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U.S. Army Corps of Engineers

New England District
Concord, Massachusetts

QUALITY ASSURANCE PROJECT PLAN

Volume IIA
Appendix A, Continued

29 March 2001 (DCN: GE-021601-AAHM)

Revised May 2003 (DCN: GE-022803-ABLZ)

Environmental Remediation Contract
General Electric (GE)/Housatonic River Project
Pittsfield, Massachusetts

Contract No. DACW33-00-D-0006

WESTON SOLUTIONS

QUALITY ASSURANCE PROJECT PLAN, FINAL (REVISED 2003)

Volume IIA—Appendix A, Continued

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Contract No. DACW33-00-D-0006

Prepared for

U.S. ARMY CORPS OF ENGINEERS
New England District
696 Virginia Road
Concord, MA 01742-2751

Prepared by

WESTON SOLUTIONS, INC.
One Wall Street
Manchester, NH 03101-1501

W.O. No. 20125.257.103.1625

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APPENDIX A-42

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF PESTICIDES AND PCBS COLLECTED ON PUF CARTRIDGES

@ Air Toxics Limited
STANDARD OPERATING PROCEDURE

ANALYSIS OF PESTICIDES and PCBs COLLECTED ON PUF CARTRIDGES

EPA Method TO-4 and Modified EPA SW-846 Methods 8081A and 8082

SOP #26

Effective Date:	10/01/98
Revision #:	2
Reason for Revision:	Clarify Procedures and QC Requirements to include SW-846 Methods

Written By:	Signature	HEIDI HAYES Print	TEAM LEADER Title	10.1.98 Date
Technical Review:	Signature	SANDIA KAO Print	CHEMIST Title	10/1/98 Date
QA Review:	Signature	Marie Jeanne deForest Print	QA Manager Title	10/1/98 Date
Laboratory Director:	Linda L. Freeman			10/1/98 Date

1.0 PURPOSE

To provide a procedural guide for the application of EPA Method TO-4 (High Volume Sampling) to the analysis of pesticides and Arochlor PCBs in ambient air collected on PUF (polyurethane foam) cartridges.

2.0 METHOD SUMMARY

Adsorbent PUF cartridges are cleaned using solvents and vacuum dried. Cartridges are sent to the field wrapped tightly in aluminum foil to prevent degradation by UV light. Following sampling the filters and cartridges are subjected to soxhlet extraction with methylene chloride, the solvent is switched to hexane and the extract concentrated. Analysis is performed using a GC/ECD (Electron Capture Detector). The Target compound list and detection limits are noted in Attachment A.

3.0 HEALTH AND SAFETY

Normal laboratory safety precautions must be used when extracting samples, preparing standards from neat materials and analyzing samples. Appropriate eye wear, gloves and lab coat should be worn when handling any chemical used in this method. All manipulation of standards, solvents, and acid and basic solutions should be done with the utmost care in the hood. MSDS for each chemical should be consulted for specific dangers and precautions. The procedures described in this SOP are designed for skilled chemists trained in the safe operation of GC/ECD and sample handling.

4.0 SAMPLE PRESERVATION, HANDLING AND STORAGE

Samples are shipped to the laboratory in 4°C ice chests. Upon receipt, the cartridges are stored in a refrigerator (4°C) until extraction. Extraction must be performed within one week of sample collection. Sample extracts are stored in a separate refrigerator (4°C) until analysis. Analysis must occur within 40 days of extraction.

5.0 INTERFERENCES AND POTENTIAL PROBLEMS

5.1 A common interference in the pesticide procedure is from phthalate esters. Phthalate esters are introduced into the system through contaminated glassware and/or when the extraction solvent contacts plastic materials. All glassware is thoroughly cleaned to minimize phthalate contamination and there is limited use of plastic materials during the extraction procedure.

5.2 Carryover from a high level sample can also create false positive results. The system is demonstrated to be clean by analysis of a hexane blank and any sample suspected of carryover contamination is re-analyzed to verify results. Scientist judgment should always be used to determine when re-analysis is necessary but a typical guideline

would be whenever the sample concentration exceeds 5 times the upper calibration limit.

6.0 EQUIPMENT AND MATERIALS

6.1 Instrument

- GC/dual ECD system equipped with a temperature programmable oven suitable for splitless injection
- Capillary column - 30 m X 0.53 mm DB-1701 with 1.5 µm film thickness. (Primary)
- Capillary column - 30 m X 0.53 mm DB-5 with 1 µm film thickness. (Secondary)
- HP Chemstation and Target Thru-put System Chromatography Software
- HP 7673 Automatic Liquid Injection System

6.2 Parameters:

- Initial Column Temperature and Hold Time: 140°C for 2 minutes
- Column Temperature Program: 20°C/minute to 200°C for 5 minutes 5°C/minute to 265°C for 5 minutes
- Final Column Temperature and Hold Time: 20°C/minute to 280°C for 5 min.
- Injector Temperature: 250°C
- Detector Temperature: 290°C
- Sample Injection Volume: 1.0µL
- Carrier Gas: Helium approximately 6 mL/minute at 50°C

7.0 REAGENTS AND SUPPLIES

- TO-4 Glass Cartridges (Graseby/General Metal Works, Village of Cleves, OH)
- Grade QMA quartz fiber filters 10.16 cm (Whatman)
- PUF plugs (Graseby/General Metal Works, Village of Cleves, OH)
- Aluminum foil
- Soxhlet extractors capable of extracting filters and adsorbent cartridges, 1.0 L flask and condenser
- Glass funnels
- Filter paper #41
- Zymark Automated Liquid Concentrator equipped with 1 mL end point
- Polyethylene gloves for handling filters and cartridges
- Vacuum oven
- Methylene Chloride - Reagent Grade
- DI Water - HPLC Grade
- Hexane - Reagent Grade
- Methanol - Reagent Grade
- Sodium Sulfate, anhydrous
- Vortex Supermixer II (Labcraft)

8.0 PROCEDURES

8.1 Preparation of Sampling Media

PUF inserts are generally 3inch cylindrical plugs. The PUF material is initially cleaned by soxhlet extraction with methylene chloride for a minimum of 18 hours at approximately 4 cycles per hour. The solvent is changed after each six hour period. Batch size varies depending on the available equipment, but generally 20 to 30 are cleaned at one time. The extracted foam is dried for two to four hours at approximately 120°C in a vacuum oven. To prepare the media for shipment, the PUF is placed into the glass sampling cartridge using polyester gloves. The cartridge is wrapped with aluminum foil followed by bubble wrap and then placed into a sealed plastic bag. To certify the batch, the final (from the third six hour period) solvent rinse is solvent exchanged to hexane and blown down to 1.0 mL and submitted for analysis. The batch is certified if all compounds are less than the required detection limit. A batch is identified by the preparation date and the type of PUF (e.g. 970508TO4 for PUF inserts prepared on 5/8/97). The PUF inserts that are not immediately being used in assembly of cartridges are placed in a glass jar or wrapped in aluminum foil and kept at ambient temperature until they are needed. The jar is labeled with the above batch ID. PUF inserts that are not used within 3 months of preparation, will be re-certified as clean prior to use.

8.2 Sample Extraction

8.2.1 Glassware Preparation: All glassware used in the extraction is prepared as follows: Wash with warm soapy water, triple rinse with tap water, triple rinse with de-ionized water, then set to dry. All glassware must be completely dry prior to use. Triple rinse with methylene choride. If glassware is not dry, a triple methanol rinse followed by a triple methylene chloride rinse may be used. The turbo vap vials must also be triple rinsed with hexane.

8.2.2 Funnels: Set up a funnel for each sample lined with #41 filter paper in the fume hood using ring stands. Add a small amount of sodium sulfate and triple rinse with hexane.

8.2.3 Extraction Procedure:

8.2.3.1 Fill each round bottom flask with approximately 700 ml methylene chloride.
8.2.3.2 Add several methylene chloride rinsed PTFE boiling chips to each flask and cover with foil.
8.2.3.3 Triple rinse each soxhlet extraction body with methylene chloride, place on flat bottom flask.
8.2.3.4 Unwrap each sample and place the sample cartridge and its quartz filter into labelled extraction soxhlets. Include a blank and spike.
8.2.3.5 Bring chiller to set point temperature of 10°C.

8.2.3.6 Add 500 ul of surrogate spiking solution to each soxhlet, including the blank and spike. Surrogate spiking solution is prepared from purchased mixes from Restek or equivalent. To prepare a 2.0 ug/ml surrogate spiking solution, 1.0 ml of a purchased mix of 200 ug/ml 2,4,5,6-Tetrachloro-m-xylene and Decachlorobiphenyl is added to a 100 ml volumetric flask and brought to volume with hexane. The surrogate spiking solution is stored at -18±5°C and expires in 6 months.

8.2.3.7 Add 500 ul of appropriate spiking solution to the spike sample (LCS). For the standard pesticide list, the spike is prepared from a purchased mix from Supelco or equivalent. An example pesticide spike is prepared as follows: 100 ul of SS TCL Pesticides Mix (Supelco) at 2000 ug/ml is added to a 100 ml volumetric flask and brought to volume with hexane to yield a final concentration of 2.0 ug/ml. This mix contains Aldrin, Alpha-BHC, Beta-BHC, Delta-BHC, Dieldrin, Endosulfan I, Endosulfan II, Endosulfan Sulfate, Endrin, Endrin Aldehyde, Endrin Ketone, Gamma-BHC, Heptachlor, Heptachlor Epoxide, Methoxychlor, 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT. If the list is PCBs only, Aroclor 1242 or any specifically requested Arochlor, is spiked as the method spike (LCS). A solution is purchased from Restek, Supelco, Ultra, or equivalent and may be prepared as follows: 1.0 ml of PP-311 Aroclor 1242 solution at 100 ug/ml purchased from Ultra is added to a 5.0 ml volumetric flask and brought to volume with hexane to yield a concentration of 20 ug/ml.

8.2.3.8 Carefully place the condenser on each soxhlet.

8.2.3.9 Turn on each heating mantle to a set point of 5.5. The orange light flashing indicates the mantle is heating.

8.2.3.10 Extract samples for a minimum of 18 hours, maintaining a chiller temperature of less than 15°C.

8.2.3.11 Turn off heating mantles at the end of the 18 hour period and allow each soxhlet to cool a minimum of 1 hour before proceeding.

8.2.3.12 Carefully remove the condenser from each soxhlet.

8.2.3.13 Drain all remaining solvent from the extractor body to the flat bottom flask by tilting the soxhlet to start the side arm siphon. Remove the soxhlets from the flat bottom flasks.

8.2.3.14 Flasks are then either transferred to the fume hood for heat reduction step (next section), or covered with foil and stored in the refrigerator.

8.2.4 Concentration:

8.2.4.1 Triple rinse each Snyder column with methylene chloride into the sample's respective flat bottom flask. Place the column on each flask.

8.2.4.2 Place the samples on hot plates using a temperature setting between 5 and 6. Samples will begin to boil and columns will chatter.

8.2.4.3 Allow to boil until sample volume is NEAR dry. Do not allow the samples to go to dryness. This will cause poor recoveries and loss of sample.

8.2.4.4 Add approximately 100 ml of Hexane through the Synder column and return to heating mantle. Again allow to boil to near dryness and add another 100 ml Hexane through the Synder column. Repeat for a third addition.

8.2.4.5 Remove sample from mantle, let cool, and rinse Synder column with hexane into round bottom flask. Remove Synder column and pour sample through a funnel lined with #41 filter paper and sodium sulfate, collecting sample extract into turbo vap vial. Rinse round bottom flask two more times with Hexane through funnel. After all solvent has drained out of the funnel, triple rinse with Hexane into the turbo vap vial.

8.2.5 Nitrogen Evaporation:

8.2.5.1 Evaporate filtered sample to just below 1.0 ml using nitrogen in the turbo vap.

8.2.5.2 Remove sample from turbo vap and adjust the volume to exactly 1.0 ml using a clean Pasteur pipette and clean hexane.

8.2.5.3 vortex the sample for five seconds.

8.2.5.4 Using a clean Pasteur pipette, transfer the 1.0 ml sample to a labeled coarse-threaded screw top vial and cap each sample.

8.2.5.5 Store vials in the refrigerator and fill out all appropriate documents.

8.2.6 PCB Cleanup Procedures:

If the target list includes Aroclors only, a sulfuric acid cleanup is used. DO NOT DO A SULFURIC ACID CLEANUP ON PESTICIDE SAMPLES AS TARGET ANALYTES WILL DEGRADE. Prior to storing sample extract vials in the refrigerator, add 100 ul concentrated sulfuric acid to each blank, spike and sample. Shake vial on the vortex mixer for 5-10 seconds. Centrifuge samples for 3-5 minutes. Store samples with sulfuric acid. When aliquots are analyzed on the GC/ECD, be careful to analyze hexane fraction only leaving the sulfuric acid layer (bottom layer) in the vial.

8.3 Sample Analysis

Analysis is carried out on a HP 5890 GC/ dual ECD system. Second column confirmation is used to positively identify pesticide results. Results are reported from the "Primary Column" analysis. However, if the results are > 40 % percent difference between the two columns, the higher result will be reported as specified in Method 8081A. Any results reported from the "Confirmation Column" analysis will be noted on the sample report.

