDF	100	21-192
^{13}C-23478-PeCDF	100	13-328
^{13}C-123478-HxCDF	100	19-202
^{13}C-123678-HxCDF	100	21-159
^{13}C-123789-HxCDF	100	17-205
^{13}C-234678-HxCDF	100	22-176
^{13}C-1234678-HpCDF	100	21-158
^{13}C-1234789-HpCDF	100	20-186
^{37}Cl-2378-TCDD	10	3.1-19.1

Table 6. OPR Recovery Limits

4.3 Data Review

4.3.1 Procedure

For quick reference, refer to the chart below.

4.3.1.1 Initial Review

- Summary form generation and organization of Ical, Ccal, Samples and QC data is conducted by the analyst.
- Analysts review data upon generation and elicit peer review.
- Data is then released to a secondary review level with the analyst's signature.
- Assemble project samples and QC data

4.3.1.2 Final Review

- Review client information and documentation.
- Complete Data Review Checklist (Section 4, Appendix A) and sign reports.
- Samples are released to clients with the data reviewer's signature after the complete package is reviewed by a QA Manager or Lab Director.

Paradigm's Quality Control Requirements for Method 1613			
QC Check	**Frequency**	**Limits**	**Corrective Action**
Method Blank	One per extraction batch.	PCDD/F< SOP RL or <10% of level in sample.	Affected samples must be re-extracted.
Initial Calibration (ICAL)	As needed to maintain acceptable CCAL, after major maintenance, or at a minimum one per year.	20% RPD for native and 35% RPD for labeled species.	An acceptable ICAL must be established before sample analysis may begin.
Mass Resolution	Before and after each 12 hour analytical sequence.	Mass resolution must be at 10,000 as estimated from a printout of a PFK peak.	MS maintenance.
Descriptor Defining Isomers	At the beginning of each 12h analytical sequence.	First and last eluters must be present within the switching times..	Perform a survey scan to identify the correct switching times.
GC Performance Isomers	At the beginning of each 12h analytical sequence.	Must be <25% valley.	GC maintenance.
OPR (LCS)	One per extraction batch.	See Table 6	Re-extract batch if low and detected. Evaluate data quality for high and non-detected.
OPRD (LCSD)	One per extraction batch.	See Table 6, ≤ 20%RSD.	If needed and fails, re-extract batch.
Extraction Standards (ES)	Every sample must receive ES before extraction.	See Table 5.	Evaluate data quality, and if needed re-extract sample.
Continuing Calibration (CCAL)	At the beginning of sample analysis every 12h.	See Table 4.	Acceptable CCAL must be established before sample analysis may begin.
Lab Sample Duplicate (DUP)	Per client request.	<25%Difference.	Flag failures.
Matrix spike/duplicate (MS/MSD)	One pair per method, per matrix, per extraction technique, per 30 days, per 20 samples.	±25% recovery, 20% RPD.	Flag failures, report OPRD.

4.3.2 Calculations

4.3.2.1 Target compound calculation

- $$\text{PCDD/PCDF (ppt)} = \frac{\text{(Sum Ion Abun. of analyte)(ES Amount)}}{\text{(Sum Ion Abun. of Int. Std)(RRF from ICal)(Amt. of Sample)}}$$

- $$\text{EDL} = \frac{\text{2.5 (Height of Noise)(Std. Amount)}}{\text{(Height of Noise from Int. STD.)(RF from ICal)(Amt. of Sample)}}$$

The instrumentation software calculates the noise level. However, manual noise determination may be employed at the reviewer's discretion in order to more accurately report peaks of interest.

4.3.2.2 Extraction Standard Recovery Calculation

- $$\text{\% Recovery} = \frac{\text{(Sum Ion Abun. of ES)(JS Amount)}}{\text{(Sum Ion Abun. of JS)(ES RRF from ICal)(ES Amount)}}$$

The clean-up standard recoveries are calculated as above, substituting the ion abundances from the individual clean-up standard for the extraction standard

4.3.3 Requests for Re-extraction

Review all supporting data, including spike profiles, extraction logs, clean-up logs, injection prep logs, observation forms, and the sample tracking forms in the folder. The project or work group folder may contain exceptions or changes to routine spiking procedures.

Check the sample for problems relating to analysis. These problems include response factors that may introduce quantitative errors, interference that could be diluted out, or any interference that causes de-tuning or chromatographic conditions that could lead to quantitative errors.

The Laboratory Supervisor or Director should be consulted when re-extraction is considered.

If re-extraction is necessary, complete the Re-Extraction Form, which indicates the sample id, re-extraction due date, and reason for re-extraction (ref. form DC18).

When the GC/MS analyst receives the form, the samples are marked "REX" in the LIMS. The Sample ID will receive an "R" suffix. If a sample requires a second or third re-extraction, the sample id suffix will change to S, then T, and so on. The sample id with the suffix is used in all paperwork. (extraction, clean-up, injection prep, and run logs).

4.4 Reference Method

"Guidelines Establishing Test Procedures for the Analysis of Pollutants; EPA Method 1613," *Federal Register*, Vol. 62(178): 48393-48442, September 15, 1997; *Final Rule*.

APPENDIX 21

STANDARD OPERATING PROCEDURES FOR FISH SAMPLE COLLECTION AND PROCESSING

PROCEDURES

1.0. Scope & Application

The purpose of this document is to provide a procedure for sampling largemouth or smallmouth bass (*Micropterus salmoides, M. dolomiueu*), brown or yellow bullhead (*Ameiurus nebulosus, A. natlis*), yellow or white perch (*Perca flavescens* and *Morone americana*), pumpkinseed (*Lepomis gibbosus*), and spottail shiner (*Notropis hudsonius),*or other substitute resident species from the Upper Hudson River. This SOP will detail the sample collection and preparation for contaminant analysis.

2.0 Summary of Method

Bass (largemouth or smallmouth), bullhead (yellow or brown), perch (yellow or white), pumpkinseed, and spottail shiner or other resident forage fish will be sampled from four locations in the Upper Hudson River; Above the Feeder Dam, Thompson Island Pool, Ft. Miller/Northumberland Pools, and the Stillwater Pool, and from Albany/Troy in the Lower Hudson River. The collection methods will include netting, electrofishing, and angling. Although electrofishing is the preferred sampling method, conditions such as water depth, habitat type, and target species and electrofishing effectiveness may warrant the use of one of the alternate collection methods.

Definitions

Beach seine – net used in shallow water to capture fish.
Caudal fin – "tail" of the fish
Cranium – skull of the fish
Dorsal fin – located at the top (dorsal side) of the fish
Gill net – Passive sampling device designed to capture fish as they swim through the water column.
Netting – Method for capturing fish that includes the use of a gill net or seine net.
Pectoral fin – first fin from the head that correspond to the arms of a land animal

3.0. Health and Safety Warnings

Health and safety concerns are documented in the Health and Safety Plan (HASP; BBL 2003).

4.0. Interferences

Potential interferences include inclement weather or equipment failure. In these instances sampling will be rescheduled so as to not compromise the integrity of the fish samples.

5.0. Personnel Qualifications

All sampling personnel are required to complete the 40-Hour HAZWOPER 29 CFR 1910.120(e) and the 8-hour refresher courses before commencing sample collection or equipment decontamination.

6.0. Equipment and Supplies

Equipment needed for fish sample collection includes:

- Laboratory grade detergent.
- Acetone.
- Hexane.
- Beach seine.
- Buoys.
- Anchors.
- Line.
- Collection buckets.
- Gill net.
- Global Positioning System (GPS).
- Sampling boat.
- Aluminum electrofishing boat equipped with live well.
- DC Generator.
- Variable voltage pulsator.
- Dip nets.
- Electrodes.
- Water temperature and conductivity meter.
- Volt meter.
- Rubber gloves and boots.
- Personal flotation devices (PFDs).

- Thermometer.
- Tape measure.
- Scale.
- Watch.
- Fish scaler.
- Dissecting (filet) knives.
- Dissecting pan/board.
- Scale envelope.
- Glass vials.
- Fish Collection Record.
- Chain of Custody Form.
- Analysis Request Form.
- Cooler(s).
- Ice.
- Aluminum Foil.
- Zip Lock Bags.
- Fish Collection Permit.
- First-aid Kit.
- Fire Extinguisher.

7.0. Collection Procedures

Decontamination

Prior to contact with fish, decontaminate all fish processing equipment (i.e., knives, scaler, etc.) in a designated decontamination area. The decontamination steps are:

1) wash with laboratory grade detergent;
2) rinse with distilled water;
3) rinse with acetone, then allow to air dry;
4) rinse with hexane, then allow to air dry;
5) rinse with distilled water.

Rinsate will be collected and placed in appropriate disposal containers.

Sample Collection

Collect fish with standard methods of netting, electrofishing, or angling. Fish retained for analysis must be within the size ranges specified in the QAPP.

Netting

For near shore shallow study areas, a beach seine may be used for the resident forage fish. The beach seine is typically used in shallow water where the net wall can extend from the surface of the water to the bottom. It is useful in the capture of near-shore species or for species that use the near-shore area seasonally or daily. In addition, the substrate needs to be relatively smooth so that the lead line of the seine drags along the bottom of the river preventing fish escapement. The fish are herded into the net as it is swept through the water. Seining will be conducted by a minimum of two people. The following outlines the procedures for seine netting:

1. Two people start together at the downstream edge of the sample location (wading or in boats).
2. One person begins extending the seine perpendicular to the shoreline until the net is straightened out or the water becomes too deep.
3. Both people begin walking parallel to the shoreline for a set distance before the deep end person begins to swing the end of the net back towards the shoreline.
4. Both ends of the net are brought together and the net hauled onto the shoreline with the captured fish.
5. Fish are removed from the net and placed into buckets for identification.

For the collection of resident sport fish, gill nets should be used when there is 100 ft of continuous depths of greater than 3 ft and little current. Fish are captured when they swim into the gill net and become entangled in the mesh of the net. A gill net consists of a net vertically suspended between a float line on top and a weighted lead line at the bottom. The mesh size of the net can consist of different sized panels or one single size for the entire length of net. To keep the net in a vertical orientation, anchors are attached to either end of the lead line and buoys are attached to either end of the float line. The lengths of the anchor and buoy lines are adjusted so that the net is suspended at the target water depth. The following describe the procedure for sampling with gill nets:

1. Setting the gill net:
   1.1 Attach anchors to both ends of the lead line and attach buoys to both ends of the float line
   1.2 Stack the gillnet in a large storage bucket by placing the end with the larger mesh size in the tub first (if the net has variable mesh sizes), and coiling the rest of the net into the tub. This procedure facilitates setting the net.
   1.3 Beginning close to shore, or in water approximately 2 m deep, remove the outer end of the net from the storage bucket and drop the anchor (attached to the lead line) and

buoy (attached to the float line) over the bow of the boat. Adjust the buoy line so that the buoy is floating and the line is relatively taut.
1.4 Begin slowly backing the boat away from the shore.
1.5 Carefully, play out the remainder of the net as the boat is moving backwards, shaking out any tangles.
1.6 Once the inner end of the net is reached, stop the boat and pull on the net until it is taut.
1.7 Drop the anchor (attached to the lead line) overboard.
1.8 Pull on the float line to make sure the net is taut.
1.9 Drop the buoy that is attached to the float line into the water. Adjust the buoy line so that the buoy is floating and the line is relatively taut.
1.10 Allow the gill net to soak for the prescribed sampling period (e.g., 1-24 hours).
2. Retrieving the gill net.
2.1 Arrive at the end of the net in deeper water and retrieve the buoy and anchor.
2.2 Begin pulling the net on board the boat and stacking it in coils in the storage bucket.
2.3 Remove fish from the net as it is brought aboard the boat and place in holding bucket.

Electrofishing

Electrofishing uses electrical currents to immobilize fish for capture for all target species. Electrofishing is less effective in deeper waters, where fish can swim and avoid the current, so this method will be limited to areas that are less than 4 meters deep. Additionally, electrofishing tends to select for larger fish of a species, and thus will not be the preferred method for collection of yearling pumpkinseed or forage fish. Electrofishing will not occur where populations of endangered species are present. All electrofishing personnel will be sufficiently trained and attend daily Health and Safety meetings reviewing procedures prior to starting work. The following outlines the procedures for electrofishing:

1. Personnel performing the electrofishing should wear appropriate health and safety gear (rubber hip or chest waders, rubber gloves, PFD).
2. Starting upstream and working downstream, position the electrofishing boat in the water.
3. Optional use of a “fish finder” may increase efficiency and aid in targeting locations for sampling.
4. Measure the water conductivity and temperature to determine the appropriate operating voltage and amperage.
5. Adjust the output voltage and amperage dials until the desired output setting is obtained without harming fish. Use pulsed output to reduce stress on fish.
6. Maintain the output for a predetermined amount of time.

7. Collect the fish with dip nets and place in live well until processing; unselected fish will be released.
8. Release all unselected fish following processing.
9. Process fish retained for analysis according to the procedures described below.

Angling

Angling uses rod and reel to passively capture fish. This method is not highly efficient and will only be used if all other methods prove to be unsuccessful. It is not anticipated that this method will be necessary, but the procedures below will be followed if this method is used:

1. Personnel performing the angling should wear appropriate health and safety gear (PFD, waders).
2. Fish will be sampled by attaching an appropriate lure to the line to catch fish.
3. Fish caught by hook and line will be identified and assessed for the need to retain for tissue analysis. All unnecessary fish will be immediately returned to the water.
4. Process fish retained for analysis according to the procedures described below.

Data Collection

Record the following data on a Fish Collection Record immediately after collection:

- the name of person(s) collecting the samples;
- GPS coordinates of starting location and approximate distance samples;
- collection date, time, and duration;
- weather conditions – temperature, wind, precipitation;
- observations on river conditions (e.g. temperature, turbidity);
- species identification (genus and species);
- sample total length (nearest mm) and weight (nearest 0.1 g);
- sample sex, if possible (fish may be cut enough to allow sexing, but do not eviscerate); and
- sample tag number.
- Fish condition, including any easily discernable diseases or deformities.

Sample Preparation

Prepare the fish according to procedures modified from the New York State Department of Environmental Conservation Fish Preparation Procedures for Contaminant Analysis. Bass, bullhead, and perch will be prepared as standard fillets as follows:

1) Scales, spines, or otoliths will be collected should the analysis of fish age be deemed appropriate. For bass and perch, all scales will be removed from fish and at least 10 scales will be placed in a scale envelope for storage. For bullhead,or other substitute species, the dorsal spine (bullhead) will be removed and placed in a scale envelope for storage. If deemed necessary, otoliths will also be removed and placed in glass vials for storage. Record the fish tag number, fish total length, weight, date, and location sampled on the envelope and/or vial.
2) Do not remove the bass or perch skin. Remove brown bullhead skin.

3) Line an examination tray with a clean piece of aluminum foil (shiny side down) and place fish in tray. Make a cut along the ventral midline of the fish from the vent to the base of the jaw.

4) Make a diagonal cut from the base of the cranium just below the gill, to the ventral side just behind the pectoral fin.

5) Remove the flesh and ribcage from one-half of the fish by cutting from the cranium along the spine and dorsal rays to the caudal fin. The ribs should remain on the fillet.

6) Place the fillet on a clean piece of aluminum foil (shiny side down). Wrap the foil and attach an identification label that includes the fish tag number, fish total length, weight, date, and location sampled. Place the wrapped fish in a pre-labeled plastic bag.

Prepare yearling pumpkinseed and other forage fish as whole fish as follows:

1) Remove several scales from fish and place at least 5 scales in a scale envelope. Record the date, time, fish tag number, fish total length, weight, and location sampled on the envelope.

2) For pumpkinseed, place individual fish on a clean piece of aluminum foil (shiny side out). For forage fish, place fish for compositing (grouping fish by size to the extent possible) on the decontaminated foil. Wrap fish in clean foil (shiny side out) and attach an identification label that includes the fish tag number, fish length(s), weight(s), date and location sampled. Place the wrapped fish in a pre-labeled plastic bag.

Transportation

Store fish at a temperature below 4° Celsius and ship immediately to the analytical laboratory, along with all Fish Collection Records, Chain of Custody, and Analysis Request documents.

Record Management

Figures B-4a and b and B-5 provide examples of fish collection field logs and COC documents respectively.

APPENDIX 22

STANDARD OPERATING PROCEDURE

Author: Chad Biski
Reviewed by:

Approved by:

James D. Daly
Assistant Laboratory Director

Northeast Analytical, Inc.
Issuing section: Organic laboratory
NE132_04.DOC
Date: 19-February-2001
Revision Number: 04

1.0 TITLE Standard operating procedures for the tissue reduction/grinding for whole body and filleted fish.

2.0 PURPOSE The purpose of this SOP is to provide procedures required to perform tissue grinding for fish samples.

3.0 SCOPE The methods in this procedure are utilized by Northeast Analytical for whole body and filleted fish samples.

4.0 COMMENT Samples are ground to homogenize the fish prior to soxhlet extraction and analysis for PCBs by SW-846 Method 8082.

5.0 SAFETY

5.1 Safety glasses, lab coat or lab apron, and disposable gloves must be worn when handling chemicals and samples.

5.2 Personnel should familiarize themselves with the necessary safety precautions by reading MSDS information covering any chemicals used to perform SOP.

6.0 REQUIREMENTS

6.1 The chemist must be certified to perform the procedure by an approved instructor.

6.2 Any problems should be brought to the attention of the supervisor and documented on the sample tracking sheet.

7.0 EQUIPMENT

7.1 Instrumentation and materials

7.1.1 Hand operated meat grinder with "fine" grinding attachment. (Eberle #10 grinder or equivalent).

7.1.2 Heavy duty Aluminum foil.

7.1.3 Stainless steel filleting knife.

7.2 Standards and Chemicals

7.2.1 Acetone: High Purity Solvent. Burdick Jackson Baxter (p/n #UN1090).

7.2.2 Alconox soap.

7.3 Glassware and apparatus

7.3.1 Pyrex baking pans (8" x 12").

7.3.2 Appropriate sized glass sample jars with teflon lined caps (4 to 32 oz size).

8.0 PROCEDURE

8.1 Sample Preparation.

8.1.1 All laboratory work surfaces should be decontaminated with Acetone before Initiating these procedures.

8.1.2 Spread Aluminum foil to cover the counter top area of the hoods.

8.1.3 Large whole fish may need to be cut up into smaller pieces before being introduced into the grinding apparatus.

8.1.4 Allow the sample to thaw slightly (slight pliability).

8.1.5 Place the sample in the grinder cup and begin grinding. Collect the reduced sample in a Pyrex pan.

8.1.6 Mix the ground sample with a gloved hand in the Pyrex pan.

8.1.7 Reintroduce the ground sample into the grinding apparatus for a second grinding.

8.1.8 Mix the re-ground sample again in the Pyrex pan and then transfer it to a labeled sample jar of appropriate size.

8.2 Instrument maintenance.

8.2.1 Disassemble the grinder and wash with Alconox soap and water after processing each sample.

8.2.2 Decontaminate all equipment; including the grinder, knives and pyrex pan with Acetone.

8.2.3 Continue with the next sample.

9.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

9.1 Pollution Prevention: see NEA168.SOP

9.2 Waste Management: see NEA054.SOP, NEA083.SOP, and NEA089.SOP

10.0 REFERENCES

10.1 **Guide to Environmental Analytical Methods** 3rd Edition, 1996, by Genium Publishing Corporation, Schenectady, NY 12304.

11.0 ATTACHMENTS

11.1 **Attachment A:** Note pages for analyst.

ATTACHMENT A
NOTES

ATTACHMENT A CONTINUED
NOTES

11 GLOSSARY

None

APPENDIX 23

STANDARD OPERATING PROCEDURE

Author: Thomas E. Herold Jr.
Reviewed by:

William A. Kotas

Approved by:

Robert Wagner
Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Organics
SOP Name: NE017_07.doc
Date: 03/10/2004
Revision: 07

1.0 TITLE Standard Operating Procedure for the extraction and cleanup of polychlorinated biphenyls from fish and biota material by SW-846 Method 3540 (Soxhlet Extraction).

2.0 PURPOSE This SOP provides the method for the extraction of polychlorinated biphenyls from fish tissue for analysis by EPA Method 8082.

3.0 SCOPE The following procedure is used by NEA for the extraction of fish tissue for PCB analysis, although it may be adapted for other biota extractions.

4.0 COMMENTS This method may be restricted to use by or under the supervision of an extraction chemist knowledgeable in the area of extraction and clean-up. The chemist should further be aware of the proper care and handling of PCBs as well.

4.1 Interferences: Laboratory contaminents including phthalate esters may be introduced during extraction and subsequent cleanup procedures. The extraction technician should exercise caution that scrupulously cleaned glassware is used and that plastic tubing and other plastic materials do not contact samples or extracts.

5.0 SAFETY Polychlorinated biphenyls should be treated with extreme caution; as a class of chemical compounds they possess both toxic and suspected carcinogenic properties. The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples.

6.0 REQUIREMENTS The chemist must have an understanding of the methods and requirements of USEPA-SW- 846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3540, 3500, 2500A. An approved instructor must also certify the chemist to perform the procedure. The chemist should have completed an acceptable demonstration of precision and accuracy before performing this method without supervision.

7.0 EQUIPMENT:

7.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO (or equivalent)

7.2 250mL Round Bottom Flask: Pyrex #4100 (or equivalent)

7.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M (or equivalent)

7.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1 (or equivalent)

7.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

7.6 Analytical Balance: Mettler AG-204 (or equivalent) used to determine sample mass.

7.7 Cellulose Extraction Thimble: Contains sample during soxhlet extraction.

7.8 Sodium Sulfate: J.T.Baker, #3375-05 Anhydrous, Granular (12-60 Mesh) (or equivalent). Washed with Dichloromethane and baked overnight at 200^0C. Used for the laboratory method blank.

7.9 Boiling Chips: Chemware PTFE Boiling Stones, P#0919120 (or equivalent)

7.10 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

7.11 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (or equivalent)

7.12 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090. (or equivalent)

7.13 TurboVap Evaporator: Zymark #ZW640-3.

7.14 TurboVap Evaporator concentrator tubes: Zymark 250mL, 0.5mL endpoint.

7.15 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL, used for liquid containment and pipette storage.

7.16 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

7.17 Vials: glass, 8 dram & 4 dram (with polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

7.18 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

7.19 Centrifuge: International Equipment Co., Model CL. (or equivalent)

7.20 Wrist Shaker: Burrell wrist action shaker, Model 75 and 88. (or equivalent)

7.21 Florisil: deactivated, Tested and Approved, see NE095.SOP

7.22 TBA Reagent: Tetrabutylammonium Hydrogen-Sulfite Reagent (prepared in the laboratory)

7.23 Mercury: Triple distilled Mercury Waste Solutions, Inc. (or equivalent)

7.24 Sulfuric Acid: Na_2SO_4 (concentrated) Malinkrodt #2468 #UN1830. (or equivalent)

7.25 Pipettes: S/P Disposable Serological Borosilicate Pipettes.
1. 1mL X 1/10
2. 5mL X 1/10
3. 10mL X 1/10
Fisher Pasteur Borosilicate glass pipette 9" #72050 (or equivalent)

7.26 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL.

7.27 4oz. Jars: Industrial Glassware

7.28 1:1 Magnesium Sulfate/Sodium Sulfate: 50%/50% by volume solvent mixture prepared in the lab.

8.0 PROCEDURES:

8.1 Sample Preparation

8.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

8.1.2 Before any steps are taken, the chemist should first review the sample job folder and review the sample container labels versus the client chain of custody.

8.1.3 The fish samples are usually received as fillets and must be processed to produce a homogenous material prior to extraction. Once the sample has been logged in, the sample is processed according to SOP NE132.SOP.

The sample is then placed in the freezer for storage until the extraction process is begun.

8.2 Procedure: Sample Extraction

8.2.1 Rinse the thimbles with Hexane, allow them to dry out in a pre-cleaned 100mL beaker in a fume hood.

8.2.2 Fill a Pyrex pan with ice cubes and cold water about 1/2 inch deep. As the samples are weighed out, place the beakers in the Pyrex pan to chill for at least 15 minutes prior to the drying step.

8.2.3 Into a pre-cleaned and tared 250mL beaker or 4oz. jar accurately weigh to the nearest 0.0001g, using an analytical balance, about 9-10 grams of tissue with a metal spatula. Record this weight in the laboratory extraction log book. Place the beaker containing the sample into the Pyrex pan to chill. Repeat for remaining samples.
Note: All samples containers are to be returned to the appropriate refrigerator. For all empty containers, see the chemical hygiene plan for proper disposal.

8.2.4 After the sample has been sufficiently chilled, add approximately 10 g. of a 1:1 mix of magnesium sulfate/sodium sulfate to the sample and mix well with the metal spatula. If the sample has not dried after a few minutes, another 10 g. may be added. Once the sample is well-dried and free flowing, transfer the sample to an extraction thimble. Set empty mixing beaker and stirring utensil aside for later rinsing into soxhlet extractor to complete sample transfer.
Note: Be careful not to add too much drying agent to the sample, if too much is added, the sample may not fit completely in the thimble. In this case the sample will have to be split into two separate soxhlets.

8.2.5 Add 200 mL of a 1:1 mixture of Hexane/Acetone to a 250 mL round bottom flask. Add several boiling chips. Place a soxhlet extractor on top of the round bottom flask. Label the round bottom with a sample number and place the corresponding thimble into the soxhlet extractor. Rinse corresponding beaker & metal spatula with a few pipettes of Hexane. Transfer into thimble. Repeat this step twice more with the same sample, and then repeat all preceding steps with remaining samples.
After all samples have been processed add the specified surrogate and matrix spikes required directly into thimble.

8.2.6 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the soxhlet extraction of the sample. Turn on chiller to cool the condensers.

8.2.7 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 5. Double check soxhlets at this time for any cracks or chips, which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

8.2.8 The samples should be extracted overnight for a minimum of 16 hours. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Once cool, rinse the inside of the condensor with several pipette volumes of Hexane. Disengage the soxhlet and condenser unit and rinse the joint off as well into the soxhlet.

8.2.9 Move soxhlet units into a chemical fume hood and flush the remaining solvent from the soxhlet extractor by tipping the soxhlet. Using a pair of long-handled tweezers, pull the thimbles out of the soxhlets one at a time and allow them to drip dry by balancing the thimbles on the tops of the soxhlets. Once dry, remove the thimbles to a Pyrex drying pan for total solvent evaporation.

8.2.10 Rinse the soxhlet with several pipettefull of Hexane and tip again to drain into the round bottom. Set aside the soxhlet at this time. Procure the same number of TurboTubes as there are samples. Using an individual TurboTube stand, label a TurboTube with the corresponding sample ID number and place in the holder. Pour the contents of the round bottom into the TurboTube, using a pipette and Hexane to rinse the last drops out of the mouth of the round bottom. Rinse the round bottom with several pipettefull of Hexane, swirl gently, and decant into same TurboTube. Repeat this step twice for same sample, then repeat all preceding steps for all other samples.

8.2.11 All glassware must be rinsed with technical grade (tech)-Acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

8.3 Solvent Reduction: TurboVap Evaporator System

8.3.1 The TurboVap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus. The TurboVap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

8.3.2 Turn the unit on (switch is located on the back side of the unit) and allow to heat up to the specified temperature for individual solvent use. This is indicated by the "Heating" display light, located above the temperate control knob on the right side of the unit. The system is at the proper temperature when the "At Temperature" light is lit. This is located above the "Heating" display light.

8.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that the gas cylinder valve and gas pressure regulators are both off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty TurboTube

into the water bath and close the lid. Make sure that the nitrogen gas cylinder valve is turned off and slowly turn on the gas pressure regulator. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4 .

8.3.4 Place the TurboTube containing the samples into the TurboVap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

8.3.5 The process for solvent (Hexane/Acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness and PCB loss may occur. Immediately notify a supervisor if an extract is blown to dryness.

8.3.6 Concentrate the solvent to approximately 10 mL. Remove the samples from the TurboVap and place in the rack. The remaining solvent will consist largely of Hexane since the Acetone component is fractionally removed at a faster rate than Hexane; however, a solvent exchange with Hexane should be completed to ensure the Acetone has been entirely removed. Fill the turbo tube back about with approximately 50mls of hexane. Proceed to concentrate the solvent to 10mls. Then remove the turbo tube and place in a rack. NOTE: Not all samples will evaporate at the same rate; sample extracts containing large amounts of petroleum or other non-volatile liquids may stop reducing before the 10.0 mL point is achieved. Samples, which stop reducing, should be removed as soon as possible.

8.3.7 Quantitatively transfer the sample extract with a disposable transfer pipette into an appropriate volumetric flask (25mL for biota extracts) with three 2mL Hexane rinses. After the sample has been transferred, rinse the disposable transfer pipette with 0.5mL of Hexane into the volumetric flask. Add Hexane to the volumetric meniscus mark. Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 8 dram vial.

8.3.8 All dirty glassware must be rinsed with tech-Acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

8.4 Sample Extract Cleanup

Most extracts of environmental samples that are to be analyzed for PCBs by gas chromatography with electron capture detection contain co-extracted xenobiotics and other interfering substances which must be removed before accurate chromatographic analysis can be performed.
Not all clean-up procedures need to be performed on every sample and several are sample matrix specific. The experience of the analyst combined with the sampling site history should guide the selection of which clean-up procedures are necessary. The sample preparation chemist in the extraction logbook records the sequence and number of repeats of cleanup steps performed.
Sample extract cleanups are performed on set volume extracts. The set volume is 25 mL for biota samples.

8.4.0 Sulfuric Acid Wash

8.4.1 The concentrated sulfuric acid treatment removes hydrocarbons and other organic compounds, which are co-extracted with the PCB residues.

8.4.2 Chill the sample to approximately 0^0C. Add 5.0 mL concentrated H_2S0_4 and shake for 30 seconds by hand, centrifuge for approximately 1 minute at a setting of 4, transfer 20mL of the Hexane layer(upper layer) to an 8 dram vial.

8.4.3 Repeat 8.4.2 if the sample extract appears to be heavily loaded (opaque) with colored material. Two to three acid washes may be required. Note: it is entirely possible that all colored material will not be removed from the extract.

8.5.0 Elemental Sulfur Clean-up

8.5.1 Elemental sulfur is soluble in the extract solvents used for biota samples. It is commonly found in many sediment/soil samples, decaying organic material, and some industrial wastes. Large amounts of sulfur can cause the electron capture detector (ECD) to signal saturate for long periods during the elution envelope of PCBs. Even small amounts of sulfur can interfere with PCB measurement as a co-eluting chromatographic peak.

8.5.2 Two techniques exist for the elimination of elemental sulfur in PCB extracts. Mercuric precipitation (Mercury Shake) and the Tetrabutylammonium (TBA) sulfite procedure. Tetrabutylammonium sulfite causes the least amount of degradation of a broad range of pesticides and organics compounds, while mercury may degrade organophosphorus and some organochlorine pesticides. The TBA procedure also has a higher capacity for samples containing high concentrations of elemental sulfur.

8.6.0 Removal of Sulfur Using Mercury

Note: Mercury is a highly toxic metal. All operations involving mercury should be performed within a hood. Prior to using mercury, the chemist should become acquainted with proper handling and emergency spill/clean-up procedures associated with this metal and must have reviewed the material safety data sheet MSDS.

8.6.1 Add 1-3 drops of mercury to the sample extracts, cap, and place on the wrist shaker for 30 min. The sulfur is converted to mercuric sulfide and precipitates out of the sample extract. A black precipitate may be seen in sample extracts containing elemental sulfur.

8.6.2 Remove the sample extracts from the wrist shaker and place in the centrifuge for 2 minutes on speed setting on #4.

8.6.3 Transfer the sample extract to a clean 8 dram vial.

8.6.4 The precipitated sulfur can be removed from the extract by performing a sulfuric acid clean-up or Florisil slurry (discussed in 8.8.0).

8.7 Removal of Sulfur using TBA Sulfite

8.7.1 The TBA procedure removes elemental sulfur by conversion to the thiosulfate ion, which is water soluble.

8.7.2 Add 2.0mL TBA Sulfite Reagent, 1.0 mL 2-propanol, and approximately 3 aliquots (using the dedicated dispenser) of sodium sulfite crystals to the extract and shake for at least 5 minutes on the wrist shaker and observe. An excess of sodium sulfite must remain in the sample extract during the procedure. If the sodium sulfite crystals are entirely consumed add one or two more aliquots to the extract and observe.

8.7.3 Place the samples on the wrist shaker for 45 minutes observing at 15 minute intervals to make sure that the sodium sulfite is not consumed. Add 5mL organic free water and shake for ten minutes.

8.7.4 Place the samples into the centrifuge and spin for approximately 2 minutes on setting #4.

8.7.5 Transfer the Hexane layer to a new 8 dram vial and cap.

8.8 Florisil Adsorption (Slurry)

8.8.1 The Florisil slurry removes co-extracted polar compounds, residual water, and residual acid and is recommended as the final cleanup step before the extract is submitted for GC analysis.

8.8.2 Add approximately 3 grams of tested and approved deactivated Florisil to each vial containing the sample extract.
SEE SUPERVISOR FOR THE APPROPRIATE FLORISIL DEACTIVATION CONCENTRATION TO BE USED.

8.8.3 Vigorously shake the vial for approximately 1 min by hand or on the wrist shaker.

8.8.4 Place the vial(s) into the centrifuge for 2 minutes on setting #4.

8.8.5 Transfer the extract to a clean 8 dram vial.

8.9 Sample Extract Storage

Sample extracts must be protected from light and stored refrigerated at 4°C (±2°C) during the analysis. After analysis is complete, sample extracts will be discarded after 60 days or can be archived in a freezer at less than -20°C for longer periods of time depending on the program requirements. The auto-sampler vial to be used for frozen storage will be filled to the neck of the vial. If the vial cannot be filled to the neck due to multiple analyses being performed, whatever remains will be placed in the vial and the volume marked. The volume level will be marked on all vials.

9.0 Extract Screening and Dilution:

9.1 PCB extracts are generally screened by GC initially to determine the approximate concentration before final analysis. Prior site history and client supplied estimates of sample concentration may be used to determine what, if any, extract dilution is necessary. Extracts of unknown concentration are generally screened at a 10 to 100 fold dilution.

9.2 The supervising chemist is responsible for determining initial screening dilutions. Extract dilutions are prepared by transferring an aliquot of the original sample extract into a vial containing the correct amount of "make up" volume of Hexane. For example, adding 1.0 mL of the extract to 9.0 mL Hexane performs a 1 to 10 dilution. The vial containing the diluted extract is labeled denoting the equivalent extract volume after the dilution; e.g. a 25mL extract diluted 1 to 10 is labeled "250X", an undiluted 25mL extract is labeled "25X".
When high dilutions are prepared, secondary (serial) dilutions of the initial diluent are prepared; e.g. a 100 fold dilution is prepared by a 1 to 10 dilution of the initial extract, then a 1 to 10 dilution of the resulting diluent.

9.3 Perform the dilution using an appropriate disposable volumetric pipette to transfer the extract and the make-up volume of Hexane. Make sure that the vial is properly labeled. Cap and invert the vial at least three times to thoroughly mix the extract with the solvent.

9.4 Transfer 1 mL of the extract to a labeled 1.5 mL GC autosampler vial. Record the screening dilution on the GC Queue Lab Sheet (Lotus-123 spreadsheet) along with the extract volume, and the sample mass. Submit the GC Queue Lab Sheet with the sample extracts to the GC analyst.

10.0 Pollution Prevention and Waste Management

10.1 Pollution Prevention: see NEA.168.SOP

10.2 Waste Management: see NEA054.SOP, NEA083.SOP, and NEA089.SOP

11.0 References

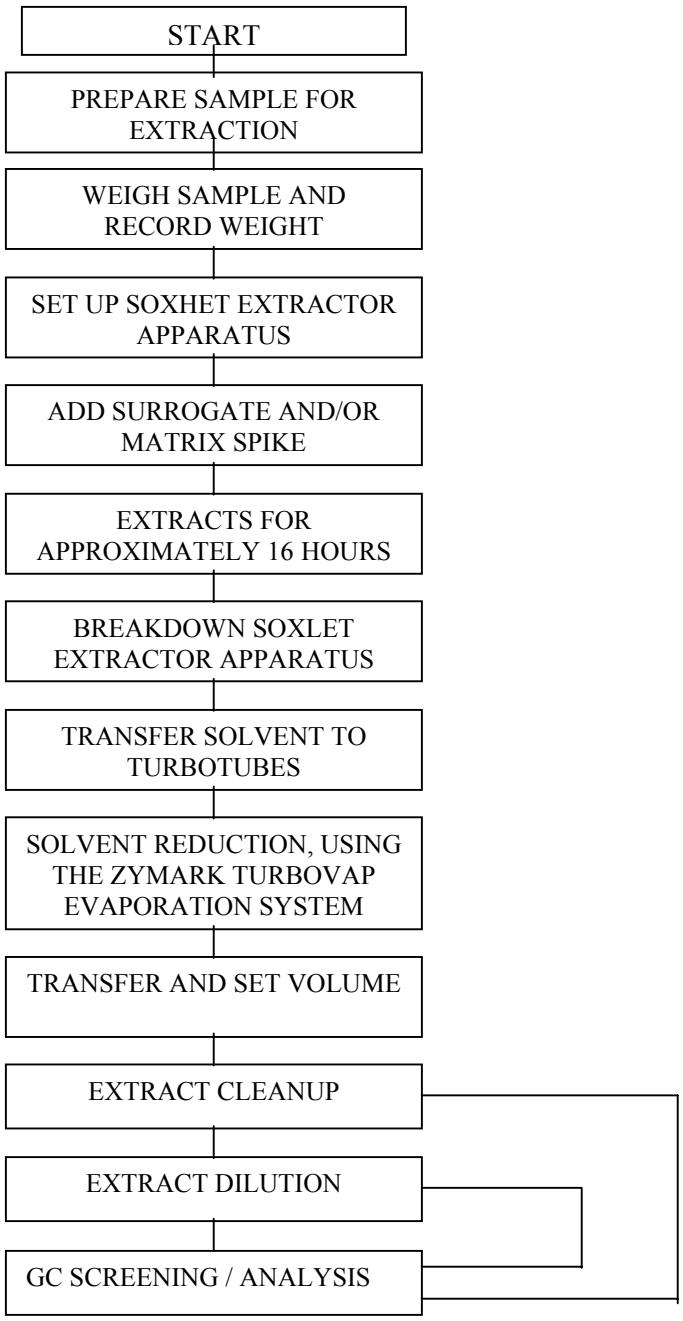
1. SW-846 methods 3500A & 3600A; United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Vol.1B, Cincinnati, OH 45268.

2. Guide to Environmental Analytical Methods, Genium Publishing Corporation, Schenectady, NY 12304.

12.0 Attachments

1. Method flow chart
2. Note page for analyst

PCBs IN FISH TISSUE/BIOTA
SOXHLET EXTRACTION/TURBO VAP EVAPORATOR



APPENDIX 24

STANDARD OPERATING PROCEDURE

Author: Chad Biski
Reviewed by:

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William A. Kotas

Approved by:

_____
James D. Daly
Assistant Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Organics
SOP Name: NE158_3.DOC
Date: 13-February-2001
Revision: 03

1.0 TITLE Standard Operating Procedure for the extraction of lipids from fish and biota material.

2.0 PURPOSE This SOP provides the method for the extraction of lipids from fish tissue.

3.0 SCOPE The following procedure is used by NEA for the extraction of fish tissue for lipid analysis, though it may in part be adapted for other biota extractions.

4.0 COMMENTS

This method may be restricted to use by or under the supervision of a chemist knowledgeable in the area of sample extraction and clean-up. The chemist should further be aware of the proper care and handling of Polychlorinated Biphenyls (PCBs) as well.

5.0 SAFETY Polychlorinated biphenyls should be treated with extreme caution; as a class of chemical compounds they possess both toxic and carcinogenic properties. The chemist should have received in-house safety training and should know the location of first aid equipment and the emergency spill/clean-up equipment, before handling any apparatus or equipment. Safety glasses and gloves must be worn when handling glassware and samples.

6.0 REQUIREMENTS

The chemist must have an understanding of the methods and requirements of USEPA-SW-846A "Test Methods for Solid Wastes" Volume 1B: Lab Manual, 3rd edition. Methods 3540, 3500, 2500A. The chemist must also be certified to perform the procedure by an approved instructor.

7.0 EQUIPMENT

7.1 Water Cooled Condenser: Pyrex 45/50 #3840-MCO.
7.2 250mL Round Bottom Flask: Pyrex #4100.

7.3 Soxhlet Repetitive Flushing (reflux) Unit: 45/50 Pyrex #3740-M.

7.4 Heating Mantle: Type "VF" laboratory heating mantle #HM0250VF1. (Or equivalent)

7.5 Heating Mantle Controller: Glass-Col #PL3122 Minitwin (or equivalent) regulates temperature control of the mantle.

7.6 Analytical Balance: Mettler ER-180A used to determine sample mass.

7.7 Cellulose Extraction Thimble: Contains sample during soxhlet extraction.

7.8 Sodium Sulfate: J.T. Baker #3375-05 Anhydrous, Granular (12-60 Mesh). Washed with dichloromethane and baked overnight at 200 C. Used for the laboratory method blank.

7.9 Boiling Chips: Chemware PTFE Boiling Stones P#0919120 (or equivalent)

7.10 Chiller: Pump driven water circulating cooling system cool flow #75 NESLABS Instruments, Inc. (or equivalent)

7.11 Hexane: High Purity Solvent Baxter (Burdick/Jackson) #UN1208. (Or equivalent)

7.12 Acetone: High Purity Solvent Baxter (Burdick/Jackson) #UN1090. (Or equivalent)

7.13 Turbo Vap Evaporator: Zymark #ZW640-3.

7.14 Turbo Vap Evaporator concentrator tubes: Zymark 250mL, 0.5mL endpoint.

7.15 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL, used for liquid containment and pipet storage.

7.16 1:1 Hexane/Acetone: 50%/50% by volume solvent mixture prepared in the lab.

7.17 Vials: glass, 8 dram & 4-dram (with polyseal sealed cap) (20 mL & 10 mL) capacity, for sample extracts.

7.18 Vial Rack: Plastic rack used to hold vials, during all phases of the extract processing.

7.19 Pipets: S/P Disposable Serological Borosilicate Pipets.

1. 1mL X 1/10
2. 5mL X 1/10
3. 10mL X 1/10
4. Fisher Pasteur Borosilicate glass pipet 9" (or equivalent)

7.20 Beakers: Assorted Pyrex: 250mL, 600mL, and 1000mL.

7.21 Weighing Boats: Tin weighing boats for percent lipid weight determination.

7.22 Metal spatula.

7.23 4oz. Jars: Industrial Glassware

8.0 PROCEDURES

8.1 Sample Preparation

8.1.1 Throughout the entire process it should be noted that if the chemist encounters any problems or difficulties with any samples or steps involved, all work should STOP! Any problems should be brought to the attention of the supervisor and documented in the extraction logbook.

8.1.2 Before any steps are taken, the chemist should first review the sample job folder and fill in the appropriate spaces on the internal sample tracking form and initial.

8.1.3 The fish samples are usually received as fillets and must be processed to produce a homogenous material prior to extraction. Once the sample has been processed, the sample is cut up into small enough pieces to fit into a standard manual meat grinder. An acetone rinsed Pyrex tray should be placed under the grinder exit to catch the minced tissue. After the fish has been ground once, it should be ground again to ensure complete homogenization of the sample. The ground fish is then placed into an appropriate-sized jar and labeled. The sample is then placed in the freezer for storage until the extraction process is begun.

8.2 Procedure: Sample Extraction

8.2.1 Rinse the thimbles with hexane, allow them to dry out in a pre-cleaned 100mL beaker in a fume hood.

8.2.2 Fill a Pyrex pan with ice cubes and cold water about 1/2 inch deep. As the samples are weighed out, place the beakers in the Pyrex pan to chill for at least 15 minutes prior to the drying step.

8.2.3 Into a pre-cleaned and tared 300mL beaker accurately weigh to the nearest 0.0001g using an analytical balance about 10 grams of tissue. Record this weight in the laboratory extraction logbook. Place the beaker containing the sample into the Pyrex pan to chill. Repeat for remaining samples.

NOTE: ALL SAMPLE CONTAINERS ARE TO BE RETURNED TO THE APPROPRIATE REFRIDGERATOR. FOR ALL EMPTY SAMPLES CONTAINERS, SEE THE CHEMICAL HYGIENE PLAN FOR PROPER DISPOSAL.

8.2.4 After the sample has been sufficiently chilled, add approximately 10 g. of a 1:1 mix of magnesium sulfate/sodium sulfate to the sample and mix well with a clean metal spatula. If the sample has not dried after a few minutes, another 10 g. may be added. Once the sample is well dried and free flowing, transfer the sample to an extraction thimble. Repeat with remaining samples. Set empty mixing beaker and stirring utensil aside for later rinsing into soxhlet extractor to complete sample transfer. **Be careful not to add too much drying agent to the sample; if too much is added, the sample may not fit completely in the thimble. In this case the sample will have to be split into two different soxhlets.**

8.2.5 Add 200 mL of a 1:1 mixture of hexane/acetone to a 250 mL round bottom flask. Add several boiling chips. Place a soxhlet extractor on top of the round bottom flask. Label the round bottom with a sample number and use a pair of long-handled tweezers to place the corresponding thimble into the soxhlet extractor. Rinse corresponding beaker & metal spatula with a few pipets of hexane. Transfer into thimble. Repeat this step twice more with the same sample, and then repeat all preceding steps with remaining samples. After all samples have been processed add the specified surrogate and matrix spikes required

directly into thimble.

8.2.6 Rinse the inside and the outside connecting joints of the condenser units that will be used to condense the extraction solvent during the soxhlet extraction of the sample. Turn on chiller to cool the condensers.

8.2.7 Place the round bottom flask with attached soxhlet extractor onto a heating mantle and attach condenser unit. Turn corresponding thermostats on to setting 5. Double check soxhlets at this time for any cracks or chips which may leak solvent. Once the solvent begins to boil, a flushing action of once every two to three minutes should be achieved.

8.2.8 The samples should be extracted overnight for a minimum of 16 hours. Once the sample has finished extracting (usually in the morning), turn the heating mantle off and allow samples to cool to room temperature. Once cool, rinse the inside of the condenser with several pipette volumes of hexane. Disengage the soxhlet and condenser unit and rinse the joint off as well into the soxhlet.

8.2.9 Move soxhlet units into a chemical fume hood and flush the remaining solvent from the soxhlet extractor by tipping the soxhlet. Using a pair of long-handled tweezers, pull the thimbles out of the soxhlets one at a time and allow them to drip dry by balancing the thimbles on the tops of the soxhlets. Once dry, remove the thimbles to a Pyrex drying pan for total solvent evaporation.

8.2.10 Rinse the soxhlet with several pipetfuls of hexane and tip again to drain into the round bottom. Set aside the soxhlet at this time. Procure the same number of turbo tubes as there are samples. Using an individual turbotube stand, label a turbotube with the corresponding sample ID number and place in the holder. Pour the contents of the round bottom into the turbotube, using a pipette and hexane to rinse the last drop out of the mouth of the round bottom. Rinse the round bottom with several pipetfuls of hexane, swirl gently, and decant into same turbo tube. Repeat this step twice for same sample, and then repeat all preceding steps for all other samples.

8.2.11 All glassware must be rinsed with technical grade (tech)-acetone or a "for rinsing-only" labeled solvent, and dried in the hood before other cleaning steps.

8.3 Solvent Reduction: TurboVap Evaporator System

8.3.1 The Turbovap evaporator system is used in place of the Kuderna Danish (KD)-concentrator apparatus.

The turbovap uses a heated water bath and positive pressure nitrogen flow/vortex action. The unit maintains a slight equilibrium imbalance between the liquid and gaseous phase of the solvent extract, which allows fractional reduction of the solvents without loss of higher boiling point analytes.

8.3.2 Turn the unit on (switch is located on the backside of the unit) and allow to heat up to the specified temperature for individual solvent use. This is indicated by the "Heating" display light, located above the temperate control knob on the right side of the unit. The system is at the proper temperature when the "At Temperature" light is lit. This is located above the "Heating" display light. The temperature of the unit should be set at 38 ± 2°C.

8.3.3 As a precaution the TurboVap system regulators should be checked to assure that no residual gas pressure remains within the system and that the gas cylinder valve and gas pressure regulators are both off before placing samples in the apparatus. Residual gas pressure may cause splashing and cross contamination of samples. To bleed the system of residual gas pressure place an empty turbo tube into the water bath and close the lid. Make sure that the nitrogen gas cylinder valve is turned off and slowly turn on the gas pressure regulator. Bleed any residual gas until the regulator output pressure gauge reads "0" psi. Proceed to 8.3.4.

8.3.4 Place the turbo tube containing the samples into the Turbovap and close the lid. Turn on the gas cylinder valve first and then begin slowly turning the pressure regulator on. Keep the gas pressure very low, until the solvent level is decreased, to avoid splashing. Increase the gas pressure as the sample reduces maintaining uniform flow throughout the reduction.

8.3.5 The process for solvent (hexane/acetone) reduction takes approximately 20-30 minutes. Do not leave the unit unattended as extracts may be blown to dryness.

8.3.6 Concentrate the solvent to approximately 10.0 mL. Remove the samples from the turbovap and place in the rack. The remaining solvent will consist largely of hexane since the acetone component is fractionally removed at a faster rate than hexane; however, a solvent exchange with hexane should be completed by filling the turbo tube up with approximately 50mls of hexane and concentrating back down to 10.0mls to ensure the acetone has been entirely removed.

NOTE: Not all samples will evaporate at the same rate; sample extracts containing large amounts of lipids or other non-volatile liquids may stop reducing before the 10.0 mL point is achieved. Samples that stop reducing should be removed as soon as possible.

8.3.7 Quantitatively transfer the sample extract with a disposable transfer pipette into an appropriate volumetric flask (25mL for biota extracts) with three 2mL hexane rinses. After the sample has been transferred, rinse the disposable transfer pipet with 0.5mL of hexane into the volumetric flask. Add hexane to the volumetric meniscus mark. Invert the volumetric flask at least three times to mix completely. Decant the contents into a pre-labeled 8-dram vial.

8.3.8 All dirty glassware must be rinsed with tech-acetone or a "For Rinsing-Only" labeled solvent and dried in the fume hood before being washed.

8.4 Sample Extract concentration

NOTE NO CLEAN-UP STEPS ARE PERFORMED FOR PERCENT LIPID DETERMINATION.

8.4.1 Weigh a pre-labeled tin weighing boat for each sample extract. Record the weight in the percent lipid log book. Place the weighing boat into the desicator for 1 hour.

8.4.2 Using a 10mL pipet, transfer 10mL of the extract into the corresponding weighing boat.

8.4.3 Concentrate the extract in the weighing boat using the nitrogen micro-blowdown. Place a maximum of 3 weighing boats at one time on the nitrogen blow down. Set the temperature at 40C and the pressure at 40 PSI.

8.4.4 After concentration has been completed, place the weighing boats into the desicator for 1 hour.

8.4.5 Weigh sample weighing boats and record the weight in the percent lipid logbook.

8.4.6 Calculate percent lipids as follows:

$$\text{PERCENT LIPIDS} = \frac{Vf - Ve \times 2.5 \times 100}{\text{Sample weight (g)}}$$

Vf = weight of tin tray with sample (g)
Ve = weight of empty tin tray (g)

9.0 Pollution Prevention and Waste Management

9.1 Pollution Prevention: see NEA168.SOP

9.2 Waste Management: see NEA054.SOP, NEA083.SOP, and NEA089.SOP

10.0 References

10.1 SW-846 methods 3500A & 3600A; United States Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Vol.1B, Cincinnati, OH 45268.

10.2 Guide to Environmental Analytical Methods, Genium Publishing Corporation, Schenectady, NY 12304.

11.0 Attachments

11.1 Note page for analyst

Note Page For Analyst

APPENDIX 25

STANDARD OPERATING PROCEDURE

Author: Anthony J. Maiello
Reviewed by:

William A. Kotas
QA Officer

Approved by:

Robert E. Wagner
Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Organics Lab
SOP Name:NE148_04.SOP
Date:10-April-2002
Revision:04

1.0 Title: **Northeast Analytical, Inc. SW 846 Method 8082-PCB Capillary Column**

Standard operating procedure for the analysis of Polychlorinated Biphenyls by Gas Chromatography with Electron Capture Detection and Total Aroclor Quantification.

2.0 Purpose

The purpose of this SOP is to provide a detailed written document for measurement of Polychlorinated Biphenyls (PCBs) according to SW-846 Method 8082 specifications.

3.0 Scope

3.1 This SOP is applicable in the determination and quantification of PCBs as outlined in EPA SW-846 Method 8082. It is applicable to the following matrices: water, soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, and tissue samples.

3.2 The following compounds can be determined by this method:

Compound	CAS Number
Aroclor 1016	12674-11-2
Aroclor-1221	1104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6

Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

3.3 In general, samples are extracted, or in the case of oils and waste solvents diluted, with a pesticide grade solvent. The extracts are further processed by concentrating or diluting, depending on the PCB concentration, and carried through a series of clean-up techniques. The sample is then analyzed by injecting onto a gas chromatographic system and detected by an electron capture detector.

3.4 This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of PCBs by gas chromatography. Each matrix requires different sample handling or special preparation procedures before analysis can be performed. Each sample will be covered separately in the extraction standard operating procedures.

4.0 Comments

4.1 One of the major sources of interference in the analysis of PCBs is that organochlorine pesticides are co-extracted from the samples. Several of the commonly found pesticides and associated degradation products (DDT, DDE, DDD) overlap the PCB profile envelope and co-elute with several PCB GC peaks and therefore cannot be accurately measured. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in the total PCB values generated.

4.2 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in PCB quantification.

5.0 Safety

5.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

5.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. The analyst should minimize manipulation of sample extracts outside of a fume hood.

5.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process

samples. The analyst should refer to the laboratory chemical hygiene plan for further safety information.

5.4 Samples remaining after analysis should be either returned to the customer for disposal or disposed of through the laboratory's disposal plan. Refer to the sample custodian for assistance in this matter and also standard operating procedure NEO54, disposal of laboratory waste.

6.0 Requirements

6.1 Extensive knowledge of this standard operating procedure and EPA SW-846 Method 8082 is required.

6.2 The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

7.0 Equipment

7.1 Instrumentation

7.1.1 Gas chromatograph: Varian Model 3400, equipped with Model 1077 split/splitless injector, temperature programmable oven, electron capture detector, Model 8100 autosampler.

7.1.2 Chromatograph Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates), will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

7.2 Glassware and Accessories

7.2.1 25 mL volummetric flasks, Class A, acid washed, (Baxter Cat. No. F4635-25)

7.2.2 5 mL volummetric flasks, Class A, acid washed (Baxter Cat. No. F4635-5)

7.2.3 10 mL volummetric flasks, Class A, acid washed (Baxter Cat. No. F 4635-10)

7.2.4 50 mL volummetric flasks, Class A, acid washed (Baxter Cat. No. F4635-50)

7.2.5 100 mL volummetric flasks, Class A, acid washed (Baxter Cat. No. F4635-100)

7.2.6 4 dram vials for sample extract storage (Kimble Opticlear, part no. 60910, code no. 60910-4)

7.2.7 8 dram vials for sample extract storage (Kimble Opticlear, part no. 60910, code no. 60910-8)

7.2.8 Pasteur pipettes (Kimble, part no. 72050)

7.2.9 250 mL beakers, glass (Baxter Cat. No. B2650-250)

7.2.10 100 mL beakers, glass (Baxter Cat. No. B2650-100)

7.2.11 Disposable 10 mL pipettes (Baxter P4650-110)

7.2.12 Disposable 5 mL pipettes (Baxter P4650-15)

7.2.13 Disposable 1.0 mL pipette (Baxter P4650-11X)

7.3 Chemicals

7.3.1 Hexane, Burdick and Jackson, (Cat.No. 216-4)

7.3.2 Acetone, Burdick and Jackson, (Cat.No.010-4)

7.3.3 Toluene, Baker, (Cat.No. 9336-03)

7.3.4 Methylene Chloride, Burdick and Jackson, (Cat. No. 300-4)

7.4 Analytical Standard Solutions

7.4.1 Aroclor Stock Standard Solutions

7.4.1.1 Polychlorinated Biphenyls - Neat commercial material for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials

that were used in products such as electric power transformers and capacitors.

7.4.1.2 Stock standards are prepared from individual Aroclor formulations by weighing an exact amount of the neat material to the nearest 0.1 mg, and dissolving and diluting to volume in a 100 mL volumetric flask with hexane. See Attachment A, Table 1 for exact weights of each compound. For DCBP, dissolve neat formulation in 10 mL of toluene and then transfer to a 100 mL volumetric flask bringing to volume with hexane.

7.4.1.3 The stock standards are transferred into Boston bottles and stored in a refrigerator at 0-6°C, protected from light.

7.4.1.4 Stock PCB standards must be replaced after one year, or sooner if comparison with certified check standards indicate a problem. See 8.5.3 for limits.

7.4.1.5 For quality control and general labeling requirements refer to standard operating procedure NE050, Preparation of Standards.

7.4.2 Calibration Standards

7.4.2.1 Calibration standards are prepared at five concentration levels using a prepared working standard. See Attachment A, Table 2 for the preparation and exact concentrations of the working standards. The following five standards make up the initial calibration curve standard set: 20 ng/mL, 100 ng/mL, 250 ng/mL, 500 ng/mL, 1000 ng/mL.

7.4.2.2 The two surrogates TCMX and DCBP are included in the A1254 calibration standards. The stock standard for TCMX is prepared by diluting 1 mL of TCMX solution (ULTRA, cat. #IST-440, at 2000 ug/mL) into a 100 mL volumetric flask resulting in a solution of TCMX at 20 PPM.

7.4.2.3 To prepare the working surrogate standard, pipet 5.0 mL of the 100ppm DCBP stock standard and 2.5 mL of the 20ppm TCMX stock standard into a 100 mL volumetric flask and bring to volume with hexane.
The final concentration of this solution will be 5.0ppm of DCBP and 0.5ppm of TCMX.

7.4.2.4 Refer to Attachment A, Table 4 for instructions on preparation of the calibration standards containing A1254 and the surrogates. Refer to Attachment A, Table 3 for

instructions on preparing the remaining calibration standards.

7.4.2.5 Transfer all calibration standards to 8 dram vials and store in a refrigerator at 0-6°C, protected from light. Calibration standards must be replaced after six months, or sooner, if comparison with check standards indicates a problem. See 8.5.3 for limits.

7.4.3 Continuing Calibration Standards

7.4.3.1 Continuing calibration check standards are prepared independently from calibration standards, by using an alternate source purchased from standard vendors. Refer to Attachment B, Tables 1-3 for instructions on preparation of these standards.

8.0 Procedure

8.1 Gas Chromatographic Operating Conditions

8.1.1 Establish the gas chromatograph (GC) operating parameters as follows:

Autosampler parameters: Multi-vial mode, ECD Attenuation and range are 1.

Refer to Attachment C for all other GC operating procedures.

Note: GC helium gas flow is optimized after instrument maintenance by adjusting nitrogen flow to elute a PCB calibration standard to a known retention time.

8.2 Data Acquisition

8.2.1 Chromatographic information will be collected and processed utilizing a computer based data acquisition workstation (Waters Associates, Millennium_32 computer network based workstation) The GC workstation acquires the millivolt detector signal, performs an analog to digital conversion and stores the digital chromatogram on the computer network's disk. The chromatography software performs all data reduction including, long term data storage on magnetic media, chromatographic peak integration, all calculations, report generation, chromatogram plots, and calibration functions.

8.3 Initial GC Calibration

8.3.1 GC calibration will be performed by the external calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

8.3.2 Establish the gas chromatographic operating parameters outlined in Section 8.1 and prepare the calibration standards at the five concentrations outlined in Section 7.4.2.

8.3.3 Inject each calibration standard using the GC autosampler and the parameters outlined in section 8.1, which are those used for actual samples.

8.3.4 For each Aroclor, 5 peaks are selected to prepare calibration curves. The peaks selected from the multi-component Aroclor formulations were based on maximizing the separation for each Aroclor (i.e., minimizing peak overlap in retention time). Consideration was also given to selecting peaks that normally did not have problems with co-elution with interfering peaks or possible co-elution with organochlorine pesticides. The determined area of the five peaks selected for calibration is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The following table lists the Aroclors that are included in the initial calibration and group number for calibration purpose.

Aroclor	Group Number
A1221	1
A1232	2
A1016	3
A1242	4
A1248	5
A1254	6
A1260	7

8.3.5 Attachment D is an example of chromatograms of standards of each Aroclor for a DB5-MS column with peaks selected for calibration labeled.

8.3.6 For the initial calibration curve to be considered valid, the percent relative standard deviation must be less than 20% over the working range. The calibration curve is used for quantification in every case and is not replaced with the average calibration factor. See attachment E

for an example of response factors and the calculation of the percent relative standard deviation.

8.4 Retention Time Windows

8.4.1 The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Make three injections of each Aroclor at a midlevel concentration throughout a minimum 72-hour time period.

8.4.2 For the 5 peaks selected for calibration of each Aroclor, calculate the standard deviation resulting from the variation in the three retention times for that peak.

8.4.3 The retention time window is defined as plus or minus three times the standard deviation of the three retention time determinations.

8.4.4 If the standard deviation of the selected peak is zero, the standard deviation of the peak eluting after it is used. If it is the last eluting peak that has zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

8.4.5 Retention time windows established in section 8.4.3 to 8.4.4 may not be practical when samples containing matrix interferences are injected onto the GC column. The default R.T. Window of +/- 0.07 minutes is employed when the established windows are too narrow. Besides using retention time windows to assign peaks for quantification, the analyst should rely on their experience in pattern recognition of multi-response chromatographic response exhibited by PCB Aroclors.

8.4.6 Attachment F provides examples of calculated retention time windows generated by the above outlined procedures.

8.5 Gas Chromatographic Analysis

8.5.1 Prior to conducting any analyses on samples, calibrate the system as specified in Section 8.3

8.5.2 To start an analytical sequence, the 500 ppb calibration standard is injected and analyzed for the seven Aroclors that the system is calibrated for, if more than 24-hours has elapsed since the last valid continuing calibration check standard. If less than 24-hours has elapsed since the last valid continuing calibration check standard,

select one 500 ppb continuing calibration check standard. Selection of the continuing calibration check standard should be based on anticipated Aroclor contamination that the samples may exhibit. Selection of the continuing calibration check standard should also be alternated among the seven Aroclors.

8.5.3 The calculated value for the continuing calibration check standard must be ±15% for it to be valid and analysis to proceed. If this criterion is exceeded, the analyst should inspect the system to determine the cause and perform maintenance as necessary. The system can then be recalibrated and sample analysis can proceed. Note that all samples which are not bracketed by valid check standards must be re-analyzed when the system is in-control.

8.5.4 The daily retention time windows must be established. Use the retention time for the selected 5 peaks of the continuing calibration check standard as the midpoint of the window for that day. If all seven Aroclors were analyzed as the initial continuing calibration check standard, then establish retention time windows using the retention time plus or minus the windows established in Section 8.4. If only one Aroclor was analyzed as the continuing calibration check standard (i.e., less than 24-hours had elapsed), use the retention time from this standard as the midpoint plus or minus the windows established in Section 8.4. to establish the daily retention time windows. For the remaining six Aroclors, go back to the previous time all seven Aroclors were analyzed as the initial calibration check standards and use those retention times plus or minus the windows established in Section 8.4 to develop daily retention time windows.

8.5.6 All succeeding continuing calibration check standards analyzed during an analysis sequence must also have a percent difference of 15% or less when compared to the initial calibration generated from the 5 point calibration curve.

8.5.7 All succeeding standards in an analysis sequence should exhibit retention times that fall within the daily retention time window established by the first continuing calibration check standard(s) of that analytical sequence. If the retention times are outside the established windows instrument maintenance must be

performed and recalibration may be required.

8.5.8 The following is the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run every tenth injection in the analytical sequence. All analytical sequences must end with a continuing calibration check standard regardless of the number of samples analyzed.

ANALYTICAL SEQUENCE

INJECTION	MATERIAL INJECTED
1	Hexane Blank
2-36	Initial Calibration Standards
37-43	Continuing Calibration Check Standard
44-52	Samples analyses, including method blanks, matrix spikes, matrix duplicates, matrix spike duplicates, and QC reference check standard. A maximum of 9 samples between continuing calibration check standards.
53	Continuing calibration check standard
54 and higher	repeat inject. 44-53 sequence

8.6 Quality Control

8.6.1 This section outlines the necessary quality control samples that need to be instituted at the time of sample extraction. The data from these quality control samples is maintained to document the quality of the data generated.

8.6.2 Each analyst must demonstrate competence in accuracy and precision on quality control samples before beginning analysis on samples. This demonstration must be on-going and be repeated if there is any modification to the method.

8.6.3 With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples an organic-free reagent water blank is processed. For soil, sediment, and solid waste samples, a laboratory sodium sulfate blank is processed. For fish and other biota samples, a sodium sulfate blank is processed. For oil samples, a PCB-free blank control oil is processed.

8.6.4 The method blank must exhibit PCB levels less than the matrix defined practical quantification limit (PQL). If the method blank exhibits PCB contamination above the reportable PQL, the samples associated with the contaminated blank should be re-extracted and analysis repeated. If there is no original sample available for re-extraction, then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank out of criteria.

8.6.5 A matrix spike is to be analyzed at a rate of 1 matrix spike per every 20 samples. Also a matrix spike duplicate or duplicate sample is to be analyzed at a rate of 1 per every 20 samples. Duplicate samples may be appropriate in place of matrix spike duplicates, for soil and waste samples, where detectable amounts of organics are present.

8.6.6 Analyze one unspiked and one spiked sample. Calculate the percent recovery based on Aroclor concentration of both samples as follows:
A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike
Percent Recovery (p) = 100 (A-B) %/T

Compare the percent recovery calculated with the lab established limits or the default limits of 70-130% if lab limits are not available. If the concentrations of the matrix spikes are *greater* than five times the calculated sample amount then the quality control limits should be applied. If the concentrations of the matrix spikes are *less* than five times the sample than there are no established limits applicable. If the percent recovery falls outside the acceptance range for the given Aroclor used as the spiking analyte, then the matrix spike recovery failed the acceptance criteria. Inform quality

control manager and document matrix spike recoveries.

A relative percent difference (RPD) must also be calculated on the matrix spike set recoveries. This is calculated as follows:

A = % recovery of matrix spike sample
B = % recovery of matrix spike duplicate sample

RPD = [(A-B)/{(A+B)/2}] x 100
where (A-B) *is taken as an absolute value*

If the concentrations of the matrix spike set are *greater* Than five times the calculated PQL then an RPD of twenty percent or less is acceptable. If the concentrations of the matrix spike set are *less* than five times the PQL than there are no established limits applicable to the RPD.

8.6.7 A QC reference check standard (laboratory control spike sample) is also prepared and analyzed. Spike one liter of laboratory organic free water, extract, and analyze. Calculate the percent recovery for the Aroclor spike and compare to the lab established limits or the default limits of 70-130% if lab limits are not available. If the percent recovery for the QC reference check standard (laboratory control spike sample) is out of criteria, the analysis is out of the control for that analyte and the problem should be immediately corrected. The entire batch of samples will need to be re-extracted and re-run.

8.6.8 Method accuracy, based on matrix spike data, is maintained by the laboratory as part of the QC program. For each sample matrix, upper and lower warning and control limits for method performance are established.

8.6.9 Surrogate compounds are added to each sample, matrix spike, matrix spike duplicates, duplicate, method blank, and QC reference check standard (laboratory control spike sample) at time of extraction. Surrogate compounds chosen for this method are tetra-chloro-meta-xylene (TCMX) and decachlorobiphenyl (DCB). The following are typical surrogate amounts added to normal encountered matrices. These amounts may be adjusted by the analyst, if PCB background levels are high and surrogates are being diluted out of analysis range.

Water: 1.0 mL of 0.05ppm TCMX/0.5ppm DCB
Soil & Sediment: 0.5 mL of 0.5ppm TCMX/5.0ppm DCB
Oil: 0.5 mL of 0.5ppm TCMX/5.0ppm DCB
Wipes: 0.5 mL of 0.5ppm TCMX/5.0ppm DCB

8.6.10 Surrogate percent recovery data for each matrix is tabulated as part of the on-going laboratory QC program. The standard deviation is calculated once enough surrogate data is available for each matrix, typically based on 25 to 30 samples. Upper and lower warning limits (p ± 2SD) and upper and lower control limits (p ± 3SD) are established.

8.6.11 Only one surrogate analyte needs to meet established control limits for the analysis to be valid. The data is compared to the lab established limits or the default limits of 70-130% if lab limits are not available. If percent surrogate recovery is not within limits for either surrogate, the following steps are required.

8.6.11.1 Review calculations that were used to generate surrogate percent recovery values to make certain there are no errors.

8.6.11.2 Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

8.6.11.3 Re-analyze the extracts that did not meet control limits, either at the previously analyzed dilution or at a more dilute level to assess if the sample matrix interfered with surrogate measurement.

8.6.11.4 If the above steps do not give satisfactory results, re-extract and re-analyze the sample. Report this data if surrogate recovery is within limits. If surrogate percent recovery is out of limits for the re-extracted samples, low or high surrogate recovery is due to matrix affects and the data can be reported as estimated and the data user is notified in the form of a case narrative.

9.0 References

9.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update, December 1996.

9.2 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants", July 1988.

9.3 Standard Methods for the Examination of Water and Waste Water, 18th Edition 1992, American Public Health Association, American Water Works Association, Water Pollution Control Federation.

9.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual", Wadsworth Center for laboratories and Research, 1988, updated 1998.

9.5 "Guide to Environmental Analytical Methods", fourth edition, Genium Publishing Corporation, 1998.

10.0 Attachments

10.1 Attachment A: PCB Standards Preparation Tables

10.2 Attachment B: PCB Continuing Calibration Tables

10.3 Attachment C: GC Operating Procedures

10.4 Attachment D: Chromatograms of PCB standards.

10.5 Attachment E: Response Factor Calculation.

10.6 Attachment F: Retention Time Windows

11.0 Glossary

Accuracy: Accuracy means the nearness of a result or the mean (±) of a set of results to the true value. Accuracy is assessed by analysis of reference samples and percent recoveries.

Analytical Batch: The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples which are analyzed together whereas the sample method sequence, the reagent lots, and manipulations are common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. ground water, sludge, ash, etc.).

Aroclor: Polychlorinated biphenyls (PCBs) were commercially produced for a variety of uses including, transformers,

capacitors, inks, paints, dedusting agents, and pesticides to list several. Monsanto Corporation was a major producer and sold PCBs under the trade name Aroclor.

Blank: A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix, however, a universal blank matrix does not exist for solid samples so sodium sulfate is used as a blank matrix. The blank is taken through the appropriate steps of the process. A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field in sealed containers and transported back to the laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

Calibration Check Standard: Standard used to determine the state of calibration of an instrument between periodic recalibration. A calibration check is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

CAS Number: An assigned number used to identify a chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts. Sequentially assigned CAS numbers identify specific chemicals, except when followed by an asterisk (*) which signifies a compound (often naturally occurring) of variable composition. The numbers have no chemical significance. The CAS number is a concise, unique means of material identification. (Chemical Abstracts Service, Division of American Chemical Society, Box 3012, Columbus, OH 43210:[614] 447-3600.)

Laboratory Control Spike: A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method is called a check sample. The level of the spike shall be at the regulatory

action level when applicable. Otherwise, the spike shall be at 5 times the estimate of the quantification limit. The matrix used shall be phase matched with the samples and well characterized: for example, reagent grade water is appropriate for an aqueous sample.

Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Environmental Sample: An environmental sample or field sample is a representative sample of any material (aqueous, nonaqueous, or multimedia) collected from any source for which determination of composition or contamination as requested or required. Environmental samples are normally classified as follows:
Drinking Water--delivered (treated or untreated) water designated as potable water;
Water/Wastewater--raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluent;
Sludge--municipal sludges and industrial sludges;
Waste--aqueous and nonaqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.

Instrument Calibration: Analysis of analytical standards for a series of different specified concentrations; used to define the quantitative response, linearity, and dynamic range of the instrument to target analytes.

Matrix: The predominant material of which the sample to be analyzed is composed. Matrix is not synonymous with phase (liquid or solid).

Matrix Spike: Aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate: A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

Method Blank: An analytical control consisting of all reagents, internal standards and surrogate standards, which is carried through the entire analytical procedure. The method blank is used to define the level of laboratory background and reagent contamination.

MSDS: Material safety data sheet. OSHA has established guidelines for the descriptive data that should be concisely provided on a data sheet to serve as the basis for written hazard communication programs. The thrust of the law is to have those who make, distribute, and use hazardous materials responsible for effective communication. See the Hazard Communication Rule, 29 CFR, Part 1910, 1200, as amended, Sec. g. See Schedule I, Sec. 12, of the Canadian Hazardous Products Act.

PCB: Polychlorinated biphenyls (PCBs) are a class of 209 individual chemical compounds (congeners), in which one to ten chlorine atoms are attached to biphenyl. Use of PCBs has made them a frequent environmental pollutant.

Precision: Precision is the agreement between a set of replicate measurements without assumption of knowledge of the true value. Precision is assessed by means of duplicate/replicate sample analysis.

Quality Control: Set of measures within a sample analysis methodology to assure that the process is in control.

Standard Curve: A standard curve is a curve which plots concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by diluting the stock analyte solution in graduated amounts which cover the expected range of the samples being analyzed. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

Stock Solution: Standard solution which can be diluted to derive other standards.

Surrogate: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference samples) and spiked

samples prior to analysis. Percent recoveries are calculated for each surrogate.

Surrogate Standard: A pure compound added to a sample in the laboratory just before processing so that the overall efficiency of
a method can be determined.

ATTACHMENT A

Table 1
PCB Stock Standard Preparation Table

PCB Formulation	Supplier	Catalog #	Std. weight(mg)	Conc.(PPM)
A1016	GE Archive	NA	93.2	932.0
A1221	GE Archive	NA	106.8	1068.0
A1232	GE Archive	NA	103.3	1033.0
A1242	GE Archive	NA	99.0	990.0
A1248	GE Archive	NA	101.9	1019.0
A1254	GE Archive	NA	99.6	996.0
A1260	GE Archive	NA	99.2	992.0
DCBP	Chem Service	F2170	10	100.0

Unless otherwise noted hexane is the solution used to make all dilutions.

Table 2
PCB Working Standard Preparation Table

PCB Stock Standards	Init. Volume(mL)	Final Volume(mL)	Conc.(PPM)
A1016	1.0	100	9.32
A1221	1.0	100	10.68
A1232	1.0	100	10.33
A1242	1.0	100	9.90
A1248	1.0	100	10.19
A1254	1.0	100	9.96
A1260	1.0	100	9.92

Table 3
PCB Calibration Standard Preparation Table

Init. Volume(mL)	Final Volume(mL)	Final Concentration (PPM)					
		A1016	A1221	A1232	A1242	A1248	A1260
5.0	50	0.932	1.068	1.033	0.990	1.019	0.992
2.5	50	0.466	0.534	0.5165	0.495	0.5095	0.496
1.25	50	0.233	0.267	0.25825	0.2475	0.2548	0.248
1.00	50	0.1864	0.2136	0.2066	0.198	0.2038	0.1984
0.500	50	0.0932	0.1068	0.1033	0.0990	0.1019	0.0992
5.0*	50	0.01864	0.02136	0.02066	0.0198	0.02038	0.01984

*This initial volume is of the nominal 0.250 ppm standard. All others are from the nominal 10 ppm standard.

Table 4
PCB A1254 Calibration Standard Preparation Table

Init. Volume(mL) A1254	Init. Volume(mL) Surrogate	Final Volume(mL)	Final Concentration(PPM)		
			A1254	TCMX	DCBP
5.0	0	50	0.996	0	0
10.0	4.0	100	0.996	0.020	0.200
25.0*	0	50	0.498	0.010	0.100
1.25	0.800	50	0.249	0.008	0.080
0.500	0.500	50	0.0996	0.005	0.050
0.100**	0.200	50	0.01992	0.002	0.020

*This initial volume is of the A1254 0.996ppm solution with surrogates.
**This initial volume is of the A1254 0.996ppm solution without surrogates.
All others are from the A1254 9.96ppm working standard.

ATTACHMENT B

Table 1
PCB Continuing Calibration Stock Standards

PCB	Supplier	Catalog #	Conc. (ug/mL)
A1016	Chem Service	F107AS	1000
A1221	Chem Service	F108AS	1000
A1232	Chem Service	F113AS	1000
A1242	Chem Service	F109AS	1000
A1248	Chem Service	F110AS	1000
A1254	Chem Service	F111AS	1000
A1260	Chem Service	F112BS	1000

Table 2
PCB Continuing Calibration Working Standards

PCB	Initial Volume(mL)	Final Volume(mL)	Concentration(PPM)
A1016	1.0	100	10
A1221	1.0	100	10
A1232	1.0	100	10
A1242	1.0	100	10
A1248	1.0	100	10
A1254	1.0	100	10
A1260	1.0	100	10

Table 3
PCB Continuing Calibration Standards

PCB	Initial Volume(mL)	Final Volume(mL)	Concentration (PPM)
A1016	2.5	50	0.500
A1221	2.5	50	0.500
A1232	2.5	50	0.500
A1242	2.5	50	0.500
A1248	2.5	50	0.500
A1254	2.5	50	0.500
A1260	2.5	50	0.500

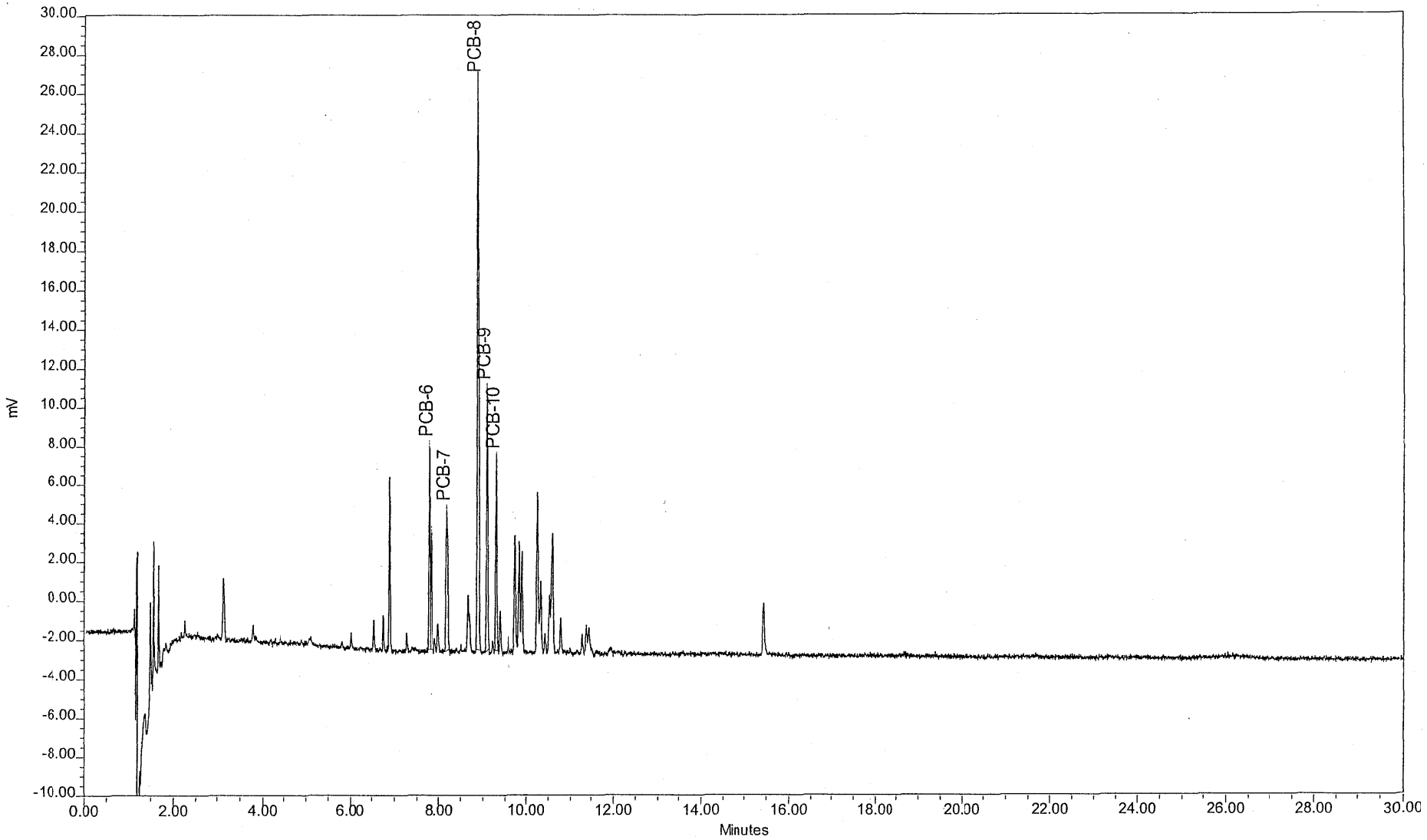
Column Type	Capillary	Capillary
Column ID	DB5-MS	DB-1
Vendor	J&W	J&W
Part Number	122-5532	122-1032
Column Length(m)	30	30
ID(mm)	0.25	0.25
Film Thick.(um)	0.25	0.25
1)Initial Col. Temp. (°C)	140	140
1)Col. Hold Time (min.)	1.0	1.0
1)Col. Temp. Rate (°C/min.)	10	10
1)Final Col. Temp. (°C)	200	200
1)Col. Hold Time (min.)	NA	NA
2)Col. Temp. Rate (°C/min.)	5	5
2)Final Col. Temp. (°C)	245	245
2)Col. Hold Time (min.)	14.50	14.50
GC Col. gas flow rate (mL/min.)	17-24	17-24
ECD autozero	Yes	Yes
Detector Temp.(°C)	300	300
Init. Injector Temp. (°C)	300	300
A/S Vial Needle Depth	85	85
A/S Solvent Select	3	3
A/S Upper Air Gap	Yes	Yes
A/S Lower Air Gap	Yes	Yes
A/S Viscosity Factor	4	1
A/S Hot Needle Time (min.)	0.05	0.05
Autosampler(A/S) Model Number	8100	8100
A/S Injection Volume (uL)	1.3	1.3
A/S Injection Time (min.)	0.01	0.01
A/S Injection Rate (uL/sec.)	Fast 4.0	Fast 4.0

A/S Solvent Inj. plug size (uL)	0.2	0.2

ATTACHMENT D
DB5-MS Chromatograms

Chromatogram Report, PCB by SW846 Method 8082

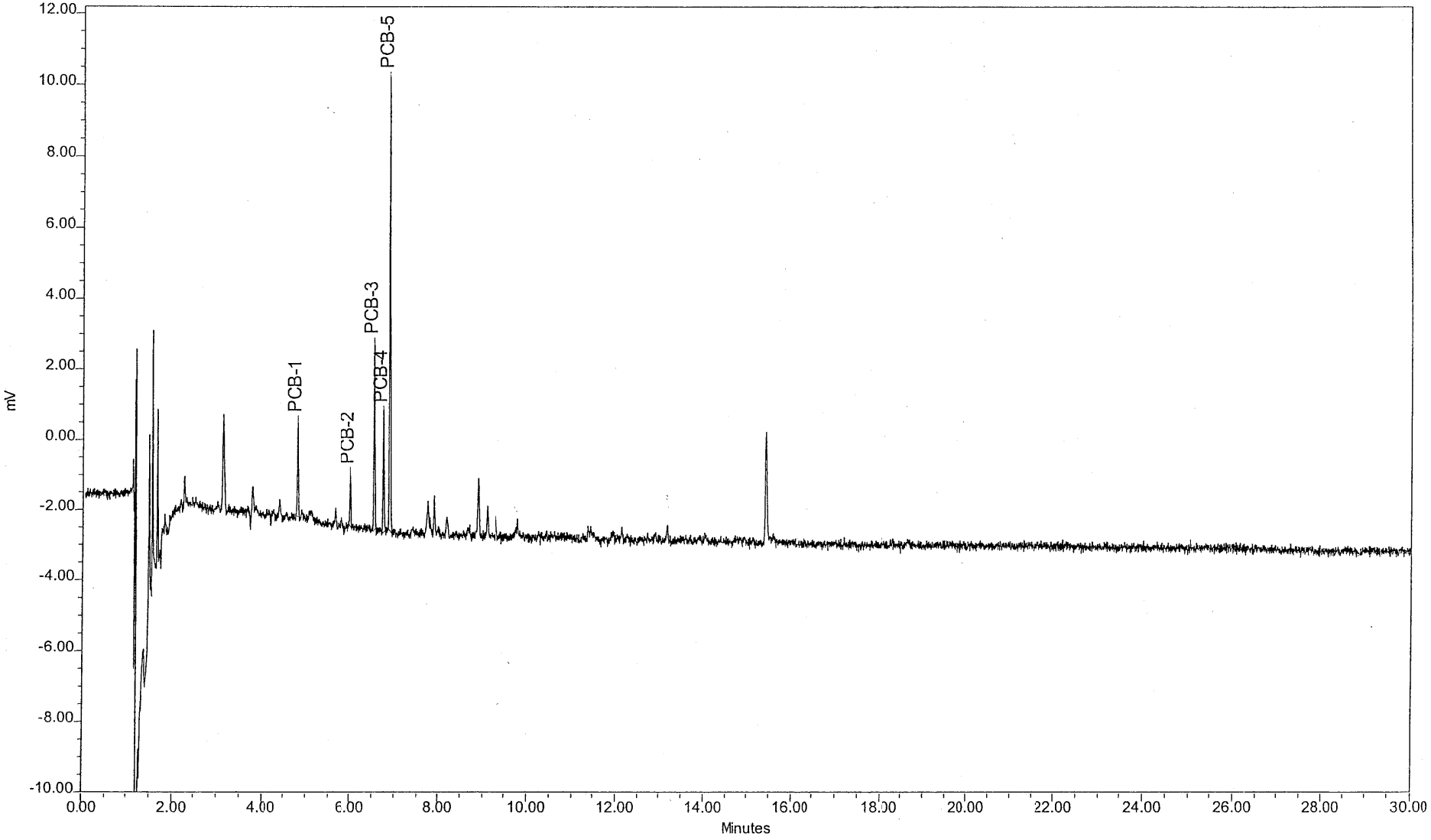
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS160818	Sample Amount:	1
Sample ID:	A1016 500 PPB	Dilution:	1
Date Acquired:	08/18/1999 10:21:00	Processing Method:	GC5_8082_081399

Chromatogram Report, PCB by SW846 Method 8082

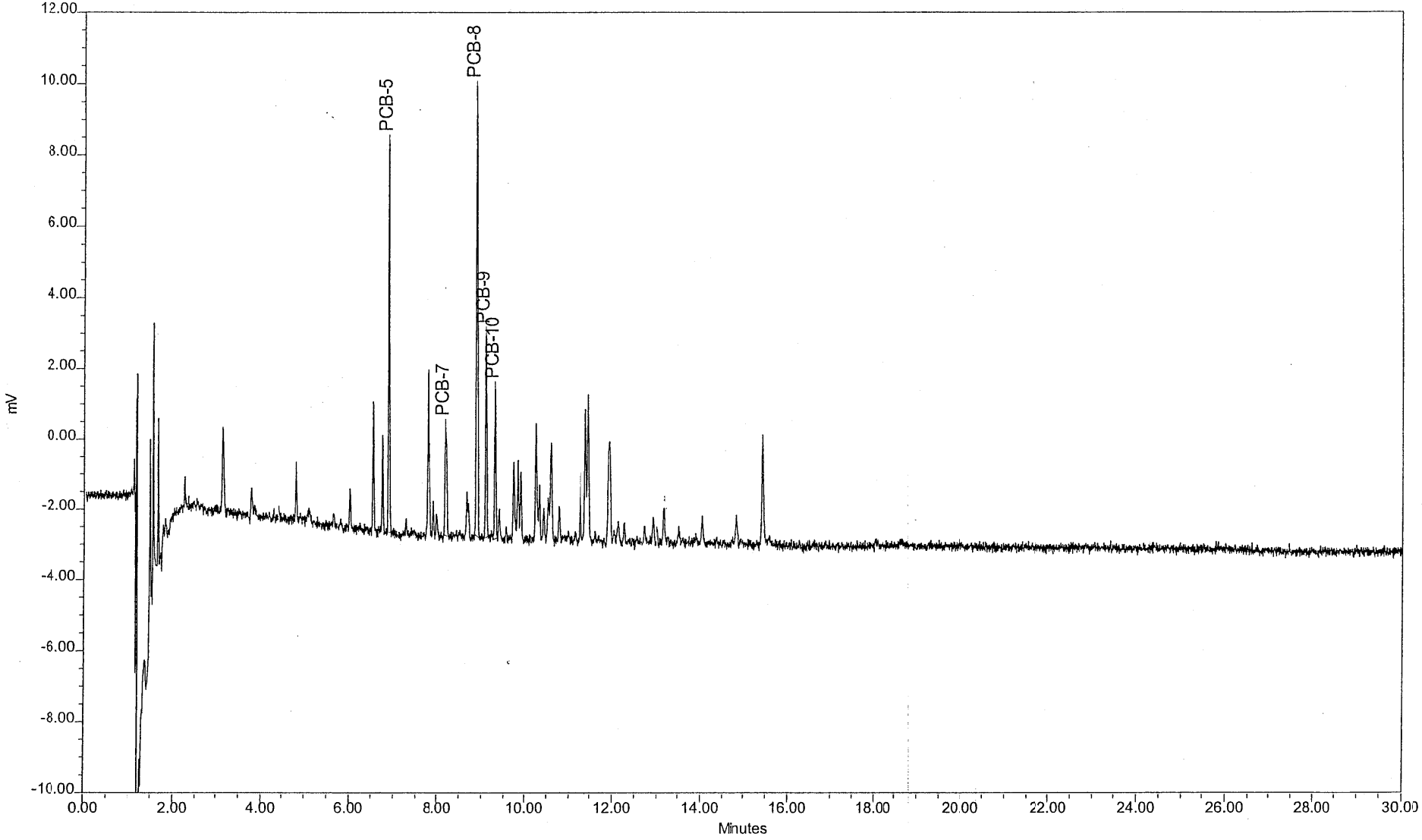
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS210818	Sample Amount:	1
Sample ID:	A1221 500 PPB	Dilution:	1
Date Acquired:	08/18/1999 10:56:10	Processing Method:	GC5_8082_081399