8.4 Calibration

Calibration is accomplished through an external standard technique. Once the data file is collected and stored it is automatically processed and reported using the Target Thruput

Software. The working range of the analytical system is defined by the range of concentrations bracketed by the five point calibration. The lowest level of the curve represents the detection limit and the highest level represents maximum concentration possible without dilution. The concentration of the field samples must be bracketed by this range. Any sample which exceeds the calibration range of the curve will be diluted with hexane until its concentration approximates the mid-point of the calibration range.

8.4.1 Initial Calibration

8.4.1.1 Standards are blended from commercially blended and certified stock solution to cover a range from 0.10 uG/sample to 2.0 uG/sample. Standards are stored in the standards freezer. One µL of each standard is analyzed. Tabulation of the peak area vs. concentration (uG/mL) is performed to generate a response factor for each level using the equation:

$$RF = A_X/C_X$$

Where: A_X = Area of the peak for the compound measured
C_X = Concentration of the compound measured (uG/mL)

8.4.1.2 Aroclor, technical Chlordane, and Toxaphene calibrations are bracket the linear range of 1.0 uG/sample to 10 uG/sample. Standards are stored in the standards freezer. Non-overlapping Aroclors can be calibrated concurrently, e.g., Aroclor 1016 and Aroclor 1260. One µL of each standard is analyzed. A minimum of four peaks are used to characterize technical Chlordane, Toxaphene and each Aroclor. In general, only Arochlor 1016/1260 mix is used to determine instrument linearity. A single mid-level standard for each remaining Aroclor is analyzed unless the project specifically requests calibration on an Aroclor by Aroclor basis. Tabulation of the peak area sum vs. concentration (uG/mL) is performed to generate a response factor for each level using the equation:

$$RF = A_X/C_X$$

Where: A_X = Sum of peak Areas of the 4 characteristic peaks for the compound measured

C_X = Concentration of the compound measured (uG/mL)

8.4.1.3 The average RF for each compound is measured and tabulated. The Percent Relative Standard Deviation (% RSD) is also measured for the five point. Linearity through the origin is assumed if the variability of the RF is within ± 20% RSD for the target compounds. The average RFs from the calibration

curve are used to calculate results. If the average RF is greater than 20% then linear regression is used.

8.5 Independent Source Check Standard

After analysis of the initial curve, an independent source check is analyzed at the mid-level of the calibration curve. See standard prep logbook for preparation details. The independent source is prepared from stock from either a different vendor or a different lot of the same vendor. Recovery must be within 80 to 120% for all compounds.

9.0 CALCULATIONS

The initial calibration response factor (RF) for each compound is used to calculate sample results using the area counts (A_X) of each target species:

A_X/RF = uG/mL
(µG/mL) X (1.0 mL final volume/sample) = **µG/sample**

10.0 QUALITY CONTROL

10.1 Initial Calibration Curve

The percent relative standard deviation (%RSD) for the initial curve must be less than or equal to 20%. If the % RSD is greater than 20% then linearity through the origin is not assumed and the analyte uses an optional linear regression calibration. A second alternative is to use the mean %RSD criterion as outlined in SW846 Method 8000B Section 7.5. If the mean %RSD criterion is used the compound(s) failing the 20% criterion requirement are noted.

10.2 Independent Source Check Standard

The independent source standard prepared at the mid-point of the multilevel calibration is analyzed immediately after the initial calibration and each time the instrument is calibrated. The independent source should agree with the primary standard within 80% to 120% recovery.

10.3 Continuing Calibration Verification

10.3.1 The continuing calibration verification (CCV) is analyzed daily prior to sample analysis. The response for each analyte should be within 15% of the initial calibration curve. If greater variability is observed, the average of all of the target analytes in the calibration table (not the average of those required for any particular project) is calculated. If the average meets the 15% criteria then the standard verification has been met. If the average deviation does not meet the 15%

criteria then a new initial calibration curve may need to be analyzed and/or fresh standards may need to be prepared.

10.3.2 The CCV is analyzed every 10 samples and at the end of the analysis sequence (i.e. end of run drift check). Both high, low and multicomponent standards are alternated. However, the analyst must verify that a pesticide standard is analyzed at the minimum of every 12 hours. The recovery of an individual component or the average of all the target components must be within 15% for these checks. Should the recovery fail to meet these limits on both the primary and confirmation column, all samples analyzed since the last valid check will be re-analyzed. However, if the standard analyzed is recovering high then samples do not need to be re-analyzed. The CCV is reported with "Q" flags to note high recoveries. If the standard analyzed is recovering low then all samples MUST be re-analyzed.

10.3.4 The retention time of every target component must be within the retention time windows established during the 72 hour retention time study for every standard analyzed. If not, the column maintenance or adjustment of chromatographic settings is performed until the analyte fall within its respective window.

10.4 LCS

Either a 1.0 µG pesticide LCS or a 10 uG PCB LCS is spiked depending on the requested target list and extracted with each set of 20 samples. All target compounds are spiked prior to extraction from a source other than the calibration standard. Recovery limits are 50% to 150% recovery. Since it is not possible to re-extract PUF samples, compounds outside the method limits will be qualified with a "Q" flag.

10.5 Surrogates

Surrogates are spiked into all samples and blanks prior to extraction. Surrogate limits are given below.

Surrogate	% Recovery
Tetrachloro-m-xylene	50-150
Decachlorobiphenyl	50-150

10.6 Method Blanks

A blank PUF cartridge will be extracted with each set of 20 samples extracted. Since it is not possible to re-extract PUF samples, compounds detected in the method blank will be qualified with a "B" flag. The "B" flag indicates that the compound was detected in the method blank and blank subtraction was not performed.

10.7 Pesticide Breakdown Evaluation Standard

Each day prior to analysis, a standard containing Endrin and p,p'-DDT is analyzed to determine breakdown. The standard is prepared as indicated standard prep logbook at 0.8 ug/ml. Breakdown must not exceed 15% for each compound and is determined as follows:

$$\text{Endrin Brkdwn} = \frac{\text{Area Endrin Aldehyde + Area Endrin Ketone}}{\text{Area Endrin + Area Endrin Aldehyde + Area Endrin Ketone}} \times 100$$

$$\text{DDT Brkdwn} = \frac{\text{Area p,p'-DDE + Area p,p'-DDD}}{\text{Area p,p'-DDT + Area p,p'-DDE + Area p,p'-DDD}} \times 100$$

10.8 Analytical Sequence

The analytical sequence begins with the Pesticide Breakdown Evaluation Standard followed immediately by the CCV. Following standard analysis a method blank is run followed by the analysis of field samples and one LCS per extraction batch. The CCV is analyzed every 10 samples and as an end check following the last sample of the day.

CCV recoveries should be ±15% of the expected value. Sample analysis cannot proceed if either the breakdown check standard, CCV or method blank analysis fails to meet acceptance criteria. If the end check standard fails re-analysis of the standard is performed. If the failure is confirmed then maintenance and re-calibration is required. The analytical sequence is repeated for each 12 hour clock.

10.9 Method Detection Limit

The limit of detection is determined in accordance with the guidelines of Appendix B, Part 136 of the Federal Register 40 CFR. The 99% confidence level is used to determine MDLs. An MDL study is performed annually.

10.10 Method Precision

Laboratory sample duplicates are analyzed at a frequency of 10%. The RPD between duplicates must be ± 20% or re-analysis is performed.

10.12 Retention Time Window Studies

A 72 hour retention time window must be established for every set of analytical columns and instruments. The lab will calculate new 72 hour windows whenever a new column is installed. Windows are established by making three injections of a mid-level calibration standard over a 72 hour period. The standard deviation of these retention times is calculated. This standard deviation is multiplied by 3 to calculate the window. The

window is applied to the daily check's R.T. The windows are used for advisory purposes and the discretion of the analyst must weight heavily on all compound identifications.

11.0 DATA VALIDATION

11.1 Manual calculation

Manual calculation is performed on a minimum of one sample per analytical sequence to validate the software has calculated and reported the results correctly. The analyst performs the calculation starting from the raw area counts through to the final result. Documentation of the calculation is done on the hardcopy quant report accompanied by signature and date. In addition, any identifiable field blanks or trip blanks should be reviewed for possible contamination. If contamination is evident, a comment is placed in the Laboratory Narrative portion of the reporting module.

11.2 Initial Data Review

As the analytical sequence is run throughout the day, the analyst verifies that the appropriate standards are analyzed, surrogate, and analyte recoveries are acceptable, and that the method blanks have no analyte detections above detection limit. As the samples are analyzed and data is generated, the analyst verifies peak integration, and that concentrations are within the linear range of the instrument. The entry in the run log is checked as acceptable and is initialed by the analyst to indicate that the data is acceptable. When the analyst compiles the data packages, the SOP for data review is followed.

11.3 Secondary Review

A thorough secondary review is performed by the QA department on a randomly chosen 10% of the final data packages. The secondary review entails verification that project and QC requirements were met. Failure to meet QC and/or project requirements results in a corrective action report and documentation. Dilution factors, analyte retention times, peak integration areas, concentration calculations, unit conversions, and detection limits are also checked. Field and trip blanks are checked and trends are observed.

Some clients requests that 100% of their final data packages undergo secondary technical review. The majority of the secondary reviews in this case are performed by the analytical supervisor. The secondary review performed by the analytical supervisor entails the same verification as that performed by the QA department. The randomly chosen 10% QA reviews typically counts towards the 100% secondary review.

12.0 WASTE DISPOSAL

All samples, standards and blank solutions are disposed of in the liquid organic waste drum located in the Hazardous Storage Area.

13.0 INSTRUMENT MAINTENANCE

Failure of DDT and Endrin to meet the breakdown check indicates active sites in the inlet system. If the breakdown check fails, the following may need to be performed: cleaning and deactivating the injection port, deactivating or replacing the injection port liner, clipping or replacing the guard column, and deactivating or replacing the "Y"-splitter.

If the daily check fails, the standard must be checked and re-prepared if needed. If the standard is acceptable, the analytical system must be evaluated. Front end maintenance as described above including septum replacement may be needed. ECDs may require thermal cleaning if a high background signal is indicated. All maintenance on the ECDs beyond thermal cleaning is performed by the manufacturer.

14.0 CORRECTIVE ACTION PROCEDURES

A request for corrective action (CAR) is initiated any time there are deviations from either the ATL SOPs or client-prescribed QC protocols, or in any instance where sample results may be adversely affected. Corrective action procedures are documented in ATLs SOP#61.

15.0 REFERENCES

SW-846 Test Methods for Evaluating Solid Waste, Third Edition, Final Update III, Revision 1, December, 1996.

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA/600/4-89/018, June 1988

Attachment A - Example Report

Attachment A - Example Report

AIR TOXICS LTD.

SAMPLE NAME: 0

ID#: 0-01A

EPA METHOD TO-4
Organochlorine Pesticides and PCBs
GC/ECD

File Name:		**Date of Collection:**	**1/0/00**
Dil. Factor:	**1**	**Date of Extraction:**	**1/1/04**
		Date of Analysis:	

Compound	Det. Limit (uG)	Amount (uG)
Aldrin	0.1	Not Detected
alpha-BHC	0.1	Not Detected
beta-BHC	0.1	Not Detected
delta-BHC	0.1	Not Detected
gamma-BHC	0.1	Not Detected
Chlordane	0.1	Not Detected
4,4'-DDD	0.1	Not Detected
4,4'-DDE	0.1	Not Detected
4,4'-DDT	0.1	Not Detected
Dieldrin	0.1	Not Detected
Endosulfan I	0.1	Not Detected
Endosulfan II	0.1	Not Detected
Endosulfan Sulfate	0.1	Not Detected
Endrin	0.1	Not Detected
Endrin Aldehyde	0.1	Not Detected
Endrin Ketone	0.1	Not Detected
Heptachlor	0.1	Not Detected
Heptachlor Epoxide	0.1	Not Detected
Methoxychlor	0.1	Not Detected
Toxaphene	1	Not Detected
Aroclor 1016	1	Not Detected
Aroclor 1221	1	Not Detected
Aroclor 1232	1	Not Detected
Aroclor 1242	1	Not Detected
Aroclor 1248	1	Not Detected
Aroclor 1254	1	Not Detected
Aroclor 1260	1	Not Detected

Surrogates	% Recovery	Method Limits
2,4,5,6-Tetrachloro-m-xylene		**50-150**
Decachlorobiphenyl		**50-150**

APPENDIX A-43

STANDARD OPERATING PROCEDURE FOR TOXICITY CHARACTERISTIC LEACHING PROCEDURE

Toxicity Characteristic Leaching Procedure
For Metals Analysis
Method 1311

Approvals and Signatures

QA Officer: Martha E. Roy Date: 12/5/94

Metals Manager: Kristine L. Aulin Date: 12/5/94

1.0 Scope and Application

1.1 The TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes.

1.2 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.3 The following parameters are tested for by this method:

Analyte	CAS #	Action Limit (mg/l)	Reporting Limit (mg/l)	Method of Analysis
Arsenic	7440-38-2	5.0	1	6010
Barium	7440-39-3	100	10	6010
Cadmium	7440-43-9	1.0	0.1	6010
Chromium	7440-43-9	5.0	1	6010
Lead	7439-92-1	5.0	1	6010
Nickel*	7440-02-0	15.0	1	6010
Silver	7440-22-4	5.0	1	6010
Zinc*	7440-66-6	250	1	6010
Selenium	7782-49-2	1.0	0.1	6010
Mercury	7439-97-6	0.2	0.04	7470

* Only for the State of Vermont

2.0 Summary of Method

2.1 For liquid wastes (i.e., those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 um glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase after particle size reduction , if needed, is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 um glass fiber filter.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

2.4 Sample Holding Times are as follows:

Table 1: Holding Times for NYS Samples

Analyte	From VTSR to TCLP Extraction	From Prep to Analysis
Mercury	5 days	26 days
Other Metals	180 days	180 days

Table 2: Holding Times for All Other Clients

Analyte	From Collection to TCLP Extraction	From Prep to Analysis
Mercury	28 days	26 days
Other Metals	180 days	180 days

4.0 Apparatus and Materials

4.1 TCLP Extractor Apparatus: The agitation apparatus is capable of rotating the extraction vessel in an end-over-end fashion at 30 +/- 2 rpm.