Chromatogram Report, PCB by SW846 Method 8082

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS320818	Sample Amount:	1
Sample ID:	A1232 500 PPB	Dilution:	1
Date Acquired:	08/18/1999 11:31:22	Processing Method:	GC5_8082_081399

Chromatogram Report, PCB by SW846 Method 8082

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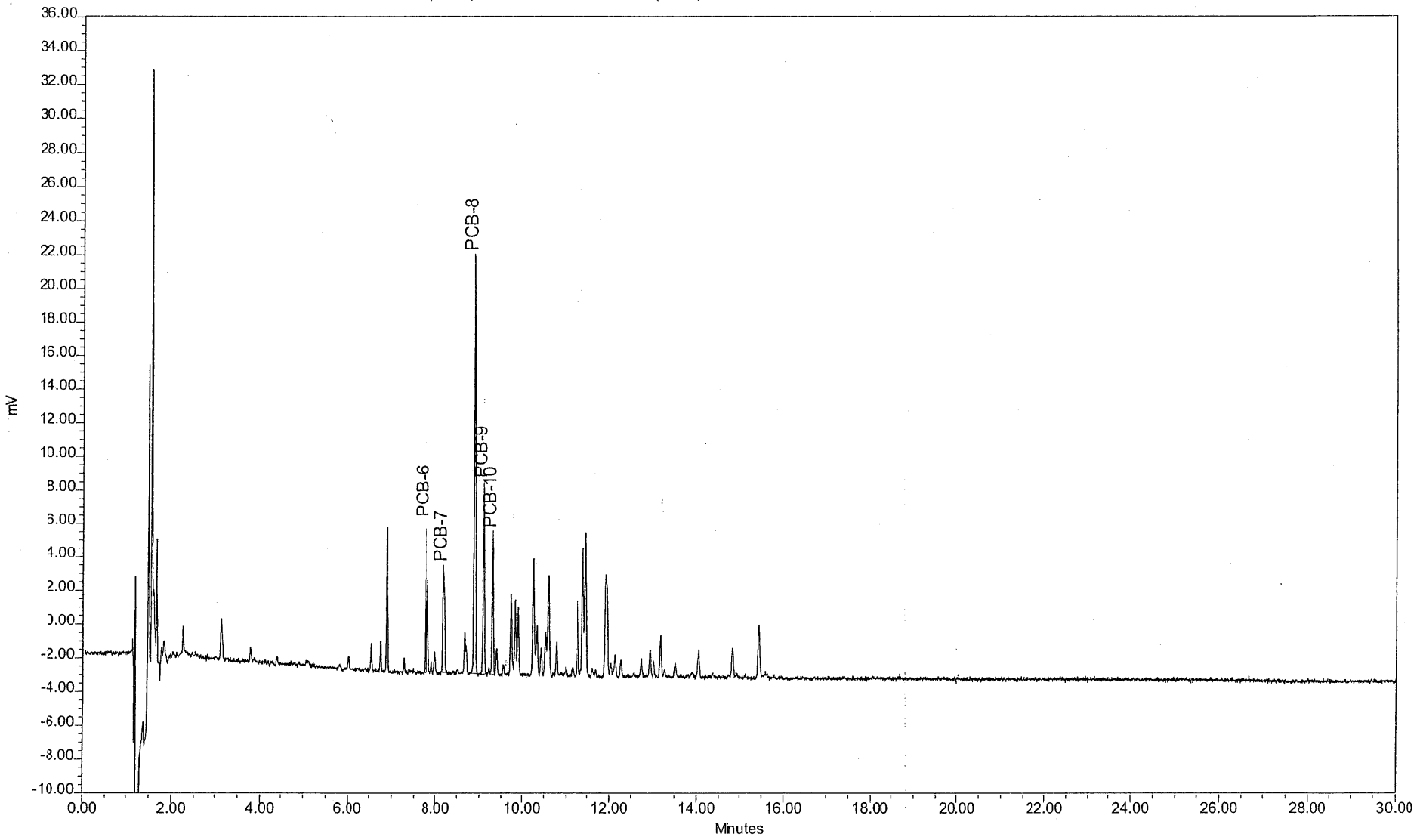
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS420818	Sample Amount:	1
Sample ID:	A1242 500 PPB	Dilution:	1
Date Acquired:	08/18/1999 12:06:31	Processing Method:	GC5_8082_081399

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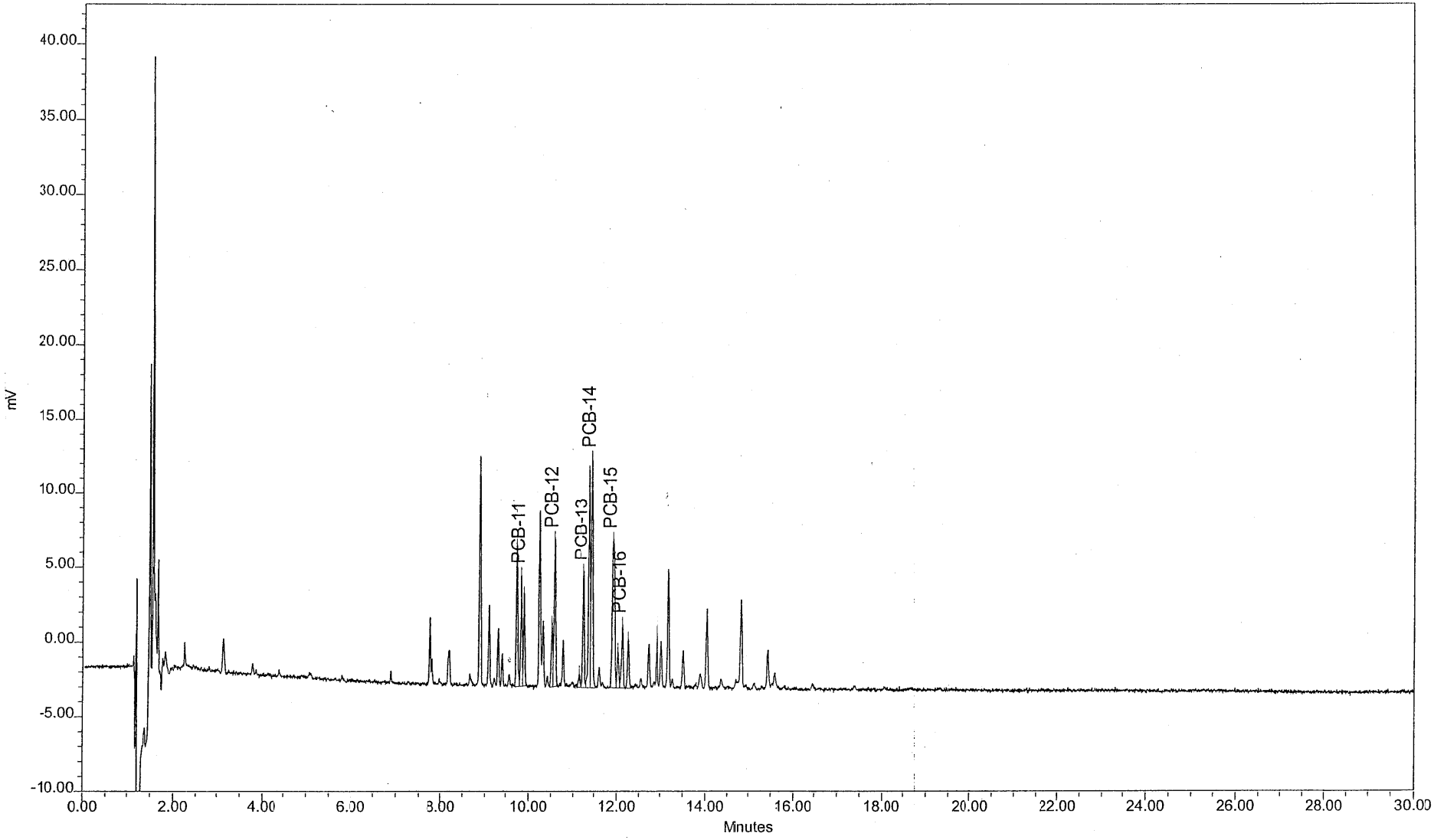
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS480818	Sample Amount:	1
Sample ID:	A1248 500 PPB	Dilution:	1
Date Acquired:	08/18/1999 12:41:43	Processing Method:	GC5_8082_081399

Chromatogram Report, PCB by SW846 Method 8082

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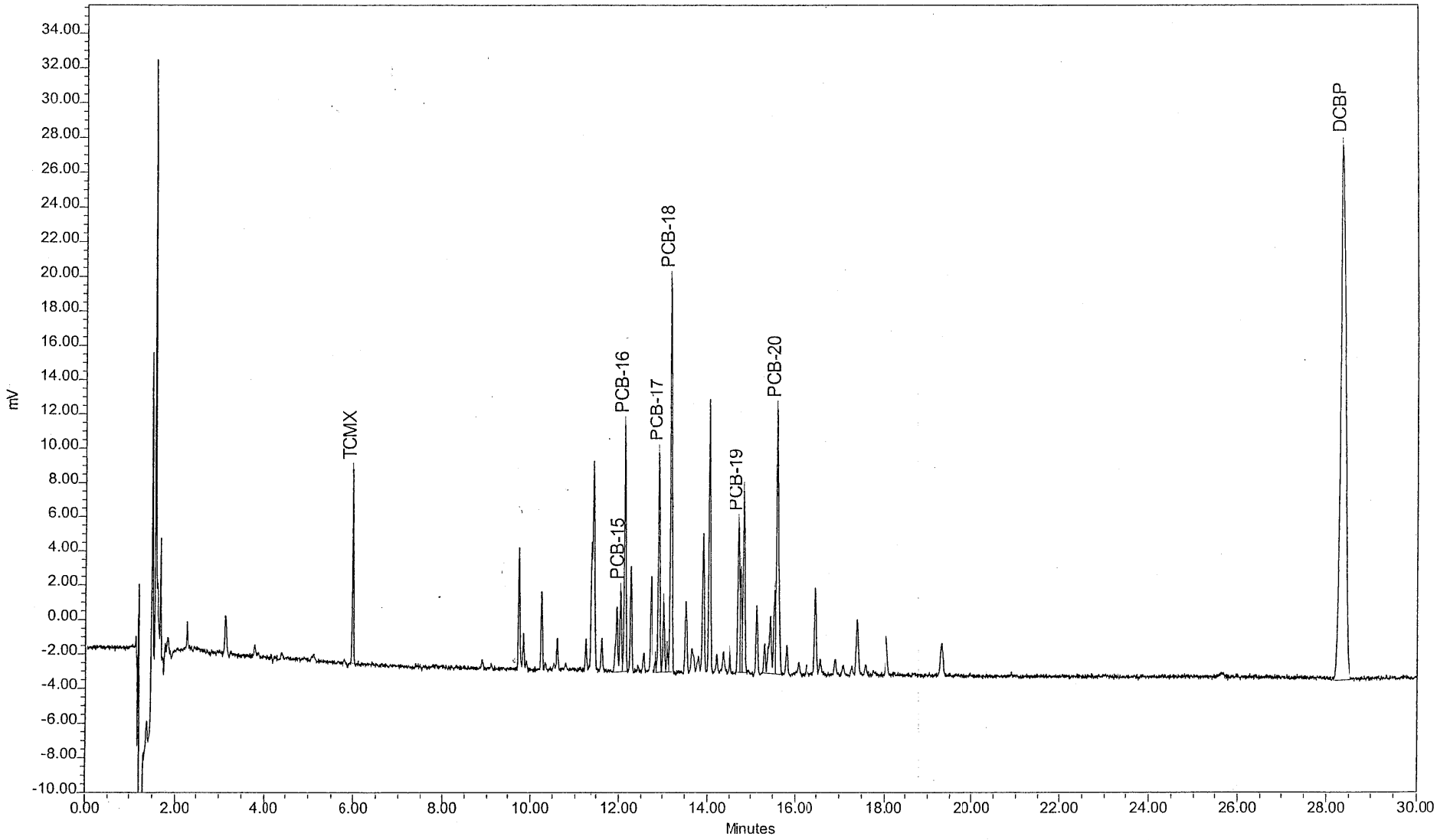
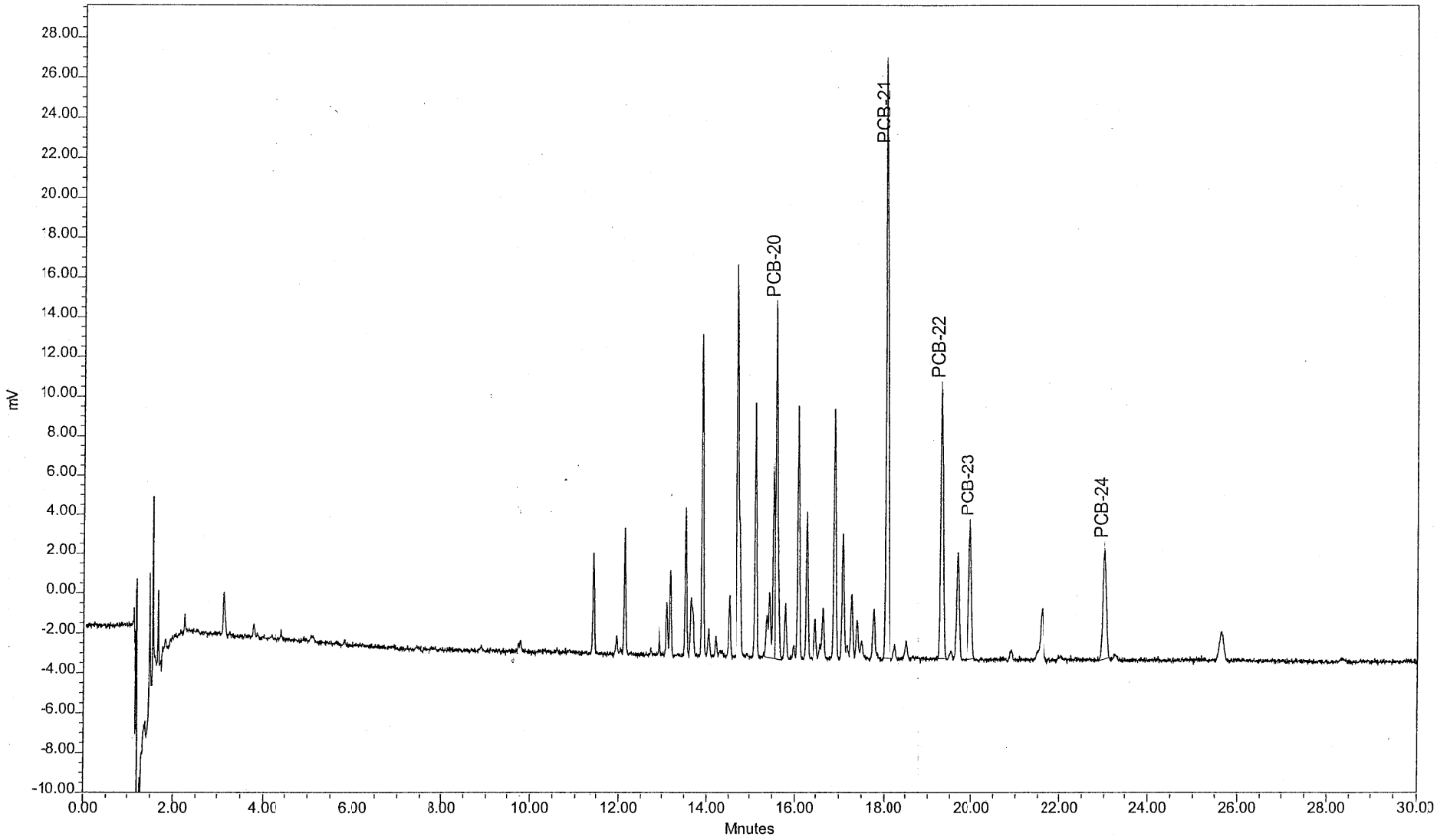
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS540818	**Sample Amount:**	1
Sample ID:	A1254 500 PPB	**Dilution:**	1
Date Acquired:	08/18/1999 1:16:54	**Processing Method:**	GC5_8082_081399

Chromatogram Report, PCB by SW846 Method 8082

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com

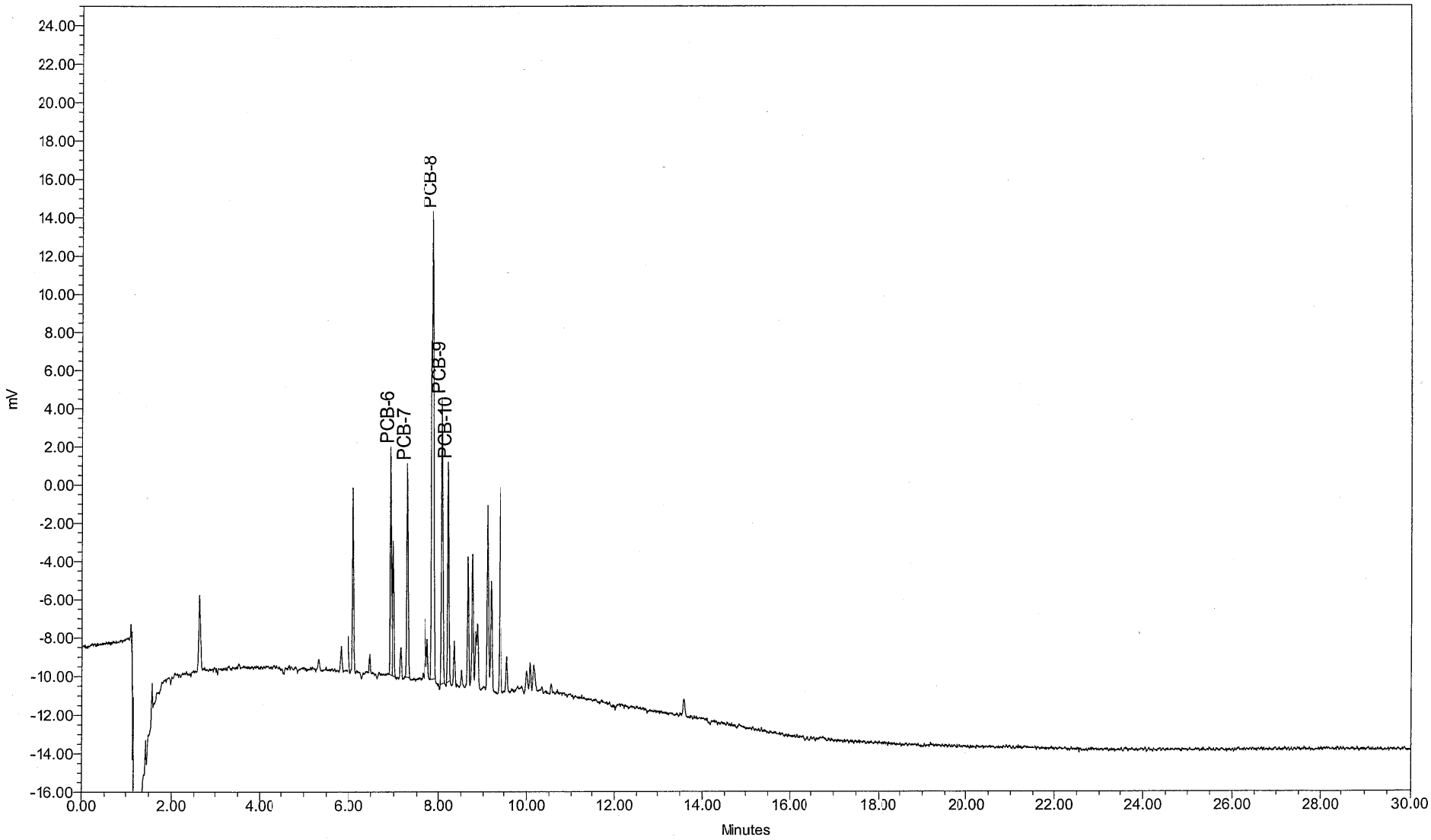


Sample Name:	CS600818	Sample Amount:	1
Sample ID:	A1260 500 PPB	Dilution:	1
Date Acquired:	08/18/1999 1:52:08	Processing Method:	GC5_8082_081399

ATTACHMENT D
DB-1 Chromatograms

Chromatogram Report, PCB by SW846 Method 8082

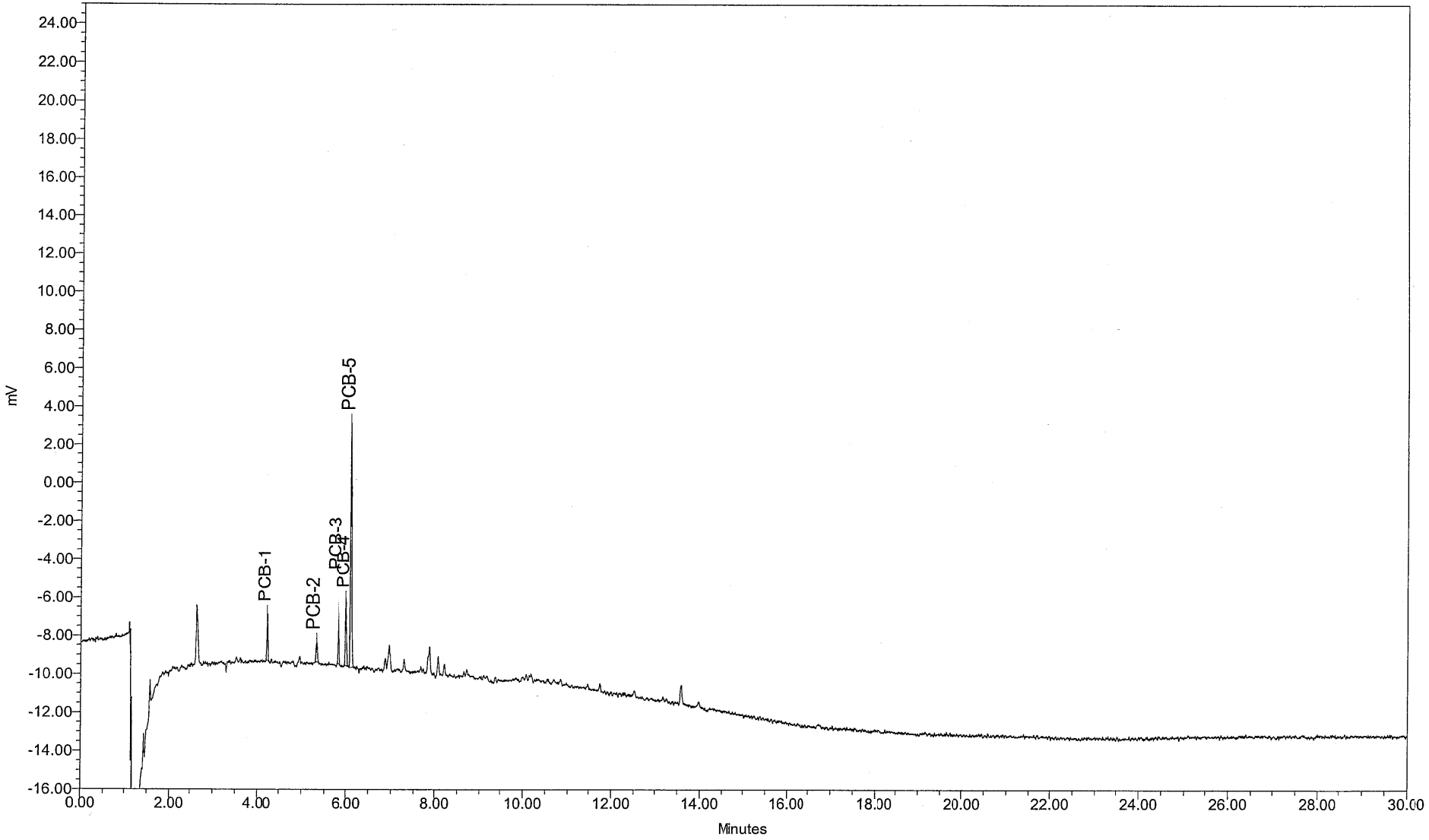
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS160725	Sample Amount:	1
Sample ID:	A1016 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 09:32:16	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

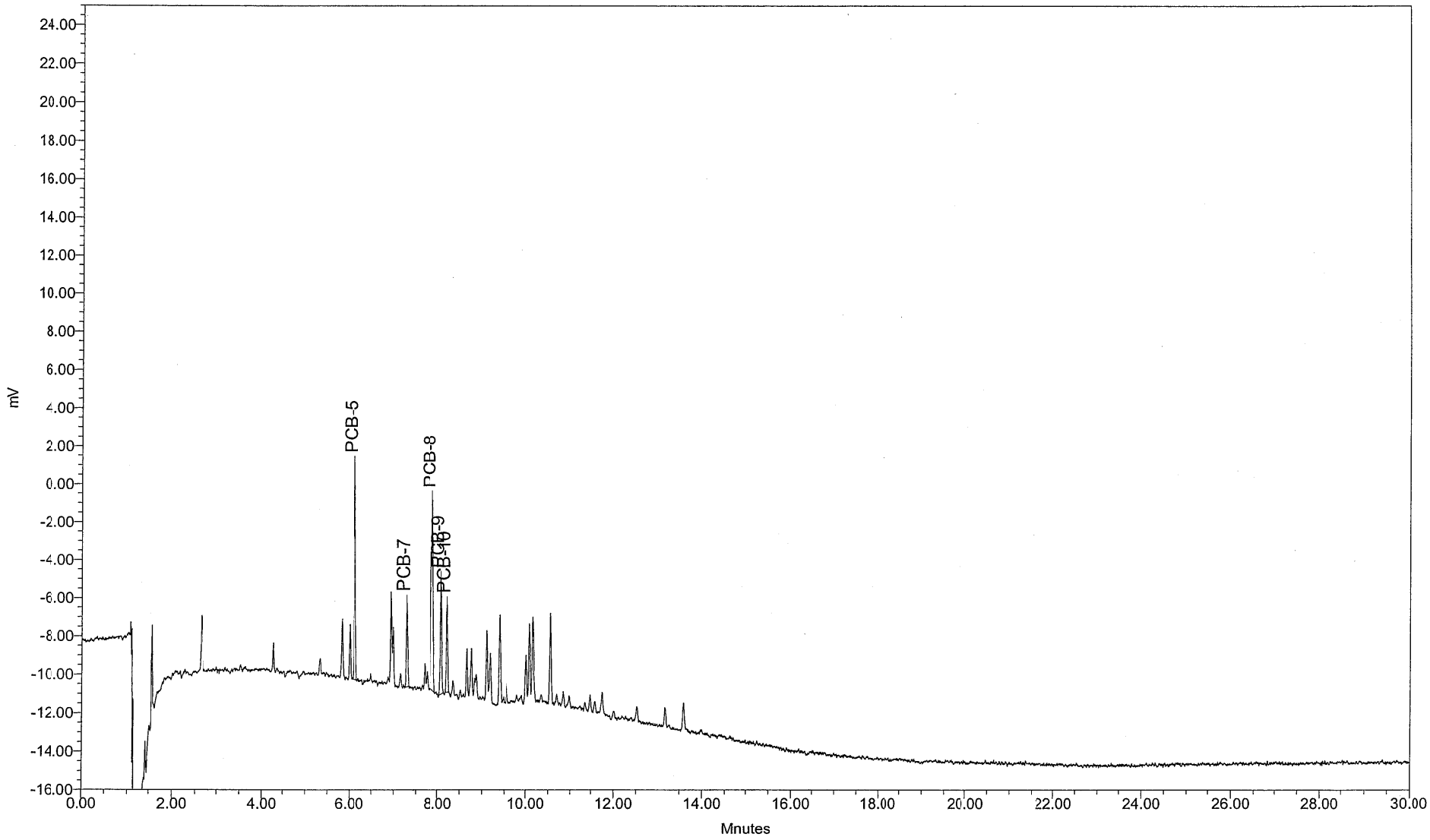
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS210725	**Sample Amount:**	1
Sample ID:	A1221 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 10:08:26	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

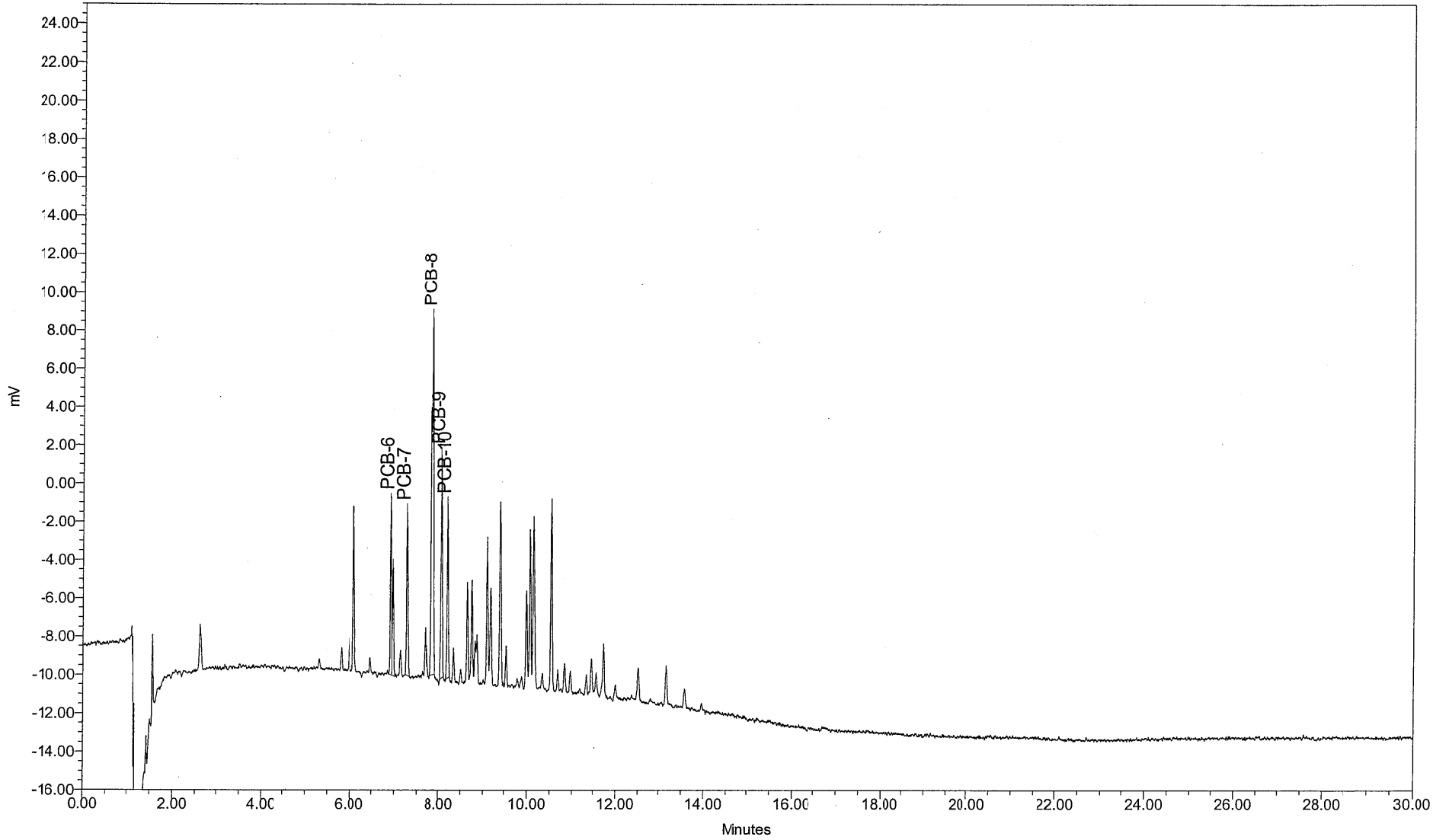
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS320725	**Sample Amount:**	1
Sample ID:	A1232 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 11:09:59	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

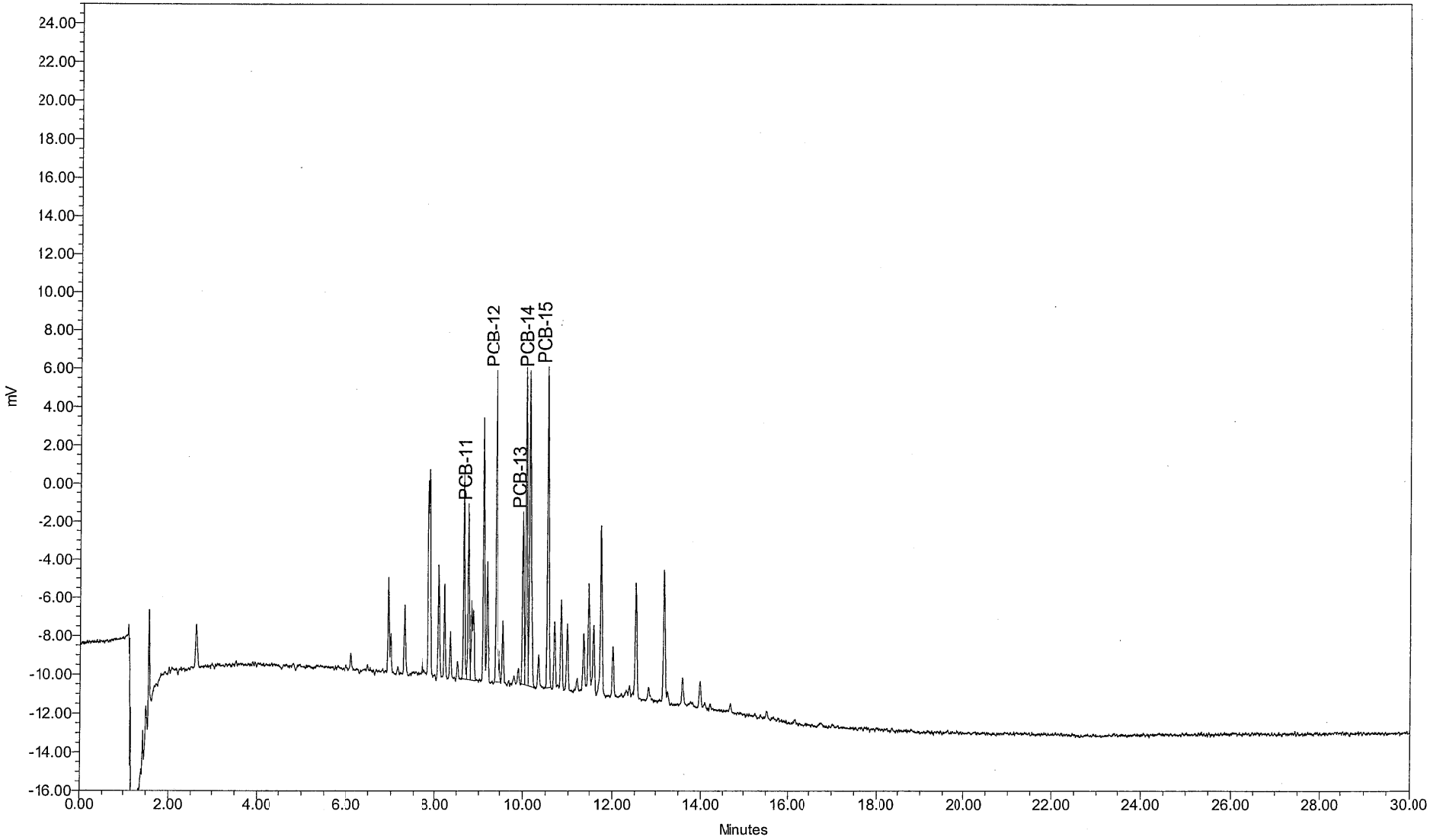
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS420725	Sample Amount:	1
Sample ID:	A1242 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 11:46:07	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

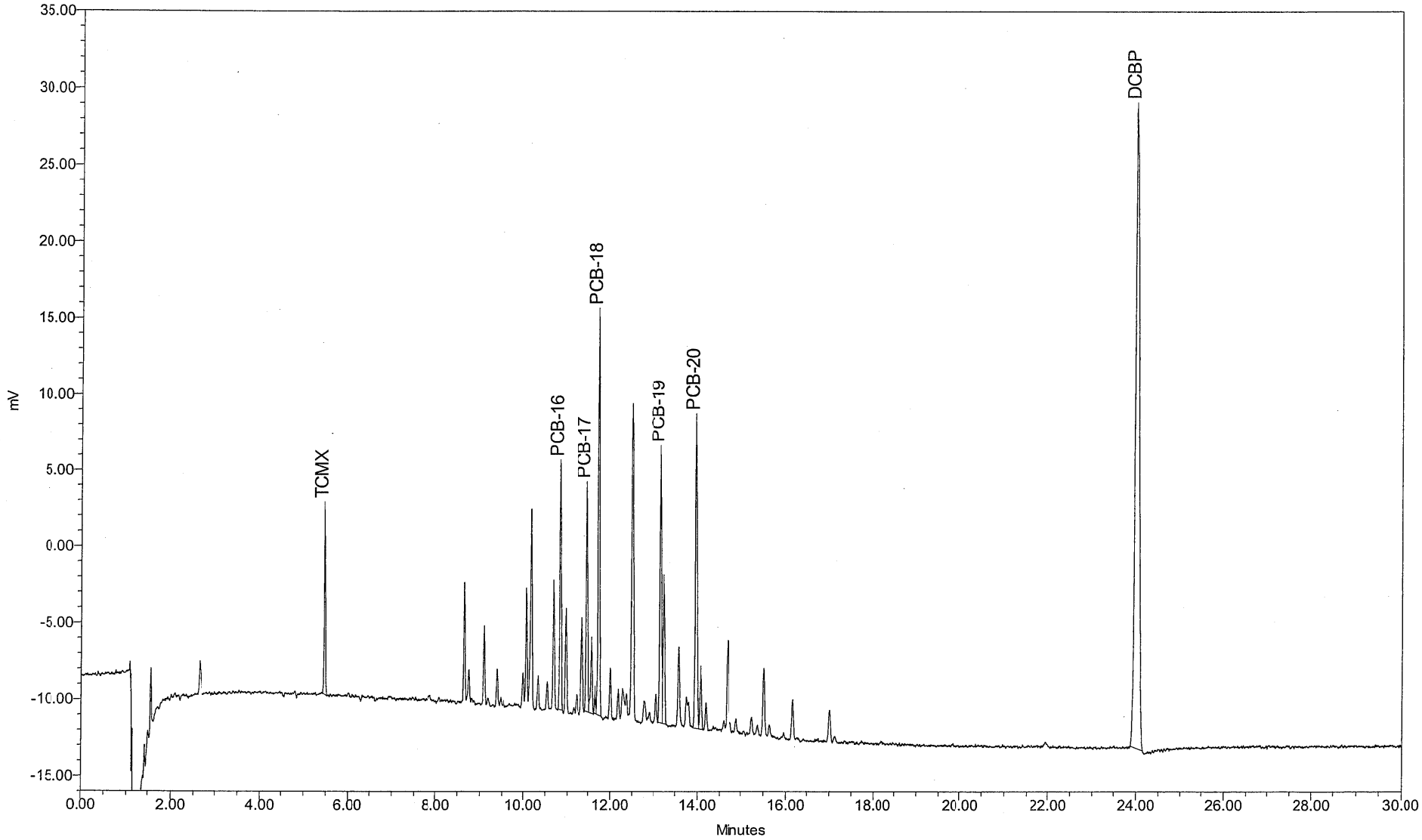
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS480725	**Sample Amount:**	1
Sample ID:	A1248 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 12:22:14	**Processing Method:**	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

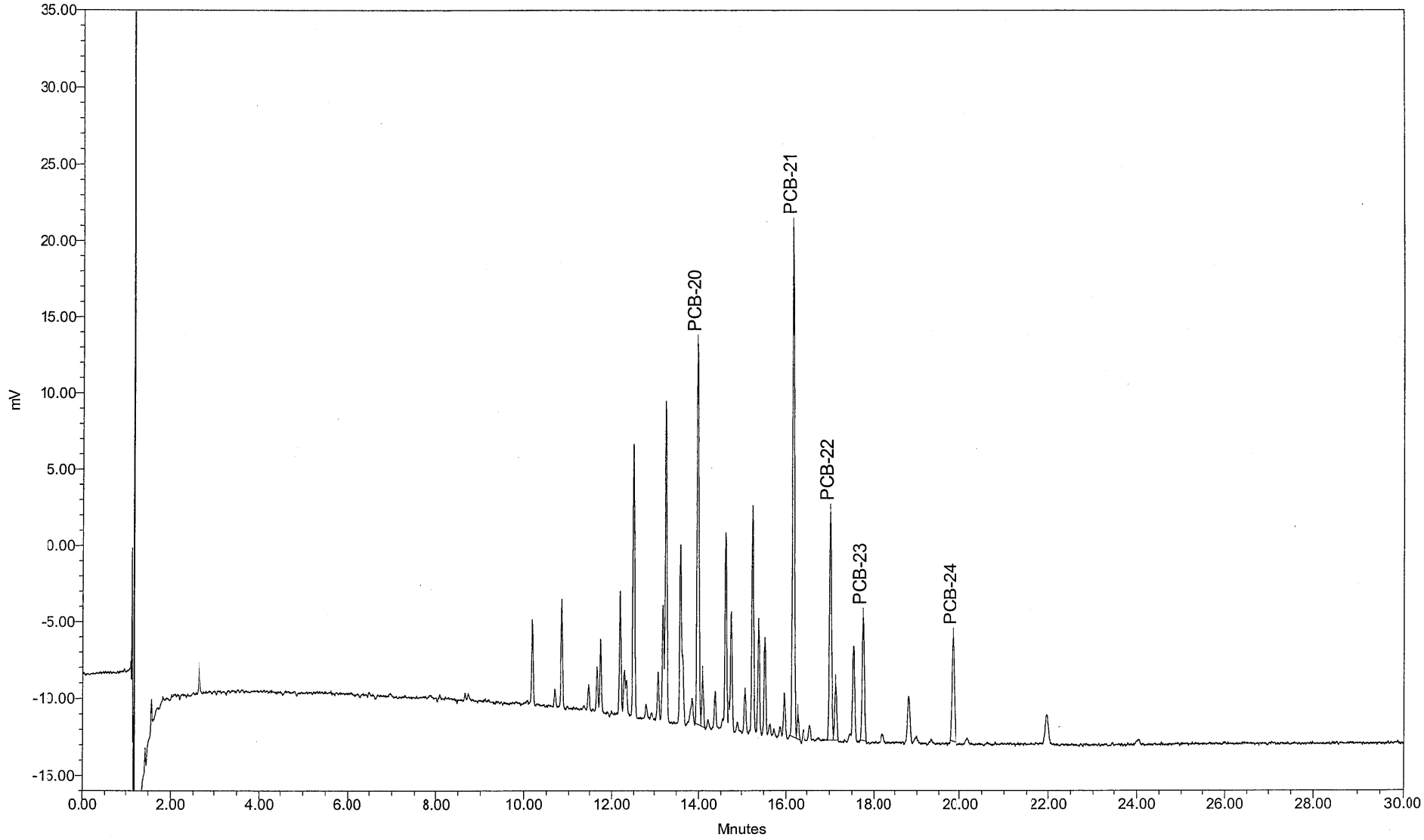
Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS540725	Sample Amount:	1
Sample ID:	A1254 500 PPB	Dilution:	1
Date Acquired:	07/26/1999 12:58:21	Processing Method:	GC7_8082_060899

Chromatogram Report, PCB by SW846 Method 8082

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	CS500725	**Sample Amount:**	1
Sample ID:	A1260 500 PPB	**Dilution:**	1
Date Acquired:	07/26/1999 13:34:27	**Processing Method:**	GC7_8082_060899

ATTACHMENT E

Calibration Report: PCB by SW-846 Method 8082

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com

System Name: Instrument 05 Sample Set Date: 08/13/1999 3:35:46 PM
Sample Set Name: GC5_8082CC_081399 Date Calibrated: 08/16/1999 2:13:22 PM
User Name: KristenV Processing Method: GC5_8082_081399
Report Method Name: 8082 CalCurve Summary by RF 01

Calibration Component Summary Table
Component Summary For RF

	Sample Name	A1254-20	A1254-16/20	A1254	A1248
1	081254A	289.400	233.718	392.161	
2	081254B	307.665	239.346	418.651	
3	081254C	309.076	237.264	412.930	
4	081254D	299.203	229.949	402.504	
5	081254E	305.003	233.686	410.308	
Mean		302.069	234.793	407.311	
Std. Dev.		8.027	3.629	10.269	
% RSD		2.7	1.5	2.5	

Calibration Component Summary Table
Component Summary For RF

	Sample Name	TCMX	PCB-15	PCB-16	PCB-17	PCB-18	DCBP
1	081254A	1743.600					2464.880
2	081254B	1905.680					2607.388
3	081254C	1838.488					2539.036
4	081254D	1852.060					2498.834
5	081254E	1873.950					2528.173
Mean		1842.756					2527.662
Std. Dev.		60.970					53.053
% RSD		3.3					2.1

Calibration Report: PCB by SW-846 Method 8082

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com

System Name: Instrument 07 Sample Set Date: 04/22/1999 14:27:01
Sample Set Name: GC7_8082_Calibration_042 Date Calibrated: 05/14/1999 11:19:00
User Name: System Processing Method: GC7_8082_051499
Report Method Name: 8082 CalCurve Summary by RF 01

Calibration Component Summary Table
Component Summary For RF

	Sample Name	A1254-16/20	A1254-20	A1260	A1260-23	A1254
1	042354A	299.563	361.997			455.381
2	042354B	273.188	342.796			450.960
3	042354C	275.873	344.896			454.235
4	042354D	272.145	342.847			452.535
5	042354E	273.574	344.877			454.616
Mean		278.868	347.483			453.545
Std. Dev.		11.648	8.179			1.782
% RSD		4.2	2.4			0.4

Calibration Component Summary Table
Component Summary For RF

	Sample Name	TCMX	PCB-17	PCB-18	PCB-19	PCB-20	DCBP
1	042354A	1954.700					2445.172
2	042354B	1969.361					2455.106
3	042354C	1991.331					2494.547
4	042354D	1933.980					2433.796
5	042354E	2000.251					2446.710
Mean		1969.925					2455.066
Std. Dev.		26.936					23.339
% RSD		1.4					1.0

ATTACHMENT F

Northeast Analytical Inc

07/06/99

Retention Time Window Study
for Aroclors (PCB) by GC/ECD
EPA Method 8082

Instrument: GC 5
Column: DB5-MS 30Meter

Analyte	PEAK	Standard 1 500 PPB R.T. Min CS__0426	Standard 2 500 PPB R.T. Min CS_0503	Standard 3 500 PPB R.T. Min CS_0511	STD. DEV Min	%RSD	Window +/- Min.
Aroclor 1016	1	7.798	7.797	7.798	0.0006	0.01	0.002
	2	8.216	8.215	8.217	0.0010	0.01	0.003
	3	8.918	8.916	8.919	0.0015	0.02	0.005
	4	9.122	9.120	9.123	0.0015	0.02	0.005
	5	9.325	9.323	9.326	0.0015	0.02	0.005
Aroclor 1221	1	4.838	4.841	4.844	0.0030	0.06	0.009
	2	6.039	6.043	6.044	0.0026	0.04	0.008
	3	6.569	6.572	6.574	0.0025	0.04	0.008
	4	6.776	6.779	6.781	0.0025	0.04	0.008
	5	6.916	6.920	6.922	0.0031	0.04	0.009
Aroclor 1232	1	6.917	6.920	6.922	0.0025	0.04	0.008
	2	8.216	8.222	8.220	0.0031	0.04	0.009
	3	8.919	8.923	8.924	0.0026	0.03	0.008
	4	9.123	9.127	9.129	0.0031	0.03	0.009
	5	9.326	9.329	9.332	0.0030	0.03	0.009
Aroclor 1242	1	7.800	7.803	7.803	0.0017	0.02	0.005
	2	8.216	8.221	8.220	0.0026	0.03	0.008
	3	8.920	8.924	8.925	0.0026	0.03	0.008
	4	9.124	9.128	9.128	0.0023	0.03	0.007
	5	9.327	9.330	9.331	0.0021	0.02	0.006
Aroclor 1248	1	9.869	9.872	9.875	0.0030	0.03	0.009
	2	10.616	10.620	10.624	0.0040	0.04	0.012
	3	11.291	11.295	11.296	0.0026	0.02	0.008
	4	11.481	11.484	11.486	0.0025	0.02	0.008
	5	11.950	11.964	11.958	0.0070	0.06	0.021
Arolcor 1254	1	12.160	12.162	12.162	0.0012	0.01	0.003
	2	12.945	12.947	12.948	0.0015	0.01	0.005
	3	13.211	13.214	13.215	0.0021	0.02	0.006
	4	14.752	14.753	14.754	0.0010	0.01	0.003
	5	15.614	15.616	15.616	0.0012	0.01	0.003
Arolcor 1260	1	15.613	15.615	15.616	0.0015	0.01	0.005
	2	18.079	18.083	18.084	0.0026	0.01	0.008
	3	19.336	19.342	19.344	0.0042	0.02	0.012
	4	20.003	20.009	20.013	0.0050	0.03	0.015
	5	23.038	23.040	23.047	0.0047	0.02	0.014
TCMX (SURROGATE)	Surr.	6.02	6.021	6.023	0.0015	0.03	0.005
DCB (SURROGATE)	Surr.	28.389	28.40	28.41	0.0093	0.03	0.028

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Northeast Analytical Inc

04/04/02

Retention Time Window Study
for Aroclors (PCB) by GC/ECD
EPA Method 8082 (Short Method)

Instrument: GC 7
Column: DB1-30Meter

Analyte	PEAK	Standard 1 50 PPB R.T. Min	Standard 2 50 PPB R.T. Min	Standard 3 50 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
Aroclor 1016		C__0401B	CS_0403	CS_0404			
	6	10.431	10.434	10.430	0.0021	0.020	0.006
	7	10.777	10.780	10.775	0.0025	0.023	0.008
	8	11.321	11.325	11.320	0.0026	0.023	0.008
	9	11.498	11.502	11.496	0.0031	0.027	0.009
	10	11.616	11.619	11.613	0.0030	0.026	0.009
Aroclor 1221		C__0401B	C__0403A	CS__0404			
	1	7.705	7.707	7.706	0.0010	0.013	0.003
	2	8.833	8.837	8.835	0.0020	0.023	0.006
	3	9.334	9.335	9.333	0.0010	0.011	0.003
	4	9.508	9.512	9.510	0.0020	0.021	0.006
	5	9.619	9.621	9.619	0.0012	0.012	0.003
Aroclor 1232		CS__0401	CS__0403	CS__0404			
	5	9.622	9.619	9.622	0.0017	0.018	0.005
	7	10.779	10.776	10.779	0.0017	0.016	0.005
	8	11.325	11.321	11.323	0.0020	0.018	0.006
	9	11.501	11.498	11.499	0.0015	0.013	0.005
	10	11.619	11.615	11.617	0.0020	0.017	0.006
Aroclor 1242		CS__0401	CS__0403	CS__0404			
	6	10.431	10.432	10.430	0.0010	0.010	0.003
	7	10.777	10.778	10.774	0.0021	0.019	0.006
	8	11.322	11.322	11.320	0.0012	0.010	0.003
	9	11.498	11.498	11.496	0.0012	0.010	0.003
	10	11.616	11.617	11.614	0.0015	0.013	0.005
Aroclor 1248		CS__0401	CS__0403	CS__0404			
	11	12.074	12.071	12.070	0.0021	0.017	0.006
	12	12.582	12.579	12.578	0.0021	0.017	0.006
	13	13.052	13.048	13.047	0.0026	0.020	0.008
	14	13.168	13.165	13.163	0.0025	0.019	0.008
	15	13.454	13.451	13.450	0.0021	0.015	0.006
Arolcor 1254		CS__0401	CS__0403	CS__0404			
	16	13.655	13.651	13.651	0.0023	0.017	0.007
	17	14.099	14.097	14.098	0.0010	0.007	0.003
	18	14.291	14.289	14.288	0.0015	0.011	0.005
	19	15.383	15.382	15.381	0.0010	0.007	0.003
	20	16.042	16.041	16.039	0.0015	0.010	0.005
Arolcor 1260		CS__0401	CS__0403	CS__0404			
	20	16.045	16.045	16.041	0.0023	0.014	0.007
	21	18.212	18.210	18.207	0.0025	0.014	0.008
	22	19.183	19.182	19.179	0.0021	0.011	0.006
	23	20.016	20.016	20.007	0.0052	0.026	0.016
	24	22.425	22.420	22.410	0.0076	0.034	0.023
TCMX (SURROGATE)	Surr.	8.988	8.986	8.987	0.0010	0.011	0.003
DCB (SURROGATE)	Surr.	27.277	27.273	27.270	0.0035	0.013	0.011

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APPENDIX 26

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE013_07.SOP

REVISION NUMBER: 07

STANDARD OPERATING PROCEDURE FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) ANALYSIS

METHOD FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) QUANTIFICATION AND IDENTIFICATION BY CAPILLARY COLUMN/GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

March 9, 2004

COPY #_____

NORTHEAST ANALYTICAL, INC.
2190 TECHNOLOGY DRIVE
SCHENECTADY, NEW YORK 12308
(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY METHOD NE013_07.SOP

REVISION 7 (3/09/2004)

TABLE OF CONTENTS

Lab Method NE013_07.SOP

Congener-Specific Polychlorinated Biphenyl (PCB) Analysis

Method for Congener-Specific Polychlorinated Biphenyl (PCB) Quantification and Identification by Capillary Column/Gas Chromatography with Electron Capture Detection

1.0 Scope

1.1 This method is applicable in the determination and quantification of Polychlorinated Biphenyls (PCB) in sediments, soils, biota, oils, water, and other solid and liquid matrices. This method is a congener-specific determination, employing a high resolution fused-silica capillary chromatographic column. The method has been, in part, developed from the following documents:

1.) "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office", prepared by Deborah L. Swackhamer, Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987. This document outlines quality assurance and quality control procedures to be followed by laboratories participating in the Green Bay Mass Balance Study. Where applicable, Northeast Analytical, Inc., will incorporate and utilize this information in quality control of data generated. Instrumental analysis and conditions (Mullin, M.D., 1985, PCB Workshop, US EPA Large Lakes Research Station, Gross Ile, MI, June.) cited in the Green Bay Mass Balance Study document will be refined to be applicable to an in-house data management software package.

2.) "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns", George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996. This journal publication provides complete assignment of all 209 PCB congeners to the GC peaks separable on a DB-1 capillary column. It also provides weight percent information for PCB congeners in Aroclor formulations used in labeling protocols for reporting purposes.

3.) "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", US EPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2. This USEPA SOP summarizes M. Mullin's congener composition of the mixed Aroclor standard used for calibration.

4.) "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10. This LLRS SOP written by M. Mullin summarizes the calibration composition of the mixed Aroclor standard reported in "Mullin, M.D., PCB Workshop, U.S. EPA Large Lakes Research Station, Grosse Ile, MI, June 1985.

1.2 This gas chromatographic capillary column method, utilizing an electron capture detector, will effectively separate 112 or more peaks representing 209 PCB congeners.

2.0 Summary of Method

2.1 This method provides detailed instructions for gas chromatographic conditions for analysis of PCBs by capillary gas chromatography.

2.2 This method utilizes a mixed Aroclor standard (Aroclor 1232/1248/1262 in the ratio of 25:18:18) for calibration. Method detection limit and practical quantitation limit will be established experimentally using the procedure in USEPA 40 CFR, Part 136, App. B.

2.3 In general, samples are first extracted with a pesticide-grade solvent. The extracts are further processed through a series of clean-up techniques. The sample is then analyzed by direct liquid injection onto the gas chromatographic column and detected by an electron capture detector. This method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

2.4 A key component of this method is the importance placed on the chromatographic separation that must be achieved for this congener specific technique. A total of 112 chromatographic peaks are detected, containing 209 PCB congeners in various ratios. This allows an almost complete profile of environmentally occurring PCBs.

2.5 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize himself with the hazards of handing the compounds used for standards and samples themselves.

3.0 Interference

3.1 One of the major sources of interference in the analysis of PCBs is that organochlorine pesticides are coextracted from the samples. A few of these ECD responding pesticides can be separated cleanly from the PCB profile by the resolving characteristics of the capillary column. Several of the commonly found pesticides and degradation products (DDT, DDE, DD) overlap the PCB profile envelope and co-elute with several of the PCB congeners found in environmental samples. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in total PCB values generated.

3.2 Sample preparation, extraction procedures, and extract clean-up protocols are covered in separate SOPs that deal exclusively with sample extraction.

3.3 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters give response on electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

4.0 Sample Archiving

4.1 Depending on program requirements, sample extracts and certain original samples (*i.e.,* Soil, sediment, tissue, and oil samples) can be retained after analysis. The sample extracts and original samples will be stored in a freezer.

5.0 Equipment and Apparatus

5.1 Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Northeast Analytical, Inc. will use a Varian Model 3800 gas chromatograph, equipped with capillary on-column injection (Septum Programmable Injector), temperature programmable oven, Model 8200 automatic sampler, and fast time constant electron capture detector. A data system (Waters Associates, Millennium_32 Workstation) for chromatographic operations and integration of detector signal is interfaced to the gas chromatograph.

5.1.1 GC Column: The gas chromatograph column to be used for analysis will be a DB-1 (J&W Company), bonded polydimethylsilicone, 30 meter fused silica capillary column with an internal diameter of 0.25mm and phase coating thickness of 0.25 microns. This column is capable of resolving 112 chromatographic peaks from the full spectrum of all PCB congeners that could be expected in an environmental sample. Refer to Appendix A and Appendix B for a complete description of PCB congeners identified in each GC chromatographic peak and achievable chromatographic separations.

5.2 Chromatograph Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates), will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

5.3 Volumetric Flasks: 10 and 100mL, ground-glass stopper. For standard preparation.

5.4 Microsyringe: 10 and 100uL for standard preparation.

5.5 Pipettes: Class A volumetric, 2mL, 5mL, and 10mL.

5.6 Vials: Glass, 10 and 20mL capacity for sample extracts.

5.7 Bottles: Glass, 120mL capacity for standard storage.

6.0 Reagents and Standards:

6.1 Solvents: Pesticide grade quality. Hexane, acetone, toluene, methylene chloride.

6.2 Octachloronaphthalene: Obtained from Ultra Scientific (Hope, RI) with a purity greater than 95%.

6.3 Polychlorinated Biphenyls: Neat commercial material or solutions for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as transformers and capacitors. Monsanto was the largest producer of PCB formulations and sold them under the tradename Aroclor.

6.4 PCB Congeners: A complete set of all 209 PCB congeners to individually verify the exact elution on the chosen chromatographic system. A subset of congeners are also used as a secondary supplemental calibration standard for those congeners that do not exist at a high enough level in the Aroclor based calibration standard. Obtained from AccuStandard or Ultra Scientific.

6.5 Stock Standard Solutions:

6.5.1 Stock standards are prepared from individual neat Aroclor formulations by weighing approximately 0.1000g to the nearest 0.2 mg and dissolving and diluting to volume in a 100mL volumetric flask with hexane. This will give a stock concentration of 1,000ug/mL.

6.5.2 The stock standard is transferred into screw-cap 120mL boston bottles and stored in a freezer, protected from light. Stock standards should be checked at frequent intervals for signs of evaporation, especially just prior to preparing calibration standards.

6.5.3 Stock PCB standards must be replaced after one year, or sooner if comparison with continuing calibration check standards indicate a problem.

6.5.4 Stock standards for the following are prepared by the above procedure:

Aroclor 1232
Aroclor 1248
Aroclor 1262

6.6 Mixed Aroclor Stock Standard at 62.7ug/mL: A stock standard is prepared at 62.7ug/mL that is used for preparing linearity standards and the calibration standard. Using a 5.0mL Class A pipette, accurately add 2.49mL of stock Aroclor 1232 standard (1,033ug/mL) to a 100mL volumetric flask. Using a 2.0mL Class A pipette, accurately add 1.82mL of stock Aroclor 1248 standard (1,019ug/mL) and 1.80mL of stock Aroclor 1262 standard (1,024ug/mL) to the same 100mL volumetric flask. Make volume to the 100mL mark with hexane.

6.6.1 Store the Mixed Aroclor Stock Standard at 62.7ug/mL in a freezer in a tightly capped bottle. This standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

6.6.2 High Linearity Standard at 31.35ug/mL: The High Linearity Standard is prepared from the 62.7ug/mL mixed Aroclor stock standard. Using a 5.0mL Class A pipette, accurately add 5.0mL of the 62.7 stock standard

into a 10mL volumetric flask. Using a 10 microliter syringe add 9.0uL of 202ug/mL octachloronaphthalene into the same 10mL volumetric flask. The octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 10ml vial and store in a freezer.

6.6.3 The 31.35ug/mL High Linearity Standard must be replaced after one year.

6.7 Calibration Standard at 6.27ug/mL: The calibration standard is prepared by combining Aroclor 1232, Aroclor 1248, and Aroclor 1262 in a 25:18:18 ratio with a final mixture concentration of 2.57ug/mL, 1.86ug/mL, and 1.84ug/mL respectively (total = 6.27ug/mL). The final concentration of the mixed standard may vary to accommodate instrument sensitivity or more closely represent sample concentrations, but the same ratio values must be maintained. These ratios are strictly maintained so that the percent composition data remains applicable, since it was developed for use under these fixed mixture parameters. The calibration standard is prepared from the 62.7ug/mL mixed Aroclor stock standard. Using a 10.0mL Class A pipette, accurately add 10.0mL of the 62.7 stock standard into a 100mL volumetric flask. Using a 100 microliter syringe add 90.0uL of 202ug/mL octachloronaphthalene into the same 100mL volumetric flask. Make to volume with hexane. The octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 120-ml boston bottle and store in a freezer.

6.7.1 The 6.27ug/mL Calibration Standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

6.8 Supplemental Congener Standard: A Supplemental Congener Standard is analyzed along with the 6.27ug/mL Calibration Standard. This standard contains congeners that exist at low levels in the mixed Aroclor standard and comprises congeners that are not typically found in Aroclor formulations, but could become important in by-product PCB analysis or the study of model experiments that use unusual PCB congeners. This standard is analyzed to supply accurate retention time information and response factors for quantification. All stock standards are purchased as solutions at 100ug/mL. All supplemental congeners are diluted (except 3-Chlorobiphenyl) to 10ug/ml in hexane by pipetting 1.0mL of the 100ug/mL stock standard into a 10mL volumetric flask and making to volume with hexane. For each congener, pipette 0.5mL of the 10ug/mL secondary stock standard into the same 100mL volumetric flask. For the 3-Chlorobiphenyl, pipette 2.0mL of the 100ug/mL stock standard into the same 100mL volumetric flask. Using a 100 microliter syringe add 90.0uL of 202ug/mL octachloronaphthalene into the same 100mL volumetric flask. Make to volume with hexane. The octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 120mL boston bottle and store in a freezer. The standard concentration is 2.00ug/mL for 3-Chlorobiphenyl and 0.050ug/mL for all other congeners in the standard. The following table lists the congeners included in this standard and the DB-1 peaks where they elute and also lists the other non-Aroclor congeners that co-elute with

these 14 congeners. The Stock Standard and Supplemental Congener Standard must be replaced after one year.

Supplemental Congener Standard

DB-1 Peak Number	IUPAC Congener Number	(IUPAC #) PCB Congener Analyzed		Conc ug/mL
3	2	(2)	3-Chlorobiphenyl	2.000
9	14	(14)	3,5-Dichlorobiphenyl	0.050
11	30	(30)	2,4,6-Trichlorobiphenyl	0.050
12	11	(11)	3,3'-Dichlorobiphenyl	0.050
19	23,34,54	(34)	2',3,5-Trichlorobiphenyl	0.050
28	36	(36)	3,3',5-Trichlorobiphenyl	0.050
30	39	(39)	3,4',5-Trichlorobiphenyl	0.050
35	62,65	(65)	2,3,5,6-Tetrachlorobiphenyl	0.050
36	35	(35)	3,3',4-Trichlorobiphenyl	0.050
41	68,96	(96)	2,2',3,6,6'-Pentachlorobiphenyl	0.050
43	57,103	(103)	2,2',4,5',6-Pentachlorobiphenyl	0.050
62	154	(154)	2,2'4,4',5,6'-Hexachlorobiphenyl	0.050
68	123	(123)	2',3,4,4',5-Pentachlorobiphenyl	0.050
70	140	(140)	2,2',3,4,4',6'-Hexachlorobiphenyl	0.050
76	127,168,184	(127)	3,3',4,5,5'-Pentachlorobiphenyl	0.050

6.9 Internal Standard: The internal standard used for capillary gas chromatography of PCBs will be octachloronaphthalene (OCN). Weigh, to the nearest 0.1 mg, 10.1mg of solid octachloronaphthalene (OCN) into a 5mL vial. Quantitatively transfer the OCN using six successive 2-mL washings of toluene to a 50mL volumetric flask. Be sure to rinse the 5mL vial walls carefully so that all OCN is completely transferred to the 50mL volumetric flask. Make the solution to volume using toluene and mix the internal standard solution by shaking the flask several times. This will give a concentration of OCN of 202ug/mL. Carefully transfer the internal standard solution to 25mL vials, tightly cap, and store in a freezer. A portion of the internal standard is transferred to a 5mL reacti-vial with a Teflon syringe-valve cap to use on a daily basis. The react-vial minimizes evaporation since the cap does not have to be removed.

6.9.1 The OCN internal standard is added to all calibration standards, continuing check standards, blanks, samples, and QC samples at the same amount. In most cases this will be achieved by spiking 9.0uL of OCN internal standard solution to 10mL of standard or sample extract to give a concentration of 0.1818ug/mL.

6.9.2 The internal standard will be added to calibration standards, sample extracts, blanks, and QC samples prior to gas chromatographic analysis. Thus, the internal standard is used as a quantification spiking standard and

will eliminate sample injection volume variations, but will not correct for analytical losses during sample preparation.

6.9.3 OCN internal standard must be replaced after one year.

6.10 Continuing Calibration Check Standards: Continuing calibration check standards at 1.27ug/mL and 0.127ug/mL are prepared from Aroclor solutions obtained from a different source (ULTRA Scientific) than the calibration standard. The continuing calibration check standard is a mixed Aroclor 1232, 1248, and 1262 in the fixed ratio used to prepare the calibration standard and must be strictly adhered to.

6.10.1 50.0ug/mL Continuing Calibration Check Stock Standards: Aroclor 1232, Aroclor 1248, and Aroclor 1262 are obtained from ULTRA Scientific at 1000ug/mL in isooctane. Using a 1.0mL Class A pipette, 0.5mL of 1000ug/mL Aroclor 1232 is transferred to a 10.0mL volumetric flask and made to volume with hexane. This procedure is repeated for Aroclor 1248 and Aroclor 1262. The 50ug/mL stock standards are transferred to a 10mL vial, tightly capped and stored in a freezer. These stock standards must be replaced after one year.

6.10.2 1.27ug/mL Continuing Calibration Check Standard with OCN: Using a 1.0mL Class A pipette transfer1.0mL of 50.0ug/mL Aroclor 1232, 0.5mL of 50.0ug/mL Aroclor 1248, and 0.5mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Using a 100 uL microsyringe, add 90.0uL of OCN internal standard (final concentration of 0.1818 ug/mL). Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing check solution will contain a total of 1.27ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

6.10.3 Transfer the 1.27ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a freezer. A new continuing check standard must be prepared every six months.

6.10.4 1.27ug/mL Continuing Calibration Check Standard without OCN: Using a 1.0mL Class A pipette transfer1.0mL of 50.0ug/mL Aroclor 1232, 0.5mL of 50.0ug/mL Aroclor 1248, and 0.5mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing check solution will contain a total of 1.27ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

6.10.5 Transfer the 1.27ug/mL Continuing Calibration Check Standard without OCN to a 120mL boston bottle, cap tightly, and store in a freezer. A new continuing calibration check standard must be prepared every six months. This continuing check standard without OCN is used to prepare the 0.127ug/mL Continuing Calibration Check Standard with OCN.

6.10.6 0.127ug/mL Continuing Calibration Check Standard with OCN: Using a 10.0mL Class A pipette transfer 10.0mL of 1.27ug/mL Continuing Calibration Check Standard without OCN to a 100mL volumetric flask. . Using a 100uL microsyringe, add 90.0uL of OCN internal standard (final concentration of 0.1818ug/mL). Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 0.127ug/mL PCB (0.050ug/mL Aroclor 1232, 0.036ug/mL Aroclor 1248, and 0.036ug/mL Aroclor 1262).

6.10.7 Transfer the 0.127ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a freezer. A new continuing calibration check standard must be prepared every six months.

7.0 Procedure

7.1 Calibration:

7.1.1 Gas chromatographic Operation Parameters: Establish the gas chromatographic operation parameters as follows:

GC Column: DB-1 (J&W, bonded polydimethylsilicone), 30 meters, 0.25 mm internal diameter, 0.25 micron phase coating.

Oven Temperature Program: 50°C for 5.0 min hold time, 50°C to 150°C at 15.0°C/min, hold 0.01minutes, 150°C to 220°C at 4.3°C/minute, hold at 220°C for 33.0 minutes.

GC Column Velocity: Approximately 30 cm/sec Helium. Column flow adjusted to elute OCN Internal Standard between 42.0 and 48.0 minutes.

Detector: Electron Capture Detector (ECD), attenuation 1, range 4.

Detector Temperature: 300°C.

Injector Temperature Program: 250°C , pulsed split injection, initial pressure at 25.0PSI, pulsed pressure at 40PSI, pulsed time 0.75 minutes, split ratio 25 (adjustable based on signal sensitivity)

Detector Make-up Gas: Approximately 65mL/min Nitrogen. Adjusted for signal sensitivity.

Autosampler: 1.0uL sample volume (adjustable based on signal sensitivity). Sample pumps 4, viscosity delay 3, sample wash 2, solvent A 2 washes, solvent B 2 washes, slow plunger OFF, sampling offset OFF, solvent A pre-wash 1, solvent B pre-wash 1.

7.1.2 Initial GC Calibration: Prior to running samples the system must be calibrated and the Continuing Calibration Check Standard must be verified.

7.1.2.1 Establish the gas chromatographic operation parameters outlined in Section 7.1.1 and prepare the appropriate calibration standards composed of a mixture of Aroclors 1232, 1248, and 1262 as outlined in Sections 6.5 through 6.10.

7.1.2.2 Chromatographic Resolution Criteria: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

7.1.2.3 Initial High Level Linearity Verification: The gas chromatograph must undergo a linearity study. A high-level three-point initial calibration check for linearity is analyzed and calculated relative response factors must meet a limit for relative standard deviation for each GC peak of less than 20%. This high level linearity verification is associated with samples with medium to high levels of PCBs for sample matrices such as biota, sediment, soil, oil, and other solid or liquid samples that contain appreciable levels of PCBs. The high level initial linearity is comprised of the following standards: 31.35ug/mL High-Level Linearity Standard, 6.27ug/mL Calibration Standard, and the 1.27ug/mL Continuing Calibration Standard.

7.1.2.4 Initial Low Level Linearity Verification: The gas chromatograph must undergo a linearity study. A low-level three-point initial calibration check for linearity is analyzed and calculated relative response factors must meet a limit for relative standard deviation for each GC peak of less than 20%. This low level linearity verification is associated with samples with low levels of PCBs for sample matrices such as water and other solid or liquid samples that contain low levels of PCBs. The low-level initial linearity is comprised of the following standards: 6.27ug/mL Calibration Standard, the 1.27ug/mL Continuing Calibration Standard, and the 0.127ug/mL Continuing Calibration Standard.

7.1.2.5 Initial 72-Hour Retention Time Window Measurement: An initial retention time study must be performed to establish retention time windows to assist in PCB peak assignment. Three high level Continuing Calibration Check standards must be analyzed over at least a 72-hour period. In addition, the Supplemental Congener Standard is analyzed three times over at least a 72-hour period. The mean retention time is calculated from these standards along with the standard deviation for each GC peak. The retention time window is established as ±3 times the determined standard deviation. If the 3 times the standard deviation value is less than 0.07 minutes a default of 0.07 minutes is applied to that GC peak. The default 0.07 minutes retention time window is the default window used in Contract Laboratory Program, Statement of Work for Organic Analysis for PCB/Pesticide analysis.

7.1.2.6 Our laboratory will use a computer based data acquisition workstation (Waters Associates, Millennium_32 workstation software), interfaced to the gas chromatograph. The workstation processes the detector signal, performs an analog to digital conversion, and stores the digitized chromatograms on the computer hard disk. All data analysis will be done on the specialized software package including peak integration, calculating calibration curves/response factors, report generation, chromatogram hardcopies, and archival of data. Calculate the response factor for each separated and identified peak.

7.1.2.7 After the above criteria are met system calibration for sample analysis can be performed. Appendix A identifies which congener and or congeners compose each resolvable GC peak in the calibration standard, along with the amount that each congener or co-eluting group of congeners are represented in the calibration standard. Throughout this document the IUPAC PCB numbering system will be used for congener identification. Appendix B is an example of an acceptable chromatogram of the calibration standard, along with peak congener labels for cross-reference to data in Appendix A. Analyze the 6.27ug/mL Calibration Standard to initiate calibration of the GC system. Also analyze the Supplemental Congener Standard to calculate relative response factors for congeners that do not exist in the 6.27ug/mL Calibration Standard. Response factors are calculated relative to the internal standard by the following equation:

$$RRF = (Ax/Ais)x(Cis/Cx)$$

Where: RRF = Relative response factor of congener(s).
Ax = Area of peak for the congener(s).
Ais = Area of peak for the internal standard.
Cx = Concentration of the congener(s).
Cis = Concentration of the internal standard.

7.2 Continuing Calibration:

7.2.1 Chromatographic Resolution:

7.2.1.1 Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

7.2.2 Response Factor Verification:

7.2.2.1 The relative response factors calculated from the calibration standard will be verified on each working day by analyzing a Continuing Calibration Check Standard, calculating the selected congener concentrations and comparing to their known concentration. A subset of six congeners and Total PCBs will be used to verify the relative response factors before samples are processed. The Percent Difference for Total PCBs must be ±15%. The six congeners include:

DB-1 PEAK NUMBER	IUPAC CONGENER NUMBER	RELATIVE PEAK LEVEL IN CALIBRATION STANDARD	PEAK CONC 1.27ug/mL CONTINUING CALIBRATION STD (ng/mL)	PERCENT DIFFERENCE LIMITS
7	6	Low level peak in standard	14.10	<30
116	205	Low level peak in standard	0.820	<30
47	70	Medium level peak in standard	25.22	<10
93	174,181	Medium level peak in standard	23.74	<10
37	104,44	high level peak in standard	31.90	<10
102	180	high level peak in standard	45.26	<10

7.2.3 After the Continuing Calibration Check Standard is analyzed, calculate the amount for these six congeners and Total PCBs and compare those values to the known concentrations by the following equation:

Percent Difference = [Amt(1)-Amt(2)]/Amt(2) x 100

Where: Amt(1) = Amount calculated for congener or Total PCBs.
Amt(2) = Known amount for congener or Total PCBs.

7.2.4 A percent difference greater than ± 30% for the two low-level peaks (7 and 116) indicates an instrument problem or unacceptable relative response factors. A percent difference greater than ± 10% for the medium level (47 and 93) and high level (37 and 102) peaks also indicates an instrument problem or unacceptable relative response factors. If any of the evaluation congeners or Total PCBs fail to meet the percent difference acceptance criteria, the guidance provided in Section 8.1.4 must be followed.

7.2.5 The percent recovery for the internal standard octachloronaphthalene (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the OCN area in the associated calibration standard. If the OCN area fails to meet the acceptance criteria, the guidance provided in Section 8.1.4 must be followed.

7.2.6 If re-calibration is performed, the Continuing Calibration Check Standard must be analyzed again and values calculated using the new relative response factors. If the Continuing Calibration Check Standard fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (*i.e.*, GC gas leak, autosampler lines plugged, broken injector liner).

7.3 Sample Preparation and Extraction

7.3.1 The following SOPs detail sample extraction procedures that are utilized in preparing samples for analysis by this analytical method:

SOP NAME	TITLE
NE005	SOXHLET EXTRACTION : SOLIDS
NE006	WATER EXTRACTION
NE017	FISH & BIOTA EXTRACTION
NE049	ANIMAL TISSUE EXTRACTION: SMALL MASS PROCEDURE
NE087	EXTRACTION FOR OIL
NE088	WIPE EXTRACTION FOR PCB
NE124	CLLE PCB EXTRACTION
NE132	FISH/BIOTA GRINDING PROCEDURES
NE140	PCB SCREENING BY GC
NE143	ASE EXTRACTION FOR PCB: SOLIDS
NE144	ASE EXTRACTION FOR WIPE: PCB
NE158	% LIPID DETERMINATION: FISH & BIOTA

7.4 Calculations:

7.4.1 SCREENING GC: External Standard Calibration:

7.4.1.1 The GC screening analysis will be done by the external standard calibration technique. See standard operating procedure NE140 for details on the PCB screening

procedures used prior to final analysis by this method. The GC will be standardized by using Aroclor 1242 and Aroclor 1260. These two Aroclor formulations incorporate most environmental PCBs found in sample extracts and provide a good estimate of PCB amount for final dilution for capillary analysis. A two level calibration curve is utilized (0.50ug/mL and 2.5ug/mL standards).

7.4.1.2 The calibration curves for each section of the PCB elution profile will be calculated using the following formula:

$$\text{Calibration factor} = \frac{\text{Amount (ug) of Aroclor}}{\text{Total area of Aroclor}}$$

The calibration curve will be a linear fit forced through zero.

7.4.2 SCREENING GC: Sample Calculations

7.4.2.1 The concentration of each Aroclor (grouped as Aroclor 1242 and Aroclor 1260 only) in a sample will be calculated based on the extract volume (not the sample weight or volume) to supply solution concentration values that show if the extract needs to be diluted for final capillary GC analysis. The solution concentration of either Aroclor 1242 or Aroclor 1260 (or both) in a sample is calculated as follows:

$$\text{Concentration (ug/mL)} = (Ax) \times (CF)$$

Where: Ax = Area of Aroclor of interest in sample
CF = Calibration factor in standard

7.4.3 Capillary GC: Internal Standard Calibration

7.4.3.1 The capillary column GC analysis will be done by the internal calibration technique. Calibration and sample quantification will be performed by a commercial GC software package. The capillary GC will be standardized by using an Aroclor mixture that encompasses all the possible PCB congeners present in environmental samples. Refer to Section 6.6 for details on the calibration standard and Aroclor ratios.

7.4.3.2 Response factors for each separated and identified peak in the standard will be calculated using the following formula:

$$RRF = (Ax/Ais) \times (Cis/Cx)$$

Where: RRF = Relative response factor of congener(s).
Ax = Area of peak for the congener(s).
Ais = Area of peak for the internal standard.
Cx = Concentration of the congener(s).
Cis = Concentration of the internal standard.

7.4.4 Capillary GC: Sample Calculations

7.4.4.1 The concentration of each identified PCB peak in a sample will be calculated based on the sample dry weight in the case of soils and sediments and wet weight for fish and biota samples.

7.4.4.2 The sample PCB concentration of each standardized PCB peak is calculated as follows:

$$\text{Concentration (ng/g)} = \frac{[(Ax)(Cis)(V)(D)]}{[(Ais)(RRF)(Ws)]}$$

Where: Ax = Peak area for congener(s) being measured.
Cis = Amount of internal standard added to sample extract.
D = Dilution factor, if sample was diluted prior to analysis.
V = Extract volume.
Ais = Peak area of added internal standard.
RRF = Relative response factor for congener(s) being measured as determined in Section 7.4.3.2.
Ws = Dry or wet weight of sample.

7.4.5 The calculated PCB concentration for each PCB peak will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results for peaks with concentrations at or above the MDL but below the RL will be reported as detects and flagged as estimated ("J"). The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

7.4.6 The Total PCB concentration will be calculated and reported as follows:

7.4.6.1 All peak results above their respective MDL (both "J" flagged and unqualified results) will be summed and compared to the sample-specific Total PCB MDL and RL.

7.4.6.2 If no peaks are detected above their respective MDL, the Total PCB results will be reported as not detected at or above the sample-specific Total PCB MDL.

7.4.6.3 If the summed peaks from are below the Total PCB MDL the result would be reported as less than ("<") the sample-specific Total PCB MDL.

7.4.6.4 If the summed peaks from are at or above the Total PCB MDL but below the Total PCB RL, the summed result will be flagged as estimated ("J").

7.4.6.5 If the summed peaks from are at or above the Total PCB RL, the Total PCB result will be reported as the unqualified numeric value.

7.4.5 Data Output and Reporting Format:

7.4.5.1 Several specialized software routines have been developed for high resolution PCB analysis to aid the data user in understanding and organizing the complex data generated from this extremely detailed analysis. Appendix C contains examples of the sample hard copy format that will be used in reporting sample information. This data is also available in electronic format as an Excel™ file.

7.4.6 Data adjustments for Hudson River water samples:

7.4.6.1 In 1997 a report was issued by General Electric to EPA (HydroQual, 1997. Development of Corrections for Analytical Biases in the 1991 – 1997 GE Hudson River PCB Database. Prepared for General Electric Company Corporate Environmental Programs, Albany, NY.) that outlined concentration corrections required for several DB-1 GC peaks containing more than one PCB congener. These PCB congeners were present in different proportions in Hudson River water samples compared to the method calibration standards. The technical details and research that support the following data conversion can be found in the above referenced document.

7.4.6.2 The EPA 1993 Reassessment Remedial Investigation and Feasibility Study (RRI/FS) Phase II Hudson River water column data were used as a qualitative benchmark for data comparison to the GE weekly Hudson River water column study. This 1993 data set was chosen because EPA collected a significant number of samples to compare to the GE weekly sampling events.

7.4.6.3 Significant concentration differences were detected in Green Bay method GC peaks 5, 8, and 14 (which are comprised of congeners IUPAC 4 and 10; IUPAC 5 and 8; and IUPAC 15 and 18, respectively) when compared to the EPA database, which determined concentrations of these congeners as individual eluting GC peaks. These congeners differ in gas chromatographic response between each other when analyzed individually. It was determined

that when these congeners were measured in Hudson River water samples as co-elutions their composition did not match the calibration standard congener composition in peaks 5, 8, and 14 and measurement was not as precise as when these congeners were determined by the EPA analytical method.

7.4.6.4 To address this measurement bias for the above peaks, a correction ratio was determined and applied to the concentration values obtained by the initial quantification. The correction ratio was derived by analysis of Hudson River water column extracts on a chromatographic system that was calibrated using individual congeners as standards and that could baseline resolve the co-elution congeners found in Green Bay method GC peaks 5, 8, and 14. These results were utilized to report a more accurate concentration value for the congeners comprising Green Bay method peaks 5, 8, and 14. The correction factors historically used were 0.65, 0.45, 1.44 for DB-1 peaks 5, 8, and 14, respectively. The correction ratios were confirmed and verified in March 2004 by conducting confirmatory analyses utilizing the gas chromatographic system that baseline resolved the six PCB congeners that required the correction ratio. GE confirmed and updated the correction factors for DB-1 peaks 5, 8 and 14 in a manner consistent with the approach described in the above report. The results of the evaluation of the correction factors for DB-1 peaks, 5, 8, and 14 were delivered to EPA via email on March 31, 2004 in a technical memorandum. Based on the findings summarized in the technical memorandum, upon initiation of the BMP, the correction factors developed based on the 2003 data set (0.61, 0.36 and 1.26) will be used to adjust DB-1 peaks 5, 8 and 14, respectively, for the bias identified in HydroQual 1997.

7.4.6.5 After the concentration values are corrected for Green Bay method peaks 5, 8, and 14 several other parameters require re-calculation prior to data reporting. These include the following: total PCB concentration, Homolog distribution, weight percent per peak, chlorination levels (ortho-Cl per biphenyl, meta+para-Cl per biphenyl, and total Cl per biphenyl), total micromoles, and average molecular weight.

8.0 Quality Control

8.1 The following table lists the Quality Control samples required for capillary gas chromatography analysis of PCBs in water, soils and sediments.

Quality Control Requirements

QC Sample	Frequency
Lab Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Continuing Cal Check	Analyzed prior to each sample batch (up to 10 samples)
Duplicate Analysis	Field generated sample – analyzed at discretion of client
Matrix Spike	One matrix spike per 20 field samples
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples

8.1.2 Laboratory Blank: The laboratory blank will monitor and assess whether the contamination or excessive interference is occurring from laboratory solvents, reagents, and glassware used in processing samples for analysis. The laboratory blank is taken through the sample extraction and clean-up procedures to include all manipulations exposed to actual samples (required volume of solvents, concentration steps, clean-up procedures, *etc*.) If the laboratory blank is positive for PCB above the reporting limit, the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis. The laboratory blank will consist of granular sodium sulfate for solids and organic free water for water samples.

8.1.2.1 Samples associated with a positive laboratory blank should be flagged when the data is reported. If a laboratory blank is positive for PCBs, the source of contamination must be located and eliminated. If the contamination occurred during the extraction procedure and more sample is available the samples will require re-extraction and re-analysis. If the contamination occurred after this step, then re-extraction may not be required and the existing extracts will be reanalyzed. Any aliquots of the extracts (*i.e.,* injection vials) which could have become contaminated will be discarded.

8.1.3 Laboratory Control Spike: A Laboratory Control Spike sample is analyzed with each extraction batch. An Aroclor is spiked into either granular sodium sulfate for solids or organic free water for liquids. This Control Spike must achieve a percent recovery of 70 to 130 percent. If the Control Spike recovery is not within limits, the cause must be tracked down and corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no more sample is available, the data must be flagged to indicate low or high Control Spike recovery.

8.1.4 Continuing Calibration Check Standard: As outlined in section 7.2, a Continuing Calibration Check Standard will be analyzed on each working day prior to sample analysis and at an interval of one Continuing Calibration Check Standard per 10 samples. The Continuing Calibration Check Standard must meet the acceptance criteria established in Section 7.2. If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the following guidance must be followed.

8.1.4.1 If samples are being run using an autoanalyzer (*i.e.,* the instrument is unattended) and a Continuing Calibration Check Standard that fails to meet the acceptance criteria is present in the analytical sequence but acceptable Continuing Calibration Check Standards are observed later in the analytical sequence, samples bracketed by acceptable Continuing Calibration Check Standards will be reported.

8.1.4.2 If the reason for the failure of the Continuing Calibration Check Standard appears to be a poor injection (or a degraded standard solution), the Continuing Calibration Check Standard will be re-injected (or reprepared and re-injected) immediately following the failed Continuing Calibration Check Standard. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the Continuing Calibration Check Standard meets all the acceptance criteria established in Section 7.2 and there is no apparent impact on the sample data (*i.e.,* acceptable internal standard areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported.

8.1.4.3 If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the calibration standard must be re-analyzed and new response factors generated. After re-calibration, the Continuing Calibration Check Standard must be analyzed again and compared to the acceptance criteria. If the Continuing Calibration Check Standard fails to meet the acceptance criteria after re-calibration, sample analysis must not proceed until the problem is corrected.

8.1.4.4 All samples that were analyzed directly before or after the continuing calibration check standard exceeded established criteria must be re-analyzed.

8.1.5 Duplicate Analysis: Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, with the sample split in the field. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike / matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

RPD = (DUP1 – DUP2)/AVG x 100

Where: RPD = Relative Percent Difference.
DUP1 = The greater of the measured values.
DUP2 = The lesser of the measured values.
AVG = Average of the two analysis.

8.1.5.1 The relative percent difference must be less than or equal to 25% if the concentration of PCB in the sample is greater than or equal to 0.5ug/g. The percent relative standard deviation must be less than or equal to 50% if the concentration of the PCB in the sample is less than 0.5ug/g.

8.1.6 Matrix Spike and Matrix Spike Duplicate: Spiked sample matrix data are analyzed to assess analytical accuracy and recovery of analytes of interest. Thus the sample is spiked and carried through sample analytical procedures including extraction, clean up, and GC analysis.

8.1.6.1 There must be sufficient sample for analysis of matrix spike/matrix spike duplicate samples and the sample must be homogeneous in PCB distribution for valid data to be produced. Preferably a sample of low level should be used in this case so that the spike level is of sufficient concentration over the background level of the chosen sample. Spike the two samples with the Aroclor matrix spike standard at a concentration approximately five times the sample concentration. Extract and analyze the two spiked samples following procedures used for actual sample analysis. Calculate the percent recovery of the matrix spike/matrix spike duplicate by the following equation:

P = A-B/T x 100

Where: P = Percent recovery, %.
A = concentration of analyte in the spike sample aliquot.
T = Known true value of the spike concentration.
B = Background concentration of PCB in the unspiked sample aliquot.

8.1.6.2 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 70% and less than or equal to 130% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

8.1.7 Surrogates: Surrogate spiking compounds monitor the exaction efficiency and sample processing procedures for each sample. Surrogate compounds are chosen which do not chromatographically interfere with the PCB target congeners and which behave similarly to the target PCB congeners during extraction and sample processing.

8.1.7.1 Surrogate spike additions are made to each field sample, method blank, and extracted QC check sample prior to extraction. Congener IUPAC 207 (2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl) or Tetra-Chloro-Meta-xylene and Decachlorobiphenyl surrogate compounds are used.

8.1.7.2 Calculate the surrogate percent recovery as follows:

% Recovery = (Surr. Amount spiked / Theoretical Spike conc.) * 100

8.1.7.3 The percent recovery limits for surrogates are:

IUPAC 207	70% - 130%
Tetra-Chloro-Meta-Xylene	70% - 130%
Decachlorobiphenyl	70% - 130%

8.1.8 Retention Time Windows:

8.1.8.1 The Initial Continuing Calibration Check Standard of the analytical sequence is used to establish the retention time window for each analyte from the retention time windows determined during the 72-hour retention time window study. The retention time window equals the absolute retention time of the Initial Continuing Calibration Check

Standard for a given batch of samples plus or minus three times the standard deviation determined in Section 7.1.2.5.

8.1.8.2 Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-residue sample analysis.