4.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 + 0.8 um, or equivalent. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 0.1 N nitric acid followed by 3 consecutive rinses with deionized distilled water (a minimum of 1 liter per rinse is recommended).

4.5 Filter Holder: When the waste is evaluated for other than volatile analytes, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered. These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimumfilter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10%) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration.

4.6 pH Meters: The meter should be accurate to +/- 0.05 units at 25°C.

4.7 Laboratory Balance: Any laboratory balance accurate to within +/- 0.01 grams may be used (all weight measurements are to be within +/- 0.1 grams).

4.8 Beaker or Erlenmeyer flask, glass, 500 mL.

4.9 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.10 Magnetic stirrer.

5.0 Reagents

5.1 Reagent grade chemicals shall be used in all tests.

5.2 Reagent water. Reagent water is defined as water in which an interferent is not observed at or above the method's detection limit of the analyte(s) of interest. For nonvolatile extrations, ASTM Type II water or equivalent meets the definition of reagent water.

5.3 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.4 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.5 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.6 Glacial acetic acid, ACS reagent grade.

5.7 Extraction fluid.

5.7.1 Extraction fluid # 1: Add 5.7 mL glacial acetic acid to 500 mL of reagent water, add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 +/- 0.05.

5.7.2 Extraction fluid # 2: Dilute 5.7 mL glacial acetic acid with reagent water to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 +/- 0.05.

Note: The pH should be checked prior to use to ensure that these fluids are made up accurately. If the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

6.0 Sample Collection and Preservation

6.1 Preservatives shall not be added to samples before extraction.

6.2 A minimum volume of 1 liter must be collected for water samples, and 100 grams for soil samples. Samples should be collected in pre-cleaned plastic or glass

containers and stored at 4°C.

6.3 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metals analysis must be acidified with nitric acid to a pH < 2, unless precipitation occurs. Sample portions that require a matrix spike analysis are spiked prior to preservation.

7.0 Procedure

7.1 Preliminary Evaluations - Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids; (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration ; (3) determination of whether the solid portion of the waste requires particle size reduction; and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste.

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Section 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Section 4.3.2 and is outlined in Sections 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

[Note: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.1.1.5 to determine the weight of the waste sample that will be filtered.]

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2 minute period), stop the filtration.

7.1.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

[NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after

applying vacuum or pressure filtration, as outlined in Section 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.]

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Section 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Section 7.1.1.5 or

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Section 7.1.1.9)}}{\text{Total weight of waste}} \times 100$$

7.1.2 If the percent solids determined in Section 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Section 7.1.3 to determine whether the solid material requires particle size reduction or to Section 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Section 7.1.1.9 is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed and to Section 7.3 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

7.1.2.2 Dry the filter and solid phase at 100 +/- 20-C until two successive weighing yield the same value within +/- 1%. Record the final weight.

[NOTE: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.]

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{(\text{Wt. of dry waste + filter}) - \text{tared wt. of filter}}{\text{Initial wt. of waste}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Section 7.2.9 if the nonvolatile TCLP is to be performed, and to Section 7.3 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Section 7.1.3) and determine the appropriate extraction fluid (Section 7.1.4). If only the volatile TCLP is to be performed, see the note in Section 7.1.4.

7.1.3 Determination of whether the waste requires particle size reduction (particle size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Section 7.3.6).

[Note: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.]

7.1.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5% and if the sample will be extracted for nonvolatile constituents (Section 7.2), determine the appropriate fluid (Section 5.7) for the nonvolatiles extraction as follows:

[NOTE: TCLP extraction for volatile constituents uses only extraction fluid #1 (Section 5.7.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 7.3.]

7.1.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500 mL beaker or Erlenmeyer flask.

7.1.4.2 Add 96.5 mL of reagent water to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 7.2.

7.1.4.3 If the pH from Section 7.1.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50°C, and hold at 50°C for 10 minutes.

7.1.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 7.2.

7.1.5 If the aliquot of the waste used for the preliminary evaluation (Sections 7.1.1 - 7.1.4) was determined to be 100% solid at Section 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Section 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Section 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Section 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Section 7.2.10 of the nonvolatile TCLP extraction.

7.2 Procedure When Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Section 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100% solid, see Section 7.1.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Section 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals.

[NOTE: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.]

7.2.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5% dry solids (Section 7.1.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5% dry solids, use the percent solids information obtained in Section 7.1.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

7.2.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through

the same filtration system.

7.2.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Section 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

[NOTE: If waste material (>1% of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Section 7.2.5, to determine the weight of the waste sample that will be filtered.]

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2 minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2 minute interval, proceed to the next 10 psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2 minute period), stop the filtration.

[NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.]

7.2.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed or stored at 4-C until time of analysis.

[NOTE: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Section 7.2.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.]

7.2.9 If the waste contains <0.5% dry solids, proceed to Section 7.2.13. If the waste contains >0.5% dry solids, and if particle size reduction of the solid was needed proceed to Section 7.2.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Section 7.2.11.

7.2.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described in Section 7.1.3. When the surface area or particle size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

[NOTE: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.q., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon coated sieve should be used to avoid contamination of the sample.]

7.2.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids} \times \text{weight of waste filtered}}{100}$$

Slowly add this amount of appropriate extraction fluid to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 +/- 2 rpm for 18 +/- 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 23 +/- 2°C during the extraction period.

[NOTE: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.q., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.]

7.2.12 Following the 18 +/- 2 hour extraction, separate the material in the

extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed if evaluating the mobility of metals.

7.2.13 Prepare the TCLP extract as follows:

7.2.13.1 If the waste contained no initial liquid phase, the filtered liquid material is defined as the TCLP extract.

7.2.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Section 7.2.12 with the initial liquid phase of the waste obtained in Section 7.2.7. This combined liquid is defined as the TCLP extract. Proceed to Section 7.2.14.

7.2.13.3 If the initial liquid phase of the waste, as obtained from Section 7.2.7, is not or may not be compatible with the filtered liquid resulting from Section 7.2.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Section 7.2.14.

7.2.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic analytes. If an analysis of the undigested extract shows that the concentration of any regulated metallic analyte exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to +/- 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted

average:

$$\text{Final Analyte Concentration} = \frac{(V1)(C1) + (V2)(C2)}{V1 + V2}$$

where:

V1 = The volume of the first phase (L).
C1 = The concentration of the analyte of concern in the first phase (mg/L).
V2 - The volume of the second phase (L).
C2 = The concentration of the analyte of concern in the second phase (mg/L).

7.2.15 Compare the analyte concentrations in the TCLP extract with the levels identified in the appropriate regulations.

7.3 Analyze a portion of the sample for Mercury following method 7470. Digest a portion of the sample by method 3010:1T and analyze by method 6010.

8.0 Quality Control

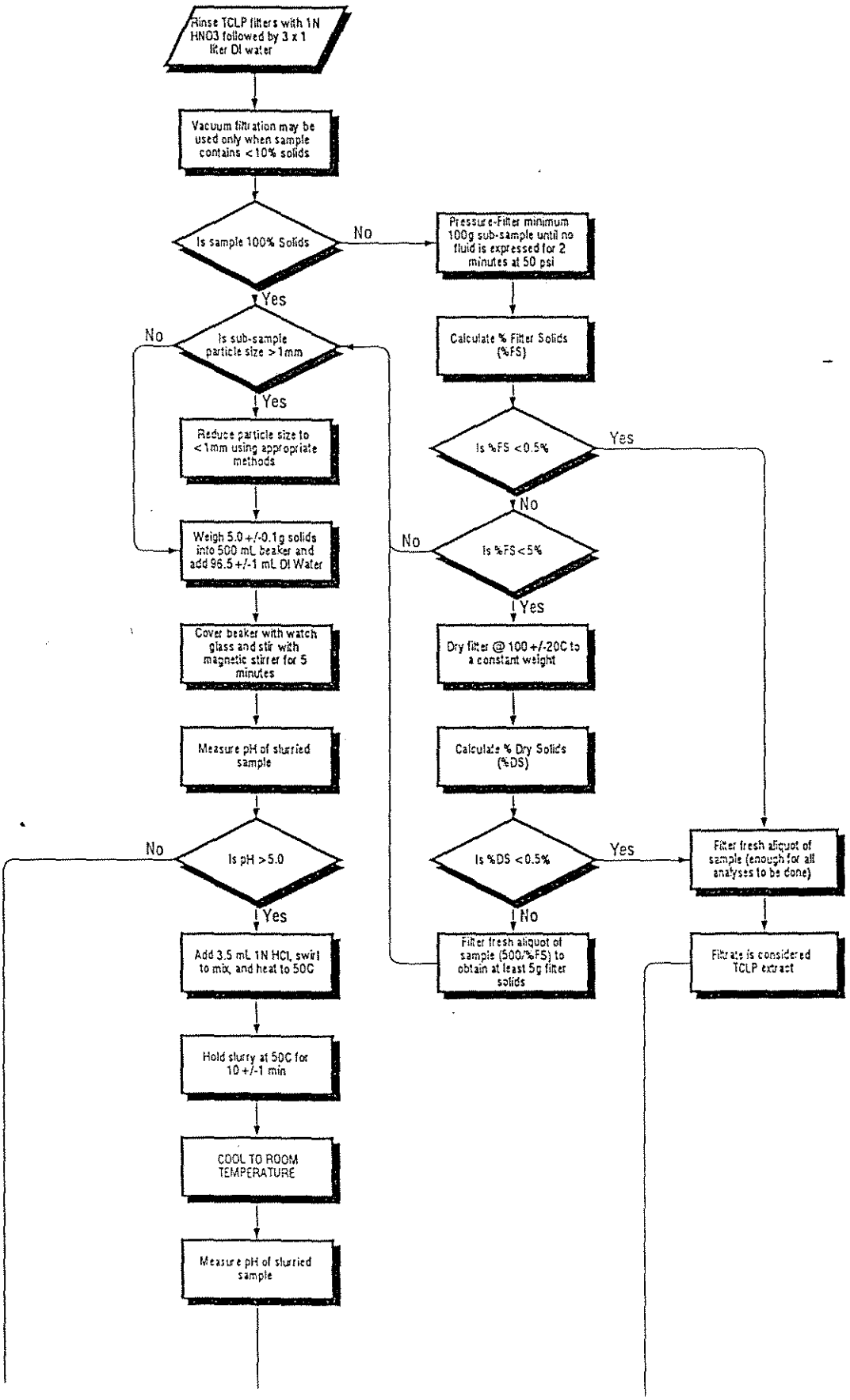
8.1 Samples are analyzed by MSA. The sample is analyzed with a minimum of two spikes. The correlation coefficient must be <0.995 or the analysis is repeated.