8.1.8.3 The PCB congener composition of DB-1 peaks is identified in Appendix A. DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. With exception of congeners IUPAC 77 and 122, the resolved peaks are found at trace levels in Aroclors (and, therefore, not present in the calibration standards) and are addressed in this method in the event they are detected. If these congeners are detected in a sample, the retention time window of the assigned DB-1 peak is set to ensure the congener is quantitated. A standard comment is included on the Congener Weight and Mole Report (see Appendix B) identifying this issue. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indicating that the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak[1]	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76*, *98*, *80*, *93*, **95**, **102**, *88*)	*80*, *88*, *93*
56 (*78*, **83**, *112*, *108*)	*108*
61 (**77**, **110**, 148)	**77**
72 (**122**, 131, 133, 142)	**122**
89 (**128**, *162*)	*162*

105 (**200**, *169*) *169*

1 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

8.1.9 Analytical Sequence Queue: A typical analytical sequence is as follows:

1)	Continuing Calibration check standard (high or low)
2)	Method Blank
3)	Lab Control Spike
4 to 10)	Samples (including Duplicates, MS/MSD)
11)	Continuing Calibration Check Standard
12 to 20)	Samples (including Duplicates, MS/MSD)
21)	Continuing Calibration Check Standard; repeat 12 to 20

9.0 Method Performance:

9.1 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at a reasonable concentration above the 0.127ug/mL continuing calibration standard and below the 6.27ug/mL calibration standard. The analyte will be added to a laboratory organic free water sample or organic free sodium sulfate sample and taken through all extraction and analytical procedures. Aroclor 1242 is used as the analyte and recovery on a total basis is used to calculate percent recovery. To be valid, Aroclor 1242 will be recovered between the limits of 70 to 130 percent. Also, a percent relative standard deviation will be calculated for the replicates will be less than or equal to 20% to be valid.

9.2 Method Detection Limit: A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures are made or at a minimum frequency of every 2 years. A minimum of seven laboratory organic free water samples or seven organic free sodium sulfate samples will be prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

$$MDL = S * t_{(n-1,\ 1\text{-}alpha=0.99)}$$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1\text{-}alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)}$ = 2.998

9.2.1 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

10.0 Data Assessment and Acceptance Criteria for Quality Control Measures and Corrective Actions for Out-of-Control Data:

10.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration check compliance.

10.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing calibration check standards.

10.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. A Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This CAR form is filed with the data and is also useful for production of case narratives that are issued with final data reports.

10.4 The Table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Linearity Verification and Initial Calibration	• Initially verify linearity through the High- and Low-Level Linearity Verifications. • The initial calibration checks for linearity are each at 3 concentration levels. • A single-point calibration is analyzed initially and when Continuing Calibration Check standard fails criteria.	• %RSD≤20% for among the relative response factors for each peak in the linearity verifications. • Relative response factors are to be calculated using area for each quantifiable peak with internal standard method.	• Re-analyze the initial calibration standard and/or evaluate/correct instrument malfunction to obtain initial calibration and continuing calibration check standards that meet criteria. • Sample results above highest linearity verification standard concentration require dilution and re-analysis.
Continuing Calibration Check Standard (CCC)	• Initially analyze a CCC immediately following a calibration standard analysis. • After the initial CCC of the sequence, a CCC must be analyzed after every 10 samples. • Analytical sequence must end with analysis of a CCC.	• ≤ 30% difference based on "true" concentration for peaks 7, 116. • ≤ 10% difference based on "true" concentration for peaks 37, 47, 93, and 102 and Total PCBs • Retention time of all quantitated peaks must be within RT window (reset with each initial CCC of a sequence) • The percent recovery for the internal standard (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the OCN area of the associated initial calibration standard. • All samples must be bracketed by CCCs that meet all criteria stated above	• If the reason for the failure of the CCC appears to be a poor injection (or a degraded standard solution), the CCC will be re-injected (or reprepared and re-injected) immediately following the failed CCC. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCC meets all the acceptance criteria and there is no apparent impact on the sample data (*i.e.,* acceptable OCN areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. • If CCC failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCC failure, correct system, if necessary, and recalibrate. Initial calibration and CCC criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCs must be re-analyzed. • If acceptable CCCs are observed later in the sequence, samples bracketed by acceptable CCCs will be reported. Samples between the failed CCC and prior/ subsequent complaint CCC will be re-analyzed.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Retention Time (RT) Windows	• Initial RT windows are established to assist in PCB peak assignment. Three high-level CCC standards and three Supplemental Congener Standards are analyzed over at least 72-hours. The mean RT and the standard deviation of each of the GC peaks are calculated. RT window is ± 3× the determined standard deviation or a default of 0.07 minute is applied (whichever is larger). • RT windows are re-centered based on the initial CCC analyzed after calibration curve or if using the first CCC of the day to start a new sequence.	• RT of CCC peaks must be within established windows in the CCs analyzed for a sequence. • Re-centering windows is allowed only once per 24 hours.	• Adjust system, re-establish RT windows, and re-calibrate if necessary.
Retention Time (RT) shift	• Each CCC analysis: RT of all quantitated peaks in the CCC is evaluated against the initial CCC following the initial calibration curve. • Each sample analysis: Rely on RT windows to identify PCB congeners to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because congener composition may shift RT for GC peaks.	• Each quantitated peak and surrogate peak should be with established windows.	• Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	• One per extraction batch of ≤20 samples of the same matrix per day. • Must be analyzed on each instrument used to analyze associated samples. • Must undergo all sample preparative procedures.	• Concentration does not exceed the total PCB method reporting limit. • Must meet surrogate criteria of 70 to 130 % recovery.	• Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. • If method blank is found to contain PCB contamination above total PCB reporting limit. Then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate method blank contamination or have client re-sample if possible.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Spike (LCS)	• One per extraction batch of ≤20 samples per matrix per day. The LCS is typically Aroclor 1242.	• Percent recovery of Aroclor 1242 on a total PCB basis must be within method limits of 70 to 130% • Must meet surrogate criteria of 70 to 130% recovery.	• Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. • If LCS recovery is still out of limits, then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate LCS failed recovery or have client re-sample if possible.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	• Normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. The MS is typically Aroclor 1242. • If requested, an MSD can be extracted an analyzed. The MSD would follow the above criteria as for the MS.	• Percent recovery for MS on a total PCB basis should be 70 to 130% • If MS/MSD is analyzed, relative percent difference (RPD) should be within 30%. • Must meet surrogate criteria of 70 to 130%(unless original unspiked sample is also outside of criteria).	• Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. • Check for errors such as calculations and spike preparation. • Check original unspiked sample results and surrogate recovery for indications of matrix effects. • If no errors are found, and the associated LCS is within 70 to 130%, then sample matrix effects are likely the cause. Note exceedence in case narrative.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Surrogates	• 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl is added to all samples and QC samples.	• Percent recovery for the surrogate should be 70 to 130%	• Re-analyze the affected sample or QC sample to determine if instrument was the cause. If surrogate passes, then report samples. • Check for errors in surrogate calculations and surrogate solutions. • If no problem is found, then re-extract and re-analyze the sample. • If re-analysis is within limits and sample extract holding time, then report only the re-analysis. • If the re-analysis is within limits, but out of extraction holding time, then report both sets of data. • If the re-extraction produces surrogate recovery still out of limits, then report both sets of data. • If no sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have client re-sample if possible.
Internal Standard	• Octachloronaphthalene (OCN) is added to all sample extracts, QC samples and calibration standards. See text for OCN amounts in calibration standards.	• The internal standard area for samples and QC samples should be 50 to 150% of the average internal standard area among the associated initial calibration standards. • The internal standard area for CCCs must be 50 to 150% of the average internal standard area among the initial calibration standards.	• Re-analyze the affected sample or standard to determine if instrument was the cause. If internal standard passes, then report samples. • For Standards – If no problem is found, prepare new standards and re-test. If problem still exists, prepare new internal standard and then prepare new standard solutions and re-test. • For Sample Extracts – If no problem is found, then follow procedures outlined above for surrogate corrective action steps for re-extraction and re-analysis.

11.0 References

11.1 US EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants," July, 1988.

11.2 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Published by: American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1995.

11.3 US EPA SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

11.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual," Wadsworth Center for Laboratories and Research, 1988.

11.5 Mullin, M.D. 1985. PCB Workshop, US EPA Large Lakes Research Station, Grosse Ile, MI, June.

11.6 M. Zell, K. Ballschmiter, Baseline Studies of the Global Pollution, III. Trace Analysis of Polychlorinated Biphenyls (PCB) by ECD Glass Capillary Gas Chromatography in Environmental Samples of Different Trophic Levels, Fresenius Z. Anal. Chem., 304, 337-349, 1980.

11.7 M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Save, "High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of All 209 PCB Congeners," Environ. Sci. Technol., Vol 18, No. 6, pp 468-476, 1984.

11.8 D.L. Swackhamer, "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office" Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987.

11.9 George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns ", Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996.

11.10 "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", USEPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2

11.11 "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10.

11.12 Contract Laboratory Program – Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration. Document OLM3.2, 1996.

APPENDIX A

Congener Composition of Multi-Aroclor Calibration Standard (6.27 ug/mL)

Congener Composition of Mixed Aroclor High-level Standard (6270ng/mL) (Aroclors 1232, 1248, 1262 in a ratio of 25:18:18)

file: S:/TEXT/SOP/ne207_appendix_A_GBcalstd.DOC

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
2	**001**	438.57
3	**002**	-
4	**003**	255.84
5	**004 010**	124.26
6	**007 009**	43.85
7	**006**	69.40
8	**005 008**	511.66
9	*014*	-
10	**019**	10.24
11	*030*	-
12	**011**	-
13	**012 013**	9.75
14	**015 018**	135.22
15	**017**	135.22
16	**024 027**	9.50
17	**016 032**	142.53
19	*023* **034** *054*	-
20	**029**	1.94
21	**026**	26.32
22	**025**	11.69
23	**031**	150.68
24	**028** *050*	192.86
25	**020** *021* **033 053**	145.16
26	**022 051**	105.99
27	**045**	32.52
28	*036*	-
29	**046**	14.62
30	*039*	-
31	**052** *069 073*	174.33
32	**043 049**	84.06
33	*038* **047**	36.55
34	**048** *075*	36.55
35	*062 065*	-
36	**035**	-
37	*104* **044**	157.16
38	**037 042 059**	95.03
39	**041 064 071** *072*	149.85
41	*068* **096**	-
42	**040**	34.36
43	**057** *103*	-
44	*058* **067** *100*	4.02
45	**063**	7.68
46	**074** *094 061*	69.44
47	**070**	124.26
48	**066** *076 098 080 093* **095 102** *088*	263.14

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
49	*055* **091** *121*	18.64
50	**056 060**	127.91
51	**084 092** *155*	65.78
52	**089**	3.66
53	**090 101**	65.78
54	*079* **099** *113*	27.04
55	**119** *150*	1.02
56	*078* **083** *112 108*	5.48
57	**097** *152 086*	20.46
58	*081* **087** *117 125* **115** *145*	42.39
59	*111 116* **085**	25.59
60	*120* **136**	27.41
61	**077 110** *148*	77.84
62	*154*	-
63	**082**	16.08
64	**151**	62.15
65	**124 135**	10.60
66	**144**	21.93
67	*107* **109** *147*	4.75
68	*123*	-
69	*106* **118** *139* **149**	146.19
70	*140*	-
71	**114 134** *143*	7.38
72	**122 131 133** *142*	1.06
73	**146** *165 188*	14.26
74	**105 132** *161*	49.52
75	**153**	107.64
76	*127 168 184*	-
77	**141**	62.13
78	**179**	53.36
79	**137**	2.74
80	**130 176**	9.50
82	**138 163 164**	98.68
83	**158** *160 186*	9.13
84	*126* **129**	0.47
85	*166* **178**	40.20
87	**175** *159*	7.31
88	*182* **187**	131.57
89	**128** *162*	3.66
90	**183**	62.13
91	**167**	1.79
92	**185**	17.17
93	**174** *181*	116.95
94	**177**	62.13
95	**156 171**	28.88
96	**157 202**	2.41
98	**173**	1.39
99	**201**	14.26
100	**172** *204*	20.46
101	*192* **197**	4.02

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
102	**180**	222.94
103	**193**	15.35
104	**191**	4.38
105	**200** *169*	15.71
106	**170**	46.78
107	**190**	15.35
108	**198**	4.38
109	**199**	153.50
110	**196 203**	157.16
111	**189**	1.46
112	**195**	20.21
113	**208**	9.02
114	*207*	3.40
115	**194**	65.78
116	**205**	4.02
117	**206**	24.85
118	*209*	0.44

1 - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low-level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.
PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 81 (176) now elutes in PK 80 (130,176)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

2 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

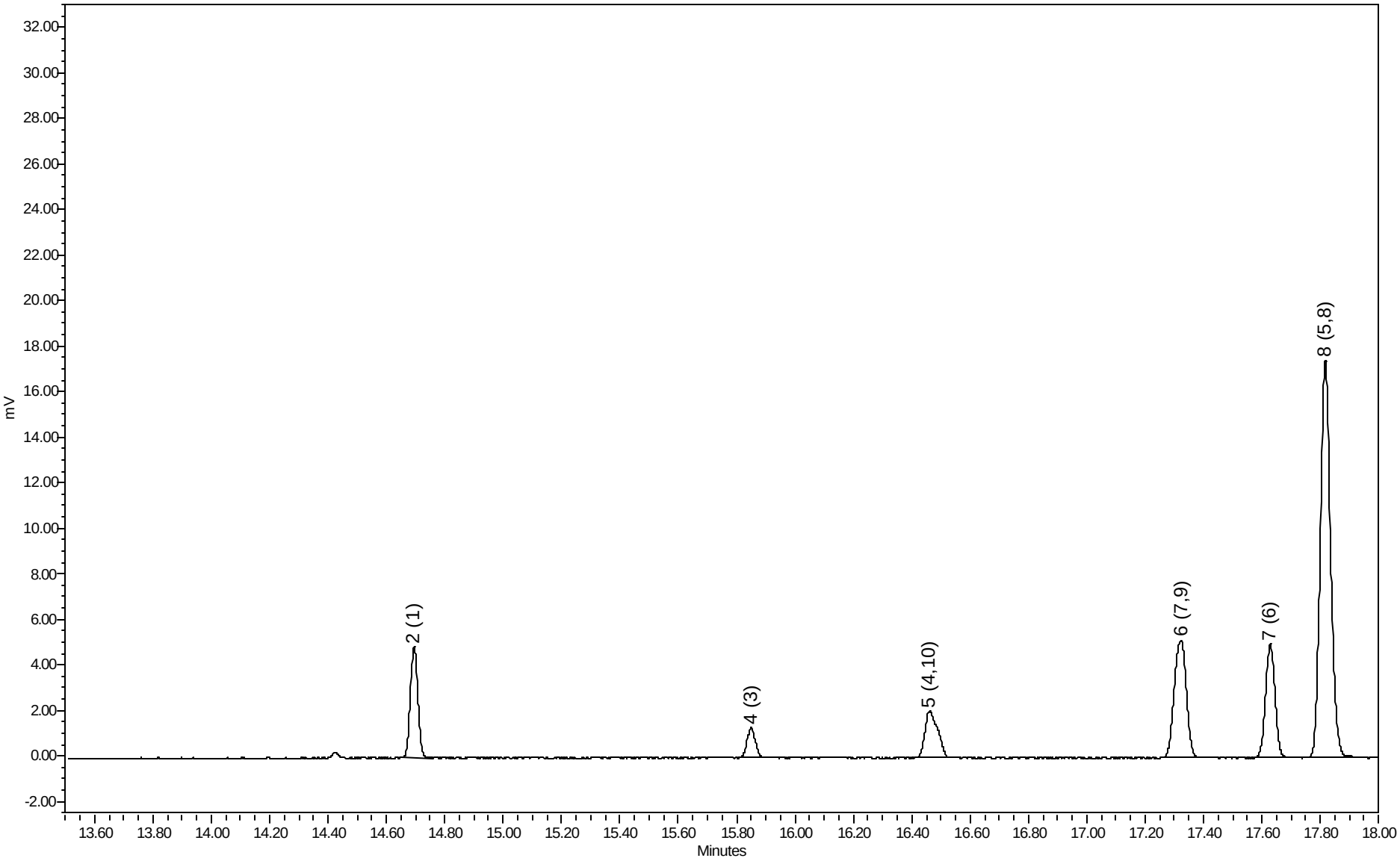
APPENDIX B

DB-1 Capillary GC Chromatograms:

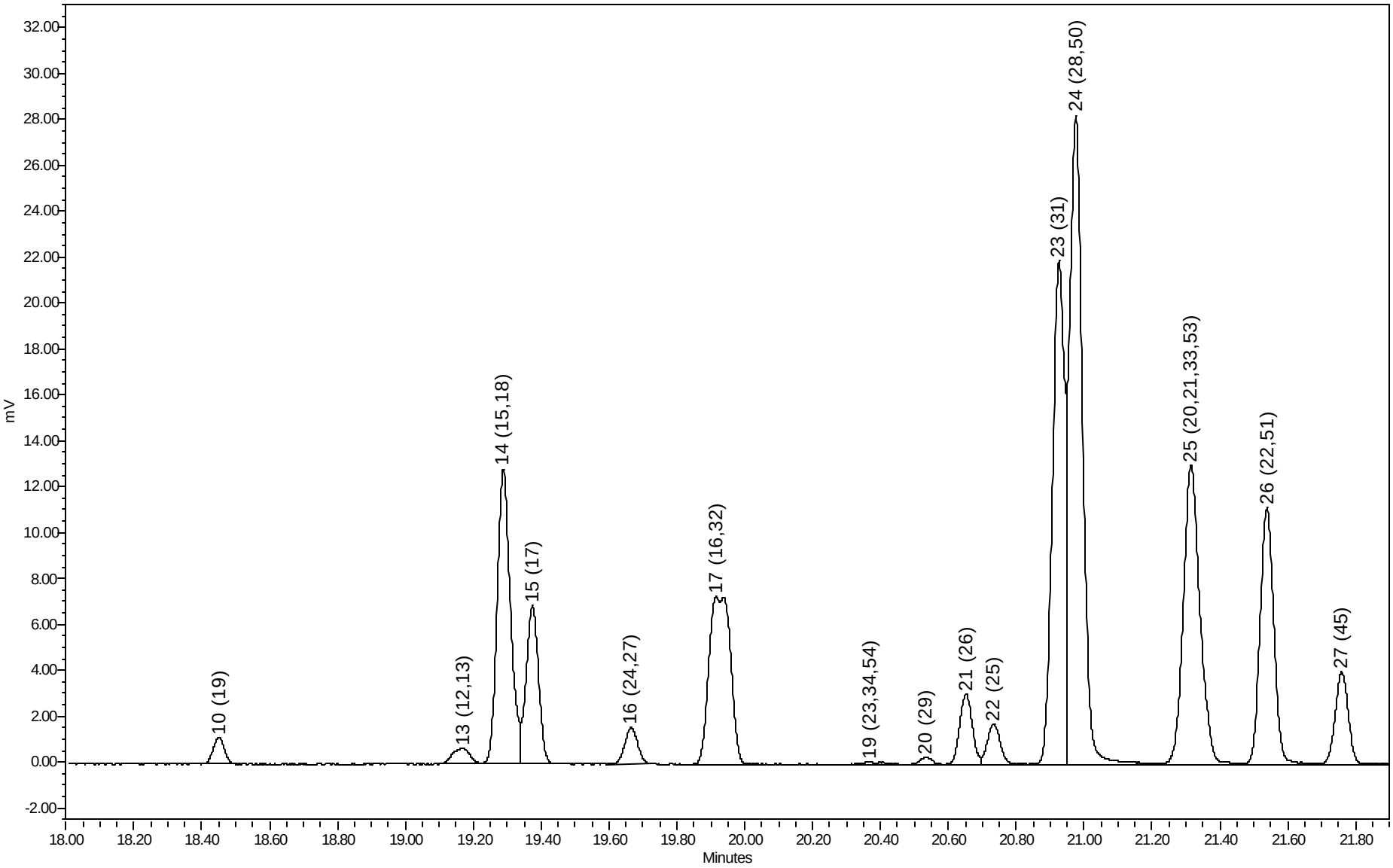
1.) 6.27 ug/mL Calibration Standard

2.) Supplemental Congener Standard

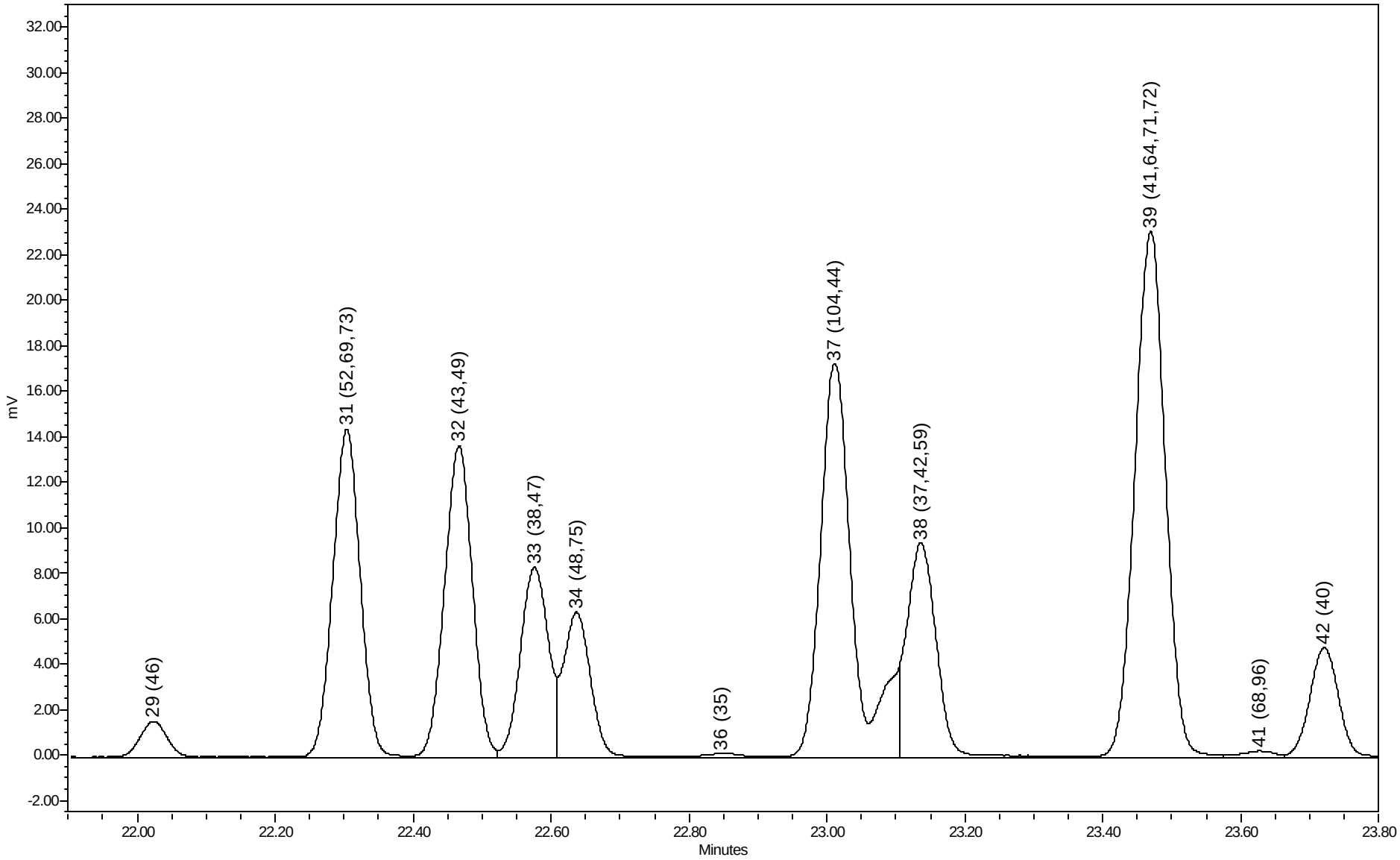
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



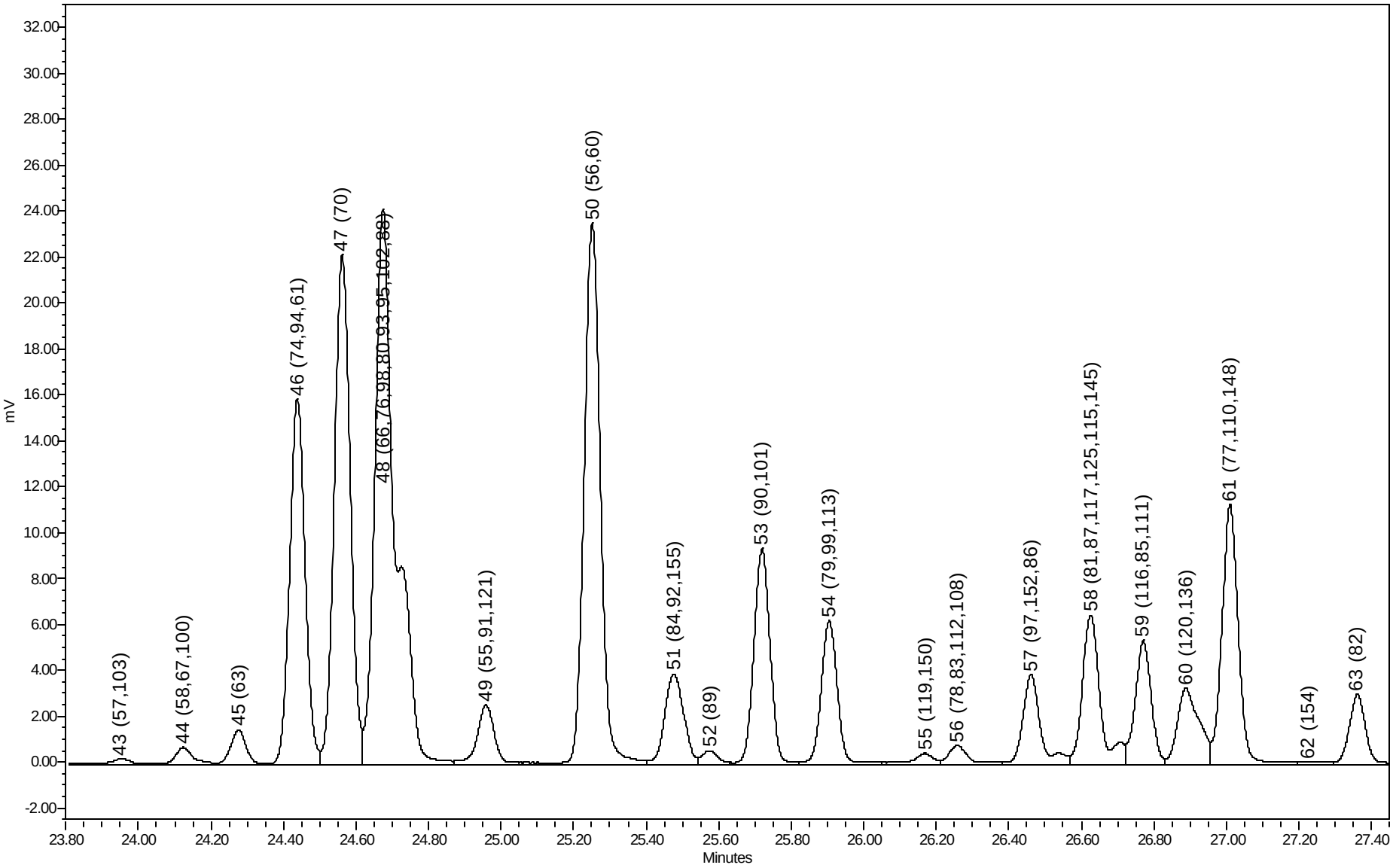
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



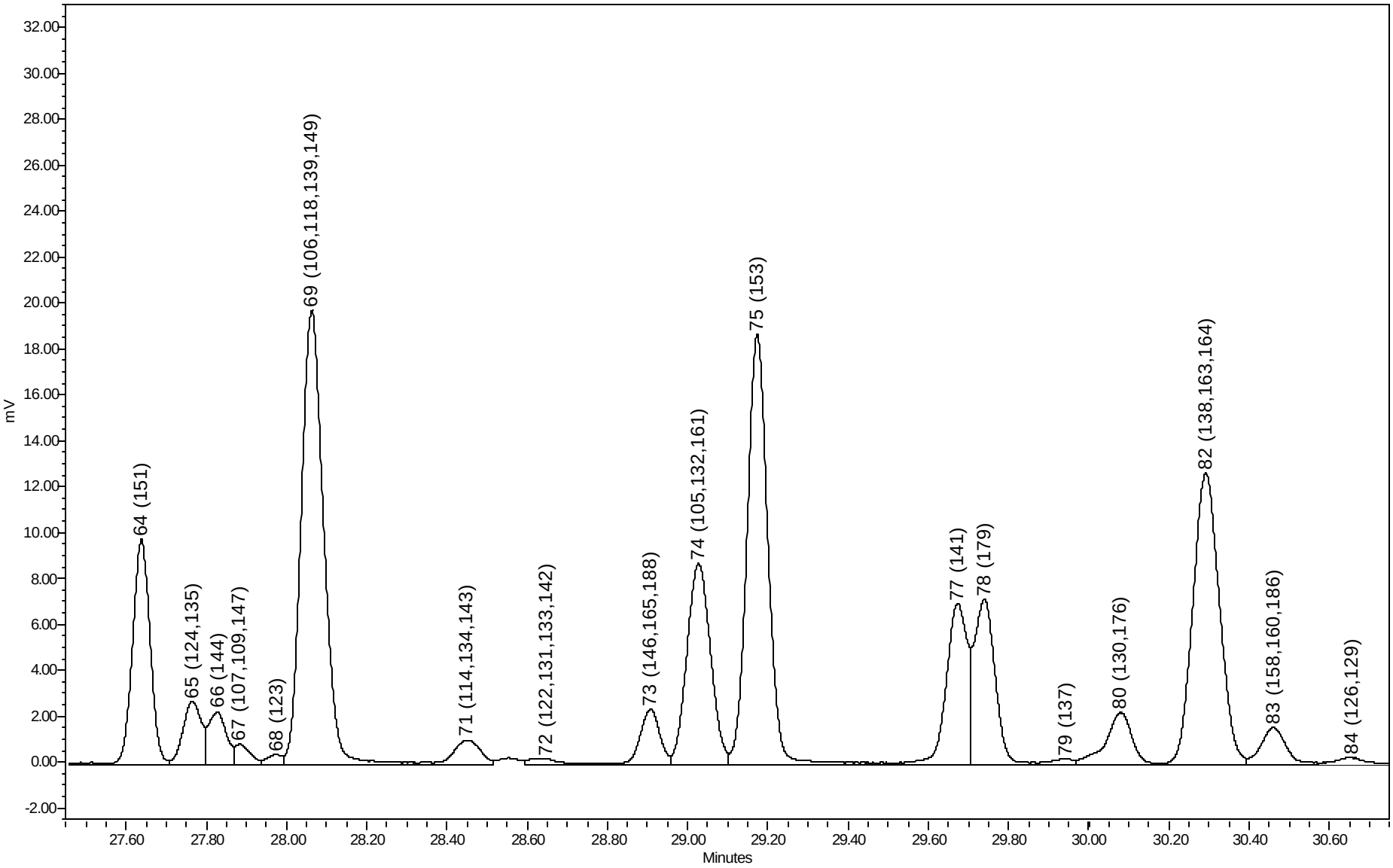
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



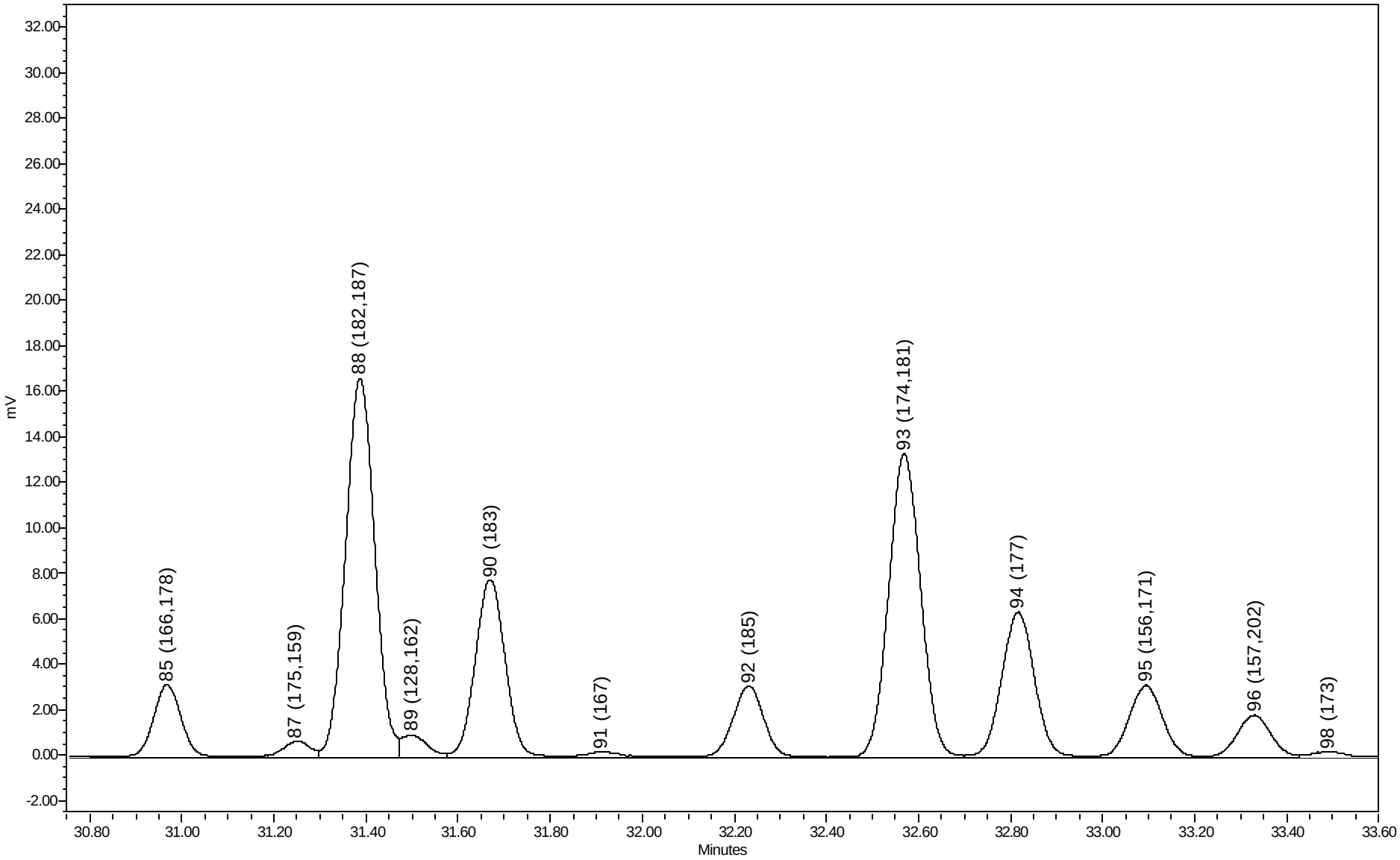
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



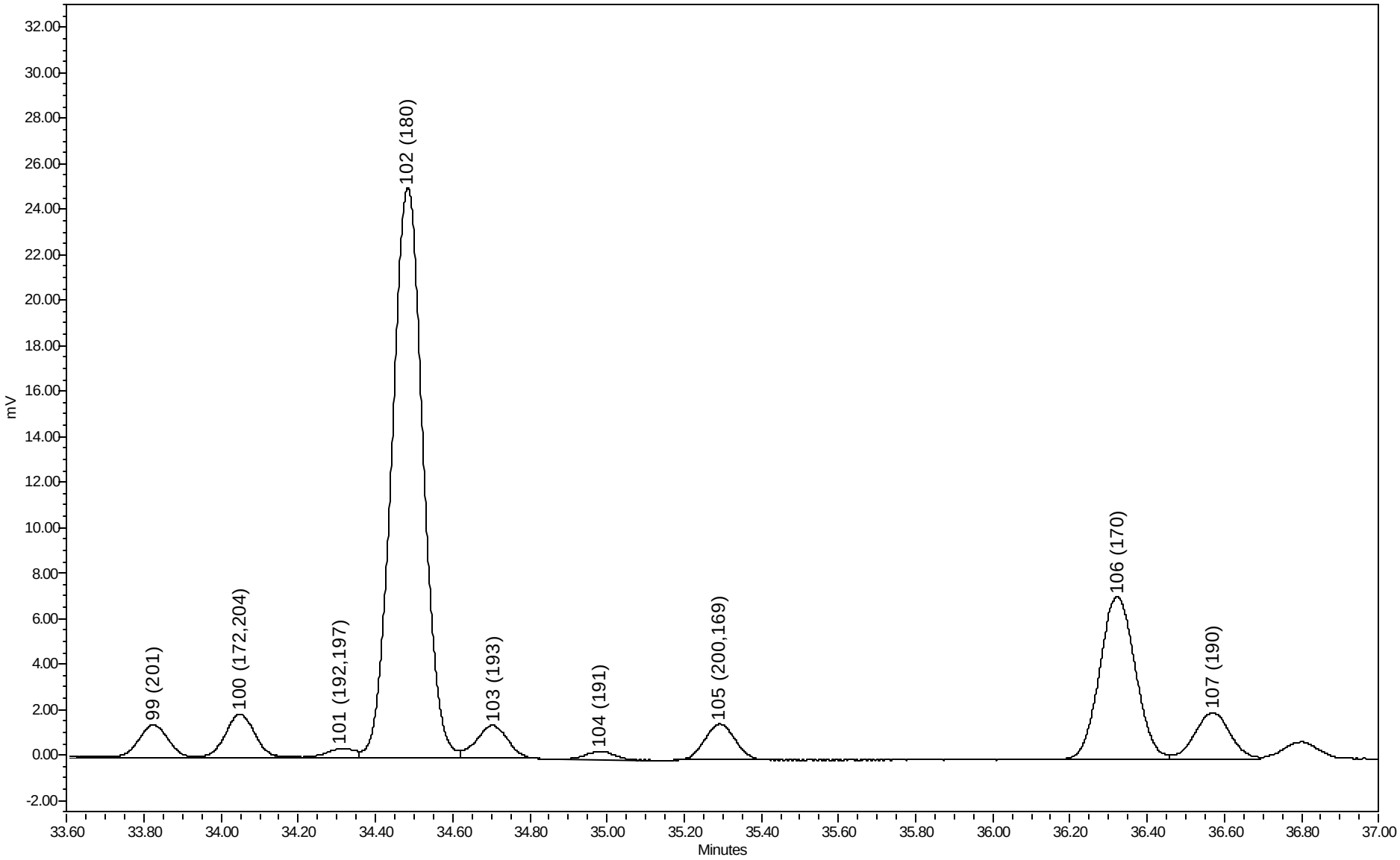
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



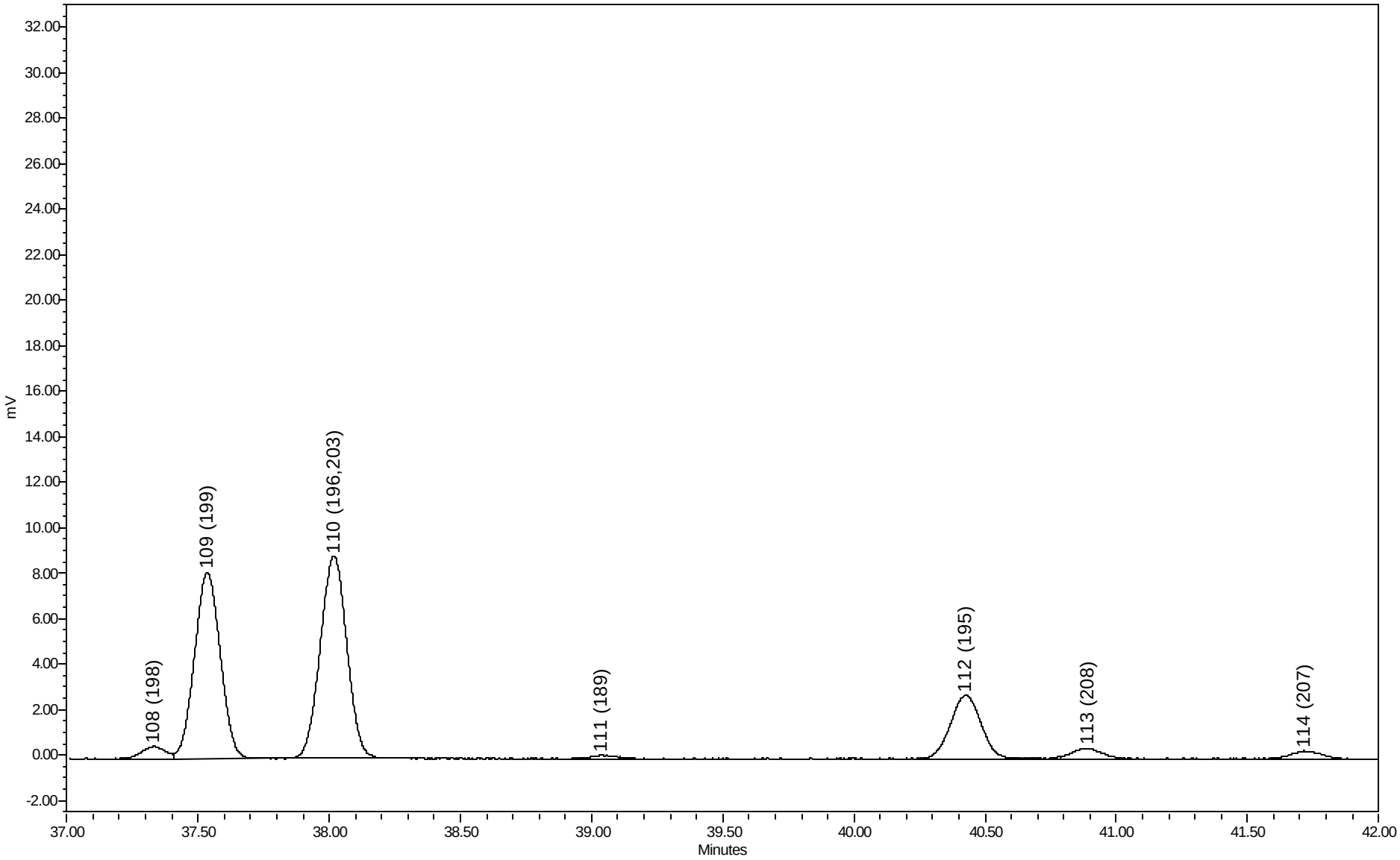
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



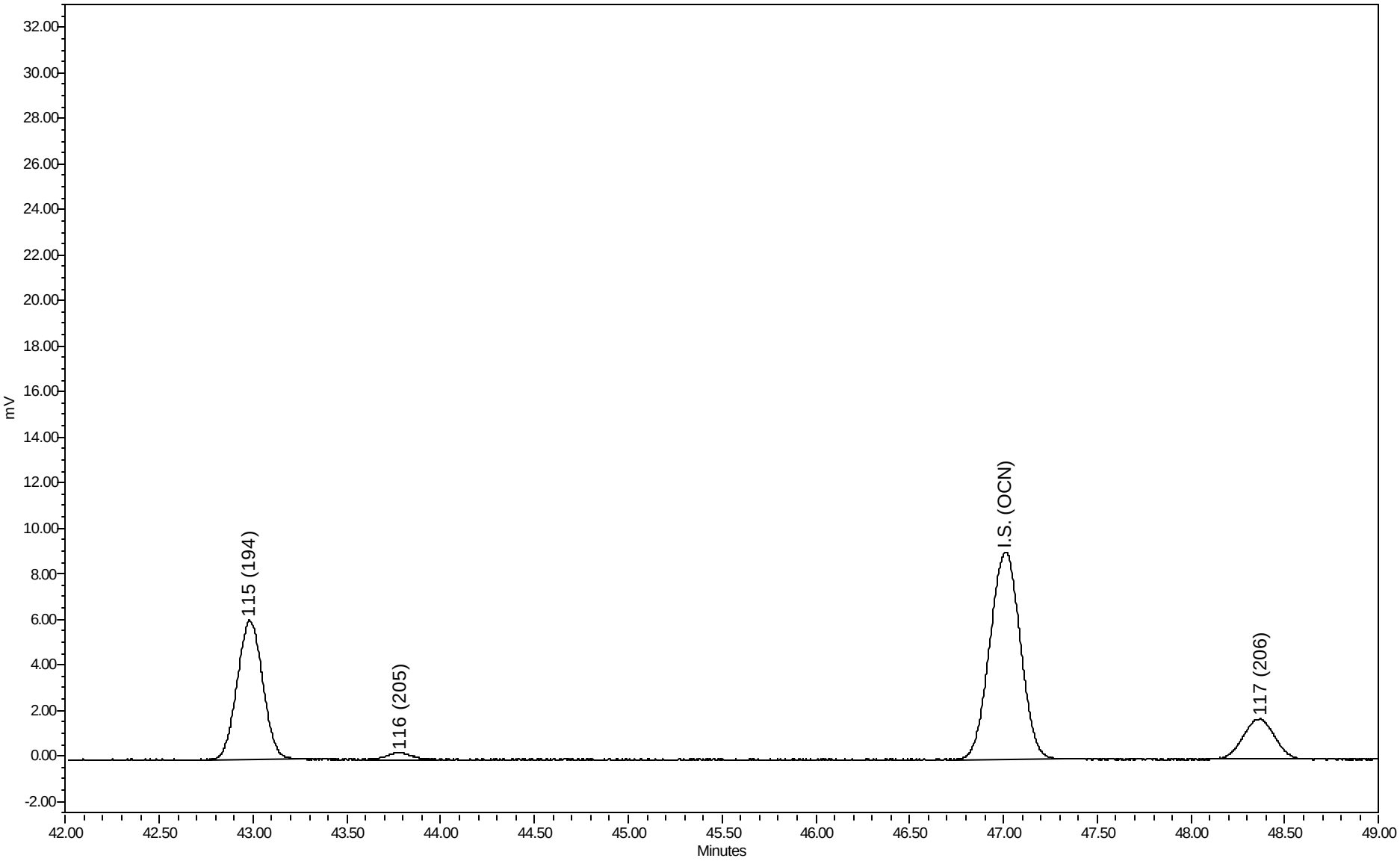
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



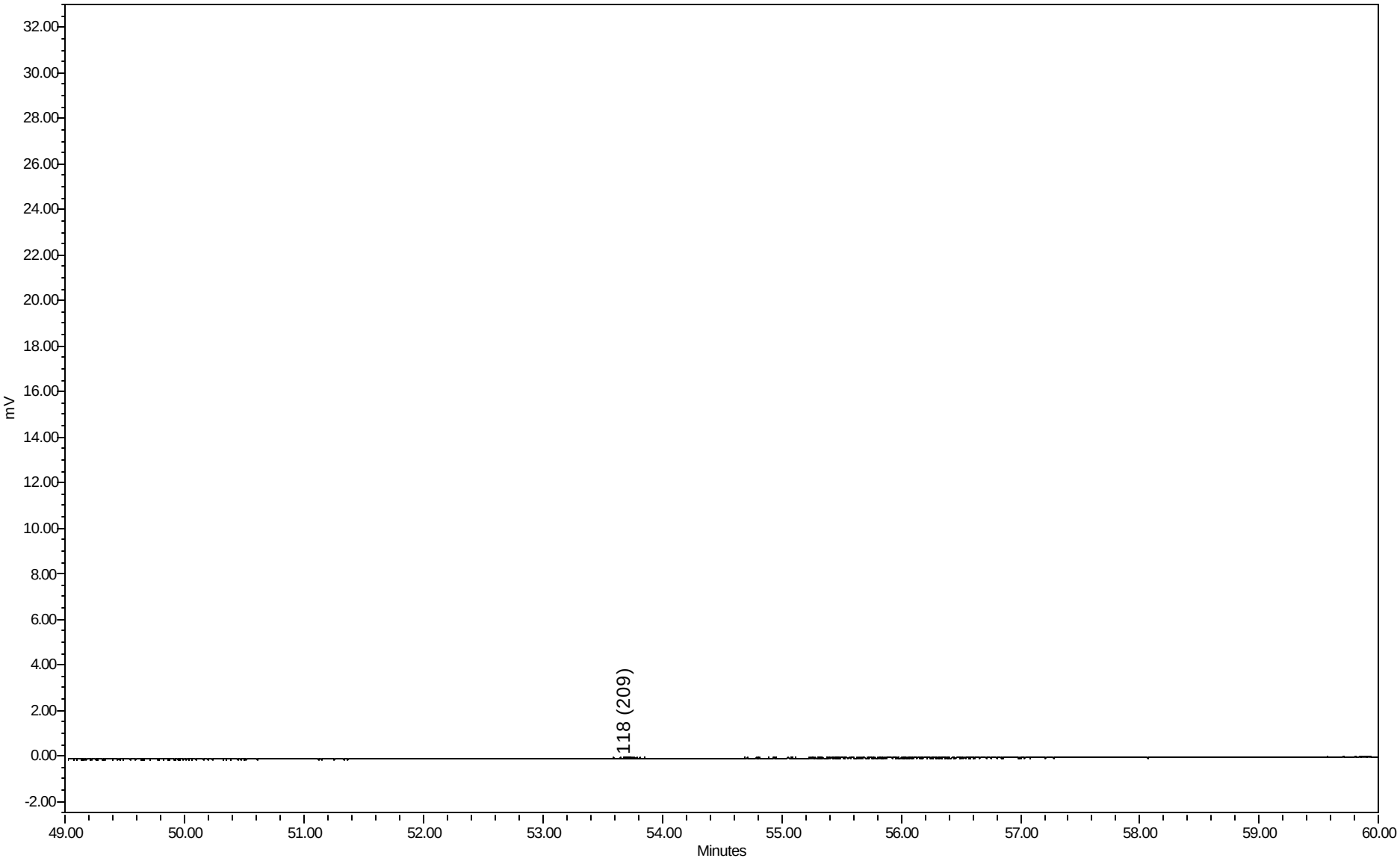
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



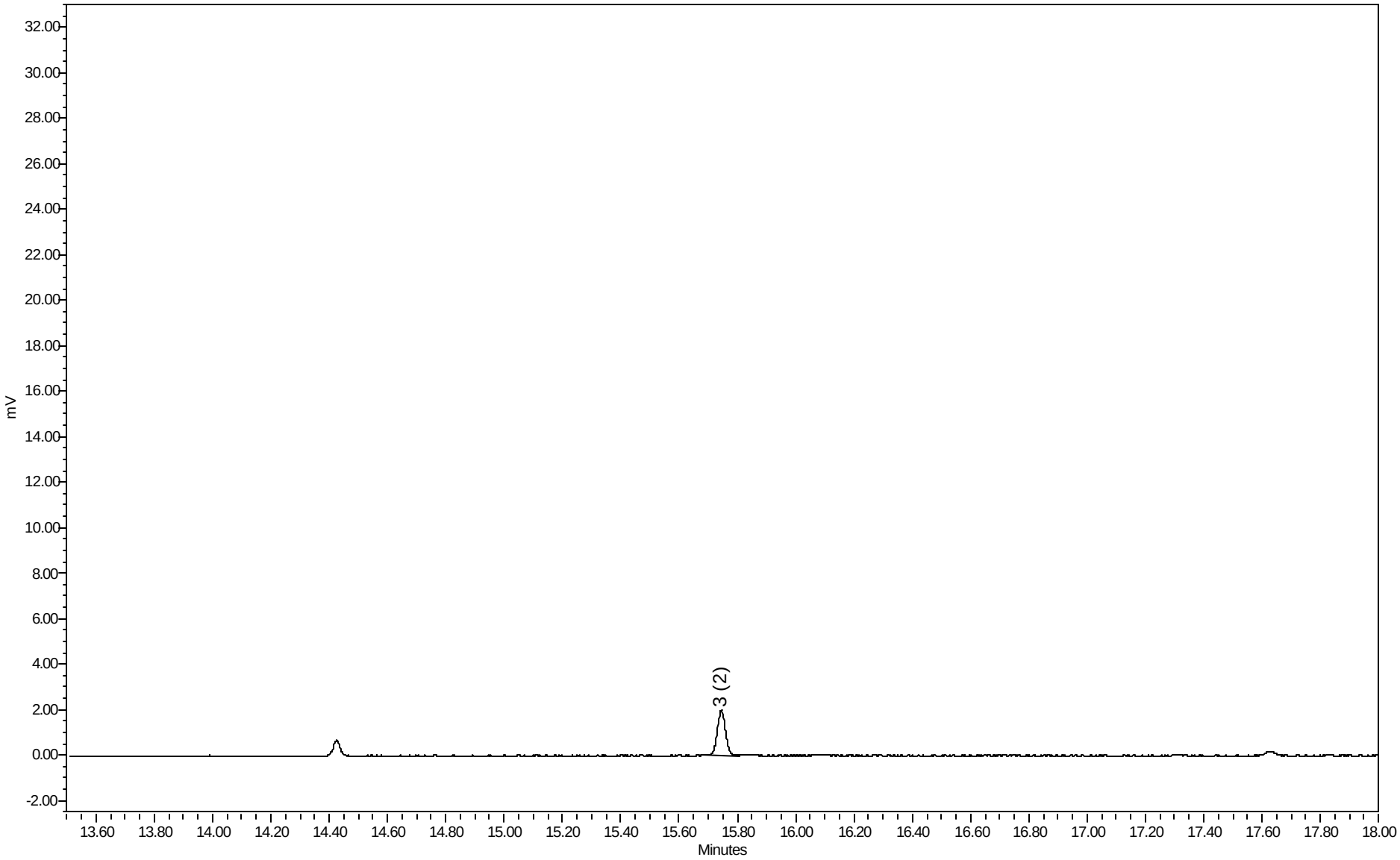
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



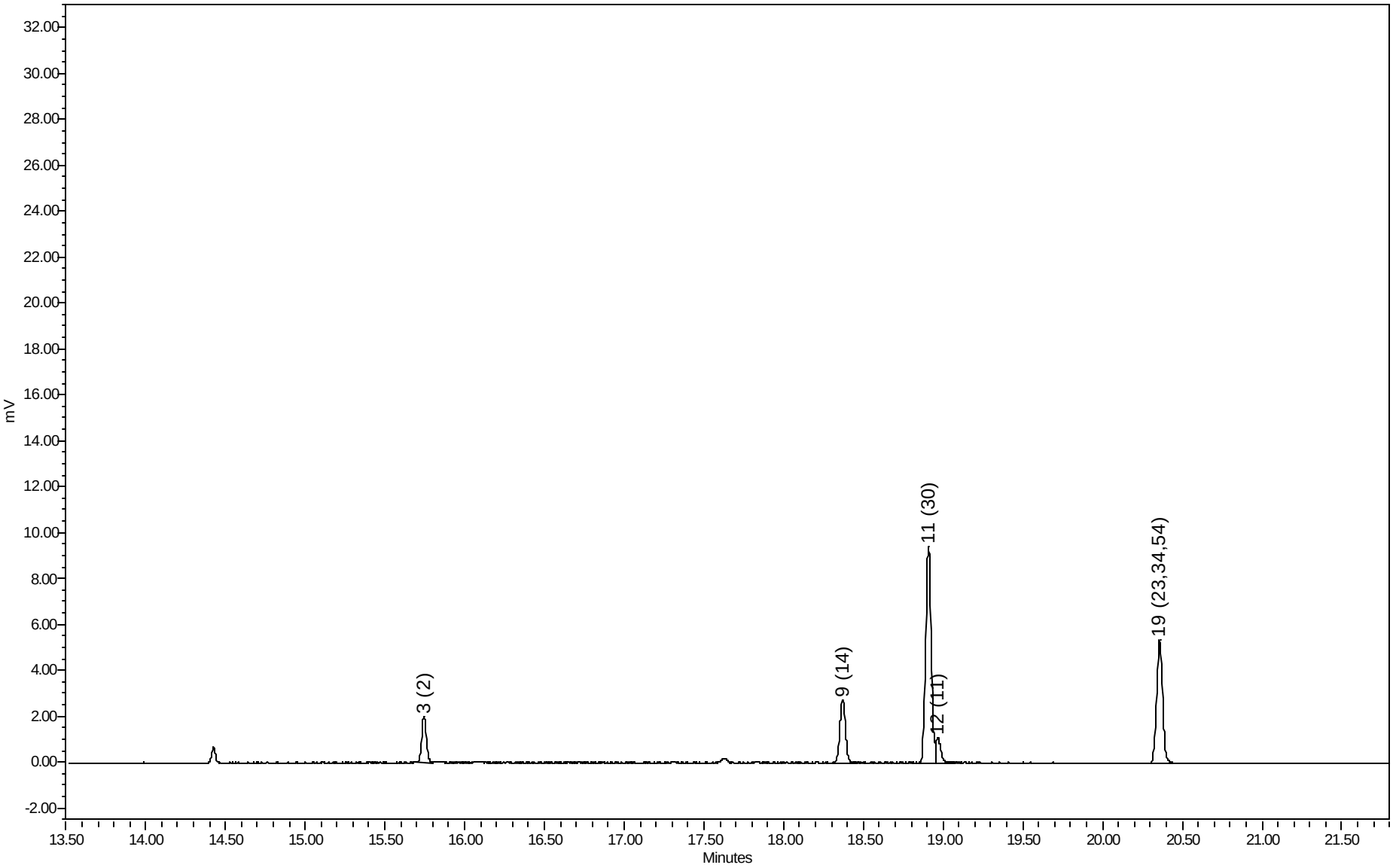
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



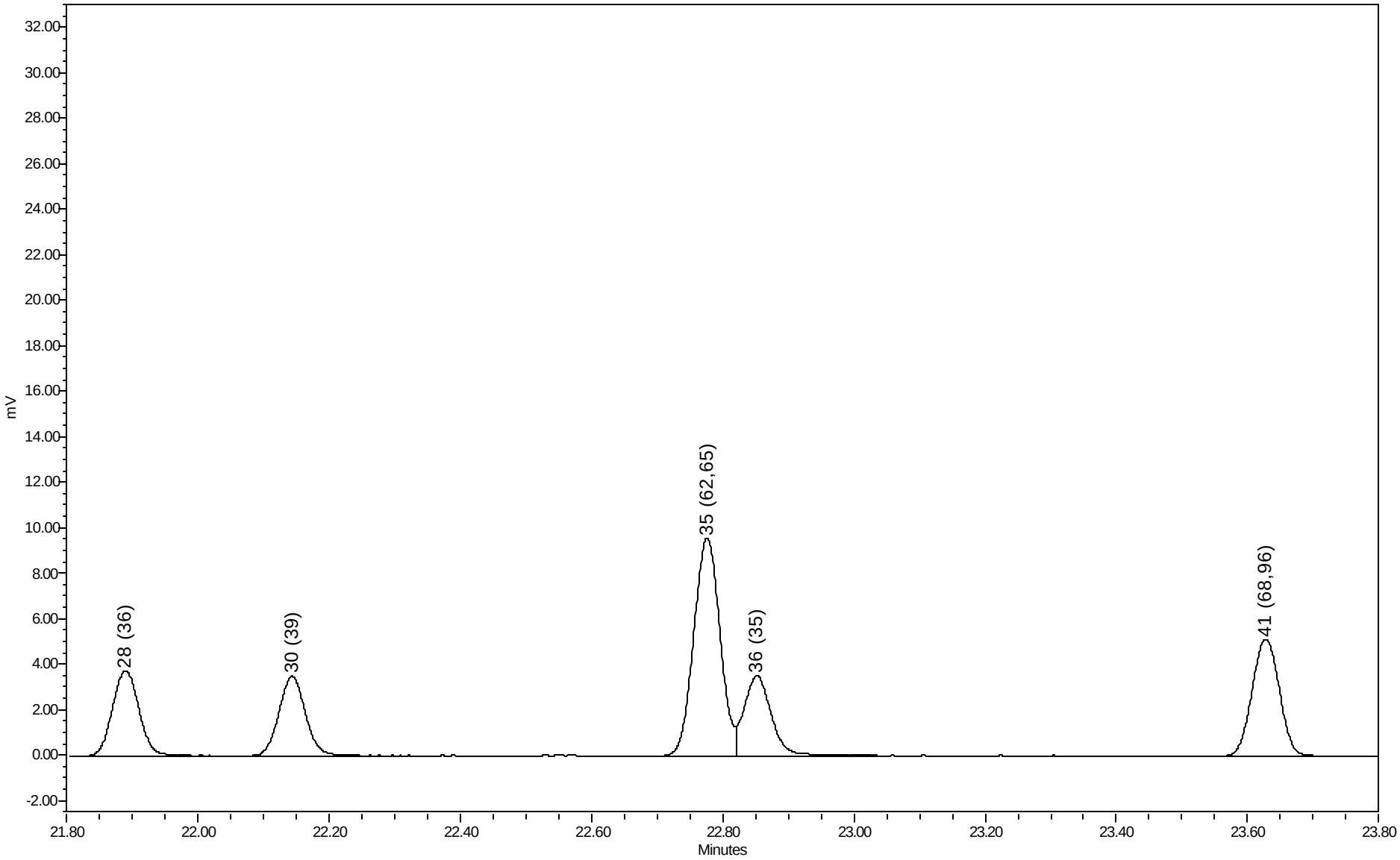
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



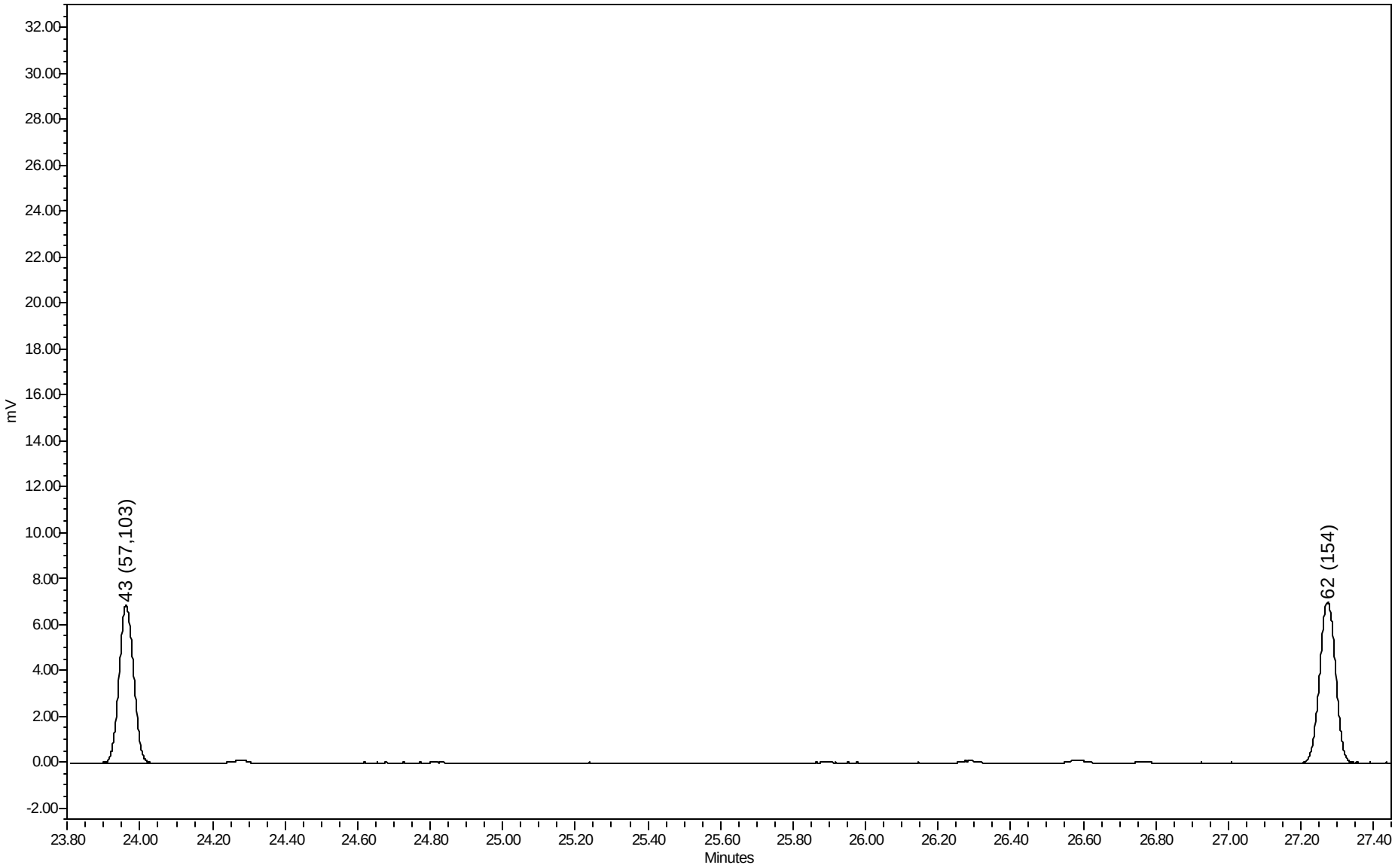
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



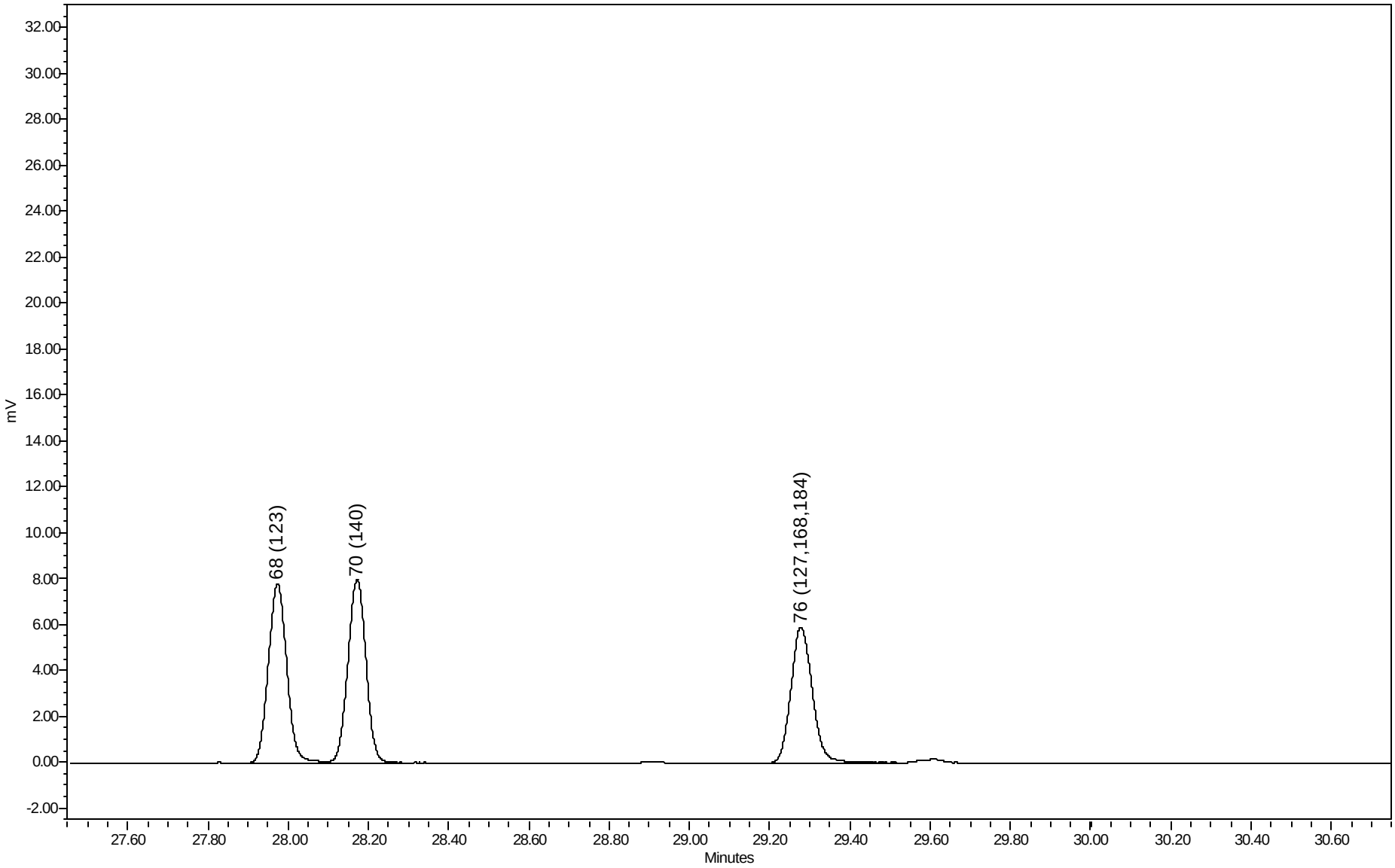
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



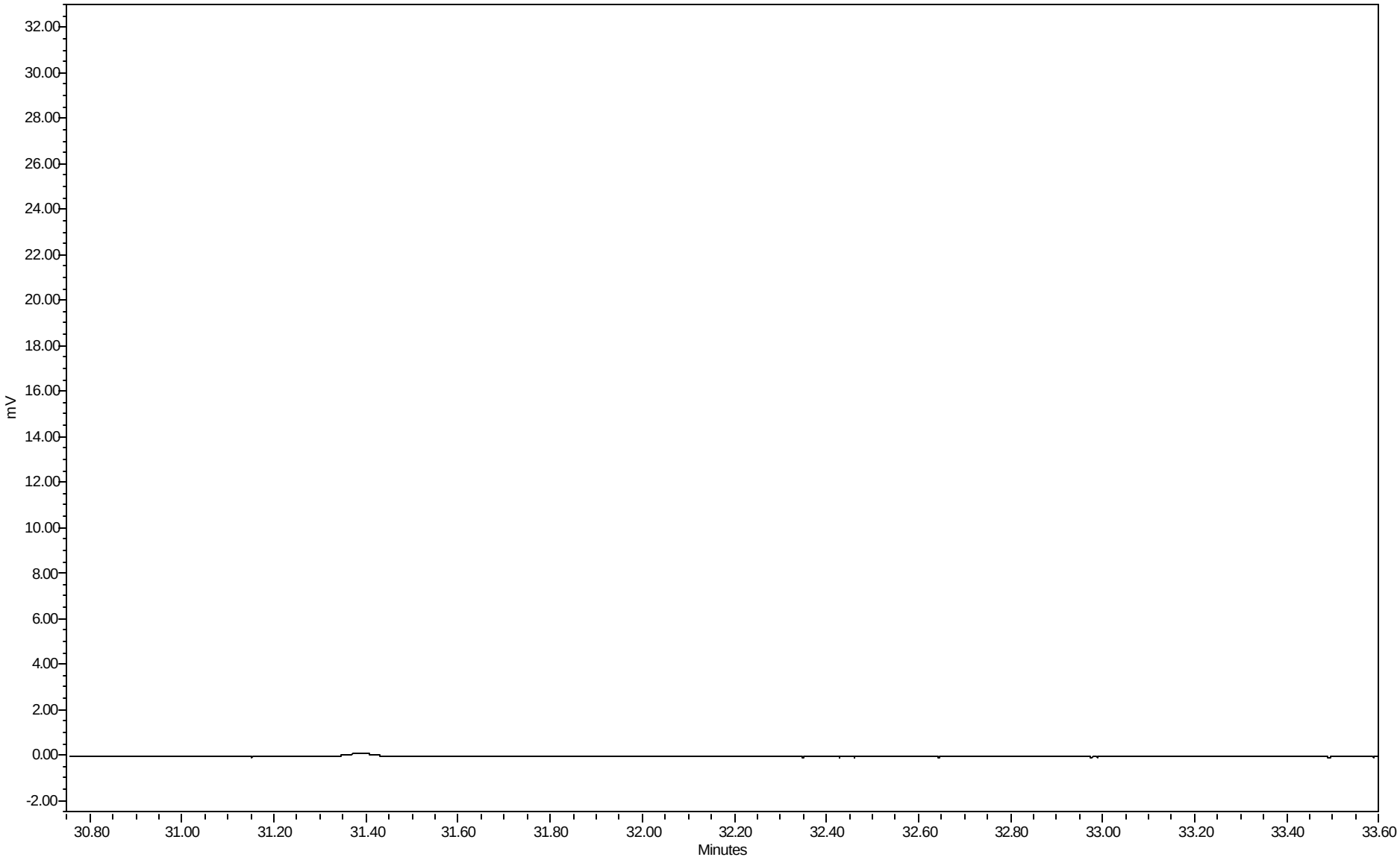
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



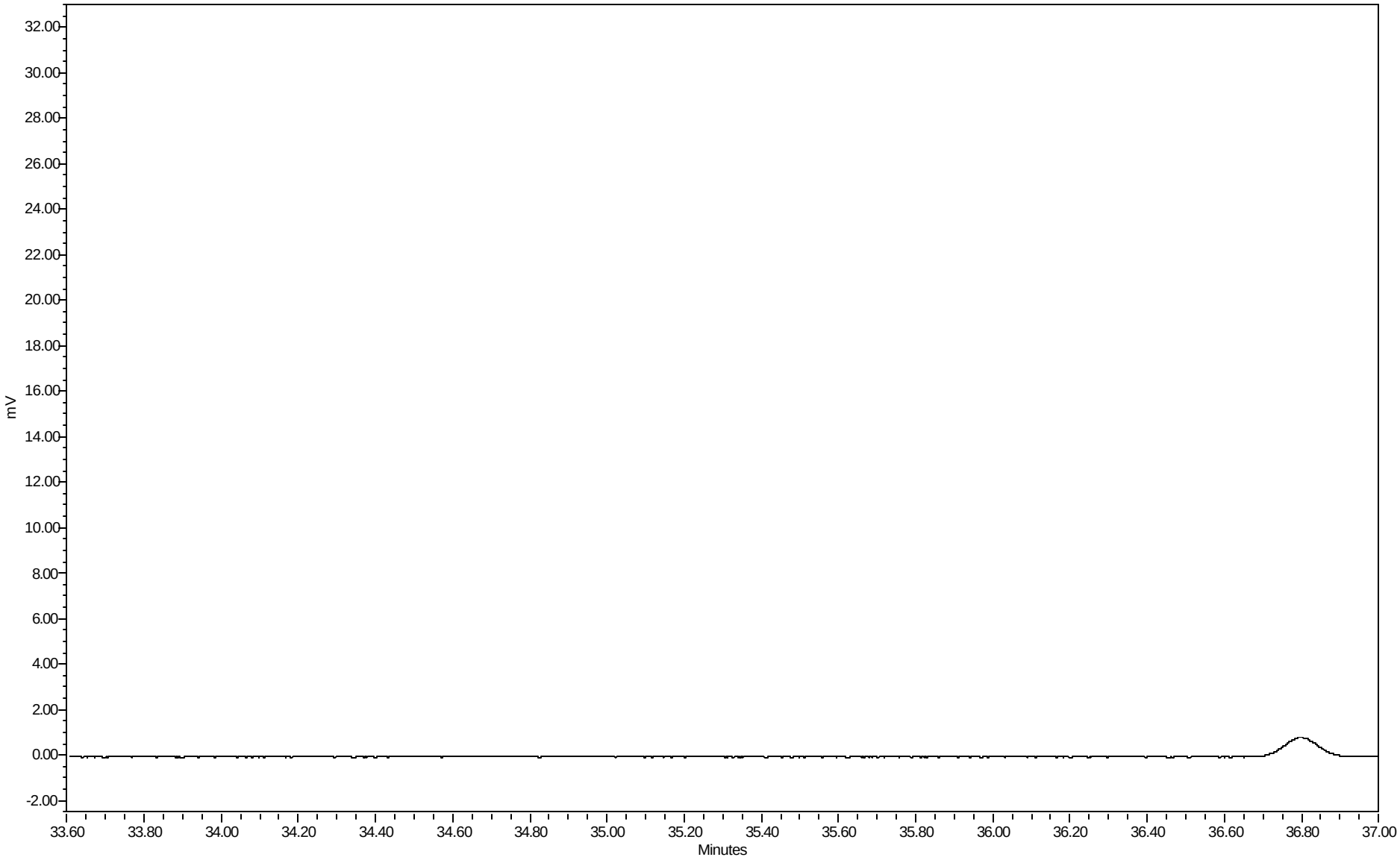
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



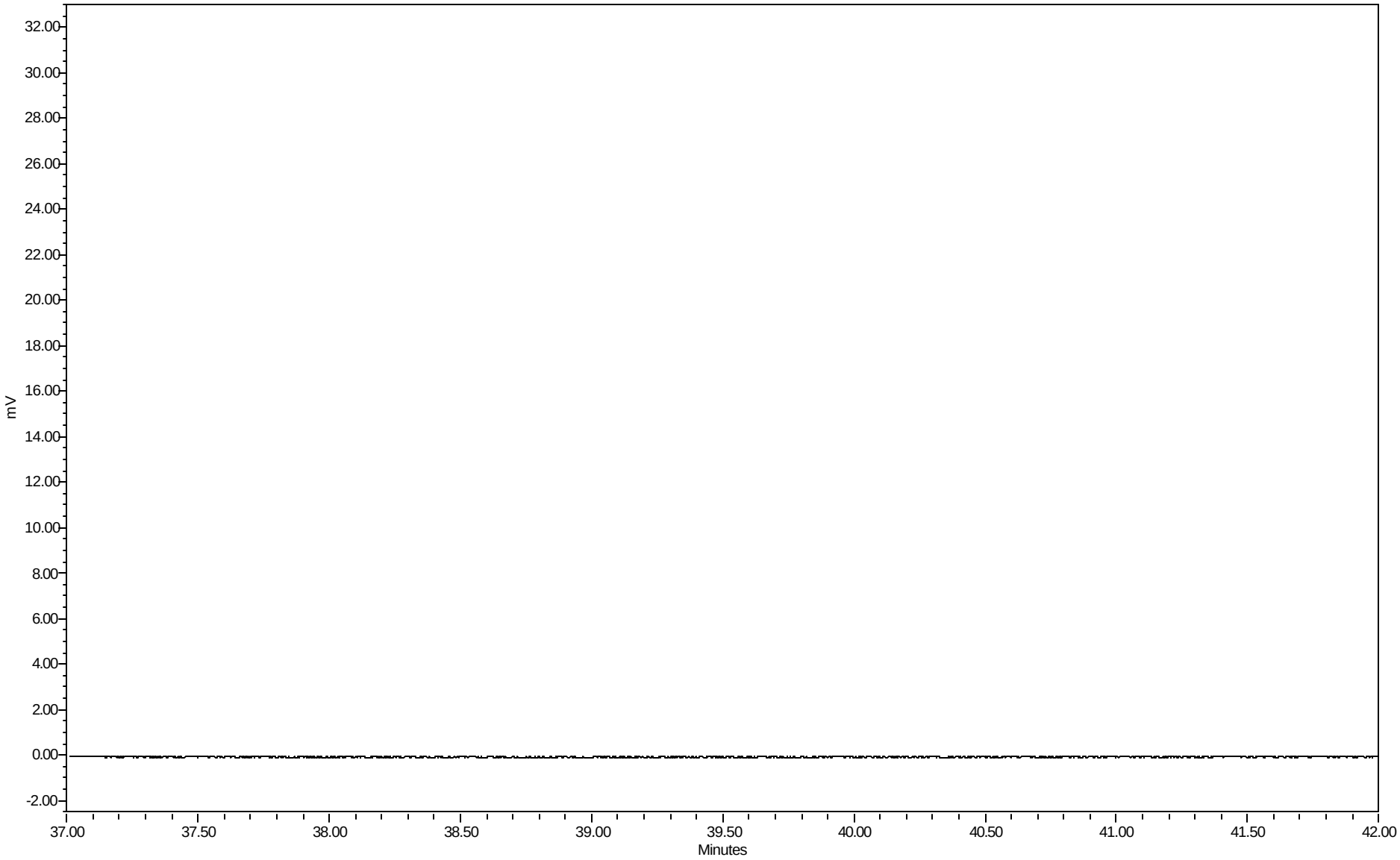
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



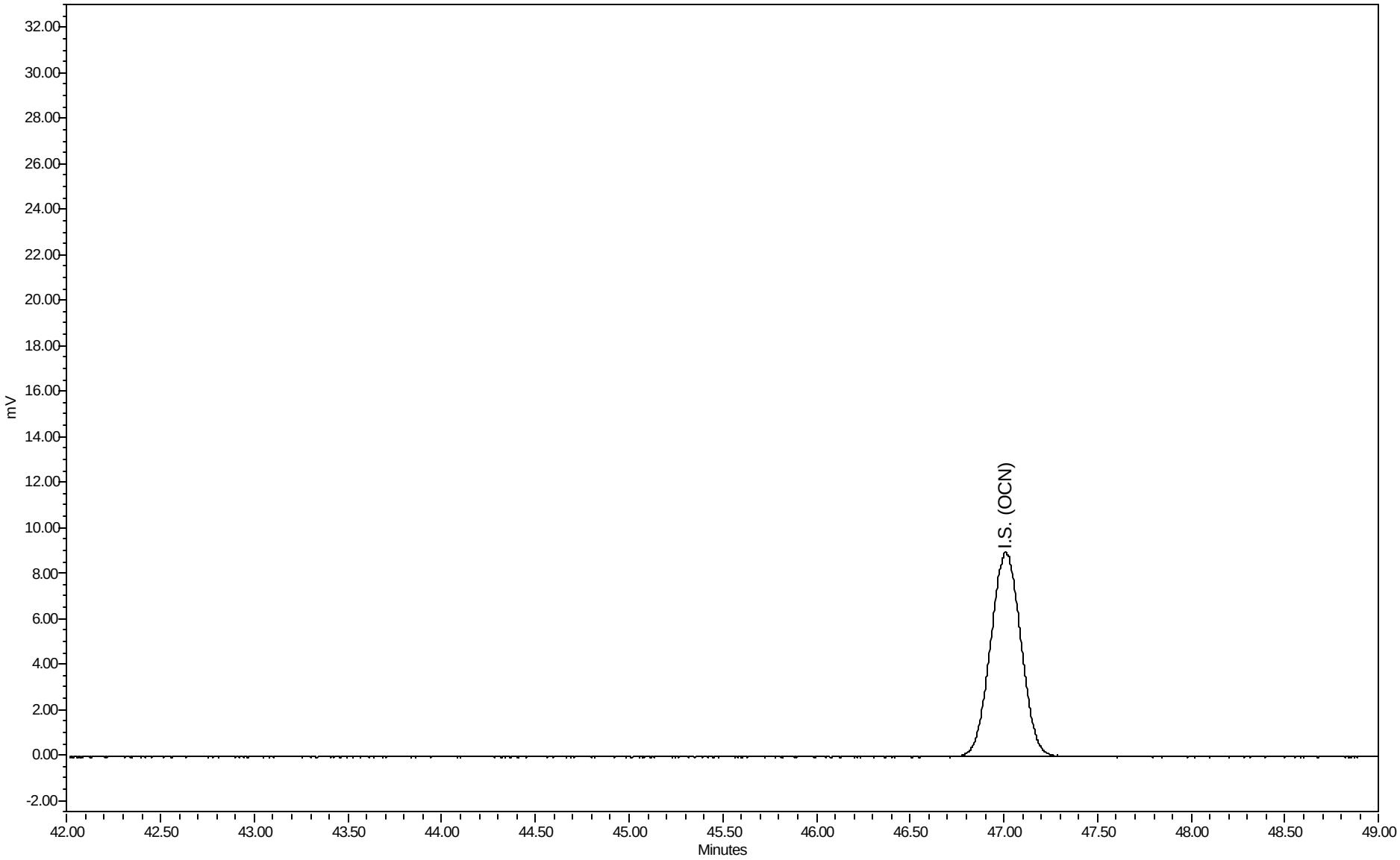
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



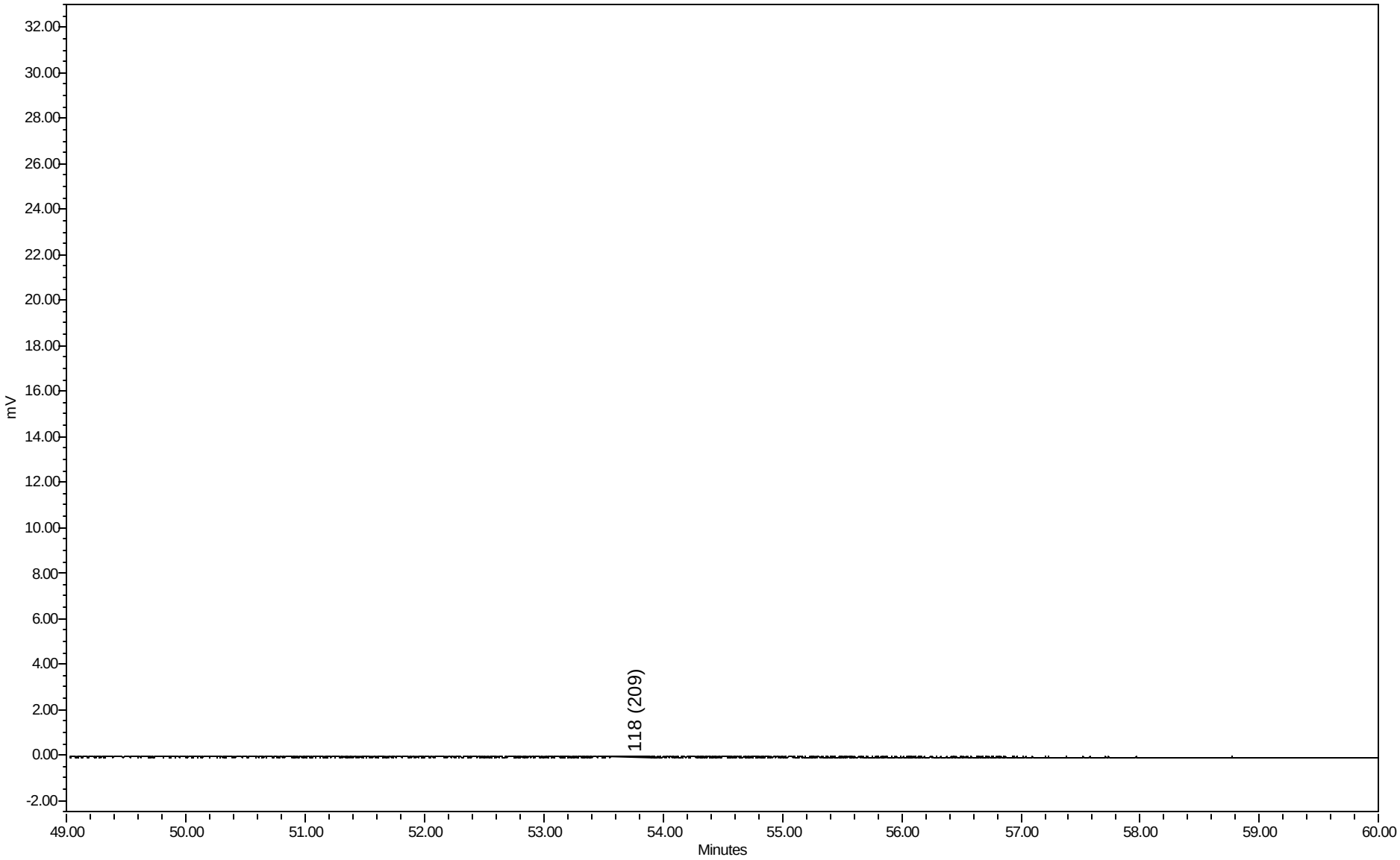
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



APPENDIX C

Example of Reporting Format

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

NEA File Name : M:\MIL2004\LIMSGC17\AH00023L.ARS

Customer : Client
Sample Description : LAB CONTROL SPIKE

Comment : This is a comment line
Date Acquired : 01/20/2004 07:15:23

Total PCBs in sample = 9.53 µg/g

PCB Homolog Distribution

Homologs	Weight %	Mole %
Mono	0.46	0.64
Di	18.08	21.08
Tri	46.10	46.94
Tetra	29.67	26.79
Penta	4.85	3.93
Hexa	0.80	0.60
Hepta	0.02	0.01
Octa	0.02	0.01
Nona	0.00	0.00
Deca	0.00	0.00

Nominal 'Aroclor' Distribution

Aroclor	Indicator Peak (PK # / IUPAC #)	Amount µg/g	Percent Sediment	Percent Biota
A1221	2/001	0.0438	3.4	3.4
A1242	23+24/31+28	1.1733	90.6	91.8
A1254SED	61/110	0.0772	6.0	
A1254BIO	***/###	0.0595		4.7
A1260	102/180	0.0009	0.1	0.1
A1268	115/194		0.0	0.0

***/### : 69+75+82/149+153+138

Ortho Cl / biphenyl Residue = 1.44

Meta + Para Cl / biphenyl Residue = 1.70

TOTAL Cl / biphenyl Residue = 3.14

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

PCB Congener Amount Report

NEA File Name : M:\MIL2004\LIMSGC17\AH00023L.ARS

Customer : Client
Sample Description : LAB CONTROL SPIKE

Comment : This is a comment line
Date Acquired : 01/20/2004 07:15:23
Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount µg/g	Nanomoles/g Sample	MDL µg/g	RL µg/g	Qual
2	14.69	188.7	162	0.0438	0.232	0.000667	0.0219	
3	15.75	188.7				0.0292	5.00	
4	15.85	188.7				0.000795	0.0128	
5	16.46	223.1	1764	0.209	0.935	0.000196	0.00621	
6	17.32	223.1	2435	0.0421	0.189	0.0000653	0.00219	
7	17.63	223.1	3342	0.120	0.537	0.000116	0.00347	
8	17.82	223.1	17401	1.20	5.40	0.000814	0.0256	
9	18.37	223.1				0.000847	0.125	
10	18.45	257.5	2222	0.0545	0.212	0.0000287	0.000512	
11	18.91	257.5				0.000564	0.125	
12	18.97	223.1				0.000663	0.125	
13	19.15	223.1	254	0.00622	0.0279	0.000189	0.000488	
14	19.29	249.0	26287	0.575	2.31	0.000317	0.00676	
15	19.38	257.5	13899	0.628	2.44	0.000219	0.00676	
16	19.67	257.5	3606	0.0510	0.198	0.0000157	0.000475	
17	19.91	257.5	25597	0.657	2.55	0.000203	0.00713	
19	20.36	267.9	246	0.00512	0.0191	0.000436	0.125	J
20	20.54	257.5	521	0.00755	0.0293	0.0000869	0.0000970	
21	20.66	257.5	7157	0.140	0.544	0.0000590	0.00132	
22	20.74	257.5	4206	0.0660	0.256	0.0000364	0.000585	
23	20.93	257.5	33906	0.538	2.09	0.000209	0.00753	
24	20.98	257.5	43359	0.636	2.47	0.000259	0.00964	
25	21.32	259.5	31800	0.605	2.33	0.000206	0.00726	
26	21.54	258.7	21441	0.421	1.63	0.000210	0.00530	
27	21.76	292.0	4999	0.0891	0.305	0.0000564	0.00163	
28	21.89	257.5				0.000822	0.125	
29	22.03	292.0	1779	0.0354	0.121	0.0000208	0.000731	
30	22.14	257.5				0.000570	0.125	
31	22.31	292.0	15791	0.393	1.35	0.000623	0.00872	
32	22.47	292.0	15240	0.191	0.654	0.000136	0.00420	
33	22.58	292.0	6365	0.0562	0.193	0.0000613	0.00183	
34	22.64	292.0	6842	0.0857	0.294	0.0000917	0.00183	
35	22.78	292.0				0.000442	0.125	
36	22.85	257.5	304	0.00828	0.0322	0.000658	0.125	J