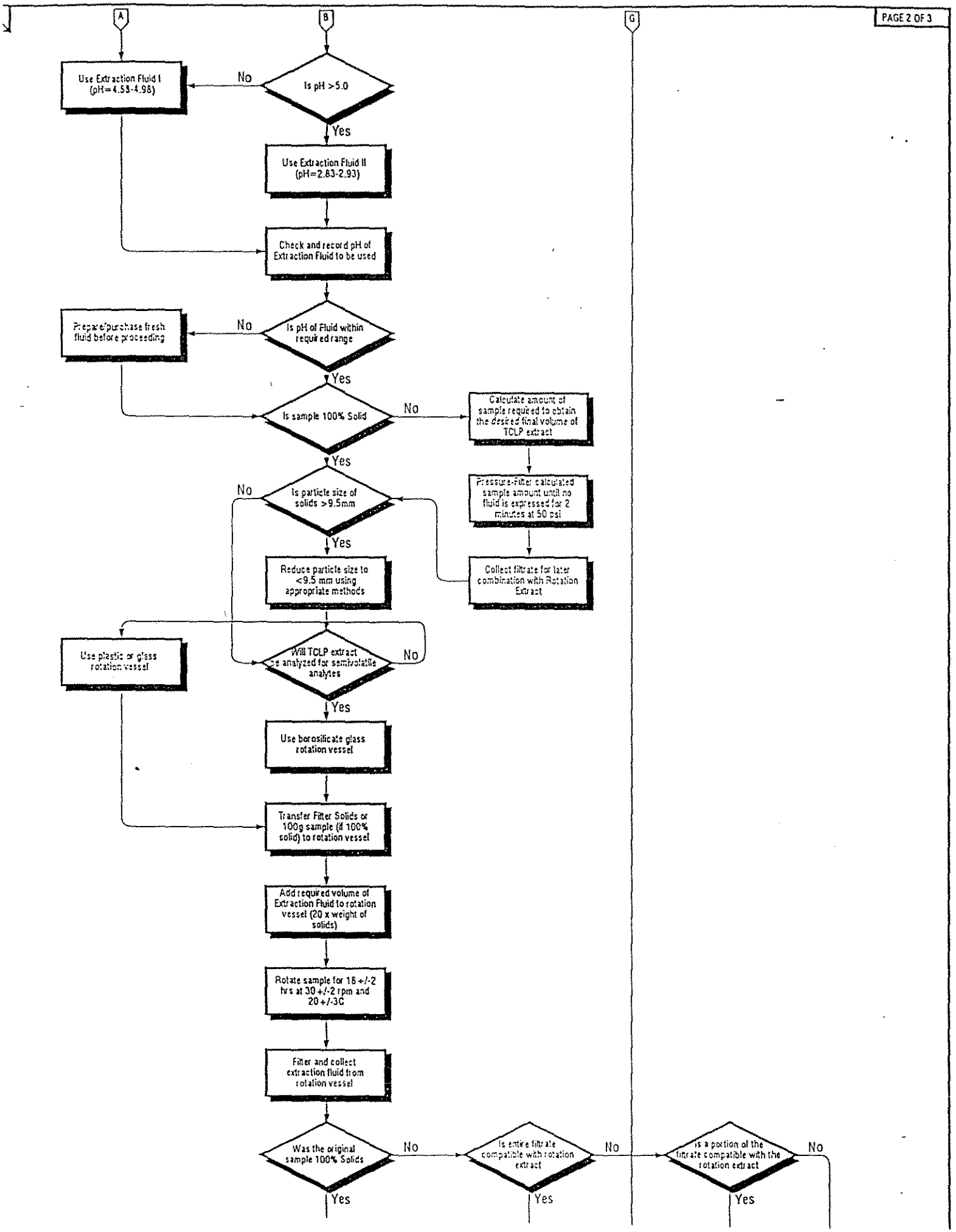
8.2 A TCLP blank is prepared, digested and analyzed with the samples. The TCLP blank will not contain any analyte above the reporting limit or the samples are reprepared.

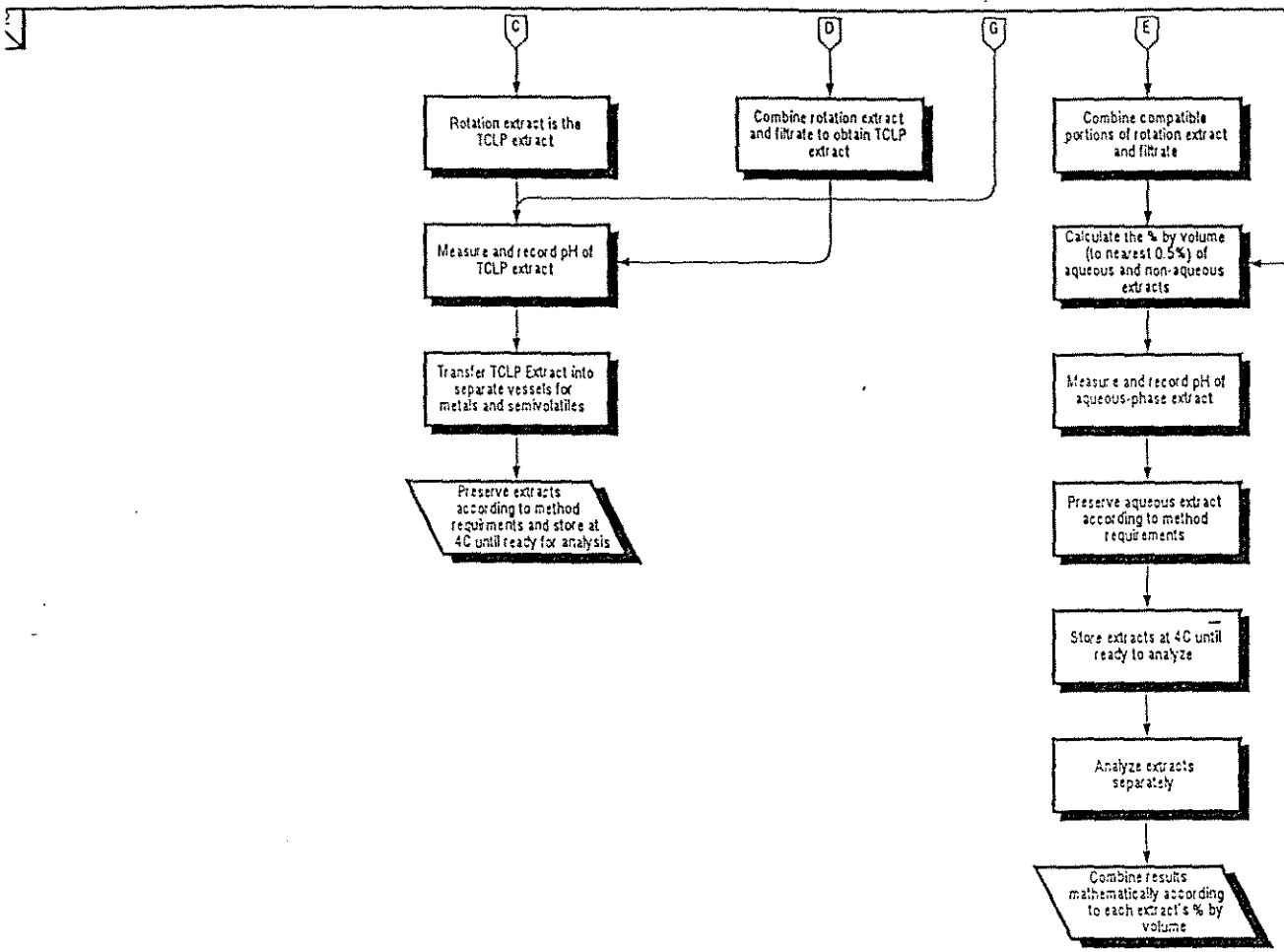
8.3 A matrix spike should be prepared with each batch of 20 samples. The sample results are not corrected for the spike recovery. The sample will be spiked with the matrix spike compounds after extraction and before preservation with HNO_3.

8.4 An aqueous LCS is digested with the TCLP Extracts. The LCS must be within the control limits of 80-120%, or the samples are redigested.

TCLP Metals/Semivolatiles (for use with TCLP Form)




A
B
G
Use Extraction Fluid I (pH=4.83-4.98)
No
Is pH >5.0
Yes
Use Extraction Fluid II (pH=2.83-2.93)
Check and record pH of Extraction Fluid to be used
Prepare/purchase fresh fluid before proceeding
No
Is pH of Fluid within required range
Yes
Is sample 100% Solid
No
Calculate amount of sample required to obtain the desired final volume of TCLP extract
Yes
Pressure-Filter calculated sample amount until no fluid is expressed for 2 minutes at 50 psi
Collect filtrate for later combination with Rotation Extract
No
Is particle size of solids >9.5mm
Yes
Reduce particle size to <9.5 mm using appropriate methods
Use plastic or glass rotation vessel
Will TCLP extract be analyzed for semivolatile analytes
No
Yes
Use borosilicate glass rotation vessel
Transfer Filter Solids or 100g sample (if 100% solid) to rotation vessel
Add required volume of Extraction Fluid to rotation vessel (20 x weight of solids)
Rotate sample for 18 +/-2 hrs at 30 +/-2 rpm and 20 +/-3C
Filter and collect extraction fluid from rotation vessel
Was the original sample 100% Solids
No
Yes
Is entire filtrate compatible with rotation extract
No
Yes
Is a portion of the filtrate compatible with the rotation extract
No
Yes


C
D
G
E
F
Rotation extract is the TCLP extract
Combine rotation extract and filtrate to obtain TCLP extract
Combine compatible portions of rotation extract and filtrate
Measure and record pH of TCLP extract
Calculate the % by volume (to nearest 0.5%) of aqueous and non-aqueous extracts
Transfer TCLP Extract into separate vessels for metals and semivolatiles
Measure and record pH of aqueous-phase extract
Preserve extracts according to method requirements and store at 4C until ready for analysis
Preserve aqueous extract according to method requirements
Store extracts at 4C until ready to analyze
Analyze extracts separately
Combine results mathematically according to each extract's % by volume

Sample ID											
Extract ID											
1. Visual Sample Evaluation											
100% solid (Skip to 3)	(✓)										
Sample is <100% Solids											
2. Filtration (Pressure Filtration is Required if Solids are ≥ 10%)											
Filter Weight	(F)										
Filtrate Vessel Weight	(V)										
Subsample Weight	(X)										
Weight of Dried Solids + Filter	(S)										
Weight of Filtrate + Vessel											
% Filter Solids = $\frac{X-(L-V)}{X} \times 100$	(%FS)										
% Dry Solids= $\frac{S-F}{X} \times 100$	(%DS)										
3.Extraction Fluid Determination											
Particle Size Reduced (1mm max)	(✓)										
Actual weight of subsample (5.0±0.1g)											
Actual volume of water (96.5 ± 1 ml)											
Initial pH (After 5 min. mixing) "pH-1"											
Volume 1N HCl (3.5 ml if pH-1 >5.0)											
Actual time at 50°C (10± 1 minutes)											
SecondpH(at room temperature)"pH-2"											
if pH-1 or pH-2 <5.0 use Fluid I	(✓)										
if pH-2>5.0 use Fluid II	(✓)										
4. Preparation for Extraction Procedure (If Sample is <0.5%FS or <0.5%DS; Filter Sample, Collect Filtrate and Skip to 6. If sample is 100% Solid, use 100 grams sample and 2000 mls Fluid.											
Particle Size Reduced(9.5mm max.)	(✓)										
$X_{grams} = \frac{100 \times DesiredFinalVolume_{mls}}{100 + (19 \times \%FS)}$	(X)										
Filtrate Vessel Weight	(V)										
Weight of Filtrate + Vessel	(L)										

Weight of Fluid Needed = 20X(VL-V1)										
pH before tumbling										
pH after tumbling										
5. TCLP Rotation (Rotate for 18± 2 hours at 23 ± 2°C and 30± 2 rpm										
Start time										
Stop time										
Filtration Complete Time										
6. Final TCLP Extract										
Volume Extract Obtained in Step 5 V1										
Volume Compatible Filtrate in Step4 V2										
Volume Non-Compatible Filtrate from Step 4 V3										
pH Combined Extract/Filtrate (V1+V2)										
Compatible PhaseRatio= $\frac{V1 + V2}{V1+V2+V3}$										
Non-Compatible Phase Ratio= $\frac{V1+V2}{V1+V2+V3}$										
Extraction Technician:		Date:								

APPENDIX A-44

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF CHLORINATED PESTICIDES IN TCLP EXTRACTS

Analysis of Chlorinated Pesticides in TCLP Extracts
Method: 8080_TCLP:AN

Approvals and Signatures

QA Officer: Martha E. Roy Date: 04/06/95

GC Manager: Gary B. Stiles Date: 4/6/95

1.0 Scope and Application

1.1 This method describes the procedures used in the analysis of prepared TCLP extracts for chlorinated pesticides.

2.0 Summary of Method

2.1 The analysis of extracts will be performed with the intent of meeting the quality control requirements of USEPA SW-846 Methods 8080. In general, the SW-846 Methods 8000 and 8080 will be followed.

2.2 Prior to sample analysis, the instrumentation is calibrated using five point calibration curves for all analytes of interest. Instrument stability is verified every five sample injections, alternating a standard to check endrin and breakdown and a mid-level standard from the individual pesticide calibration to check instrument stability. The gas chromatograph is set up with two columns of different polarity: one used for quantitation, the second for confirmation.

2.3 The compounds of interest for TCLP analysis are a sublist of 8080. The TCLP extracts may also be analyzed using the 8080 method if all QC criteria are met for this method.

3.0 Apparatus and Materials

3.1 Gas Chromatograph: An analytical system equipped with a packed or

split/splitless injection port, two electron captures, and an auto-sampler.

3.2 Data System: The data system must be capable of handling a minimum of 200 chromatographic peaks per detector. Fison's vax based multi-chrom version 2.0 is used for this analysis.

3.3 Fused Silica Capillary Columns: The intent of using a two column system is to confirm identifications from the quantitation column with the second column. Capillary columns which may be used include the following:

3.3.1 RTX-5, 95% dimethyl - 5% diphenyl polysiloxane or equivalent.

3.3.2 RTX-1, 100% dimethyl polysiloxane or equivalent.

3.3.3 RTX-35, 65% dimethyl - 35% diphenyl polysiloxane or equivalent.

3.3.4 RTX-1701, 14% cyanopropylphenyl - 86% methyl polysiloxane or equivalent.

3.3.5 DB-17, 50% dimethyl - 50% diphenyl polysiloxane or equivalent.

4.0 Reagents and Standards

4.1 Solvents

4.1.1 Hexane - JT Baker, Resi-Analyzed, Cat #JT9262-3

4.1.2 Acetone - JT Baker, Resi-Analyzed, Cat #JT9254-3

4.2 Standards

4.2.1 Technical Chlordane and Toxaphene.

Five Point Calibration Concentration (ug/L)

Compound	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Toxaphene	500	1000	2000	4000	8000
Tech. Chlordane	50	100	200	400	800

4.2.2 Pesticide Standard Mix A

The following pesticide analytes are combined in the same standard solution.

Five Point Calibration Concentration (ug/L)

Compound	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Tetrachloro-m-xylene	5.0	10	20	40	80
gamma-BHC	5.0	10	20	40	80
heptachlor	5.0	10	20	40	80
heptachlor epoxide	5.0	10	20	40	80
endrin	10	20	40	80	160
methoxychlor	50	100	200	400	800
decachlorobiphenyl	10	20	40	80	160

4.2.3 Breakdown Check Standard

Compound	Standard Concentration (ug/L)
tetrachloro-m-xylene	20
endrin	50
4,4'-DDT	100
decachlorobiphenyl	20

5.0 Instrument Set-Up

5.1 GC Configuration: A five meter deactivated guard column is installed into the injection port. The guard column is connected using a "y" connector to the two analytical columns, which are each installed into an electron capture detector.

5.2 Operating Conditions: Operating conditions are used as guidelines to starting an analytical method. Conditions may change depending on the types of columns used (including different manufacturers).

Initial Temperature: 130 °C
Time 1: 1 minute

Rate: 6 °/min
Final Temperature: 270 °C
Time 2: 5 minutes
Injection Port Temperature: 225 °C
Detector Temperature: 310 °C
Injection Volume: 2 uL
Carrier Gas Flow: 10 ml/min He
ECD Make-up Gas: 60 ml/min % Argon/methane

6.0 Initial Calibration

Prior to sample analysis, a five point calibration for each pesticide and Aroclor mix is analyzed, and breakdown of endrin are verified to be within acceptable limits. A typical calibration can be found in Table 1.

6.1 The initial calibration must meet the following controls:

6.1.1 For quantitation, the correlation coefficient must be≥0.995 using linear regression.

6.1.2 Breakdown of endrin must each be less than 20%.

7.0 Continuing Calibration:

As indicated in the analytical sequence in section 6.0, there are three standards used for checking instrument stability.

7.1 Breakdown Check Standard (BCS): The BCS is analyzed every 10 sample injections to monitor endrin breakdown as described in section 6.1.2. If the breakdown criteria are not met, the analysis must be stopped and injection port maintenance performed. The GC must be recalibrated after this maintenance as described in section 6.0.

7.2 The mid-level pesticide mix standard is analyzed every 10 sample injections.

In order to continue the analysis, the check standards must meet the following criteria:

7.2.1 The peak response must be≤ 15% of the initial calibration standard

(injection 4 or 9) for quantitation. The peak response must be ≤ 20% of the initial calibration standard for confirmation. Both columns may be used for quantitation as long as QC passes.

7.2.2 Retention time must fall within the established windows for both quantitation and confirmation analysis.

7.2.2.1 0.32 mm ID columns must be within ± 0.04 minutes of the initial calibration.

7.2.2.2 0.53 mm ID columns must be within ± 0.05 minutes for gamma-BHC, alpha-BHC, beta-BHC, delta-BHC, heptachlor, tetrachloro-m-xylene and aldrin, ± 0.07 for all other compounds.

7.2.3 If these quality control criteria are not met, standards may be reinjected a second time. If they still fail, GC maintenance must be performed to correct the problem and re-calibration is required.

7.3 If the GC has been left idle for more than 8 hours, the following standards must be acquired and pass QC limits before sample analysis begins.

7.3.1 Breakdown Check Standard
7.3.2 Mid-level pesticide standard

7.4 When the sample analysis is completed, the analytical sequence must end with the mid-level pesticide standard.

8.0 Sample Extract Preservation

8.1 Sample extracts are preserved in a refrigerator at 4 °C.

8.2 Sample extracts must be analyzed within 40 days of sample extraction.

9.0 Quality Control (QC)

9.1 Method Blank: One per extraction batch, Sample Delivery Group (SDG), or every 20 samples. All analytes must be less than the quantitation limit.

9.2 Surrogate Spike Compounds: Method blank and samples are fortified with surrogate spike before extraction begins. Surrogate compounds and concentrations are identified below.

Compound	Recovery Limits (%)
tetrachloro-m-xylene	60-150
decachlorobiphenyl	60-150

Recovery limits are presented from USEPA Method OLM01 for Method 8080. Although recovery limits are advisory, if recovery of any surrogate compound is outside of these limits, then the sample analysis is thoroughly reviewed and the sample extract may be reanalyzed or possibly re-extracted depending on circumstances. The client will be notified of any gross deficiencies in surrogate recovery to discuss possible corrective action.

9.3 Matrix spike/matrix spike duplicate: An MS/MSD analysis is required every 20 samples. The MS/MSD analysis consists of spiking two aliquots of the same sample with matrix spike before extraction begins. Recovery limits for analytes which may be used as matrix spikes are listed below. These recovery limits are generated from method 8080.

Compound	**8080**
gamma-BHC (Lindane)	32-127
Heptachlor	34-111
Heptachlor Epoxide	37-142
Endrin	30-147
Methoxychlor	37-142*
Tech. Chlordane	45-119
Toxaphene	41-126

* Heptachlor epoxide recovery used for methoxychlor

Recovery limits are advisory, if recovery of any matrix compound is outside of these limits, then the sample analysis is thoroughly reviewed and the sample extract may be reanalyzed or possibly re-extracted depending on circumstances. The client will be notified of any gross deficiencies in matrix recovery to discuss possible corrective action.

Matrix spike results will be reviewed in conjunction with surrogate recoveries to evaluate method performance.

10.0 Compound List and Limits of Reporting

Compound	Quantitation Limit in Extract (ug/L)	TCLP Water (mg/L)
gamma-BHC (Lindane)	5.0	0.1
Heptachlor	5.0	0.003
Heptachlor epoxide	5.0	0.003
Endrin	10.0	0.005
Methoxychlor	50.0	1.0
Tech. Chlordane	50	0.01
Toxaphene	500	0.1

The quantitaion limits assume the following extraction information:

TCLP 8080 water- 1 liter sample concentrated to a 10 ml extract volume

11.0 Reporting

Results will be reported from the quantitation analysis. If both columns meet quality control requirements for quantitation, the lower value will be reported. If the above is true, and if the confirmation analysis result is lower than the quantitation analysis result by more than 50 percent, the confirmation result may be reported, if justified. Compounds will not be identified and reported below the reporting limit.

12.0 Standard Qualifiers

U = Compound not detected at or above reporting limit.
D = Compound concentration is reported from a secondary dilution of the sample.

Table 1: Analytical Sequence

inj	Lab ID
1.	Breakdown Check Std
2.	Pesticide Mix A-1
3.	Pesticide Mix A-2
4.	Pesticide Mix A-3
5.	Pesticide Mix A-4
6.	Pesticide Mix A-5
7.	Toxaph 500 ppb
8.	Toxaph 1000 ppb
9.	Toxaph 2000 ppb
10.	Toxaph 4000 ppb
11.	Toxaph 8000 ppb
12.	T-CHLOR 50 ppb
13.	T-CHLOR 100 ppb
14.	T-CHLOR 200 ppb
15.	T-CHLOR 400 ppb
16.	T-CHLOR 800 ppb
17-21.	5 Samples
22.	Breakdown Check Standard
23-27.	5 samples
28.	Pesticide Mix A-3

APPENDIX A-45

STANDARD OPERATING PROCEDURE FOR ANALYSIS OF HERBICIDES IN TCLP EXTRACTS

Analysis of Chlorinated Herbicides in TCLP Extracts
Method: 8151_TCLP:AN

Approvals and Signatures

QA Officer: Martha E. Roy Date: 4/6/95

GC Manager: Gary B Stidham Date: 4/6/95

1.0 Scope and Application

1.1 This method is used to determine the concentration of chlorinated herbicides in sample extracts.

2.0 Summary of Method

2.1 This method provides the sample preparation and gas chromatographic conditions that will be applied to analyze chlorinated herbicides using USEPA SW-846 Methods 8000 and 8151. Detection limits are presented in Section 11.0

2.2 Prior to sample analysis, the instrumentation is calibrated using five point calibration curves for all analytes of interest. Instrument stability is verified every ten sample injections with the mid point standard. The gas chromatograph is set up with two columns of different polarity: one used for quantitation, the second for confirmation.

2.3 The compounds of interest are a sublist of 8151. The TCLP extracts may also be analyzed using the 8151 method if all QC criteria of this method are met.

3.0 Sample Preparation

3.1 Samples are prepared following extraction procedures of the USEPA SW-846 methodology. In general, 20 mL of a TCLP extract is extracted and concentrated to 10 ml. The final extract solvent is hexane.

4.0 Apparatus and Materials

4.1 Gas Chromatograph: An analytical system equipped with a packed or split/splitless injection port, two electron captures, and an auto-sampler.

4.2 Data System: The data system must be capable of handling a minimum of 200 chromatographic peaks per detector. Fison's Vax based multi-chrom version 2.0 is used for this analysis.

4.3 Fused Silica Capillary Columns: The intent of using a two column system is to confirm identifications from the quantitation column with the second column. Capillary columns which may be used include the following:

4.3.1 RTX-35, 65% dimethyl - 35% diphenyl polysiloxane or equivalent.

4.3.2 RTX-1701, 14% cyanopropylphenyl - 86% methyl polysiloxane or equivalent.

4.3.3 RTX-5, 95% dimethyl - 5% diphenyl polysiloxane or equivalent.

5.0 Reagents and Standards

5.1 Solvents

5.1.1 Hexane - JT Baker, Resi-Analyzed, Cat #JT9262-3

5.1.2 Acetone - JT Baker, Resi-Analyzed, Cat #JT9254-3

5.2 Standards

Five Point Calibration Concentration (ug/L as acid form)

Compound	Herb Mix A	Herb Mix B	Herb Mix C	Herb Mix D	Herb Mix E
2,4-D	94	190	380	750	1500
Silvex	9.5	19	38	76	150
DCAA (2,4-DA)	94	190	370	750	1500

6.0 GC Set-Up

6.1 GC Configuration: A five meter deactivated guard column is installed into the injection port. The guard column is connected using a "y" connector to the two analytical columns, which are each installed into an electron capture detector.

6.2 Operating Conditions: Operating conditions are used as guidelines to starting an analytical method. Conditions may change depending on the types of columns used (including different manufacturers)

Initial Temperature: 60 °C
Time 1: 2 minute
Rate: 6°/min
Final Temperature: 270°C
Time 2: 5 minutes
Injection Port Temperature: 225°C
Detector Temperature: 310°C
Injection Volume: 2 uL
Carrier Gas Flow: 10 ml/min He
ECD Make-up Gas: 60 ml/min % Argon/methane

7.0 Initial Calibration: Prior to sample analysis, a five point calibration for each chlorinated herbicide mix is analyzed. A typical calibration is as follows:

Analytical Sequence

inj	Lab ID	inj	Lab ID
1.	HerbMixA	7.	PIBLK
2.	HerbMixB	8-17.	Samples
3.	HerbMixC	18.	PIBLK
4.	HerbMixD	19.	HerbMixC
5.	HerbMixE		
6.	SSS		

Note: SSS is a secondary source standard.

7.1 The initial calibration must meet the following controls:

7.1.1 For quantitation, the correlation coefficient (r) must be ≥0.995 using a linear regression ($r^2 \geq 0.990$), or if average response factor is used ≤20%RSD.

8.0 Continuing Calibration:

As indicated in the analytical sequence in section 6.0, there is one standard used for checking instrument stability.

8.1 The Herb Mix C standard must be analyzed every 10 sample injections. In order to continue the analysis, the check standards must meet the following criteria:

8.1.1 The peak response must be± 15% of the initial calibration standard for quantitation.

8.1.2 Retention times (of chromatographic peaks used for quantitation and confirmation analysis) must fall within the established windows.

8.1.2.1 0.32 mm ID columns must be within ± 0.04 minutes of the initial calibration.

8.1.2.2 0.53 mm ID columns must be within ± 0.05 minutes of the initial calibration.

8.1.3 If these quality control criteria are not met, standards may be reinjected a second time. If they still fail, GC maintenance must be performed to correct the problem and re-calibration is required.

8.14 For this project the intent is to report samples encompassed with passing initial and closing standards.

8.2 If the GC has been left idle for more than 8 hours, the following standard must be acquired and pass QC limits before sample analysis begins.

8.2.1 Herb Mix C

8.3 When the sample analysis is completed, the analytical sequence must end with the

Herb Mix C standard.

9.0 Sample Extract Preservation

9.1 Sample extracts are preserved in a refrigerator at 4°C.

9.2 Sample extracts must be analyzed within 40 days of sample extraction.

10.0 Quality Control (QC)

10.1 Method Blank: One per extraction batch, Sample Delivery Group (SDG), or every 20 samples. All analytes must be less than the quantitation limit. If a method blank fails, all samples in the associated extraction group must be re-extracted.

10.2 Surrogate Standard Compounds: Method blank and samples are fortified with surrogate spike before extraction begins. Surrogate compounds and concentrations are identified below.