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount µg/g	Nanomoles/g Sample	MDL µg/g	RL µg/g	Qual
37	23.01	292.0	20852	0.338	1.16	0.000250	0.00786	
38	23.14	272.4	17729	0.342	1.25	0.000131	0.00475	
39	23.47	292.0	25240	0.312	1.07	0.000256	0.00749	
41	23.63	326.4	176	0.00339	0.0104	0.000828	0.125	J
42	23.72	292.0	5764	0.0858	0.294	0.0000698	0.00172	
43	23.96	298.9	267	0.00395	0.0132	0.000443	0.125	J
44	24.12	298.9	1247	0.0135	0.0451	0.00000693	0.000201	
45	24.28	292.0	1249	0.0139	0.0476	0.0000152	0.000384	
46	24.44	292.0	13045	0.110	0.378	0.000132	0.00347	
47	24.56	292.0	22643	0.241	0.827	0.000191	0.00621	
48	24.68	293.5	26880	0.430	1.47	0.000367	0.0132	
49	24.97	324.7	2104	0.0298	0.0917	0.0000436	0.000932	
50	25.25	292.0	23794	0.245	0.841	0.000174	0.00640	
51	25.48	326.4	2877	0.0824	0.252	0.000109	0.00329	
52	25.58	326.4	278	0.00424	0.0130	0.000161	0.000183	
53	25.72	326.4	4053	0.0537	0.164	0.000190	0.00329	
54	25.91	326.4	2770	0.0232	0.0710	0.0000542	0.00135	
55	26.17	326.4	153	0.000780	0.00239	0.0000254	0.0000512	
56	26.26	326.4	524	0.00780	0.0239	0.000177	0.000274	
57	26.46	326.4	2393	0.0225	0.0690	0.0000294	0.00102	
58	26.63	326.4	4311	0.0495	0.152	0.0000777	0.00212	
59	26.77	326.4	2317	0.0218	0.0667	0.0000386	0.00128	
60	26.93	360.9	1552	0.0181	0.0501	0.0000486	0.00137	
61	27.01	315.8	5847	0.0772	0.244	0.000123	0.00389	
62	27.23	360.9				0.000612	0.125	
63	27.36	326.4	1847	0.0186	0.0571	0.0000282	0.000804	
64	27.64	360.9	81	0.00100	0.00277	0.000101	0.00311	J
65	27.79	350.5	256	0.00192	0.00548	0.0000386	0.000530	
66	27.81	360.9	94	0.00175	0.00485	0.0000372	0.00110	
67	27.89	336.8	446	0.00635	0.0189	0.00000918	0.000237	
68	27.98	326.4	149	0.00173	0.00530	0.000531	0.125	J
69	28.09	337.5	4388	0.0492	0.146	0.000243	0.00731	
70	28.17	360.9				0.000547	0.125	
71	28.47	347.8	378	0.00384	0.0110	0.000230	0.000369	
72	28.59	336.8	57	0.000340	0.00101	0.0000569	0.0000569	
73	28.93	360.9	182	0.00196	0.00543	0.0000259	0.000713	
74	29.03	347.8	4059	0.0327	0.0941	0.0000827	0.00248	
75	29.18	360.9	420	0.00397	0.0110	0.000157	0.00538	J
76	29.28	360.9				0.000668	0.125	
77	29.68	360.9				0.000122	0.00311	
78	29.74	395.3				0.000148	0.00267	
79	29.95	360.9				0.0000928	0.000137	
80	30.09	360.9				0.0000169	0.000475	
82	30.29	360.9	640	0.00631	0.0175	0.000143	0.00493	
83	30.47	360.9				0.0000213	0.000457	
84	30.66	360.9	99	0.000210	0.000582	0.0000165	0.0000236	
85	30.98	395.3				0.0000930	0.00201	
87	31.26	395.3				0.00000999	0.000366	
88	31.39	395.3				0.000208	0.00658	
89	31.51	360.9	165	0.00111	0.00308	0.0000122	0.000183	
90	31.68	395.3				0.0000863	0.00311	

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount µg/g	Nanomoles/g Sample	MDL µg/g	RL µg/g	Qual
91	31.92	360.9				0.0000101	0.0000897	
92	32.24	394.3				0.0000277	0.000859	
93	32.58	394.3				0.000158	0.00585	
94	32.82	394.3				0.0000888	0.00311	
95	33.10	382.2				0.0000731	0.00144	
96	33.34	429.8				0.00000475	0.000121	
98	33.50	395.3				0.0000568	0.0000695	
99	33.83	429.8	33	0.000390	0.000907	0.0000297	0.000713	J
100	34.05	395.3				0.0000374	0.00102	
101	34.32	429.8				0.0000121	0.000201	
102	34.47	395.3	91	0.000850	0.00215	0.000317	0.0111	J
103	34.71	395.3				0.0000328	0.000768	
104	34.97	395.3	54	0.000670	0.00169	0.000148	0.000219	
105	35.30	429.8				0.0000293	0.000786	
106	36.33	395.3				0.0000726	0.00234	
107	36.57	395.3				0.0000260	0.000768	
108	37.35	429.8				0.00000968	0.000219	
109	37.65	429.8	99	0.00160	0.00372	0.000251	0.00768	J
110	38.03	429.8				0.000218	0.00786	
111	39.07	395.3				0.0000798	0.0000798	
112	40.44	429.8				0.0000605	0.00101	
113	40.91	464.2				0.0000203	0.000451	
114	41.73	464.2				.0000000000	.0000000000	
115	43.00	429.8				0.0000881	0.00329	
116	43.79	429.8				0.0000833	0.000201	
117	48.38	464.2				0.0000453	0.00124	
118	53.74	498.6				0.0000187	0.0000222	

Concentration = 9.53 µg/g

Total Micromoles = 0.036

Average Molecular Weight = 262.4

Number of Calibrated Peaks Found = 69

Internal Standard Retention Time = 47.03 Minutes

Internal Standard Peak Area = 68991.0

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

Congener Weight and Mole Report

NEA File Name : M:\MIL2004\LIMSGC17\AH00023L.ARS

Customer : Client
Sample Description : LAB CONTROL SPIKE

Comment : This is a comment line
Date Acquired : 01/20/2004 07:15:23
Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
2	14.69	1:1	**001**	0.3567	2	0.460	0.639	2
3	15.75	1:0	**002**	0.3853	3	-	-	3
4	15.85	1:0	**003**	0.3880	4	-	-	4
5	16.46	2:2	**004 010**	0.4039	2-2 ; 26	2.187	2.573	5
6	17.32	2:1	**007 009**	0.4236	24 ; 25	0.441	0.519	6
7	17.63	2:1	**006**	0.4304	2-3	1.258	1.479	7
8	17.82	2:1	**005 008**	0.4346	23 ; 2-4	12.633	14.857	8
9	18.37	2:0	*014*	0.4462	35	-	-	9
10	18.45	3:3	**019**	0.4474	26-2	0.572	0.582	10
11	18.91	3:2	*030*	0.4572	246	-	-	11
12	18.97	2:0	**011**	0.4584	3-3	-	-	12
13	19.15	2:0	**012 013**	0.4622	34 ; 3-4	0.065	0.077	13
14	19.29	2:0 3:2	**015 018**	0.4650	4-4 ; 25-2	6.031	6.355	14
15	19.38	3:2	**017**	0.4668	24-2	6.590	6.714	15
16	19.67	3:2	**024 027**	0.4721	236 ; 26-3	0.535	0.545	16
17	19.91	3:2	**016 032**	0.4783	23-2 ; 26-4	6.890	7.020	17
19	20.36	3:1 4:4	*023* **034** *054*	0.4856	235 ; 35-2 ; 26-26	0.054	0.053	19
20	20.54	3:1	**029**	0.4889	245	0.079	0.081	20
21	20.66	3:1	**026**	0.4912	25-3	1.470	1.498	21
22	20.74	3:1	**025**	0.4926	24-3	0.693	0.706	22
23	20.93	3:1	**031**	0.4965	25-4	5.640	5.747	23
24	20.98	3:1 4:3	**028** *050*	0.4969	24-4 ; 246-2	6.669	6.795	24
25	21.32	3:1 4:3	**020** *021* **033 053**	0.5031	23-3 ; 234 ; 34-2 ; 25-26	6.346	6.417	25
26	21.54	3:1 4:3	**022 051**	0.5074	23-4 ; 24-26	4.415	4.477	26
27	21.76	4:3	**045**	0.5109	236-2	0.935	0.840	27
28	21.89	3:0	*036*	0.5135	35-3	-	-	28
29	22.03	4:3	**046**	0.5157	23-26	0.371	0.334	29
30	22.14	3:0	*039*	0.5172	35-4	-	-	30
31	22.31	4:2	**052** *069 073*	0.5209	25-25 ; 246-3 ; 26-35	4.127	3.708	31
32	22.47	4:2	**043 049**	0.5236	235-2 ; 24-25	2.003	1.800	32
33	22.58	4:2	*038* **047**	0.5262	345 ; 24-24	0.590	0.530	33
34	22.64	4:2	**048** *075*	0.5267	245-2 ; 246-4	0.899	0.808	34
35	22.78	4:2	*062 065*	0.5289	2346 ; 2356	-	-	35
36	22.85	3:0	**035**	0.5302	34-3	0.087	0.089	36
37	23.01	5:4 4:2	*104* **044**	0.5333	246-26 ; 23-25	3.547	3.187	37
38	23.14	3:0 4:2	**037 042 059**	0.5352	34-4 ; 23-24 ; 236-3	3.586	3.454	38
39	23.47	4:2	**041 064 071** *072*	0.5406	234-2 ; 236-4 ; 26-34 ; 25-35	3.271	2.939	39
41	23.63	5:4	*068* **096**	0.5435	24-35 ; 236-26	0.036	0.029	41
42	23.72	4:2	**040**	0.5446	23-23	0.900	0.809	42
43	23.96	4:1 5:3	**057** *103*	0.5489	235-3 ; 246-25	0.041	0.036	43
44	24.12	4:1 5:3	*058* **067** *100*	0.5517	23-35 ; 245-3 ; 246-24	0.141	0.124	44
45	24.28	4:1	**063**	0.5534	235-4	0.146	0.131	45
46	24.44	4:1 5:3	**074** *094 061*	0.5570	245-4 ; 235-26 ; 2345	1.157	1.040	46

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
47	24.56	4:1	**070**	0.5595	25-34	2.533	2.276	47
48	24.68	4:1 5:3	**066** *076 098 080 093* **095 102** *088*	0.5609	24-34 ; 345-2 ; 246-23 ; 35-35 ; 2356-2 ; 236-25 ; 245-26 ; 2346-2	4.516	4.037	48
49	24.97	4:1 5:3	*055* **091** *121*	0.5658	234-3 ; 236-24 ; 246-35	0.312	0.252	49
50	25.25	4:1	**056 060**	0.5701	23-34 ; 234-4	2.575	2.314	50
51	25.48	5:3 6:4	**084 092** *155*	0.5739	236-23 ; 235-25 ; 246-246	0.864	0.695	51
52	25.58	5:3	**089**	0.5761	234-26	0.044	0.036	52
53	25.72	5:2	**090 101**	0.5788	235-24 ; 245-25	0.563	0.452	53
54	25.91	5:2	*079* **099** *113*	0.5814	34-35 ; 245-24 ; 236-35	0.243	0.196	54
55	26.17	5:2 6:4	**119** *150*	0.5860	246-34 ; 236-246	0.008	0.007	55
56	26.26	5:2	*078* **083** *112 108*	0.5874	345-3 ; 235-23 ; 2356-3 ; 2346-3	0.082	0.066	56
57	26.46	5:2 6:4	**097** *152 086*	0.5903	245-23 ; 2356-26 ; 2345-2	0.236	0.190	57
58	26.63	5:2	*081* **087** *117 125* **115** *145*	0.5929	345-4 ; 234-25 ; 2356-4 ; 345-26 ; 2346-4 ; 2346-26	0.519	0.417	58
59	26.77	5:2	*116* **085** *111*	0.5953	23456 ; 234-24 ; 235-35	0.228	0.184	59
60	26.93	6:4	*120* **136**	0.5971	245-35 ; 236-236	0.190	0.138	60
61	27.01	4:0 5:2	**077 110** *148*	0.5998	34-34 ; 236-34 ; 235-246	0.809	0.673	61
62	27.23	6:3	*154*	0.6039	245-246	-	-	62
63	27.36	5:2	**082**	0.6055	234-23	0.195	0.157	63
64	27.64	6:3	**151**	0.6101	2356-25	0.010	0.008	64
65	27.79	5:1 6:3	**124 135**	0.6129	345-25 ; 235-236	0.020	0.015	65
66	27.81	6:3	**144**	0.6139	2346-25	0.018	0.013	66
67	27.89	5:1 6:3	*107* **109** *147*	0.6152	234-35 ; 235-34 ; 2356-24	0.067	0.052	67
68	27.98	5:1	*123*	0.6166	345-24	0.018	0.015	68
69	28.09	5:1 6:3	*106* **118** *139* **149**	0.6186	2345-3 ; 245-34 ; 2346-24 ; 236-245	0.516	0.401	69
70	28.17	6:3	*140*	0.6202	234-246	-	-	70
71	28.47	5:1 6:3	**114 134** *143*	0.6256	2345-4 ; 2356-23 ; 2345-26	0.040	0.030	71
72	28.59	5:1 6:3	**122 131 133** *142*	0.6289	345-23 ; 2346-23 ; 235-235 ; 23456-2	0.004	0.003	72
73	28.93	6:2	**146** *165 188*	0.6342	235-245 ; 2356-35 ; 2356-246	0.021	0.015	73
74	29.03	5:1 6:3	**105 132** *161*	0.6364	234-34 ; 234-236 ; 2346-35	0.343	0.259	74
75	29.18	6:2	**153**	0.6393	245-245	0.042	0.030	75
76	29.28	6:2	*127 168 184*	0.6412	345-35 ; 246-345 ; 2346-246	-	-	76
77	29.68	6:2	**141**	0.6488	2345-25	-	-	77
78	29.74	7:4	**179**	0.6499	2356-236	-	-	78
79	29.95	6:2	**137**	0.6537	2345-24	-	-	79
80	30.09	6:2 7:4	**130 176**	0.6565	234-235 ; 2346-236	-	-	80
82	30.29	6:2	**138 163 164**	0.6605	234-245 ; 2356-34 ; 236-345	0.066	0.048	82
83	30.47	6:2	**158** *160 186*	0.6639	2346-34 ; 23456-3 ; 23456-26	-	-	83
84	30.66	6:2	*126* **129**	0.6674	345-34 ; 2345-23	0.002	0.002	84
85	30.98	7:3	*166* **178**	0.6735	23456-4 ; 2356-235	-	-	85
87	31.26	7:3	**175** *159*	0.6790	2346-235 ; 2345-35	-	-	87
88	31.39	7:3	*182* **187**	0.6816	2345-246 ; 2356-245	-	-	88
89	31.51	6:2	**128** *162*	0.6838	234-234 ; 235-345	0.012	0.008	89
90	31.68	7:3	**183**	0.6871	2346-245	-	-	90
91	31.92	6:1	**167**	0.6919	245-345	-	-	91
92	32.24	7:3	**185**	0.6980	23456-25	-	-	92
93	32.58	7:3	**174** *181*	0.7046	2345-236 ; 23456-24	-	-	93
94	32.82	7:3	**177**	0.7094	2356-234	-	-	94
95	33.10	6:1 7:3	**156 171**	0.7149	2345-34 ; 2346-234	-	-	95
96	33.34	8:4	**157 202**	0.7195	234-345 ; 2356-2356	-	-	96
98	33.50	7:3	**173**	0.7226	23456-23	-	-	98
99	33.83	8:4	**201**	0.7294	2346-2356	0.004	0.002	99
100	34.05	7:2	**172** *204*	0.7339	2345-235 ; 23456-246	-	-	100
101	34.32	8:4	*192* **197**	0.7392	23456-35 ; 2346-2346	-	-	101
102	34.47	7:2	**180**	0.7427	2345-245	0.009	0.006	102
103	34.71	7:2	**193**	0.7471	2356-345	-	-	103
104	34.97	7:2	**191**	0.7527	2346-345	0.007	0.005	104
105	35.30	8:4	**200** *169*	0.7588	23456-236 ; 345-345	-	-	105
106	36.33	7:2	**170**	0.7799	2345-234	-	-	106
107	36.57	7:2	**190**	0.7850	23456-34	-	-	107
108	37.35	8:3	**198**	0.8007	23456-235	-	-	108

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
109	37.65	8:3	**199**	0.8050	2345-2356	0.017	0.010	109
110	38.03	8:3	**196 203**	0.8149	2345-2346 ; 23456-245	-	-	110
111	39.07	7:1	**189**	0.8365	2345-345	-	-	111
112	40.44	8:3	**195**	0.8647	23456-234	-	-	112
113	40.91	9:4	**208**	0.8743	23456-2356	-	-	113
114	41.73	9:4	*207*	0.8909	23456-2346	-	-	114
115	43.00	8:2	**194**	0.9177	2345-2345	-	-	115
116	43.79	8:2	**205**	0.9342	23456-345	-	-	116
117	48.38	9:3	**206**	1.0294	23456-2345	-	-	117
118	53.74	10:4	*209*	1.1406	23456-23456	-	-	118

Concentration = 9.53 µg/g

Total Micromoles = 0.036

Average Molecular Weight = 262.4

Number of Calibrated Peaks Found = 69

[1] - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)

PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

[2] - IUPAC congener numbers listed in **boldface** font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in *italic* font were absent or present below 0.05 weight percent.

[3] - PCB congener identification is denoted by position of the chlorine atoms on each ring of the biphenyl molecule. Designation used in this report has unprimed chlorines separated from prime chlorines by a hyphen that represents separation of the biphenyl rings.

[4] - DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indication the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76, 98, 80, 93*, **95**, **102**, *88*)	*80, 88, 93*
56 (*78,* **83**, *112, 108)*	*108*
61 (**77, 110**, *148*)	**77**
72 (**122**, *131, 133, 142*)	**122**
89 (**128**, *162*)	*162*
105 (**200**,*169*)	*169*

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE013_07.SOP

REVISION NUMBER: 07

STANDARD OPERATING PROCEDURE FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) ANALYSIS

METHOD FOR CONGENER-SPECIFIC POLYCHLORINATED BIPHENYL (PCB) QUANTIFICATION AND IDENTIFICATION BY CAPILLARY COLUMN/GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION

March 9, 2004

COPY #_____

NORTHEAST ANALYTICAL, INC.
2190 TECHNOLOGY DRIVE
SCHENECTADY, NEW YORK 12308
(518) 346-4592

STANDARD OPERATING PROCEDURE

LABORATORY METHOD NE013_07.SOP

REVISION 7 (3/09/2004)

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Lab Method NE013_07.SOP

Congener-Specific Polychlorinated Biphenyl (PCB) Analysis

Method for Congener-Specific Polychlorinated Biphenyl (PCB) Quantification and Identification by Capillary Column/Gas Chromatography with Electron Capture Detection

1.0 Scope

1.1 This method is applicable in the determination and quantification of Polychlorinated Biphenyls (PCB) in sediments, soils, biota, oils, water, and other solid and liquid matrices. This method is a congener-specific determination, employing a high resolution fused-silica capillary chromatographic column. The method has been, in part, developed from the following documents:

1.) "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office", prepared by Deborah L. Swackhamer, Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987. This document outlines quality assurance and quality control procedures to be followed by laboratories participating in the Green Bay Mass Balance Study. Where applicable, Northeast Analytical, Inc., will incorporate and utilize this information in quality control of data generated. Instrumental analysis and conditions (Mullin, M.D., 1985, PCB Workshop, US EPA Large Lakes Research Station, Gross Ile, MI, June.) cited in the Green Bay Mass Balance Study document will be refined to be applicable to an in-house data management software package.

2.) "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns", George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996. This journal publication provides complete assignment of all 209 PCB congeners to the GC peaks separable on a DB-1 capillary column. It also provides weight percent information for PCB congeners in Aroclor formulations used in labeling protocols for reporting purposes.

3.) "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", US EPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2. This USEPA SOP summarizes M. Mullin's congener composition of the mixed Aroclor standard used for calibration.

4.) "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10. This LLRS SOP written by M. Mullin summarizes the calibration composition of the mixed Aroclor standard reported in "Mullin, M.D., PCB Workshop, U.S. EPA Large Lakes Research Station, Grosse Ile, MI, June 1985.

1.2 This gas chromatographic capillary column method, utilizing an electron capture detector, will effectively separate 112 or more peaks representing 209 PCB congeners.

2.0 Summary of Method

2.1 This method provides detailed instructions for gas chromatographic conditions for analysis of PCBs by capillary gas chromatography.

2.2 This method utilizes a mixed Aroclor standard (Aroclor 1232/1248/1262 in the ratio of 25:18:18) for calibration. Method detection limit and practical quantitation limit will be established experimentally using the procedure in USEPA 40 CFR, Part 136, App. B.

2.3 In general, samples are first extracted with a pesticide-grade solvent. The extracts are further processed through a series of clean-up techniques. The sample is then analyzed by direct liquid injection onto the gas chromatographic column and detected by an electron capture detector. This method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

2.4 A key component of this method is the importance placed on the chromatographic separation that must be achieved for this congener specific technique. A total of 112 chromatographic peaks are detected, containing 209 PCB congeners in various ratios. This allows an almost complete profile of environmentally occurring PCBs.

2.5 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize himself with the hazards of handing the compounds used for standards and samples themselves.

3.0 Interference

3.1 One of the major sources of interference in the analysis of PCBs is that organochlorine pesticides are coextracted from the samples. A few of these ECD responding pesticides can be separated cleanly from the PCB profile by the resolving characteristics of the capillary column. Several of the commonly found pesticides and degradation products (DDT, DDE, DD) overlap the PCB profile envelope and co-elute with several of the PCB congeners found in environmental samples. The analyst must be careful in chromatographic pattern review and flag peaks that are suspected of being contaminated so that they are not included in total PCB values generated.

3.2 Sample preparation, extraction procedures, and extract clean-up protocols are covered in separate SOPs that deal exclusively with sample extraction.

3.3 Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters give response on electron capture detectors, usually as late eluting peaks and can interfere in PCB quantification.

4.0 Sample Archiving

4.1 Depending on program requirements, sample extracts and certain original samples (*i.e.,* Soil, sediment, tissue, and oil samples) can be retained after analysis. The sample extracts and original samples will be stored in a freezer.

5.0 Equipment and Apparatus

5.1 Gas Chromatograph: Complete system for high resolution, capillary column capability and all required accessories. Northeast Analytical, Inc. will use a Varian Model 3800 gas chromatograph, equipped with capillary on-column injection (Septum Programmable Injector), temperature programmable oven, Model 8200 automatic sampler, and fast time constant electron capture detector. A data system (Waters Associates, Millennium_32 Workstation) for chromatographic operations and integration of detector signal is interfaced to the gas chromatograph.

5.1.1 GC Column: The gas chromatograph column to be used for analysis will be a DB-1 (J&W Company), bonded polydimethylsilicone, 30 meter fused silica capillary column with an internal diameter of 0.25mm and phase coating thickness of 0.25 microns. This column is capable of resolving 112 chromatographic peaks from the full spectrum of all PCB congeners that could be expected in an environmental sample. Refer to Appendix A and Appendix B for a complete description of PCB congeners identified in each GC chromatographic peak and achievable chromatographic separations.

5.2 Chromatograph Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates), will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

5.3 Volumetric Flasks: 10 and 100mL, ground-glass stopper. For standard preparation.

5.4 Microsyringe: 10 and 100uL for standard preparation.

5.5 Pipettes: Class A volumetric, 2mL, 5mL, and 10mL.

5.6 Vials: Glass, 10 and 20mL capacity for sample extracts.

5.7 Bottles: Glass, 120mL capacity for standard storage.

6.0 Reagents and Standards:

6.1 Solvents: Pesticide grade quality. Hexane, acetone, toluene, methylene chloride.

6.2 Octachloronaphthalene: Obtained from Ultra Scientific (Hope, RI) with a purity greater than 95%.

6.3 Polychlorinated Biphenyls: Neat commercial material or solutions for standard preparation. These materials are multi-component mixtures of PCB congeners and are the actual materials that were used in products such as transformers and capacitors. Monsanto was the largest producer of PCB formulations and sold them under the tradename Aroclor.

6.4 PCB Congeners: A complete set of all 209 PCB congeners to individually verify the exact elution on the chosen chromatographic system. A subset of congeners are also used as a secondary supplemental calibration standard for those congeners that do not exist at a high enough level in the Aroclor based calibration standard. Obtained from AccuStandard or Ultra Scientific.

6.5 Stock Standard Solutions:

6.5.1 Stock standards are prepared from individual neat Aroclor formulations by weighing approximately 0.1000g to the nearest 0.2 mg and dissolving and diluting to volume in a 100mL volumetric flask with hexane. This will give a stock concentration of 1,000ug/mL.

6.5.2 The stock standard is transferred into screw-cap 120mL boston bottles and stored in a freezer, protected from light. Stock standards should be checked at frequent intervals for signs of evaporation, especially just prior to preparing calibration standards.

6.5.3 Stock PCB standards must be replaced after one year, or sooner if comparison with continuing calibration check standards indicate a problem.

6.5.4 Stock standards for the following are prepared by the above procedure:

Aroclor 1232
Aroclor 1248
Aroclor 1262

6.6 Mixed Aroclor Stock Standard at 62.7ug/mL: A stock standard is prepared at 62.7ug/mL that is used for preparing linearity standards and the calibration standard. Using a 5.0mL Class A pipette, accurately add 2.49mL of stock Aroclor 1232 standard (1,033ug/mL) to a 100mL volumetric flask. Using a 2.0mL Class A pipette, accurately add 1.82mL of stock Aroclor 1248 standard (1,019ug/mL) and 1.80mL of stock Aroclor 1262 standard (1,024ug/mL) to the same 100mL volumetric flask. Make volume to the 100mL mark with hexane.

6.6.1 Store the Mixed Aroclor Stock Standard at 62.7ug/mL in a freezer in a tightly capped bottle. This standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

6.6.2 High Linearity Standard at 31.35ug/mL: The High Linearity Standard is prepared from the 62.7ug/mL mixed Aroclor stock standard. Using a 5.0mL Class A pipette, accurately add 5.0mL of the 62.7 stock standard into a 10mL volumetric flask. Using a 10 microliter syringe add 9.0uL of

202ug/mL octachloronaphthalene into the same 10mL volumetric flask. The octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 10ml vial and store in a freezer.

6.6.3 The 31.35ug/mL High Linearity Standard must be replaced after one year.

6.7 Calibration Standard at 6.27ug/mL: The calibration standard is prepared by combining Aroclor 1232, Aroclor 1248, and Aroclor 1262 in a 25:18:18 ratio with a final mixture concentration of 2.57ug/mL, 1.86ug/mL, and 1.84ug/mL respectively (total = 6.27ug/mL). The final concentration of the mixed standard may vary to accommodate instrument sensitivity or more closely represent sample concentrations, but the same ratio values must be maintained. These ratios are strictly maintained so that the percent composition data remains applicable, since it was developed for use under these fixed mixture parameters. The calibration standard is prepared from the 62.7ug/mL mixed Aroclor stock standard. Using a 10.0mL Class A pipette, accurately add 10.0mL of the 62.7 stock standard into a 100mL volumetric flask. Using a 100 microliter syringe add 90.0uL of 202ug/mL octachloronaphthalene into the same 100mL volumetric flask. Make to volume with hexane. The octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 120-ml boston bottle and store in a freezer.

6.7.1 The 6.27ug/mL Calibration Standard must be replaced after one year, or sooner, if comparison with continuing check standards indicate a problem.

6.8 Supplemental Congener Standard: A Supplemental Congener Standard is analyzed along with the 6.27ug/mL Calibration Standard. This standard contains congeners that exist at low levels in the mixed Aroclor standard and comprises congeners that are not typically found in Aroclor formulations, but could become important in by-product PCB analysis or the study of model experiments that use unusual PCB congeners. This standard is analyzed to supply accurate retention time information and response factors for quantification. All stock standards are purchased as solutions at 100ug/mL. All supplemental congeners are diluted (except 3-Chlorobiphenyl) to 10ug/ml in hexane by pipetting 1.0mL of the 100ug/mL stock standard into a 10mL volumetric flask and making to volume with hexane. For each congener, pipette 0.5mL of the 10ug/mL secondary stock standard into the same 100mL volumetric flask. For the 3-Chlorobiphenyl, pipette 2.0mL of the 100ug/mL stock standard into the same 100mL volumetric flask. Using a 100 microliter syringe add 90.0uL of 202ug/mL octachloronaphthalene into the same 100mL volumetric flask. Make to volume with hexane. The octachloronaphthalene is used as an internal standard for instrument calibration. Transfer the standard solution to a 120mL boston bottle and store in a freezer. The standard concentration is 2.00ug/mL for 3-Chlorobiphenyl and 0.050ug/mL for all other congeners in the standard. The following table lists the congeners included in this standard and the DB-1 peaks where they elute and also lists the other non-Aroclor congeners that co-elute with these 14 congeners. The Stock Standard and Supplemental Congener Standard must be replaced after one year.

Supplemental Congener Standard

DB-1 Peak Number	IUPAC Congener Number	(IUPAC #) PCB Congener Analyzed		Conc ug/mL
3	2	(2)	3-Chlorobiphenyl	2.000
9	14	(14)	3,5-Dichlorobiphenyl	0.050
11	30	(30)	2,4,6-Trichlorobiphenyl	0.050
12	11	(11)	3,3'-Dichlorobiphenyl	0.050
19	23,34,54	(34)	2',3,5-Trichlorobiphenyl	0.050
28	36	(36)	3,3',5-Trichlorobiphenyl	0.050
30	39	(39)	3,4',5-Trichlorobiphenyl	0.050
35	62,65	(65)	2,3,5,6-Tetrachlorobiphenyl	0.050
36	35	(35)	3,3',4-Trichlorobiphenyl	0.050
41	68,96	(96)	2,2',3,6,6'-Pentachlorobiphenyl	0.050
43	57,103	(103)	2,2',4,5',6-Pentachlorobiphenyl	0.050
62	154	(154)	2,2'4,4',5,6'-Hexachlorobiphenyl	0.050
68	123	(123)	2',3,4,4',5-Pentachlorobiphenyl	0.050
70	140	(140)	2,2',3,4,4',6'-Hexachlorobiphenyl	0.050
76	127,168,184	(127)	3,3',4,5,5'-Pentachlorobiphenyl	0.050

6.9 Internal Standard: The internal standard used for capillary gas chromatography of PCBs will be octachloronaphthalene (OCN). Weigh, to the nearest 0.1 mg, 10.1mg of solid octachloronaphthalene (OCN) into a 5mL vial. Quantitatively transfer the OCN using six successive 2-mL washings of toluene to a 50mL volumetric flask. Be sure to rinse the 5mL vial walls carefully so that all OCN is completely transferred to the 50mL volumetric flask. Make the solution to volume using toluene and mix the internal standard solution by shaking the flask several times. This will give a concentration of OCN of 202ug/mL. Carefully transfer the internal standard solution to 25mL vials, tightly cap, and store in a freezer. A portion of the internal standard is transferred to a 5mL reacti-vial with a Teflon syringe-valve cap to use on a daily basis. The react-vial minimizes evaporation since the cap does not have to be removed.

6.9.1 The OCN internal standard is added to all calibration standards, continuing check standards, blanks, samples, and QC samples at the same amount. In most cases this will be achieved by spiking 9.0uL of OCN internal standard solution to 10mL of standard or sample extract to give a concentration of 0.1818ug/mL.

6.9.2 The internal standard will be added to calibration standards, sample extracts, blanks, and QC samples prior to gas chromatographic analysis. Thus, the internal standard is used as a quantification spiking standard and will eliminate sample injection volume variations, but will not correct for analytical losses during sample preparation.

6.9.3 OCN internal standard must be replaced after one year.

6.10 Continuing Calibration Check Standards: Continuing calibration check standards at 1.27ug/mL and 0.127ug/mL are prepared from Aroclor solutions obtained from a different source (ULTRA Scientific) than the calibration standard. The continuing calibration check standard is a mixed Aroclor 1232, 1248, and 1262 in the fixed ratio used to prepare the calibration standard and must be strictly adhered to.

6.10.1 50.0ug/mL Continuing Calibration Check Stock Standards: Aroclor 1232, Aroclor 1248, and Aroclor 1262 are obtained from ULTRA Scientific at 1000ug/mL in isooctane. Using a 1.0mL Class A pipette, 0.5mL of 1000ug/mL Aroclor 1232 is transferred to a 10.0mL volumetric flask and made to volume with hexane. This procedure is repeated for Aroclor 1248 and Aroclor 1262. The 50ug/mL stock standards are transferred to a 10mL vial, tightly capped and stored in a freezer. These stock standards must be replaced after one year.

6.10.2 1.27ug/mL Continuing Calibration Check Standard with OCN: Using a 1.0mL Class A pipette transfer1.0mL of 50.0ug/mL Aroclor 1232, 0.5mL of 50.0ug/mL Aroclor 1248, and 0.5mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Using a 100 uL microsyringe, add 90.0uL of OCN internal standard (final concentration of 0.1818 ug/mL). Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing check solution will contain a total of 1.27ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

6.10.3 Transfer the 1.27ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a freezer. A new continuing check standard must be prepared every six months.

6.10.4 1.27ug/mL Continuing Calibration Check Standard without OCN: Using a 1.0mL Class A pipette transfer1.0mL of 50.0ug/mL Aroclor 1232, 0.5mL of 50.0ug/mL Aroclor 1248, and 0.5mL of 50.0ug/mL Aroclor 1262 into a 100mL volumetric flask. Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing check solution will contain a total of 1.27ug/mL PCB (0.500ug/mL Aroclor 1232, 0.360ug/mL Aroclor 1248, and 0.360ug/mL Aroclor 1262).

6.10.5 Transfer the 1.27ug/mL Continuing Calibration Check Standard without OCN to a 120mL boston bottle, cap tightly, and store in a freezer. A new continuing calibration check standard must be prepared every six months. This continuing check standard without OCN is used to prepare the 0.127ug/mL Continuing Calibration Check Standard with OCN.

6.10.6 0.127ug/mL Continuing Calibration Check Standard with OCN: Using a 10.0mL Class A pipette transfer 10.0mL of 1.27ug/mL Continuing Calibration Check Standard without OCN to a 100mL volumetric flask. . Using a 100uL microsyringe, add 90.0uL of OCN internal standard (final concentration of 0.1818ug/mL). Make to volume with hexane and mix well by shaking and inverting flask several times. The prepared continuing calibration check solution will contain a total of 0.127ug/mL

PCB (0.050ug/mL Aroclor 1232, 0.036ug/mL Aroclor 1248, and 0.036ug/mL Aroclor 1262).

6.10.7 Transfer the 0.127ug/mL Continuing Calibration Check Standard with OCN to a 120mL boston bottle, cap tightly, and store in a freezer. A new continuing calibration check standard must be prepared every six months.

7.0 Procedure

7.1 Calibration:

7.1.1 Gas chromatographic Operation Parameters: Establish the gas chromatographic operation parameters as follows:

GC Column: DB-1 (J&W, bonded polydimethylsilicone), 30 meters, 0.25 mm internal diameter, 0.25 micron phase coating.

Oven Temperature Program: 50°C for 5.0 min hold time, 50°C to 150°C at 15.0°C/min, hold 0.01minutes, 150°C to 220°C at 4.3°C/minute, hold at 220°C for 33.0 minutes.

GC Column Velocity: Approximately 30 cm/sec Helium. Column flow adjusted to elute OCN Internal Standard between 42.0 and 48.0 minutes.

Detector: Electron Capture Detector (ECD), attenuation 1, range 4.

Detector Temperature: 300°C.

Injector Temperature Program: 250°C , pulsed split injection, initial pressure at 25.0PSI, pulsed pressure at 40PSI, pulsed time 0.75 minutes, split ratio 25 (adjustable based on signal sensitivity)

Detector Make-up Gas: Approximately 65mL/min Nitrogen. Adjusted for signal sensitivity.

Autosampler: 1.0uL sample volume (adjustable based on signal sensitivity). Sample pumps 4, viscosity delay 3, sample wash 2, solvent A 2 washes, solvent B 2 washes, slow plunger OFF, sampling offset OFF, solvent A pre-wash 1, solvent B pre-wash 1.

7.1.2 Initial GC Calibration: Prior to running samples the system must be calibrated and the Continuing Calibration Check Standard must be verified.

7.1.2.1 Establish the gas chromatographic operation parameters outlined in Section 7.1.1 and prepare the appropriate calibration standards composed of a mixture of Aroclors 1232, 1248, and 1262 as outlined in Sections 6.5 through 6.10.

7.1.2.2 Chromatographic Resolution Criteria: Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and 15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

7.1.2.3 Initial High Level Linearity Verification: The gas chromatograph must undergo a linearity study. A high-level three-point initial calibration check for linearity is analyzed and calculated relative response factors must meet a limit for relative standard deviation for each GC peak of less than 20%. This high level linearity verification is associated with samples with medium to high levels of PCBs for sample matrices such as biota, sediment, soil, oil, and other solid or liquid samples that contain appreciable levels of PCBs. The high level initial linearity is comprised of the following standards: 31.35ug/mL High-Level Linearity Standard, 6.27ug/mL Calibration Standard, and the 1.27ug/mL Continuing Calibration Standard.

7.1.2.4 Initial Low Level Linearity Verification: The gas chromatograph must undergo a linearity study. A low-level three-point initial calibration check for linearity is analyzed and calculated relative response factors must meet a limit for relative standard deviation for each GC peak of less than 20%. This low level linearity verification is associated with samples with low levels of PCBs for sample matrices such as water and other solid or liquid samples that contain low levels of PCBs. The low-level initial linearity is comprised of the following standards: 6.27ug/mL Calibration Standard, the 1.27ug/mL Continuing Calibration Standard, and the 0.127ug/mL Continuing Calibration Standard.

7.1.2.5 Initial 72-Hour Retention Time Window Measurement: An initial retention time study must be performed to establish retention time windows to assist in PCB peak assignment. Three high level Continuing Calibration Check standards must be analyzed over at least a 72-hour period. In addition, the Supplemental Congener Standard is analyzed three times over at least a 72-hour period. The mean retention time is calculated from these standards along with the standard deviation for each GC peak. The retention time window is established as ±3 times the determined standard deviation. If the 3 times the standard deviation value is less than 0.07 minutes a default of 0.07 minutes is

applied to that GC peak. The default 0.07 minutes retention time window is the default window used in Contract Laboratory Program, Statement of Work for Organic Analysis for PCB/Pesticide analysis.

7.1.2.6 Our laboratory will use a computer based data acquisition workstation (Waters Associates, Millennium_32 workstation software), interfaced to the gas chromatograph. The workstation processes the detector signal, performs an analog to digital conversion, and stores the digitized chromatograms on the computer hard disk. All data analysis will be done on the specialized software package including peak integration, calculating calibration curves/response factors, report generation, chromatogram hardcopies, and archival of data. Calculate the response factor for each separated and identified peak.

7.1.2.7 After the above criteria are met system calibration for sample analysis can be performed. Appendix A identifies which congener and or congeners compose each resolvable GC peak in the calibration standard, along with the amount that each congener or co-eluting group of congeners are represented in the calibration standard. Throughout this document the IUPAC PCB numbering system will be used for congener identification. Appendix B is an example of an acceptable chromatogram of the calibration standard, along with peak congener labels for cross-reference to data in Appendix A. Analyze the 6.27ug/mL Calibration Standard to initiate calibration of the GC system. Also analyze the Supplemental Congener Standard to calculate relative response factors for congeners that do not exist in the 6.27ug/mL Calibration Standard. Response factors are calculated relative to the internal standard by the following equation:

$$RRF = (Ax/Ais)x(Cis/Cx)$$

Where:	RRF	=	Relative response factor of congener(s).
	Ax	=	Area of peak for the congener(s).
	Ais	=	Area of peak for the internal standard.
	Cx	=	Concentration of the congener(s).
	Cis	=	Concentration of the internal standard.

7.2 Continuing Calibration:

7.2.1 Chromatographic Resolution:

7.2.1.1 Chromatographic resolution is measured by peak height to valley height for two pairs of closely eluting peaks. The peak valley height formed between DB-1 peaks 14 and

15 must be equal to or less than the half height of peak 15. The peak valley height formed between DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. This peak resolution must be established initially and maintained throughout sample analysis.

7.2.2 Response Factor Verification:

7.2.2.1 The relative response factors calculated from the calibration standard will be verified on each working day by analyzing a Continuing Calibration Check Standard, calculating the selected congener concentrations and comparing to their known concentration. A subset of six congeners and Total PCBs will be used to verify the relative response factors before samples are processed. The Percent Difference for Total PCBs must be ±15%. The six congeners include:

DB-1 PEAK NUMBER	IUPAC CONGENER NUMBER	RELATIVE PEAK LEVEL IN CALIBRATION STANDARD	PEAK CONC 1.27ug/mL CONTINUING CALIBRATION STD (ng/mL)	PERCENT DIFFERENCE LIMITS
7	6	Low level peak in standard	14.10	<30
116	205	Low level peak in standard	0.820	<30
47	70	Medium level peak in standard	25.22	<10
93	174,181	Medium level peak in standard	23.74	<10
37	104,44	high level peak in standard	31.90	<10
102	180	high level peak in standard	45.26	<10

7.2.3 After the Continuing Calibration Check Standard is analyzed, calculate the amount for these six congeners and Total PCBs and compare those values to the known concentrations by the following equation:

Percent Difference = [Amt(1)-Amt(2)]/Amt(2) x 100

Where: Amt(1) = Amount calculated for congener or Total PCBs.
Amt(2) = Known amount for congener or Total PCBs.

7.2.4 A percent difference greater than ± 30% for the two low-level peaks (7 and 116) indicates an instrument problem or unacceptable relative response factors. A percent difference greater than ± 10% for the medium level (47 and 93) and high level (37 and 102) peaks also indicates an instrument problem or unacceptable relative response factors. If any of the evaluation congeners or Total PCBs fail to meet the percent difference acceptance criteria, the guidance provided in Section 8.1.4 must be followed.

7.2.5 The percent recovery for the internal standard octachloronaphthalene (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the OCN area in the associated calibration standard. If the OCN area fails to meet the acceptance criteria, the guidance provided in Section 8.1.4 must be followed.

7.2.6 If re-calibration is performed, the Continuing Calibration Check Standard must be analyzed again and values calculated using the new relative response factors. If the Continuing Calibration Check Standard fails to meet the percent difference criteria after re-calibration, sample analysis must not proceed until the problem is found and corrected (*i.e.*, GC gas leak, autosampler lines plugged, broken injector liner).

7.3 Sample Preparation and Extraction

7.3.1 The following SOPs detail sample extraction procedures that are utilized in preparing samples for analysis by this analytical method:

SOP NAME	TITLE
NE005	SOXHLET EXTRACTION : SOLIDS
NE006	WATER EXTRACTION
NE017	FISH & BIOTA EXTRACTION
NE049	ANIMAL TISSUE EXTRACTION: SMALL MASS PROCEDURE
NE087	EXTRACTION FOR OIL
NE088	WIPE EXTRACTION FOR PCB
NE124	CLLE PCB EXTRACTION
NE132	FISH/BIOTA GRINDING PROCEDURES
NE140	PCB SCREENING BY GC
NE143	ASE EXTRACTION FOR PCB: SOLIDS
NE144	ASE EXTRACTION FOR WIPE: PCB
NE158	% LIPID DETERMINATION: FISH & BIOTA

7.4 Calculations:

7.4.1 SCREENING GC: External Standard Calibration:

7.4.1.1 The GC screening analysis will be done by the external standard calibration technique. See standard operating procedure NE140 for details on the PCB screening procedures used prior to final analysis by this method. The GC will be standardized by using Aroclor 1242 and Aroclor 1260. These two Aroclor formulations incorporate most environmental PCBs found in sample extracts and provide a good estimate of PCB amount for final dilution for capillary analysis. A two level calibration curve is utilized (0.50ug/mL and 2.5ug/mL standards).

7.4.1.2 The calibration curves for each section of the PCB elution profile will be calculated using the following formula:

$$\text{Calibration factor} = \frac{\text{Amount (ug) of Aroclor}}{\text{Total area of Aroclor}}$$

The calibration curve will be a linear fit forced through zero.

7.4.2 SCREENING GC: Sample Calculations

7.4.2.1 The concentration of each Aroclor (grouped as Aroclor 1242 and Aroclor 1260 only) in a sample will be calculated based on the extract volume (not the sample weight or volume) to supply solution concentration values that show if the extract needs to be diluted for final capillary GC analysis. The solution concentration of either Aroclor 1242 or Aroclor 1260 (or both) in a sample is calculated as follows:

Concentration (ug/mL) = (Ax) x (CF)

Where: Ax = Area of Aroclor of interest in sample
CF = Calibration factor in standard

7.4.3 Capillary GC: Internal Standard Calibration

7.4.3.1 The capillary column GC analysis will be done by the internal calibration technique. Calibration and sample quantification will be performed by a commercial GC software package. The capillary GC will be standardized by using an Aroclor mixture that encompasses all the possible PCB congeners present in environmental samples. Refer to Section 6.6 for details on the calibration standard and Aroclor ratios.

7.4.3.2 Response factors for each separated and identified peak in the standard will be calculated using the following formula:

$$RRF = (Ax/Ais)x(Cis/Cx)$$

Where:
RRF = Relative response factor of congener(s).
Ax = Area of peak for the congener(s).
Ais = Area of peak for the internal standard.
Cx = Concentration of the congener(s).
Cis = Concentration of the internal standard.

7.4.4 Capillary GC: Sample Calculations

7.4.4.1 The concentration of each identified PCB peak in a sample will be calculated based on the sample dry weight in the case of soils and sediments and wet weight for fish and biota samples.

7.4.4.2 The sample PCB concentration of each standardized PCB peak is calculated as follows:

$$\text{Concentration (ng/g)} = \frac{[(Ax)(Cis)(V)(D)]}{[(Ais)(RRF)(Ws)]}$$

Where:
- Ax = Peak area for congener(s) being measured.
- Cis = Amount of internal standard added to sample extract.
- D = Dilution factor, if sample was diluted prior to analysis.
- V = Extract volume.
- Ais = Peak area of added internal standard.
- RRF = Relative response factor for congener(s) being measured as determined in Section 7.4.3.2.
- Ws = Dry or wet weight of sample.

7.4.5 The calculated PCB concentration for each PCB peak will be compared to its respective sample-specific reporting limit (RL) and method detection limit (MDL). The results for peaks with concentrations at or above the MDL but below the RL will be reported as detects and flagged as estimated ("J"). The results for peaks with concentrations at or above the RL would be reported as unqualified numeric values.

7.4.6 The Total PCB concentration will be calculated and reported as follows:

7.4.6.1 All peak results above their respective MDL (both "J" flagged and unqualified results) will be summed and compared to the sample-specific Total PCB MDL and RL.

7.4.6.2 If no peaks are detected above their respective MDL, the Total PCB results will be reported as not detected at or above the sample-specific Total PCB MDL.

7.4.6.3 If the summed peaks from Section 12.2.3.1 are below the Total PCB MDL the result would be reported as less than ("<") the sample-specific Total PCB MDL.

7.4.6.4 If the summed peaks from Section 12.2.3.1 are at or above the Total PCB MDL but below the Total PCB RL, the summed result will be flagged as estimated ("J").

7.4.6.5 If the summed peaks from Section 12.2.3.1 are at or above the Total PCB RL, the Total PCB result will be reported as the unqualified numeric value.

7.4.5 <u>Data Output and Reporting Format</u>:

7.4.5.1 Several specialized software routines have been developed for high resolution PCB analysis to aid the data user in understanding and organizing the complex data generated from this extremely detailed analysis. Appendix C contains examples of the sample hard copy format that will be used

in reporting sample information. This data is also available in electronic format as an Excel™ file.

7.4.6 Data adjustments for Hudson River water samples:

7.4.6.1 In 1997 a report was issued by General Electric to EPA (HydroQual, 1997. Development of Corrections for Analytical Biases in the 1991 – 1997 GE Hudson River PCB Database. Prepared for General Electric Company Corporate Environmental Programs, Albany, NY.) that outlined concentration corrections required for several DB-1 GC peaks containing more than one PCB congener. These PCB congeners were present in different proportions in Hudson River water samples compared to the method calibration standards. The technical details and research that support the following data conversion can be found in the above referenced document.

7.4.6.2 The EPA 1993 Reassessment Remedial Investigation and Feasibility Study (RRI/FS) Phase II Hudson River water column data were used as a qualitative benchmark for data comparison to the GE weekly Hudson River water column study. This 1993 data set was chosen because EPA collected a significant number of samples to compare to the GE weekly sampling events.

7.4.6.3 Significant concentration differences were detected in Green Bay method GC peaks 5, 8, and 14 (which are comprised of congeners IUPAC 4 and 10; IUPAC 5 and 8; and IUPAC 15 and 18, respectively) when compared to the EPA database, which determined concentrations of these congeners as individual eluting GC peaks. These congeners differ in gas chromatographic response between each other when analyzed individually. It was determined that when these congeners were measured in Hudson River water samples as co-elutions their composition did not match the calibration standard congener composition in peaks 5, 8, and 14 and measurement was not as precise as when these congeners were determined by the EPA analytical method.

7.4.6.4 To address this measurement bias for the above peaks, a correction ratio was determined and applied to the concentration values obtained by the initial quantification. The correction ratio was derived by analysis of Hudson River water column extracts on a chromatographic system that was calibrated using individual congeners as standards and that could baseline resolve the co-elution congeners found in Green Bay method GC peaks 5, 8, and 14. These results were utilized to report a more accurate concentration

value for the congeners comprising Green Bay method peaks 5, 8, and 14. The correction factors historically used were 0.65, 0.45, 1.44 for DB-1 peaks 5, 8, and 14, respectively. The correction ratios were confirmed and verified in March 2004 by conducting confirmatory analyses utilizing the gas chromatographic system that baseline resolved the six PCB congeners that required the correction ratio. GE confirmed and updated the correction factors for DB-1 peaks 5, 8 and 14 in a manner consistent with the approach described in the above report. The results of the evaluation of the correction factors for DB-1 peaks, 5, 8, and 14 were delivered to EPA via email on March 31, 2004 in a technical memorandum. Based on the findings summarized in the technical memorandum, upon initiation of the BMP, the correction factors developed based on the 2003 data set (0.61, 0.36 and 1.26) will be used to adjust DB-1 peaks 5, 8 and 14, respectively, for the bias identified in HydroQual 1997.

7.4.6.5 After the concentration values are corrected for Green Bay method peaks 5, 8, and 14 several other parameters require re-calculation prior to data reporting. These include the following: total PCB concentration, Homolog distribution, weight percent per peak, chlorination levels (ortho-Cl per biphenyl, meta+para-Cl per biphenyl, and total Cl per biphenyl), total micromoles, and average molecular weight.

8.0 Quality Control

8.1 The following table lists the Quality Control samples required for capillary gas chromatography analysis of PCBs in water, soils and sediments.

Quality Control Requirements

QC Sample	Frequency
Lab Blank	With each sample batch (up to 20 samples)
Lab Control Spike	With each sample batch (up to 20 samples)
Continuing Cal Check	Analyzed prior to each sample batch (up to 10 samples)
Duplicate Analysis	Field generated sample – analyzed at discretion of client
Matrix Spike	One matrix spike per 20 field samples
Matrix Spike Duplicate	One matrix spike duplicate per 20 field samples

8.1.2 Laboratory Blank: The laboratory blank will monitor and assess whether the contamination or excessive interference is occurring from laboratory solvents, reagents, and glassware used in processing samples for analysis. The laboratory blank is taken through the sample extraction and clean-up procedures to include all manipulations exposed to actual samples (required volume of solvents, concentration steps, clean-up procedures, *etc*.) If the laboratory blank is positive for PCB above the reporting limit, the contamination must be traced down and eliminated before samples can be processed and analyzed. If non-PCB contamination occurs that interferes with PCB quantification, it too must be traced down and eliminated before proceeding with sample analysis. The laboratory blank will consist of granular sodium sulfate for solids and organic free water for water samples.

8.1.2.1 Samples associated with a positive laboratory blank should be flagged when the data is reported. If a laboratory blank is positive for PCBs, the source of contamination must be located and eliminated. If the contamination occurred during the extraction procedure and more sample is available the samples will require re-extraction and re-analysis. If the contamination occurred after this step, then re-extraction may not be required and the existing extracts will be reanalyzed. Any aliquots of the extracts (*i.e.,* injection vials) which could have become contaminated will be discarded.

8.1.3 Laboratory Control Spike: A Laboratory Control Spike sample is analyzed with each extraction batch. An Aroclor is spiked into either granular sodium sulfate for solids or organic free water for liquids. This Control Spike must achieve a percent recovery of 70 to 130 percent. If the Control Spike recovery is not within limits, the cause must be tracked down and corrected. If there is sufficient sample, the samples associated with the Laboratory Control Spike that failed must be re-extracted and re-analyzed. If no more sample is available, the data must be flagged to indicate low or high Control Spike recovery.

8.1.4 Continuing Calibration Check Standard: As outlined in section 7.2, a Continuing Calibration Check Standard will be analyzed on each working day prior to sample analysis and at an interval of one Continuing Calibration Check Standard per 10 samples. The Continuing Calibration Check Standard must meet the acceptance criteria established in Section 7.2. If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the following guidance must be followed.

8.1.4.1 If samples are being run using an autoanalyzer (*i.e.,* the instrument is unattended) and a Continuing Calibration Check Standard that fails to meet the acceptance criteria is present in the analytical sequence but acceptable Continuing Calibration Check Standards are observed later

in the analytical sequence, samples bracketed by acceptable Continuing Calibration Check Standards will be reported.

8.1.4.2 If the reason for the failure of the Continuing Calibration Check Standard appears to be a poor injection (or a degraded standard solution), the Continuing Calibration Check Standard will be re-injected (or reprepared and re-injected) immediately following the failed Continuing Calibration Check Standard. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the Continuing Calibration Check Standard meets all the acceptance criteria established in Section 7.2 and there is no apparent impact on the sample data (*i.e.,* acceptable internal standard areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported.

8.1.4.3 If the Continuing Calibration Check Standard fails to meet the acceptance criteria, the calibration standard must be re-analyzed and new response factors generated. After re-calibration, the Continuing Calibration Check Standard must be analyzed again and compared to the acceptance criteria. If the Continuing Calibration Check Standard fails to meet the acceptance criteria after re-calibration, sample analysis must not proceed until the problem is corrected.

8.1.4.4 All samples that were analyzed directly before or after the continuing calibration check standard exceeded established criteria must be re-analyzed.

8.1.5 Duplicate Analysis: Duplicate analysis of the same sample is performed to assess method precision. A duplicate can also be performed as a blind duplicate, with the sample split in the field. The analysis of a duplicate sample precludes that PCBs are to be found at appreciable levels in samples. If this is not known the analysis of matrix spike / matrix spike duplicates provide more consistent quality control information. The relative percent difference of the two measurements on the sample is calculated on total PCB concentration by the following equation:

$$RPD = (DUP1 - DUP2)/AVG \times 100$$

Where: RPD = Relative Percent Difference.
DUP1 = The greater of the measured values.
DUP2 = The lesser of the measured values.
AVG = Average of the two analysis.

8.1.5.1 The relative percent difference must be less than or equal to 25% if the concentration of PCB in the sample is greater than or equal to 0.5ug/g. The percent relative standard

deviation must be less than or equal to 50% if the concentration of the PCB in the sample is less than 0.5ug/g.

8.1.6 Matrix Spike and Matrix Spike Duplicate: Spiked sample matrix data are analyzed to assess analytical accuracy and recovery of analytes of interest. Thus the sample is spiked and carried through sample analytical procedures including extraction, clean up, and GC analysis.

8.1.6.1 There must be sufficient sample for analysis of matrix spike/matrix spike duplicate samples and the sample must be homogeneous in PCB distribution for valid data to be produced. Preferably a sample of low level should be used in this case so that the spike level is of sufficient concentration over the background level of the chosen sample. Spike the two samples with the Aroclor matrix spike standard at a concentration approximately five times the sample concentration. Extract and analyze the two spiked samples following procedures used for actual sample analysis. Calculate the percent recovery of the matrix spike/matrix spike duplicate by the following equation:

$$P = A-B/T \times 100$$

Where: P = Percent recovery, %.
A = concentration of analyte in the spike sample aliquot.
T = Known true value of the spike concentration.
B = Background concentration of PCB in the unspiked sample aliquot.

8.1.6.2 Matrix spike recovery information is used to assess the long-term precision and accuracy of the method for each encountered matrix. Matrix spike/matrix spike duplicate results are not used alone to qualify an extraction batch. Generally, percent recovery for MS/MSD samples should be greater than or equal to 70% and less than or equal to 130% based on the total PCB concentration. If the percent recovery is outside the limits, all calculations should be checked and the data should be narrated to describe possible matrix interference.

8.1.7 Surrogates: Surrogate spiking compounds monitor the exaction efficiency and sample processing procedures for each sample. Surrogate compounds are chosen which do not chromatographically interfere with the PCB target congeners and which behave similarly to the target PCB congeners during extraction and sample processing.

8.1.7.1 Surrogate spike additions are made to each field sample, method blank, and extracted QC check sample prior to extraction. Congener IUPAC 207 (2,2',3,3',4,4',5,6,6'-

Nonachlorobiphenyl) or Tetra-Chloro-Meta-xylene and Decachlorobiphenyl surrogate compounds are used.

8.1.7.2 Calculate the surrogate percent recovery as follows:

% Recovery = (Surr. Amount spiked / Theoretical Spike conc.) * 100

8.1.7.3 The percent recovery limits for surrogates are:

IUPAC 207	70% - 130%
Tetra-Chloro-Meta-Xylene	70% - 130%
Decachlorobiphenyl	70% - 130%

8.1.8 Retention Time Windows:

8.1.8.1 The Initial Continuing Calibration Check Standard of the analytical sequence is used to establish the retention time window for each analyte from the retention time windows determined during the 72-hour retention time window study. The retention time window equals the absolute retention time of the Initial Continuing Calibration Check Standard for a given batch of samples plus or minus three times the standard deviation determined in Section 7.1.2.5.

8.1.8.2 Besides using the retention time window to assign peaks for quantification, the analyst should also rely on their experience in pattern recognition of multi-residue sample analysis.

8.1.8.3 The PCB congener composition of DB-1 peaks is identified in Appendix A. DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. With exception of congeners IUPAC 77 and 122, the resolved peaks are found at trace levels in Aroclors (and, therefore, not present in the calibration standards) and are addressed in this method in the event they are detected. If these congeners are detected in a sample, the retention time window of the assigned DB-1 peak is set to ensure the congener is quantitated. A standard comment is included on the Congener Weight and Mole Report (see Appendix B) identifying this issue. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indicating that the assigned DB-1 peak includes the presence of the resolved congener. The

DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak[1]	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76*, *98*, *80*, *93*, **95**, **102**, *88*)	*80*, *88*, *93*
56 (*78*, **83**, *112*, *108*)	*108*
61 (**77**, **110**, 148)	**77**
72 (**122**, 131, 133, 142)	**122**
89 (**128**, *162*)	*162*
105 (**200**, *169*)	*169*

1 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

8.1.9 Analytical Sequence Queue: A typical analytical sequence is as follows:

1)	Continuing Calibration check standard (high or low)
2)	Method Blank
3)	Lab Control Spike
4 to 10)	Samples (including Duplicates, MS/MSD)
11)	Continuing Calibration Check Standard
12 to 20)	Samples (including Duplicates, MS/MSD)
21)	Continuing Calibration Check Standard; repeat 12 to 20

9.0 Method Performance:

9.1 Precision and Accuracy Determination: Precision and accuracy data is obtained for the method by analyzing four laboratory control spikes at a reasonable concentration above the 0.127ug/mL continuing calibration standard and below the 6.27ug/mL calibration standard. The analyte will be added to a laboratory organic free water sample or organic free sodium sulfate sample and taken through all extraction and analytical procedures. Aroclor 1242 is used as the analyte and recovery on a total basis is used to calculate percent recovery. To be valid, Aroclor 1242 will be recovered between the limits of 70 to 130 percent.

Also, a percent relative standard deviation will be calculated for the replicates will be less than or equal to 20% to be valid.

9.2 Method Detection Limit: A method detection limit will be determined for this method whenever major modification to the extraction or analysis procedures are made or at a minimum frequency of every 2 years. A minimum of seven laboratory organic free water samples or seven organic free sodium sulfate samples will be prepared with the mixed Aroclor calibration standard at a low level and taken through all extraction and analytical procedures. Method detection limit data will be determined for each chromatographic peak (comprising one or more PCB congeners) based on the following equation:

$$MDL = S * t_{(n-1,\ 1\text{-}alpha=0.99)}$$

Where:

S = Standard deviation of the replicate analyses
n = Number of replicates
$t_{(n-1,\ 1\text{-}alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1

For example: t for 8 replicates = $t_{(7,0.99)} = 2.998$

9.2.1 The determined MDL must be less than the concentration spiked but greater than one tenth (1/10) the spiked concentration. If not, repeat the MDL determination at an appropriate spike concentration for affected analytes.

10.0 Data Assessment and Acceptance Criteria for Quality Control Measures and Corrective Actions for Out-of-Control Data:

10.1 The GC analyst is responsible for generating the data and also is the initial individual to review the data. This would include inspection of the chromatographic data, processing the raw data, producing all required data forms, inspection of calibration curves for compliance, surrogate recovery, laboratory control spike recovery, matrix spike/matrix spike duplicate recovery, and continuing calibration check compliance.

10.2 Once the initial review of the data is performed by the analyst, decisions are made at that time to accept the data if all criteria are met or to reject sample data if any of the quality control parameters or limits are out of control. Depending on the situation, samples requiring re-extraction will be notified to the appropriate extraction personnel, sample extracts requiring re-injection will be queued for analysis, new calibrations may have to be performed, or samples re-analyzed due to failing continuing calibration check standards.

10.3 The analyst may also consult with the quality control officer as to the best form of action to take or if the situation warrants corrective action beyond routine practices. A Corrective Action Report (CAR) is issued to document the problem found, steps taken to resolve the problem, and what samples were affected. This

CAR form is filed with the data and is also useful for production of case narratives that are issued with final data reports.

10.4 The Table below outlines the data assessment, acceptance criteria, and corrective action procedures for out-of-control data.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Linearity Verification and Initial Calibration	• Initially verify linearity through the High- and Low-Level Linearity Verifications. • The initial calibration checks for linearity are each at 3 concentration levels. • A single-point calibration is analyzed initially and when Continuing Calibration Check standard fails criteria.	• %RSD≤20% for among the relative response factors for each peak in the linearity verifications. • Relative response factors are to be calculated using area for each quantifiable peak with internal standard method.	• Re-analyze the initial calibration standard and/or evaluate/correct instrument malfunction to obtain initial calibration and continuing calibration check standards that meet criteria. • Sample results above highest linearity verification standard concentration require dilution and re-analysis.
Continuing Calibration Check Standard (CCC)	• Initially analyze a CCC immediately following a calibration standard analysis. • After the initial CCC of the sequence, a CCC must be analyzed after every 10 samples. • Analytical sequence must end with analysis of a CCC.	• ≤ 30% difference based on "true" concentration for peaks 7, 116. • ≤ 10% difference based on "true" concentration for peaks 37, 47, 93, and 102 and Total PCBs • Retention time of all quantitated peaks must be within RT window (reset with each initial CCC of a sequence) • The percent recovery for the internal standard (OCN) in the Continuing Calibration Check Standard must be within 50-150% of the OCN area of the associated initial calibration standard. • All samples must be bracketed by CCCs that meet all criteria stated above	• If the reason for the failure of the CCC appears to be a poor injection (or a degraded standard solution), the CCC will be re-injected (or reprepared and re-injected) immediately following the failed CCC. This can only occur if the instrument is being attended by an analyst. If upon re-injection, the CCC meets all the acceptance criteria and there is no apparent impact on the sample data (*i.e.,* acceptable OCN areas and surrogate recoveries are observed), the analytical sequence will continue and samples will not be reanalyzed. The associated sample data will be reported. • If CCC failure was not due to a poor injection (or degraded standard solution) or the instrument was unattended at the time of the CCC failure, correct system, if necessary, and recalibrate. Initial calibration and CCC criteria must be met before sample analysis may begin. Samples that are not bracketed by complaint CCCs must be re-analyzed. • If acceptable CCCs are observed later in the sequence, samples bracketed by acceptable CCCs will be reported. Samples between the failed CCC and prior/ subsequent complaint CCC will be re-analyzed.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Retention Time (RT) Windows	• Initial RT windows are established to assist in PCB peak assignment. Three high-level CCC standards and three Supplemental Congener Standards are analyzed over at least 72-hours. The mean RT and the standard deviation of each of the GC peaks are calculated. RT window is ± 3× the determined standard deviation or a default of 0.07 minute is applied (whichever is larger). • RT windows are re-centered based on the initial CCC analyzed after calibration curve or if using the first CCC of the day to start a new sequence.	• RT of CCC peaks must be within established windows in the CCs analyzed for a sequence. • Re-centering windows is allowed only once per 24 hours.	• Adjust system, re-establish RT windows, and re-calibrate if necessary.
Retention Time (RT) shift	• Each CCC analysis: RT of all quantitated peaks in the CCC is evaluated against the initial CCC following the initial calibration curve. • Each sample analysis: Rely on RT windows to identify PCB congeners to report. Also use pattern recognition and professional judgment for peaks that shift from RT windows, because congener composition may shift RT for GC peaks.	• Each quantitated peak and surrogate peak should be with established windows.	• Inspect chromatographic system for malfunction, correct problem. Perform re-analysis if necessary.
Method Blank	• One per extraction batch of ≤20 samples of the same matrix per day. • Must be analyzed on each instrument used to analyze associated samples. • Must undergo all sample preparative procedures.	• Concentration does not exceed the total PCB method reporting limit. • Must meet surrogate criteria of 70 to 130 % recovery.	• Re-analyze method blank to determine if instrument contamination was the cause. If method blank re-analysis passes, then report samples. • If method blank is found to contain PCB contamination above total PCB reporting limit. Then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate method blank contamination or have client re-sample if possible.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Laboratory Control Spike (LCS)	• One per extraction batch of ≤20 samples per matrix per day. The LCS is typically Aroclor 1242.	• Percent recovery of Aroclor 1242 on a total PCB basis must be within method limits of 70 to 130% • Must meet surrogate criteria of 70 to 130% recovery.	• Re-analyze LCS to determine if instrument was the cause. If LCS passes, then report samples. • If LCS recovery is still out of limits, then re-extract and re-analyze all associated samples. If no sample exists for re-extraction, report data flagged to indicate LCS failed recovery or have client re-sample if possible.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	• Normal method procedure is to extract and analyze a matrix spike sample. One MS per extraction batch of ≤20 samples per matrix per day. The MS is typically Aroclor 1242. • If requested, an MSD can be extracted an analyzed. The MSD would follow the above criteria as for the MS.	• Percent recovery for MS on a total PCB basis should be 70 to 130% • If MS/MSD is analyzed, relative percent difference (RPD) should be within 30%. • Must meet surrogate criteria of 70 to 130%(unless original unspiked sample is also outside of criteria).	• Re-analyze MS and/or MSD to determine if instrument was the cause. If MS and/or MSD pass, then report samples. • Check for errors such as calculations and spike preparation. • Check original unspiked sample results and surrogate recovery for indications of matrix effects. • If no errors are found, and the associated LCS is within 70 to 130%, then sample matrix effects are likely the cause. Note exceedence in case narrative.

Quality Control Acceptance Criteria and Corrective Action Plan

Quality Control Item	Frequency	Acceptance Criteria	Corrective Action
Surrogates	• 2,2',3,3',4,4',5,6,6'-Nonachlorobiphenyl is added to all samples and QC samples.	• Percent recovery for the surrogate should be 70 to 130%	• Re-analyze the affected sample or QC sample to determine if instrument was the cause. If surrogate passes, then report samples. • Check for errors in surrogate calculations and surrogate solutions. • If no problem is found, then re-extract and re-analyze the sample. • If re-analysis is within limits and sample extract holding time, then report only the re-analysis. • If the re-analysis is within limits, but out of extraction holding time, then report both sets of data. • If the re-extraction produces surrogate recovery still out of limits, then report both sets of data. • If no sample exists for re-extraction, report data flagged to indicate surrogate failed recovery or have client re-sample if possible.
Internal Standard	• Octachloronaphthalene (OCN) is added to all sample extracts, QC samples and calibration standards. See text for OCN amounts in calibration standards.	• The internal standard area for samples and QC samples should be 50 to 150% of the average internal standard area among the associated initial calibration standards. • The internal standard area for CCCs must be 50 to 150% of the average internal standard area among the initial calibration standards.	• Re-analyze the affected sample or standard to determine if instrument was the cause. If internal standard passes, then report samples. • For Standards – If no problem is found, prepare new standards and re-test. If problem still exists, prepare new internal standard and then prepare new standard solutions and re-test. • For Sample Extracts – If no problem is found, then follow procedures outlined above for surrogate corrective action steps for re-extraction and re-analysis.

11.0 References

11.1 US EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants," July, 1988.

11.2 Standard Methods for the Examination of Water and Wastewater, 19th Edition, Published by: American Public Health Association, American Water Works Association, Water Pollution Control Federation, 1995.

11.3 US EPA SW-846, "Test Methods for Evaluating Solid Waste Physical/Chemical Methods," Office of Solid Waste and Emergency Response, 3rd Edition, 1986 and its updates.

11.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual," Wadsworth Center for Laboratories and Research, 1988.

11.5 Mullin, M.D. 1985. PCB Workshop, US EPA Large Lakes Research Station, Grosse Ile, MI, June.

11.6 M. Zell, K. Ballschmiter, Baseline Studies of the Global Pollution, III. Trace Analysis of Polychlorinated Biphenyls (PCB) by ECD Glass Capillary Gas Chromatography in Environmental Samples of Different Trophic Levels, Fresenius Z. Anal. Chem., 304, 337-349, 1980.

11.7 M.D. Mullin, C.M. Pochini, S. McCrindle, M. Romkes, S.H. Save, "High-Resolution PCB Analysis: Synthesis and Chromatographic Properties of All 209 PCB Congeners," Environ. Sci. Technol., Vol 18, No. 6, pp 468-476, 1984.

11.8 D.L. Swackhamer, "Quality Assurance Plan, Green Bay Mass Balance Study, 1. PCBs and Dieldrin, US EPA Great Lakes National Program Office" Quality Assurance Coordinator, Field and Analytical Methods Committees, University of Minnesota, December 11, 1987.

11.9 George M. Frame, Robert E. Wagner, James C. Carnahan, John F. Brown, Jr., Ralph J. May, Lynn A. Smullen, and Donna L. Bedard, "Comprehensive, Quantitative, Congener-Specific Analyses of Eight Aroclors and Complete PCB Congener Assignments on DB-1 Capillary GC Columns ", Chemosphere, Vol. 33, No. 4, pp. 603-623, 1996.

11.10 "Standard Operating Procedure for the Gas Chromatographic Analysis of Hydrophobic Organic Contaminant Extracts from Great Lakes Water Samples", USEPA Great Lakes National Program Office, 77 West Jackson Boulevard, Chicago, IL 60604-2590, GLNPO Organics SOP – 10, 6/1/94:Revision 2

11.11 "Biphenyls and Halogenated Pesticides by High Resolution Gas Chromatography", M.D. Mullin, Large Lakes Research Station, LLRS-SOP-ORG-013, revision 2, August 3, 1990, p 1-10.

11.12 Contract Laboratory Program – Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration. Document OLM3.2, 1996.

APPENDIX A

Congener Composition of Multi-Aroclor Calibration Standard (6.27 ug/mL)

Congener Composition of Mixed Aroclor High-level Standard (6270ng/mL) (Aroclors 1232, 1248, 1262 in a ratio of 25:18:18)

file: S:/TEXT/SOP/ne207_appendix_A_GBcalstd.DOC

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
2	**001**	438.57
3	**002**	-
4	**003**	255.84
5	**004 010**	124.26
6	**007 009**	43.85
7	**006**	69.40
8	**005 008**	511.66
9	*014*	-
10	**019**	10.24
11	*030*	-
12	**011**	-
13	**012 013**	9.75
14	**015 018**	135.22
15	**017**	135.22
16	**024 027**	9.50
17	**016 032**	142.53
19	*023* **034** *054*	-
20	**029**	1.94
21	**026**	26.32
22	**025**	11.69
23	**031**	150.68
24	**028** *050*	192.86
25	**020** *021* **033 053**	145.16
26	**022 051**	105.99
27	**045**	32.52
28	*036*	-
29	**046**	14.62
30	*039*	-
31	**052** *069 073*	174.33
32	**043 049**	84.06
33	*038* **047**	36.55
34	**048** *075*	36.55
35	*062 065*	-
36	**035**	-
37	*104* **044**	157.16
38	**037 042 059**	95.03
39	**041 064 071** *072*	149.85
41	*068* **096**	-
42	**040**	34.36
43	**057** *103*	-
44	*058* **067** *100*	4.02
45	**063**	7.68
46	**074** *094 061*	69.44
47	**070**	124.26
48	**066** *076 098 080 093* **095 102** *088*	263.14

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
49	*055* **091** *121*	18.64
50	**056 060**	127.91
51	**084 092** *155*	65.78
52	**089**	3.66
53	**090 101**	65.78
54	*079* **099** *113*	27.04
55	**119** *150*	1.02
56	*078* **083** *112 108*	5.48
57	**097** *152 086*	20.46
58	*081* **087** *117 125* **115** *145*	42.39
59	*111 116* **085**	25.59
60	*120* **136**	27.41
61	**077 110** *148*	77.84
62	*154*	-
63	**082**	16.08
64	**151**	62.15
65	**124 135**	10.60
66	**144**	21.93
67	*107* **109** *147*	4.75
68	*123*	-
69	*106* **118** *139* **149**	146.19
70	*140*	-
71	**114 134** *143*	7.38
72	**122 131 133** *142*	1.06
73	**146** *165 188*	14.26
74	**105 132** *161*	49.52
75	**153**	107.64
76	*127 168 184*	-
77	**141**	62.13
78	**179**	53.36
79	**137**	2.74
80	**130 176**	9.50
82	**138 163 164**	98.68
83	**158** *160 186*	9.13
84	*126* **129**	0.47
85	*166* **178**	40.20
87	**175** *159*	7.31
88	*182* **187**	131.57
89	**128** *162*	3.66
90	**183**	62.13
91	**167**	1.79
92	**185**	17.17
93	**174** *181*	116.95
94	**177**	62.13
95	**156 171**	28.88
96	**157 202**	2.41
98	**173**	1.39
99	**201**	14.26
100	**172** *204*	20.46
101	*192* **197**	4.02

DB-1 Peak Number [1]	IUPAC # [2]	Amount ng/mL
102	**180**	222.94
103	**193**	15.35
104	**191**	4.38
105	**200** *169*	15.71
106	**170**	46.78
107	**190**	15.35
108	**198**	4.38
109	**199**	153.50
110	**196 203**	157.16
111	**189**	1.46
112	**195**	20.21
113	**208**	9.02
114	*207*	3.40
115	**194**	65.78
116	**205**	4.02
117	**206**	24.85
118	*209*	0.44

1 - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low-level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.
PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)
PK 81 (176) now elutes in PK 80 (130,176)
PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

2 - IUPAC congener numbers listed in boldface font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in italic font were absent or present below 0.05 weight percent.

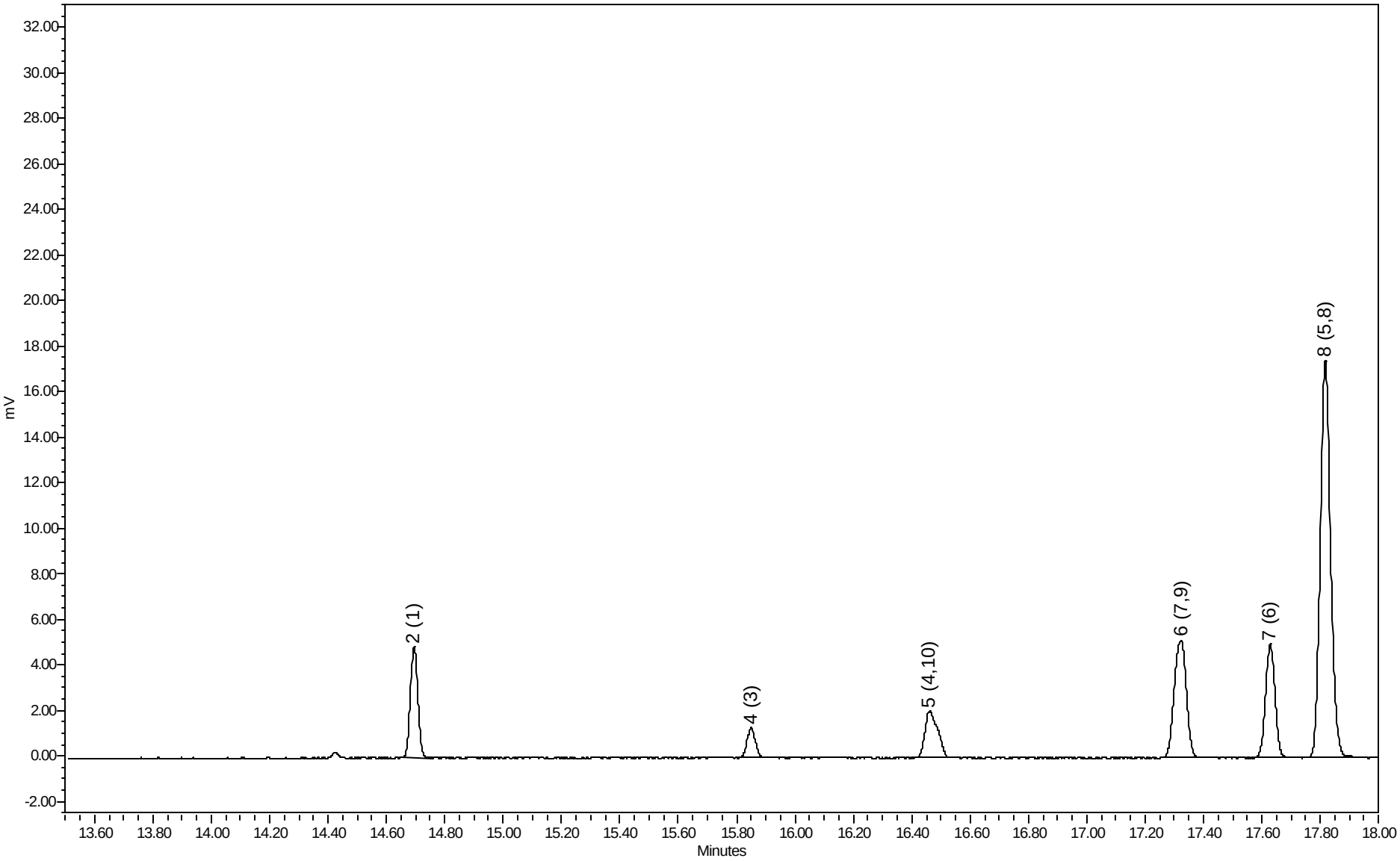
APPENDIX B

DB-1 Capillary GC Chromatograms:

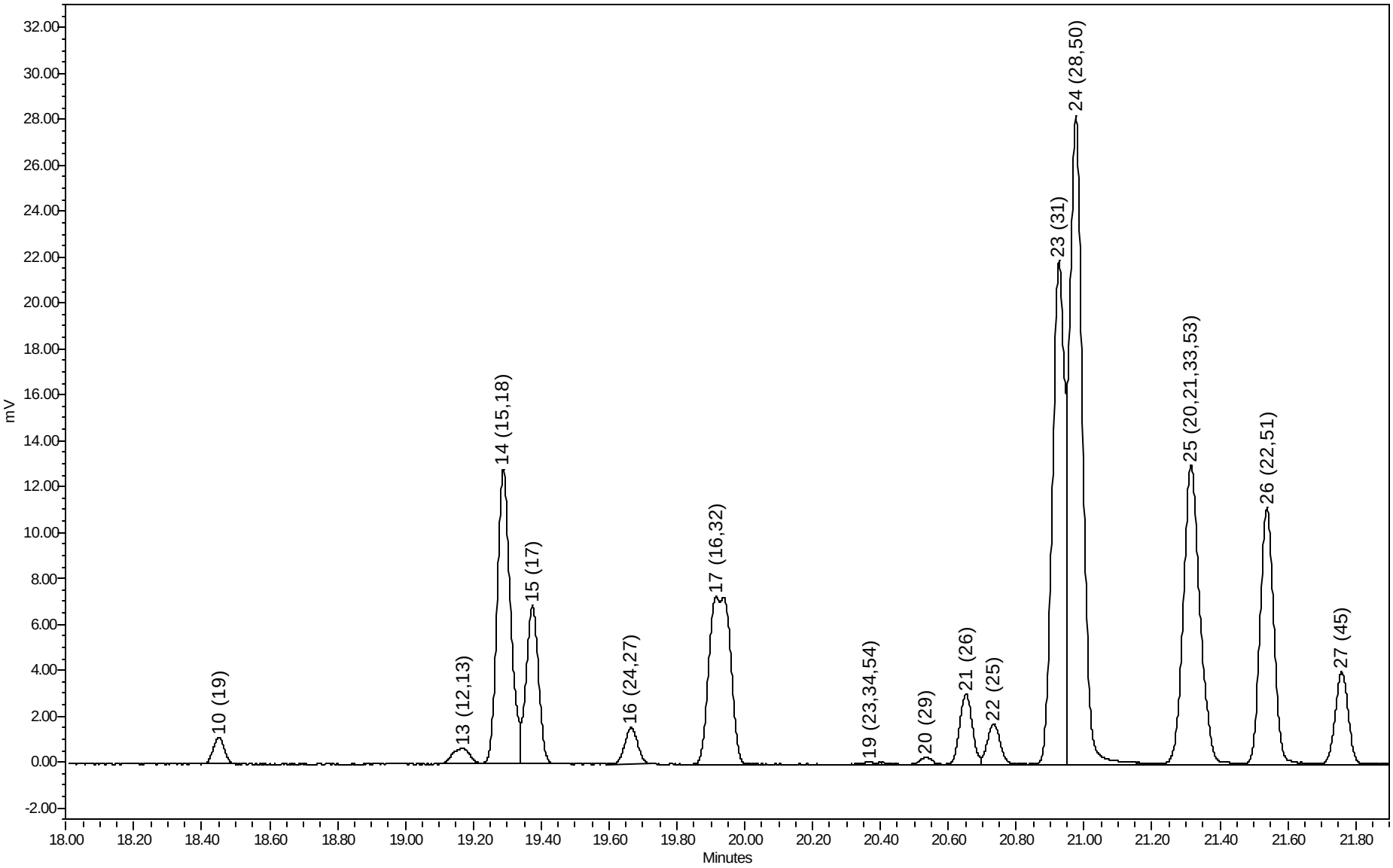
1.) 6.27 ug/mL Calibration Standard

2.) Supplemental Congener Standard

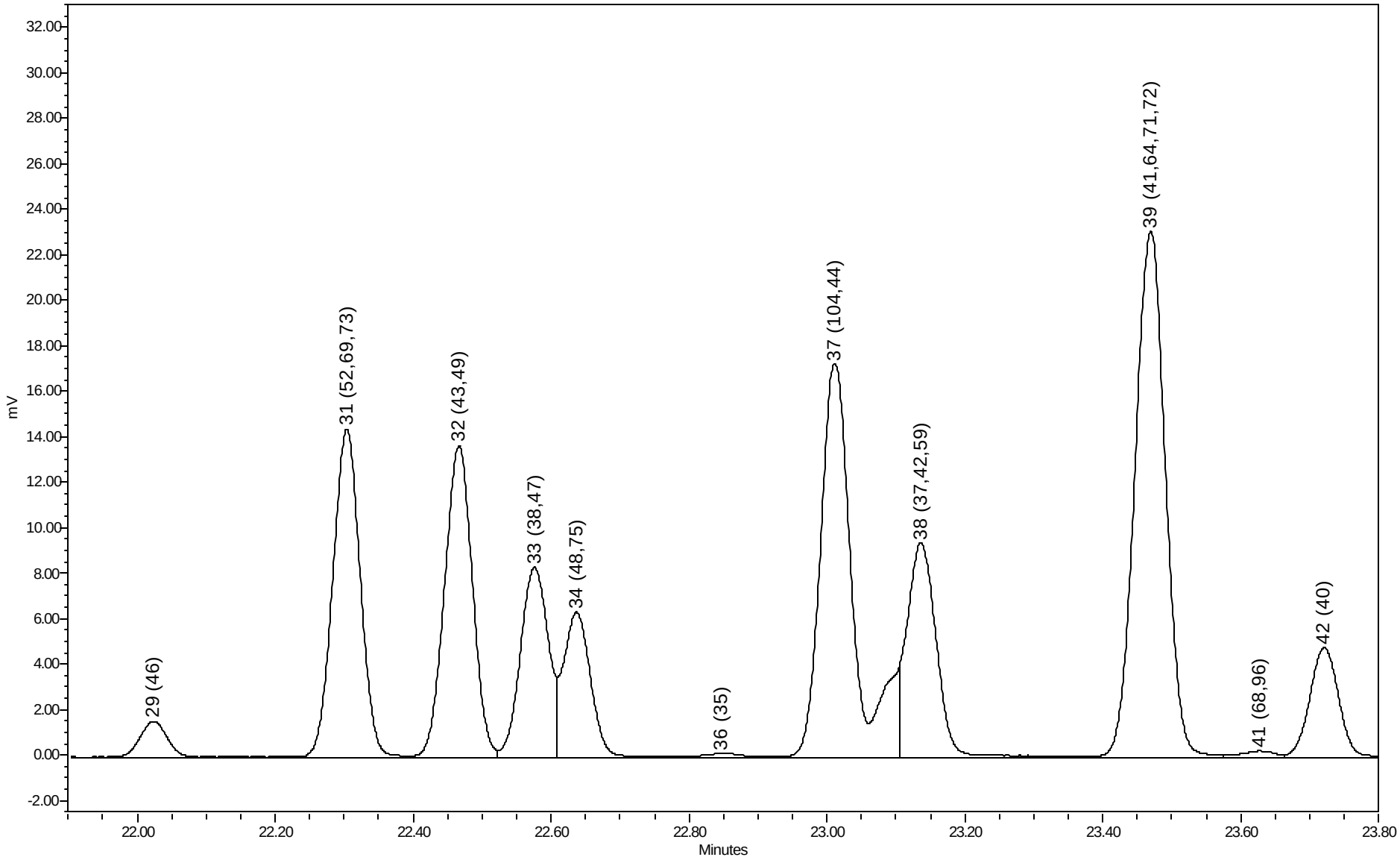
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



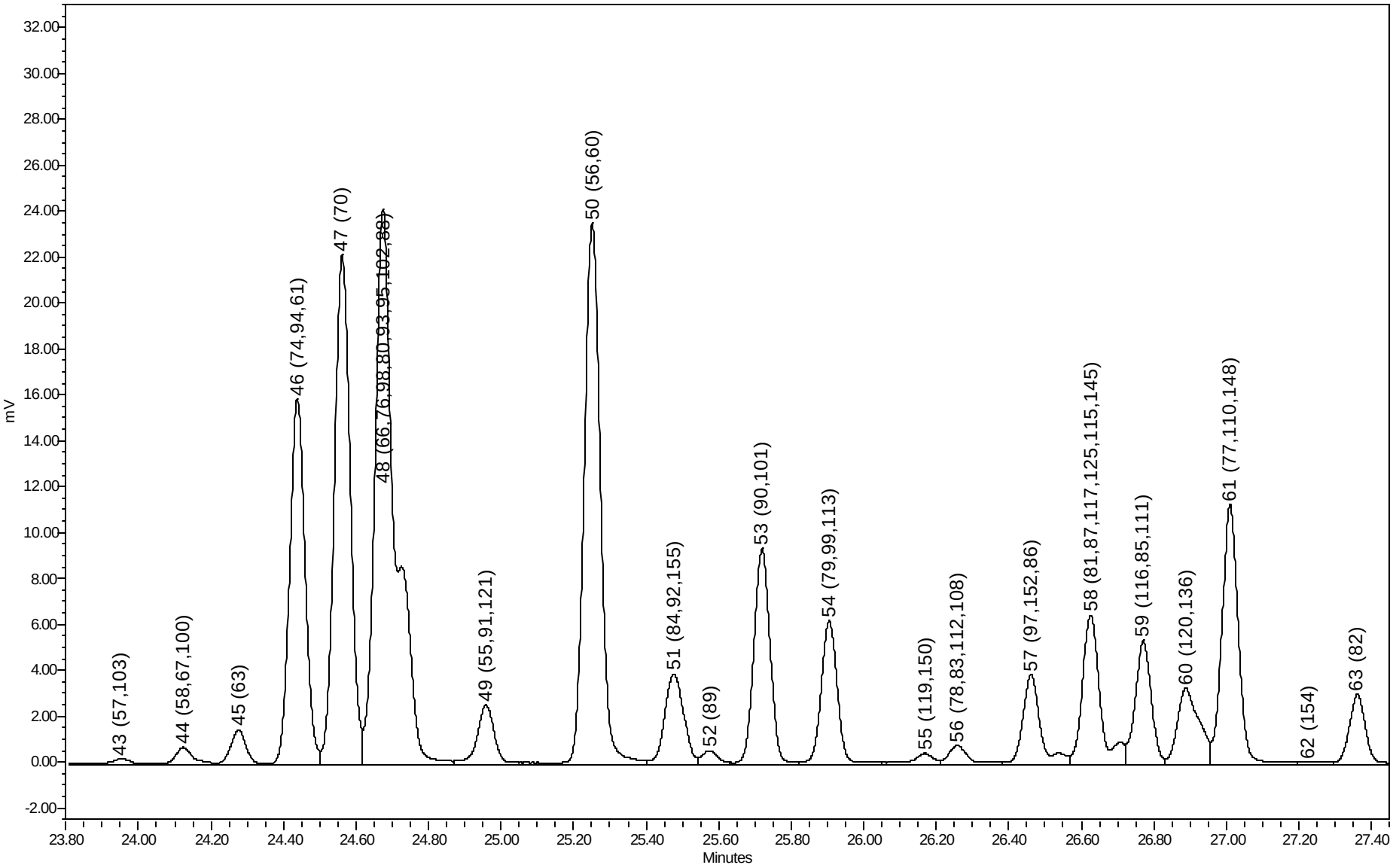
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