Compound	Water	Soils/ Sediment
DCAA (2,4-DA)	40-150	40-150

Although recovery limits are advisory, if recovery of any surrogate compound is outside of these limits, then the sample analysis is thoroughly reviewed and the sample extract may be reanalyzed and possibly re-extracted if the surrogate recovery confirms low. The client will be notified of any gross deficiencies in surrogate recovery to discuss possible corrective action.

10.3 Matrix Spike/Matrix Spike Duplicate: An MS/MSD analysis is required every 20 samples. The MS/MSD analysis consists of spiking two aliquots of the same sample with matrix spike before extraction beings. Recovery limits for analytes used as matrix spikes are listed below. These recovery limits are generated from each specific method.

Compound	Water	Soils/ Sediment	RPD
2,4-D	40-150	40-150	30
Silvex	40-150	40-150	30

Although recovery limits are advisory, if recovery of any matrix compound is outside of these limits, then the sample analysis is thoroughly reviewed and the sample extract may be reanalyzed or possibly re-extracted depending on circumstances. The client will be notified of any gross deficiencies in matrix recovery to discuss possible corrective action.

Matrix spike results will be reviewed in conjunction with surrogate recoveries to evaluate method performance.

11.0 Compound List and Quantitation Limits (QL)

Compound	TCLP (mg/L) QL
2,4-D	1.0
Silvex	0.1

11.1 Calculations

Quantitation of Water Sample:

$$\text{conc. in ext (ug/L)} \times \frac{\text{ext vol (L)}}{\text{spl. vol. (L)}} \times \text{D.F.} = \text{ug/L}$$

D.F. = Dilution Factor

12.0 Reporting

Results will be reported from the quantitation analysis. The quantitation limit is to be used as the reporting limit. Compound concentrations will not be reported below the quantitation limit (QL).

13.0 Standard Qualifiers

U = Compound not detected at or above reporting limit
E = Compound concentration exceeds the calibration range.
D = Compound concentration is reported from a secondary dilution of the sample.

APPENDIX A-46

STANDARD OPERATING PROCEDURE FOR METHOD 6010 TCLP ANALYSIS BY INDUCTIVELY COUPLED PLASMA SPECTROSCOPY

Method 6010_TCLP
TCLP Analysis by
Inductively Coupled Plasma Spectroscopy

Approvals and Signatures

QA Officer: Martha E. Roy Date: 2/21/95

Metals Manager: Kristine L. Aubin Date: 02/21/95

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements, including metals, in solution. The method is applicable to all of the elements below. TCLP extracts require digestion prior to analysis.

1.2 Elements for which the 6010_TCLP method is applicable are listed below. Detection limits will meet those specified in the Statement of Work (SOW).

Analyte	CAS #	Aqueous Reporting Limit (ug/l) Trace ICP	Aqueous Reporting Limit (ug/l) ICP3
Barium	7440-39-3	10000	10000
Cadmium	7440-43-9	100	100
Chromium	7440-43-9	1000	1000
Copper	7440-50-8	1000	1000
Lead	7439-92-1	1000	1000
Nickel	7440-02-0	1000	1000
Silver	7440-22-4	1000	1000
Zinc	7440-66-6	1000	1000
Arsenic	7440-38-2	1000	1000
Selenium	7782-49-2	100	100
Tin	7440-31-5	1000	1000

2.0 Summary of Method

2.0 The samples must be digested by the suitable EPA digestion procedure method 3010:1T.

2.1 This method describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background photo-multiplier-correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

2.2 Each metal is quantified at specific wavelengths of light emitted as the electrons relax to lower energy states. The sample is analyzed by multiple integrations (3 injections for ICP3 and 2 injections for the Trace ICP) and the average integration is converted to a concentration from a calibration curve.

Element	**Specified Wavelengths**	
	Trace ICP	**ICP3**
Barium	493.409	493.409
Cadmium	226.502	228.802
Chromium	267.716	267.716
Copper	324.754	324.754
Lead	220.353	220.353
Nickel	231.604	231.604
Silver	328.068	328.068
Zinc	213.856	213.856
Arsenic	189.042	193.696
Selenium	196.026	196.026
Tin	189.900	189.989

(a) The wavelengths listed are used because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

3.0 Interferences

3.1 Since metals emit light at more than one wavelength, the emission peak for a target analyte may be overlapped by that of another metal. The additive effect of this interference causes the target concentration to read artificially high. When common elements such as Al, Fe, or Mg are present in high concentrations, spectral overlap produces an apparent concentration of the interfered target analyte, even in its absence. These apparent or interference concentrations are measured independently, allowing correction of the target analyte concentration. Other spectral interferences can be minimized using background corrections or alternate emission wavelengths for the target analyte.

3.2 Matrix matching and dilution are used to correct for viscosity and surface tension changes between samples.

3.3 Interelement correction factors are determined annually and applied automatically by the instrument.

4.0 Apparatus and Materials

4.1 Two instruments are currently in use:

- Thermo Jarrell-Ash Trace (Trace) simultaneous inductively coupled plasma emission spectrometer. System includes 150 position autosampler and computer control. (3/94)

- Thermo Jarrell-Ash Enviro II (ICP3) simultaneous and sequential inductively coupled plasma emission spectrometer. System includes 150 position autosampler and computer control. (1/92)

4.2 Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary

argon inlet is recommended, as are increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where coordination factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

4.3 Class A volumetric flasks

4.4 Class A volumetric pipets

5.0 Digestate Storage and Handling

5.1 Digestates are stored at room temperature in a secured area.

5.2 Digestates must be analyzed within 180 days after sample receipt.

6.0 Reagents

6.1 ASTM Type 1 water

6.2 All blanks and standards are in a 5% HCl, 2% HNO_3 matrix.

6.3 Argon

6.4 Stock Standard Solutions (for Calibration use) purchased from SPEX

6.5 Calibration Check Standards (for Initial and Continuing Calibration) purchased from Inorganic Ventures

6.6 Interference Check Solutions made from standards purchased from SPEX or Inorganic Ventures

7.0 Calibration Preparation

7.1 All calibration standards are prepared from SPEX Plasma Standard stock

solutions. See Table 1 at the end of this SOP for the concentrations of calibration standards.

7.2 Intermediate standard solutions are made by quantitively transferring aliquots of concentrated stock standards into a volumetric flask containing ASTM Type 1 water and an aliquot of HNO_3/HCl. When the appropriate metals standards have been added, the solution is brought to volume. The resulting intermediate standard solution is in a 5% HCl, 2% HNO_3 matrix.

7.3 Working standards are made by quantitatively diluting the intermediate standard to the needed concentrations.

7.4 Intermediate and working standards are stored at room temperature in storage bottles. These standards are kept until their expiration date.

8.0 Instrument Calibration

8.1 Each instrument is calibrated according to the manufacturer's recommendations . After the torch is ignited and the instrument's parameters are recorded (See the Maintenance Logs attached at the end of this SOP), the calibration standards are placed in an autosampler. A 5% HCl, 2% HNO_3 matrix solution is used for the calibration blank.

During calibration, multiple integrations (2 for the Trace ICP and 3 for ICP3) are performed per standard. There is a 120 second rinse between standards.

8.2 Initial calibration is performed once per batch.

9.0 Calculations

9.1 The final concentration of an element in the sample is determined in the following way:

Aqueous Samples:

$$\text{Dil} \times \frac{\text{ug from the instrument}}{\text{l}} \times \frac{\text{mls digestate}}{\text{mls original sample volume}} = \text{ug/l in sample}$$

10.0 Quality Control

10.1 Instrument Detection Limits (IDL's) are determined quarterly for all the elements of interest and their established wavelength. The IDL's are determined by analyzing a standard at 3-5 times the detection limit seven (7) times on three (3) non-consecutive days. The resulting average standard deviation is than multiplied by 3 to determine the IDL. IDL's must be below the reporting limit or the IDL experiment must be repeated. If instrument sensitivity is improved than the experiment is repeated.

10.2 Interelement Correction Factors

Interelement Correction Factors are determined annually for spectral interference due to Al, Ca, Fe, and Mg and are determined for both ICP instruments at all wavelengths used for each analyte reported by ICP. A 100 ppm stock solution of each interferent is analyzed and any result found above the negative or positive value of the instrument detection limit is recorded within the instrument. The result in ppb is divided by the concentration of interferent in ppb to determine the IEC constant. This number is entered into IEC tables of the instrument. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg may be determined in the same fashion and reported if they were applied.

10.3 Linear Range

The linear range verification check standard is analyzed and reported quarterly for each element analyzed by ICP. The analytically determined concentration of this standard shall be within 5% of the true value. This concentration is the upper limit of the ICP linear range and any result found above this limit, must be diluted and reanalyzed.

10.4 Dilute and reanalyze samples that are more concentrated than the linear calibration limit.

10.5 Analyze the method blank (prep) per sample batch to determine if contamination or any memory effects are occurring. If the blank is contaminated with any of the elements of interest, and the sample concentration for that element is <10 times the blank; the sample must be redigested and reanalyzed.

10.6 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank and a check standard. The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and reanalyze the previous ten samples.

The results of the calibration blank must be within the control limit of ± the reporting limit (CRDL), if not terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

10.7 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check sample. Results should be within +/- 20% of the true value. If not terminate the analysis, correct the problem, recalibrate, and reanalyze the samples.

10.8 Analyze one matrix spike sample per batch of twenty samples of the same matrix. The matrix spike sample is spiked during the digestion process and treated like any other sample. The control limits for the matrix spike are 75-125%. If any element fails to meet this criteria the samples are flagged with the "N" qualifier for that element. A post digestion spike as described below is performed in the event that the matrix spike analyses is flagged with an N.

10.9 A LRS (Linear Range Standard) is analyzed at the beginning of the run to verify the upper linear range. The highest calibration standard is analyzed for all analytes reported and the found concentration must be within 5% of the true value. If the measurements exceed ± 5%, the instrument is recalibrated for the effected analytes.

10.10 A CRDL standard is analyzed at the beginning of each run to verify linearity near the CRDL. Although there are no contract specified control limits on this standard at this time, the laboratory uses ± 25% as a warning there may be a problem.

10.11 All samples and extracted preparation blanks are analyzed by the method of standard addition. The correlation coefficient for the standard addition analyses must be ≥ 0.995.

10.12 Instrument maintenance is done on a daily basis. Please see the attached maintenance logs.

10.13 The following qualifiers are used for metals analysis:

E (furnace)-	Analytical cup spike recovery is less than 40%. An explanatory note is included on the specific form to which this applies.
E (ICP)-	The reported value is estimated because of the presence of interference.
M-	Duplicate injection precision is not met.
N-	Matrix spiked sample recovery not within control limits.
S-	The reported value was determined by the Method of Standard Additions.
+-	Correlation coefficient for the MSA is less than 0.995.
W-	Post digestion spike for Furnace AA analysis is out of control limits (85-115%), while sample concentration is less than 50% of spike concentration.
*-	Duplicate analysis not within control limits.
B-	Entered if the reported value is less than the Contract Required Detection Limit (CRDL) but greater than the Instrument Detection Limit (IDL).
U-	Entered if the analyte was analyzed for but not detected, less than IDL.

Table 1: Calibration Standards (ug/L)

Element	Trace ICP Standards		ICP3 Standards	
Barium	0	1000	0	5000
Cadmium	0	500	0	500
Chromium	0	1000	0	1000
Copper	0	1000	0	5000
Lead	0	1000	0	5000
Nickel	0	1000	0	1000
Silver	0	500	0	500
Zinc	0	1000	0	5000
Tin	0	1000	0	1000
Arsenic	0	500	0	5000
Selenium	0	500	0	5000

Table 2: Method of Standard Additions

Element	Standard 0	Standard 1	Standard 2
Barium	0	500	1000
Cadmium	0	200	400
Chromium	0	400	800
Copper	0	400	800
Lead	0	500	1000
Nickel	0	400	800
Silver	0	200	400
Zinc	0	400	800

Element	Standard 0	Standard 1	Standard 2
Tin	0	1000	2000
Arsenic	0	1000	2000
Selenium	0	500	1000

Daily maintenance: ICP3 Analyst_____
Date_____

---

10 PPM Cu Profile: Peak intensity: _____
S.S. Offset: _____
Meter Setting: _____

Peristaltic Pump Tubing:

Advanced: Yes_____ No_____
Replaced: Yes_____ No_____

Instrument Running Properly: Yes_____ No_____
(If "No" continue, If "Yes" disregard the following.)

Instrument out of control due to :

1) Pump tubing needing replacement. _____
2) Autosampler not functioning properly. _____
3) Torch needing cleaning. _____
4) Nebulizer being clogged. _____
5) Other. _____
Explanation for other_____
_____
_____

Corrective Action taken:

1) Pump tubing replaced or advanced. _____
2) Auto sampler repaired. _____
3) Torch cleaned. _____
4) Nebulizer cleaned. _____
5) Other. _____
Explanation:_____
_____
_____

Return to control: Batch _____
Analyst Initials _____

Daily maintenance: ICP4-TRACE Analyst_____
Date_____

---

5 PPM As Profile: Peak intensity: _____
S.S. Offset: _____
Meter Setting: _____

Peristaltic Pump Tubing:

Advanced: Yes_____ No_____
Replaced: Yes_____ No_____

Instrument Running Properly: Yes_____ No_____
(If "No" continue, If "Yes" disregard the following.)