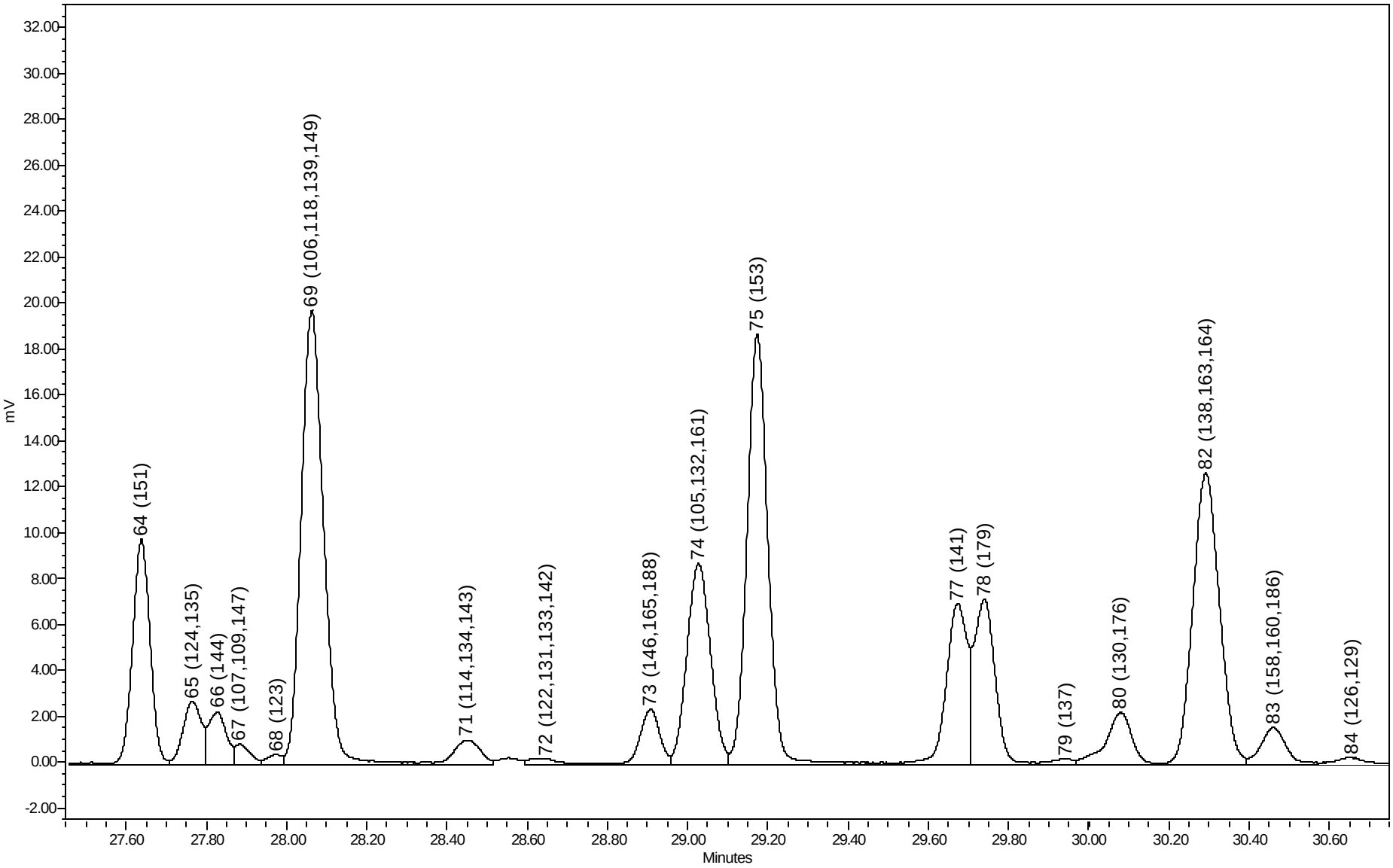
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



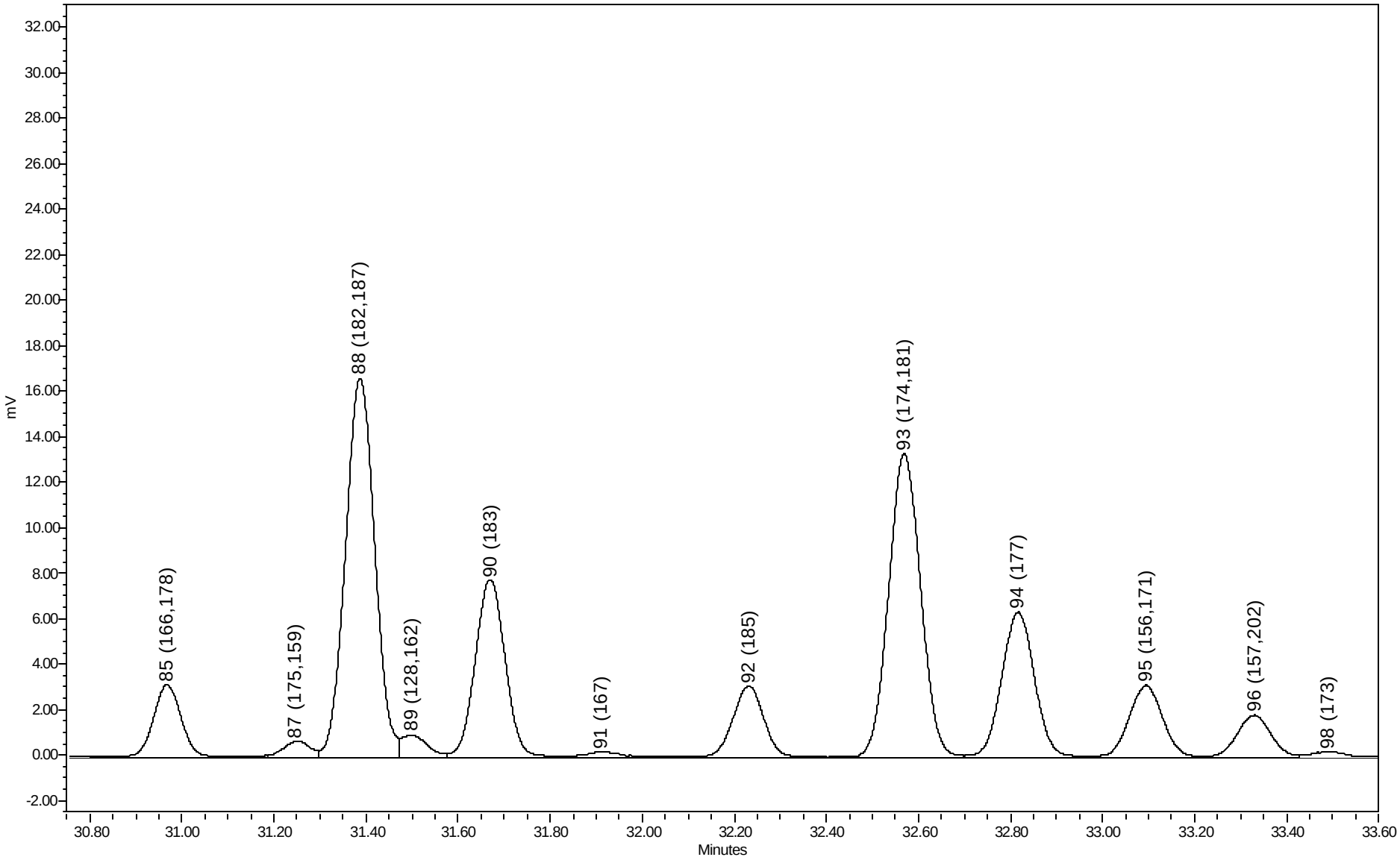
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



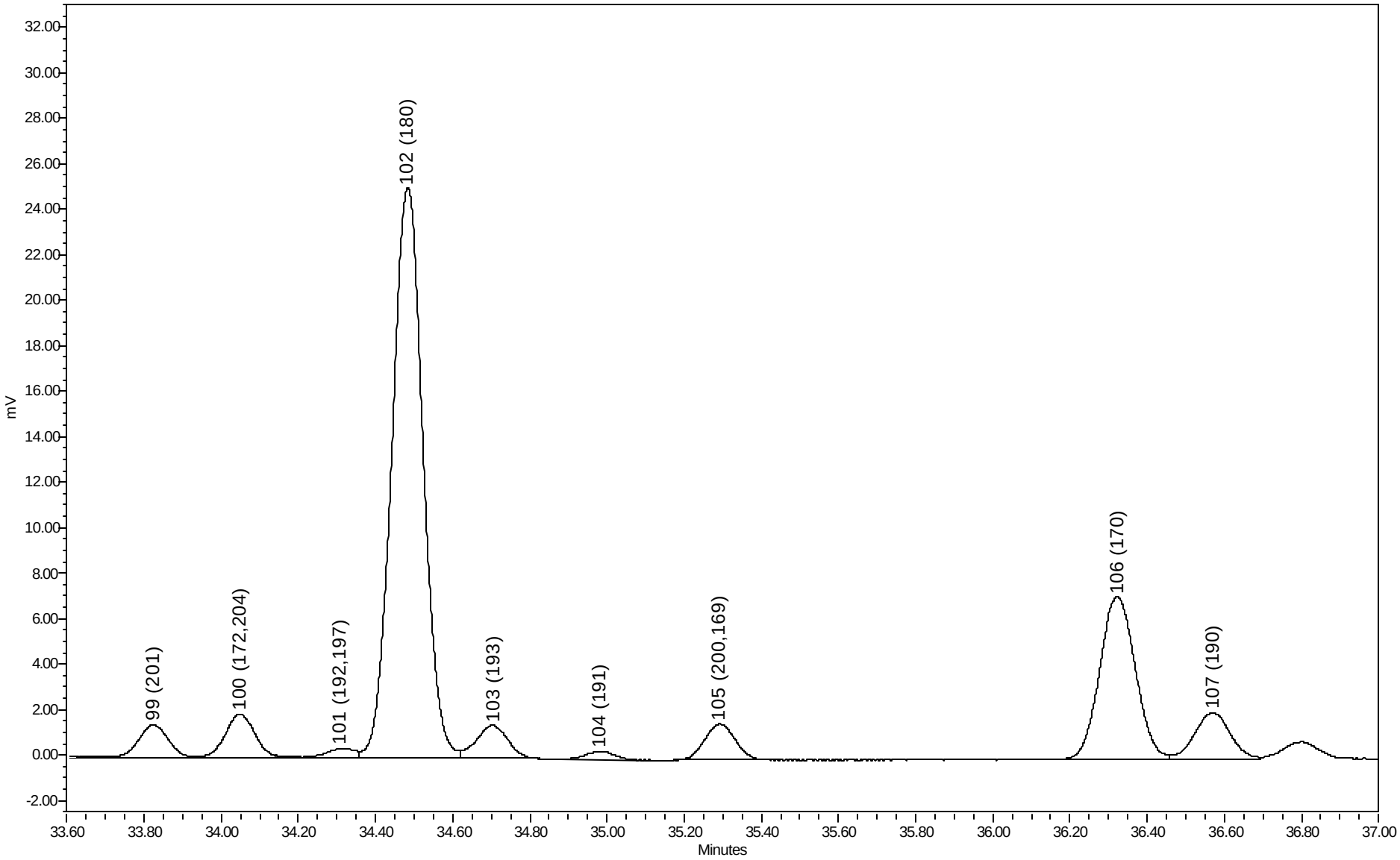
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



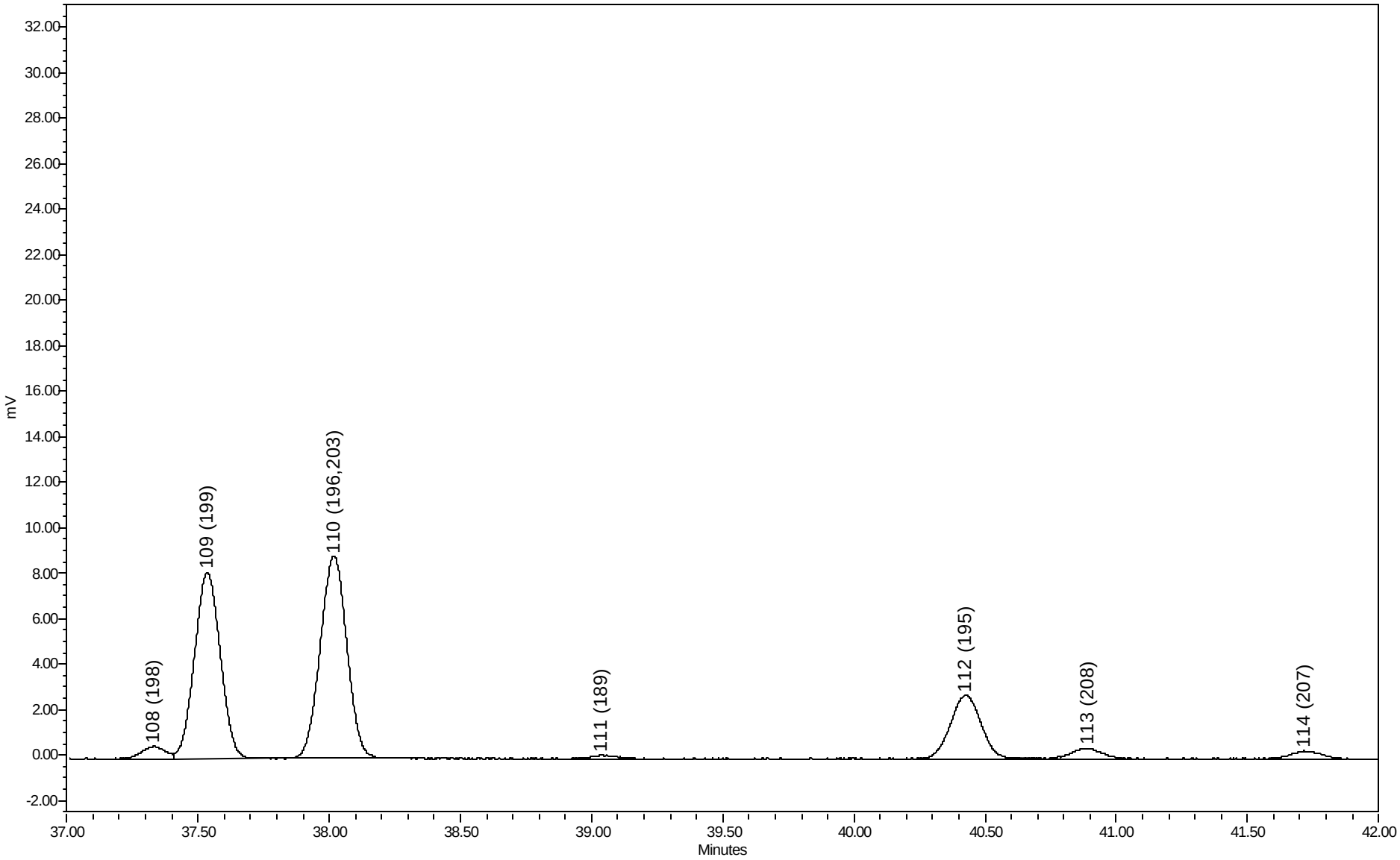
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



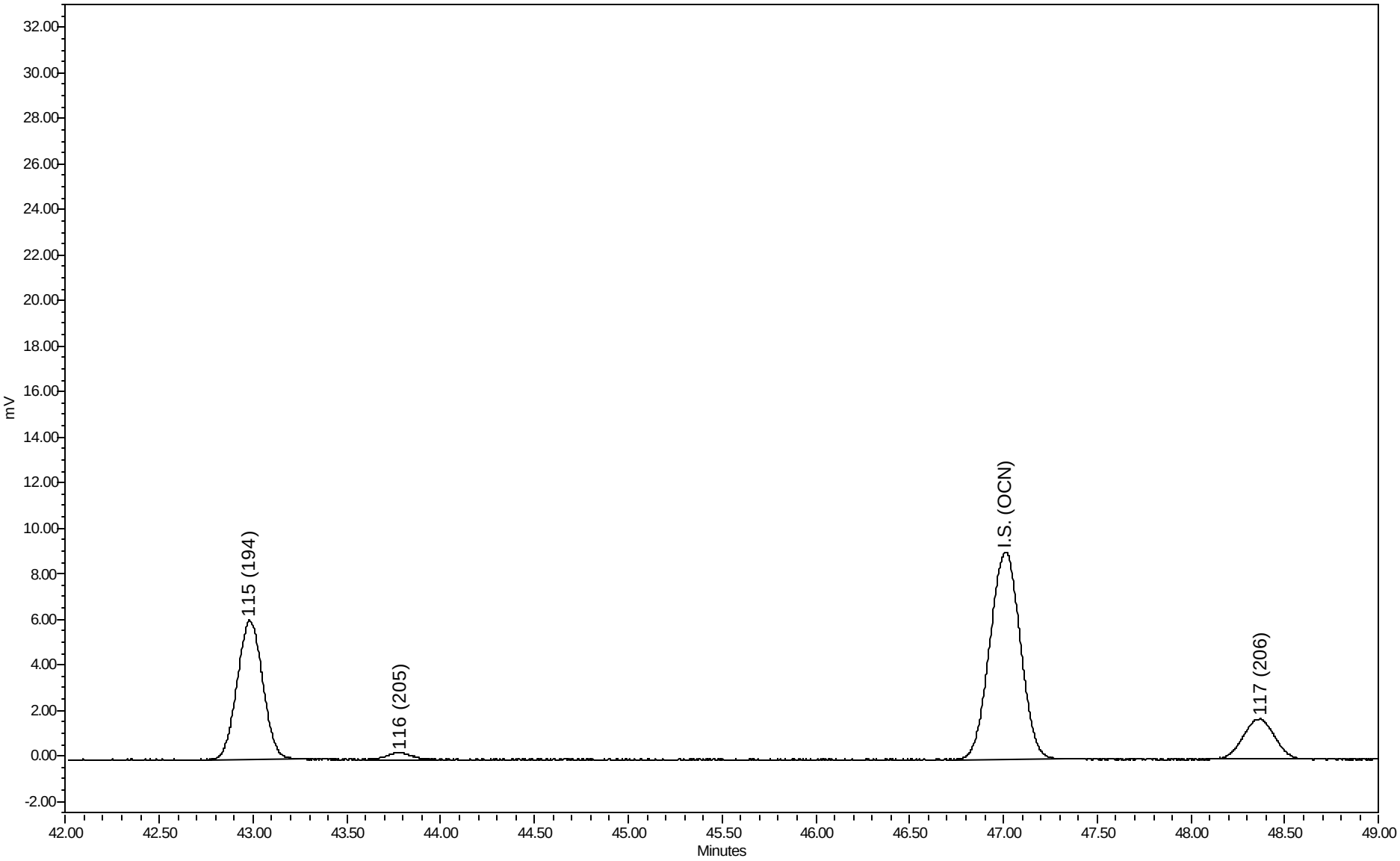
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



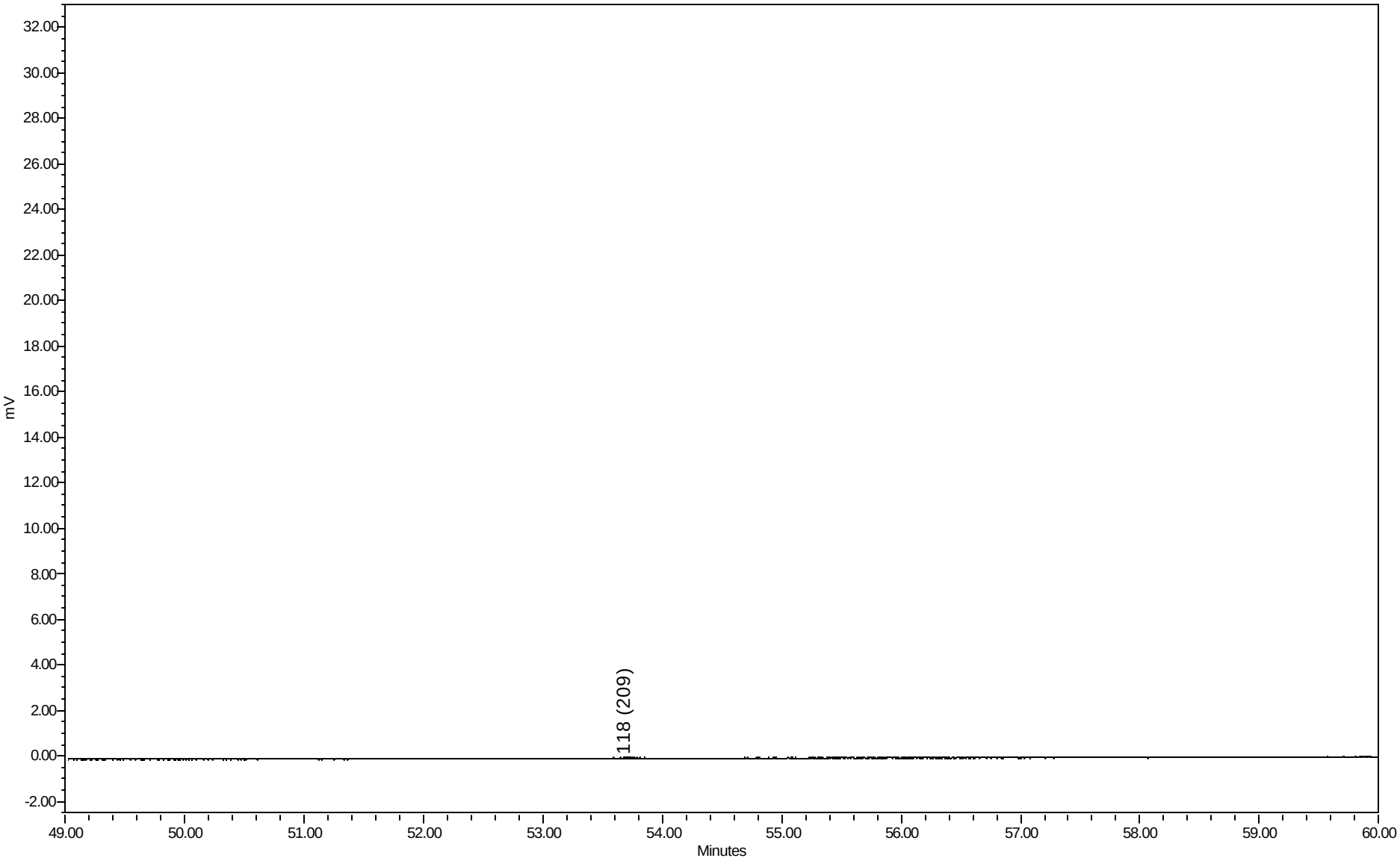
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



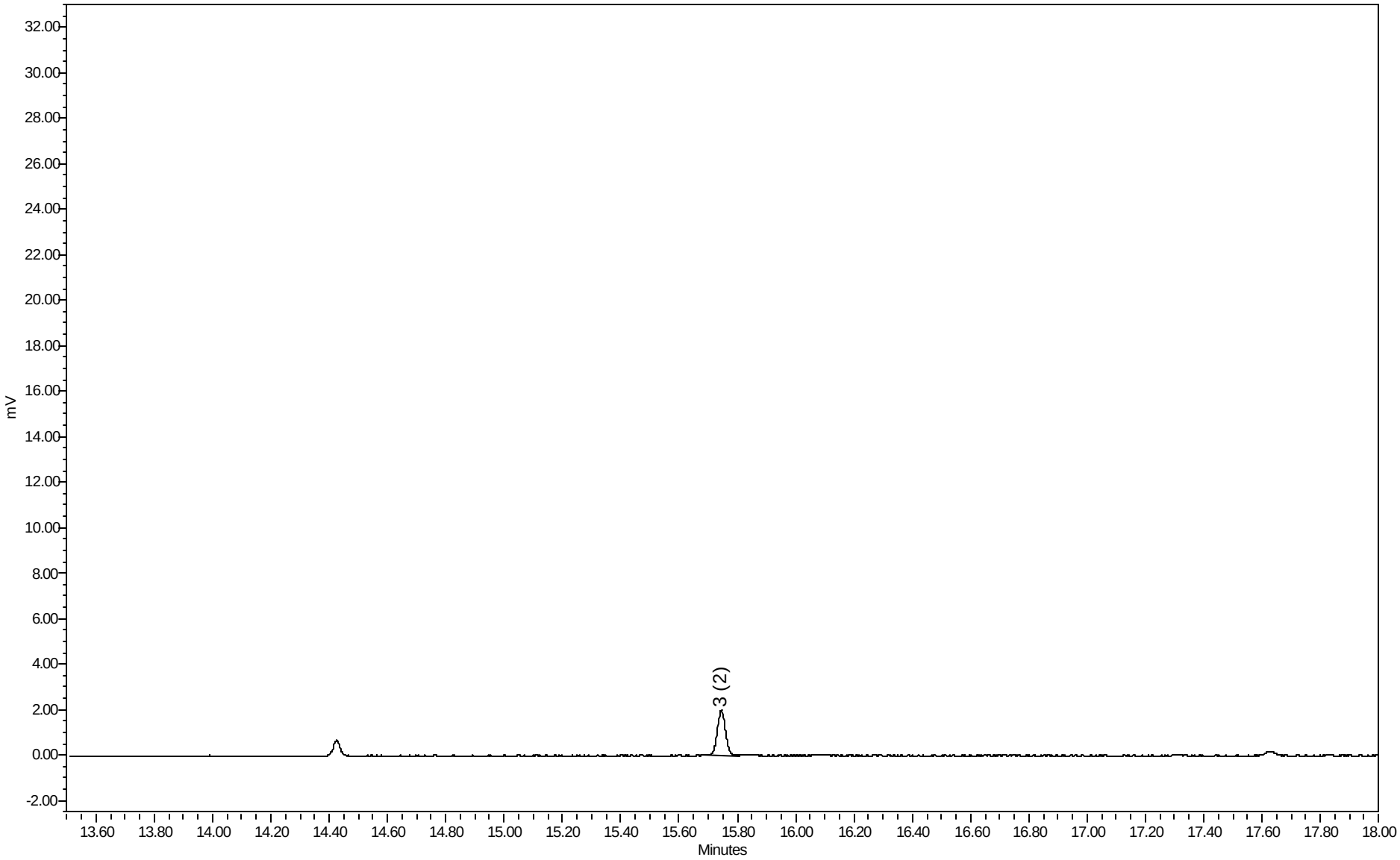
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



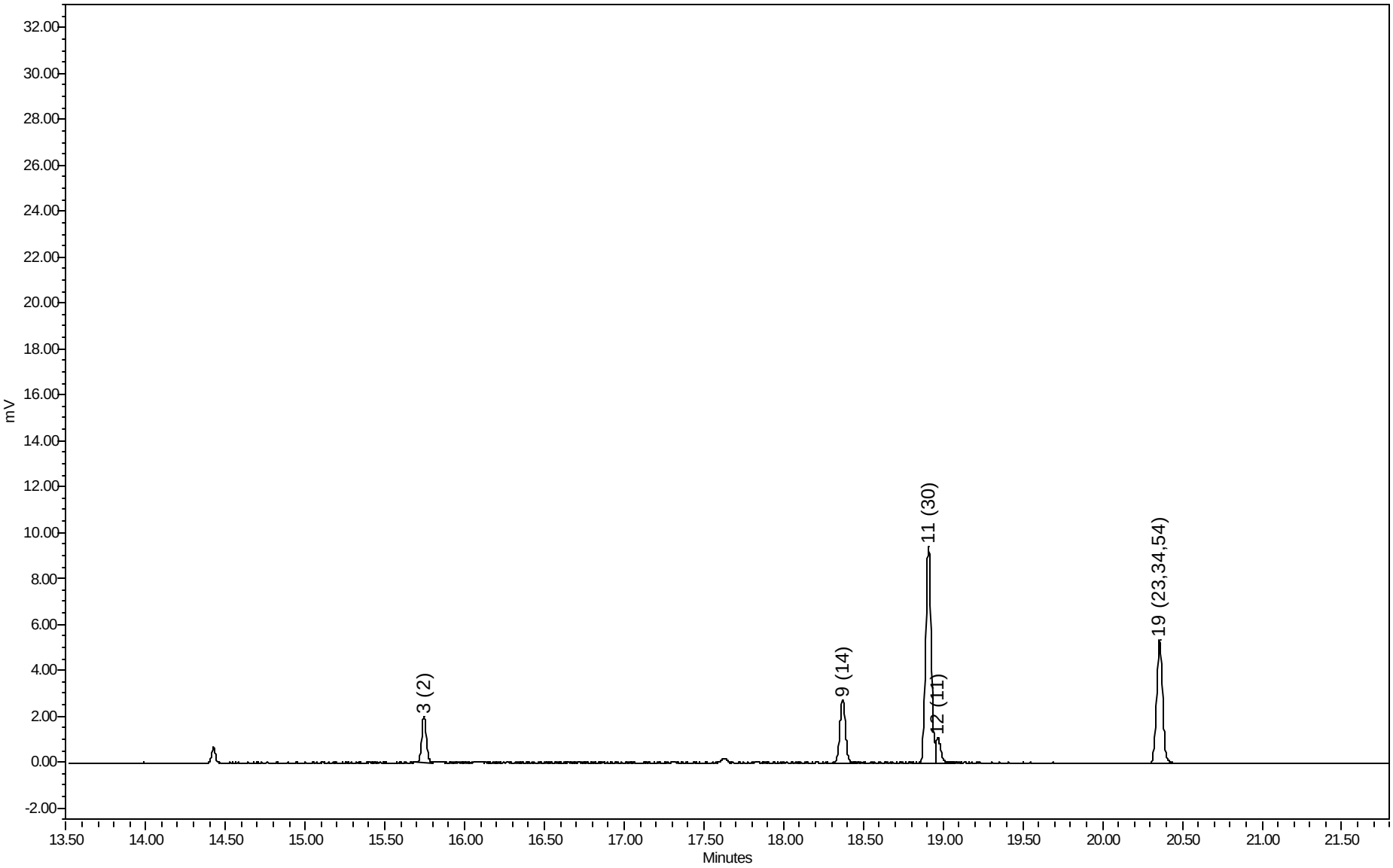
Composition Chromatogram of Aroclor Calibration Mixture (6.27 ug/mL)



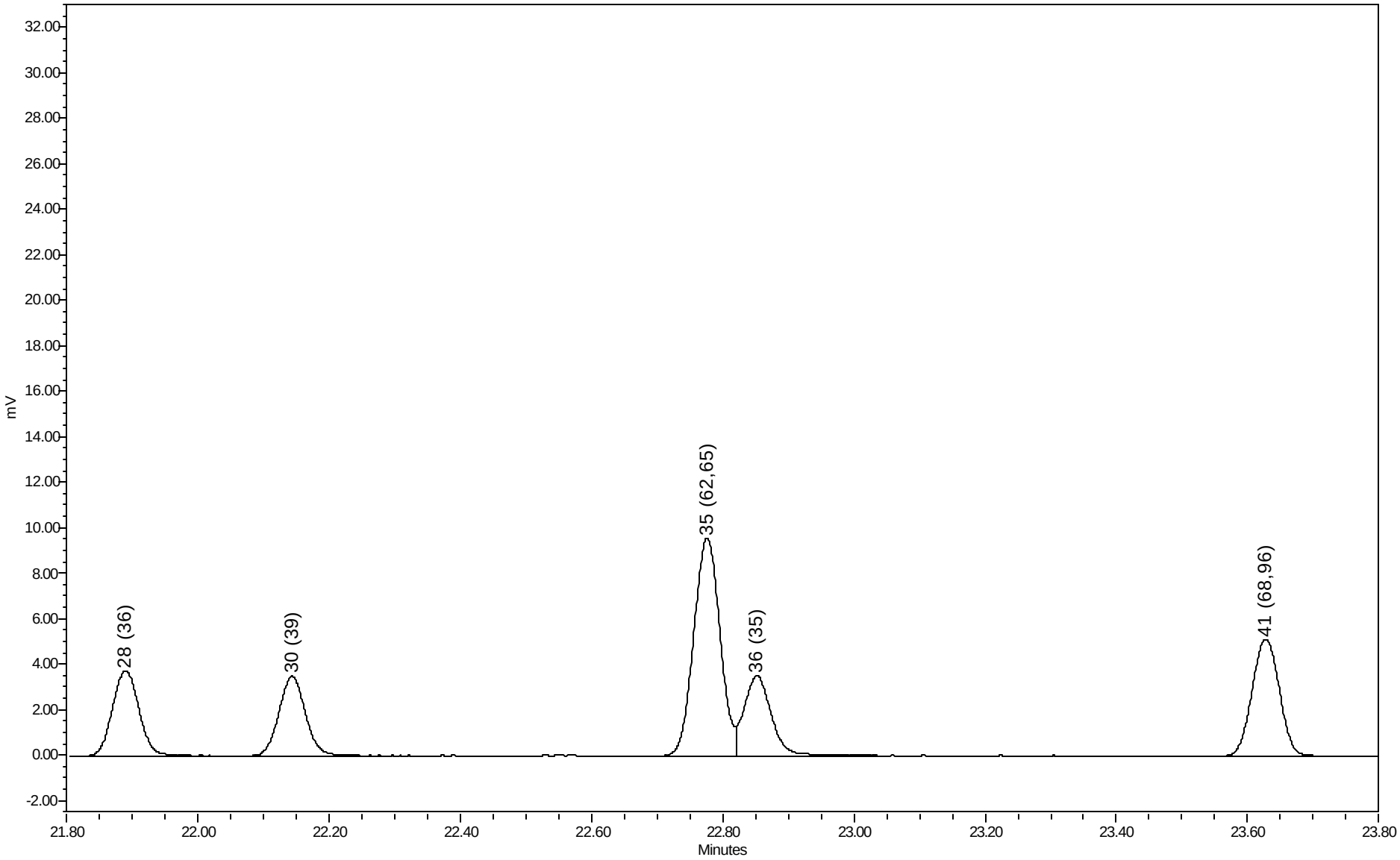
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



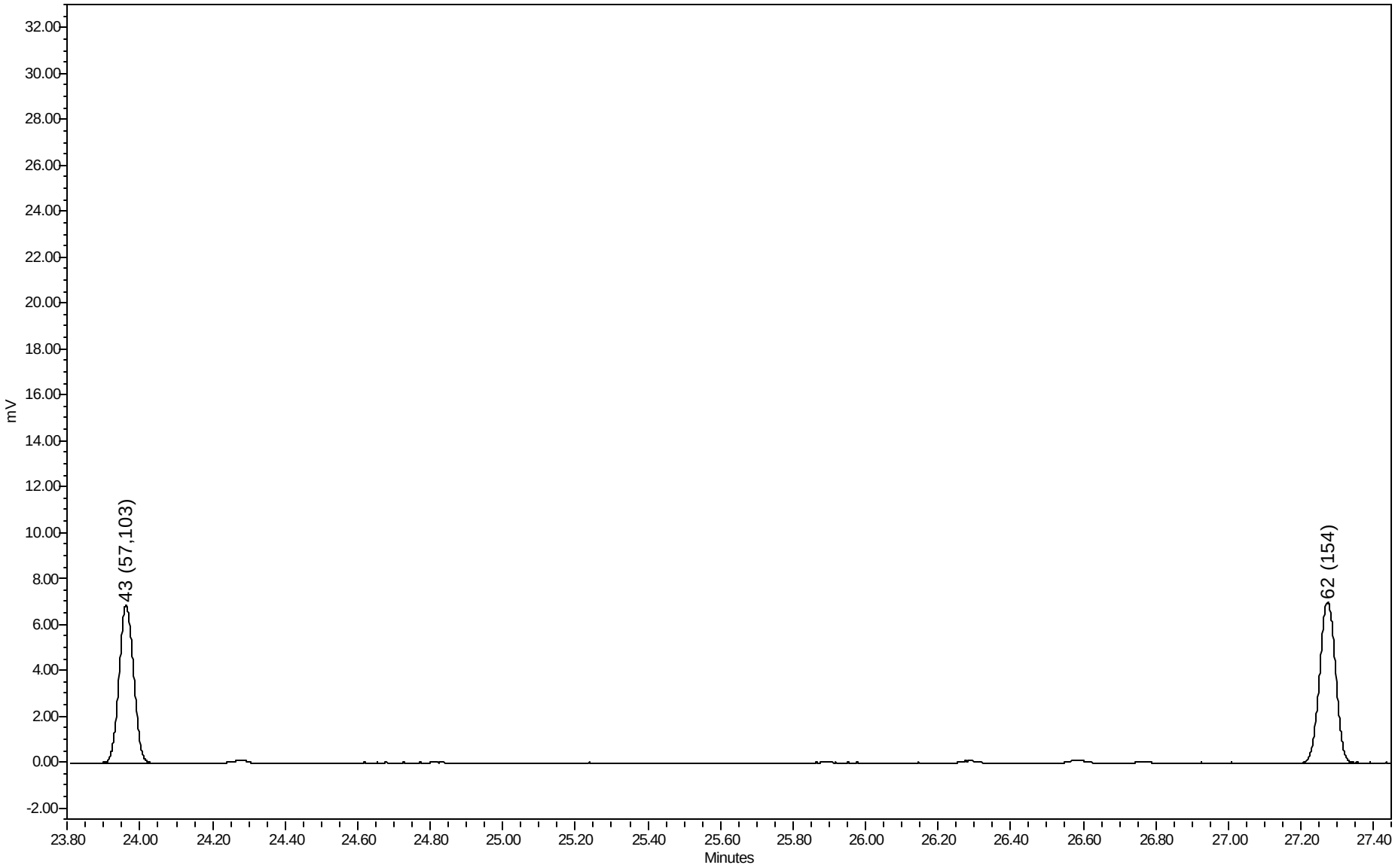
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



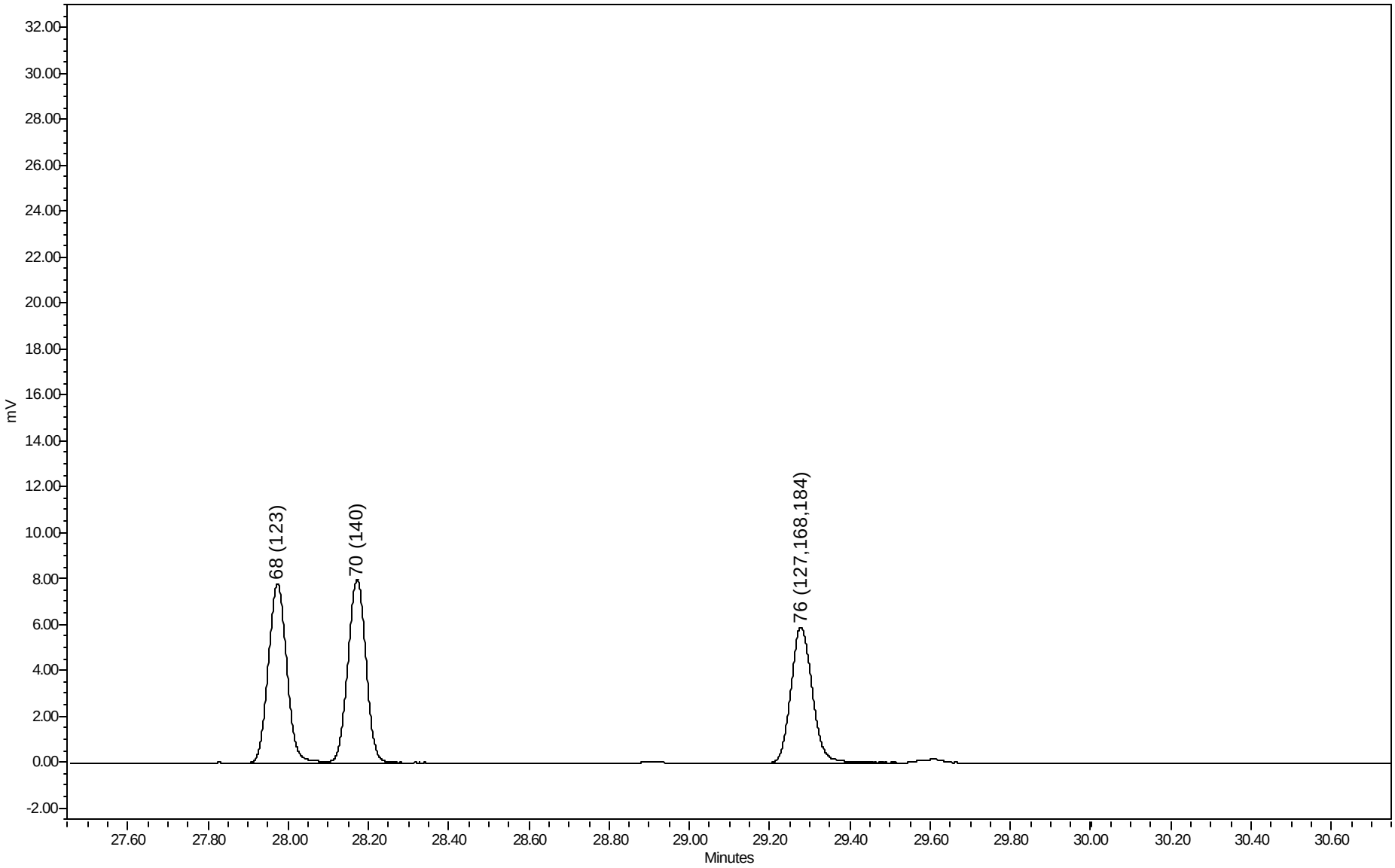
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



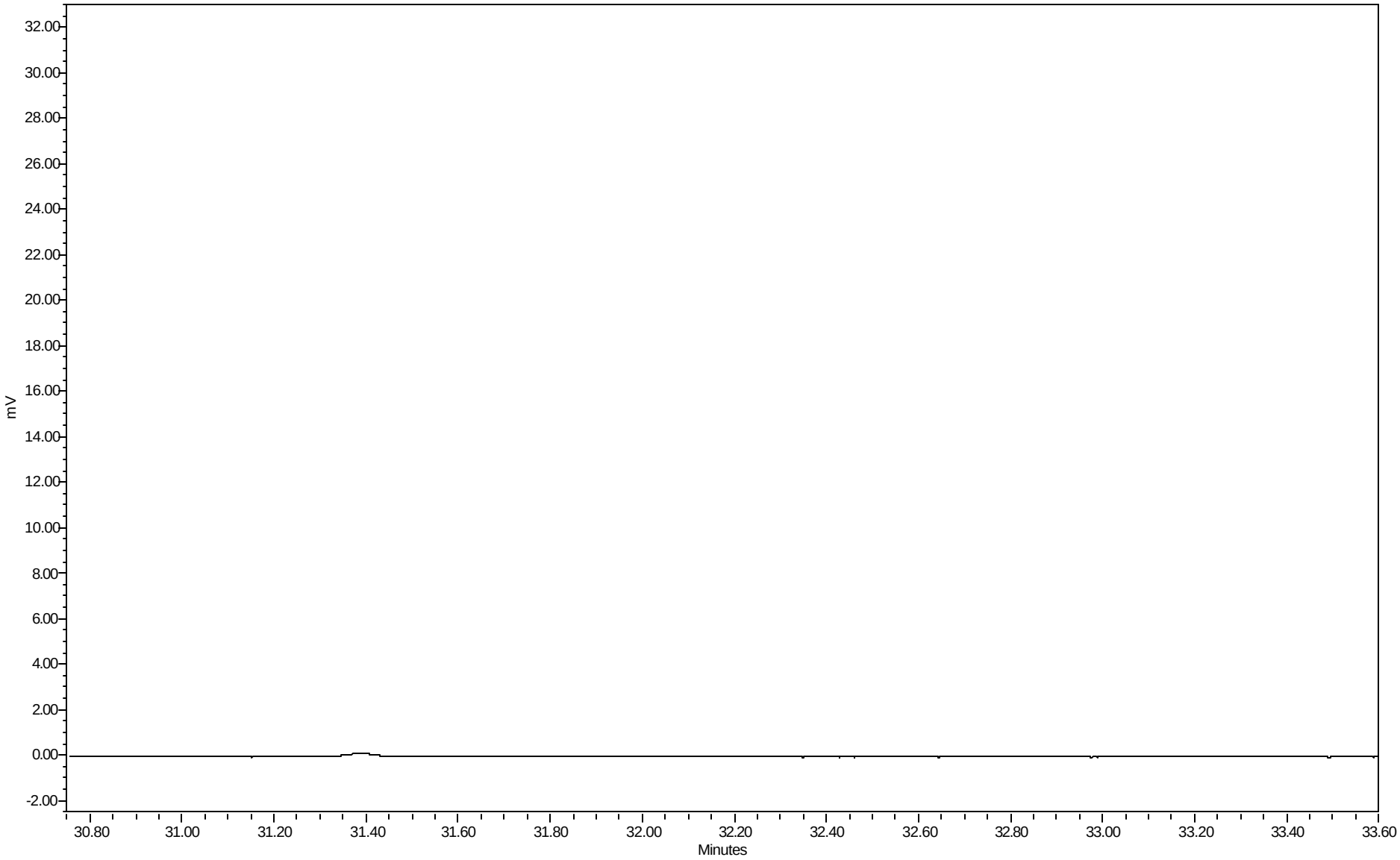
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



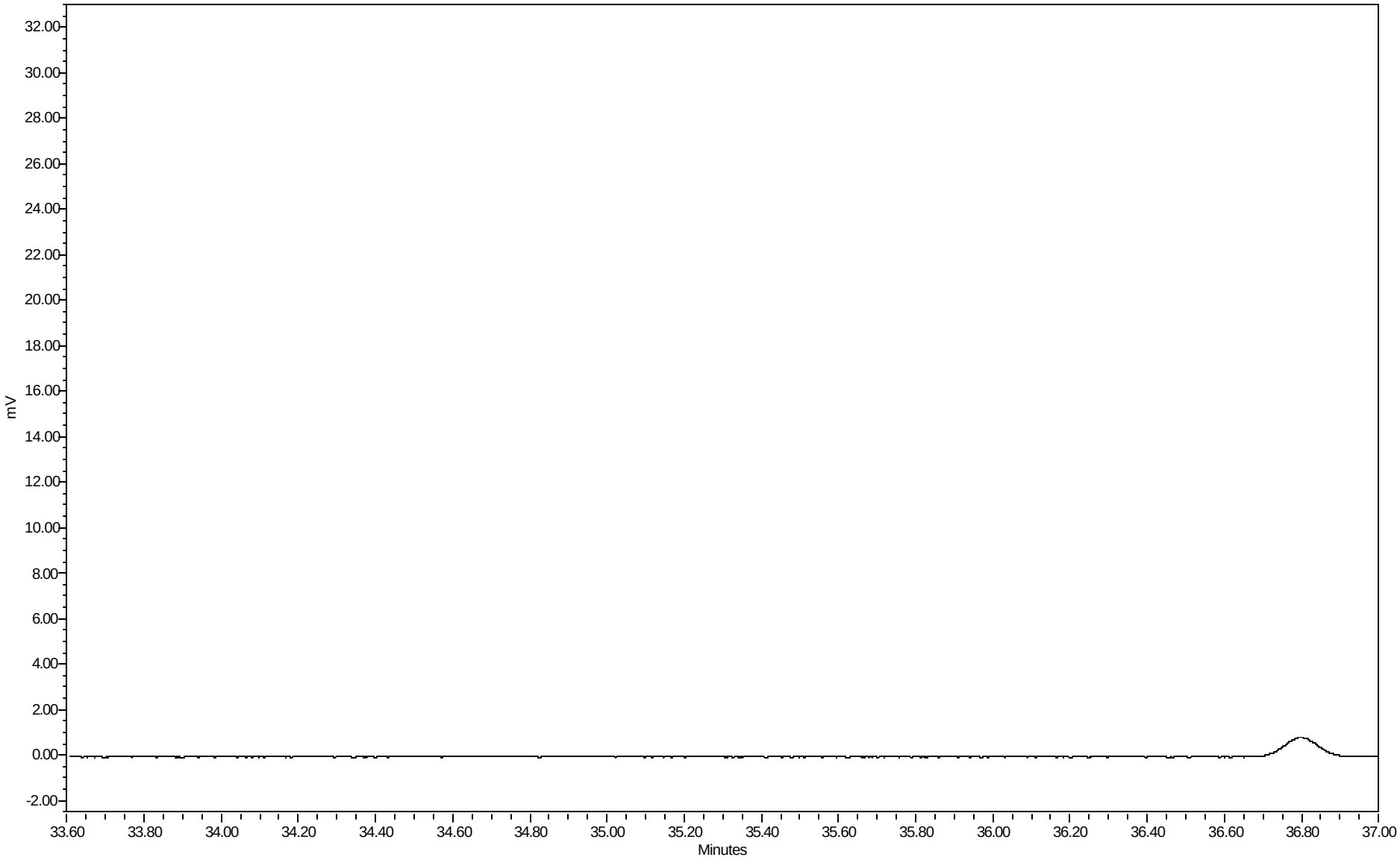
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



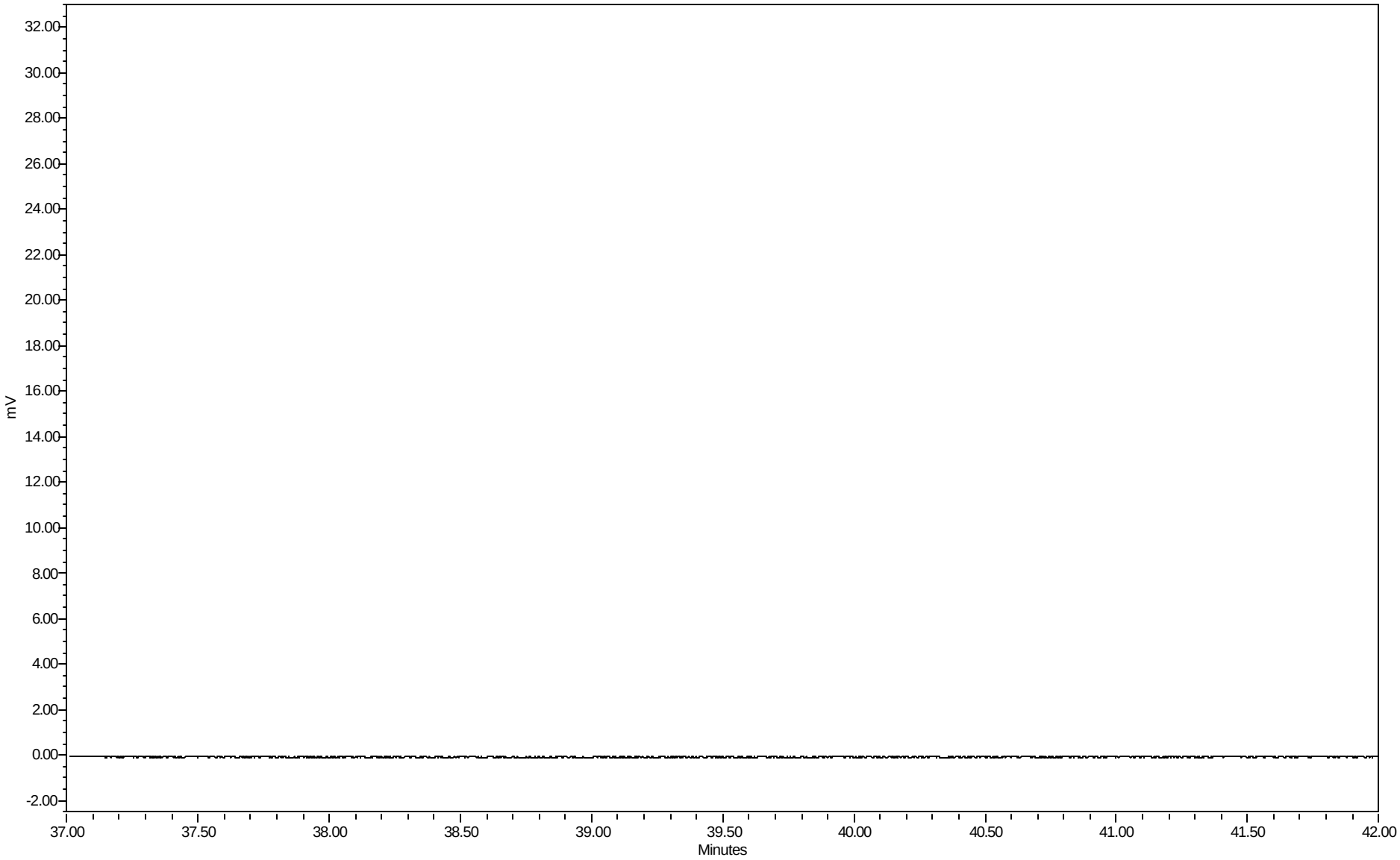
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



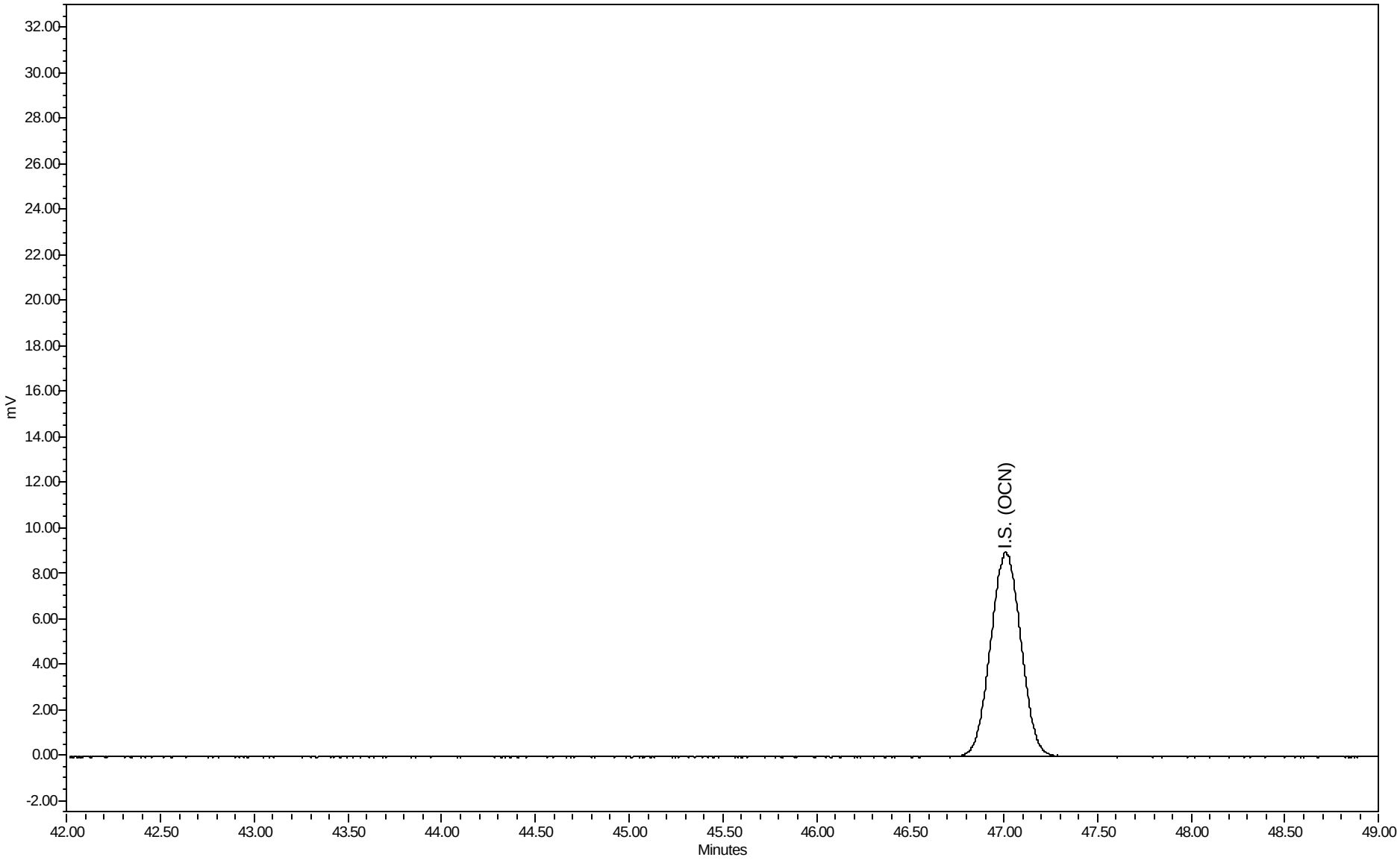
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



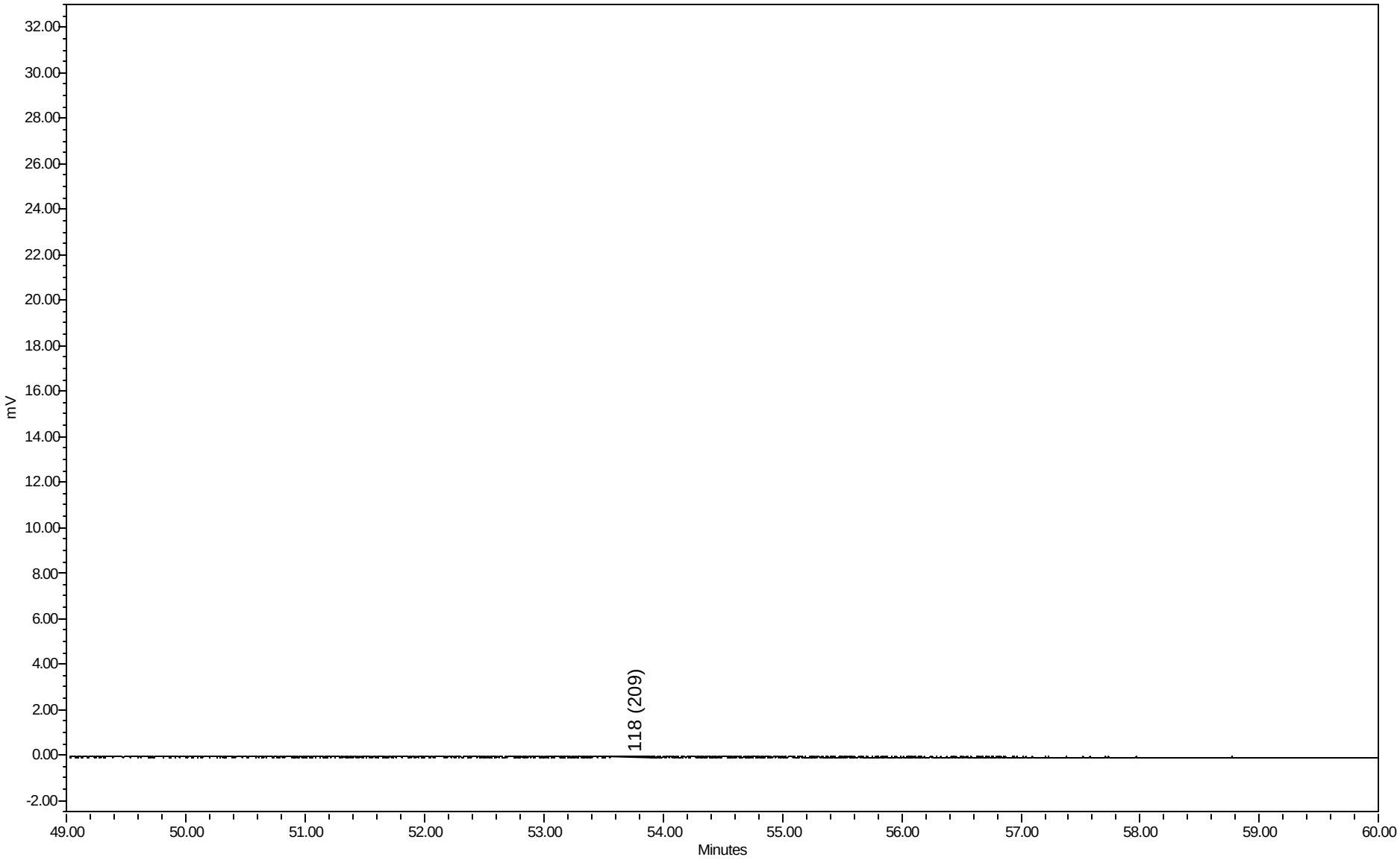
Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



Composition Chromatogram of Supplemental congener Standard (2000 / 50.0 ng/mL)



APPENDIX C

Example of Reporting Format

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

NEA File Name : M:\MIL2004\LIMSGC17\AH00023L.ARS

Customer : Client
Sample Description : LAB CONTROL SPIKE

Comment : This is a comment line
Date Acquired : 01/20/2004 07:15:23

Total PCBs in sample = 9.53 µg/g

PCB Homolog Distribution

Homologs	Weight %	Mole %
Mono	0.46	0.64
Di	18.08	21.08
Tri	46.10	46.94
Tetra	29.67	26.79
Penta	4.85	3.93
Hexa	0.80	0.60
Hepta	0.02	0.01
Octa	0.02	0.01
Nona	0.00	0.00
Deca	0.00	0.00

Nominal 'Aroclor' Distribution

Aroclor	Indicator Peak (PK # / IUPAC #)	Amount µg/g	Percent Sediment	Percent Biota
A1221	2/001	0.0438	3.4	3.4
A1242	23+24/31+28	1.1733	90.6	91.8
A1254SED	61/110	0.0772	6.0	
A1254BIO	***/###	0.0595		4.7
A1260	102/180	0.0009	0.1	0.1
A1268	115/194		0.0	0.0

***/### : 69+75+82/149+153+138

Ortho Cl / biphenyl Residue = 1.44

Meta + Para Cl / biphenyl Residue = 1.70

TOTAL Cl / biphenyl Residue = 3.14

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

PCB Congener Amount Report

NEA File Name : M:\MIL2004\LIMSGC17\AH00023L.ARS

Customer : Client
Sample Description : LAB CONTROL SPIKE

Comment : This is a comment line
Date Acquired : 01/20/2004 07:15:23
Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount µg/g	Nanomoles/g Sample	MDL µg/g	RL µg/g	Qual
2	14.69	188.7	162	0.0438	0.232	0.000667	0.0219	
3	15.75	188.7				0.0292	5.00	
4	15.85	188.7				0.000795	0.0128	
5	16.46	223.1	1764	0.209	0.935	0.000196	0.00621	
6	17.32	223.1	2435	0.0421	0.189	0.0000653	0.00219	
7	17.63	223.1	3342	0.120	0.537	0.000116	0.00347	
8	17.82	223.1	17401	1.20	5.40	0.000814	0.0256	
9	18.37	223.1				0.000847	0.125	
10	18.45	257.5	2222	0.0545	0.212	0.0000287	0.000512	
11	18.91	257.5				0.000564	0.125	
12	18.97	223.1				0.000663	0.125	
13	19.15	223.1	254	0.00622	0.0279	0.000189	0.000488	
14	19.29	249.0	26287	0.575	2.31	0.000317	0.00676	
15	19.38	257.5	13899	0.628	2.44	0.000219	0.00676	
16	19.67	257.5	3606	0.0510	0.198	0.0000157	0.000475	
17	19.91	257.5	25597	0.657	2.55	0.000203	0.00713	
19	20.36	267.9	246	0.00512	0.0191	0.000436	0.125	J
20	20.54	257.5	521	0.00755	0.0293	0.0000869	0.0000970	
21	20.66	257.5	7157	0.140	0.544	0.0000590	0.00132	
22	20.74	257.5	4206	0.0660	0.256	0.0000364	0.000585	
23	20.93	257.5	33906	0.538	2.09	0.000209	0.00753	
24	20.98	257.5	43359	0.636	2.47	0.000259	0.00964	
25	21.32	259.5	31800	0.605	2.33	0.000206	0.00726	
26	21.54	258.7	21441	0.421	1.63	0.000210	0.00530	
27	21.76	292.0	4999	0.0891	0.305	0.0000564	0.00163	
28	21.89	257.5				0.000822	0.125	
29	22.03	292.0	1779	0.0354	0.121	0.0000208	0.000731	
30	22.14	257.5				0.000570	0.125	
31	22.31	292.0	15791	0.393	1.35	0.000623	0.00872	
32	22.47	292.0	15240	0.191	0.654	0.000136	0.00420	
33	22.58	292.0	6365	0.0562	0.193	0.0000613	0.00183	
34	22.64	292.0	6842	0.0857	0.294	0.0000917	0.00183	
35	22.78	292.0				0.000442	0.125	
36	22.85	257.5	304	0.00828	0.0322	0.000658	0.125	J

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount µg/g	Nanomoles/g Sample	MDL µg/g	RL µg/g	Qual
37	23.01	292.0	20852	0.338	1.16	0.000250	0.00786	
38	23.14	272.4	17729	0.342	1.25	0.000131	0.00475	
39	23.47	292.0	25240	0.312	1.07	0.000256	0.00749	
41	23.63	326.4	176	0.00339	0.0104	0.000828	0.125	J
42	23.72	292.0	5764	0.0858	0.294	0.0000698	0.00172	
43	23.96	298.9	267	0.00395	0.0132	0.000443	0.125	J
44	24.12	298.9	1247	0.0135	0.0451	0.00000693	0.000201	
45	24.28	292.0	1249	0.0139	0.0476	0.0000152	0.000384	
46	24.44	292.0	13045	0.110	0.378	0.000132	0.00347	
47	24.56	292.0	22643	0.241	0.827	0.000191	0.00621	
48	24.68	293.5	26880	0.430	1.47	0.000367	0.0132	
49	24.97	324.7	2104	0.0298	0.0917	0.0000436	0.000932	
50	25.25	292.0	23794	0.245	0.841	0.000174	0.00640	
51	25.48	326.4	2877	0.0824	0.252	0.000109	0.00329	
52	25.58	326.4	278	0.00424	0.0130	0.000161	0.000183	
53	25.72	326.4	4053	0.0537	0.164	0.000190	0.00329	
54	25.91	326.4	2770	0.0232	0.0710	0.0000542	0.00135	
55	26.17	326.4	153	0.000780	0.00239	0.0000254	0.0000512	
56	26.26	326.4	524	0.00780	0.0239	0.000177	0.000274	
57	26.46	326.4	2393	0.0225	0.0690	0.0000294	0.00102	
58	26.63	326.4	4311	0.0495	0.152	0.0000777	0.00212	
59	26.77	326.4	2317	0.0218	0.0667	0.0000386	0.00128	
60	26.93	360.9	1552	0.0181	0.0501	0.0000486	0.00137	
61	27.01	315.8	5847	0.0772	0.244	0.000123	0.00389	
62	27.23	360.9				0.000612	0.125	
63	27.36	326.4	1847	0.0186	0.0571	0.0000282	0.000804	
64	27.64	360.9	81	0.00100	0.00277	0.000101	0.00311	J
65	27.79	350.5	256	0.00192	0.00548	0.0000386	0.000530	
66	27.81	360.9	94	0.00175	0.00485	0.0000372	0.00110	
67	27.89	336.8	446	0.00635	0.0189	0.00000918	0.000237	
68	27.98	326.4	149	0.00173	0.00530	0.000531	0.125	J
69	28.09	337.5	4388	0.0492	0.146	0.000243	0.00731	
70	28.17	360.9				0.000547	0.125	
71	28.47	347.8	378	0.00384	0.0110	0.000230	0.000369	
72	28.59	336.8	57	0.000340	0.00101	0.0000569	0.0000569	
73	28.93	360.9	182	0.00196	0.00543	0.0000259	0.000713	
74	29.03	347.8	4059	0.0327	0.0941	0.0000827	0.00248	
75	29.18	360.9	420	0.00397	0.0110	0.000157	0.00538	J
76	29.28	360.9				0.000668	0.125	
77	29.68	360.9				0.000122	0.00311	
78	29.74	395.3				0.000148	0.00267	
79	29.95	360.9				0.0000928	0.000137	
80	30.09	360.9				0.0000169	0.000475	
82	30.29	360.9	640	0.00631	0.0175	0.000143	0.00493	
83	30.47	360.9				0.0000213	0.000457	
84	30.66	360.9	99	0.000210	0.000582	0.0000165	0.0000236	
85	30.98	395.3				0.0000930	0.00201	
87	31.26	395.3				0.00000999	0.000366	
88	31.39	395.3				0.000208	0.00658	
89	31.51	360.9	165	0.00111	0.00308	0.0000122	0.000183	
90	31.68	395.3				0.0000863	0.00311	

DB-1 Peak Number [1]	Retention Time	Molecular Weight	Peak Area	Amount µg/g	Nanomoles/g Sample	MDL µg/g	RL µg/g	Qual
91	31.92	360.9				0.0000101	0.0000897	
92	32.24	394.3				0.0000277	0.000859	
93	32.58	394.3				0.000158	0.00585	
94	32.82	394.3				0.0000888	0.00311	
95	33.10	382.2				0.0000731	0.00144	
96	33.34	429.8				0.00000475	0.000121	
98	33.50	395.3				0.0000568	0.0000695	
99	33.83	429.8	33	0.000390	0.000907	0.0000297	0.000713	J
100	34.05	395.3				0.0000374	0.00102	
101	34.32	429.8				0.0000121	0.000201	
102	34.47	395.3	91	0.000850	0.00215	0.000317	0.0111	J
103	34.71	395.3				0.0000328	0.000768	
104	34.97	395.3	54	0.000670	0.00169	0.000148	0.000219	
105	35.30	429.8				0.0000293	0.000786	
106	36.33	395.3				0.0000726	0.00234	
107	36.57	395.3				0.0000260	0.000768	
108	37.35	429.8				0.00000968	0.000219	
109	37.65	429.8	99	0.00160	0.00372	0.000251	0.00768	J
110	38.03	429.8				0.000218	0.00786	
111	39.07	395.3				0.0000798	0.0000798	
112	40.44	429.8				0.0000605	0.00101	
113	40.91	464.2				0.0000203	0.000451	
114	41.73	464.2				.0000000000	.0000000000	
115	43.00	429.8				0.0000881	0.00329	
116	43.79	429.8				0.0000833	0.000201	
117	48.38	464.2				0.0000453	0.00124	
118	53.74	498.6				0.0000187	0.0000222	

Concentration = 9.53 µg/g

Total Micromoles = 0.036

Average Molecular Weight = 262.4

Number of Calibrated Peaks Found = 69

Internal Standard Retention Time = 47.03 Minutes

Internal Standard Peak Area = 68991.0

Northeast Analytical Inc
2190 Technology Drive
Schenectady , NY 12308
(518) 346-4592 Fax (518) 381-6055

Congener Weight and Mole Report

NEA File Name : M:\MIL2004\LIMSGC17\AH00023L.ARS

Customer : Client
Sample Description : LAB CONTROL SPIKE

Comment : This is a comment line
Date Acquired : 01/20/2004 07:15:23
Type for Mixed Peak Deconvolution = S

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
2	14.69	1:1	**001**	0.3567	2	0.460	0.639	2
3	15.75	1:0	**002**	0.3853	3	-	-	3
4	15.85	1:0	**003**	0.3880	4	-	-	4
5	16.46	2:2	**004 010**	0.4039	2-2 ; 26	2.187	2.573	5
6	17.32	2:1	**007 009**	0.4236	24 ; 25	0.441	0.519	6
7	17.63	2:1	**006**	0.4304	2-3	1.258	1.479	7
8	17.82	2:1	**005 008**	0.4346	23 ; 2-4	12.633	14.857	8
9	18.37	2:0	*014*	0.4462	35	-	-	9
10	18.45	3:3	**019**	0.4474	26-2	0.572	0.582	10
11	18.91	3:2	*030*	0.4572	246	-	-	11
12	18.97	2:0	**011**	0.4584	3-3	-	-	12
13	19.15	2:0	**012 013**	0.4622	34 ; 3-4	0.065	0.077	13
14	19.29	2:0 3:2	**015 018**	0.4650	4-4 ; 25-2	6.031	6.355	14
15	19.38	3:2	**017**	0.4668	24-2	6.590	6.714	15
16	19.67	3:2	**024 027**	0.4721	236 ; 26-3	0.535	0.545	16
17	19.91	3:2	**016 032**	0.4783	23-2 ; 26-4	6.890	7.020	17
19	20.36	3:1 4:4	*023* **034** *054*	0.4856	235 ; 35-2 ; 26-26	0.054	0.053	19
20	20.54	3:1	**029**	0.4889	245	0.079	0.081	20
21	20.66	3:1	**026**	0.4912	25-3	1.470	1.498	21
22	20.74	3:1	**025**	0.4926	24-3	0.693	0.706	22
23	20.93	3:1	**031**	0.4965	25-4	5.640	5.747	23
24	20.98	3:1 4:3	**028** *050*	0.4969	24-4 ; 246-2	6.669	6.795	24
25	21.32	3:1 4:3	**020** *021* **033 053**	0.5031	23-3 ; 234 ; 34-2 ; 25-26	6.346	6.417	25
26	21.54	3:1 4:3	**022 051**	0.5074	23-4 ; 24-26	4.415	4.477	26
27	21.76	4:3	**045**	0.5109	236-2	0.935	0.840	27
28	21.89	3:0	*036*	0.5135	35-3	-	-	28
29	22.03	4:3	**046**	0.5157	23-26	0.371	0.334	29
30	22.14	3:0	*039*	0.5172	35-4	-	-	30
31	22.31	4:2	**052** *069 073*	0.5209	25-25 ; 246-3 ; 26-35	4.127	3.708	31
32	22.47	4:2	**043 049**	0.5236	235-2 ; 24-25	2.003	1.800	32
33	22.58	4:2	*038* **047**	0.5262	345 ; 24-24	0.590	0.530	33
34	22.64	4:2	**048** *075*	0.5267	245-2 ; 246-4	0.899	0.808	34
35	22.78	4:2	*062 065*	0.5289	2346 ; 2356	-	-	35
36	22.85	3:0	**035**	0.5302	34-3	0.087	0.089	36
37	23.01	5:4 4:2	*104* **044**	0.5333	246-26 ; 23-25	3.547	3.187	37
38	23.14	3:0 4:2	**037 042 059**	0.5352	34-4 ; 23-24 ; 236-3	3.586	3.454	38
39	23.47	4:2	**041 064 071** *072*	0.5406	234-2 ; 236-4 ; 26-34 ; 25-35	3.271	2.939	39
41	23.63	5:4	*068* **096**	0.5435	24-35 ; 236-26	0.036	0.029	41
42	23.72	4:2	**040**	0.5446	23-23	0.900	0.809	42
43	23.96	4:1 5:3	**057** *103*	0.5489	235-3 ; 246-25	0.041	0.036	43
44	24.12	4:1 5:3	*058* **067** *100*	0.5517	23-35 ; 245-3 ; 246-24	0.141	0.124	44
45	24.28	4:1	**063**	0.5534	235-4	0.146	0.131	45
46	24.44	4:1 5:3	**074** *094 061*	0.5570	245-4 ; 235-26 ; 2345	1.157	1.040	46

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
47	24.56	4:1	**070**	0.5595	25-34	2.533	2.276	47
48	24.68	4:1 5:3	**066** *076 098 080 093* **095 102** *088*	0.5609	24-34 ; 345-2 ; 246-23 ; 35-35 ; 2356-2 ; 236-25 ; 245-26 ; 2346-2	4.516	4.037	48
49	24.97	4:1 5:3	*055* **091** *121*	0.5658	234-3 ; 236-24 ; 246-35	0.312	0.252	49
50	25.25	4:1	**056 060**	0.5701	23-34 ; 234-4	2.575	2.314	50
51	25.48	5:3 6:4	**084 092** *155*	0.5739	236-23 ; 235-25 ; 246-246	0.864	0.695	51
52	25.58	5:3	**089**	0.5761	234-26	0.044	0.036	52
53	25.72	5:2	**090 101**	0.5788	235-24 ; 245-25	0.563	0.452	53
54	25.91	5:2	*079* **099** *113*	0.5814	34-35 ; 245-24 ; 236-35	0.243	0.196	54
55	26.17	5:2 6:4	**119** *150*	0.5860	246-34 ; 236-246	0.008	0.007	55
56	26.26	5:2	*078* **083** *112 108*	0.5874	345-3 ; 235-23 ; 2356-3 ; 2346-3	0.082	0.066	56
57	26.46	5:2 6:4	**097** *152 086*	0.5903	245-23 ; 2356-26 ; 2345-2	0.236	0.190	57
58	26.63	5:2	*081* **087** *117 125* **115** *145*	0.5929	345-4 ; 234-25 ; 2356-4 ; 345-26 ; 2346-4 ; 2346-26	0.519	0.417	58
59	26.77	5:2	*116* **085** *111*	0.5953	23456 ; 234-24 ; 235-35	0.228	0.184	59
60	26.93	6:4	*120* **136**	0.5971	245-35 ; 236-236	0.190	0.138	60
61	27.01	4:0 5:2	**077 110** *148*	0.5998	34-34 ; 236-34 ; 235-246	0.809	0.673	61
62	27.23	6:3	*154*	0.6039	245-246	-	-	62
63	27.36	5:2	**082**	0.6055	234-23	0.195	0.157	63
64	27.64	6:3	**151**	0.6101	2356-25	0.010	0.008	64
65	27.79	5:1 6:3	**124 135**	0.6129	345-25 ; 235-236	0.020	0.015	65
66	27.81	6:3	**144**	0.6139	2346-25	0.018	0.013	66
67	27.89	5:1 6:3	*107* **109** *147*	0.6152	234-35 ; 235-34 ; 2356-24	0.067	0.052	67
68	27.98	5:1	*123*	0.6166	345-24	0.018	0.015	68
69	28.09	5:1 6:3	*106* **118** *139* **149**	0.6186	2345-3 ; 245-34 ; 2346-24 ; 236-245	0.516	0.401	69
70	28.17	6:3	*140*	0.6202	234-246	-	-	70
71	28.47	5:1 6:3	**114 134** *143*	0.6256	2345-4 ; 2356-23 ; 2345-26	0.040	0.030	71
72	28.59	5:1 6:3	**122 131 133** *142*	0.6289	345-23 ; 2346-23 ; 235-235 ; 23456-2	0.004	0.003	72
73	28.93	6:2	**146** *165 188*	0.6342	235-245 ; 2356-35 ; 2356-246	0.021	0.015	73
74	29.03	5:1 6:3	**105 132** *161*	0.6364	234-34 ; 234-236 ; 2346-35	0.343	0.259	74
75	29.18	6:2	**153**	0.6393	245-245	0.042	0.030	75
76	29.28	6:2	*127 168 184*	0.6412	345-35 ; 246-345 ; 2346-246	-	-	76
77	29.68	6:2	**141**	0.6488	2345-25	-	-	77
78	29.74	7:4	**179**	0.6499	2356-236	-	-	78
79	29.95	6:2	**137**	0.6537	2345-24	-	-	79
80	30.09	6:2 7:4	**130 176**	0.6565	234-235 ; 2346-236	-	-	80
82	30.29	6:2	**138 163 164**	0.6605	234-245 ; 2356-34 ; 236-345	0.066	0.048	82
83	30.47	6:2	**158** *160 186*	0.6639	2346-34 ; 23456-3 ; 23456-26	-	-	83
84	30.66	6:2	*126* **129**	0.6674	345-34 ; 2345-23	0.002	0.002	84
85	30.98	7:3	*166* **178**	0.6735	23456-4 ; 2356-235	-	-	85
87	31.26	7:3	**175** *159*	0.6790	2346-235 ; 2345-35	-	-	87
88	31.39	7:3	*182* **187**	0.6816	2345-246 ; 2356-245	-	-	88
89	31.51	6:2	**128** *162*	0.6838	234-234 ; 235-345	0.012	0.008	89
90	31.68	7:3	**183**	0.6871	2346-245	-	-	90
91	31.92	6:1	**167**	0.6919	245-345	-	-	91
92	32.24	7:3	**185**	0.6980	23456-25	-	-	92
93	32.58	7:3	**174** *181*	0.7046	2345-236 ; 23456-24	-	-	93
94	32.82	7:3	**177**	0.7094	2356-234	-	-	94
95	33.10	6:1 7:3	**156 171**	0.7149	2345-34 ; 2346-234	-	-	95
96	33.34	8:4	**157 202**	0.7195	234-345 ; 2356-2356	-	-	96
98	33.50	7:3	**173**	0.7226	23456-23	-	-	98
99	33.83	8:4	**201**	0.7294	2346-2356	0.004	0.002	99
100	34.05	7:2	**172** *204*	0.7339	2345-235 ; 23456-246	-	-	100
101	34.32	8:4	*192* **197**	0.7392	23456-35 ; 2346-2346	-	-	101
102	34.47	7:2	**180**	0.7427	2345-245	0.009	0.006	102
103	34.71	7:2	**193**	0.7471	2356-345	-	-	103
104	34.97	7:2	**191**	0.7527	2346-345	0.007	0.005	104
105	35.30	8:4	**200** *169*	0.7588	23456-236 ; 345-345	-	-	105
106	36.33	7:2	**170**	0.7799	2345-234	-	-	106
107	36.57	7:2	**190**	0.7850	23456-34	-	-	107
108	37.35	8:3	**198**	0.8007	23456-235	-	-	108

DB-1 Peak Number [1]	Retention Time	T-CL:O-CL	IUPAC # [2]	RRT	Congeners [3]	Weight Percent	Mole Percent	DB-1 Peak Number [1]
109	37.65	8:3	**199**	0.8050	2345-2356	0.017	0.010	109
110	38.03	8:3	**196 203**	0.8149	2345-2346 ; 23456-245	-	-	110
111	39.07	7:1	**189**	0.8365	2345-345	-	-	111
112	40.44	8:3	**195**	0.8647	23456-234	-	-	112
113	40.91	9:4	**208**	0.8743	23456-2356	-	-	113
114	41.73	9:4	*207*	0.8909	23456-2346	-	-	114
115	43.00	8:2	**194**	0.9177	2345-2345	-	-	115
116	43.79	8:2	**205**	0.9342	23456-345	-	-	116
117	48.38	9:3	**206**	1.0294	23456-2345	-	-	117
118	53.74	10:4	*209*	1.1406	23456-23456	-	-	118

Concentration = 9.53 µg/g

Total Micromoles = 0.036

Average Molecular Weight = 262.4

Number of Calibrated Peaks Found = 69

[1] - Note that 5 DB-1 peaks (PK18, PK40, PK81, PK86, PK97) have been removed from the DB-1 peak numbering scheme. The following low level congeners that were designated as separately eluting peaks have been determined to co-elute with another congener. The DB-1 peak numbers are no longer required for these congeners, but the original DB-1 numbering system has remained intact for all other peaks.

PK 18 (23) now elutes in PK 19 (23,34,54)
PK 40 (68) now elutes in PK 41 (68,96)

PK 86 (166) now elutes in PK 85 (166,178)
PK 97 (157) now elutes in PK 96 (157,202)

[2] - IUPAC congener numbers listed in **boldface** font were found to be present in at least one of the Aroclors at or above 0.05 weight percent. These congeners should be considered the primary congeners existing in a peak composed of co-eluting congeners. IUPAC congener numbers listed in *italic* font were absent or present below 0.05 weight percent.

[3] - PCB congener identification is denoted by position of the chlorine atoms on each ring of the biphenyl molecule. Designation used in this report has unprimed chlorines separated from prime chlorines by a hyphen that represents separation of the biphenyl rings.

[4] - DB-1 peaks may include one or more coeluting PCB congeners. In the case of some peaks, the congeners assigned to the peak consist of coeluting congeners and a congener that is resolved or is just slightly out of the normal retention time window of ± 0.07 minutes. If detection of one of the resolved congeners occurs, a comment will be included in the report narrative indication the assigned DB-1 peak includes the presence of the resolved congener. The DB-1 peaks consisting of coeluting congeners and a congener that is resolved are as follows:

DB-1 Peak	Resolved Congener (IUPAC #)
37 (**44**, *104*)	*104*
48 (**66**, *76, 98, 80, 93*, **95**, **102**, *88*)	*80, 88, 93*
56 (*78,* **83**, *112, 108)*	*108*
61 (**77, 110**, *148*)	**77**
72 (**122**, *131, 133, 142*)	**122**
89 (**128**, *162*)	*162*
105 (**200**,*169*)	*169*

APPENDIX 27

STANDARD OPERATING PROCEDURE

NORTHEAST ANALYTICAL, INC.

NE131_03.SOP
REVISION NUMBER: 03

STANDARD OPERATING PROCEDURE FOR THE ANALYSIS OF ORGANOCHLORINE PESTICIDES BY EPA METHOD 8081A

AUGUST 25, 1999

COPY

STARDARD OPERATING PROCEDURE

Author: Kristen E. Voigt
Reviewed by:

_____
Name & Functional Area

Approved by:

James D. Daly
Assistant Laboratory Director

Northeast Analytical, Inc.
Issuing Section: Organics Lab
SOP Name: NE131_03.SOP
Date: 25-August-1999
Revision: 03

1.0 Title:

Northeast Analytical,Inc. SW 846 Method 8081A PESTICIDE

Standard operating procedure for the analysis of Pesticides by Gas Chromatography with Electron Capture Detection.

2.0 Purpose

The purpose of this SOP is to provide a detailed written document for measurement of Pesticides according to SW-846 Method 8081A specifications.

3.0 Scope

3.1 This SOP is applicable in the determination of Pesticides as outlined in EPA SW-846 Method 8081A. It is applicable to the following matrices: water, soil, sediment, sludge, oil, fuel oil, waste solvent, fish, other aquatic animals, and tissue samples.

3.2 The following compounds can be determined by this method:

Compound	CAS Number
Aldrin	309-00-2
Alpha-BHC	319-84-6
Alpha Chlordane	5103-71-9
Beta-BHC	319-85-7
Delta-BHC	319-86-8
Gamma-BHC (Lindane)	58-89-9
Gamma Chlordane	5103-74-2
Chlordane(Technical)	12789-03-6
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33212-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
4,4'-Methoxychlor	72-43-5
Toxaphene	8001-35-2

3.3 In general, samples are extracted, or in the case of oils and waste solvents diluted, with a pesticide grade solvent. The extracts are further processed by concentrating or diluting, depending on the Pesticide concentration. The sample is then analyzed by direct injection onto a gas chromatographic system and detected by an electron capture detector.

3.4 This SOP provides detailed instructions for gas chromatographic conditions, calibration, and analysis of Pesticides by capillary column gas chromatography.

4.0 Comments

4.1 Interference

Laboratory contamination can occur by introduction of plasticizers (phthalate esters) into the samples through the use of flexible tubing. Samples and extracts should not be exposed to plastic materials. Phthalate esters respond on electron capture detectors, usually as late eluting peaks, and can interfere in Pesticide quantification.

5.0 Safety

5.1 Safety glasses and disposable gloves must be worn when handling samples and extracts.

5.2 All manipulations of sample extracts should be conducted inside a chemical fume hood. The analyst should minimize manipulation of sample extracts outside of a fume hood.

5.3 Safe laboratory practices should be followed by the analyst at all times when conducting work in the lab. The analyst should refer to the reference file of material safety data sheets to familiarize themselves with the precautions of handling applicable solvents and chemicals used to process samples. The analyst should refer to the laboratory chemical hygiene plan for further safety information.

5.4 Samples remaining after analysis should be either returned to the customer for disposal or disposed of through the laboratory's disposal plan. Refer to the sample custodian for assistance in this matter and also standard operating procedure NEO54, disposal of laboratory waste.

6.0 Requirements

6.1 Extensive knowledge of this standard operating procedure and EPA SW-846 method 8081A is required.

6.2 The analysis portion of this method should be performed by a skilled chemist or by an analyst trained in the quantification of trace organics by gas chromatography.

6.3 Method Detection Limit (MDL): Prepare eight MDL samples and a method blank for the compounds of interest. Analyze the samples and blank according to the procedures set forth in this document. Calculate the MDL by multiplying the standard deviation of eight MDL measurements by 2.998. For the MDL to be valid, it must be greater than the 1/10 the amount spiked but not greater than the amount spiked.

6.4 Precision and Accuracy: An initial demonstration of precision and accuracy must be performed and documented prior to the analysis of any environmental samples. Prepare four replicates of a 1 liter lab fortified aqueous method blank. The samples should contain each of the single response target analytes at a concentration of approximately 10 ng/L. Extract and analyze the samples and compare the percent recovery to lab established limits. If lab established limits are not available then the interim limits for percent recovery (70-130%) may be used. Multi-response analytes should be measured separately.

7.0 Equipment

7.1 Instrumentation

7.1.1 Gas chromatograph: Varian Model 3400, equipped with Model 1077 split/splitless injector, temperature programmable oven, electron capture detector, Model 8100 autosampler.

7.1.2 Chromatograph Data System: A data system for measuring peak height and peak area. A Millennium_32 computer network based workstation (Waters Associates), will be employed to capture detector response and digitally store the chromatographic information. This system will allow for chromatographic review of data from the gas

chromatograph, electronic peak integration for precise calculations, database structuring of the analytical information, and archival capabilities.