Instrument out of control due to :

1) Pump tubing needing replacement. _____
2) Autosampler not functioning properly. _____
3) Torch needing cleaning. _____
4) Nebulizer being clogged. _____
5) Other. _____
Explanation for other_____
_____
_____

Corrective Action taken:

1) Pump tubing replaced or advanced. _____
2) Auto sampler repaired. _____
3) Torch cleaned. _____
4) Nebulizer cleaned. _____
5) Other. _____
Explanation:_____
_____
_____

Return to control: Batch _____
Analyst Initials _____

APPENDIX A-47

STANDARD OPERATING PROCEDURE FOR PCB CONGENERS BY LRMS

PCB CONGENERS BY LRMS

SOP 3-38

29 March 1999

Approved:

C. Stephen Parsons Author	Date
Bruce N. Colby President	Date

1.0 INTRODUCTION

The purpose of this SOP is to describe the procedure for determining the presence of polychlorinated biphenyls in environmental samples. This procedure follows the details that are found in USEPA Method 680, 1668 and 8082 Mono- through Deca-chlorinated biphenyls by isotope dilution HRGC/LRMS. Internal Standards (labeled spiking solutions), Recovery Standards and Calibration Standards as used in this SOP are optimized for the use of LRMS. Sample Characterization, Extraction and Cleanup are recorded on Pacific Analytical's "Pesticide Extraction Log". Report and Analysis QC data are reported on Forms taylored after Method 1668.

2.0 SAMPLE CHARACTERIZATION AND ALIQUOT DETERMINATION

A sample is determined to be of one of four categories: soil/sediment, water, filter paper, or chemical waste for the purposes of this method:

Soil/sediment is defined as a portion of wet soil/sediment which does not contain oil, but which may contain other solids such as stones, vegetation, etc. The sample should not contain an obvious liquid phase. After homogenization, a 10 gram aliquot of soil/sediment is taken for extraction.

Water sample is defined as a single phase system that is primarily water but may contain very small amounts of floating, suspended and/or settled particulate matter. Multiphases should not be present. After homogenization, a 1 Liter aliquot of water sample is taken for extraction.

Filter paper sample is defined as a filter paper and solid matrix obtained from the filtration of an aliquot of water.

Chemical waste sample includes sample matrices of oils, stillbottoms, oily sludge, oil-laced soil and surface water heavily contaminated with matrices listed above. The sample may contain particulates and an obvious non-aqueous liquid phase. After homogenization, a 1 gram aliquot of chemical waste is taken for extraction.

3.0 SAMPLE EXTRACTION

Aqueous samples are spiked with internal standards. The sample is extracted using liquid liquid extraction. The extraction solvent is methylene chloride.

Solid samples are spiked with internal standards. The sample is extracted using sonication. The extraction solvent is 1:1 methylene chloride:acetone..

Filter papers are placed into a soxhlet extractor and spiked with internal standards. The sample is extracted for 18 to 24 hours using petroleum ether as a solvent.

Chemical waste samples are spiked with internal standards and placed into a soxhlet-Dean Stark (SDS) apparatus. The SDS apparatus is charged with toluene and operated for 16 to 24 hours. Water trapped in the Dean Stark apparatus is measured and discarded periodically.

4.0 SAMPLE CLEANUP

The extracts are processed through two types of cleanup processes: Liquid liquid partitioning with acid/base washes, and acidified silica gel column chromatography.

Sample extracts are solvent exchanged to hexane and brought to 50 mL in a 250 mL separatory funnel. The sample is partitioned with 50 mL of sulfuric acid. The sulfuric acid layer is discarded. The sample is then washed with 50 mL of distilled water. The sample is subsequently partitioned with 50 mL of a 6N sodium hydroxide solution. The aqueous layer is discarded. The sample is subsequently partitioned with distilled water.

After base/acid washing the solvent is concentrated to about 100 uL using a Kuderna-Danish apparatus and nitrogen blow down. The extract is diluted to 1 mL with hexane. The 1 mL extract is placed on a pastuer pipet plugged with glass wool and containing 1 grams of 40% sulfuric acid impregnated silica gel. The column is eluted with 10 mL of hexane and the eluate is collected. The sample eluate is concentrated to 100 uL.

5.0 HRGC/LRMS CALIBRATION:

HRGC/LRMS calibration consists of three operations: LRMS mass calibration, HRGC/LRMS selective ion monitoring calibration and window defining, and HRGC/LRMS Relative Response Factor (RRF) determination and RRF linearity.

The LRMS is tuned with FC-43. Optimum results for FC-43 for mass calibration may be achieved by scanning from 210 to 510 amu every one second or less, utilizing 70 volts (nominal) electron energy in the electron ionization mode.

Prior to the calibration of the HRGC/LRMS system, it is necessary to establish the appropriate switching times for the SIM descriptors and to verify the chromatographic resolution. The switching times are determined by the analysis of the individual congener solutions.

The column used for the analysis is a 60 meter SPB-Octyl column..

Overall GC/MS performance is verified by the ability to initially calibrate the instrument running a minimum of 5 calibration points, and performing ongoing calibration checks. The standards are analyzed to determine ion abundance ratios, minimum levels, signal-to-noise ratios and absolute retention times. Measure the Selective Ion Current Profile (SICP) areas for each analyte and compute the ion abundance ratios as specified in the Table 3.0.

The peaks representing the native analytes in the CS1 and other standards must have a signal to noise ratio (S/N) greater than 2.5. The peaks representing the labeled analytes in the CS1 and other standards must have a S/N ratio greater than 10.

The five calibration standards, CS1, CS2, CS3, CS4, and CS5 are analyzed. A calibration curve encompassing the concentration range is prepared for each compound to be determined. The Relative Response (RR) (native to labeled) vs. concentration is plotted or computed using average response factor or point to point. Relative Response using both the primary and secondary m/z's is determined according to the procedure below:

$$RR = \frac{(A_n^{\,1} + A_n^{\,2})C_l}{(A_l^{\,1} + A_l^{\,2})C_n}$$

Where:

A_n^1 and A_n^2 are the areas of the primary and secondary m/z's for the native compound.

A_l^1 and A_l^2 are the areas of the primary and secondary m/z's for the labeled compound.

C_l is the concentration of the labeled compound in the calibration standard.

C_n is the concentration of the native compound in the calibration standard.

Table 1.0

LIST OF TARGETED PCB CONGENERS

BZ#	Compound ID:	Retention Time on SPB-Octyl	BZ#	Compound ID:	Retention Time on SPB-Octyl
1	2-chlorobiphenyl	5.97	114	2,3,4,4',5-pentachlorobiphenyl	25.06
3	4-chlorobiphenyl	7.15	105	2,3,3',4,4'-pentachlorobiphenyl	25.83
8	2,4'-dichlorobiphenyl	8.72	184	2,2',3,4,4',6,6'-heptachlorobiphenyl	26.11
18	2,2',5-trichlorobiphenyl	9.89	153	2,2',4,4',5,5'-hexachlorobiphenyl	26.62
15	4,4'-dichlorobiphenyl	10.41	168	2,2',4,4',5,5' -hexachlorobiphenyl	26.69
28	2,4,4'-trichlorobiphenyl	12.27	138	2,2',3,4,4',5'-hexachlorobiphenyl	28.22
52	2,2',5,5'-tetrachlorobiphenyl	13.47	158	2,3,3',4,4',6-hexachlorobiphenyl	28.71
49	2,2',4,5'-tetrachlorobiphenyl	13.84	126	3,3',4,4',5-pentachlorobiphenyl	29.64
44	2,2',3,5'-tetrachlorobiphenyl	14.32	128	2,2',3,3',4,4' -hexachlorobiphenyl	29.89
37	3,4,4'-trichlorobiphenyl	15.17	187	2,2',3,4',5,5',6-heptachlorobiphenyl	30.61
70	2,3',4',5-tetrachlorobiphenyl	17.29	183	2,2',3,4,4',5',6-heptachlorobiphenyl	30.79
74	2,4,4',5-tetrachlorobiphenyl	17.39	177	2,2',3,3',4',5,6-heptachlorobiphenyl	31.73
66	2,3',4,4'-tetrachlorobiphenyl	17.60	202	2,2',3,3',5,5',6,6'-octachlorobiphenyl	31.89
101	2,2',4,5,5'--pentachlorobiphenyl	19.15	167	2,3',4,4',5,5'-hexachlorobiphenyl	32.17
90	2,2',3,4',5--pentachlorobiphenyl	19.17	156	2,3,3',4,4',5-hexachlorobiphenyl	33.71
99	2,2',4,4',5-pentachlorobiphenyl	19.74	157	2,3,3',4,4',5'-hexachlorobiphenyl	33.78
119	2,3',4,4',6-pentachlorobiphenyl	20.24	180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35.76
87	2,2'3,4,5'-pentachlorobiphenyl	20.39	170	2,2',3,3',4,4',5-heptachlorobiphenyl	37.68
110	2,3,3',4',6-pentachlorobiphenyl	21.17	169	3,3',4,4',5,5'-hexachlorobiphenyl	38.36
115	2,3,4,4',6-pentachlorobiphenyl	21.31	201	2,2',3,3'4,5,5',6'-octachlorobiphenyl	38.71
81	3,4,4',5-tetrachlorobiphenyl	21.34	195	2,2',3,3',4,4',5,6-octachlorobiphenyl	41.86
77	3,3',4,4'-tetrachlorobiphenyl	21.92	189	2,3,3',4,4',5,5'-heptachlorobiphenyl	42.19
151	2,2',3,5,5',6-hexachlorobiphenyl	22.15	207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	42.94
149	2,2',3,4',5',6-hexachlorobiphenyl	23.14	194	2,2',3,3',4,4',5,5'-octachlorobiphenyl	45.45
123	2',3,4,4',5-pentachlorobiphenyl	24.06	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	48.98
118	2,3',4,4',5-pentachlorobiphenyl	24.44	209	decachlorobiphenyl	51.49

TABLE 2.0

LABELED SPIKING SOLUTION

BZ #	Compound ID:	Label:	Concentration:
3	4-Monochlorobiphenyl	$^{13}C_6$	1 uG/mL
15	4,4'-Dichlorobiphenyl	$^{13}C_{12}$	1 uG/mL
28	2,4,4'-Trichlorobiphenyl	$^{13}C_{12}$	1 uG/mL
52	2,2',5,5'-Tetrachlorobiphenyl	$^{13}C_{12}$	1 uG/mL
118	2,3',4,4',5-Pentachlorobiphenyl	$^{13}C_{12}$	1 uG/mL
153	2,2'4,4'5,5'-Hexachlorobiphenyl	$^{13}C_{12}$	1 uG/mL
180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	$^{13}C_{12}$	1 uG/mL
194	2,2',3,3',4,4',5,5'-Octachlorobiphenyl	$^{13}C_{12}$	1 uG/mL
208	2,2',3,3',4,5,5',6,6'-Nonachlorobiphenyl	$^{13}C_{12}$	1 uG/mL
209	Decachlorobiphenyl	$^{13}C_{12}$	1 uG/mL

Compounds in the calibration standards are of two types: compounds with labeled analogs and compounds with labeled isomers. Compounds with labeled analogs are determined using isotope dilution, and compounds with labeled isomers are determined using a labeled isomer as an internal standard.

For compounds with a labeled analog, if the Relative Response for any compound over the range of the five point curve has a coefficient of variation of less than 20, then an average Relative Response may be used for that compound. Otherwise, a segmented curve or second order fit curve using all five points of the calibration will be used.

For compounds not having a labeled analog in the calibration sequence, calibration is performed by the internal standard method. The Response Factors (RFs) for the compounds are computed in the same manner as for compounds with labeled analogs by substituting the response for the primary and secondary ion of the labeled isomer with that of the labeled analog.

For compounds not having a labeled analog, if the Response Factor for any compound over the range of the five point curve has a coefficient of variation of less than 35, then an average Relative Response may be used for that compound. Otherwise, a segmented curve or second order fit curve using all five points of the calibration will be used.

TABLE 3.0

CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDDs/PCDFs

ANALYTE	SELECTED IONS	THEORETICAL ION ABUNDANCE	CONTROL LIMITS
MCB	188/190	3.0769	2.60 - 3.54
DCB	222/224	1.5385	1.30 - 1.77
TriCB	256/258	1.0256	0.87 - 1.18
TetraCB	290/292	0.769	0.65 - 0.89
PeCB	326/328	1.5385	1.32 - 1.78
HxCB	360/362	1.2315	1.05 - 1.43
HpCB	394/396	1.0256	0.88 - 1.20
OCB	428/430	0.879	0.76 - 1.02
NCB	462/464	0.769	0.65 - 0.89
DecaCB	498/500	1.1547	0.98 - 1.33
Internal Standards			
$^{13}C_6$-4-MCB	194/196	3.0769	2.60 - 3.54
$^{13}C_{12}$-4,4'-DiCB	234/236	1.5385	1.30 - 1.77
$^{13}C_{12}$-2,4,4'-TriCB	268/270	1.0256	0.87 - 1.18
$^{13}C_{12}$-2,2',5,5'-TetraCB	302/304	0.769	0.65 - 0.89
$^{13}C_{12}$-2,3',4,4',5-PeCB	338/340	1.5385	1.32 - 1.78
$^{13}C_6$-2,2',4,4',5,5'-HcCB	372/374	1.2315	1.05 - 1.43
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	406/408	1.0256	0.88 - 1.20
$^{13}C_{12}$-2,2'3,3',4,4'5,5'-OCB	440/442	0.879	0.76 - 1.02
$^{13}C_{12}$-2,2'3.3',4,5,5'6,6'-NCB	474/476	0.769	0.65 - 0.89
$^{13}C_{12}$-DecaCB	510/512	1.1547	0.98 - 1.33
Recovery Standard			
d_{14}-p-Terphenyl	244/243	0.1428	0.10 - 0.18

6.0 HRGC/LRMS ANALYSIS:

Once the operating conditions of the system have been established necessary to meet the system calibration criteria sample, analysis may begin. At the beginning of each 12-hour shift HRGC resolution and verification of RRF values must be monitored to verify that the HRGC\LRMS is within QC criteria. For these tests, analysis of the column resolution mix and the CS3 calibration verification standard are used to verify all system performance criteria. Acceptance criteria for calibration verification can be found in Table 5 and Table 6..