7.2 Glassware and Accessories

7.2.1 25 mL volumetric flasks, Class A, acid washed, (Baxter Cat. No. F4635-25)

7.2.2 5 mL volumetric flasks, Class A, acid washed (Baxter Cat. No. F4635-5)

7.2.3 10 mL volumetric flasks, Class A, acid washed (Baxter Cat. No. F 4635-10)

7.2.4 50 mL volumetric flasks, Class A, acid washed (Baxter Cat. No. F4635-50)

7.2.5 100 mL volumetric flasks, Class A, acid washed (Baxter Cat. No. F4635-100)

7.2.6 4 dram vials for sample extract storage (Kimble Opticlear, part no. 60910, code no. 60910-4)

7.2.7 8 dram vials for sample extract storage (Kimble Opticlear, part no. 60910, code no. 60910-8)

7.2.8 Pasteur pipettes (Baxter, part no. P5216-2A)

7.2.9 250 mL beakers, glass (Baxter Cat. No. B2650-250)

7.2.10 100 mL beakers, glass (Baxter Cat. No. B2650-100)

7.2.11 Disposable 10 mL pipettes (Baxter P4650-110)

7.2.12 Disposable 5 mL pipettes (Baxter P4650-15)

7.2.13 Disposable 1.0 mL pipette (Baxter P4650-11X)

7.3 Chemicals

7.3.1 Hexane, Burdick and Jackson, (Cat.No.216-4)

7.3.2 Acetone, Burdick and Jackson, (Cat.No.010-4)

7.3.3 Methylene Chloride, Burdick and Jackson (Cat. No. 300-4)

7.4 Analytical Standard Solutions

7.4.1 All primary stock standards, with the exception of Organochlorine Pesticides and the Performance Evaluation Mixture, are stored in a freezer, protected from light. The Organochlorine Pesticides and the Performance Evaluation Mixture are stored at ambient temperature. Stock standards must be disposed of after expiration date listed.

7.4.2 All secondary stock solutions and all subsequent Pesticide standard dilutions are stored in a refrigerator at 0-6°C, protected from light, and must be replaced after six months, or sooner if comparison with Performance Evaluation Mixture indicates a problem. See 8.6.2 for limits.

7.4.3 For quality control and general requirements refer to standard operating procedure NE050, Preparation of Standards.

7.4.4 See Attachment A for instructions on preparing stock standards.

7.5 Calibration Standards

7.5.1 See Attachment A for instructions on preparing calibration and working standards.

7.5.2 Transfer all calibration and working standards to 4 or 8 dram vials and store in a refrigerator. These standards must be replaced after six months, or sooner, if comparison with Performance Evaluation Mixture indicates a problem. See 8.6.2 for limits.

8.0 Procedure

8.1 Gas Chromatographic Operating Conditions

8.1.1 Establish the gas chromatograph (GC) operating parameters as follows:

Refer to Attachment B for specific program parameters for GCs, columns, and autosamplers.

Note: GC helium gas flow is optimized after instrument maintenance by adjusting nitrogen flow to elute a PCB calibration standard to a known retention time.

8.1.2 All autosamplers are operated in the multi-vial mode.

8.2 Data Acquisition

8.2.1 Chromatographic information will be collected and processed utilizing a computer based data acquisition workstation (Waters Associates, Millennium_32 computer network based workstation) The GC workstation acquires the millivolt detector signal, performs an analog to digital conversion and stores the digital chromatogram on the computer network's disk. The chromatography software performs all data reduction including, long term data storage on magnetic media, chromatographic peak integration, all calculations, report generation, chromatogram plots, and calibration functions.

8.3 Initial GC Calibration

8.3.1 GC calibration will be done by the external calibration procedure. Prior to running samples the system must be calibrated and system performance must be verified.

8.3.2 Establish the gas chromatographic operating parameters outlined in Section 8.1 and prepare the calibration standards at the various concentrations outlined in Sections 7.4 and 7.5.

8.3.3 A calibration curve is prepared from a minimum of five calibration standards. Select the calibration standards based on the system sensitivity. Inject each calibration standard using the GC Autosampler and the parameters outlined in section 8.1, which are those used for actual samples.

8.3.4 For Technical Chlordane and Toxaphene, 5 peaks are used for quantification. Consideration was given to selecting peaks that normally did not have problems with co-elution with interfering peaks. The area of the five peaks is processed by the data workstation as a group, combining the area for calculations of the calibration factors. The single component pesticides are processed by the data workstation individually by area. The following table compiles the Pesticides that are included in the initial calibration and the approximate retention time of calibration peaks for a DB-1 column.

Compound	Peak Number	Retention Time
Technical Chlordane	1	7.900
	2	8.340
	3	10.578
	4	11.027
	5	11.269
Toxaphene	1	12.570
	2	12.798
	3	13.776
	4	14.115
	5	14.758

TCMX (Surrogate)	NA	5.474
Alpha-BHC	NA	5.994
Gamma-BHC	NA	6.578
Beta-BHC	NA	6.238
Heptachlor	NA	8.332
Delta-BHC	NA	6.672
Aldrin	NA	9.166
Heptachlor Epoxide	NA	9.996
Gamma Chlordane	NA	10.573
Alpha Chlordane	NA	11.023
Endosulfan I	NA	10.934
P,P'-DDE	NA	11.556
Dieldrin	NA	11.621
Endrin	NA	12.133
P,P'-DDD	NA	12.577
Endosulfan II	NA	12.203
P,P'-DDT	NA	13.798
Endrin Aldehyde	NA	12.630
Endosulfan Sulfate	NA	13.371
Methoxychlor	NA	15.467
Endrin Ketone	NA	14.616
DCB (Surrogate)	NA	24.036

8.3.5 Attachment C includes chromatograms of the three individual pesticide standards with selected peaks labeled.

8.3.6 For the calibration curve to be considered valid, the percent relative standard deviation of the response factors must be less than 20% for the calibration standards. See attachment D for an example of response factors and the percent relative standard deviation.

8.3.7 The calibration curve is used for quantification in every case and is not replaced with the average calibration factor.

8.4 Retention Time Windows

8.4.1 The GC system should be checked by the analyst to make sure it is functioning properly before establishing retention time windows. Select a calibration standard for each of the three individual pesticides and inject each standard three times within a 72-hour time period.

8.4.2 For each peak calculate the standard deviation resulting from the variation in the three retention times for that peak.

8.4.3 The retention time window is defined as plus or minus three times the standard deviation of the three retention time determinations.

8.4.4 If the standard deviation of the selected peak is zero, the standard deviation of the peak eluting after it is used. If it is the last eluting peak that has zero for the standard deviation, then substitute the standard deviation of the peak eluting before the last peak.

8.4.5 Retention time windows are established by the mid-level standard of the calibration curve. If the continuing calibration checks fall outside of these windows update the windows using the previous check standard. If the retention times are still outside the established windows instrument maintenance must be performed and recalibration may be required.

8.4.6 Besides using retention time windows to assign peaks for quantification, the analyst should primarily rely on their experience in pattern recognition of multi-response analytes such as Technical Chlordane and Toxaphene.

8.4.7 Attachment E is an example of calculated retention time windows generated by the above outlined procedures.

8.5 Gas Chromatographic Analysis

8.5.1 Prior to conducting any analyses on samples, calibrate the system as specified in Section 8.3.

8.5.2 The following is an example of the order that initial calibration standards, continuing calibration check standards, method blanks, QC samples, and samples are placed in an analytical sequence. A continuing calibration check standard is run every tenth injection in the analytical sequence. All analytical sequences must end with a continuing calibration check standard regardless of the number of samples analyzed. See section 8.6 for information relating to quality control.

ANALYTICAL SEQUENCE

INJECTION	MATERIAL INJECTED
1	Hexane Blank
2-16	Initial Calibration Standards
17	Performance Evaluation Mixture
18-20	Continuing Calibration Check Standards
21-29	Samples analyses, including method blanks, matrix spikes, matrix duplicates, matrix spike duplicates, and QC reference check standard. A maximum of 9 samples between continuing calibration check standards.
30	Continuing calibration check standard
31 and higher	repeat inject. 21-30 sequence

*The initial calibration standard sequence may be altered due to sensitivity of the instrument.

8.6 Quality Control

8.6.1 This section outlines the necessary quality control samples that need to be analyzed to meet method 8081A specifications. The data from these quality control samples is maintained to document the quality of the data generated.

8.6.2 **Performance Evaluation Mixture:** This mixture is analyzed after every calibration curve is generated. The performance evaluation mixture has certain criterion that must be met in order for the data to be considered valid. Two of the analytes included in the mixture are Endrin and P,P'-DDT. Endrin breaks down into Endrin Aldehyde and Endrin Ketone. P,P'-DDT breaks down into P,P'-DDE and P,P'-DDD. The percentage of breakdown must be ±15% percent for each individual compound. All components in mixture must be within 15 percent of true value.

8.6.3 **Continuing Calibration Check Standard (CCCS):** The initial CCCS consists of three standards. Use the midlevel standard of the three pesticide compounds. These standards are analyzed after the Performance Evaluation Mixture. Selection of the succeeding CCCS should be alternated among the three Pesticide curves and is analyzed after every nine injections and at the end of an analytical sequence. Analysis time in between check standards must not exceed 24 hours. The percent recoveries must be between ±15% of the true value.

If this criterion is exceeded, the analyst should inspect the system to determine the cause and perform maintenance as necessary. The system can then be recalibrated and sample analysis can proceed. Note that all samples which are not bracketed by valid check standards must be re-analyzed when the system is in-control.

8.6.4 **Method Blank:** With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. The method blank must exhibit Pesticide levels less than the matrix defined practical quantification limit (PQL). If the method blank exhibits Pesticide contamination above the reportable PQL, the samples associated with the contaminated blank should be re-extracted and analysis repeated. If there is no original sample available for re-extraction, then the results should be flagged with a "B" indicating blank contamination. The value measured in the blank is reported for those samples associated with the particular blank which is out of criteria.

8.6.5 **Laboratory Control Spike (LCS):** With each batch of 20 or less samples to be extracted an LCS is processed. The LCS is carried through all stages of sample preparation and measurement steps. Spike one liter of laboratory organic free water, extract and analyze. Calculate the percent recovery for the LCS. The recovery must fall within lab established limits or the default of 70-130% in order for the result to be considered valid. If the percent recovery for the LCS is out of criteria, the analysis is out of control for that analyte and the problem should be immediately corrected. Re-extraction of the entire batch of samples may be required.

8.6.6 **Matrix Spike:** A matrix spike and spike duplicate is to be analyzed at a rate of 1 matrix spike set per every 20 samples. Duplicate samples may be appropriate in place of matrix spike duplicates, for soil and waste samples, where detectable amounts of organics are present.

8.6.7 Analyze one unspiked and one spiked sample. Calculate the percent recovery based on Pesticide concentration of both samples as follows:

A = concentration of spiked sample
B = concentration of unspiked sample (background)
T = known true value of the spike
Percent Recovery (p) = {(A-B)/T} x 100

Compare the percent recovery calculated with the lab established limits or the default limits of 70-130% if lab limits are not available. If the percent recovery falls outside the acceptance range for the given Pesticides used as spiking analytes, then the matrix spike recovery failed the acceptance criteria. Inform quality control manager and document matrix spike recoveries. If the concentrations of the matrix spikes are *greater* than five times the calculated sample amount then the quality control limits should be applied. If the concentrations of the matrix spikes are *less* than five times the sample than there are no established limits applicable.

A relative percent difference (RPD) must also be calculated on the matrix spike set recoveries. This is calculated as follows:

A = % recovery of matrix spike sample
B = % recovery of matrix spike duplicate sample

RPD = [(A-B)/{(A+B)/2}] x 100
where (A-B) *is taken as an absolute value*

If the concentrations of the matrix spike set are *greater* than five times the calculated PQL then an RPD of twenty percent or less is acceptable. If the concentrations of the matrix spike set are *less* than five times the PQL than there are no established limits applicable to the RPD.

8.6.8 **Surrogates:** Surrogate compounds are added to each sample, matrix spike, matrix spike duplicates, duplicate, method blank, and LCS at time of extraction. Surrogate compounds chosen for this method are tetra-chloro-meta-xylene (TCMX) and decachlorobiphenyl (DCB). The following are typical surrogate amounts added to normal matrices. These amounts may be adjusted if the pesticide background levels are high and surrogates are being diluted out of analysis range.

Water: 0.2 mL of 0.1 ppm TCMX/1.0 ppm DCB
Soil & Sediment: 0.1 mL 0.5 ppm TCMX/5.0 ppm DCB

Only one surrogate analyte needs to meet established control limits for the analysis to be valid. The recovery must fall within lab established limits or 70–130% if lab limits are not available for the analysis to be valid.

If percent surrogate recovery is not within laboratory established limits for either surrogate, the following steps are required.

Review calculations that were used to generate surrogate percent recovery values to make certain there are no errors.

Check by GC analysis surrogate solutions used during sample extraction steps to ensure that no problems exist with spiking solutions.

If the above steps do not lead to satisfactory results then consult with Organics manager to resolve the situation. Samples containing out of limits surrogate recoveries must be narrated. This documentation must be retained with the samples' raw data.

9.0 References

9.1 U.S. EPA SW-846 "Test Methods for Evaluating Solid Waste; Volume 1B Laboratory Manual Physical/Chemical Methods", Office of Solid Waste and Emergency Response, Third Edition, Final Update III, December 1996.

9.2 U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants", July 1988.

9.3 Standard Methods for the Examination of Water and Waste Water, 18th Edition 1992, American Public Health Association, American Water Works Association, Water Pollution Control Federation.

9.4 New York State Department of Health, "Environmental Laboratory Approval Program Certification Manual", Wadsworth Center for laboratories and Research, 1988, updated 1998.

9.5 “Guide to Environmental Analytical Methods", fourth edition, Genium Publishing Corporation, 1998.

10.0 Attachments

10.1 Attachment A: Standard Preparation Procedure.

10.2 Attachment B: GC Program Parameters

10.3 Attachment C: Chromatograms of three pesticide standards.

10.4 Attachment D: Response Factor Calculation.

10.5 Attachment E: Retention Time Window Study.

11.0 Glossary

Continuing Calibration Check Standard (CCCS): Standard used to determine the state of calibration of an instrument between periodic recalibration.

CAS Number: An assigned number used to identify a chemical. CAS stands for Chemical Abstracts Service, an organization that indexes information published in Chemical Abstracts by the American Chemical Society and that provides index guides by which information about particular substances may be located in the abstracts. Sequentially assigned CAS numbers identify specific chemicals, except when followed by an asterisk (*) which signifies a compound (often naturally occurring) of variable composition. The numbers have no chemical significance. The CAS number is a concise, unique means of material identification. (Chemical Abstracts Service, Division of American Chemical Society, Box 3012, Columbus, OH 43210: [614] 447-3600.)

Duplicate: A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

Initial Calibration: Analysis of analytical standards for a series of different specified concentrations; used to define the linearity and dynamic range of the response of the analytical detector or method.

Matrix Spike: Aliquot of a sample (water or soil) fortified (spiked) with known quantities of specific compounds and subjected to the entire analytical procedure in order to indicate the appropriateness of the method for the matrix by measuring recovery.

Matrix Spike Duplicate: A second aliquot of the same matrix as the matrix spike (above) that is spiked in order to determine the precision of the method.

Method Blank: With each batch of samples to be extracted a method blank is processed. The method blank is carried through all stages of sample preparation and measurement steps. For water samples an organic-free reagent water blank is processed. For soil, sediment, and solid waste samples, a laboratory sand blank is processed. For fish and other biota samples, a sodium sulfate blank is processed.

Pesticide: Organic compounds used for eradication of unwanted insects.

Surrogate: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference samples) and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

NOTES

NOTES

ATTACHMENT A

Primary Stock Solutions

Pesticide Solutions	Supplier	Catalog #	Conc. (ug/mL)
Organochlorine Pesticides	ULTRA	US-127	2000
Technical Chlordane	ULTRA	PP-151	100
Toxaphene	ULTRA	PP-271	100
Performance Evaluation Mixture	ULTRA	CLP-250	10-250
DCBP	Chem Service	F2170	Neat
TCMX	ULTRA	IST-440	2000

Unless otherwise noted hexane is the solution used to make all dilutions.

Secondary Stock Solutions

Pesticide Solutions	Initial Volume(mL)	Final Volume(mL)	Final Conc.(ug/mL)
DCBP*	10.0 mg	100	100
TCMX	1.0	100	20
Organochlorine Pesticides 1	1.0	10.0	200
Organochlorine Pesticides 2**	1.0	100	2.0
Technical Chlordane	1.0	100	1.0
Toxaphene	1.0	10.0	10.0
Performance Evaluation Mixture(1)	1.0	10.0	1.0-25.0
Performance Evaluation Mixture(2)	1.0	100	0.01-0.250

*DCBP is dissolved in toluene (10 mL), sonicated to solubilize, and transferred to 100 mL volumetric. Solvent for DCBP: 10 mL toluene and 90 mL hexane.
**Add 2.0 mL of 100 ug/mL DCBP surrogate and 10.0 mL of 20 ug/mL TCMX surrogate.

Attachment A cont'd

Calibration and Working Standards

Organochlorine Pesticide Standards

Initial Conc.(ug/mL)	Initial Volume(uL)	Final Volume(mL)	Final Conc.(ng/mL)
2.0	400	10.0	80.0
2.0	250	10.0	50.0
2.0	125	10.0	25.0
2.0	100	10.0	20.0
2.0	75.0	10.0	15.0
2.0	50.0	10.0	10.0
2.0	25.0	10.0	5.0
0.020	1.0	10.0	2.0
0.010	1.0	10.0	1.0

Technical Chlordane Standards

Initial Conc.(ug/mL)	Initial Volume(mL)	Final Volume(mL)	Final Conc.(ug/mL)
100	1.0	100	1.0
1.0	7.5	10.0	0.750
1.0	5.0	10.0	0.500
1.0	3.5	10.0	0.350
1.0	2.5	10.0	0.250
1.0	1.0	10.0	0.100
1.0	0.500	10.0	0.05

Attachment A cont'd

Toxaphene Standards

Initial Conc.(ug/mL)	Initial Volume(uL)	Final Volume(mL)	Final Conc.(ug/mL)
10.0	1000	10.0	1.0
10.0	750	10.0	0.750
10.0	500	10.0	0.500
10.0	350	10.0	0.350
10.0	250	10.0	0.250
10.0	100	10.0	0.100

ATTACHMENT B

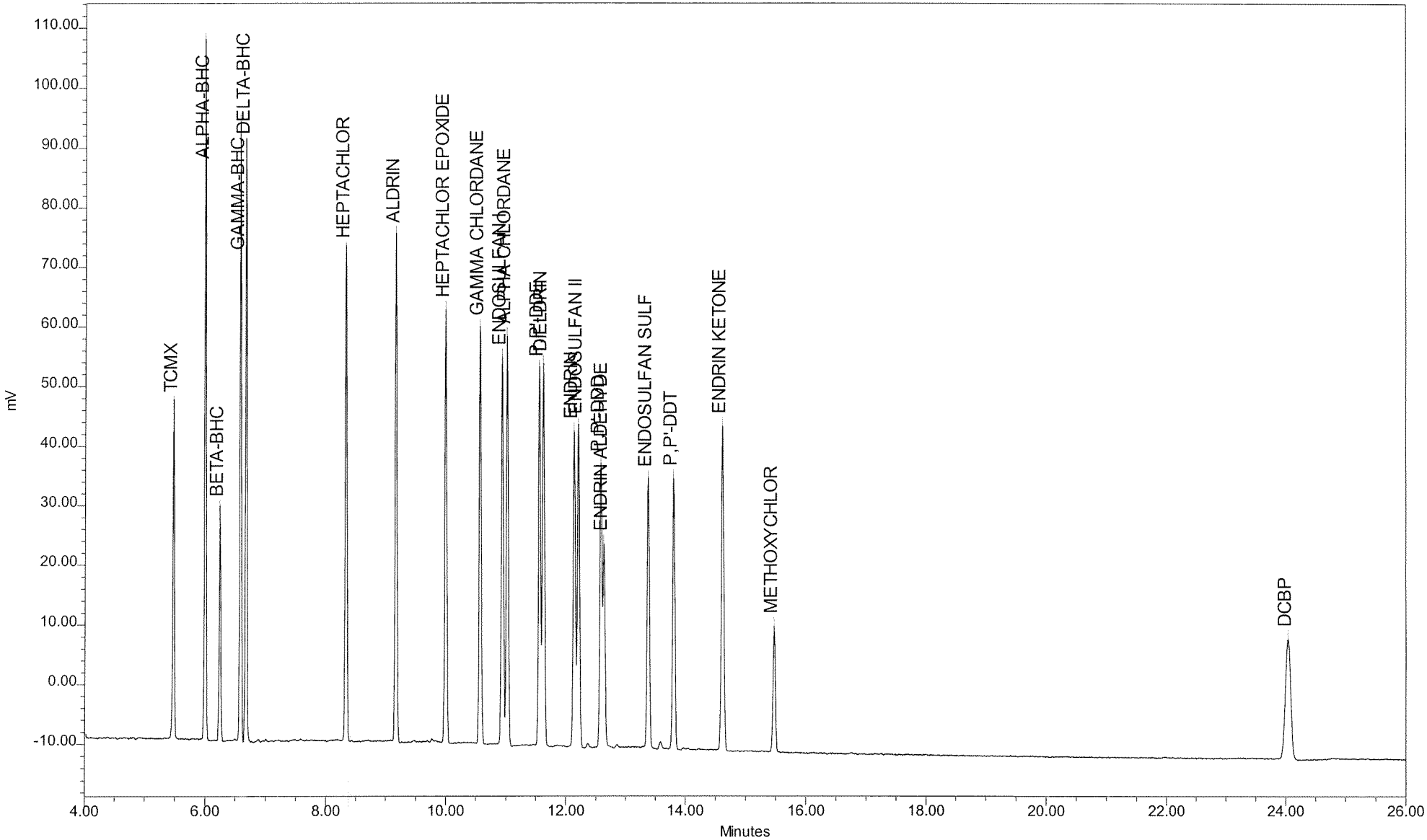
Gas Chromatograph Operating Procedures

Column Type	Capillary	Capillary
Column ID	DB-5MS	DB-1
Vendor	J&W	J&W
Part Number	122-5532	122-1032
Column Length(m)	30	30
ID(mm)	0.25	0.25
Film Thick.(um)	0.25	0.25
1) Initial Col. Temp. (^{o}C)	140	140
1) Initial Col. Hold Time	1	1
1) Col. Temp. Rate (^{o}C/min.)	10	10
1) Final Col. Temp. (^{o}C)	200	200
1) Col. Hold Time (min.)	NA	NA
2) Col. Temp. Rate (^{o}C/min.)	5	5
2) Final Col. Temp. (^{o}C)	245	245
2)Col. Hold Time (min.)	14.5	14.5
GC Col. gas flow rate (mL/min.)	17-24	17-24
ECD Attenuation	1	1
ECD Range	1	1
ECD autozero	Yes	Yes
Detector Temp.(^{o}C)	300	300
Init. Injector Temp. (^{o}C)	300	300
Injector Hold Time (min.)	NA	NA
Injector Temp. Rate (^{o}C/min.)	NA	NA
Final Injector Temp. (^{o}C)	NA	NA
Injector Hold Time (min.)	NA	NA
Autosampler(A/S) Model Number	8100	8100
A/S Injection Volume (uL)	1.2	1.2
A/S Injection Time (min.)	0.01	0.01
A/S Injection Rate (uL/sec.)	Fast 4.0	Fast 4.0

ATTACHMENT C

Chromatogram Report, Pesticide by SW846 Method 8081A

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com

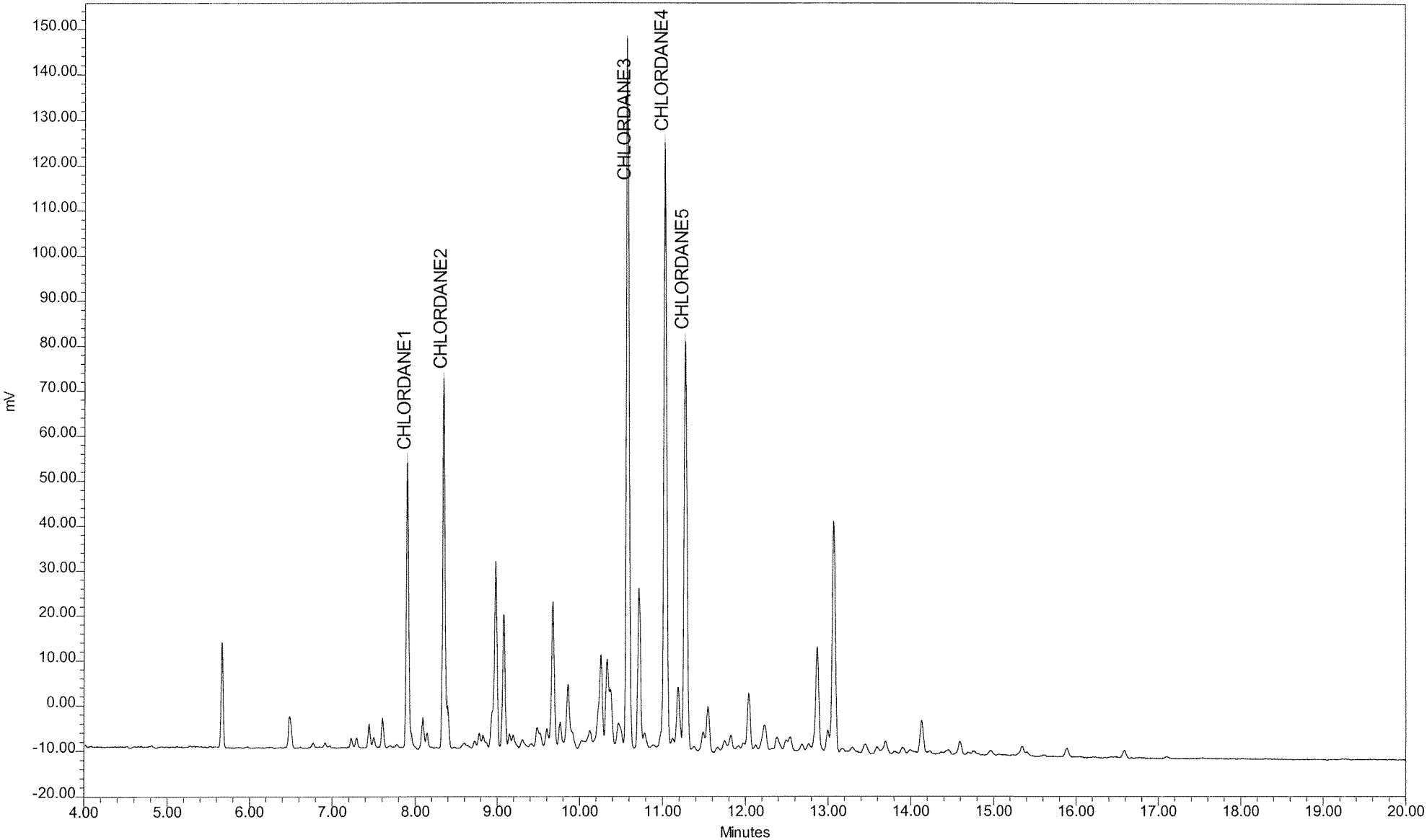


Sample Name:	**PST0701H**	**Sample Amount:**	**1**
Sample ID:	**PEST 50.0 PPB**	**Dilution:**	**1**
Date Acquired:	**07/01/1999 10:31:56**	**Processing Method:**	**NEA_8081_Pest_07029**

ATTACHMENT C CONT.

Chromatogram Report, Pesticide by SW846 Method 8081A

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com

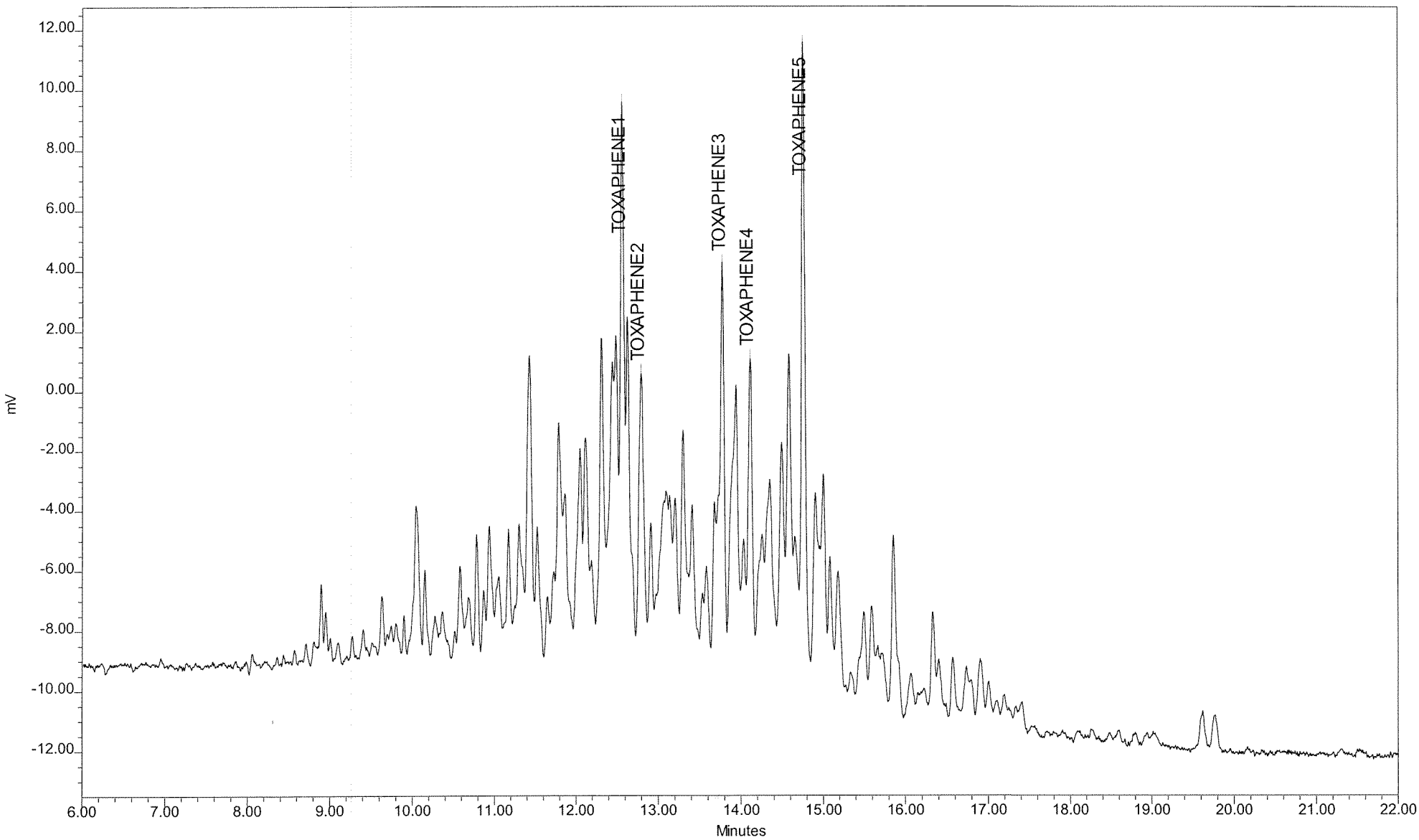


Sample Name:	CHL0701G	**Sample Amount:**	1
Sample ID:	CHLORDANE 1000 PPB	**Dilution:**	1
Date Acquired:	07/02/1999 2:41:27	**Processing Method:**	NEA_8081_CT_070299

ATTACHMENT C CONT.

Chromatogram Report, Pesticide by SW846 Method 8081A

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518)-346-4592 Fax: (518)-381-6055 e-mail: nelab@aol.com



Sample Name:	TOX0701F	**Sample Amount:**	1
Sample ID:	TOXAPHENE 1000 PPB	**Dilution:**	1
Date Acquired:	07/02/1999 11:48:43	**Processing Method:**	NEA_8081_CT_070299

ATTACHMENT D

Calibration Report: Pesticide by SW-846 Method 8081A

Northeast Analytical, Inc., 2190 Technology Drive, Schenectady, NY 12308
Phone: (518) 346-4592 Fax: (518) 381-6055 e-mail: nelab@aol.com

System Name:	Instrument 07	Sample Set Date:	07/01/1999 5:27:48 PM
Sample Set Name:	GC7_8081CC_070199	Date Calibrated:	07/02/1999 3:34:51 PM
User Name:	KristenV	Processing Method:	NEA_8081_CT_070299

Calibration Component Summary Table
Component Summary For RF

	Sample Name	CHLORDANE
1	CHL0701A	1237.375
2	CHL0701B	1248.860
3	CHL0701C	1239.550
4	CHL0701D	1198.142
5	CHL0701E	1139.058
6	CHL0701F	1168.128
7	CHL0701G	1190.361
Mean		1203.068
Std. Dev.		41.046
% RSD		3.4

ATTACHMENT E

Northeast Analytical Inc

02/17/98

Retention Time Window Study
for Organochlorine Pesticides by GC
EPA Method 8081A
Instrument: GC6 Column: DB608 0.53mm ID

Analyte	Standard 1 50 PPB R.T. Min	Standard 2 50 PPB R.T. Min	Standard 3 50 PPB R.T. Min	STD. DEV Min	%RSD	Window +/- Min.
TCMX (SURR)	5.96	5.99	6.01	0.0252	0.42	0.08
ALPHA-BHC	7.72	7.75	7.78	0.0300	0.39	0.09
GAMMA-BHC	8.65	8.68	8.71	0.0300	0.35	0.09
BETA-BHC	8.85	8.88	8.9	0.0252	0.28	0.08
HEPTACHLOR	9.37	9.41	9.43	0.0306	0.32	0.09
DELTA-BHC	9.67	9.7	9.73	0.0300	0.31	0.09
ALDRIN	10.09	10.13	10.16	0.0351	0.35	0.11
HEPTACHLOR EPOX	11.34	11.38	11.4	0.0306	0.27	0.09
GAMMA CHLORDANE	11.69	11.73	11.75	0.0306	0.26	0.09
ALPHA CHLORDANE	12.04	12.08	12.1	0.0306	0.25	0.09
ENDOSULFAN I	12.08	12.12	12.14	0.0306	0.25	0.09
P,P'-DDE	12.64	12.7	12.72	0.0416	0.33	0.12
DIELDRIN	12.8	12.85	12.87	0.0361	0.28	0.11
TOXAPHENE 1						
ENDRIN	13.77	13.84	13.86	0.0473	0.34	0.14
P,P'-DDD	14.17	14.24	14.27	0.0513	0.36	0.15
ENDOSULFAN II	14.33	14.4	14.43	0.0513	0.36	0.15
TOXAPHENE 2						
TOXAPHENE 3	14.47	14.46	14.39	0.0436	0.30	0.13
P,P'-DDT	15.19	15.27	15.3	0.0569	0.37	0.17
TOXAPHENE 4						
ENDRIN ALDEHYDE	15.5	15.58	15.61	0.0569	0.37	0.17
ENDOSULFAN SULF	15.98	16.07	16.11	0.0666	0.41	0.20
TOXAPHENE 5						
METHOXYCHLOR	19.19	19.31	19.34	0.0794	0.41	0.24
ENDRIN KETONE	19.37	19.48	19.51	0.0737	0.38	0.22
DCB (SURR)	24.8	24.96	25	0.1058	0.42	0.32
CHLORDANE 1	9.06	9.05	9.06	0.0058	0.06	0.02
CHLORDANE 2	9.41	9.41	9.41	0.0000	0.00	0.00
CHLORDANE 3						
CHLORDANE 4	12.08	12.09	12.08	0.0058	0.05	0.02

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APPENDIX 28

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB Congener data generated by Northeast Analytical, Inc.'s analytical SOP NE207_03 for the General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to the analytical SOP as applicable to the General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the PCB Congener data provided by the analytical laboratory will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by laboratory-developed analytical methods; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- Northeast Analytical, Inc. (NEA)- Standard Operating Procedure for the Congener-Specific Polychlorinated Biphenyl (PCB) Analysis (Low-level Calibration Method) (SOP NE207_03.DOC, Rev. 03; 03/08/04).

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (SOP HW-23B, Rev. 1.0, May, 2002).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB Congener data based on an evaluation of information presented in the data package deliverables. Compliance to NEA's analytical SOP as applicable to General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

The data reviewer should contact the project laboratory to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB Congener data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

The data reviewer's criteria for evaluating the usability of the PCB Congener data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis. It should be noted that the project manager should be consulted when "professional judgment" use is indicated on the attached table.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgment should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Sediment/soil samples should be extracted within 14 days of sample collection. Tissue samples (which have been frozen to <-18°C upon laboratory receipt) should be extracted within 1 year of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Initial Calibration	%RSD should be ≤20% for the three- or four-point calibration curve for each peak. In addition, the correlation coefficient (r) for each calibration curve must be ≥0.995. <u>Chromatographic Resolution</u> Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	If r is <0.995 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. Use professional judgment to qualify "not-detected" results as estimated ("UJ"). If r is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Continuing Calibration Check (CCC) Standards	The %differences are calculated for Total PCBs and six selected PCB congeners (IUPAC #s 6, 205, 70, 174, 181, 104, 44, and 180) comparing the selected congener concentrations with the known concentrations. The % difference for Total PCBs must be ≤15%. The % differences for PCB congeners #s 6 and 205 (low-level peaks) must be ≤30%. The % differences for the other four medium and high-level peaks must be ≤15%. If a %difference fails, this may indicate unacceptable RRFs or an instrument problem. The area of the internal standard Octachloronapthalene (OCN) in the CCC standard must be within 50-150% of the average area for OCN among the initial calibration standards. Chromatographic Resolution Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. Professional judgment should be used to determine the impact of an out-of-criteria continuing calibration check relative to the PCB Congeners for which %differences have not been calculated. If Total PCBs has 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If Total PCBs has %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the low-level PCB Congeners have 30%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the low-level PCB Congeners have %D>30% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the medium or high-level PCB Congeners have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the medium or high-level PCB Congeners have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If Total PCBs or the select PCB Congeners have %D>90% with the response indicating a sensitivity decrease qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment for qualification if the internal standard area for OCN or chromatographic resolution fails the usability criteria.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Internal Standard – Octachloronaphthalene (OCN)	Area counts of the internal standard peaks for all CCCs, QC samples, and samples should be ±50% of the average internal standard area observed among the associated initial calibration standards. Retention time (RT) for any internal standard should be within the RT window.	If a sample area count is outside of criteria (±50% of the average area among the associated initial calibration standards), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low sample area counts (<25% of the average area among the associated initial calibration standards) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as unusable ("UR"). If a CCC standard or QC sample area count is outside of the criteria (±50% of the average area among the associated initial calibration standards), use professional judgment to qualify data. If an internal standard RT is outside of the RT window and no peaks are observed in the sample chromatogram, qualification is not necessary. Use professional judgment if peaks are observed in the sample chromatogram.
Retention Time Windows (See Note #1 for additional information.)	All PCB congener(s) retention times (RTs) should be within the established RT windows in the CCCs. RT windows for samples are defined as the absolute RT of the Initial CCC Standard for a given analytical sequence ±0.07 minutes.	If the CCC RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCC standards, the direction of the RT drift should be applied to the sample chromatograms.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Blanks (See Note #2 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target PCB Congener is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("U*") and revise the MDL to the value of the positive result. If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #3 for additional information.)	Use 60-140% for acceptance limits.	If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Laboratory Control Samples/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 60-140% for Total PCBs. For precision (if LCSD is provided), use RPD limits of 20% for aqueous samples and 40% for solid samples.	If the recovery is >140%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <60% but ≥10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (If performed)	For accuracy, use recovery limits of 60-140% for Total PCBs. For precision between MS and MSD, use criteria specified in the Field/ Laboratory Duplicate criteria (next item).	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a PCB Congener is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >140%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <60% but ≥10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision criteria for any PCB Congener or Total PCBs are not met, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).
Field/Laboratory Duplicate (See Note #4 for additional information)	Use QAPP-Specified Limits. (Use ½ the RL as a numerical value for any "not-detected" results in the difference calculations).	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgment if a soil/sediment sample has a percent solid content <10%.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Compound Quantitation (See Notes #5 and 6 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. .	If a target PCB Congener result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgment to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target PCB Congener is <RL but ≥MDL, qualify positive results as estimated ("J"). If any PCB Congener has been qualified as estimated due to any reason stated in this SOP, qualify the associated positive result for Total PCBs as estimated ("J").
System Performance (See Note #6 for additional information.)	Professional judgment should be used when assessing the degradation of system performance during analyses.	Use professional judgment to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

1. f a RT shift is observed in an associated CCC and the sample chromatograms reveal peaks, use expanded RT windows and the surrogate shifts to evaluate for potential false positives and false negatives. If a possible false positive is observed, the reported positive sample result for the PCB Congener outside of the RT window may replace the MDL/RL and the result may be qualified as "not-detected" ("U"), depending on professional judgment. If a possible false negative is observed, the potential positive result may be quantitated and added to the result field and may be qualified as tentative ("N"), depending on professional judgment.

   If the chromatograms reveal peaks that interfere with potential detection of a target PCB Congener, qualify the MDL/RL for "not-detected" results as estimated ("UJ") or unusable ("UR"), depending on the level of the interference. Qualify reported positive results for the PCB Congener as unusable ("R") or raise the MDL and RL above the level of detection, depending on professional judgment.

   In addition to RT windows, the laboratory will be relying on its experience in pattern recognition of multi-peak response PCB chromatograms as well as historical data.

2. The frequency of equipment/rinse blanks is determined during the sampling event. The results of an equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

based upon a comparison with the associated blank having the highest concentration of a contaminant.

Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

3. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

4. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Solid duplicate results are expected to have greater variance than aqueous duplicate results.

5. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

6. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- High background levels or shifts in absolute RTs of internal standards
- Excessive baseline rise at elevated temperature
- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

Furthermore, one of the major sources of interference in PCB Congener analysis is co-extracted organochloride pesticides and associated pesticide breakdown products (*e.g.* DDT, DDD, DDE). Sulfuric acid, Florisil®, and sulfur cleanups (if performed) remove many non-target interferences but review the chromatographic pattern and peak RTs for potential interference.

APPENDIX 29

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate inorganic data generated by US EPA Method 200.8 for the General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 200.8 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the inorganic data provided by the project laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Inorganic Data Review" (2/94; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by US EPA Method 200.8; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (2/94).

- US EPA Method 200.8.

- STL – Pittsburgh Standard Operating Procedure "Analysis of Metals by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) for Methods 200.8, 6020 & ILM05.2" (SOP No. PITT-MT-0020, 7/01/03).

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region III, Modifications to Natural Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the inorganic data based on evaluation of information presented in the data package deliverables. Compliance with US EPA Method 200.8 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of certain deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. In addition, the data reviewer should contact the project laboratories if feasible to request the correction of all correctable deficiencies that impact sample results or that the data reviewer was unable to correct prior to the submittal of the QAR, if time allows. Any laboratory resubmittals as a result of such requests will be discussed in the comments substation of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the inorganic data based on an evaluation of the information presented in the data package deliverables. The findings of the inorganic data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier subsection of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the

quantitation/reporting limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

The data reviewer's criteria for evaluating the usability of the inorganic data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Metals Data Generated by US EPA Method 200.8. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved with nitric acid to pH≤2. Solid samples should be preserved to 4±2°C.	If pH is >2 and the laboratory did not adjust the pH and allow the sample to sit for 16 hours before digestion, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Solid samples should not be qualified due to out-of-criteria temperature upon receipt.
Technical Holding Time	All matrices should be analyzed within 6 months of sample collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded (>1 year from date of sample collection), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration	Should be established with a minimum of one blank and three standards. Correlation coefficients (r) should be ≥0.995.	Use professional judgement if the minimum number of standards was not used or if instrument was not calibrated daily and/or not calibrated each time set up. If r is <0.995 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance (See Note #1 for additional information)	The coefficient of variation (C.V.) for multiple injections/integrations should be ≤20% for multiple injections/integrations when the result is >than the reporting limit (RL). Samples should not display negative results with absolute values >2× the method detection limit (MDL).	If C.V. is >20%, qualify positive results greater than the RL as estimated ("J") and do not qualify "not-detected" results. If a negative result >5× MDL, qualify the "not-detected" result as unusable ("UR"). If an analyte displays a negative result >2× MDL, qualify the "not-detected" result as estimated ("UJ").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Initial Calibration Verification (ICV)	For accuracy, use recovery limits of 90-110%.	**Qualify samples for an entire analytical sequence.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Continuing Calibration Verification (CCV)	For accuracy, use recovery limits of 90-110% for the CCVs.	**Qualify samples analyzed before and after a non-compliant CCV.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
PQL/CRI/RLV Standard	For accuracy, use recovery limits of 80-120%.	**Qualify samples analyzed before and after a non-compliant PQL/CRI standard.** If an analyte recovery is >120%, qualify positive results ≤3× the spike level as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <80% but ≥50%, qualify positive results ≤ 3× the spike level as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is <50%, qualify positive results ≤3× the spike level as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If an analyte recovery is >150%, qualify positive results ≤ 3× the spike level as unusable ("R"), qualify positive results >3× the spike level but ≤5× as the spike level estimated ("J"), and do not qualify "not-detected" results.
Initial Calibration Blank (ICB)/Continuing Calibration Blank (CCB)/Preparation Blank (PB)/Field Blank/Equipment Blank (See Note #2 for additional information.)	The highest positive result (greater than the MDL) in the blanks associated with a sample should be summarized and utilized for evaluation of contamination.	For ICBs and CCBs qualify samples per analytical sequence; for PBs, field blanks, and equipment blanks qualify per batch and for SDG. If an analyte is detected in the blank but not in the associated samples, no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("U*") and revise the MDL to the value of the positive result. If the positive result qualified "U*" is ≤RL, the RL should be used as reported. If the positive result qualified "U*" is >RL, the value of the positive result should be used as the revised RL. If a sample result is >5× blank result, qualification is not required. If a blank has a negative result with an absolute value >2× MDL, qualify positive results ≤5× the absolute value of the blank result as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Interference Check Sample Analysis (ICSA/ICSAB) (See Note #3 for additional information.)	For accuracy, use recovery limits of 80-120% for ICSA/ICSAB. The absolute value of analytes not present in ICSA solution should be <2× MDL.	Qualify samples analyzed before and after ICSA/ICSAB standard. Sample data are acceptable if the concentrations of interferents (*i.e.*, Al, Ca, Fe, and Mg) in the samples are ≤ 50% of the respective ICSA concentrations. For samples with concentrations of interferents (*i.e.*, Al, Ca, Fe, and Mg) >50% of the respective concentrations in the ICSA, qualify as follows: If an ICSAB recovery is > 120%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an ICSAB recovery is 50-79%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an ICSAB recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If positive results are observed in the ICSA for non-ICSA analytes that are >2× MDL, qualify positive results up to 5× ICSA concentration in samples with high (>50% ICSA interferents) interferents as estimated ("J") and do not qualify "not-detected" results. If negative results with an absolute value >2× MDL are observed in the ICSA for non-ICSA analytes, qualify positive results up to 5× the concentration observed in the ICSA in samples with high (>50% ICSA interferents) interferents as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Laboratory Control Sample (LCS) (See Note #4 for additional information.)	For accuracy, use recovery limits of 85-115% for aqueous samples and 70-130% for solid samples.	For aqueous samples, if a recovery is >115% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For aqueous samples, if a recovery is <85% but ≥50%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For aqueous samples, if a recovery is >150%, qualify all positive results as unusable ("R") and do not qualify "not-detected" results. For aqueous samples, if a recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). For solid samples, if a recovery is >130%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For solid samples, if a recovery is <70% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For solid samples, if recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #5 for additional information.)	For accuracy, use recovery limits of 70-130%. For precision, use the Field/ Laboratory Duplicate criteria (next page).	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD results can be used to evaluate precision. If a recovery is >130%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If a recovery is <70% but ≥30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If a recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Serial Dilution Analysis	%D<10% if original undiluted concentration is >50× MDL.	If %D is >10%, qualify positive results as estimated ("J") and do not qualify "not-detected" results.

Table for the Validation of Metals Generated by US EPA Method 200.8

Quality Control Item(s)	Usability Criteria	Action(s)
Field Duplicate/Laboratory Duplicate (See Notes #5 and #6 for additional information.)	Use QAPP-specified limits. (Use ½ the RL as the numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for non-compliant analyte in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Total vs. Dissolved Comparison	When the dissolved result is greater than the total result: use default limits of ± RL if at least one result is <10× RL. Use default limit of percent difference <10% if both results are ≥10× RL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× MDL and the difference is >5× MDL, qualify positive results and "not-detected" results as unusable ("R/UR"). If both results are ≥10× MDL and the percent difference is >50%, qualify positive results as unusable ("R").
Percent Solids	Soil/sediment samples with < 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a soil/sediment sample has a percent solid content <10%.
Analyte Quantitation	Samples with results that are >90% of the linear range should be reanalyzed at a dilution.	If a target analyte result is >90% of the linear range, qualify the positive result as estimated ("J"). If a target analyte result is <RL but ≥MDL, qualify positive results as estimated ("J").
Internal Standards	Intensities of the internal standards in the samples must be within 70-130% those in the associated calibration blank.	If the intensity of any internal standards in the samples is not within 70-130% that in the associated calibration blank and the laboratory did not dilute and reanalyze the sample, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ") for elements associated with the internal standard.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information of the intended use and required quality of the data is available, the reviewer should include the assessment of the usability of the data within the given content.

Notes for the Validation of Metals Data Generated by US EPA Method 200.8

1. Due to the nature of ICP/MS data, the MDL may be very low such that 5× the MDL may be below the project reporting limit (RL). If the MDL is very low, use professional judgement to determine if the RLs should be qualified due to negative sample results.

2. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. When evaluating blank contamination, sample weights, volumes, and initial dilution factors should be taken into account. Sample results should not be blank corrected.

   The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was collected for a several-day sampling event, results would be applied to all samples in the SDG).

3. When comparing ICSA results to sample results, the units of each should be the same (*i.e.*, if the sample results are in mg/kg and the ICSA results are in µg/L, convert the ICSA results to mg/kg before comparing the results.) If the negative interference in the ICSA solution is comparable (similar level) to the negative values observed in the CCBs, the negative ICSA values should not be utilized for qualification. If the negative interference in the ICSA solution is not comparable to the negative values observed in the CCBs, the negative ICSA values should be utilized for qualification.

Notes for the Validation of Metals Data Generated by US EPA Method 200.8

4. The spike level for the solid LCS should be compared to the RL. Use professional judgement if the spike level is not sufficiently greater than the RL (*i.e.*, the lower recovery limit should not be less than the RL).

5. The laboratory may choose to analyze an MSD instead of a laboratory duplicate. The laboratory may include a post-digestion matrix spike (PDS) analysis. The PDS results are not utilized for qualification; however, the results are utilized to evaluate the MS/MSD recoveries.

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicates should be applied to all samples in a batch. It is also expected that solid duplicate results will have a greater variance than aqueous duplicate results.

APPENDIX 30

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate mercury data generated by US EPA Method 245.1 for General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 245.1, SW-846 Methods 7470A and 7471A, and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the mercury data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (2/94; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by US EPA Method 245.1 or SW-846 Methods 7470A or 7471A; this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel form available in R:/Templates/Chemistry/XCELForms:

- Inorganic field duplicate comparison Rev 1-01.xls
- Inorganic triplicate comparison Rev 1-01.xls
- Total versus dissolved comparison Rev 1-01.xls

Chemistry Applications:

- FIT
- Methods Database

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (2/94).

- US EPA Method 245.1.

- SW-846 Methods 7470A and 7471A.

- Northeast Analytical, Inc.'s "Standard Operating Procedures for the Preparation and Analysis of Mercury in Samples According to EPA 1994 Method for the Chemical Analysis of Water

and Wastes 245.1, Test Methods for Evaluating Solid Waste SW-846 7471, and NYSDOH ELAP Requirements." (NE025_04.doc, Revision 4, 6/12/03).

- Severn Trent Laboratories (STL) Pittsburgh's SOP "Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW846 7470A and MCAWW 245.1." (C-MT-0005, Revision 3, 4/1/03).

- Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

- Region III, Modifications to National Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the mercury data based on evaluation of information presented in the data package deliverables. Compliance with US EPA Method 245.1, SW-846 Methods 7470A and 7471A, and/or other reference documents (*e.g.,* analytical SOPs) as applicable to the General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be

evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic Data Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by the General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such request will be discussed in the comments subsection of the QAR and will be included as an attachment of the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the mercury data based on an evaluation of the information presented in the data package deliverables. The findings of the mercury data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic Data Qualifier Section of the QAR. Each qualification will indicate that the affected sample result(s) has been flagged with representative

qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation/reporting limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

The data reviewer's criteria for evaluating the usability of the mercury data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

Quality Control Item	Usability Criteria	Action(s)
Temperature and Conditions Upon Receipt	Aqueous samples should be preserved to pH ≤2 with HNO_3. Solid/soil samples should be preserved to 4±2°C.	If pH is >2 and the laboratory did not adjust the pH and allow the sample to sit for 16 hours before digestion, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Solid/soil samples should not be qualified due to out-of-criteria temperatures.
Technical Holding Time	Aqueous and soil/sediment matrices should be analyzed within 28 days of sample collection. Tissue matrices (which have been frozen to <-18°C upon receipt at the laboratory) should be analyzed within one year of sample collection.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded *i.e.*, twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information.)	Calibration should be daily and each time the instrument is set up, with at least one blank and five standards. The correlation coefficient (r) should be ≥ 0.995.	Use professional judgement if the appropriate number of standards is not used or if the instrument was not calibrated daily and/or not calibrated each time set up. If the r is <0.997 but ≥0.850, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r is <0.850, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance	Samples should not display negative results with an absolute value >2× the method detection limit (MDL).	If a negative result with an absolute value >2× MDL is observed, qualify the "not-detected" result as estimated ("UJ").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

Quality Control Item	Usability Criteria	Action(s)
Quality Control Sample (QCS)/Initial Calibration Verification (ICV)	For accuracy, use recovery limits of 90-110%.	**Qualify samples for an entire analytical sequence.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Instrument Performance Check (IPC)/Continuing Calibration Verification (CCV)	For accuracy, use recovery limits of 90-110% for the subsequent IPCs/CCVs.	**Qualify samples analyzed before and after a non-compliant CCV.** If an analyte recovery is >110% but ≤125%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If an analyte recovery is <90% but ≥75%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If an analyte recovery is >125%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. If an analyte recovery is <75%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

Quality Control Item	Usability Criteria	Action(s)
PRDL/CRA/RLV standard	For accuracy, use recovery limits 80-120%.	Qualify samples analyzed before and after a non-compliant PRDL/CRA standard. If the recovery is >120% but ≤150%, qualify positive results ≤ 2 × the spike level as estimated ("J") and do not qualify "not-detected" results. If the recovery is <80% but ≥ 50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recovery is <50%, qualify positive results ≤ 2 × the spike level as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the recovery is >150%, qualify positive results ≤ 2 × the spike level as unusable ("R"), qualify positive results >2× the spike level but ≤5× the spike level as estimated ("J"), and do not qualify "not-detected" results.
Initial Calibration Blank (ICB)/ Continuing Calibration Blank (CCB)/ Preparation Blank (PB)/Field Blank/Equipment Blank (See Note #2 for additional information.)	The highest positive result (greater than the MDL) in the blanks associated with a sample should be summarized and utilized for the evaluation of contamination.	For ICBs and CCBs, qualify samples per analytical sequence; for PBs, field blanks, and equipment blanks, qualify per batch and/or SDG. If mercury is detected in blank but not in sample, no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("U*") and revise the MDL to the value of the positive result. If the positive result qualified "U*" is ≤RL, the RL should be used as reported. If the positive result qualified "U*" is >RL, the value of the positive result should be used as the revised RL. If sample is >5× blank result, qualification is not required. If a blank has a negative result with an absolute value >2 × MDL, qualify positive results ≤ 5 × the absolute value of the blank result as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

Quality Control Item	Usability Criteria	Action(s)
Laboratory Fortified Blank (LFB)/Laboratory Control Sample (LCS) (See Note #3 for additional information.)	For accuracy, use recovery limits of 80-120% for aqueous samples and 70-130% for solid samples.	For aqueous samples, if the recovery is >120% but ≤150%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <80%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For aqueous samples, if the recovery is >150%, qualify positive results as unusable ("R") and do not qualify "not-detected" results. For aqueous samples, if the recovery is <50%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). For solid samples, if the recovery is >130%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. For solid samples, if the recovery is <70% but ≥30%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). For solid samples, if the recovery is <30%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

Quality Control Item	Usability Criteria	Action(s)
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (See Note #4 for additional information.)	For accuracy use recovery limits of 75-125%. For precision, use the criteria for Field/Laboratory Duplicates (next item).	Data should not be qualified due to %Rs (or RPDs calculated using %Rs) that are outside of criteria if the original concentration of an analyte is >4× the spiking level for that analyte. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >125%, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <75% but ≥30%, qualify all positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify all "not-detected" results in all associated samples as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field Duplicate/Laboratory Duplicate (See Notes #4 and #5 for additional information.)	Use QAPP-specified limits. (Use ½ the RL as the numerical value for a "not-detected" result in the RPD calculation.)	If the criteria are not met, qualify positive results for the non-compliant analyte in original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Total vs. Dissolved Comparisons	When the dissolved result is greater than the total result: use default limits of ± RL when at least one result is <10× RL. Use default limits of percent differences <10% when both results are ≥ 10× RL.	If the criteria are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If at least one result is <10× RL and the differences is >5× RL, qualify positive and "not-detected" results as unusable ("R/UR"). If both results are ≥10× RL and the percent difference is >50%, qualify positive results as unusable ("R").

Table for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

Quality Control Item	Usability Criteria	Action(s)
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a soil/sediment sample has a percent solid content <10%.
Analyte Quantitation	Samples with results that are > the calibration range should be reanalyzed at a dilution.	If a target analyte result is > the calibration range, qualify the positive result as estimated ("J"). If a target analyte result is <RL but ≥MDL, qualify positive results as estimated ("J").
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

1. Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, samples should be evaluated for false positives. If the concentration intercept is negative, samples should be evaluated for false negatives. Furthermore, samples should not display negative values >2× the MDL.

   The laboratory may utilize a non-linear regression curve fit. Due to different software programs, it may not be possible to reproduce the laboratory results.

2. Generally, if more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. When evaluating blank contamination, sample weights, volumes, and initial dilution factors should be taken into account. Sample results should not be blank corrected.

   The frequency of equipment blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (if only one blank was collected for a several-day sampling event; results would be applied to all samples in the SDG).

3. The spike level for the solid LCS/LFB should be compared to the RL. Use professional judgement if the spike level is not sufficiently greater than the RL (*i.e.*, the lower recovery limit should not be less than the RL).

Notes for the Validation of Mercury Data Generated by US EPA Method 245.1 or SW-846 Methods 7470A and 7471A

4. The laboratory may choose to analyze a matrix spike duplicate instead of a laboratory duplicate.

5. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate results should be applied to all samples in a batch. It is expected that solid duplicate results will have a greater variance than aqueous duplicate results.

APPENDIX 31

(Note: The SOP for data validation of GFAA Thallium data is not included because Thallium will be analyzed by method 200.8 along with the other TAL metals.)

APPENDIX 32

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that Environmental Standards' data reviewers will use to validate wet chemistry and conventional parameter data generated by the ASTM and US EPA Methods for General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to the applicable ASTM and US EPA Method and/or other reference documents (*e.g.*, analytical SOP) as applicable to General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the wet chemistry and conventional parameter data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review" (2/94) (National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by the Contract Laboratory Program (CLP) protocol. As such, it is not directly applicable to validation of data generated by ASTM and US EPA Methods; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared from one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELForms:

Inorganic field duplicate comparison Rev1-01.xls
Inorganic field triplicate comparison Rev1-01.xls

Chemistry Applications:

FIT
Methods Database

3.0 REFERENCE DOCUMENTS

US EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review (2/94).

ASTM and US EPA Methods.

Northeast Analytical Inc.'s "Standard Operating Procedure for the Determination of Non-Filterable Residue (or Total Suspended Solids) According to EPA 1979 Method 160.2," (NE117_02.SOP, Revision 2, 2/25/02).

Northeast Analytical Inc.'s "Standard Operating Procedure for the Determination of Total and Particulate Organic Carbon According to Tekmar-Dohrmann Application Note TOC-011," (NE128_03.SOP, Revision 3, 2/10/00).

St. Peter-Bender Lab's SOP "Nitrogen, Nitrate-Nitrite Method 353.3 (Spectrophotometric, Cadmium Reduction)"

St. Peter-Bender Lab's SOP "Phosphorus, All Forms (Colorimetric, Ascorbic Acid, Single Reagentt)"

St. Peter-Bender Lab's SOP "Nitrite-N (Nitrogen, Nitrite-N) (Spectrophotometric, Manual)"

St. Peter-Bender Lab's SOP "Kjeldahl Nitrogen, Total Digestion, Nessierization (TKN as N)"

Region II, Evaluation of Metals Data for the Contract Laboratory Program (CLP) (1/92) Validation of Inorganics.

Region I, EPA – New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

Region III, Modifications to Natural Functional Guidelines for Inorganic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the wet chemistry and conventional parameter data based on an evaluation of information presented in the data package deliverables. Compliance to the ASTM or US EPA Method and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Inorganic and Conventional Parameter Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or any certain aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to the submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections necessary for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would take a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as

a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the wet chemistry and conventional parameter data based on an evaluation of the information presented in the data package deliverables. The findings of the wet chemistry and conventional parameter data usability assessment will be described in terms of certain qualifications of the data that the project team should consider in order to best utilize the data. These qualifications will be presented in the Inorganic and Conventional Parameter Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, common contaminants that were not qualified, unusable results (R/UR), estimated results (J/UJ), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

The data reviewer's criteria for evaluating the usability of the wet chemistry and conventional parameter data and the resultant qualifications will be as stated in the attached Table for the Validation of Wet chemistry and Conventional Parameter Data Generated by ASTM and US EPA Procedures. It should be noted that the Project

Manager should be consulted when directed to use "professional judgement" in the attached table.

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by the ASTM and US EPA Procedures

Quality Control Item	Usability Criteria	Action
Temperature and Conditions Upon Receipt	QAPP-specified.	For samples that are required to be stored at 4°±2°C: If temperature >10°C, but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgment should be used if less than 8 hours had lapsed from collection to receipt to determine if the qualification above applies. If aqueous samples have pH values outside of required criteria, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Technical Holding Time	Samples should be analyzed within the QAPP-specified holding times.	If the sample analysis was performed >holding time but ≤ 2 × the holding time, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the sample analysis was performed >2 × the holding time, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Calibration (See Note #1 for additional information)	Laboratory-specified limit or use default of correlation coefficient (r) (linear) or coefficient of determination (COD) (quadratic) ≥0.995 if limits are not provided.	Use professional judgement when evaluating correlation coefficients and coefficients of determination (r or COD). If r or COD <0.995 (or laboratory limit) but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Independent Calibration Verification Standard (ICV) and Continuing Calibration Verification Standard (CCV)	ICV and CCV Recoveries (%R) should be 85-115% for dissolved and suspended organic carbon. Laboratory-specified limits if performed for other parameters (not applicable to all parameters).	If the ICV or CCV %R>upper limit qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the ICV or CCV 55%≤%R<lower limit qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the ICV or CCV %R <55%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by the ASTM and US EPA Procedures

Quality Control Item	Usability Criteria	Action
Blanks (Preparation and/or Continuing Calibration Blanks) (See Note #2 for additional information)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target analyte is found in blank but not in the associated sample(s) no action is needed. If sample >RL, but <5× blank result, qualify the positive results as "not detected" ("U*"). If sample is positive, but <RL and <5× blank result, qualify the positive result as "not-detected" ("U*"). If sample result >5× blank result no qualification is necessary.
Laboratory Control/In-House Reference Sample	For accuracy, use laboratory-specified limits.	Data should not be qualified due to %Rs that are outside of criteria if the original concentration of a compound is > 4 × spiking level for that compound. If the recovery is >upper limit, qualify positive results in all associated samples in batch as estimated ("J") and do not qualify "not-detected" results. If the recovery is 30%≤%R<lower limit, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Laboratory Fortified Matrix Sample (MS)	For accuracy, use laboratory-specified limits.	Data should not be qualified due to %Rs that are outside of criteria if the original concentration of a compound is > 4 × spiking level for that compound. If the recovery is >upper limit, qualify positive results in all associated samples in batch as estimated ("J") and do not qualify "not-detected" results. If the recovery is 30%≤%R<lower limit, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ"). If the recovery is <30%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by the ASTM and US EPA Procedures

Quality Control Item	Usability Criteria	Action
Field/Laboratory Duplicate (See Note #3 for additional information)	Use QAPP-specified limits for Field Duplicate comparison. Use laboratory-specified limits for Laboratory Duplicate (Use ½ the RL as the numerical value for comparison if the analyte was "not-detected")	If the field duplicate criteria are not met, qualify positive results for the non-compliant analyte in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the laboratory duplicate criteria are not met, qualify positive results in the all associated samples in batch as estimated ("J") and qualify "not-detected" results in all associated samples in batch as estimated ("UJ").
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a soil/sediment sample has a percent solid content <10%.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data that were not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include his assessment of the usability of the data within the given context.

Notes for the Validation of Wet Chemistry and Conventional Parameter Data Generated by ASTM and US EPA Procedures

1. Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive then the samples should be evaluated for false positives. If the concentration intercept is negative then the samples should be evaluated for false negatives.

2. The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (unless only one was collected for a several-day sampling event; results would be applied to all samples in the SDG). In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

3. Duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. Field duplicate sample results should only be applied to the original sample and its field duplicate. Laboratory duplicate should be applied to all samples in a batch. It is also expected that solid duplicate results will have a greater variance than aqueous duplicate results.

APPENDIX 33

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB Congener data generated by Northeast Analytical, Inc.'s analytical SOP NE013_07 for the General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to the analytical SOP as applicable to the General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the PCB Congener data provided by the analytical laboratory will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by laboratory-developed analytical methods; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls
- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- Northeast Analytical, Inc. (NEA)- Standard Operating Procedure for the Congener-Specific Polychlorinated Biphenyl (PCB) Analysis (SOP NE013_07.SOP, Rev. 07; 03/09/2004).

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (SOP HW-23B, Rev. 1.0, May, 2002).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB Congener data based on an evaluation of information presented in the data package deliverables. Compliance to NEA's analytical SOP as applicable to General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratory to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB Congener data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

The data reviewer's criteria for evaluating the usability of the PCB Congener data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis. It should be noted that the project manager should be consulted when "professional judgment" use is indicated on the attached table.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgment should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Sediment/soil samples should be extracted within 14 days of sample collection. Tissue samples (which have been frozen to <-18°C upon laboratory receipt) should be extracted within 1 year of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Initial High Level Linearity Verification (To confirm linearity; not used for quantitation)	%RSD should be ≤20% for the three relative response factors (RRFs). Chromatographic Resolution Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	If both the Low- and High-Level Linearity Verifications have been performed and only one of the verifications do not meet criteria, qualify positive results based on the concentration range and use the Low-Level Linearity Verification to assess "not-detected" results. If target PCB Congeners have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target PCB Congeners have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If target PCB Congeners have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Initial Low Level Linearity Verification (To confirm linearity; not used for quantitation)	%RSD should be ≤20% for the three RRFs. Chromatographic Resolution Peak valley heights between NEA DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, NEA DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	If both the Low- and High-Level Linearity Verifications have been performed and only one of the verifications do not meet criteria, qualify positive results based on the concentration range that failed and use the Low-Level Linearity Verification to assess "not-detected" results. If target PCB Congeners have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target PCB Congeners have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If target PCB Congeners have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment for qualification if the chromatographic resolution fails the usability criterion.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Initial 72-hour Retention Time Window Measurement (See Note #1 for additional information.)	Initial RT windows are established to assist in PCB peak assignment. Three high-level Continuing Calibration Check standards and three Supplemental Congener Standards are analyzed over at least 72-hours. The mean RT and the standard deviation of each of the GC peaks are calculated. RT window is ± 3× the determined standard deviation or a default of 0.07 minute is applied (whichever is larger).	If the initial RT windows are not calculated correctly, use professional judgment for qualification.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Continuing Calibration Check (CCC) Standards	The %differences are calculated for Total PCBs and six selected PCB congeners (IUPAC #s 6, 205, 70, 174, 181, 104, 44, and 180) comparing the selected congener concentrations with the known concentrations. The % difference for Total PCBs must be ≤ 15%. The % differences for PCB congeners #s 6 and 205 (low-level peaks) must be ≤30%. The % differences for the other four medium and high-level peaks must be ≤10%. If a %difference fails, this may indicate unacceptable RRFs or an instrument problem. The area of the internal standard Octachloronapthalene (OCN) in the CCC standard must be within 50-150% of the average area for OCN among the initial calibration standards. Chromatographic Resolution Peak valley heights between DB-1 peaks 14 and 15 must be equal to or less than half the height of peak 15. Also, DB-1 peaks 74 and 75 must be equal to or less than one-third the height of peak 74. Must be established initially.	Qualification is for all samples on both sides of the out-of-criteria calibration standards. Professional judgment should be used to determine the impact of an out-of-criteria continuing calibration check relative to the PCB Congeners for which %differences have not been calculated. If Total PCBs have 15%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If Total PCBs have %D>15% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the low-level PCB Congeners have 30%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the low-level PCB Congeners have %D>30% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If the medium or high-level PCB Congeners have 10%<%D≤90% with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the medium or high-level PCB Congeners have %D>10% with the response indicating a sensitivity increase, qualify positive results as estimated ("J") and use professional judgment to qualify "not-detected" results. If Total PCBs or the select PCB Congeners have %D>90% with the response indicating a sensitivity decrease qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment for qualification if the internal standard area for OCN or the chromatographic resolution fails the usability criteria.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Internal Standard – Octachloronaphthalene (OCN)	Area counts of the internal standard peaks for all CCCs, QC samples, and samples should be ±50% of the average internal standard area observed among the associated initial calibration standards. Retention time (RT) for any internal standard should be within the RT window.	If a sample area count is outside of criteria (±50% of the average area among the associated initial calibration standards), qualify positive results for compounds quantitated using that internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as estimated ("UJ"). If extremely low sample area counts (<25% of the average area among the associated initial calibration standards) are reported, qualify positive results for compounds quantitated using the extremely low internal standard as estimated ("J") and qualify "not-detected" results for compounds quantitated using that internal standard as unusable ("UR"). If a CCC standard or QC sample area count is outside of criteria (±50% of the average area among the associated initial calibration standards), use professional judgment to qualify data. If an internal standard RT is outside of the RT window and no peaks are observed in the sample chromatogram, qualification is not necessary. Use professional judgment if peaks are observed in the sample chromatogram.
Retention Time Windows (See Note #1 for additional information.)	All target compound retention times (RTs) should be within the established RT windows. RT windows for samples are defined as the absolute RT of the Initial Continuing Calibration Check Standard for a given analytical sequence ±3× the standard deviation determined in the 72-hour period. If this RT window is less than 0.07 minute then a default of 0.07 minute is applied.	If the CCCstandard RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCC standards, the direction of the RT drift should be applied to the sample chromatograms.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Blanks (See Note #2 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target PCB Congener is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("U*") and revise the MDL to the value of the positive result. If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.
Surrogates (See Note #3 for additional information.)	Use 70-130% for acceptance limits.	If the recoveries of one or more surrogates are > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Laboratory Control Samples/Laboratory Control Sample Duplicate (LCS/LCSD)	For accuracy, use recovery limits of 70-130% for Total PCBs. For precision (if LCSD is provided), use RPD limits of 20% for aqueous samples and 40% for solid samples.	If the recovery is >130%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is <70% but ≥10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results for all PCB Congeners and Total PCBs in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (If performed)	For accuracy, use recovery limits of 70-130% for Total PCBs. For precision between MS and MSD, use criteria specified in the Field/ Laboratory Duplicate criteria (next item).	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a PCB Congener is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is >130%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is <70% but ≥10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive results for all PCB Congeners and Total PCBs in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision criteria for any PCB Congener or Total PCBs are not met, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).
Field/Laboratory Duplicate (See Note #4 for additional information)	Use QAPP-Specified Limits. (Use ½ the RL as a numerical value for any "not-detected" results in the difference calculations).	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgment if a soil/sediment sample has a percent solid content <10%.

Table for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

Quality Control Item	Usability Criteria	Action
Compound Quantitation (See Notes #5 and 6 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. .	If a target PCB Congener result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgment to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target PCB Congener is <RL but ≥MDL, qualify positive results as estimated ("J"). If any PCB Congener has been qualified as estimated due to any reason stated in this SOP, qualify the associated positive result for Total PCBs as estimated ("J").
System Performance (See Note #6 for additional information.)	Professional judgment should be used when assessing the degradation of system performance during analyses.	Use professional judgment to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgment to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

1. If a RT shift is observed in an associated CCC and the sample chromatograms reveal peaks, use expanded RT windows and the surrogate shifts to evaluate for potential false positives and false negatives. If a possible false positive is observed, the reported positive sample result for the PCB Congener outside of the RT window may replace the MDL/RL and the result may be qualified as "not-detected" ("U"), depending on professional judgment. If a possible false negative is observed, the potential positive result may be quantitated and added to the result field and may be qualified as tentative ("N"), depending on professional judgment.

   If the chromatograms reveal peaks that interfere with potential detection of a target PCB Congener, qualify the MDL/RL for "not-detected" results as estimated ("UJ") or unusable ("UR"), depending on the level of the interference. Qualify reported positive results for the PCB Congener as unusable ("R") or raise the MDL and RL above the level of detection, depending on professional judgment.

   In addition to RT windows, the laboratory will be relying on its experience in pattern recognition of multi-peak response PCB chromatograms as well as historical data.

2. The frequency of equipment/rinse blanks is determined during the sampling event. The results of an equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

based upon a comparison with the associated blank having the highest concentration of a contaminant.

Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

3. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

4. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Solid duplicate results are expected to have greater variance than aqueous duplicate results.

5. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

Notes for the Validation of PCB (Congener) Data Generated by NEA's SOP for Congener-Specific PCB Analysis

6. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- High background levels or shifts in absolute RTs of internal standards
- Excessive baseline rise at elevated temperature
- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

Furthermore, one of the major sources of interference in PCB Congener analysis is co-extracted organochloride pesticides and associated pesticide breakdown products (*e.g.* DDT, DDD, DDE). Sulfuric acid, Florisil®, and sulfur cleanups (if performed) remove many non-target interferences but review the chromatographic pattern and peak RTs for potential interference.

APPENDIX 34

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate PCB data generated by SW-846 Method 8082 for the General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8082 and/or other reference documents (*e.g.*, analytical SOPs) as applicable to the General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the PCB data provided by the analytical laboratories will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by the Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Method 8082; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

- Organic field duplicate comparisons Rev1-01.xls

- Organic field quadruplicate comparison Rev1-01.xls
- Organic field triplicate comparison Rev1-01.xls
- Aroclor.xls

Chemistry Applications:

- FIT
- Methods Database
- Target version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

- US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

- SW-846 Method 8082.

- Northeast Analytical Inc.'s SOP "Northeast Analytical, Inc. SW 846 8082 – PCB Capillary Column," (NE148_04.SOP, Revision 4, 4/10/02).

- Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

- Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8082 (Rev 2. 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the PCB data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8082 and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to submittal of the QAR (if feasible and sanctioned by to General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as

a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the PCB data based on an evaluation of the information presented in the data package deliverables. The findings of the PCB data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) to General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination (U*), unusable results (R/UR), estimated results (J/UJ), tentative identifications of target compound results (N), field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

The data reviewer's criteria for evaluating the usability of the PCB data and the resultant qualifications will be as stipulated on the attached Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082. It should be noted that the project manager should be consulted when "professional judgement" use is indicated on the attached table.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected results as estimated ("UJ"). If temperature is > 20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory. Professional judgement should be used if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days of sample collection. Sediment/soil samples should be extracted within 14 days of sample collection. Tissue samples (which have been frozen to <-18°C upon laboratory receipt) should be extracted within 1 year of sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #1 for additional information.)	%RSD should be ≤20%. For the calibration curve, r (linear) or coefficient of determination (COD; quadratic) must be ≥0.99.	If target Aroclors have 20%< %RSD ≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target Aroclors have 50%< %RSD ≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target Aroclors have %RSD > 90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgment when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Continuing Calibration Verification (CCV) (See Note #2 for additional information.)	%drift or %difference should be ≤15% (or %recovery within ±15%).	Qualification is for all samples on both sides of the out-of-criteria calibration standards. If target Aroclors have 15%<%D≤90% (or 10%≤%R<85%), with the response indicating a sensitivity decrease, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target Aroclors have %D>15% with the response indicating a sensitivity increase (or %R>115%), qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target Aroclors have %D>90% with the response indicating a sensitivity decrease (or %R<10%), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Standard Reference Material (Tissue only)	Use recovery limits provided in the QAPP.	If the recovery is > the laboratory's upper acceptance limit, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is < the laboratory's lower acceptance limit but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR").
Retention Time Windows (See Note #3 for additional information.)	All target Aroclor peak retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory or 3× the standard deviation of three non-sequential standards over a 72-hour period.	If the CCV RT windows are not within the specified RT windows, evaluate sample chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCV, the direction of the RT drift should be applied to the sample chromatograms.
Blanks (See Note #4 and Note #9 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target Aroclor is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("U*") and revise the MDL to the value of the positive result. If the positive result qualified "U*" is <RL, the RL should be used as reported. If the positive result qualified "U*" is ≥RL, the value of the positive result should be used as the revised RL. If a sample result is >5× blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on the GC), qualify the positive results as unusable ("R") due to interference.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Surrogates (See Note #5 for additional information.)	Use laboratory acceptance limits.	If the recoveries of one or more surrogates are > the laboratory's upper acceptance limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < the laboratory's lower acceptance limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Matrix Spike/Matrix Spike Duplicate (MS/MSD) (If performed)	Use laboratory acceptance limits for recovery. For precision, use the criteria for Field/ Laboratory Duplicate (next page).	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of an Aroclor is >4× the spiking level for that compound. RPDs calculated using MS/MSD results can be used to evaluate precision. If the recovery is > the laboratory's upper acceptance limit, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the recovery is < the laboratory's lower acceptance limit but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify the "not-detected" result. If the precision criteria (see field duplicate usability criteria) for non-spiked compounds are not met, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native samples as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
Laboratory Control Samples (LCS)	Use laboratory acceptance limits for recovery.	If the recovery is > the laboratory's upper acceptance limit, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery is < the laboratory's lower acceptance limit but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR").
Field/Laboratory Duplicate (See Note #6 for additional information)	Use QAPP-specified limits for precision. (Use ½ the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for the out-of-criteria compounds in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Sediment/soil samples with less than 50% solid content require qualification.	If a sediment/soil sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a sediment/soil sample has a percent solid content <10%.
Compound Quantitation and Qualitative Identification (See Notes #3, #7, and #8 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution. All sample chromatograms must be evaluated to determine whether the laboratory correctly identified the correct Aroclor based upon pattern recognition, peak retention times, and qualititative matching with the associated calibration standards.	If a target Aroclor result exceeds the instrument calibration range, qualify positive result as estimated ("J"). Use professional judgement to determine whether sample reanalyses and dilutions should be compared to the original analyses. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target Aroclor is <RL but ≥MDL, qualify positive results as estimated ("J"). It any positive result for a target Aroclor has been qualified as estimated ("J") due to any reason in this SOP, qualify the associated Total PCBs result as estimated ("J"). Use professional judgement to determine whether qualititative identifications are accurate and whether data qualification is necessary.

Table for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

Quality Control Item	Usability Criteria	Action
System Performance (See Note #8 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

1. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r ≥0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgment when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

2. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration verification standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this within the QAR support documentation.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

The Aroclor in the continuing calibration verification (CCV) standard analysis is alternated among the Aroclors and also may be based on any Aroclors observed in the samples. Each Aroclor CCV should be considered to be representative of all Aroclors; therefore, if the %D>15% for a CCV, all Arolcors should be qualified according to the actions stated in this SOP.

3. Use professional judgement when evaluating sample chromatograms. The Aroclor patterns should be evaluated when an RT shift is observed. If the Aroclor pattern is present, qualification is not necessary. If a RT shift is observed in an associated CCC and the sample chromatograms reveal peaks, use expanded RT windows and the surrogate shifts to evaluate for potential false positives and false negatives. If a possible false positive is observed, the reported positive sample result for the Aroclors outside of the RT window may replace the MDL/RL and the result may be qualified as "not-detected" ("U"), depending on professional judgment. If a possible false negative is observed, the potential positive result may be quantitated and added to the result field and may be qualified as tentative ("N"), depending on professional judgment.

   If the chromatograms reveal peaks that interfere with potential detection of a target Aroclor, qualify the MDL/RL for "not-detected" results as estimated ("UJ") or unusable ("UR"), depending on the level of the interference. Qualify reported positive results for the PCB Congener as unusable ("R") or raise the MDL and RL above the level of detection, depending on professional judgment.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

4. The frequency of equipment/rinse blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected in the same day, unless only one blank was collected for a several-day sampling event. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

   Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank.

5. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

6. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Solid duplicate results are expected to have greater variance than aqueous duplicate results.

Notes for the Validation of PCB (Aroclor) Data Generated by SW-846 Method 8082

7. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

8. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- High background levels or shifts in absolute RTs of internal standards
- Excessive baseline rise at elevated temperature
- Extraneous peaks
- Loss of resolution
- Peak tailing or peak splitting that may result in inaccurate quantitation

APPENDIX 35

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards, Inc. data reviewer will use to validate polychlorinated dibenzodioxin (dioxin) and polychlorinated dibenzofuran (furan) organic data generated by US EPA Method 1613B for General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to US EPA Method 1613B and/or other reference documents (*e.g.*, analytical SOPs), as applicable to General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the dioxin/furan organic data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Validation" (8/02) (National Functional Guidelines). It should be noted that the National Functional Guidelines applies strictly to data generated by the Contract Laboratory Program (CLP) protocol. As such, it is not directly applicable to validation of data generated by US EPA Method 1613B; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared from one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and all data qualifier codes, or a data summary spreadsheet of the qualified analytical results will be included in the analytical results section of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

Organic field duplicate comparison Rev 1-01.xls
Organic field quadruplicate comparison Rev 1-01.xls
Organic field triplicate comparison Rev 1-01.xls

Chemistry Apps

FIT
Methods database

3.0 REFERENCE DOCUMENTS

US EPA Method 1613B (10/94)

Paradigm's SOPs for "Sample Processing" (Revision DC37.030603.15) and "1613 Data Analysis and Reporting" (Revision DC38.120602.7)

US EPA Contract Laboratory Program National Functional Guidelines for Chlorinated Dioxin/Furan Data Validation (8/02)

Region III – SOP for Dioxin/Furan Data Validation (Draft 3/99)

Region IV – Data Validation SOP for Polychlorinated Dibenzodioxin and Polychlorinated Dibenzofurans Analysis by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (9/96)

Region II – Data Validation SOP for EPA Method 1613, Revision A (Revision 2 9/99)

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the dioxin/furan data based on an evaluation of information presented in the data package deliverables. Compliance to US EPA Method 1613B and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or any certain aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of deficiencies prior to the submittal of the QAR (if feasible and sanctioned by General Electric Company) at a minimum corrections necessary for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would take a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the dioxin/furan organic data based on an evaluation of the information presented in the data package deliverables. The findings of the dioxin/furan organic data usability assessment will be described in terms of certain qualifications of the data that the project team should consider in order to best utilize the data. These qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank qualification, common contaminants that were not qualified, unusable results ("R/UR"), estimated results ("J/UJ"), field duplicate comparison and a general qualifier for all results reported the quantitation limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

The data reviewer's criteria for evaluating the usability of the dioxin/furan organic data and the resulting qualifications will be as stated in the attached Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B. It should be noted that the Project Manager should be consulted when directed to use "professional judgement" in the attached table.

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4°±2°C	Due to the stability of PCDDs and PCDFs, there is no direct impact on data usability due to receipt temperatures outside the specified range.
Holding Time (See Note #1 for additional information.)	Aqueous and soil/sediment samples should be extracted within 30 days of sample collection and analyzed within 45 days of extraction. Tissue samples (which have been frozen to <-18°C upon laboratory receipt) should be extracted within one year after sample collection and analyzed within 40 days of extraction.	If holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If holding time is grossly exceeded (>twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Chromatographic Resolution (Isomer Specificity Test Standard, See Note #2 for additional information)	Should be analyzed at the beginning of each 12-hour period of sample and standard analysis. The % valley between unlabeled 2,3,7,8-TCDD and all other unlabeled TCDD should be <25%. The RT of the first and last eluting isomers are used to establish the RT windows for each congener class of PCDD/PCDF compounds.	Use professional judgement if the Isomer Specificity Test Standard was not analyzed at the required frequency. If the % valley between unlabeled 2,3,7,8-TCDD and all other unlabeled TCDD is >25%, qualify positive results for 2,3,7,8-TCDD as estimated ("J").
Window Defining Mix (WDM) (See Note #2 for additional information)	Should be analyzed at the beginning of each 12-hour period of sample and standard analysis.	If frequency is not met, qualify positive results for total homologues as estimated ("J").
Instrument Performance-Mass Spectrometer Performance (PFK)	Should be analyzed at the beginning of each 12-hour period during which samples are to be analyzed and prior to the analysis of the initial and continuing calibration standards. A static resolving power of at least 10,000 (10% valley definition) should be demonstrated at appropriate masses before any analysis is performed and at the end of each 12-hour period.	Use professional judgement if the mass calibration was not performed at the required frequency or if the resolving power was less than 10,000.

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #3 for additional information)	Should be established with a minimum of 5 different concentration levels. The %RSD should be ≤20% for the 17 unlabeled standards and ≤35% for the labeled reference compounds. The relative ion abundance ratios should be within the limits specified in Note #3. The retention times of all target compounds, internal standards, and recovery standard should be within the windows established. The two monitored ions for each homologue should be present and should maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ions. The signal-to-noise (S/N) ratio for the GC signals present in the selected ion current profiles (SICPs) should be ≥ 10.	If the %RSD >20% but ≤90% (for unlabeled), qualify positive result as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the %RSD >90% (for unlabeled), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). If the relative ion abundance ratios for the two quantitation ions of the target compounds, internal standard, and/or recovery standards were not with the stated range, qualify positive results as unusable ("R"). Qualify positive results associated with the out of criteria ion abundance ratio internal standards and/or recovery standards. If the retention time of any target compound, internal standard, and/or recovery standard is not within the established retention time windows (±10 seconds of retention times in the WDM), qualify all data as unusable ("R/UR"). If the two monitored ions for a native isomer are not present and/or did not maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ion, qualify positive results as "not-detected" ("U") (the reported concentration with be reported at the detection limit). If the S/N ratio was <10, qualify "not-detected" results as unusable ("UR").

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Continuing Calibration (See Notes #3 and #4 for additional information)	Should be analyzed at the beginning of each 12-hour shift. The relative ion abundance ratios should be within the limits specified in Note #3. The recoveries (%Rs) should be within the limits specified in Note #4. The retention times for all compounds should be within the windows established. The two monitored ions for each homologue should be present and should maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ions. The signal-to-noise (S/N) ratio for the GC signals present in the SICPs should be ≥ 10.	If the unlabeled target compound recovery < lower limit but ≥ 50% of the lower limit, qualify positive result as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the unlabeled target compound recovery is > the upper limit but ≤ 150% of the upper limit, qualify positive result as estimated ("J"). If the unlabeled target compound recovery is < 50% of the lower limit or > 150% of the upper limit, qualify positive and "not-detected" results as unusable ("R/UR"). If the relative ion abundance ratio for the two quantitation ions are not within the specified range, qualify positive results as unusable ("R"). If the retention time of any target compound is not within the specified retention time window, qualify positive results as unusable ("R"). If the two monitored ions for a native isomer are not present and/or did not maximize simultaneously within 3 seconds of the corresponding ^{13}C-labeled isomer ion, qualify positive results as "not-detected" ("U") (the reported concentration with be reported at the detection limit). If the S/N ratio was <10, qualify "not-detected" results as unusable ("UR").
Internal Standards and Recovery Standards	Added to all samples and standards. %Rs should be within the limits specified in Note #4. The relative ion abundance ratios should be within the limits specified in Note #3. The retention times should be within the windows established.	Use professional judgement to determine if qualification is necessary due to relative ion abundance ratio being outside the specified range and if the retention times are not within the windows established. If the %R is > upper limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the %R is < lower limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the %R is <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Blanks (See Note #5 for additional information)	Summarize all results greater than the estimated detection limit (EDL). The highest positive results associated with a sample should be utilized for evaluation of contamination.	If a target compound is found in blank but not in the associated sample(s), no action is taken. If a sample result is ≤5× the blank result, qualify the results as "not-detected" ("U*"). The value of the positive result should be used as the revised EDL. If a sample result >5× (or 10× for OCDD only) blank result, no qualification is necessary. If gross contamination exists (*i.e.*, saturated peaks by GC/MS), qualify samples as unusable ("R") due to interference.

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicates (MS/MSD) (If performed)	For accuracy, use laboratory acceptance limits. For precision, use RPD limit of 40% for all matrices.	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if original concentration of a compound is > 4× spiking level for that compound. RPDs calculated using MS/MSD results can still be used to evaluate precision. If the recovery is > upper limit, qualify positive results for that compound in the native sample as estimated ("J") and do not qualify "not-detected" results. If the recovery is < lower limit but ≥10%, qualify positive results for that compound in the native sample as estimated ("J") and qualify "not-detected" results for that compound in the native sample as estimated ("UJ"). If the recovery is <10%, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results for that compound in the native samples as unusable ("UR"). If the precision is >20%, qualify positive results for that compound in the native sample as estimated ("J") and do not qualify "not-detected" results. If the precision criteria (See field duplicate usability criteria) for non-spiked compounds are not met, qualify positive results in the native sample as estimated ("J") and qualify "not-detected" results in the native sample as estimated ("UJ"). If a field duplicate of the native (unspiked) sample was collected and analyzed, the field duplicate should also be qualified if the MS/MSD %Rs or RPD are outside of criteria as stated above for the native sample.
Ongoing Precision and Recovery (OPR) Standard	%Rs should be within the limits specified in Note #4. The relative ion abundance ratios should be within the limits specified in Note #3. The retention times should be within the windows established.	If the recovery for a target compound is outside of the acceptance criteria, qualify all positive results and "not-detected" results as unusable ("UR").

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Field Duplicate/Laboratory Duplicate (See Note #6 for additional information)	QAPP-Specified Limits (Use ½ the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results in original sample, and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Qualification is for sediment/soil samples with less than 50% solid content.	If a sediment/soil sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a sediment/soil sample has a percent solid content <10%.
Target Compound Identification (See Note #7 for additional information)	For 2,3,7,8-substitued isomers for which an isotopically labeled internal standard is present, the absolute RT at the maximum peak height should be within –1 to +3 seconds of the RT of the corresponding labeled standard. For non-2,3,7,8-substituted isomers, the RT should be within the established window. The two quantitation ions for the compounds, internal standards, and recovery standards should maximize simultaneously (within 2 seconds). The relative ion abundance ratios should be within the limits specified in Note #3. All integrated ion current for each characteristic ion of the target compound should have an S/N ratio ≥2.5. The identification of a peak as a PCDF can only be made if no signal having a S/N ≥2.5 is detected at the same time in the corresponding polychlorinated diphenyl ether (PCDPE) channel. Any results reported for 2,3,7,8-TCDF should be confirmed on a DB-225 column.	Use professional judgement to determine if the result should be changed to "not-detected" or flagged "EMPC" if one or more of the identification criteria specified was not met. Use professional judgement if a PCDPE peak was detected at the same retention time as a reported PCDF result.

Table for the Validation of Polychlorinated Dibenzo-*p*-dioxin (PCDD) and Polychlorinated Dibenzofuran (PCDF) Data Generated by US EPA Method 1613B

Quality Control Item	Usability Criteria	Action
Compound Quantitation and Detection Limits	The laboratory should reextract samples (utilizing a smaller sample aliquot) with compound concentrations above the instrument calibration range.	If a target compound result exceeds the instrument calibration range, qualify the positive result as estimated ("J"). If a target compound result is below the low calibration standard concentration, qualify the positive result as estimated ("J"). If the laboratory performed a dilution of a sample that had a target compound result that exceeded the instrument calibration range instead of reextracting a smaller sample aliquot, qualify positive results for the dilution analysis as estimated ("J").
System Performance (See Note #8 for additional information)	Professional judgement should be used when assessing the degradation of the system performance during analyses.	Professional judgement should be used to qualify the data if it is determined that the system performance has degraded during sample analysis.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data that were not qualified based on the QC previously addressed. Write a brief narrative to give the user an indication of the analytical limitation of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include the assessment of the usability of the data within the given context.

Notes for the Validation of PCDD and PCDF Data Generated by the US EPA Method 1613B

1. The holding time of extraction within 30 days of sample collection is a recommendation; however, since PCDDs and PCDFs are very stable in many matrices, the holding time may be as high as one year. Use professional judgement when evaluating samples that were extracted beyond the 30-day holding time.

2.

DB-5 Column GC Retention Time WDM

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

DB-5 Column TCDD Isomer Specificity Test Standard

1,2,3,4-TCDD	1,2,3,7-TCDD
1,2,3,9-TCDD	2,3,7,8-TCDD

DB-225 Column TCDF Isomer Specificity Test Standard

2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

3. If the initial calibration %RSD is >50% but ≤90%, the linearity of the first three initial calibration standards for the compound should be evaluated. If the first three initial calibration standards for the compound are linear then do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, then qualify "not-detected" results as estimated ("UJ").

   Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive then the samples should be evaluated for false positives. If the concentration intercept is negative then the samples should be evaluated for false negatives.

Relative Ion Abundance Criteria for PCDDs and PCDFs

PCDDs	Relative Intensity
Tetra	0.65-0.89
Penta	1.32-1.78
Hexa	1.05-1.43
Hepta	0.88-1.20
Octa	0.76-1.02
PCDFs	**Relative Intensity**
Tetra	0.65-0.89
Penta	1.32-1.78
Hexa	1.05-1.43
Hexa[1]	0.43-0.59
Hepta	0.88-1.20
Hepta[2]	0.37-0.51
Octa	0.76-1.02

1 - used only for ^{13}C-HxCDF (internal standard)
2 - used only for ^{13}C-HpCDF (internal standard)

4.

Acceptance Criteria for Performance Tests When All PCDD/PCDF Are Tested

PCDD/PCDF	Concentration (ng/ml)	OPR (ng/ml)	Verification (ng/ml)
2,3,7,8-TCDD	10	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	35-71	39-65
1,2,3,7,8-PeCDF	50	40-67	41-60
2,3,4,7,8-PeCDF	50	34-80	41.61
1,2,3,4,7,8-HxCDD	50	35-82	39-64
1,2,3,6,7,8-HxCDD	50	38-67	39-64
1,2,3,7,8,9-HxCDD	50	32-80	41-61
1,2,3,4,7,8-HxCDF	50	36-67	45-56
1,2,3,6,7,8-HxCDF	50	42-65	44-57
1,2,3,7,8,9-HxCDF	50	39-65	45-56
2,3,4,6,7,8-HxCDF	50	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	39-69	43-58
OCDD	100	78-144	79-126
OCDF	100	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	26-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	21-158	78-129

Acceptance Criteria for Performance Tests When All PCDD/PCDF Are Tested

PCDD/PCDF	Concentration (ng/ml)	OPR (ng/ml)	Verification (ng/ml)
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	20-186	77-129
$^{13}C_{12}$-OCDD	200	26-397	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.1-19.1	7.9-12.7

Acceptance Criteria for Performance Tests When Only Tetra Compounds Are Tested

PCDD/PCDF	Concentration (ng/ml)	OPR (ng/ml)	Verification (ng/ml)
2,3,7,8-TCDD	10	7.3-14.6	8.2-12.3
2,3,7,8-TCDF	10	8.0-14.7	8.6-11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-141	85-117
$^{13}C_{12}$-2,3,7,8-TCDF	100	26-126	76-131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.7-15.8	8.3-12.1

Acceptance Criteria for Labeled Compound Recovery in Samples When All PCDD/PCDFs Are Tested

PCDD/PCDF	Concentration (ng/ml)	Recovery (ng/ml)	Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28-130	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147	29-147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28-136	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138	26-138
$^{13}C_{12}$-OCDD	200	34-313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5-19.7	35-197

Acceptance Criteria for Labeled Compound Recovery in Samples When Only Tetra Compounds Are Tested

PCDD/PCDF	Concentration (ng/ml)	Recovery (ng/ml)	Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31.137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2-16.4	42-164

5. The frequency of equipment blanks is determined during the sampling event. The results of a equipment/rinse blank should be applied to all samples collected using the same equipment (equipment/rinse blanks only) on the same day (unless only one was collected for a several-day sampling event; results would be applied to all samples in the SDG). In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant.

6. Duplicate samples may be taken and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that solid duplicate results will have a greater variance than aqueous duplicate results.

7. US EPA Method 1613B (Section 16.6) requires that a result meet all identification criteria or the result should not be reported. The sample should undergo reextraction with additional cleanup to remove any interference. Therefore, the laboratory should not be reporting the estimated maximum possible contamination (EMPC) results. If the presence of a reported positive is questioned (mostly due to chlorinated ether interference or if ratio/retention times are out), quality the result as "EMPC".

8. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. high background levels or shifts in absolute retention times of internal standards
   b. excessive baseline rise at elevated temperatures
   c. extraneous peaks
   d. loss of resolution
   e. peak tailing or peak splitting that may result in inaccurate quantitation

APPENDIX 36

1.0 OBJECTIVES

This standard operating procedure (SOP) describes procedures that the Environmental Standards data reviewers will use to validate organochloride pesticide data generated by SW-846 Method 8081A for General Electric Company's Hudson River Baseline Monitoring Program. Validation will be performed to assess the compliance of the sample data to SW-846 Method 8081A and/or other reference documents (*e.g.*, analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program. In addition, the usability of the pesticide data provided by the analytical laboratory(ies) will be determined based on the general guidance provided in the "US EPA Contract Laboratory National Functional Guidelines for Organic Data Review" (10/99; National Functional Guidelines). It should be noted that the National Functional Guidelines apply strictly to data generated by Contract Laboratory Program (CLP) protocol and are not directly applicable to validation of data generated by SW-846 Method 8081A; therefore, this SOP presents the specific data qualification actions that will be used for validation.

The validation findings will be presented in a quality assurance review (QAR) that will be prepared for one or more sample delivery groups (SDGs). Copies of annotated analytical results summaries (Form I's), including any changes to the analytical results and data qualifier codes or a data summary spreadsheet of the qualified analytical results, will be included in the support documentation of the QAR.

2.0 EVALUATION TOOLS

Excel forms available in R:/Templates/Chemistry/XCELforms:

Organic field duplicate comparisons Rev1-01.xls
Organic field quadruplicate comparison Rev1-01.xls
Organic field triplicate comparison Rev1-01.xls

Chemistry Applications:

FIT
Methods Database
Target Version 4.1 data processing software

3.0 REFERENCE DOCUMENTS

US EPA Contract Laboratory Program National Functional Guidelines for Organic Data Review (10/99).

SW-846 Method 8081A.

Northeast Analytical, Inc.'s "Standard Operating Procedure for the Analysis of Organochlorine Pesticides by EPA Method 8081A," (NE131_03.SOP, Revision 3, 8/25/99)

Region I, EPA-New England Data Validation Functional Guidelines for Evaluating Environmental Analyses (12/96).

Region II, Standard Operating Procedure for the Validation of Organic Data Acquired Using SW-846 Method 8081A (Rev 2. 12/96).

- Region III, Modifications to National Functional Guidelines for Organic Data Review (9/94).

4.0 PROCEDURE

4.1 EVALUATION OF METHOD COMPLIANCE

The data reviewer will assess the method compliance of the pesticide data based on an evaluation of information presented in the data package deliverables. Compliance to SW-846 Method 8081A and/or other reference documents (*e.g.,* analytical SOPs) as applicable to General Electric Company's Hudson River Baseline Monitoring Program (as directed by the Project Manager) will be evaluated as part of the assessment. In addition, the deliverables will be evaluated for reporting errors and inconsistencies. The findings of the method compliance assessment will be described in terms of deficiencies and comments about the data/deliverables. The deficiencies/comments will be presented in three subdivisions (*i.e.*, correctable deficiencies, noncorrectable deficiencies, and comments) of the Organic Data Evaluation Section of the QAR. Each deficiency and comment discussed in the QAR will indicate any subsequent impact on the usability of the data or will identify aspect(s) of the data that could not be evaluated due to the deficiency.

The data reviewer should contact the project laboratories to request the correction of certain deficiencies prior to submittal of the QAR (if feasible and sanctioned by General Electric Company). At a minimum, corrections required to allow for a full evaluation of the usability of the data should be requested. Such correctable deficiencies may include sample result errors, missing data deliverables, or calculation errors that would require a significant amount of the data reviewer's time to correct. Any laboratory resubmittals as a result of such requests will be discussed in the comments subdivision of the QAR and included as an attachment to the QAR.

4.2 DETERMINATION OF DATA USABILITY

The data reviewer will determine the usability of the pesticide data based on an evaluation of the information presented in the data package deliverables. The findings of the pesticide data usability assessment will be presented in terms of data qualifications that the project team should consider in order to best utilize the data; these qualifications will be presented in the Organic Data Qualifier subsection of the QAR. Each qualification discussed in the QAR will indicate that the affected sample result(s) has been flagged with a representative qualifier code(s) in the General Electric Company's database to provide, at a glance, an indication of the quantitative and qualitative reliability of each analytical result. In general, the qualifier statements will be presented in the QAR in the following order: blank contamination, unusable (R/UR) results, tentative identifications of target compound results (N), estimated (J/UJ) results, field duplicate comparison, and a general qualifier for all results reported below the quantitation limit (if applicable to General Electric Company's Hudson River Baseline Monitoring Program).

The data reviewer's criteria for evaluating the usability of the pesticide data and the resultant qualifications will be as stipulated on the attached Table for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A. It should be noted that the Project Manager should be consulted when "professional judgement" use is indicated on the attached table.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Temperature Upon Receipt	4±2°C	If temperature is >6°C but ≤10°C, no action is required. If temperature is > 10°C but ≤20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If temperature is >20°C, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Note time of collection relative to receipt at laboratory; use professional judgement if < 8 hours has elapsed from collection to receipt at the laboratory to determine if qualification due to elevated temperature applies.
Technical Holding Time	Aqueous samples should be extracted within 7 days after sample collection. Sediment/soil samples should be extracted within 14 days after sample collection. Tissue samples (which have been frozen to <-18°C upon laboratory receipt) should be extracted within one year after sample collection. All matrices should be analyzed within 40 days after extraction.	If a holding time is exceeded, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a holding time is grossly exceeded (*i.e.*, > twice the holding time), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
GC Instrument Performance (See Note #1 for additional information.)	% Breakdown for 4,4′-DDT and endrin should be ≤15% for both GC columns.	Use professional judgement to determine if the associated sample data should be qualified if the instrument performance standard was not analyzed at the proper frequency. See Note #1 for action if the instrument performance standard criteria are not met.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Initial Calibration (See Note #2 for additional information.)	%RSD should be ≤20%. Calibration curve should have r (linear) or coefficient of determination (COD; quadratic) must be ≥0.99.	If target compounds have 20%<%RSD≤50%, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If target compounds have 50%<%RSD≤90%, qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %RSD>90%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR"). Use professional judgement when evaluating correlation coefficients (r) and coefficients of determination (COD). If r (linear) or COD (quadratic) is <0.99 but ≥0.85, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If r or COD is <0.85, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").
Continuing Calibration Verification (CCV) (See Note #3 for additional information.)	%drift or %difference (%D) should be ≤15% (or %recovery within ±15%).	Qualification is for all samples on both sides of the out-of-criteria calibration standards. If target compounds have 15%<%D≤90% with the response indicating a sensitivity decrease (or 10%≤%R<85%), qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If target compounds have %D>15% with the response indicating a sensitivity increase (or %R>115%), qualify positive results as estimated ("J") and use professional judgement to qualify "not-detected" results. If target compounds have %D>90% with the response indicating a sensitivity decrease (or %R<10%), qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Retention Time Windows (See Note #4 for additional information.)	All target compound retention times (RTs) should be within the established RT windows. RT windows should be estimated or defined by the laboratory as 3× the standard deviation of three non-sequential standards over a 72-hour period.	If the CCV RT windows are not within the specific RT windows, evaluate the chromatograms for false positives and false negatives. If a constant drift in RT is observed in the bracketing CCVs, the direction of the RT drift should be applied to the sample chromatograms.
Blanks (See Note #5 and Note #10 for additional information.)	Summarize all results greater than the method detection limit (MDL) present in the blanks. The highest positive result associated with a sample should be utilized for evaluation of contamination.	If a target compound is found in the blank but not in the associated sample(s), no action is required. If a sample result is ≤5× the blank result, qualify the positive result as "not detected" ("U*") and revise the MDL to the value of the positive result. If the positive result qualified "U*" is ≤RL, the RL should be used as reported. If the positive result qualified "U*" is >RL, the value of the positive result should be used as the revised RL. If a sample result is >5× the blank result, qualification is not required. If gross contamination exists (*i.e.*, saturated peaks on both GC columns), qualify the positive results as unusable ("R") due to interference.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Surrogates (See Note #6 for additional information.)	Use laboratory acceptance limits.	If samples are analyzed on two columns, samples should only be qualified if the out-of-criteria surrogate result is reported from the same column as the sample results. If the recoveries of one or more surrogates are > the laboratory's upper acceptance limit, qualify positive results as estimated ("J") and do not qualify "not-detected" results. If the recoveries of one or more surrogates are < the laboratory's lower acceptance limit but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If the recoveries of one or more surrogates are <10%, qualify positive results as estimated ("J") and qualify "not-detected" results as unusable ("UR").

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Use laboratory acceptance limits for recovery. For precision, use the criteria for Field/Laboratory Duplicates (next page).	Data should not be qualified due to %Rs (or RPDs calculated on %Rs) that are outside of criteria if the original concentration of a compound is 4× the spiking level for that compound. RPDs calculated using MS/MSD result can be used to evaluate precision. If the recovery is > the laboratory's upper acceptance limit, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" results. If the recovery is < the laboratory's lower acceptance limit but ≥10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as estimated ("UJ"). If the recovery is <10%, qualify the positive result in the native sample as estimated ("J") and qualify the "not-detected" result in the native sample as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify the positive result in the native sample as estimated ("J") and do not qualify "not-detected" result. If the precision criteria (see field duplicate usability criteria) are not met for non-spiked compounds, qualify the positive result as estimated ("J") and qualify the "not-detected" result as estimated ("UJ"). If a field duplicate of the native sample was collected and analyzed, the field duplicate sample should also be qualified if an MS/MSD recovery or RPD is outside of criteria (as stated above for the native sample).

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	Use laboratory acceptance limits for recovery. For precision, use the criteria for Field/Laboratory Duplicates (next page).	If the recovery > the laboratory's upper acceptance limit, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results. If the recovery < the laboratory's lower acceptance limit but ≥10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as estimated ("UJ"). If the recovery is <10%, qualify positive results in all associated samples as estimated ("J") and qualify "not-detected" results in all associated samples as unusable ("UR"). If the precision between recoveries exceeds the RPD criterion, qualify positive results in all associated samples as estimated ("J") and do not qualify "not-detected" results.
Field or Laboratory Duplicate (See Note #7 for additional information.)	Use QAPP-specified limits. (Use ½ the RL as a numerical value for any "not-detected" results in the RPD calculations).	If the criteria are not met, qualify positive results for the non-compliant compound in the original sample and its duplicate as estimated ("J") and qualify "not-detected" results as estimated ("UJ").
Percent Solids	Soil/sediment samples with less than 50% solid content require qualification.	If a soil/sediment sample has a percent solid content <50% but ≥10%, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). Use professional judgement if a soil/sediment sample has a percent solid content <10%.
Compound Quantitation (See Note #8 for additional information.)	Samples with results that exceed the instrument calibration range should be reanalyzed at a dilution.	If a target compound result exceeds the instrument calibration range, qualify positive results as estimated ("J"). Use professional judgement when evaluating sample reanalyses and dilutions. If criteria (see field duplicate usability) between the original sample results and the reanalysis sample results are not met, qualify positive results as estimated ("J") and qualify "not-detected" results as estimated ("UJ"). If a target compound result is <RL but ≥MDL, qualify positive results as estimated ("J").

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Quality Control Item	Usability Criteria	Action
System Performance (See Note #9 for additional information.)	Professional judgement should be used when assessing the degradation of system performance during analyses.	Use professional judgement to qualify the data if it is determined that system performance degraded during sample analyses.
Overall Assessment of Data	Assess overall quality of the data. Review available materials to assess the quality, keeping in mind the additive nature of the analytical problems.	Use professional judgement to determine the need to qualify data not qualified based on the QC previously discussed. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, include the assessment of the usability of the data within the given context.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

1. $$\%\ \text{breakdown for 4,4′ - DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{peak areas (DDT + DDE + DDD)}} \times 100$$

$$\%\ \text{breakdown for Endrin} = \frac{\text{Total Endrin degradation peak area (Endrin aldehyde + Endrin ketone)}}{\text{peak areas (Endrin + Endrin aldehyde + Endrin ketone)}} \times 100$$

Qualification Due to High 4,4′-DDT (or Endrin) Breakdown				
Column # / Met criteria?	If 4,4′-DDT (or Endrin):	And if 4,4′-DDD and/or 4,4′-DDE (or Endrin ketone and/or Endrin aldehyde):	Then flag 4,4′-DDT (or Endrin):	And flag **positives** for 4,4′-DDD and/or 4,4′-DDE (or Endrin ketone and/or Endrin aldehyde):
(1)/no (2)/yes	+ +	any +'s +'s or ND's	"J" column (1) OK column (2)	"JN" column (1) "N" column (2)
(1)/no (2)/yes	ND + > RL^+	any +'s +'s or ND's	ND "R"	"JN" column (1) "N" column (2)
(1)/no (2)/yes	ND + < RL^+	any +'s +'s or ND's	ND OK	"JN" column (1) "N" column (2)
(1)/no (2)/yes	+ +	all ND's +'s or ND's	*	NA
(1)/no (2)/yes	ND + or ND	all ND's +'s or ND's	ND OK	NA
(1)/no (2)/yes	+ or ND ND	+'s or ND's +'s or ND's	ND OK	OK
(1)/no (2)/no	ND + or ND	any +'s any +'s	ND "R"	"JN"
(1)/no (2)/no	+ +	any +'s any +'s	"J"	"JN"
(1)/no (2)/no	+ ND	all ND's any +'s	ND "R"**	NA
(1)/no (2)/no	+ +	all ND's all ND's	*	NA
(1)/no (2)/no	+ or ND ND	+'s or ND's all ND's	ND OK	NA

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

Where:

+ A peak was observed in the RT window for this pesticide on the corresponding GC column indicating a tentative identification for this pesticide. The positive result may quantitate to be below, at, or above the MDL.

ND Not Detected regardless of the MDL (flat baseline was observed in the area of the chromatogram where this compound would elute if it were truly present in the sample).

NA Not Applicable. Pesticide was not detected and only positive results are impacted.

* Although high breakdown was indicated by the associated standard on at least one column used for analysis, this positive result for 4,4′-DDT (or Endrin) has not been qualified because the breakdown components were not detected in the sample analysis on the noncompliant column(s). It is questionable, however, whether the peak(s) used for identification on the noncompliant column(s) truly represents 4,4′-DDT (or Endrin) because high breakdown was indicated by the associated standard. It is highly unusual not to detect the breakdown components in the presence of 4,4′-DDT (or Endrin).

** This "not-detected" result for 4,4′-DDT (or Endrin) has been qualified as unusable ("UR") because the breakdown components were observed in the sample analysis on this column on which high breakdown was indicated by the associated standard. However, it should be noted that the breakdown components were not detected in the sample analysis on the other column on which high breakdown was also indicated by the associated

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

standard. It is questionable whether the peak used for identification on this other column truly represents 4,4′-DDT (or Endrin) because high breakdown was indicated by the associated standard on this other column. It is highly unusual not to detect the breakdown components in the presence of 4,4′-DDT (or Endrin).

2. If the initial calibration curve %RSD>50%, the linearity of the first three initial calibration standards should be evaluated. If the first three initial calibration standards for the compound are linear (*i.e.*, r > 0.99), do not qualify "not-detected" results. If the first three initial calibration standards for the compound are not linear, qualify "not-detected" results as estimated ("UJ").

   Use professional judgement when evaluating the concentration intercept of a calibration curve. If the concentration intercept is positive, the samples should be evaluated for false positives. If the concentration intercept is negative, the sample should be evaluated for false negatives.

   Positive results should only be qualified if the results were reported from the out-of-criteria column. If samples are analyzed on two columns and an out-of-criteria initial calibration is reported on either column, the sample should be evaluated for tentative positive results. If a tentative positive result is observed on the compliant column, qualify "not-detected" results (laboratory should only report positive results that have been confirmed on a second column) as estimated ("UJ"). If an out-of-criteria initial calibration is reported on both columns, qualify "not-detected" results as estimated ("UJ") whether or not tentative positive results were observed.

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

3. If instrument instability (*i.e.*, several continuing calibration standards with compounds exhibiting both increasing and decreasing sensitivity throughout an analytical sequence) is observed in the analysis of sequential continuing calibration standards, "not-detected" results may be qualified as estimated ("UJ") due to instrument sensitivity of a continuing calibration standard response that is greater than the initial calibration standard response (increase in instrument sensitivity).

   If the continuing calibration verification standard is %D>15% in the direction of increased instrument sensitivity and it is determined that "not-detected" results should not be qualified, the data reviewer should note this within the QAR support documentation.

   Positive results should only be qualified if the results were reported for the out-of-criteria column. If samples are analyzed on two columns and an out-of-criteria CCV is reported on either column, the samples should be evaluated for tentative positive results. If a tentative positive result is observed on the compliant column, qualify "not-detected" results (laboratory should only report positive results that have been confirmed on a second column) as estimated ("UJ"). If an out of criteria CCV is reported on both columns, qualify "not-detected" results as estimated ("UJ") whether or not tentative positive results were observed.

4. Use professional judgement when evaluating sample chromatograms. If a RT shift is observed in an associated CCC and the sample chromatograms reveal peaks, use expanded RT windows and the surrogate shifts to evaluate for potential false positives and false negatives. If a possible false positive is observed, the reported positive sample

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

result for the target compounds outside of the RT window may replace the MDL/RL and the result may be qualified as "not-detected" ("U"), depending on professional judgment. If a possible false negative is observed, the potential positive result may be quantitated and added to the result field and may be qualified as tentative ("N"), depending on professional judgment.

If the chromatograms reveal peaks that interfere with potential detection of a targetcompound qualify the MDL/RL for "not-detected" results as estimated ("UJ") or unusable ("UR"), depending on the level of the interference. Qualify reported positive results for the target compound as unusable ("R") or raise the MDL and RL above the level of detection, depending on professional judgment.

5. The frequency of field/equipment/rinse blanks is determined during the sampling event. The results of a field/equipment/rinse blank should be applied to all samples collected on the same day, unless only one blank was collected for a several-day sampling event. In instances when more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant.

   Instrument blank contamination should be applied to samples bracketing the contaminated instrument blank. If a positive result for a target compound is detected on the first column and not on the second column, the positive results should be qualified as tentative in all associated samples ("N"). Use professional judgement to determine if the result should be qualified as "not-detected" ("U*").

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

6. The surrogate recovery limits do not apply to samples analyzed at greater than five-fold dilutions. Qualification of the data is not necessary if the surrogate is diluted beyond detection. Generally, a greater than five-fold dilution will affect the ability to even detect the surrogate. Write a comment in the QAR addressing the issue that sample-specific method performance based on surrogate recoveries could not be evaluated due to the dilution required for sample analysis.

7. Duplicate samples may be collected and analyzed as an indication of overall precision. Field duplicate analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates that measure only laboratory performance. Laboratory duplicate results and field duplicate results apply only to the original sample and the laboratory/field duplicate. Solid duplicate results will have greater variance than aqueous duplicate results.

8. If a sample result exceeds the instrument calibration range (lower dilution analysis) or is less than the RL (secondary dilution), do not utilize this result when comparing an original analysis and a diluted reanalysis.

   If the laboratory provides the dual-column results for samples and both columns are quantitative, evaluate the %D between the results reported for both columns. If the sample results are ≥5× RL and the %D is >40% but ≤90%, qualify positive results as estimated ("J"). If the sample results are ≥5× RL and the %D is >90%, qualify positive results as unusable ("R"). If sample results are <5× RL and the difference between

Notes for the Validation of Organochlorine Pesticide Data Generated by SW-846 Method 8081A

columns is >±2×RL, qualify results as estimated ("J") and qualify "not-detected" results as estimated ("UJ").

9. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

- high background levels or shifts in absolute RTs of internal standards
- excessive baseline rise at elevated temperature
- extraneous peaks
- loss of resolution
- peak tailing or peak splitting that may result in inaccurate quantitation

APPENDIX 37

GENERAL ELECTRIC COMPANY
HUDSON RIVER BASELINE MONITORING PROGRAM
ELECTRONIC DATA DELIVERABLE SPECIFICATIONS

Introduction

The purpose of this document is to describe the processing of the analytical data received from the laboratory and includes the required specifications of the electronic data deliverable (EDD) along with the field sample data import format.

File Format

All data from the laboratory must be stored in an ASCII file using a tab-delimited standard format. Maximum length of text fields is indicated in the parentheses under Column Datatype. If the information is less than the maximum length, do not pad the record with spaces.

Each record must be terminated with a carriage return/line feed (i.e., standard DOS text file). The file can be produced using any software with the capability to create ASCII files. Date is reported as MM/DD/YY (month/day/year) and time as HH:MM (hour:minute). Time uses a 24 hour clock, thus 3:30 p.m. will be reported as 15:30.

Five files are required: one each for field samples, laboratory samples, tests, results, and batches. The files must have valid DOS (8.3) filenames. The filename extensions are used to indicate the file type as follows:

*.FDW for field sample rows (**water column samples**)
*.FDF for field sample rows (**fish samples only**)
*.SMP for laboratory sample rows
*.TST for test rows
*.RES for result rows
*.BCH for batch rows

The field sample files (*.FDW and *.FDF) are required files that will originate from the field contractor. Since field data collection requirements are different for the water column and fish programs, there is a different EDD specification for each. Only **one** field sample file should be submitted by the field contractor depending on the type of samples collected (water column (*.FDW) or fish (*.FDF) samples). The filename for the field sample deliverable is defined as the date of the file's creation.

One additional field file (*.EVT) is required if the FDF field sample file is submitted. This file will contain all sampling event-specific information (e.g., location name, event date, weather conditions). In contrast, the FDF file discussed above will contain all sample-specific information (i.e., individual or composite fish) collected during any given event.

The 8-character portion filenames for the lab generated files must be the same for each group of four files. Filename conventions are defined as the sample delivery group. It is anticipated that all four files will be prepared and loaded into the database together in one group.

Data Integrity Rules

If a field is to be considered part of the primary key of a table, it is indicated below by the presence of "PK" in the *PK* column. The combination of values in each primary key must be unique within the file. Also, referential integrity must be enforced between tables. That is, the values of sys_sample_code present in the Result and Test tables must also be present in the Sample table.

The key fields in the test table may appear complicated, so they are discussed further here. By default, only two fields are defined as part of a unique key: sys_sample_code and lab_anl_method_name. This means that each combination of sample ID and lab method can be used to uniquely define a lab test event. For this project, we are going to store retests or re-dilutions as separate test events. In order to achieve this, include analysis_date and analysis_time as part of the unique key of test. This will allow multiple occurrences of a given combination of sample ID and lab method, provided that analysis date and time is different for each retest. Other common situations are discussed below. The fields that are included as part of the unique key on test are indicated below by the presence of "PK" in the *PK* column. These fields are part of the uniqueness constraint needed by the data management user, so they must be required in the EDD.

A. The data management users intend to import the full suite of test level information, including column-number and analysis-time. **Both the column number and analysis time are required for this project.**

B. Some metal analyses can be done on unfiltered samples (to obtain total concentrations) or can be done on filtered samples (to get dissolved concentrations). The data management users need to use the same method name value for both of these tests, and therefore require another field to distinguish between these test types. **Population of the total or dissolved field is required for this project.**

Null Format

Many fields are optional, and the list of valid values may be defined in a project or lab specific manner as determined by the laboratory and project manager. When a field is <u>not</u> listed as required, this means that a null or blank may be appropriate. However, the blank value must still be surrounded by tabs. In other words, the number of fields is always the same, whether or not the fields include data is optional.

OPL Naming Convention of Field Samples

Field samples being submitted to the data management system follow the standard Organization, Project, Location (OPL) naming structure. As an example, a water column field sample ID of 'RTN-040101-SW-' designates:

Organization = RTN
Project = 040101
Location = SW

The field sample ID describes a water sample collected as part of the routine monitoring program (RTN) on January 1, 2004 (040101) at the Stillwater monitoring station (SW). An additional code is added after the location to indicate if a location is a composite (C) or transect point (T) location, followed by a number indicating the composite ID number, or point along the transect, to complete the unique field sample ID (C01, T01, T02, etc.). All field samples submitted to the analytical laboratories (included in the .FDW file) will be composite (C) samples; transect (T) ID's will only be used for recording surface water quality (SWQ) parameters measured at each point along the transect (not included in the .FDW file). The SWQ measurements are linked to the composite sample ID based on the OPL portion of the field sample ID.

There are to be no dashes used within in the OPL naming convention. For example, the sample collection date should be characterized as 040101 and not 04-01-01. There is to be no deviation in this regard due to system requirements.

The contractor is responsible to let the lab know the proper Organization, Project, Location (OPL) structure to append to the field sample id on the chain of custody. If the field on the chain of custody is too small for the new sample naming convention, please place the proper OPL codes in the comments field so the lab can append the information to the field sample name. If this information is not present the EDD will fail EDD checks and will be returned to the data generator for corrections.

Lab QC samples, while having no real sampling location, should also follow the OPL naming convention.

Lab QC samples will use the concatenation of LABQC and the SDG for the location code, while maintaining the same organization and project codes. Use the internal laboratory sample ID at the end to identify the sample. For example a method blank QC sample (A3910) for the project mentioned above would look like RTN-040101-LABQC[*SDG*]-A3910.

Examples

Below are examples of sample types to be used in the project, showing when fields need to be populated and when it is not necessary to populate fields.

QC fields in a normal field sample (i.e., Sample_type_code = ENV)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that all QC fields are blank.

cas_rn	Result value	QC original conc	QC spike added	QC spike measured	QC spike recovery	QC dup original conc	QC dup spike added	QC dup spike measured	QC dup spike recovery
93-76-5	1.56								
94-75-7	3.17								
94-82-6	2.31								

QC fields in a normal field sample with surrogates (i.e., Sample_type_code = ENV)

The following table shows a subset of the fields in the result file for a normal field sample. Notice that QC fields are blank except on surrogate rows.

cas_rn	Result value	Result unit	Result type code	QC original conc	QC spike added	QC spike measured	QC spike recovery
93-76-5	1.56	mg/l	TRG				
94-75-7	3.17	mg/l	TRG				
PHEN2F		mg/l	SUR		12.5	12.9	103

QC fields in a matrix spike (i.e., Sample_type_code = MS)

The following table shows some of the fields in the result file for a matrix spike sample. Notice that all "dup" QC fields are blank, and that the result_value field is not needed. Also, the qc_rpd field would be blank for these rows.

cas_rn	Result value	QC original conc	QC spike added	QC spike measured	QC spike recovery	QC dup original conc	QC dup spike added	QC dup spike measured	QC dup spike recovery
93-76-5		1.56	4.18	5.36	90.9				
94-75-7		3.17	4.18	7.15	95.2				
94-82-6		2.31	4.22	5.66	79.3				

QC fields in a matrix spike duplicate (i.e., Sample_type_code = SD)

The following table shows a subset of the fields in the result file for a matrix spike duplicate sample. Notice that all "dup" QC fields are completed, and that the result_value field is not needed. **Also, the qc_rpd field would be completed for these rows.**

cas_rn	Result value	QC original conc	QC spike added	QC spike measured	QC spike recovery	QC dup original conc	QC dup spike added	QC dup spike measured	QC dup spike recovery
93-76-5						1.56	4.23	5.70	97.8
94-75-7						3.17	4.23	7.62	105
94-82-6						2.31	4.13	5.33	73.1

QC fields in an LCS (i.e., laboratory control sample, blank spike, Sample_type_code = LCS)
The following table shows a subset of the fields in the result file for an LCS sample. **The qc_rpd field would be blank for these rows.**

cas_rn	Result value	QC original conc	QC spike added	QC spike measured	QC spike recovery	QC dup original conc	QC dup spike added	QC dup spike measured	QC dup spike recovery
93-76-5			5.00	5.26	105				
94-75-7			1.00	1.02	102				
94-82-6			12.5	12.9	103				

Retests

The following table shows how to report retests in an example where a sample was retested at dilution. The end user would see the first two constituents (75-25-2, and 67-66-3) in the initial test, and constituent 95-95-4 in the diluted retest. The other results would be "turned off" by setting the reportable_result field to "No".

Test_type	cas_rn	result_value	reportable_result
initial	75-25-2	1.2	Yes
initial	67-66-3	3.4	Yes
initial	95-95-4	100	No
retest	75-25-2	0	No
retest	67-66-3	0	No
retest	95-95-4	78.3	Yes

Second Columns

The following table shows how to report first and second column confirmation results. The end user would see the first and third constituents (75-25-2, and 95-95-4) as "primary" in the first column, and constituent 67-66-3 as "primary" in the second column. The other results would be "turned off" by setting the reportable_result field to "No".

column_number	cas_rn	result_value	reportable_result
1C	75-25-2	1.2	Yes
1C	67-66-3	3.4	No
1C	95-95-4	5.6	Yes
2C	75-25-2	1.3	No
2C	67-66-3	3.7	Yes
2C	95-95-4	5.4	No

Units

Units are to be reported consistently for the duration of the project. The result_unit field is required to be reported as specified in the reference values. Associated measurements (i.e., reporting detection limit, method detection limit) should be reported consistently with the result units.

Surface Water Quality (SWQ) Parameter Measurements

For this project, water samples submitted for analysis will be point samples taken from the flow centroid or composite samples taken along a transect. At each sampling point, SWQ parameters (temperature, pH, specific conductivity, dissolved oxygen, and turbidity) will be measured. Composite and centroid samples are the only samples that will have analytical tests requested, and should therefore be the only samples included in the .FDW file submitted by the field contractor. SWQ parameters will be collected using a probe equipped with a datalogger. Prior to sampling, the datalogger will be pre-programmed with the appropriate field sample IDs (consistent with the OPL naming convention discussed above). ASCII files containing the results from the data logger will be uploaded to a computer and submitted by the field contractor; these SWQ results will then be directly uploaded to the data management system.

Field Sample Import Format (*.FDW) - Water Column Samples

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value, including blanks and duplicates. This field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: the first sample on the chain would be COC042602-001, second sample would be COC042602-002, etc.). This file should only contain field samples, including field blanks, equipment blanks, and field duplicates. This table should not include laboratory samples. **Required.**
2	sample_name	Text(30)		required		Unique field sample ID. Each sample must have a unique value. **The Organization, Project, Location naming convention, as described on page 2, must be followed.**
3	sample_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of sample matrix. For example, soil samples must be distinguished from ground water samples. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g., TCLP leachates), so this field is required at the sample level. For valid value list, consult the reference values supplied for this project.
4	sample_type_code	Text(10)		required	Yes	Code which distinguishes between different types of samples. For valid value list, consult the reference values supplied for this project.
5	sample_source	Text(10)		required	Yes	This field identifies where the sample came from, either **Field** or **Lab**. In this import, this should always be **Field**.
6	parent_sample_code	Text(20)		required if applicable		Must be blank for normal field samples. The value of "sys_sample_code" that uniquely identifies the sample that was the source of this sample.
7	sample_date	Date		required		Date sample was collected (in MM/DD/YY format).
8	sample_time	Time		required		Time of sample collection in 24-hr (military) HH:MM format.
9	location_name	Text(30)		required		Name of sampling location (e.g.,

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
						Stillwater). For valid value list, consult the reference values supplied for this project.
10	start_depth	Text(5)				Beginning depth (top) of sample.
11	end_depth	Text(5)				Ending depth (bottom) of sample.
12	depth_unit	Text(15)				Unit of measurement for the sample begin and end depths.
13	test_requested	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for this project.
14	preservative_chemical	Text(50)		required if applicable		If sample is preserved, enter type of preservative in this field (use chemical symbol). If sample is unpreserved, this field must be null.
15	preservative_temperature	Text(5)		required if applicable		Temperature to which sample is cooled in the format of number and unit without the degree symbol (i.e. if temp. is 4 degrees Celsius it should be reported as “4C” not “4°C”).
16	chain_of_custody	Text(15)		required		Chain of custody identifier. A single sample may be assigned to only one chain of custody.
17	sent_to_lab_date	Date		required		Date sample was sent to lab (in MM/DD/YY format for EDD). Not included in the laboratory EDD.
18	sampler_initials	Text(5)				Initials of sample processing custodian.
19	num_containers	Integer		required		Number of sample containers.
20	sample_archived	Yes/No			Yes	Indicates if a sample was archived.
21	epa_split	Yes/No			Yes	Indicates if the sample was chosen as a split by the USEPA.
22	tat_expected	Double		required		Expected turn-around-time in number of business days for laboratory results.
23	sample_type	Text(20)		required	Yes	Indicates type of water sample collected (e.g., center channel, transect composite, E-W composite).
24	comments	Text(255)				General comments or field observations at time of sample collection (optional).
25	matrix_spike_yn	Yes/No		required	Yes	“Y” if the sample was chosen for matrix spike analysis, “N” if not chosen.
26	matrix_spike_dup_yn	Yes/No		required	Yes	“Y” if the sample was chosen for matrix spike duplicate analysis, “N” if not chosen.
27	lab_dup_yn	Yes/No		required	Yes	“Y” if the sample was chosen for lab duplicate analysis, “N” if not chosen.
28	partition_parent_sample	Text(30)		required if applicable		Field sample ID of parent sample for particulate/dissolved phase study samples.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
29	volume	Text(15)		required	Yes	Indicates if sample is routine or high-volume sample for PCB analysis (e.g., ROUTINE, HIGH).
30	t1	Text(10)				Distance from 0 (west shore) for EDI location 1, in feet.
31	t2	Text(10)				Distance from 0 (west shore) for EDI location 2, in feet.
32	t3	Text(10)				Distance from 0 (west shore) for EDI location 3, in feet.
33	t4	Text(10)				Distance from 0 (west shore) for EDI location 4, in feet.
34	t5	Text(10)				Distance from 0 (west shore) for EDI location 5, in feet.
35	t6	Text(10)				Distance from 0 (west shore) for EDI location 6, in feet.

Fish Sampling Event Data Format (*.EVT)

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sampling_event_id	Text(15)	PK	required		Unique sampling event ID. Used to link fish sample data with event data.
2	station_id	Text(5)		required	Yes	Sampling location abbreviation.
3	station_name	Text(50)		required	Yes	Full location name.
4	sample_collect_method	Text(5)		required	Yes	Indicates fish sample collection method (e.g., NET, ES, ANG).
5	event_start_date	Date		required		Date sampling event initiated (in MM/DD/YY format).
6	event_start_time	Time		required		Beginning time of sampling event in 24-hr (military) HH:MM format.
7	event_end_date	Date		required		Date sampling event completed (in MM/DD/YY format).
8	event_end_time	Time		required		Ending time of sampling event in 24-hr (military) HH:MM format.
9	start_northing	Text(20)		required		Northing coordinate of upstream end of sampling location (NY state plane east NAD83).
10	start_easting	Text(20)		required		Easting coordinate of upstream end of sampling location (NY state plane east NAD83).
11	end_northing	Text(20)		required		Northing coordinate of downstream end of sampling location (NY state plane east NAD83).
12	end_easting	Text(20)		required		Easting coordinate of downstream end of sampling location (NY state plane east NAD83).
13	coordinate_unit	Text(15)		required		Unit of measurement for the northing and easting coordinates. The accepted value is ‘ft’ for feet.
14	water_temp	Text(5)				Temperature (in degrees C) of water at beginning of sampling event.
15	turbidity	Text(10)				Turbidity of water at beginning of sampling event.
16	turbidity_units	Text(5)				Unit of measurement for turbidity. The accepted value is ‘NTU’.
17	conductivity	Text(10)				Conductivity of water at beginning of sampling event.
18	conductivity_units	Text(5)				Unit of measurement for conductivity. The accepted value is ‘mS/cm’.
19	weather	Text(100)				Weather conditions during sampling event.
20	comments	Text(255)				General comments or field observations (optional).
21	sampler_initials	Text(5)				Initials of sampler.

Field Sample Import Format (*.FDF) - Fish Samples

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value, including blanks and duplicates. This field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: the first sample on the chain would be COC042602-001, second sample would be COC042602-002, etc.). This file should only contain field samples, including field blanks, equipment blanks, and field duplicates. This table should not include laboratory samples. **Required**
2	sample_name	Text(30)		required		Unique field sample ID. Each sample must have a unique value. **The Organization, Project, Location naming convention, as described on page 2, must be followed.**
3	sample_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of sample matrix. For example, soil samples must be distinguished from ground water samples. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g. TCLP leachates), so this field is required at the sample level. For valid value list, consult the reference values supplied for this project.
4	sample_type_code	Text(10)		required	Yes	Code which distinguishes between different types of samples. For valid value list, consult the reference values supplied for this project.
5	sample_source	Text(10)		required	Yes	This field identifies where the sample came from, either **Field** or **Lab**. In this import, this should always be **Field**.
6	parent_sample_code	Text(20)		required if applicable		Must be blank for normal field samples. The value of "sys_sample_code" that uniquely identifies the sample that was the source of this sample.
7	sample_date	Date		required		Date sample was collected (in MM/DD/YY format).
8	sample_time	Time		required		Time sample was collected in 24-hr (military) HH:MM format.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
9	test_requested	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for this project.
10	preservative_chemical	Text(50)		required if applicable		If sample is preserved, enter type of preservative in this field (use chemical symbol). If sample is unpreserved, this field must be null.
11	preservative_temperature	Text(5)		required if applicable		Temperature to which sample is cooled in the format of number and unit without the degree symbol (i.e., if temp. is 4 degrees Celsius it should be reported as "4C" not "4°C").
12	chain_of_custody	Text(15)		required		Chain of custody identifier. A single sample may be assigned to only one chain of custody.
13	sent_to_lab_date	Date		required		Date sample was sent to lab (in MM/DD/YY format for EDD). Not included in the laboratory EDD.
14	num_containers	Integer		required		Number of sample containers.
15	sample_archived	Yes/No				Indicates if a sample was archived.
16	epa_split	Yes/No				Indicates if the sample was chosen as a split by the USEPA.
17	tat_expected	Double		required		Expected turn-around-time in number of business days for laboratory results.
18	composite_yn	Yes/No		required	Yes	Indicates if sample is a composite.
19	num_in_composite	Integer		required if applicable		If composite sample, indicates number of fish in composite.
20	species_code	Text(20)		required	Yes	NYSDEC abbreviations for species of fish sample. For valid value list, consult the reference values supplied for this project.
21	total_length	Text(10)		required		Total length of fish sample for individuals (nearest mm).
22	length_unit	Text(5)		required		Unit of measurement for length. The accepted value is 'mm' for millimeters.
23	weight	Text(10)		required		Total weight of fish sample for individuals (nearest 0.1 grams).
24	weight_unit	Text(5)		required		Unit of measurement for weight. The accepted value is 'g' for grams.
25	sex	Text(5)			Yes	Sex of fish sample ('M', 'F', or 'U').
26	age	Text(5)				Age of individual fish (not determined in field; hold space to be filled in later if desired).
27	sample_prep	Text(20)		required	Yes	Indicates type of sample collected (e.g., fillet, offal, whole body).
28	general_description	Text(255)				General comments or field observations at time of sample collection (optional).

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
29	matrix_spike_yn	Yes/No		required	Yes	"Y" if the sample was chosen for matrix spike analysis, "N" if not chosen.
30	matrix_spike_dup_yn	Yes/No		required	Yes	"Y" if the sample was chosen for matrix spike duplicate analysis, "N" if not chosen.
31	lab_dup_yn	Yes/No		required	Yes	"Y" if the sample was chosen for lab duplicate analysis, "N" if not chosen.
32	archive_only	Yes/No		required	Yes	'Y" if tissue was collected but not submitted for analysis, "N" if submitted for analysis.
33	sampling_event_id	Text(15)		required		Event ID for fish sample. Used to link event information to sample information.
34	cpue_id	Text(30)				Corresponding ID from "catch per unit effort" sampling.

Sample Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (i.e., COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. This table should **only** contain laboratory - generated samples, including lab blanks, blank spikes, matrix spikes, matrix spike duplicates, and laboratory replicates. This table should not include field samples. **Required.**
2	lab_sample_id	Text(60)		required		Laboratory sample identifier. **The Organization, Project, Location naming convention, as described on page 2, must be followed. Required.**
3	sample_type_code	Text(10)		required	Yes	Code which distinguishes between different types of sample. For valid value list, consult the reference values supplied for the project.
4	sample_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of sample matrix. For example, soil samples must be distinguished from ground water samples. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g., TCLP leachates), so this field is required at the sample level. For valid value list, consult the reference values supplied for the project.
5	sample_source	Text(10)		required	Yes	Must be "Lab" for internally generated laboratory QC samples. For example, a matrix spike duplicate sample would be a "Lab" sample.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
6	parent_sample_code	Text(20)		required where applicable		The value of "sys_sample_code" that uniquely identifies the sample that was the source of this sample. For example, the value of this field for a laboratory replicate sample would identify the normal sample of which this sample is a replicate (same sys_sample_code as replicate without the "LR" designation). Required in the laboratory EDD for all laboratory "clone" samples (e.g., spikes and duplicates). Must be blank for samples that have no parent (e.g., lab blanks and lab control samples). This field must be filled out for those samples which have "parents."
7	Comment	Text(255)				Sample comments as necessary (optional).
8	sample_date	Date				Must be blank for laboratory generated samples. Date of sample collection in MM/DD/YY format. **Will be a blank field for this project.**
9	sample_time	Time				Must be blank for laboratory generated samples. Time of sample collection in 24-hr (military) HH:MM format. **Will be a blank field for this project.**
10	standard_solution_source	Text(20)				Relevant only for laboratory-generated samples. Textual description of the source of standard solutions as needed for certain laboratory samples (e.g., LCS).

Test Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. **Required.**
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the ref values supplied for this project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/DD/YY format. Must refer to the beginning of the analysis for this project.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:MM format. Must refer to the beginning of the analysis for this project. Note that this field, combined with the "analysis_date" field is used to distinguish between retests and reruns. Please ensure that retests have "analysis_date" and/or "analysis_time" different from the original test event (and fill out the test_type field as needed).
5	total_or_dissolved	Text(1)	PK	required	Yes	It must be either "T" for total (metal) concentration, "D" for dissolved or filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Required, it must be either "1C" for first column analyses, "2C" for second col-umn analyses, or "NA" for analyses for which neither "1C" nor "2C" is applic-able. If any "2C" tests are report-ed, then there must be corresponding "1C" tests present also. Also, laboratories will be reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	lab_matrix_code	Text(10)		required	Yes	Code which distinguishes between different types of lab sample matrix. The matrix of the sample as analyzed may be different from the matrix of the sample as retrieved (e.g., TCLP leachates). Valid values include “W” and “S”.
9	analysis_location	Text(2)		required	Yes	Must be either "FI" for field instrument or probe, "FL" for mobile field laboratory analysis, or "LB" for fixed-based laboratory analysis.
10	basis	Text(10)		required	Yes	It must be either "Wet" for wet-weight basis reporting, "Dry" for dry-weight basis reporting, or "NA" for tests for which this distinction is not applicable.
11	dilution_factor	Text(4)		required		Effective test dilution factor.
12	prep_method	Text(35)		required if applicable	Yes	Laboratory sample preparation method name or description. For valid values consult the reference list supplied for the project.
13	prep_date	Date		required if applicable		Date of sample preparation in MM/DD/YY format. Must refer to the end of the prep for this project.
14	prep_time	Time		required if applicable		Time of sample preparation in 24-hr (military) HH:MM format. Must refer to the end of the prep for this project.
15	leachate_method	Text(15)		required if applicable		Laboratory leachate generation method name or description. A list of valid method names is not required for the laboratory EDD unless otherwise specified by the project manager.
16	leachate_date	Date		required if applicable		Date of leachate preparation in MM/DD/YY format. Must refer to the end of the leachate for this project.
17	leachate_time	Time		required if applicable		Time of leachate preparation in 24-hr (military) HH:MM format. Must refer to the end of the leachate for this project.
18	lab_name_code	Text(10)		required		Unique identifier of the laboratory. Must be consistent throughout the project.
19	data_package_level	Text(10)		required	Yes	Data package level. Values are “A”, “B”, or “AB”.
20	lab_sample_id	Text(20)		required		Laboratory sample identifier.
21	percent_moisture	Text(5)		required		Percent moisture of the sample portion used in this test; this value may vary from test to test for any sample. Numeric format is "NN.MM", i.e., 70.1% could be reported as "70.1" but not as "70.1%".
22	subsample_amount	Text(14)		required		Amount of original sample used in sample preparation.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
23	subsample_amount_ unit	Text(15)		required		Unit of measurement for subsample amount.
24	analyst_name	Text(30)				Name or initials of laboratory analyst. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
25	instrument_id	Text(50)				Instrument identifier. This is an optional field for the laboratory EDD unless otherwise specified by the project manager.
26	sample_receipt_date	Date		required		Must be blank for laboratory generated samples. Date of sample collection in MM/DD/YY format.
27	sample_receipt_time	Time		required		Must be blank for laboratory generated samples. Time of sample collection in 24-hr (military) HH:MM format.
28	sample_delivery_group	Text(10)		required		Sample delivery group.
29	Comment	Text(255)				Comments about the test as necessary.
30	final_volume	Text(15)		required if applicable		The final amount/volume of the sample, extract, or digestate after sample preparation.
31	final_volume_unit	Text(15)		required if applicable		The unit of measure that corresponds to the final volume.

Result Import Format

#	Attribute Name	Type	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a sequential three digit number that is typed on the Chain-of-Custody to the left of each sample (ex: COC042602-001), followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. **Required.**
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for the project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/DD/YY format. Must refer to the beginning of the analysis for this project.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:MM format. Must refer to the beginning of the analysis for this project. Note that this field, combined with the "analysis_date" field is used to distinguish between retests and reruns. Please ensure that retests have "analysis_date" and/or "analysis_time" different from the original test event (and fill out the test_type field as needed).
5	total_or_dissolved	Text(1)	PK	required	Yes	It must be either "T" for total (metal) concentration, "D" for dissolved or filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	Required, it must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable. If any "2C" tests are reported, then there must be corresponding "1C" tests present. Also, laboratories are reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table.

#	Attribute Name	Type	PK	Required	Ref. Value?	Attribute Definition
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	cas_rn	Text(15)	PK	required	Yes	Chemical Abstracts Registry Number for the parameter if available. Otherwise consult the reference values supplied for this project.
9	chemical_name	Text(60)		required	Yes	Chemical name is used only in review of EDD. For valid value list, consult the reference values supplied for the project. **Required.**
10	result_value	Text(20)		required where applicable		Analytical result reported at the project specified number of significant digits. Must be blank for non-detects.
11	result_error_delta	Text(20)				Error range applicable to the result value; typically used only for radiochemistry results.
12	result_type_code	Text(10)		required	Yes	Must be either "TRG" for a target or regular result, and "SUR" for surrogates.
13	reportable_result	Text(10)		required	Yes	Must be either "Yes" for results which are considered to be reportable, or "No" for other results. This field has many purposes. For example, it can be used to distinguish between multiple results where a sample is retested after dilution. It can also be used to indicate which of the first or second column result should be considered primary. The proper value of this field in both of these two examples should be provided by the laboratory (only one result should be flagged as reportable).
14	detect_flag	Text(2)			Yes	Must be either "Y" for detected analytes or "N" for non-detects.
15	lab_qualifiers	Text(7)		required	Yes	Qualifier flags assigned by the laboratory. For valid value list, consult the reference values supplied for the project.
16	organic_yn	Yes/No		required	Yes	Must be either "Y" for organic constituents or "N" for inorganic constituents.
17	method_detection_limit	Text(20)		required		Method detection limit. Required for all results for which such a limit is appropriate.
18	reporting_detection_limit	Text(20)		required		Detection limit that reflects conditions such as dilution factors and moisture content. Required for all results for which such a limit is appropriate.
19	quantitation_limit	Text(20)		required		Concentration level above which results can be quantified with confidence. It must reflect conditions such as dilution factors and moisture content. Required for all results for which such a limit is appropriate.

#	Attribute Name	Type	PK	Required	Ref. Value?	Attribute Definition
20	result_unit	Text(15)		required if applicable	Yes	Units of measurement for the result. For valid value list, consult the reference values supplied for the project.
21	detection_limit_unit	Text(15)		required		Units of measurement for the detection limit(s).
22	tic_retention_time	Text(8)				Retention time in seconds for tentatively identified compounds. TICs will not be used on this project.
23	result_comment	Text(255)				Result specific comments.
24	qc_original_conc	Text(14)		required where applicable		The concentration of the analyte in the original (unspiked) sample. This field is required for matrix spikes and not necessary for surrogate compounds or LCS samples (where the original concentration is assumed to be zero). If original (unspiked) sample is a non-detect, then populate this field with a "0" as opposed to the detection limit. For matrix spikes, if using an original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit original sample result, as opposed to "0".
25	qc_spike_added	Text(14)		required where applicable		The concentration of the analyte added to the original sample. Required for matrix spikes, surrogate compounds, and LCSs.
26	qc_spike_measured	Text(14)		required where applicable		The measured concentration of the analyte. Use zero for spiked compounds that were not detected in the sample. Required for matrix spikes, surrogate compounds, and LCSs.
27	qc_spike_recovery	Text(14)		required where applicable		The percent recovery calculated. Always required for spikes, surrogate compounds, and LCSs. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
28	qc_dup_original_conc	Text(14)		required where applicable		The concentration of the analyte in the original sample. Is required for matrix spike duplicates and lab replicates only. If original sample is a non-detect, then populate this field with a "0" as opposed to the detection limit. For matrix spike duplicates, if using an original sample result that is less than the reporting limit for background correction, then populate this field with the below reporting limit original sample result, as opposed to "0".
29	qc_dup_spike_added	Text(14)		required where applicable		The concentration of the analyte added to the original sample. Required for matrix spike duplicates.
30	qc_dup_spike_measured	Text(14)		required		The measured concentration of the analyte

#	Attribute Name	Type	PK	Required	Ref. Value?	Attribute Definition
				where applicable		in the duplicate (for background corrected matrix spike duplicates). Use zero for spiked compounds that were not detected in the sample. Required for matrix spike duplicates and lab replicates.
31	qc_dup_spike_recovery	Text(14)		required where applicable		The duplicate percent recovery calculated. Always required for spike or LCS duplicates, surrogate compounds, and any other spiked and duplicated sample. Also complete the qc_spike_recovery field. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
32	qc_rpd	Text(8)		required where applicable		The relative percent difference calculated. Required for duplicate samples as appropriate. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
33	qc_spike_lcl	Text(8)		required where applicable		Lower control limit for spike recovery. Required for spikes, spike duplicates, surrogate compounds, LCS and any spiked sample. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
34	qc_spike_ucl	Text(8)		required where applicable		Upper control limit for spike recovery. Required for spikes, spike duplicates, surrogate compounds, LCS and any spiked sample. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
35	qc_rpd_cl	Text(8)		required where applicable		Relative percent difference control limit. Required for any duplicated sample. Report as percentage multiplied by 100 (e.g., report "120%" as "120").
36	qc_spike_status	Text(10)		required where applicable		Used to indicate whether the spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank. Required for matrix spikes, surrogate compounds, and LCSs.
37	qc_dup_spike_status	Text(10)		required where applicable		Used to indicate whether the duplicate spike recovery was within control limits. Use the "*" character to indicate failure, otherwise leave blank. Required for any spiked and duplicated sample.
38	qc_rpd_status	Text(10)		required where applicable		Used to indicate whether the relative percent difference was within control limits. Use the "*" character to indicate failure, otherwise leave blank. Required for any duplicated sample.

Batch Import Format

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
1	sys_sample_code	Text(25)	PK	required		Unique sample identifier. Each sample must have a unique value, including spikes and duplicates. Laboratory QC samples must also have unique identifiers. For matrix spike, matrix spike duplicate, and laboratory replicate samples, this field must be populated as follows: COC#, which is "COC" followed by a number, then a dash (-), then the Item#, which is a three digit number that is typed on the Chain-of-Custody to the left of each sample, followed by "MS" for matrix spike, "SD" for matrix spike duplicate, or "LR" for laboratory replicate. **Required.**
2	lab_anl_method_name	Text(35)	PK	required	Yes	Laboratory analytical method name or description. For valid value list, consult the reference values supplied for this project.
3	analysis_date	Date	PK	required		Date of sample analysis in MM/DD/YY format. May refer to either beginning or end of the analysis long as it is consistent throughout the project.
4	analysis_time	Time	PK	required		Time of sample analysis in 24-hr (military) HH:MM format. May refer to either beginning or end as long as it is consistent throughout the project. Note that this field, combined with the "analysis_date" field is used to distinguish between retests and reruns. Please ensure that retests have "analysis_date" and/or "analysis_time" different from the original test event (and fill out the test_type field as needed).
5	total_or_dissolved	Text(1)	PK	required	Yes	It must be either "T" for total (metal) concentration, "D" for dissolved or filtered (metal) concentration, or "N" for organic (or other) constituents for which neither "total" nor "dissolved" is applicable.
6	column_number	Text(2)	PK	required	Yes	If required, then it must be either "1C" for first column analyses, "2C" for second column analyses, or "NA" for analyses for which neither "1C" nor "2C" is applicable. If any "2C" tests are reported, then there must be corresponding "1C" tests present. Also, laboratories will be reporting which of the two columns is to be considered "primary". This distinction is handled by the "reportable_result" field in the result table.

#	Attribute Name	Column Datatype	PK	Required	Ref. Value?	Attribute Definition
7	test_type	Text(10)	PK	required	Yes	Type of test. Valid values include "initial", "reextract", and "reanalysis".
8	test_batch_type	Text(10)	PK	required	Yes	Lab batch type. Valid values include "Prep", "Analysis", and "Leach". Additional valid values may optionally be provided by the project manager. This is a required field for all batches.
9	test_batch_id	Text(20)		required		Unique identifier for all lab batches. Must be unique within a database. For example, the same identifier can not be used for a prep batch and an analysis batch.

APPENDIX 38

OBJECTIVE

This Standard Operating Procedure (SOP) describes the requirements for the data packages that will be generated as part of the Baseline Monitoring Program (BMP). This SOP applies to the contractor(s) involved in analytical data generation and reporting. All data packages generated for the BMP must be provided in an Adobe Acrobat (.PDF) file format. The laboratory will be notified of the samples that will undergo data validation. For these samples, the laboratory will be required to generate hard copy data packages as well as the Adobe Acrobat (.PDF) file format.

SECTION A-9 DATA PACKAGE DELIVERABLES

The following sections describe in detail the types of data packages designed for the Baseline Monitoring Program. These details are provided to allow several participating laboratories to produce data packages that are similar in format, order of presentation, and content. The data packages detailed in Section A-9.1 have been developed based on deliverables specified in the US EPA Contract Laboratory Program Statement of Work (CLP SOW). The CLP SOW has additional details concerning data packages that are specific to the CLP analyses. The most recent Statement of Work should be referenced for details concerning CLP-style data packages. Note: the summary forms provided in these data packages should be in similar format and content to the Contract Laboratory Program (CLP) forms listed (as references) next to the form title. These CLP forms references are only provided as guidance on content and format and should be modified by the laboratory to meet specific method requirements. Section A-9.2 provides details concerning specific contents of the data deliverables described in Section A-9.1.

The data package deliverables are categorized into two distinct levels as follows:

Level A - Case Narrative, analytical results, and Chain-of-Custody Records for the sample delivery group (SDG).

Level B - Fully documented data package.

The Level A data package is a basic "results-only" style of data package that includes a cover letter, SDG narrative, field Chain-of-Custody Records, analytical results summaries, and a glossary of qualifier codes. The Level B package resembles the information required by the CLP SOW. This type of package includes all information provided in Level A package but also includes summary forms for quality control procedures and all sample and quality control raw data to support the results reported.

A-9.1 Data Package Contents and Order of Presentation

The laboratory will be required to submit supporting documentation for the reported analytical results. The supporting documentation and the analytical results will be reported in one of two data package delivery categories. The categories are defined below. The data package deliverables must be submitted in the order in which the deliverables appear in the text. The laboratory need not include the documentation for any fraction not required for an SDG.

A-9.1.1 General Format for Level B Deliverables

For some analyses, Level B Sample Data Package deliverables may be requested. A Level A Data Package will also be required with the Level B package as a summary package.

The Level B Sample Data Package shall include data for analyses of all samples in one SDG, including field samples, reanalyses, secondary dilutions, blanks, laboratory control samples, matrix spikes, matrix spike duplicates, and/or laboratory duplicates. The complete Sample Data Package is divided into the units as described below. Units for each analytical fraction have been detailed. If the analysis of that fraction was not required for samples in the SDG, the fraction-specific unit is not a required deliverable. The Sample Data Package must be complete before submission and must be consecutively paginated. The Sample Data Package will be arranged in the following order:

A) Cover Letter/Letter of Transmittal signed by the laboratory manager.

B) Title Page

C) Table of Contents

D) Sample Delivery Group (SDG) Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name; SDG number; GE sample identifications; laboratory sample numbers; and detailed documentation of any quality control, sample, shipment, and/or analytical problems encountered in processing (preparing and analyzing) the samples reported in the data package. A glossary of qualifier codes used in the SDG must also be provided.

The laboratory must also include any technical and administrative problems encountered, corrective actions taken and method of resolution, and an explanation of all flagged edits (i.e., exhibit edits) on quantitation reports.

Additionally, the SDG Narrative must be signed and dated by the laboratory manager.

E) Field and Internal (Laboratory) Chain-of-Custody Records and Sample Receipt Documentation Log

Copies of both the external and internal Chain-of-Custody Records for all samples within the SDG must be included in the deliverables. A description of the condition and temperature of the samples upon laboratory receipt (*i.e.*, custody seal condition, container status) must be provided for each Chain-of-Custody Record/sample cooler.

F) GC/MS Volatile Organic Data.

1. Quality Control (QC) Summary.

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II VOA).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III VOA).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III VOA).

d. Method Blank Summary (modified CLP SOW288 Form IV VOA) -- arranged in chronological order by date of analysis of the blank, by instrument.

e. GC/MS Tuning and Mass Calibration Summary (modified CLP SOW288 Form V VOA) -- arranged in chronological order, by instrument.

f. Internal Standard Area and Retention Time Summary (modified CLP SOW288 Form VIII VOA) -- arranged in chronological order, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for volatile samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Target Compound Results (modified CLP SOW288 Form I VOA).

b. Reconstructed total ion chromatogram (RIC) and quantitation reports.

c. Copies of raw spectra and copies of background-subtracted mass spectra of each target compound identified in the sample and corresponding background-subtracted target compound standard mass spectra.

d. Exhibit work sheet (including example calculations showing how sample results are calculated using the initial calibration and sample responses for at least one sample).

3. Standards Data

a. Initial Calibration Data (modified CLP SOW288 Form VI VOA and associated volatile standard RICs and quantitation reports) -- for all initial calibrations associated with analyses in the SDG, in chronological order, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

b. Continuing Calibration Data (modified CLP SOW288 Form VII VOA and associated volatile standard RICs and quantitation reports) -- for all continuing calibrations associated with analyses in the SDG, in chronological order, by instrument.

4. Raw QC Data

a. For each GC/MS tuning and mass calibration (in chronological order, by instrument):

1. Bromofluorobenzene (BFB) bar graph spectrum.

2. BFB mass listing.

b. Method/Storage Blank Data - in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

iii. Copies of raw spectra and copies of background-subtracted mass spectra of each target compounds identified in the blank and corresponding background-subtracted target compound standard mass spectra.

c. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

d. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

e. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I VOA).

ii. RIC and quantitation reports.

G) GC/MS Semivolatile Organic Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II SV).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III SV).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III SV).

d. Method Blank Summary (modified CLP SOW288 Form IV SV) -- arranged in chronological order by date of analysis of the blank, by instrument.

e. GC/MS Tuning and Mass Calibration Summary (modified CLP SOW288 Form V SV) -- arranged in chronological order, by instrument.

f. Internal Standard Area and Retention Time Summary (modified CLP SOW288 Form VIII SV-1, SV-2) -- arranged in chronological order, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries, followed by the raw data for semivolatile samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

b. RIC and quantitation report.

c. Copies of raw spectra and copies of background-subtracted mass spectra of each target compound identified in the sample and corresponding background-subtracted target compound standard mass spectra.

d. UV traces from Gel Permeation Chromatography (GPC) chromatograms cleanup (if performed).

e. Exhibit work sheet (including example calculations showing how sample results are calculated using the initial calibration and sample responses for at least one sample).

3. Standards Data

a. Initial Calibration Data (modified CLP SOW288 Form VI SV-1, SV-2 and associated semivolatile standard RICs and quantitation reports) -- for all initial calibrations associated with analyses in the SDG, in chronological order, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

b. Continuing Calibration Data (modified CLP SOW288 Form VII SV-1, SV-2 and associated semivolatile standard RICs and quantitation reports) -- for all continuing calibrations associated with analyses in the SDG, in chronological order, by instrument.

4. Raw QC Data

a. For each GC/MS tuning and mass calibration (in chronological order, by instrument):

i. Decafluorotriphenylphosphine (DFTPP) bar graph spectrum.

ii. DFTPP mass listing.

b. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

iii. Copies of raw spectra and copies of background-subtracted mass spectra of each target compounds identified in the blank and corresponding background-subtracted target compound standard mass spectra.

c. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

d. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

e. Matrix Spike Duplicate Data

i. Target Compound Results (modified CLP SOW288 Form I SV-1, SV-2).

ii. RIC and quantitation reports.

H) GC Organochlorine Pesticide Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III PEST).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III PEST).

d. Method Blank Summary (modified CLP SOW288 Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for organochlorine pesticide samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary (modified CLP SOW288 Form I PEST).

b. Copies of organochlorine pesticide chromatograms.

c. Copies of organochlorine pesticide chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts.

e. Exhibit work sheet (including example calculation showing how sample results are calculated using initial calibration standard and sample responses for at least one sample).

f. UV traces from GPC cleanup (if performed).

g. If organochlorine pesticides are confirmed by GC/MS, the laboratory must submit copies of raw spectra and copies of background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra. For multi-component pesticides confirmed by GC/MS, the laboratory will submit mass spectra of three major peaks of multi-component compounds from samples and standards.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data (Initial Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], organochlorine pesticide standard chromatograms, and integration reports) -- for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data (Continuing Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], organochlorine pesticide standard chromatograms, and integration reports) -- for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibrations.

d. 4,4′-DDT and Endrin Breakdown Data (Percent Breakdown Summary Form, organochlorine pesticide chromatograms and integration reports) -- for each standard associated with SDG in chronological order by GC column, by instrument.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. Organochlorine pesticide chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written over the peaks or printed over the peaks, or retention times shall be written over the peaks, and a separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution.

f. Raw Florisil® data, arranged in chronological order.

i. Chromatographs and data system reports for the analysis of the Florisil® cartridge performance check.

ii. Chromatographs and data system reports for the standards used to quantify compounds in the Florisil® cartridge performance check analysis (*i.e.*, INDA, INDB, and the 2,4,5-trichlorophenol standards).

I) GC Polychlorinated Biphenyl (PCB) Data

1. QC Summary

a. Surrogate Percent Recovery Summary (modified CLP SOW288 Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary (modified CLP SOW288 Form III PEST).

c. Laboratory Control Sample Summary (modified CLP SOW288 Form III PEST).

d. Method Blank Summary (modified CLP SOW288 Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for PCB samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary (modified CLP SOW288 Form I PEST).

b. Copies of PCB chromatograms.

c. Copies of PCB chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts. The integration reports or data system printouts must include all peaks not just the peaks corresponding to the target analytes.

e. Exhibit work sheets (including example calibration showing how sample results are calculated using initial calibration and sample responses for at least one sample).

f. UV traces from GPC (if performed).

g. If PCBs are confirmed by GC/MS, then the laboratory must submit copies of raw spectra and background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra. The laboratory will submit mass spectra of three major peaks of multi-component compounds from samples and standards for each PCB result confirmed by GC/MS.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data -- Initial Calibration Summary Form (inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.), PCB standard chromatograms, and integration reports for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data -- Continuing Calibration Summary Form (inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.), PCB standard chromatograms, and integration reports for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibration.

4. Raw QC data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results (modified CLP SOW288 Form I PEST).

ii. PCB chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written or printed over the peaks, or retention times shall be written over the peaks, and a

separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution (or used to assess the Aroclor pattern).

f. Raw Florisil® data, arranged in chronological order:

i. Chromatographs and data system reports for the analysis of the Florisil® cartridge performance check.

ii. Chromatographs and data system reports for the standards used to quantify compounds in the Florisil® cartridge performance check analysis (*i.e.*, INDA, INDB, and the 2,4,5-trichlorophenol standards).

J) GC Herbicide Data

1. QC Summary

a. Surrogate Percent Recovery Summary ("CLP SOW288-like" Form II PEST).

b. Matrix Spike/Matrix Spike Duplicate Summary ("CLP SOW288-like" Form III PEST).

c. Laboratory Control Sample Summary ("CLP SOW288-like" Form III PEST).

d. Method Blank Summary ("CLP SOW288-like" Form IV PEST) -- arranged in chronological order by date of analysis of the blank, by instrument.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for herbicide samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary ("CLP SOW288-like" Form I PEST).

b. Copies of herbicide chromatograms.

c. Copies of herbicide chromatograms from second GC column confirmation (if performed).

d. GC integration reports or data system printouts.

e. Exhibit work sheets (including example calculation showing how sample results are calculated using initial calibration and sample responses for at least one sample).

f. UV traces from GPC (if performed).

g. If herbicides are confirmed by GC/MS, the laboratory must submit copies of raw spectra and copies of background-subtracted mass spectra of target compounds that are identified in the sample and corresponding background-subtracted target compound standard mass spectra.

3. Standards Data

a. Analytical Sequence Form -- in chronological order, by GC column, by instrument for all samples and quality control analyses.

b. Initial Calibration Data (Initial Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], herbicide standard chromatograms, and integration reports) -- for each initial calibration associated with SDG in chronological order, by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

c. Continuing Calibration Data (Continuing Calibration Summary Form [inclusive of retention time windows, calibration factors, %RSDs, %Ds, etc.], herbicide standard chromatograms, and integration

reports) -- for each continuing calibration associated with SDG in chronological order, by GC column, by instrument following the associated initial calibrations.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

b. Laboratory Control Sample Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

c. Matrix Spike Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

d. Matrix Spike Duplicate Data:

i. Target Compound Results ("CLP SOW288-like" Form I PEST).

ii. Herbicide chromatograms and integration reports.

e. UV traces from GPC cleanup (if performed).

i. UV traces for the initial calibration standards and blanks. Compound names shall be written or printed over the peaks, or retention times shall be written over the peaks and a separate table listing compounds and retention times shall be provided.

ii. Chromatographs and data system reports for all standards used to quantify compounds in the GPC blanks.

iii. Chromatographs and data system reports for the GPC calibration check solution and all standards used to quantify compounds in the GPC calibration check solution (or used to assess the Aroclor pattern).

K) GC/MS Dioxin/Furan Data

1. Quality Control (QC) Summary

a. Matrix Spike/Matrix Spike Duplicate Summary.

b. Ongoing Precision and Recovery (ORP) Summary.

c. Method Blank Analysis Summary.

2. Sample Data

Sample data shall be arranged in packets consisting of the Analytical Results Summaries followed by the raw data for dioxin/furan samples. These sample packets should then be placed in increasing alphanumeric order by GE sample identification. The order of each sample packet is as follows:

a. Analytical Results Summary.

For each sample including peak retention times, ion ratios, reported concentrations, Estimated Detection Limit (EDL) designation, and internal standard recoveries.

b. Calculation of Toxicity Equivalence.

c. Dioxin/Furan Review Worksheet and Quantitation Report. The quantitation reports must include all information required to reproduce reported positive results and EDL results.

d. Extracted Ion Current Profile (EICP) Chromatograms.

e. Second Column Confirmation Data (if necessary; will include A-9.1.1.K, Section 2, items a, b, c, and d).

f. Exhibit work sheets (including example calibration showing how sample results are calculated using initial calibration and sample responses for at least one sample. The calculations should cover positive results and EDL results).

3. Standards Data

a. Mass spectrometer performance standard data for each calibration associated with the SDG, in chronological order by GC column, by instrument.

b. Window-defining mix and isotope ratio data for each calibration associated with the SDG, in chronological order by GC column, by instrument. The retention time windows must be summarized for reference.

c. Isomer Specificity Test Standard Summary and raw data in chronological order by GC column, by instrument.

d. Initial Calibration Data (Initial Calibration Summary Form, quantitation report, and EICP Chromatograms) for each initial calibration associated with the SDG, in chronological order by GC column, by instrument. If a curve equation is utilized, the laboratory must provide the curve equation and coefficient of determination.

e. Continuing Calibration Data (Continuing Calibration Summary Form, quantitation report, and EICP Chromatograms) for each continuing calibration associated with the SDG, in chronological order, by GC column, by instrument.

4. Raw QC Data

a. Blank Data -- in chronological order, by instrument:

i. Analytical Results Summary.

For each blank including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

b. OPR Standard Data:

i. Analytical Results Summary.

For each OPR standard including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

c. Matrix Spike Data:

i. Analytical Results Summary.

For each matrix spike including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

d. Matrix Spike Duplicate Data:

i. Analytical Results Summary.

For each matrix spike duplicate including peak retention times, ion ratios, reported concentrations, EDL designation, and internal standard recoveries.

ii. Dioxin/Furan Review Worksheet and Quantitation Report.

iii. EICP Chromatograms.

5. GC/MS Instrument Run Logs.

L) Inorganic Data for ICP or ICP/MS

1. Cover Page for the Inorganic Analyses Data Package.

2. Sample Results Summaries (modified CLP SOW390 Form I-INs) -- for all samples in the SDG, arranged in increasing alphanumeric order by GE sample identification.

3. Quality Control and Quarterly Verification of Instrument Parameters Summaries:

a. Initial and Continuing Calibration Verification summaries (modified CLP SOW390 Form II [PART 1]-INs).

b. Detection Limit Standards summaries (if performed, modified CLP SOW390 Form II [PART 2]-INs).

c. Blanks summaries (modified CLP SOW390 Form III-INs).

d. ICP Interference Check Sample summaries (modified CLP SOW390 Form IV-INs).

e. Matrix Spike/Matrix Spike Duplicate Sample Recovery summary (modified CLP SOW390 Form V [PART 1]-IN).

f. Post-Digest Spike Sample Recovery forms (modified CLP SOW390 Form V [PART 2]-IN).

g. Duplicates summary (modified CLP SOW390 Form VI-IN).

h. Laboratory Control Sample summary (modified CLP SOW390 Form VII-IN)

i. Method of Standard Addition Results summary (modified CLP SOW390 Form VIII-IN).

j. ICP Serial Dilution summary (modified CLP SOW390 Form IX-IN).

k. Method Detection Limits (MDL) and Reporting Limits (modified CLP SOW390 Form X-IN).

l. ICP Interelement Correction Factors (if performed, modified CLP SOW390 Form XI [PART 1]-IN).

m. ICP Linear Ranges (if performed, modified CLP SOW390 Form XII-INs).

n. Preparation Logs (modified CLP SOW390 Form XIII-INs).

o. Analytical Run Logs (modified CLP SOW390 Form XIV-INs).

4. ICP/MS Data Package will also include the following additional forms. The forms for ICP analysis listed A-9.1.1.K Sections 1-3 are also required using the SOW1091-LCIN protocol.

a. Linear Range Standard Summary (if performed, modified CLP For IV-LCIN).

b. ICP and ICP/MS Interference Check Sample (modified CLP Form VI-LCIN).

c. ICP/MS Tuning and Response Factor Criteria (modified CLP Form XIV-LCIN).

d. ICP/MS Internal Standards Summary (modified Form XV-LCIN).

5. Raw Data

For each reported value, the contracted laboratories will provide all raw data used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, and all sample analysis results. This statement does not apply to the Quarterly Verifications Parameters submitted as part of each data package (Section A-9.1.1.L, items 3k-3m). Raw data must contain all instrument readouts used for the sample results. Each exposure or instrumental reading must be provided, including those readouts that may fall below the MDL. All AA and ICP instruments must provide a legible hard copy of the direct real-time instrument readout (*i.e.,* strip charts, printer tapes, etc.). A photocopy of the instrument's direct sequential readout must be included. A hard copy of the instrument's direct instrument readout for cyanide must be included if the instrumentation has the capability.

The order of raw data in the data package shall be ICP-AES, ICP/MS, flame AA, furnace AA, mercury, and cyanide. All flame and furnace AA data will be grouped by element.

M) Wet Chemistry/Conventionals Data

The wet chemistry data will be arranged in the following order by individual parameter requested for the samples in the SDG.

1. Analytical Results Summaries -- for all samples in the SDG, arranged in increasing alphanumeric order by GE sample identification.

2. Quality Control Summaries

   a. Initial and Continuing Calibration Verification summaries.

   b. Blanks summaries.

   c. Spike Sample/Spike Duplicate Recovery summary.

   d. Duplicates summary.

   e. Laboratory Control Sample summary.

   f. Analytical Run Logs for instrumental analyses.

3. Raw Data

   For each reported value, the contracted laboratories will provide all raw data (instrument printouts or logbook pages) used to obtain that value. This applies to all required QA/QC measurements, instrument standardization, as well as all sample analysis results. Raw data must contain all instrument readouts/logbooks pages used for the sample results. Each exposure or instrumental reading must be provided, including those readouts/logbook pages that may fall below the quantitation limit. A photocopy of the instrument's direct sequential readout must be included if the instrumentation has the capability.

P) Preparation Logs

1. TCLP Extraction Logs (if TCLP extraction was performed).

2. Volatile Extraction Logs (if medium-level volatile analyses were performed).

3. Semivolatile Extraction Logs.

4. Organochlorine Pesticide/PCB Extraction Logs.

5. Herbicide Extraction Logs.

6. Dioxin/Furan Extraction Logs.

7. Metals Digestion Logs.

8. Wet Chemistry Preparation Logs (by parameter).

A-9.1.3 General Format for Level A Deliverables

A Level A Data Package will be prepared concurrently with each complete Sample Data Package prepared for quality assurance review. The Level A Data Package shall contain data for all samples in one SDG. All Level A Data Packages will be arranged in the following order:

A) Cover Letter/Letter of Transmittal

B) SDG Narrative

This document shall be clearly labeled "SDG Narrative" and shall contain: laboratory name, SDG number, GE sample identifications, laboratory sample numbers, and detailed documentation of any quality control, sample, shipment, and/or analytical problems encountered in processing (preparing and analyzing) the samples reported in the data package. A glossary of qualifier codes used in the SDG must also be provided.

The laboratory must also include any technical and administrative problems encountered, and corrective actions taken. An explanation of all flagged edits (*i.e.,* exhibit edits) on quantitation reports must be included in the SDG Narrative.

Additionally, the SDG Narrative must be signed and dated by the laboratory manager.

C) Field and Internal (Laboratory) Chain-of-Custody Records and Sample Receipt Documentation Log

Copies of both the external and internal Chain-of-Custody Records for all samples within the SDG must be included in the deliverables. A description of the condition and temperature of the samples upon laboratory receipt (*i.e.*, custody seal condition, container status) must be provided for each Chain-of-Custody Record/sample cooler.

D) Analytical Results Summaries, grouped by fraction, and submitted in the same order of fractions as the Level B Deliverables.

A-9.2 Deliverables Reporting Requirements for GC/MS Volatile and Semivolatile Organic Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identifier, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. If the requirement of a summary form is not applicable to a particular sample, standard, or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that sample, standard, or blank.

A) 1. An analysis summary of the results for all target compounds for all sample analyses, matrix spike analyses, matrix spike duplicate analyses, laboratory control sample analyses, and method/storage blank analyses must be supplied. The summary must include an entry for each target compound, date(s) and time(s) of analysis, GE sample identification, laboratory sample number, date of sample collection, sample matrix, sample weight, sample percent solids, heated or unheated purge, column type(s), column internal diameter, dilution factor, solid extract volume, solid aliquot volume,

concentration units, and sample results. For semivolatile analyses, date of sample extraction, final extract volume, injection volume, and an indication of whether the GPC cleanup was performed (yes/no) is also required. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the GE required quantitation limit and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range, then the positive result for the particular compound should be flagged with a "D." If the compound is still above the calibration rage after a dilution is performed on the sample, then the compound should be flagged with an "E."

2. The raw data for the sample analyses, method blank analyses, and storage blank analyses by GC/MS methodologies will include the RICs, mass spectra for all target compounds identified, and quantitation reports for the target compounds and surrogates. The raw data for the matrix spike and matrix spike duplicate analyses will include the RIC and quantitation report for the target compounds. These are required only for Level B Deliverables.

B) A surrogate percent recoveries summary for all of the reported analyses (samples, blanks, *etc*.). The surrogate recovery forms should be segregated by method (*i.e*., high-level solid samples separate from low-level solid samples). The summary form should also include the surrogate recovery limits and the laboratory should flag the compounds that do not meet the recovery limits, on the summary form.

C) A matrix spike/matrix spike duplicate concentration and percent recovery/relative percent difference summary for each matrix spike/matrix spike duplicate pair analyzed. The matrix spike/matrix spike duplicate summary form will indicate the GE identification of the unspiked sample, the MS/MSD sample, the spike concentrations, the matrix, and the concentrations of the compounds present in the unspiked sample and the MS/MSD sample. The summary form should also include the MS/MSD recovery criteria and RPD criterion. The laboratory should flag the compounds that do not meet the criteria. A similar form for the LCS must be included with the deliverables.

D) A method/storage blank summary form for each method/storage blank which identifies the samples associated with each method/storage blank. The date of analysis, time of analysis, file number, and matrix of the method/storage blank must also be reported on the summary form. Storage blanks are only required for volatiles analysis.

E) 1. A GC/MS tuning summary which summarizes the percent abundances for the mass ions of interest and the acceptance criteria for the mass ions. Additionally, the summary must include a list of the sample and QC sample analyses (sample names, file numbers, and dates and times of analysis) associated with the GC/MS tune. The summary should indicate the instrument identification, date and time of analysis, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the GC/MS tuning summary, consisting of a summary of the mass ion abundances and a mass spectral representation of the tuning peak.

F) 1. For the internal standard calibration method, an initial calibration summary for each initial calibration performed, summarizing all of the relative response factors for each calibration standard, the average relative response factor, and the relative standard deviation among the relative response factors. If a calibration curve equation is utilized, the laboratory must summarize the curve equation and the coefficient of determination. Additionally, the summary should indicate the compounds that must meet a minimum relative response factor or a maximum relative standard deviation criterion and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the file identifications of the analyses, the dates and times of calibration commencement and completion, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the initial calibration, consisting of the reconstructed ion chromatogram and the raw quantitation report for each calibration standard. This is a requirement for the Level B Deliverables only.

G) 1. For the internal standard calibration method, a continuing calibration summary for each continuing calibration standard analyzed, summarizing the average relative response factors of the initial calibration associated with the continuing calibration standard, the relative response factors of the continuing calibration standard, and the percent differences between the

average relative response factors of the initial calibration and the relative response factors of the continuing calibration. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. Additionally, the summary must indicate the compounds that are subject to a minimum relative response factor criterion, the compounds that are subject to a maximum percent difference criterion, and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the date of the initial calibration, the date and time of analysis, column type, diameter of the column, and the type of purge (heated or unheated for volatiles) used to analyze the samples.

2. The raw data for the continuing calibration, consisting of the reconstructed ion chromatogram and the raw quantitation report for each calibration standard. This is a requirement only for the Level B Deliverables.

H) An internal standard area counts summary, containing a summary of the area counts and retention times for the internal standards for a continuing calibration. The summary must indicate the acceptance windows for the internal standard retention times and area counts. This summary must supply a comparison of the continuing calibration internal standards to the mid-level initial calibration internal standards. Additionally, the summary must include a listing of the internal standard retention times and area counts for all of the samples, method blanks, matrix spikes, and matrix spike duplicates associated with the continuing calibration standard.

I) A copy of all of the extraction log information for semivolatiles is required. At a minimum, the extraction information must include the date the extraction was

started, the date the extraction was completed, the initial sample weight or volume, final extraction volume, laboratory sample number, the amount and concentration of surrogate spike added, and the amount and concentration of matrix spike solution added. Additionally, the extraction log should indicate if a cleanup procedure was performed on the sample. If a medium-level extraction was performed for the volatiles analysis, all extraction logs for this analysis will be required. For volatile organics analyses that require weighing sample aliquots in the field, copies of the field measurement documentation will be included in this section.

A-9.3 Deliverables Reporting Requirements for Organochlorine Pesticide, PCB, and Herbicide Analysis

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (i.e., recovery ranges, relative percent difference limits, etc.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identification, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. If the requirement of a summary form is not applicable to a particular sample, standard or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that requirement.

A) 1. An analysis summary of the concentrations of all target compounds for all sample analyses, matrix spike analyses, matrix spike duplicate analyses, and blank analyses. The blank analyses must consist of all of the extraction

(method) blank analyses, injection blank analyses, and any blanks associated with cleanup procedures. The summary must include dates and times of analysis, GE sample identifications, laboratory sample numbers, dates of sample collection, date of sample receipt, dates of sample extraction, sample matrices, sample weights or volumes, sample percent solids, column types, column internal diameters, dilution factors, initial extract volumes/weights, final extract volumes, concentration units, the type of cleanup performed, and sample results. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the GE required quantitation limit and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range then the positive result for the particular compound should be flagged with a "D." If the compound is still above the calibration range after a dilution is performed on the sample, then the positive result for the compound should be flagged with an "E."

2. The raw data for the sample analyses, matrix spike analyses, matrix spike duplicate analyses, and blank analyses, consisting of the chromatograms indicating the surrogate peaks and target compound peaks and quantitation reports for the target compounds and surrogates. This is a requirement only for the Level B Deliverables.

B) A surrogate percent recovery summary for all of the reported analyses (samples, blanks, *etc*.). The surrogate recovery forms should be segregated by matrix and

method (*i.e.*, medium-level solid samples separate from low-level solid samples). The summary form should also include the surrogate recovery limits and the laboratory should flag the compounds that do not meet the recovery limits on the summary form.

C) A matrix spike/matrix spike duplicate concentration and percent recovery/relative percent difference summary for each matrix spike/matrix spike duplicate pair analyzed. The matrix spike/matrix spike duplicate summary form will indicate the GE identification of the unspiked sample, the MS/MSD sample, the spike concentrations, the matrix, and the concentrations of the compounds present in the unspiked sample and the MS/MSD sample. The summary form should also include the MS/MSD recovery criteria and RPD criterion. The laboratory should flag the compounds that do not meet the criteria. A similar form for the LCS should be included with the deliverables.

D) A method blank summary form for each method blank, identifying the samples associated with each method blank. The date, time, lab file number, and matrix of the method blank must also be reported on the summary form.

E) Initial Calibration Data: A summary of the initial calibration retention times, mean retention time, and a retention time window for all target compounds and surrogates must be provided for all initial calibrations. A second summary of the initial calibration standard calibration factors, average calibration factors, and relative standard deviations for all target compounds and surrogates must also be provided for all initial calibrations. If a calibration curve equations is utilized the laboratory must supply the curve equation and the coefficient of determination. Both summaries should include the SDG number, instrument identification, GC column

type and diameter, date(s) of analysis, the concentration level for each initial calibration standard (as a multiplication factor of the low calibration standard), and the acceptance limit for the relative standard deviation. Copies of the pesticide, herbicide, and PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverables). Each initial calibration associated with the SDG must be presented in chronological order, by GC column and by instrument.

F) Continuing Calibration Data: A summary of the observed retention times, calculated compound concentrations, true concentrations, percent differences, and retention time window from the initial calibration (or from the daily retention time window update) must be provided for all continuing calibration standards. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. The summary should list the SDG number, GC column type and diameter, date and time of analysis, laboratory sample number, initial calibration dates, and acceptance limits. Copies of the pesticide, herbicide, and PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverable). Each continuing calibration associated with an SDG must be presented in chronological order, by GC column and by instrument.

G) 4,4′-DDT and Endrin Breakdown Data (organochlorine pesticides only): A summary of the observed 4,4′-DDT, endrin, and combined percent breakdowns must be presented for each breakdown check performed. (Alternatively, if this data is obtained from a continuing calibration standard rather than a specific breakdown standard, this information may be reported on the associated continuing calibration summary form.) The summary should list the SDG number, GC column type and

diameter, date and time of analysis, laboratory sample number, initial calibration dates, and acceptance limits. Copies of the pesticide/PCB standard chromatograms and integration reports associated with summaries should immediately follow the summary (only for the Level B Deliverables). Each breakdown summary associated with an SDG must be presented in chronological order, by GC column and by instrument.

H) A summary of the analytical sequence for each column and instrument used for the analysis of the project samples. The summary must contain the GC column number, the internal diameter of the column, initial calibration dates associated with the sequence, the instrument identification, the mean retention time(s) for the surrogate(s) utilized, a listing of the GE sample names, the laboratory sample numbers, dates and times of analysis, and the retention times for the surrogate(s). The summary should also indicate the retention time window for all surrogates used and any surrogate retention times that do not meet the acceptance criterion. The summary must contain all of the analyses for the samples, blanks, initial calibration standards, and continuing calibration standards associated with the sequence. All sequences will begin with an initial calibration and will terminate with a continuing calibration or breakdown check standard that meets all acceptance criteria.

I) When a GPC cleanup procedure is required for the samples, a summary for each check standard associated with the GPC calibration. The summary must contain the GPC column identification, the calibration date of the GPC column, the GC column(s) used for the analysis of the standard, the GC column internal diameter, the theoretical concentrations of the compounds in the GPC standard, the observed concentrations of the GPC standard, the percent recovery for each compound in the GPC standard, the GE sample identification, laboratory sample number, and the

date(s) of analysis for all samples associated with the GPC standard. The limits for each compound in the GPC standard should be listed on the summary form. The laboratory should flag any compound if the percent recovery was not within the control limits.

J) When a Florisil® cartridge cleanup procedure is required for the samples, a summary for each check standard associated with a Florisil® cartridge lot. The summary must contain the Florisil® cartridge lot number, the date of analysis of the Florisil® cartridge check standard, the GC column(s) used for the analysis of the standard, the GC column internal diameter(s), the theoretical concentrations of the compounds in the Florisil® cartridge check standard, the observed concentrations of the Florisil® cartridge check standard, the percent recovery for each compound in the Florisil® cartridge check standard, the GE sample identifications, the laboratory sample number, and the date(s) of analysis for all samples in the data deliverable associated with each lot of Florisil® cartridges.

K) Second column confirmation may be performed for all pesticide, PCB, and herbicide analyses when there is a positive result reported for a project sample. When the laboratory performs a dual column quantitative analysis for organochlorine pesticides, PCBs, and herbicides, a summary of the identified compounds and observed concentrations for the two columns utilized for sample analyses is required. The summary must contain the GE sample identification, the laboratory sample number, the dates and times of analysis, the instruments used for analysis, the GC columns, the GC column internal diameters, the retention time windows for each peak used to quantitate the compound, the observed retention time for each peak used to quantitate the compound, the calculated concentration for each peak

used, the mean concentration for each column for each compound identified, and the percent difference between the mean concentrations calculated for each column.

If the percent difference between the results for the analyte from the two GC columns is greater than 40% for the analysis, then the higher of the two values is reported and flagged with a "P." Finally, the "C" flag is used when the identification of a pesticide result is confirmed by GC/MS.

A-9.4 Deliverables Reporting Requirements for Dioxin/Furan Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e*., recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any recoveries that are outside of the acceptance criteria. The raw data associated with the samples, blanks, and standards must clearly identify the GE sample identifier, the laboratory sample number, the instrument, the laboratory file number for the analysis, and the peak areas/heights and retention times that correspond to the compounds of interest observed in all analyses reported. The raw data must provide all information necessary to reproduce all reported positive and EDL results. If the requirement of a summary form is not applicable to a particular sample, standard, or blank, the requirement should still appear on the form; however, no entry will be necessary on the form for that requirement.

A) 1. An analysis summary of the results for all target compounds for all sample analyses, second column confirmation analyses, matrix spike analyses, ORP standard analyses, and method blank analyses must be supplied. The

summary must include an entry for each target 2,3,7,8-substituted compound and total homologue concentrations, date(s) and time(s) of analysis, GE sample identification, laboratory sample number, date of sample collection, date of sample preparation, sample matrix, sample weight, sample percent solids, column type(s), column internal diameter(s), dilution factor, concentrated extract volume, concentration units, peak retention times, isotope ratios, and sample results. If positive results below the lowest calibration standard are reported, they must be flagged as estimated ("J") on the analysis summary. "Not-detected" results will be represented by the EDL and a "U" flag. If a compound was detected in a sample as well as in the method blank associated with the sample, the result must be flagged with a "B" on the summary form. Additionally, if a dilution is performed on a sample because a target compound is above the calibration range, then the positive result for the particular compound should be flagged with a "D". If the compound is still above the calibration rage after a dilution is performed on the sample, the positive result for the compound should be flagged with an "E".

2. The raw data for the sample analyses and method blank analyses by GC/MS methodologies, consisting of the EICP, quantitation reports for the target compounds, the associated areas or height for each peak within the established retention time window, and all other information required to reproduce all reported positive and EDL results. The raw data for the matrix spike and matrix spike duplicate analyses will include the EICP chromatogram and quantitation report for the target compounds.

B) A matrix spike concentration and percent recovery summary for each matrix spike analyzed is required. The matrix spike summary form will indicate the GE identification of the unspiked sample, the sample, the matrix, and the concentrations of the compounds present in the unspiked and spiked sample. The summary form should also include the MS recovery criteria. The laboratory should mark the compounds that do not meet the specified criteria. A similar form for the OPR standard should be included with the deliverables.

C) A method blank summary form for each method blank that identifies the samples associated with each method blank. The date of extraction, date of analysis, time of analysis, lab file number, sample weight, and matrix of the method blank must also be reported on the summary form.

D) A mass spectrometer performance summary for each mass spectrometer performance standard analyzed should identify the sample number, lab file identification, date and time of analysis, instrument identification, GC column identification, and static resolving power.

E) A window defining mix summary form for each window defining analysis should identify the sample number, lab file identification, date and time of analysis, instrument identification, and GC column identification. This form should include the retention time of the first eluting and last eluting isomer for each congener group.

F) An isomer specificity test standard summary should identify the sample number, file number, instrument ID, date and time of analysis, the GC column and instrument identification, and the percent valley determination between $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-1,2,3,4-TCDD. In addition, if second column confirmation is required,

percent valley for 2,3,7,8-TCDD and the closest isomers should be calculated and reported.

G) A summary of the analytical sequence for each column and instrument used for the analysis of the project samples. The summary must contain the GC column number, the internal diameter of the column, initial calibration dates associated with the sequence, the instrument identification, a listing of the GE sample names, the laboratory sample numbers, and dates and times of analysis. The summary must contain all of the analyses for the samples, blanks, initial calibration standards, and the continuing calibration standards associated with the sequence.

H) 1. An initial calibration summary for each initial calibration performed, summarizing all of the relative response factors for each calibration standard, the average relative response factor, and the relative standard deviation among the relative response factors. If calibration curve equations are utilized, the laboratory must supply the curve equation and coefficient of determination. Additionally, the summary should indicate maximum relative standard deviation and minimum relative response factor criteria as well as the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the dates and times of calibration commencement and completion, column type, and diameter of the column.

2. The raw data for the initial calibration, consisting of the EICPs and the raw quantitation report for each calibration standard.

I) 1. A continuing calibration summary for each continuing calibration standard analyzed, summarizing the average relative response factors of the initial calibration associated with the continuing calibration standard, the relative response factors of the continuing calibration standard, and the percent differences between the average relative response factors of the initial calibration and the relative response factors of the continuing calibration, and the isotope ratios and retention times. If calibration curve equations are utilized the laboratory must summarize the true concentration, observed concentration, and the percent drift. Additionally, the summary must indicate the compounds that are subject to a minimum relative response factor criterion, the compounds that are subject to a maximum percent difference criterion, and the compounds that did not meet the acceptance criteria. The summary should indicate the instrument identification, the date of the initial calibration, the date and time of analysis, column type, and diameter of the column.

2. The raw data for the continuing calibration, consisting of the EICPs and the raw quantitation report for each calibration standard.

A-9.5 Deliverables Reporting Requirements for Inorganic Analyses

The laboratory will be required to submit the following information as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e.,* recovery ranges, relative percent difference limits, *etc*.) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any quality control results that are outside the acceptance criteria. All instrument raw data printouts for the points discussed below must be provided in an orderly

fashion. This applies to all required QA/QC measurements, and instrument standardization, as well as sample analysis results. Additionally, all associated extraction, digestion, and distillation logs must be supplied. The order of the raw data in the data package shall be ICP-AES, ICP/MS, flame AA (if performed), furnace AA (if performed), and mercury. All flame and furnace AA data shall be grouped by element. All raw data shall be grouped by analysis date for all analytical results.

A) 1. A sample reference list for all samples present in an SDG. This reference list must summarize and correlate the laboratory sample number, the GE designated sample identification, and any laboratory code (*i.e.*, truncation of GE designated sample number by the laboratory) for each sample in an SDG.

2. A Table of Contents listing page numbers associated with information such as:

a. Methodology Summary

b. Case Narrative

c. Sample Results

d. Quality Control Data

e. Verification of Instrument Parameters

f. Preparation and Analysis Logs

g. Raw Data, including but not limited to:

i. ICP-AES, ICP/MS, Flame AA, GFAA, and Mercury Data

ii. Digestion Logs

iii. Confirmation Data

h. Chain-of-Custody Records

B) Analysis summaries of the concentrations of all target analytes for all sample analyses. The summary must include the GE designated sample number, the laboratory sample number, date of sample collection, date of sample receipt, sample matrix, sample percent solids, concentration units, sample results, data qualifier codes, analysis method codes, description of sample before and after analysis, and any comments relating to the sample.

C) A summary of the initial and continuing calibration verifications for each calibration performed. This summary will include the concentrations observed as well as the true value of the analyte in the initial and continuing calibrations. A percent recovery will be summarized based on the observed and true values for each analyte.

D) A summary of the Detection Limit (DL) standard analyses for both Atomic Absorption (AA) and Inductively Coupled Plasma (ICP) analyses. This summary will include the concentrations observed as well as the true value of the analyte in the DL standard. A percent recovery will be summarized based on the observed and true values for each analyte.

E) A summary of the initial and continuing laboratory blank analyses for each calibration performed. This summary will include the concentrations (positive or negative) observed of any analyte in the initial and continuing blank analyses at values greater than the MDL. The summary should also include the concentrations of any analyte observed in the laboratory preparation blank associated with each calibration sequence performed by the laboratory.

F) A summary of the ICP interference check sample analysis for each analytical sequence performed. This form will summarize the true and found values (positive, negative, or zero) of all analytes present in Solutions A and AB of the ICP interference check sample analysis. This form will also summarize the percent recoveries of the analytes/interferences present in the standards.

G) A summary of the pre-digestion matrix spike analysis. This form will summarize the percent recovery control limit for each analyte. Also, the sample result, the spike sample result, and the spike-added amount must be summarized on this form for all parameters analyzed. The laboratory-calculated percent recovery as well as the laboratory qualifier stating whether the calculated percent recovery was within control limits must also be summarized on this form.

H) A summary of the post-digestion matrix spike analysis. This form will require the same information described in item G.

I) A summary of the laboratory duplicate analysis. This form will summarize the percent differences observed between the sample and laboratory duplicate analyses. The appropriate control limits must be specified by the laboratory, and a summary of

the sample and laboratory duplicate analyses must be provided. The percent solids for the sample and the duplicate sample should be included on the summary form.

J) A summary of the Laboratory Control Sample (LCS) analysis. This form will summarize the percent recovery, control limits, and true and found values for the solid sample analyses.

K) A summary of any required Method of Standard Additions (MSA) determinations. This form will summarize the concentrations and absorbencies of all samples and analytes that require analysis by MSA. The correlation coefficient for the MSA analysis will be calculated and summarized on this form. Also, the sample concentration determined from the MSA determination will be summarized on this form.

L) A summary of the ICP Serial Dilution analyses performed by the laboratory. This summary will show the result of the initial sample analysis (in aqueous units, as observed from the raw data), the result of the five-fold serial dilution analysis, and the percent difference between the two analyses.

M) The summaries necessary for the verification of instrument parameters. These include an Method Detection Limit and Reporting Limit Summary, an ICP Interelement Correction Factor Summary (if performed) for each ICP used for analysis, and an ICP Linear Range Summary (if performed) for each ICP used for analysis.

N) The analysis log summaries. These include a Sample Preparation log that provides the sample identification; the preparation date; the sample weight (in grams) used;

and the digestion volume (in mL) used and an Analysis Run Log that provides the instrument identification, the sample identification, any dilution factors employed in the analysis, the date and time of analysis, the method of analysis, and the parameters analyzed. Additionally, the GFAA post-digestion analytical spike sample recoveries are listed on the Analysis Run Log.

A-9.6 Deliverables Reporting Requirements for Wet Chemistry/Conventionals Analysis

The laboratory will be required to submit the information detailed in Sections A-9.5 A) -C), A-9.5, E) and A-9.5, G) - J) and A-9.5-N as support documentation for the reported analytical results. The quality control summary forms must include the acceptance criteria (*i.e.*, recovery ranges, relative percent difference limits, *etc.*) and spike-added amounts (where applicable). Additionally, the quality control summary forms must indicate any quality control results that are outside the acceptance criteria. All instrument raw data printouts for the points discussed in the above mentioned sections must be provided in an orderly fashion. This applies to all required QA/QC measurements, and instrument standardization, as well as sample analysis results. Additionally, a direct sequential readout must be included if the instrument has the capability.

APPENDIX 39

1.0 OBJECTIVES

This Standard Operating Procedure (SOP) describes the procedures that the auditor will use for performing field audits and the reporting of the audit findings. Field audits will be performed to provide GE with an indication of the quality of the field services that are being provided by the field contractor(s) as part of the Baseline Monitoring Program (BMP) and to ensure that the field contractor(s) are adhering to project requirements. This SOP applies to the contractor(s) involved in field data collection and the auditor.

2.0 EQUIPMENT

Not applicable.

3.0 SUPPORTING SOPs and DOCUMENTS

Applicable Field Sampling SOPs

Quality Assurance Project Plan (QAPP)

Health and Safety Plan

4.0 PROCEDURE

4.1 SCHEDULING

The frequency of field audits will be identified in the appropriate QAPP. When it has been determined that the performance of a field audit is necessary, the auditor will coordinate a date and time for the audit with GE which consider both the field schedule and any deadline necessary to meet the needs of the BMP. The majority of the audits will be unannounced to the field contractors.

4.2 PRE-AUDIT PREPARATION

Once a field audit is scheduled, the auditor will review the applicable QAPP and determine and review the applicable SOPs. The checklists to be used for auditing the GE BMP water sampling and fish sampling are included as Attachment 1. The individual sampling and field procedures SOPs applicable to the tasks being audited will provide the specific criteria against which the audit will be performed.

4.3 GENERAL AUDIT APPROACH

Upon arrival at the project site, the auditor will initiate a meeting with the appropriate field personnel (site manager) to give a brief introduction of what they can expect to occur during the field audit. This introduction focuses on several key points. The auditor(s) will identify that they will be performing the audit with the aid of a checklist that has been prepared by the auditor.

The checklist guides the auditor(s) through the field task in the basic order that events are expected to occur. Another key point that will be made is that the auditor(s) will focus their questions toward the field personnel who actually perform the work and **not** their supervisors. Field supervisors may be present during the audit but may not answer the questions for the field personnel unless specifically requested to provide an answer. In addition, the auditor will ask questions regarding appropriate general field service protocols during this initial meeting.

The field audit checklist should include the following 9 sections as appropriate to the activities being performed. The field audit will be performed in the basic order defined by the checklist, depending on the task being performed. Subdivisions of the following sections will be necessary and will be dependent on the type of work being performed.

The approach of the audit on the following topics is described in greater detail in the subsequent sections of this SOP. The narrative of the field audit report will also follow the subject order of the checklist but will give the audit findings and recommendations in sufficient detail that the checklist will not be included with the report.

1. Field Documentation/Records
2. Decontamination Procedures
3. Sampling/Field Procedures
4. Sample Containers
5. Sample Packaging and Shipment
6. Chain-of-Custody
7. Health and Safety/Personal Protective Equipment
8. Other
9. Summary

Finally, following the audit, the auditor(s) will convene another meeting with the field management personnel in order to debrief them on the audit findings. The debriefing meeting should accomplish several goals. First, the field personnel must be made aware of the major points of the audit findings. This way, any statements made in the field audit report will not be a surprise to the contractor, and the contractor is given a chance to respond to the findings before the report is written. Their responses can then be incorporated into the field audit report by the auditor. Secondly, the auditor(s) should emphasize that recommendations will be made even to the best of contractors. The major goals of a field audit is to determine the quality of services being provided by the contractor, document that appropriate procedures are being used, and to identify problems (or potential problems) so that appropriate corrective action can be initiated by the contractor. The extent of the impact of the recommendation(s) will be indicated in

the report. Additionally, the audit should stress when correct field procedures were in use.

4.4 FIELD DOCUMENTATION/RECORDS

The auditor(s) must evaluate the contractor's documentation procedures throughout the audit, and should verify that all pertinent information is being neatly recorded in a logbook for all field events. The minimum information to be entered in the logbook should include: on-site personnel and their arrival and departure times; weather conditions; calibration and background settings of monitoring equipment; location of collected samples; time of collection; the required sample analysis; relevant observations; photograph log; adherence to and/or deviations from the QAPP; and other pertinent information.

4.5 DECONTAMINATION PROCEDURES

The auditor(s) will verify that the decontamination areas are established in a clean portion of the site and that correct decontamination procedures are being followed. The personnel performing the decontamination of the sampling equipment should be using the decontamination materials specified in the appropriate SOP and should be performed in the exact order listed in the SOP. Care should be taken to limit the amount of decontamination wastes generated during the cleaning process. The decontamination wastes should be properly managed and stored per SOP until appropriate disposal arrangements are made.

4.6 SAMPLE CONTAINERS

The auditor(s) will verify that the contractor is using laboratory supplied, pre-cleaned sample containers for analytical samples. The containers should be of the proper type

(i.e. glass, plastic, metal), volume, and material (i.e. amber or clear glass). Any cracked or broken sample containers should not be used and should be discarded. The appropriate preservatives should already be placed in the sample containers by the laboratory, or they may be added to the sample containers in the field. Once the sample is collected and placed in the sample container, the container should be legibly labeled or preprinted with the following information; sample ID, date, time, sampler's initials, analysis, and project name and number.

4.7 SAMPLING/FIELD PROCEDURES

The auditor(s) must evaluate the procedures the contractor utilizes during the collection of samples and other field activities. Samples may be collected from various medias (i.e., surface water and fish) and for various purposes (i.e., chemical analysis). The method of sample collection will also vary and will require assorted types of equipment to insure the proper collection of the sample. The auditor(s) must verify that a proper method of sample collection and proper equipment are being used for the media being sampled and the intended purpose of the sample collection. Deviations to the applicable QAPP should be noted by the auditor(s).

4.8 SAMPLE PACKAGING AND SHIPMENT

After environmental samples have been collected, placed in sample containers, labeled and temporarily stored on-site, they should be packaged and shipped to the laboratory for chemical analysis per SOP. The auditor(s) will verify that the transport device (e.g., ice chest) to be used for shipment of the samples is cleaned of any obvious debris and old shipping labels are removed. The auditor(s) will check to see that the transport device is lined with an absorbent material and a plastic bag. The samples will be checked to see if they are individually wrapped or protected and properly aligned in the transport device so

that they do not touch each other. The samples should then be packed using an approved packing material and iced down (with the exception of liquid samples for metal analysis) with sufficient "wet" ice or ice pack to keep the samples at 4 degrees Celsius. Packing tape and signed custody seals should be used to seal the transport device. Shipping air bills and content caution content labels (e.g., Fragile, This End Up, etc.) should be attached to the outside of the shipping container.

4.9 CHAIN-OF-CUSTODY

The auditor(s) will verify that the chain-of-custody record and procedures are being properly completed per SOP. As soon as practicable after sample collection, the following information must be recorded on the chain-of-custody form; project name and number, sampler(s), sample ID, date, time, type of sample (grab or composite), number of containers, sample analysis, remarks, and signature (when being relinquished). The field audit will include a determination that proper handling and transfer of chain-of-custody documentation is occurring.

4.10 HEALTH AND SAFETY/PERSONAL PROTECTIVE EQUIPMENT

The auditor(s) will observe the field personnel to verify that they are following the guidelines of the Health and Safety Plan. The auditor will make only general observations about the health and safety practices. The auditor(s) will check to see that the field personnel are wearing the specified protective clothing and equipment for the level of protection specified by the health and safety officer. The auditor(s) will also verify that the appropriate types of personal monitoring equipment is being used, and that personnel using the equipment are knowledgeable with the operation of the equipment.

4.11 OTHER

Due to the wide range of field services being performed on this project, the above discussed list of items may not always completely address the extent of the audit. At the auditor's discretion, other checklist items may be added to ensure that a complete audit is performed.

4.12 SUMMARY

The auditor(s) must summarize the major points of the field audit findings and the overall evaluation of the quality of service provided by the contractor. The summary should also reflect the overall attitude that the contractor has toward quality assurance and quality control.

4.13 REPORT FORMAT

The field audit report must contain the following sections in the following order. It must also contain a completed checklist as an attachment.

1. Introduction
2. Executive Summary
3. Audit Findings

The introduction should summarize who performed the audit, when the audit was performed, the name and address of the contractor, and the contractor's role in the BMP. The Executive Summary should address the major findings of the field audit along with the possible impact on the quality of the contractor's service. The Audit Findings should follow the major headings of the checklist summarizing the findings presented on the

checklist along with any recommendations for improvement or corrective action. The report will be signed by the auditor(s) who performed the audit.

5.0 TRAINING

The auditor's conducting the field audit must have demonstrated knowledge in field quality assurance/quality control practices. This knowledge will include experience in geological and hydrogeological investigations, sample collection of various media, health and safety training, and technical report writing.

ATTACHMENT 1

GENERAL ELECTRIC COMPANY
HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

Project Location: _____

Environmental Standards' Job #: _____

Date(s) of Field Audit: _____

Time(s) of Field Audit: _____

Environmental Standards' Auditor: _____

GENERAL ELECTRIC COMPANY

HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.	Page 1 of 7

Pre-Task Planning

General	YES	NO	NA	COMMENTS
Are personnel and responsibilities defined?				
Are GEHR project-specific SOPs and the QAPP present and in use?				
Is a site-specific map on-site showing sampling locations?				
What are the weather conditions?				

COMMENTS ON PRE-TASK PLANNING:

GENERAL ELECTRIC COMPANY

HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.				Page 2 of 7
Water Column Sample Collection				
Supplies and Equipment	YES	NO	NA	COMMENTS
Are all sampling vessels equipped with:				
-Required safety equipment				
-Positioning system (GPS, spuds, anchors)				
-USGS style Depth Integrating Sampler (DH-59 or equivalent)				
-Portable Bridge Crane				
-Portable winch w/ precise two-directional line speed control				
-Laptop computer with Printer (with Microsoft Access 2002)				
-Disposable gloves				
-Laboratory-supplied organic-free water				
-Field Log				
-Chain of Custody forms and labels for containers				
-Sample Containers				
-Resealable food storage bags				
-Cooler with temperature blank and ice				
-Trash bags				
-YSI 6920 (or equivalent) multi-parameter probe w/ 100 ft of cable				
-Data logger				
-Data transfer cable				
-Calibration fluids for water quality parameter measurement				

GENERAL ELECTRIC COMPANY

HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.				Page 3 of 7
Water Column Sample Collection				
Pre-Sample Collection	YES	NO	NA	COMMENTS
Was the multi-parameter probe (YSI 6920 or equivalent) calibrated using the calibration fluids as per the instrument manufacturer's instructions at the beginning of each sampling day?				
Does the instrument data logger have sufficient memory and battery power for the day's sampling event?				
Are the date and time on the instrument data logger accurate?				
Were the probe measurements only taken after 5 minutes of any vessel traversing near the sampling location (bridge location) or setting spuds or other anchoring device (boat access)?				
Was the probe lowered to mid-depth in the water column and did at least 30 seconds pass by before the readings were logged with the data logger?				
Were consecutive measurements (at least one minute apart) taken to verify probe stability at least once per day?				
If the consecutive measurements appeared to be off by 20% or more, was the probe recalibrated and the consecutive readings repeated?				
At the end of each day, was the probe immersed in calibration fluid to assess instrument drift or loss of calibration? What were the results?				
For samples to be collected by boat access, are vessels navigated to within 10 ft. of previously defined target coordinates?				
Were the actual GPS coordinates recorded?				
Prior to sample collection, were measurements for temperature, dissolved oxygen (DO), pH, conductivity, and turbidity obtained using the probe?				
For bridge locations, was a portable bridge crane maneuvered into position above the sampling location (unless the depth-integrating sampler was to be lowered and retrieved manually)?				
For samples to be collected by boat access, was a portable crane with line speed control set up?				
Did field personnel put on a new pair of disposable gloves prior to sample collection?				

GENERAL ELECTRIC COMPANY

HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.	Page 4 of 7

Water Column Sample Collection

Sample Collection	YES	NO	NA	COMMENTS
Was a new sample collection vessel placed in the depth integrating sampler (1 qt for centroid locations or 1 pt For EDI locations)? Note the same container should be used at all EDI sub-stations for each location.				
Did field personnel determine the proper amount of sample that will be required from each station or sub station to fill all sample containers for a location? The volume must be adjusted such that approximately equal volume will be collected at each sub-station and that little or no sample is collected that is not needed to fill sample containers.				
Was the sampler properly calibrated to the water depth and river flow conditions to produce the desired sample volume (*i.e.*, was the proper size [¼", 3/16", 3/8"] nozzle installed)?				
Was the sampler lowered until 75% of the water depth was reached (distance to be determined during prior surveying)?				
Once the 75% water depth was reached, was the sampler retrieved using the same approximate line speed used to deploy the sampler?				
Once the sampler was retrieved, was the sample vessel no more than approximately 90% filled and not significantly below the desired volume? If not, was the sample discarded and the sampling procedures adjusted accordingly until the appropriate sample volume was collected?				
Multiple sampler deployments will be required to obtain sufficient sample volume. Each time the sampler is retrieved, is the amount of sample distributed to each sample container based on the estimated number of sample deployments?				
Do the sample containers and volumes used meet the QAPP specifications (Section B3 and Table B-5)?				
Were the sample containers labeled appropriately (Section B3 of the QAPP)?				
Was the sample collection vessel used at each station placed in a re-sealable plastic bag and labeled with the date, time, and station (the sample vessel is to be submitted to the laboratory)?				

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BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.				Page 5 of 7
Water Column Sample Collection				
Sample Collection (Cont.)	YES	NO	NA	COMMENTS
Was each sample container placed in a re-sealable plastic storage bag and placed in a cooler with ice to chill the samples to approximately 4°C?				
Was a temperature blank placed in each cooler?				
Were proper Chain-of-Custody procedures followed as specified in Section B3 of the QAPP?				
Were the appropriate QA/QC samples collected? (Record which QA/QC of the following were collected for the event) -Blind duplicate samples? -Matrix spike samples? -Matrix spike duplicate/laboratory duplicate samples? -Equipment blank samples?				
Are equipment blanks prepared in the following manner: -Field personnel wears disposable gloves -A decontaminated ¼ inch nozzle and a new sample collection vessel are placed in the depth integrating sampler -Laboratory-supplied organic-free water is poured into the sample collection vessel -When nearly full, the sample collection vessel is removed and distributed to appropriately labeled sample containers -The process is repeated until adequate sample volume is obtained -After collection, the equipment blank is handled in a manner that is consistent with all other environmental samples				
Are the samples sent to each laboratory daily by courier or overnight delivery?				
Are all field data recorded in the field database via laptops and a hard copy of field log printed after each sample collection?				

GENERAL ELECTRIC COMPANY

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BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.				
Water Column Sample Collection				
Sample Collection (Cont.)	YES	NO	NA	COMMENTS
COMMENTS ON WATER COLUMN SAMPLE COLLECTION:				

GENERAL ELECTRIC COMPANY

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BASELINE MONITORING PROGRAM - WATER COLUMN

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.	Page 7 of 7

Training

General	YES	NO	NA	COMMENTS
Have the field personnel completed the following Training Requirements prior to the beginning of the project: -Any specialized training -OSHA 40-hour documentation needed prior to start -Medical surveillance clearance also needed prior to start				

COMMENTS ON TRAINING:

GENERAL ELECTRIC COMPANY

HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - FISH

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

Project Location: _____

Environmental Standards' Job #: _____

Date(s) of Field Audit: _____

Time(s) of Field Audit: _____

Environmental Standards' Auditor: _____

GENERAL ELECTRIC COMPANY

HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - FISH

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.				
Pre-Task Planning				
General	YES	NO	NA	COMMENTS
Are personnel and responsibilities defined?				
Are GEHR project-specific SOPs and the QAPP present and in use?				
Is a site-specific map on-site showing sampling locations?				
What are the weather conditions?				
COMMENTS ON PRE-TASK PLANNING:				

ENVIRONMENTAL STANDARDS, INC.				Page 2 of 12
Fish Sample Collection				
Supplies and Equipment	YES	NO	NA	COMMENTS
The need for the equipment listed below will vary based on the specific type of sampling taking place during the audit: -Required safety equipment -Positioning system (GPS, anchors) -Laboratory grade detergent -Distilled water -Acetone and Hexane -Collection buckets -Beach seine -Buoys -Line -Gill net - Sampling Boat or aluminum electrofishing boat equipped with live well -DC generator -Variable voltage pulsator -Dip nets -Electrodes -Water temperature and conductivity meter -Volt meter -Thermometer -Tape measure -Scale -Watch -Fish Scaler -Dissecting pan/board -Scale envelopes -Glass vials -Fish collection record -Chain of Custody and Analytical Request forms -Cooler with temperature blank and ice -Aluminum foil -Zip lock bags -Fish collection permit				

ENVIRONMENTAL STANDARDS, INC.				Page 3 of 12
Fish Sample Collection				
Pre-Sample Collection	YES	NO	NA	COMMENTS
Was the fish processing equipment properly decontaminated in the following manner in a designated area prior to contact with the fish? -Washed with laboratory detergent -Rinsed with distilled water -Rinsed with acetone and then, allowed to air dry -Rinsed with hexane and then, allowed to air dry -Rinsed with distilled water				
Was the rinsate from the equipment decontamination procedure collected and placed in appropriate disposal containers?				

GENERAL ELECTRIC COMPANY

HUDSON RIVER PCBs SITE

BASELINE MONITORING PROGRAM - FISH

SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.	Page 4 of 12

Fish Sample Collection

Netting using a Beach Seine	YES	NO	NA	COMMENTS
Was a beach seine appropriately used for near shore shallow study areas? -Where the net wall can extend from the surface of the water to the bottom -For capture of near-shore species or for species that use the near-shore area seasonally or daily -Where the substrate is relatively smooth so that the lead line of the seine drags along the bottom of the river preventing fish escapement				
Did two people start together at the downstream edge of the sample location (either wading or in boats)?				
Did one of the two people begin to extend the seine perpendicular to the shoreline until the net was straightened out or the water became too deep?				
Did both people begin walking parallel to the shoreline for a set distance before the deep end person began to swing the end of the net back to the shoreline?				
Were both ends of the net brought together and the net hauled onto the shoreline with the captured fish?				
Were the fish removed from the net and placed into buckets for identification?				
Were caught fish identified and assessed for the need to retain such that all unnecessary fish were immediately returned to the water?				

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SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

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Fish Sample Collection

Netting using a Gill Net	YES	NO	NA	COMMENTS
Was the gill net used when there is 100 ft of continuous depths of greater than 3 ft and little current?				
Were anchors attached to both ends of the lead line and buoys attached to both ends of the float line?				
Was the gill net stacked in a large storage tub by placing the end with the larger mesh size in the tub first (for variable mesh sizes) and coiling the rest of the net into the tub?				
Beginning close to the shore or in water approximately 2 m deep, was the outer end of the net removed from the storage tub and the anchor attached to the lead line and buoy attached to the float line dropped over the bow of the boat?				
Was the buoy line adjusted so that the buoy is floating and the line was relatively taut?				
As the boat slowly moved backwards from the shore, was the remainder of the net let out while shaking out any tangles?				
Once the inner end of the net was reached, was the boat stopped and the net pulled until it was taut?				
Was the anchor attached to the lead line dropped overboard and the float line pulled to make sure the net was taut?				
Was the buoy attached to the float line dropped in the water and the buoy line adjusted so that the buoy was floating and the line was relatively taut?				
Was the gill net allowed to soak the prescribed sampling period (*e.g.*, 1-24 hours)?				
Was the gill net retrieved by first arriving at the end of the net in the deeper water and retrieving the buoy and anchor?				
Was the net pulled on board and stacked in coils in the storage tub?				
Were the fish removed from the set as it was brought aboard and placed into the holding bucket?				
Were caught fish identified and assessed for the need to retain such that all unnecessary fish were immediately returned to the water?				

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Fish Sample Collection

Electrofishing	YES	NO	NA	COMMENTS
Was electrofishing only used in areas less than 4 meters deep?				
Was electrofishing used for fish other than yearling pumpkinseed or forage fish?				
Did field personnel ensure that electrofishing was not used where endangered species were present?				
Did field personnel wear appropriate health and safety gear (rubber hip or chest waders, rubber gloves, personal floatation devices)?				
Was the elctrofishing boat positioned in the water in order to start upstream and work downstream?				
Was the water conductivity and temperature measured in order to determine the appropriate operating voltage and amperage?				
Was the output voltage and amperage adjusted until the desired setting was obtained without harming the fish?				
Was pulsed output used to reduce the stress on the fish?				
Was the output maintained for the predetermined amount of time?				
Were the fish collected with dip nets and placed in the live well until processing?				
After processing, were all unselected fish released?				

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Fish Sample Collection

Angling	YES	NO	NA	COMMENTS
Was angling used only after all other methods proved unsuccessful?				
What type of lure was used to catch the fish?				
Were caught fish identified and assessed for the need to retain such that all unnecessary fish were immediately returned to the water?				

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Fish Sample Collection				
General	YES	NO	NA	COMMENTS
After a successful fish collection, was the following information entered into the Field Collection Record: -Names of field personnel collecting the samples -Date -Time and duration of collection -Actual GPS coordinates of the starting location and approximate distance of samples -Weather conditions (temperature, wind, precipitation) -Observations of river conditions (*e.g.,* temperature, turbidity) -Species identification (genus and species) -Sample total length (nearest mm) and weight (to nearest 0.1 g) -Sample sex, if possible -Sample tag number				
If fish were cut to determine sex, did field personnel not eviscerate the fish?				
Was the balance used for weighing the fish calibrated? How?				
After processing, were fish stored at a temperature below 4°C and shipped immediately to the analytical laboratory along with all Fish collection Records, Chains-of-Custody, and Analysis Request documents?				
Was a temperature blank placed in each cooler?				
Were proper Chain-of-Custody procedures followed as specified in Section B3 of the QAPP?				
Were the appropriate QA/QC samples collected? (Record which QA/QC of the following were collected for the event) -Blind duplicate samples? -Matrix spike samples? -Matrix spike duplicate/laboratory duplicate samples? -Equipment blank samples?				
Are the samples sent to each laboratory daily by courier or overnight delivery?				

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FIELD AUDIT CHECKLIST

ENVIRONMENTAL STANDARDS, INC.				
Fish Sample Collection				
General (Cont.)	YES	NO	NA	COMMENTS

COMMENTS ON FISH SAMPLE COLLECTION:

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Fish Sample Processing				
Bass, Bullhead, Perch	YES	NO	NA	COMMENTS
If the analysis of the fish age was deemed appropriate, were the scales, spines, or otoliths collected as follows? -For bass and perch, were all scales removed from the fish and at least 5 scales placed in a scale envelope for storage? -For bullhead, was the dorsal spine removed and placed in a scale envelope for storage? -Were otoliths removed and placed in glass vials for storage if deemed necessary? -Was the fish tag number, fish total length, weight, date, and location sampled recorded on the envelope and/or vial?				
Was the skin removed from all brown bullheads but not from any bass or perch?				
Was the examination tray lined with a clean piece of aluminum foil (shiny side down) and the fish place on the lined tray?				
Was the fish cut along the ventral midline of the fish from the vent to the base of the jaw?				
Was a diagonal cut made from the base of the cranium to just below the fill, to the ventral side just behind the pectoral fin?				
Was the flesh removed from the ribcage from one-half of the fish by cutting from the cranium along the spine and dorsal rays to the caudal fin?				
Did the ribs remain on the fillet?				
Was the fillet placed on a clean piece of aluminum foil (shiny side down) and wrapped?				
Was an identification label that included the fish tag number, fish total length and weight, date, and location sampled attached to the wrapped fish?				
Was the wrapped, labeled fish placed in a pre-labeled plastic bag?				

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FIELD AUDIT CHECKLIST

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Fish Sample Processing

Yearling Pumpkinseed and Other Forage Fish	YES	NO	NA	COMMENTS
Were several scales removed from the fish and at least 5 scales placed in a scale envelope?				
Were the date, time, fish tag number, fish total length, weight, and location sample recorded on the scale envelope?				
For pumkinseed, was an individual fish placed on a clean piece of aluminum foil (shiny side out)?				
For forage fish, were fish for compositing (grouped by size to the extent possible) placed on the decontaminated foil?				
Were the fish wrapped in the aluminum foil and an identification label that includes the fish tag number, fish length(s), weight(s), date and location sampled attached?				
Were the wrapped fish placed in a pre-labeled bag?				

COMMENTS ON FISH SAMPLE PROCESSING:

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SAMPLING AND ANALYSIS

FIELD AUDIT CHECKLIST

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Training

General	YES	NO	NA	COMMENTS
Have the field personnel completed the following Training Requirements prior to the beginning of the project: -Any specialized training -OSHA 40-hour documentation needed prior to start -Medical surveillance clearance also needed prior to start				

COMMENTS ON TRAINING:

APPENDIX 40

1.0 OBJECTIVES

This Standard Operating Procedure (SOP) describes the procedures that the auditor will use for performing analytical laboratory audits and the reporting of the audit findings. Analytical laboratory audits will be performed to provide GE with an indication of the quality of the data that are being provided by the laboratories as part of the Baseline Monitoring Program (BMP) and to ensure that the laboratories are adhering to project requirements. This SOP applies to the laboratories and the auditor.

2.0 EQUIPMENT

Not applicable.

3.0 SUPPORTING SOPs and DOCUMENTS

Applicable Analytical SOPs.

Quality Assurance Project Plan (QAPP).

Health and Safety Plan

Applicable Laboratory Quality Assurance Manual (LQAM)

4.0 PROCEDURE

4.1 SCHEDULING

The frequency of laboratory audits will be identified in the appropriate QAPP. When it has been determined that the performance of a laboratory audit is necessary, the auditor will initiate contact with the designated project laboratory. The auditor and the laboratory will mutually determine a date and time for the audit which is convenient for both parties and which is within any deadline necessary to meet the needs of the QAPP. If necessary, unannounced audits may be performed.

4.2 PRE-AUDIT PREPARATION

At the time the laboratory audit is scheduled, the auditor will request any laboratory documents that would aid in the effectiveness of the audit if received prior to the audit. Such documents will include the LQAM and all analytical Standard Operating Procedures (SOPs) which are applicable to the analytical work being performed by the laboratory.

Prior to the audit, the auditor will review all documents provided by the laboratory. In the laboratory audit report, a statement will be made as to the appropriateness and thoroughness of these documents in terms of the needs of the QAPP. In addition, the auditor will take notes upon this initial review that will aid in verifying that the laboratory is following the procedures described in the documents. Any deviations from the documents will also be noted in the laboratory audit report.

4.3 GENERAL AUDIT APPROACH

Upon arrival at the designated project laboratory, the auditor will initiate a meeting with the appropriate laboratory personnel (analytical laboratory supervisor(s) and quality assurance supervisor) to give a brief introduction of what they can expect to occur during the laboratory audit. This introduction focuses on several key points. The auditor(s) will identify that they will be performing the audit with the aid of a checklist that has been prepared by the auditor. The checklist will not be provided to the laboratory at any time.

This checklist guides the auditor(s) through the laboratory in the basic order that samples are processed through the laboratory starting with sample receipt and ending with data reporting. Another key point that will be made is that the auditor(s) will focus their questions toward the technicians and analysts who actually perform the work and **not** their supervisors. Laboratory supervisors may be present during the laboratory audit but may not answer the questions for the

technicians/analysts unless the technicians/analysts cannot answer a given question. In addition, the auditor will ask questions regarding appropriate general laboratory information during this initial meeting.

The audit checklist is a proprietary document and has not been included with this SOP. It contains significant specific detail on the audit criteria and evaluation. The laboratory evaluation checklist includes the following eight sections. The laboratory audit will be performed in the basic order defined by the checklist, depending on the layout of the laboratory being audited. Subdivisions of the following sections will be necessary and will be dependent on the types of analytical work being performed for the BMP at the designated laboratory. The approach of the audit on the following topics is described in greater detail in the subsequent sections of this SOP. In addition to the following topics, the auditor(s) will also be evaluating the overall sample tracking throughout the audit and the communication between the various sections of the laboratory (with a special regard to how holding times are met). The narrative of the laboratory audit report will also follow the subject order of the checklist but will give the audit findings and recommendations in sufficient detail that the checklist will not be included with the report.

1. Organization and Personnel
2. Sample Receipt and Storage Area
3. Sample Preparation Area
4. Sample Analysis Instrumentation
5. Documentation
6. Quality Control Manual
7. Data Handling
8. Summary

Finally, following the audit, the auditor(s) will initiate another meeting with the appropriate laboratory personnel in order to debrief them on the audit findings. The debriefing meeting should accomplish several goals. First, the laboratory personnel must be made aware of the major points of the audit findings. This way, any statements made in the laboratory audit report will not be a surprise to the laboratory and the laboratory is given a chance to respond to the findings before the report is written. Their responses can then be incorporated into the laboratory audit report. Secondly, the auditor(s) should emphasize that recommendations will be made even to the best of laboratories. The major goal of a laboratory audit is to determine the quality of data which is currently being generated by the laboratory and to identify problems (or potential problems) so that appropriate corrective action can be initiated by the laboratory. However, laboratory audits are also attended to give all laboratories, no matter their level of quality, ideas on how to become a better laboratory. The extent of the impact of the recommendation(s) will be indicated in the report.

4.4 ORGANIZATION AND PERSONNEL

The auditor(s) must evaluate the size and experience of the organization and the number, working hours, experience, and education of the personnel in the context of the BMP analytical work which is being performed by the laboratory being audited. The general information about the organization and personnel should be addressed by the auditor(s) during the initial introduction meeting. The experience and education of the personnel are best evaluated at a later date by obtaining the staff's resumes during this introductory meeting. However, if the resumes or some other similar summaries are not available, questions of this nature must be asked by the auditor(s) throughout the audit.

4.5 SAMPLE RECEIPT AND STORAGE AREA

The auditor(s) should interview the designated sample custodian in this area of the laboratory. If a sample custodian has not been designated by the laboratory, the auditor(s) must interview any personnel responsible for receiving and logging in samples upon receipt at the laboratory. The auditor(s) must determine whether the laboratory personnel do anything to compromise the integrity of the samples during the check-in process, such as subjecting samples to any procedures which might lead to contamination or allowing temperature-preserved samples to warm to room temperature. In addition, the auditor(s) must verify that the laboratory personnel check and record all appropriate information regarding the condition of the samples upon receipt (i.e., Chains-of-Custody, cooler temperature, preservation, etc.). Furthermore, the auditor(s) must determine whether the sample storage area(s) are kept at the proper well-documented temperatures without any possibility of cross-contamination of samples. Finally, the auditor(s) must verify that the laboratory properly documents the condition of the samples upon receipt and that the information is determined from the check-in procedure. It must also be determined whether the tracking system in which the samples have been logged is adequate to ensure that holding times are being met.

4.6 SAMPLE PREPARATION AREA

The auditor(s) must evaluate the overall appearance and appropriateness of the size of the sample preparation area and the condition of the facility and equipment in the sample preparation area. The auditor(s) must verify that the equipment, water, and standards used in sample preparation are appropriately calibrated, stored, and/or maintained and that all appropriate information regarding these issues is properly documented. While in this area, the auditor(s) must interview the sample preparation technicians responsible for the preparations for the analyses of concern for the BMP. During the interviews, the auditor(s) must determine whether the sample preparation technicians follow good laboratory practices as well as the required analytical preparation methods. The auditor(s) must evaluate whether the laboratory is introducing the appropriate type and number of quality control samples at this point and that the sample technicians' procedures or equipment do not introduce possible contamination (i.e., glassware is cleaned properly) or inaccuracies (i.e., proper glassware and standards are used correctly). The auditor(s) must also evaluate the laboratory's sample tracking system through this area to verify that holding times are properly tracked. Finally, the auditor(s) must verify whether all preparation procedures are appropriately documented.

4.7 SAMPLE ANALYSIS INSTRUMENTATION

In the various sample analysis instrumentation areas of the laboratory, the auditor(s) must interview the analyst(s) responsible for the analyses of concern for the BMP. When possible, analysts will also be observed performing assigned tasks. The auditor(s) must evaluate whether the instrumentation used for the analyses of concern for the BMP is appropriate and is properly maintained. Through the interviews with the analysts and observations of actual tasks, it must be determined if each instrument is calibrated (according to the associated analytical method) with well-documented calibration standards at the required frequency and that these instrument

calibrations are properly documented. The auditor(s) must determine if method detection limit studies have been performed on each instrument used for analysis. In addition, the auditor(s) must determine if standards and quality control samples are being analyzed at an appropriate frequency and whether appropriate quality control limits are being utilized for these analyses. The analysts' practices must be evaluated for their attention to the quality control results and to the possibility of instrument carryover. The auditor(s) must evaluate whether appropriate corrective actions are being taken when standard or quality control results are out of the method-required or laboratory-determined limits. Finally, the auditor(s) must determine whether all the analysis procedures and results are properly documented.

4.8 DOCUMENTATION

The auditor(s) must evaluate the laboratory's documentation procedures throughout the audit. It should be determined if well-labeled, neat, bound notebooks are being used to document and trace standards, calibrations, laboratory procedures, and any other routine quality control check. The auditor(s) must examine notebooks and observe whether they have been properly reviewed at the laboratory and that there are no obliterations.

The auditor(s) must also evaluate the data package preparation practices. Such practices include the system used for the collection of various hard copy data, validation of results prior to data package release, completeness checks, generation of cover letters or case narratives, and retention of data packages at the laboratory.

4.9 QUALITY CONTROL MANUAL

The appropriateness and thoroughness of the laboratory's quality control manual, as well as the LQAM and analytical SOPs, must be evaluated prior to the audit. However, throughout the audit, the auditor(s) must verify if the laboratory is actually following the practices defined in their documents. Any deviations from the documented procedures must be discussed in the laboratory audit report.

4.10 DATA HANDLING

The auditor(s) must determine whether the laboratory's data handling procedures are adequate. Proper data handling techniques include the checking of calculations by a second person, documenting calculations, recording all corrective actions taken on rejected data, and properly documenting detection limits and quality control results. In addition, data must be retained at the laboratory for an appropriate amount of time.

4.11 SUMMARY

The auditor(s) must summarize the major points of the laboratory audit findings and the overall impact on the quality of the data issued from the laboratory. The summary should also reflect the overall attitude that the laboratory has toward quality assurance and quality control.

4.12 REPORT FORMAT

The laboratory audit report must contain the following sections in the following order. It must also contain a completed checklist as an attachment.

1. Introduction
2. Executive Summary
3. Audit Findings

The introduction should summarize who performed the audit, when the audit was performed, the name and location of the laboratory, and the laboratory's role in the BMP. The Executive Summary should address the major findings of the laboratory audit along with the possible impact on the laboratory's data quality. The Audit Findings should follow the major headings of the checklist summarizing the findings presented on the checklist along with any recommendations for improvement or corrective action. The report will be signed by the auditor(s) who performed the audit.

5.0 TRAINING

The auditors conducting the laboratory audit must have demonstrated knowledge in laboratory quality assurance/quality control practices. This knowledge will include experience in analytical data validation and having conducted at least two prior laboratory audits.

APPENDIX 41

DESCRIPTION OF PCB SAMPLING FREQUENCY ANALYSIS

PCB loads during baseline and during dredging were simulated by performing a bootstrap sampling from historical data collected between 2000 and 2002 at TID-PRW2 and Schuylerville. Simulated baseline load values were compared with simulated load values during dredging. This analysis was performed separately for each month (May – November) and repeated 10,000 times.

PCB load values during the baseline period were simulated by randomly sampling with replacement from the historical data. To simulate weekly monitoring, 12 values were chosen with replacement from the historical data set (3 years of baseline monitoring X 4 weeks per month). These 12 values were averaged to determine the monthly mean and confidence interval of the baseline load.

PCB load values during dredging were simulated in the same way, except that the simulation involved daily sampling, and an additional load was added to mimic a PCB release from the dredging operation. Each day, one value was sampled (with replacement) from the historical data set. To start the simulation, 7 simulation days were so created for the Evaluation Standard (28 for Control). Then, for each of the following 60 days, values were again randomly sampled, and a specified load added to each, to simulate a PCB release. Seven-day or 28-day running averages were calculated. The first day of elevated load was called day 1.

A series of such simulations was performed, differing in the additional load added to baseline. For each dredging simulation, a separate baseline bootstrap average was calculated. The computer program tracked the first day on which the running average during dredging was significantly different from, and was at least 300 or 600 g/day greater than, the average during baseline. The results were summarized by computing the probability that the monitoring program would not capture an exceedance within 7 or 28 days of its beginning.

Results for the Evaluation and Control Standards were as follows. When the simulated baseline is exceeded by exactly 300 or 600 g/d for exactly 7 or 28 days, approximately 50% of the time one concludes loads are greater than 300 or 600, and about 50% of time one concludes the opposite, as expected (See Tables below). The power of the monitoring program can be seen when evaluating results when the dredging loads exceed baseline by a slightly different amounts. For example, when dredging loads are 100 g/d less than the trigger values (i.e., either 200 g/d or 500 g/d), then there is up to a 31% chance of concluding that the standards have been exceeded (a “type I error”); in this way, the program provides a level of conservatism. On the other hand, when dredging loads are 100 g/d greater than the trigger values (i.e., either 400 g/d or 700 g/d, then the power of the program to detect the exceedance is generally greater than 80 percent (minimum is 57 percent; power = 1 – probability of type II error). Note that after 14 days

of loading at 400 g/d, the power has increased to at least 79 percent. After 60 days of loading at 700 g/d, the power has increased to at least 90 percent (See Tables below).

Probability of concluding that the standards have been exceeded at TID-PRW2

Month	Evaluation Standard (7-d average)			Control Standard (28-d average)		
	300 g/d added	200 g/d added[1]	400 g/d added[2]	600 g/d added	500 g/d added[1]	700 g/d added[2]
May	*52%*	*25%*	*78% (94%)*[4]	*50%*	*14%*	*86% (96%)*[3]
June	*52%*	*15%*	*87% (98%)*	*51%*	*7%*	*94% (99%)*
July	*51%*	*8%*	*94% (99%)*	*50%*	*2%*	*98% (99%)*
Aug	*51%*	*3%*	*96% (100%)*	*50%*	*1%*	*100% (100%)*
Sep	*49%*	*4%*	*97% (100%)*	*51%*	*0.3%*	*99% (100%)*
Oct	*51%*	*19%*	*84% (96%)*	*50%*	*8%*	*91% (97%)*
Nov	*50%*	*7%*	*95% (99%)*	*51%*	*1%*	*98% (100%)*

[1]For exceedances less than the standard, this represents the type I error.
[2]For exceedances greater than the standard, this represents the power of the program.
[3]Values in parentheses represent results 60 days after the exceedance began.
[4]Values in parentheses represent results 14 days after the exceedance began.

Probability of concluding that the standards have been exceeded at Schuylerville

Month	Evaluation Standard (7-d average)			Control Standard (28-d average)		
	300 g/d added	200 g/d added[1]	400 g/d added[2]	600 g/d added	500 g/d added[1]	700 g/d added[2]
May	*41%*	*27%*	*57% (79%)*[4]	*50%*	*26%*	*74% (90%)*[3]
June	*51%*	*31%*	*71% (88%)*	*50%*	*20%*	*80% (93%)*
July	*48%*	*29%*	*69% (85%)*	*51%*	*21%*	*80% (92%)*
Aug	*51%*	*5%*	*95% (100%)*	*49%*	*1%*	*99% (100%)*
Sep	*51%*	*13%*	*90% (98%)*	*50%*	*4%*	*95% (99%)*
Oct	*51%*	*30%*	*74% (89%)*	*51%*	*19%*	*83% (93%)*
Nov	*51%*	*24%*	*81% (94%)*	*49%*	*12%*	*87% (96%)*

[1]For exceedances less than the standard, this represents the type I error.
[2]For exceedances greater than the standard, this represents the power of the program.
[3]Values in parentheses represent results 60 days after the exceedance began.
[4]Values in parentheses represent results 14 days after the exceedance began.

APPENDIX 42

ANALYSIS OF THE STATISTICAL POWER OF THE COMPARISON BETWEEN TRANSECT DATA AND GRAB SAMPLES

The Baseline Monitoring Program (BMP) includes paired water column measurements at the historical and baseline monitoring stations using the historical and baseline monitoring sampling protocols, respectively, to determine whether the historical data may be combined with the baseline data. The BMP calls for the collection of 9 monthly single-point samples at TID-PRW2 and 12 at Schuylerville. The goal of the analysis presented here is to determine the power associated with this program to distinguish possible differences between the historical single-point data and transect data.

Sokal and Rohlf (1995, Box 9.14) and Cochran and Cox (1957, p.19) presented an equation describing the number of samples required to distinguish between two uncorrelated populations of values. The transect and single-point data are paired, however. Therefore, the equation is modified here for an analysis of paired data. The modified equation is used to estimate the power associated with 9 monthly samples.

Number of Samples Required - Unpaired analysis

The number of samples required to detect a specified difference (δ) between two populations, at a significance level of α and with a power of P is given by (Sokal and Rohlf 1995, Cochran and Cox (1957):

$$n \geq 2\left(\frac{s}{\delta}\right)^2 \left[t_{\alpha,\nu} + t_{2(1-P),\nu}\right]^2 \qquad (1)$$

where:

n = required number of samples
s = standard deviation of the data (assuming similar values for the two populations; also assuming that s ~ σ, the parametric standard devation)
δ = difference between the population means that it is desired to detect
α = significance level of the test of the difference between the two populations
ν = degrees of freedom
P = power = desired probability that a difference will be found to be significant, if it is as small as δ
t = critical values of Student's t distribution

This equation is derived as follows:

The difference between the average transect concentration and the average grab sample concentration (i.e. the unpaired analysis) is described by a t distribution (Sokal and Rohlf 1995):

$$t_1 = \frac{d_u}{\sqrt{\frac{2s^2}{n}}} \qquad (2)$$

where:

$d_u = \frac{\sum(x_{1,i})}{n} - \frac{\sum(x_{2,i})}{n}$ = difference between the means for the unpaired analysis

$x_{1,i}$ = concentration measured in transect sample *i*

$x_{2,i}$ = concentration measured in the grab sample *i*

t_1 in Equation 2 is the same as $t_{\alpha,\nu}$ in Equation 1. The value for t_1 is calculated using the appropriate degrees of freedom (2(n-1)) and is compared with a critical value of t calculated for a probability of $p_1 = \alpha = 0.05$. The denominator in Equation 2 is the standard error of the difference.

To evaluate the power of a sampling program, one specifies a probability (P) that a specified true difference (δ) will be correctly identified as significant. The difference between d_u and δ is also described by a t distribution, with the same standard error for d_u:

$$t_2 = \frac{d_u - \delta}{\sqrt{\frac{2s^2}{n}}} \quad (3)$$

t_2 in Equation 3 is the same as $t_{2(1-P),\nu}$ in Equation 1. The probability associated with t_2 is p_2. Note that since a 2-sided t test will be used (for consistency with the calculation of t_1), the power (P) is given by:

$$P = (1 - \frac{1}{2} p_2) \quad (4)$$

Combining Equations 2, 3 and 4 results in Equation 1.

Number of Samples Required - Paired Analysis

Equation 1 considers two populations of unpaired data. The planned comparisons between transect and grab data permit a paired data analysis, which should, in principle, have greater power. For paired data, the equation describing the required number of samples must be derived for a comparison between the population of differences and a single value (= 0, the null hypothesis for the difference between the two populations of values), as opposed to the comparison between two populations that formed the basis for Equation 1. The number of samples required to distinguish one population from a parametric value is slightly different Equation 1:

$$n \geq \left(\frac{s_{dif}}{\delta} \right)^2 \left[t_{\alpha,\nu} + t_{2(1-P),\nu} \right]^2 \quad (5)$$

This is derived as follows. For the paired test, the value of t_1 is given by:

$$t_1 = \frac{d_p}{\sqrt{\frac{s_{dif}^2}{n}}} \quad (6)$$

where:

$$d_p = \frac{\sum \left(x_{1,i} - x_{2,i} \right)}{n} - 0$$

s_{dif} = standard deviation of the difference between the paired data sets

The value of t_2 is given by:

$$t_2 = \frac{d_p - \delta}{\sqrt{\frac{s_{dif}^2}{n}}} \quad (7)$$

Combining Equations 4, 6 and 7 gives Equation 5. This equation is used in the power calculation described below.

Equation 5 differs from Equation 1, because the standard error is derived for a test of the difference between a population of numbers (the differences $d_i = x_{1,i} - x_{2,i}$) and a single value (0), and not the difference between two populations of numbers (grab and transect samples). The standard deviation of the difference between two random variables depends on the correlation between them (Sokal and Rohlf 1995):

$$s^2_{dif} = s_1^2 + s_2^2 - 2rs_1s_2 \quad (8)$$

where:

s_1 = standard deviation of the transect samples
s_2 = standard deviation of grab samples
r = correlation coefficient between the transect and grab samples

Assuming that the standard deviations of each of the two populations are approximately equal ($s_1 \sim s_2 = s$), this becomes:

$$s^2_{dif} = 2s^2(1-r) \quad (9)$$

Power Calculation

The sample size was set equal to 9. The significance level α was set equal to 0.05. The analysis was performed for a range of differences, δ. For each value of δ, the power (P), or the probability of declaring the transect and grab data to be different when in fact they differ by δ, was calculated.

The correlation coefficient was estimated using the PRW2 and Schuylerville data. The overall correlation coefficient between data collected on the same date at PRW2 and at Schuylerville (from 1997 to 2003) was 0.84. This sets a lower bound estimate of the expected correlation between transect data and grab samples, because the PRW2 and Schuylerville stations are separated by a distance of 7 miles, while the grab station at PRW2 and the nearby transect station will be separated by a distance of about 1 mile. The power analysis was performed for r = 0.84 and, because this value is likely to be lower than the true value for this comparison, for r = 0.90.

The standard deviation was also estimated from the historical data. In this analysis, the values of both σ and δ are specified as proportions of the mean: this is acceptable, because it is the ratio between δ and s that is required in Equation 9. Values of 0.65 and 0.57 were calculated for the coefficient of variation (= standard deviation / mean) for TID - PRW2 and Schuylerville, respectively. A value of s = 0.6 is used here. This value was used in Equation 4 to determine the standard deviation in the statistical test (s_{dif}).

Parameters are summarized below:

Description	**Parameter**	**Value**
Sample size	n	9
Degrees of freedom	ν	n – 1 = 8
Significance level	α	0.05
Correlation coefficient	r	0.84, 0.90
Standard deviation (as a proportion of the mean)	$\sqrt{(s^2_{dif})}$	$\sqrt{[2s^2(1-r)]}$ $= \sqrt{[2 \times 0.6^2 \times (1-r)]}$
Difference to be detected (as a proportion of the mean)	δ	0 – 80%

The results of the analysis consist of the calculated power of this program to detect a given true difference, δ, using Equation 9. Results for a range of values of δ are presented in Figure 1. For example, with a correlation coefficient equal to 0.84, we can be about 85% sure that a true difference of 40% will be detected at the 5% level of significance. With a correlation coefficient of 0.90, we can be about 85% sure that a true difference of 30% will be detected. We can be more than 95% sure that a true difference of 50% will be detected if r = 0.84, and that a true difference of 40% will be detected if r = 0.90. Based on these results, the power of the program as presented is deemed sufficient.

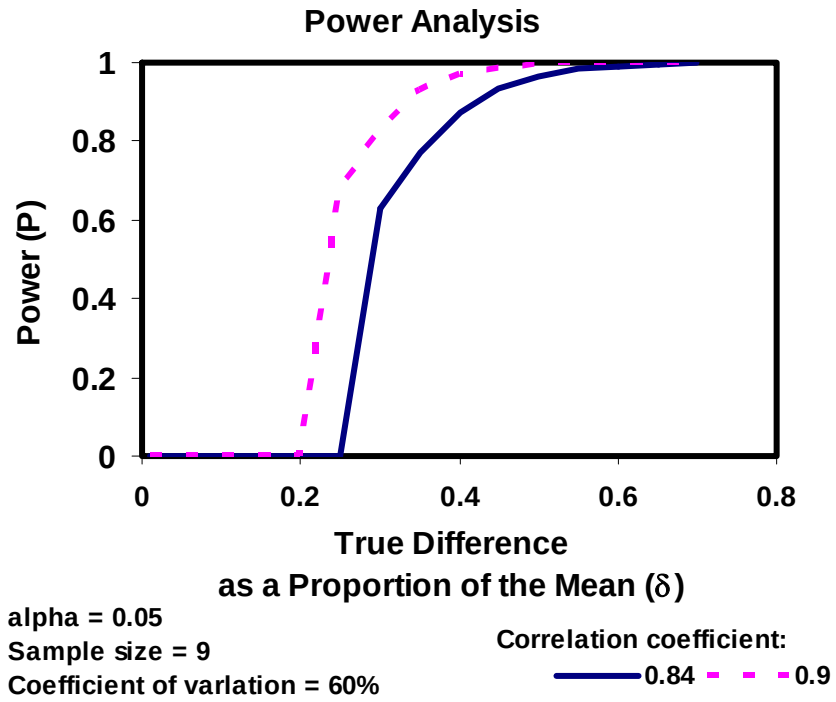

Figure 1. Relationship between a specified true difference between transect and grab samples (δ in Equation 9) and the power of the BMP to detect that difference (P in Equation 8).

APPENDIX 43

APPENDIX 43
DESCRIPTION OF TSS SAMPLING FREQUENCY ANALYSIS

This appendix provides details for the analysis presented in Section A7.2.8 of the text which shows that during baseline monitoring, semiweekly TSS sampling in May and June and weekly sampling from July through November is sufficient.

The goal of this analysis was to estimate the sample size during baseline monitoring that is sufficient to meet the goals of the Resuspension Performance Standard. A simulation approach was taken. Using the historical water column TSS data, a bootstrap analysis was performed simulating both the results of the planned baseline monitoring program and the results of monitoring during dredging. For the simulation of conditions during dredging, this analysis included elevated TSS concentrations and focused on answering the question: what is the likelihood that an increase in TSS concentration greater than the Resuspension Standard far-field Evaluation and Control levels would be observed and declared to be significantly different from background, that is, what is the likelihood that such an increase would lead to the conclusion that additional action was necessary?

Total suspended solids during baseline and during dredging were simulated by performing a bootstrap sampling from low flow data (less than or equal to 10,000 cfs at Fort Edward) collected between 1997 and 2003 at TID-PRW2 and 1991 and 2003 at Schuylerville. One data point was rejected as an outlier as identified on probability plots of TSS in each month (see Figure 1). The bootstrap analysis was performed separately for each month (May – November) and repeated 5,000 times.

TSS values during the baseline period were simulated by randomly sampling with replacement from the historical data. To simulate semiweekly monitoring in May and June, 24 values were chosen with replacement from the historical data set (3 years of baseline monitoring X 4 weeks per month X 2 samples per week). To simulate weekly monitoring in July through November, 12 values were chosen with replacement from the historical data set (3 years of baseline monitoring X 4 weeks per month X 1 sample per week). These simulated values were averaged to determine the monthly mean and standard deviation of the baseline TSS.

TSS values during dredging were simulated over the course of a period lasting approximately two days. During this two-day period, one value was sampled (with replacement) every 3 hours from the historical data set. To calculate 6-hour average concentrations for the Evaluation Standard, running averages of pairs of consecutive samples were calculated. To simulate a 9-hour dredge day for the Concern Standard throughout the simulated period, running averages of 3 consecutive values were calculated. To simulate a 24-hour average, running averages of 8 consecutive samples were calculated. To simulate a TSS release, after the first few simulated samples, a specified TSS concentration was added to each value. For each dredging simulation, a separate baseline bootstrap average was calculated.

A series of such simulations was performed, differing in the amount of additional TSS added to baseline. The computer program tracked the first day on which the running average during dredging was significantly different from, and was at least 12 or 24 mg/L greater than, the average during baseline. The results were summarized by computing the probability that the monitoring program would not capture an exceedance within 6 hours (Evaluation Standard), or 9 or 24 hours (Concern Standard).

Results for the Evaluation and Control Standards were as follows. When the simulated baseline is exceeded by exactly 12, 24 or 24 mg/L for exactly 6, 9 or 24 hours, respectively, 27-50% of the time one

concludes that TSS increase is greater than 12 or 24 mg/L, and about 50-73% of time one concludes the opposite (see Tables below). The power of the monitoring program can be seen when evaluating results when the TSS during dredging exceeds baseline by a slightly different amounts. For example, when the TSS during dredging is 4 mg/L less than the trigger values (i.e., either 8 mg/L or 20 mg/L), then there is up to a 16% chance of concluding that the standards have been exceeded (a "type I error"); in this way, the program provides a level of conservatism.

On the other hand, when the TSS during dredging is 4 mg/L greater than the trigger values (i.e., either 16 mg/L or 28 mg/L), then the power of the program to detect the exceedance is greater than 95 percent (power = 1 – probability of type II error; see Tables below).

Probability of concluding that the standards have been exceeded at TID-PRW2

Month	**Evaluation Standard (6-hour average)**			**Control Standard (9-hour average)**			**Control Standard (24-hour average)**		
	12 mg/L added	8 mg/L added[1]	16 mg/L added[2]	24 mg/L added	20 mg/L added[1]	28 mg/L added[2]	24 mg/L added	20 mg/L added[1]	28 mg/L added[2]
May[3]	28%	14%	99 %	27%	14%	99 %	40%	4%	99%
June[3]	30%	15%	98 %	28%	12%	98 %	40%	4%	99%
July	40%	0%	100%	42%	0%	100%	46%	0%	100%
Aug	38%	0%	100%	43%	0%	100%	49%	0%	100%
Sep	46%	0%	100%	47%	0%	100%	50%	0%	100%
Oct	43%	0%	100%	45%	0%	100%	50%	0%	100%
Nov	40%	0%	100%	45%	0%	100%	50%	0%	100%

[1]For exceedances less than the standard, this represents the type I error.
[2]For exceedances greater than the standard, this represents the power of the program.
[3]During baseline monitoring, sampling frequency is twice a week in May and June, once a week in other months.

Probability of concluding that the standards have been exceeded at Schuylerville

Month	**Evaluation Standard (6-hour average)**			**Control Standard (9-hour average)**			**Control Standard (24-hour average)**		
	12 mg/L added	8 mg/L added[1]	16 mg/L added[2]	24 mg/L added	20 mg/L added[1]	28 mg/L added[2]	24 mg/L added	20 mg/L added[1]	28 mg/L added[2]
May[3]	32%	16%	96%	30%	15%	97%	42%	6%	98%
June[3]	34%	12%	100%	35%	7%	100%	44%	1%	100%
July	38%	3%	100%	42%	0%	100%	48%	0%	100%
Aug	42%	1%	100%	47%	0%	100%	48%	0%	100%
Sep	36%	0%	100%	39%	0%	100%	48%	0%	100%
Oct	42%	0%	100%	45%	0%	100%	49%	0%	100%
Nov	43%	0%	100%	47%	0%	100%	49%	0%	100%

[1]For exceedances less than the standard, this represents the type I error.
[2]For exceedances greater than the standard, this represents the power of the program.
[3]During baseline monitoring, sampling frequency is twice a week in May and June, once a week in other months.

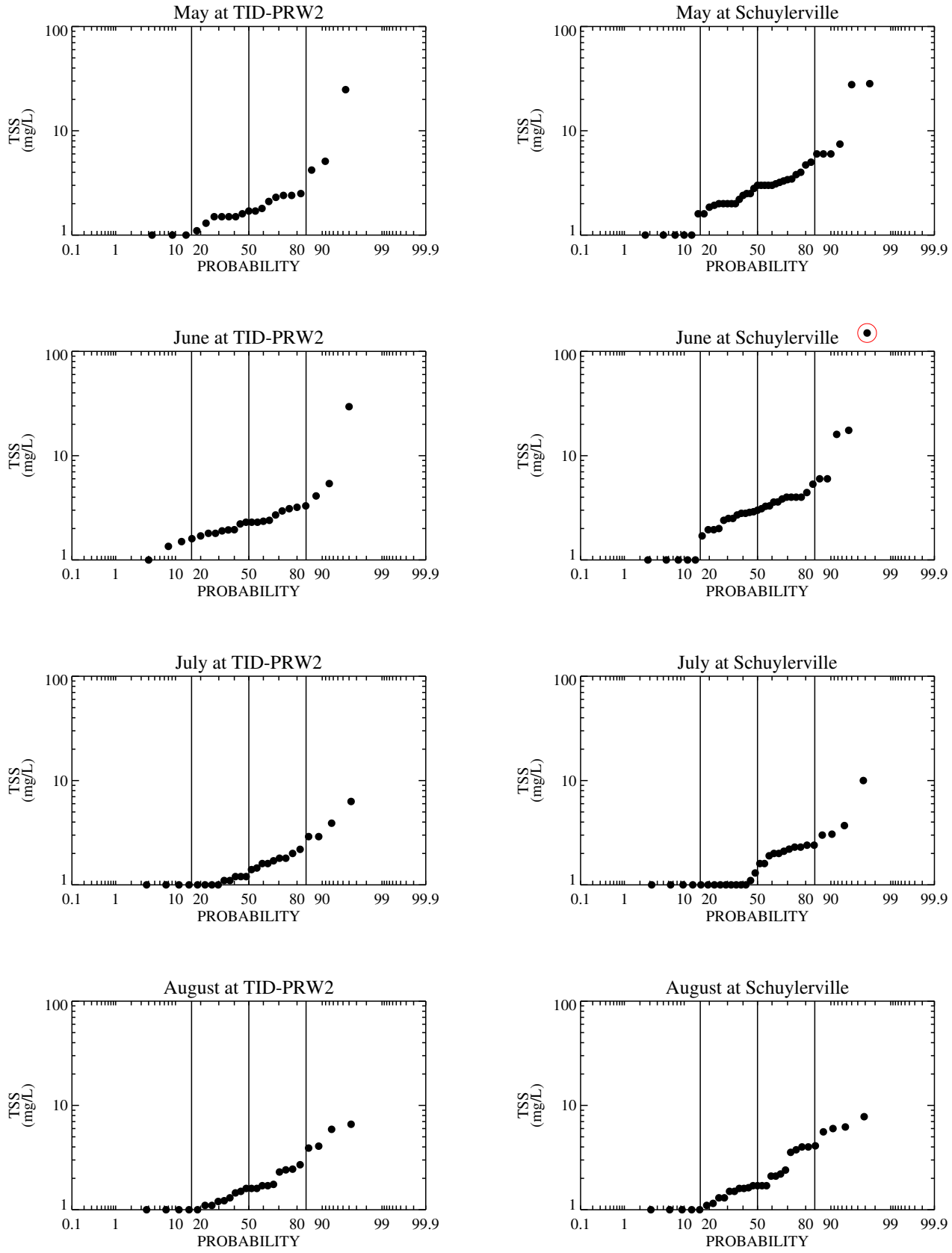

Figure 1a. Probability plots of total TSS by month at TID-PRW2 and Schuylerville.

Data source: GE database data collected from 1997 through 2003 at TID-PRW2 and 1991 through 2003 at Schuylerville. Duplicates are averaged. Non-detects were set to 1 mg/L. Circled point was rejected as an outlier. Measurements taken at high flow (>10,000 cfs at Fort Edward) have been excluded.

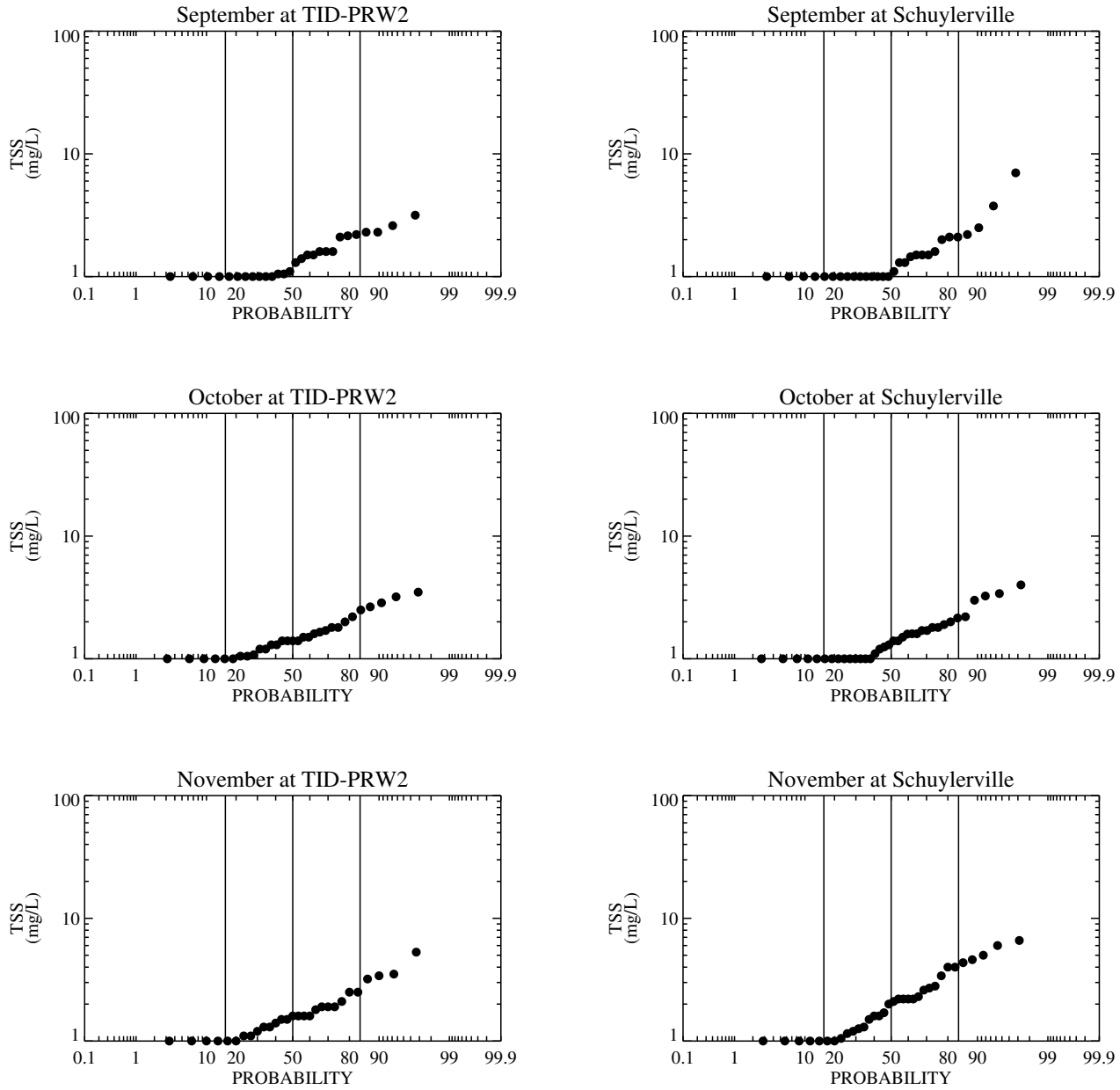

Figure 1b. Probability plots of total TSS by month at TID-PRW2 and Schuylerville.

Data source: GE database data collected from 1997 through 2003 at TID-PRW2 and 1991 through 2003 at Schuylerville.
Duplicates are averaged. Non-detects were set to 1 mg/L.
Measurements taken at high flow (>10,000 cfs at Fort Edward) have been excluded.

APPENDIX 44

STANDARD OPERATING PROCEDURE FOR COLLECTION OF WATER COLUMN SAMPLES FOR DISSOLVED METAL ANALYSIS

PROCEDURES

1.0. Scope & Application

This Standard Operating Procedure (SOP) is applicable to the collection of water column samples for dissolved Target Analyte List (TAL) metals analysis for the Hudson River Baseline Monitoring Program, and is based on USEPA's Method 1669 for sampling ambient water for trace metals (USEPA 1996).

2.0. Summary of Method

This method involves the use of a multiple aliquot depth integrating sampler to collect water column samples, as defined in Appendix 1. Composite samples will be prepared for the dissolved metals analysis in the same manner described in Appendix 1 for other parameters. The sampler will be coated with epoxy to minimize exposure of water samples from coming into contact with metal equipment.

Before samples are collected, the sample collection vessels and sample containers will be cleaned by the laboratory using detergent, mineral acids, and reagent water. Reagent water is defined as water prepared by the laboratory in which the analytes of interest and potentially interfering substances are not detected at the Method Detection Limit (MDL) of the analytical method(s). After cleaning, sample containers will be filled with weak acid solution, and individually double-bagged using resealable plastic bags. Sample collection vessels will be placed in plastic bags to minimize contact with metal or atmospheric deposition of particles containing metal.

Upon arrival at the sampling site, one member of a two-person sampling team will be designated to perform duties that may result in contact with potential contaminants, and will not perform any tasks that result in direct contact with samples ("dirty hands"). The second member will perform all activities that may result in contact with the sample containers or transfer of the sample ("clean hands"). Sampling personnel are required to wear clean gloves (without talc) at all times when handling sampling equipment and containers.

The epoxy-coated multiple aliquot depth integrating sampler will be deployed, and a sample aliquot for dissolved metals analysis will be collected in one of the sample collection vessels. Upon completion of preparation of the composite sample at a transect location, filtration will be performed through a 0.45 µm filter. The resulting filtrate will be placed in an appropriate container, double bagged, and placed in a cooler with ice prior to delivery to the laboratory. Preservation of samples with dilute nitric acid will be

performed immediately upon arrival at the laboratory, where the samples will be allowed to equilibrate for a minimum of 48 hours prior to analysis. Appropriate field documentation will be maintained using a computerized sample tracking system.

3.0. Health and Safety Warnings

Health and safety issues are addressed in the project Health and Safety Plan (HASP; BBL, 2003).

4.0. Contamination and Interferences

Potential sources of trace metals contamination during sampling include metallic or metal-containing sampling equipment, containers, personal protective equipment (PPE) (e.g. gloves that contain zinc due to the presence of talc), reagent water, and improperly cleaned and stored equipment. Additionally, atmospheric inputs such as dirt and dust from automobile exhaust, tobacco smoke, nearby roads, bridges, wires, and poles can result in sample contamination. Several of the sampling stations are on bridges that carry automobile and truck traffic. If contamination due to environmental conditions on the bridges is suspected and is persistent, the locations and procedures for collecting samples for dissolved metals analysis will be reevaluated. If laboratory analyses indicate that Hudson River water contains substances that interfere in the determination of dissolved metals, additional sample volume will be collected to allow the laboratory to identify and address interference problems.

5.0. Personnel Qualifications

All field personnel are required to take a 40-hour OSHA Hazardous Waste Operations training course and annual refresher courses, and participate in a medical monitoring program prior to engaging in any field collection activities as required in 29 CFR 1910.120. Additionally, field personnel will be under the direct supervision of qualified professionals who are experienced in performing the tasks required for sample collection.

6.0. Equipment and Supplies

Equipment needed for collection of water samples for dissolved metals analysis includes:

- Epoxy-coated multiple aliquot depth integrating sampler
- Pre-cleaned glass sample collection vessels
- Pre-cleaned fluoropolymer or glass sample containers
- Portable glove bag/box
- Peristaltic pump
- Pre-cleaned tubing for peristaltic pump
- Pre-cleaned polyethylene fittings for connecting pump to filter

- Filter – 0.45 µm, 15 mm diameter or larger, tortuous-path capsule filters (Gelman Supor 12175 or equivalent)
- Power source for peristaltic pump
- Disposable gloves (talc free)
- Reagent water (free of metals; supplied by laboratory)
- 5 gallon plastic carboy (for storage of dilute acid wastes from pre-cleaned sample containers)
- Plastic (polyethylene) resealable food storage bags
- Plastic (polyethylene) food wrap
- Plastic (polyethylene) trash bags
- Dedicated, clean cooler with ice
- All equipment necessary for collection of routine water samples (see Appendix 1)
    - Portable bridge crane
    - Boat and motor equipped w/anchors or spuds
    - Portable winch w/precise two-directional line speed control
    - Global Positioning System (GPS)
    - Lap top computer and printer
    - Field log

7.0. Water Sample Collection and Filtration

Sampling Locations

Sample locations are defined in Section B1.1 of the main text of the QAPP, and will be consistent with those locations used for the routine sampling described in Appendix 1. Samples will be collected from the centroid (center of the channel) at the following locations:

- Bakers Falls Bridge
- Rogers Island (Rt. 197 Bridge; east/west channel composite)
- Waterford (Rt. 4 Bridge; spring high flow only)
- Albany (near RM 145; boat access)
- Poughkeepsie (near RM 76; boat access)

Samples will be collected along transects using the EDI sampling method at the following locations:

- Thompson Island (boat access)
- Schuylerville (Rt. 29 Bridge, east/west channel composite)
- Stillwater (Bridge)
- Above Lock 1 (boat access)
- Waterford (Rt. 4 Bridge)
- Mohawk River at Cohoes (Rt. 32 Bridge)

Sampling Procedures

1. Locate the desired sampling station. The locations of sampling stations and substations on bridges will be predetermined based on historical center channel sampling locations or bathymetric and flow velocity surveys conducted in accordance with the SOP for measuring velocity profiles included as Appendix 3 of this QAPP. If these surveys indicate that significant changes in the proportion of discharge assigned to each sub-area under various river flows at EDI stations occurs, the locations of the sampling substations may be shifted based on river flow, as defined in Appendix 1. Stations on the Bakers Falls and Rt. 197 Bridges will be consistent with historical sampling locations.
2. Maneuver a portable crane into position above the sampling location.
3. From this point forward, sample handling procedures will follow USEPA's "clean hands/dirty hands" protocols whenever handling materials that may come in contact with the sample to be filtered and submitted for dissolved metals analysis. One person of the two person sampling crew will be designated to perform the "clean hands" duties, while the other will perform the "dirty hands" duties.
4. Both sampling personnel will put on two pairs of talc-free disposable gloves. The outer pair of gloves will be changed any time there is potential for the outer gloves coming in contact with potential contaminants.
5. "Clean hands" will place the pre-cleaned sample collection vessels in the epoxy coated multiple aliquot depth integrating sampler. One set of sample collection vessels will be used at each station; however, the same vessels will be used at all EDI sub-stations for each sampling event.
6. As defined in Appendix 1, determine the amount of sample that will be required from each station or sub-station to fill all sample containers, including any duplicate or split samples. The volume of sample will be adjusted so that an approximately equal volume of sample will be collected at each sub-station, and that little or no sample is collected that is not needed to fill sample containers (i.e., collection of excess sample will be avoided and, to the extent possible, all of the sample collected will be put into containers.
7. When the sampler is retrieved, "clean hands" will remove the sample collection vessels and inspect to confirm that the approximate target volume has been collected. Recalibrate the deployment speed as necessary if sample volumes are not correct (Appendix 1).
8. Once the sampler is calibrated so that an acceptable sample volume is collected, the sample will be transferred from the collection vessel to pre-cleaned containers by "clean hands". Pre-cleaned sample containers will be pre-labeled and double bagged using resealable food storage bags, and placed in a clean, dedicated (to Hudson River dissolved metals analyses work) cooler.
9. Sample containers will be labeled in accordance with Section B3 of the main text. "Dirty hands" will retrieve the sampler and steady it while "clean hands" removes the sample collection vessels. "Dirty hands" will open the cooler and the outer plastic bag containing the appropriate sample container.[both should change gloves after handling the sampler and prior to opening the outer and inner bags] "Clean hands" will then open the inner plastic bag, poor the dilute acid solution out into a carboy container designated for waste storage.

10. "Clean hands" then transfer the contents of the collection vessel to the sample container to the predetermined level marked on the container (see discussion below), place the cap back on the container, and close the inner bag. "Dirty hands" will then close the outer bag, and place the double bagged container back in the cooler. This process will be repeated at each sub-station until the all sub-stations have been sampled along one transect.

Sample Filtration

Upon completing collection of the composite sample at each sampling location, samples will be filtered in the field to permit subsequent analysis for dissolved metals.

1. Set up the filtration system inside the glove bag, using the shortest runs of tubing possible.
2. "Dirty hands" places the peristaltic pump immediately outside of the glove bag and passes the cleaned tubing through a small hole in the glove bag. "Clean hands" attaches the tubing to the capsule filter inside the glove bag. Also, attach a short length of tubing to the outlet of the capsule filter for filling containers after filtration.
3. "Dirty hands" opens the cooler and the outside bag, allowing "clean hands" to remove the water sample from the inner storage bag and place the sample inside the glove bag. "Clean hands" also places the capsule filter, two clean empty sample bottles, a bottle containing reagent water, and a bottle for waste in the glove bag.
4. "Clean hands" opens the reagent water bottle and places the end of the pump tubing in the bottle.
5. "Dirty hands" starts the pump and pumps approximately 200 mL of reagent water through the tubing and filter into the waste bottle. "Clean hands" then moves the outlet tubing to a clean bottle and collects the remaining reagent water as a blank.
6. "Dirty hands" stops the pump. "Clean hands" removes the lid of the sample bottle and places the intake end of the tubing in the bottle.
7. "Dirty hands" starts the pump and passes approximately 50 mL through the tubing and filter into the remaining clean sample bottle and then stops the pump.
8. "Clean hands" uses the filtrate to rinse the bottle, discards the waste sample, and returns the outlet tube to the sample bottle.
9. "Dirty hands" starts the pump and the remaining sample is processed through the filter and collected in the sample bottle.
10. "Clean hands" replaces the lid on the bottle, and places the bottle in a new bag, and seals the bag. "Clean hands" then places the first bag into a second new bag held by "dirty hands".
11. "Dirty hands" seals the outer bag, and places the double-bagged sample bottle into the cooler for subsequent delivery to the laboratory.

8.0. Sample Handling and Preservation

Sample containers will be labeled prior to sample collection in accordance with labeling requirements specified in Section B3 and Figure B-5. Samples will be collected, filtered, and placed in containers in accordance with the procedures described in Section 7 above. Each container will be placed in two re-sealable food storage bags (double bagged, one inside the other), and placed in a clean cooler dedicated to dissolved metals analysis for the Hudson River. The samples will be chilled with ice to approximately 4° C. A temperature blank will be placed in each cooler for use by the laboratory to measure the temperature of samples upon submittal. Samples will be shipped by overnight delivery to the laboratory at the end of each day and preserved with nitric acid upon arrival. Samples will be allowed to equilibrate after preservation for a minimum of 48 hours prior to analysis. Chain of custody procedures will be followed, as specified in Section B3 of this QAPP.

9.0. Data and Records Management

All data from water sample collection will be recorded in the field database (Microsoft Access®) provided by QEA using a laptop computer. Upon completion of sampling at one location, all data from the location will be entered into the database and the field log for that location printed and the hard copy stored in the field notebook. This will limit the risk of losing sample information due to computer failure. Blank field log sheets can also be used to record information manually in case difficulties with data entry using the computer are encountered. Manually recorded data will be transcribed into the field database at the end of each day.

10.0. Quality Control and Quality Assurance (QA/QC)

QA/QC procedures are defined in Section B5 of this QAPP, and include the collection of field QA/QC samples. Field QA/QC samples to be collected are blind duplicate samples, equipment blank samples, and matrix spike samples. One set of field QA/QC samples will be collected for each sampling event. Blind duplicate samples and matrix spike samples will be prepared by filling additional appropriately marked containers at pre-selected sampling stations (both samples will not be collected at the same station). The station where these samples are collected will be rotated randomly for each sampling event. Equipment blank samples will be prepared as follows:

1. Prepare for “clean hands/dirty hands” procedures (put on new disposable gloves).
2. Place a pre-cleaned sample collection vessel in the epoxy coated multiple aliquot depth integrating sampler (“clean hands”).
3. “Clean hands” will slowly pour laboratory supplied reagent water into the nozzle and fill the sample collection vessel while “dirty hands” hold the sampler stable.
4. When the desired volume is reached, “clean hands” remove the sample collection vessel and distribute to appropriately labeled sample containers using “clean hands/dirty hands” procedures specified in Section 7 above.
5. Repeat as necessary to provide adequate sample volume.

6. Filter the field blank sample using techniques identical to those used to filter environmental samples, as described in Section 7 above.
7. After collection, handle equipment blank samples in a manner that is consistent with all other environmental samples.

11.0. References

Appendix 1 – Water Sampling SOP

Appendix 3 - SOP for Determining Equal Discharge Increments (Hydrologic Surveys)

BBL. 2003. Revised Health and Safety Plan.

USEPA. 1996. Method 1669. Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. U.S. Environmental Protection Agency. Office of Water Engineering and Analysis Division (4303). July, 1996.

USGS. 1999. Techniques of Water-Resources Investigations of the United States Geological Survey. Book 9. Chapter 4.1.1.A. Isokinetic, Depth-Integrated Sampling Methods. September, 1999.