Sample extracts are spiked with 10 uL of recovery standard. Care must be taken to ensure that the 10 uL of recovery standard is mixed well with the 100 uL of sample in hexane.

An aliquot of the spiked extract is injected into the HRGC/LRMS system using splitless injection.

Quantitative Determination:

Quantitation is of two types: Compounds with labeled analogs are determined using isotope dilution, and compounds with labeled isomers are determined using the internal standard method.

For compounds with labeled analogs, Relative Response Factors are used in conjunction with calibration data. Assuming that labeled concentrations in extracts and calibration standards are the same, the following equation is used for quantitation:

$$C_{ex}\ (nG/uL) = \frac{(A_n^{\,1} + A_n^{\,2})\ C_x}{(A_1^{\,1} + A_1^{\,2})\ RR}$$

Where:

C_{ex} is the concentration in the extract., and
C_x is the concentration of the labeled analog in the extract.

For compounds not having a labeled analog quantitation is performed by the internal standard method. The Response Factors (RFs) for the compounds are substituted for the RR value in the above equation and values are calculated in the same manner as for compounds with labeled analogs. The C_X value would be the labeled isomer concentration used as an internal standard.

The concentration of the native compound in the sample is computed using the concentration of the compound in the extract and the weight for solids or volume for liquids as follows:

$$Concentration = \frac{(C_{ex} * V_{ex})}{W_s}$$

Where,

V_{es} is the extract volume in mL.
W_S is the sample weight in kG or volume in Liters.

TABLE 4.0

QA/QC ACCEPTANCE CRITERIA

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Instrument Performance Check	Prior to initial and calibration verification	Visual Inspection of. FC-43.	1. Evaluate 2. Retune
Initial Calibration	Five point calibration for all analytes prior to sample analysis	Isotope Dilution or internal standard, see Method 680.	1. Evaluate 2. Recalibrate when QC criteria not met.
Identification/Retention Times	Obtained from Individual Standards	Checked with Calibration Check standard	1. Evalutate 2. Recalibrate when QC criteria not met.
Ion Ratios	Initial and Verification Calibration, Samples	+/- 15%	1. Evaluate 2. Retune
Signal to Noise/Interferences	Low point Calibration	10 times noise	1. Evaluate 2. Retune
Calibration Verification	Daily, before sample analysis and every 12 hour shift.	+/- 30%	1. Evaluate 2. Recalibrate when QC criteria not met.
Internal Standards	All data	See Table 5.	1. Evaluate 2. Re-analyze when QC criteria not met.
Method Blank	1/batch/matrix or 20 samples whichever is frequent	No targets above MDL.	1. Evaluate 2. Re-extract if targets above MDL.
Ongoing Precision and Recovery (OPR	1/batch/matrix or 20 samples whichever is most frequent	See Table 5. .	1. Evaluate 2. Re-extract if targets out of QC.

TABLE 5.0

NATIVE SPIKE ACCURACY AND PRECISION LIMITS

	Water		Soil	
Spike Compound	% Recovery	RPD	%Recovery	RPD
PCB-1	70-140	NA	70-140	NA
PCB-3	70-140	NA	70-140	NA
PCB-4	70-140	NA	70-140	NA
PCB-15	70-140	NA	70-140	NA
PCB-18	70-140	NA	70-140	NA
PCB-28	70-140	NA	70-140	NA
PCB-37	70-140	NA	70-140	NA
PCB-44	60-140	NA	60-140	NA
PCB-49	70-140	NA	70-140	NA
PCB-52	60-140	NA	60-140	NA
PCB-66	70-140	NA	70-140	NA
PCB-70	70-140	NA	70-140	NA
PCB-74	70-140	NA	70-140	NA
PCB-77	70-160	NA	70-160	NA
PCB-81	70-140	NA	70-140	NA
PCB-87/115	70-140	NA	70-140	NA
PCB-90/101	70-140	NA	70-140	NA
PCB-99	70-140	NA	70-140	NA
PCB-110	70-140	NA	70-140	NA
PCB-119	70-140	NA	70-140	NA
PCB-118	64-160	NA	64-160	NA
PCB-123	14-330	NA	14-330	NA
PCB-105	68-160	NA	68-160	NA
PCB-114	14-330	NA	14-330	NA
PCB-126	68-160	NA	68-160	NA
PCB-151	70-140	NA	70-140	NA
PCB-128/167	64-170	NA	64-170	NA
PCB-138/158	70-140	NA	70-140	NA
PCB-149	70-140	NA	70-140	NA
PCB-153/168	70-140	NA	70-140	NA
PCB-156	70-140	NA	70-140	NA
PCB-157	64-170	NA	64-170	NA
PCB-169	64-170	NA	64-170	NA
PCB-170	70-140	NA	70-140	NA
PCB-177	70-140	NA	70-140	NA
PCB-180	70-140	NA	70-140	NA
PCB-183	70-140	NA	70-140	NA
PCB-184	70-140	NA	70-140	NA
PCB-187	70-140	NA	70-140	NA
PCB-189	70-140	NA	70-140	NA
PCB-201	70-140	NA	70-140	NA
PCB-202	70-140	NA	70-140	NA
PCB-194	70-140	NA	70-140	NA
PCB-195	70-140	NA	70-140	NA
PCB-206	70-140	NA	70-140	NA
PCB-207	70-140	NA	70-140	NA
PCB-209	70-140	NA	70-140	NA

TABLE6.0

LABELED SPIKE ACCURACY AND PRECISION LIMITS

	Water		Soil	
Spike Compound	% Recovery	RPD	%Recovery	RPD
^{13}C-PCB-3	25-150	NA	25-150	NA
^{13}C-PCB-15	25-150	NA	25-150	NA
^{13}C-PCB-28	25-150	NA	25-150	NA
^{13}C-PCB-52	25-150	NA	25-150	NA
^{13}C-PCB-118	13-328	NA	13-328	NA
^{13}C-PCB-153	17-205	NA	17-205	NA
^{13}C-PCB-180	20-186	NA	20-186	NA
^{13}C-PCB-194	25-150	NA	25-150	NA
^{13}C-PCB-208	25-150	NA	25-150	NA
^{13}C-PCB-209	25-150	NA	25-150	NA

APPENDIX A-48

STANDARD OPERATING PROCEDURE FOR PESTICIDE/PCB EXTRACTION AND CONCENTRATION OF SOIL SAMPLES BY METHOD 3550B

TITLE: Pesticide/PCB Extraction and Concentration of Soil Samples by Method 3550B			
Original Author: T. Kanalley		Revision Author: G. Rudz	
Implementation Date: 10/11/99		Last Annual Review Date: 9/27/99	
File Information: L:\SOPs\Final\EXT\EXT19.ene-10/11/99 11:03 AM			
Revision: 5	Status: Final	Method: SW-846, 3550B	Minor Revision Date: None

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the sample preparation procedure for extraction and concentration of organochlorine pesticides and PCB in soil and solid waste samples. Samples may be prepared for pesticide analysis only SOP GC.72 (Method 8081A), PCB analysis only SOP GC.73 (Method 8082) or both pesticide and PCB analysis GC.14 (Method 8081).

2.0 METHOD SUMMARY

2.1 Samples are mixed with sodium sulfate (drying agent), surrogate spiking solution is added, sonicated three times with solvent and the solvent decanted. The extract is concentrated and solvent exchanged to hexane using a Kuderna-Danish apparatus on a steam bath.

2.2 Alternative PCB spiking information is provided should PCBs be the only target analytes. This PCB spiking information can be used to supplement the normal Pesticide Spike if requested.

3.0 HEALTH AND SAFETY

3.1 All employees should protect themselves at a minimum with safety glasses, protective gloves and a lab coat. For more information see the E & E Inc., Analytical Services Center Chemical Hygiene Plan, located in the QA Library Island shelf 2.

3.2 All glassware should be inspected for flaws or ragged edges before use. Do not use damaged glassware.

3.1 Pollution Prevention – Purchase chemicals based on expected usage, shelf life, and disposal cost. Prepare standard volumes on anticipated usage. Make appropriately sized dilutions and use serial dilutions where practical.

4.0 REFERENCES

4.1 Method 3550B, (Rev. 2, 12/96), SW-846 Update III, June 1997.
4.2 Analysis SOPs GC.14, GC.72, GC.73.
4.3 Use checklist C-048 for analyst and peer review.
4.4 Training SOP QA.5, A.23, and A.29.
4.5 Data Review SOP A.25.
4.6 Laboratory Quality Assurance Manual.
4.7 MDL SOP A.18.
4.8 Corrective Action Procedure, QA.1.

5.0 DEFINITIONS/ACRONYMS

5.1 Batch – A group of samples that behave similarly with respect to the sampling or testing procedures being employed which are processed as a unit. If the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

5.2 Method Blank (MB) – an analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank is used to document contamination resulting from the analytical process.

5.3 Matrix – The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

5.4 Matrix Spike (MS) – an aliquot of sample 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 sample matrix.

5.5 DCB, TCMX – Decachlorobiphenyl and tetrachlorometaxylene, respectively; all are method surrogates.

5.6 Matrix Spike Duplicate /MSD – an intra-laboratory split sample spiked with identical concentrations of analytes. They are used to document the precision and bias of a method in a given sample matrix.

5.7 Laboratory Control Sample/LCS – a known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

6.0 INTERFERENCES/POTENTIAL PROBLEMS

6.1.1 Phthalates may cause false positives. Plasticware may not be used. Latex gloves must not contact inside of glassware.

7.0 INSTRUMENTATION AND EQUIPMENT

- Ultrasonic Disruptor with ¾" Titanium Horn
- Sonabox
- 400-mL Thick Walled Beakers
- 100-mm Drying Funnel
- Glass Wool (Fisher or equivalent)
- Filter paper (Whatman 41 or equivalent)
- Kuderna-Danish Apparatus (K-D)
  - Concentrator Tube, 10-mL graduated
  - 500-mL Evaporation Flask (Kontes K-507001-500 or equivalent)
  - Snyder Column, micro (569261-031 or equivalent)
  - Snyder Column, 3 ball macro (Kontes K-503000-0121 or equivalent)
- Boiling Chips, 10/40 mesh, Fisher or equivalent
- Water Bath heated with concentric ring cover
- Balance, Top-loading (readable to .001g or better)
- 15-ml Glass Vials with screw cap PTFE lined tops
- Benchtop Centrifuge (Fisher or equivalent)
- Spatula, Stainless Steel
- 1.0-mL pipettes or syringe
- 16-oz. jars

- Stainless Steel Spoonula
- Sparkleen (or equivalent)
- 2% Heikol-e
- NOCHROMIX
- Zymark Turbovap
- Turbovap Tubes

8.0 REAGENTS AND MATERIALS

8.1 See Table 8-1, Summary of Standard, Reagents, and Consumables.

Table 8-1

SUMMARY OF STANDARD AND REAGENTS

Description	Source	Concentration
Methylene Chloride ($MeCl_2$), ultra resi analyzed	JT Baker or Equivalent	Neat
Acetone ultra resi grade	JT Baker or Equivalent	Neat
Hexane, ultra resi grade	JT Baker or Equivalent	Neat
Sodium Sulfate, Na_2SO_4 (anhydrous)	JT Baker or Equivalent	Stored @ 120°C
ASTM Type II Water	In-house Laboratory System	Neat
Pesticide Matrix Spike Mix	Restek or Equivalent	See Table 8-3
Pesticide Surrogate Mix	Restek or Equivalent	200 µg/mL TCMX and DCB
Aroclor 1016/1260	Restek or Equivalent	1000 µg/mL each
Toxaphene	Restek or equivalent	1000 µg/mL
Sand	Play Sand or Equivalent	NA

Revision: 5	Status: Final	Method: SW-846, 3550B	Minor Revision Date: None

8.2 Standard Solution Preparation

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	Amount of Stock Diluted to	Final Concentration
Ar 1660 PCB Spike	Aroclor 1016/1260	250 µL to 50 mL with acetone	5 µg/mL
8081A Pestcide/ PCB Surrogate	Pesticide Surrogate Mix	100 µL Pesticide Surrogate Mix to 100 mL with acetone	0.2 µg/mL TCMX and DCB
8081A Pesticide Spike	Pesticide Matrix Spike Mix (See Table 8-3)	100 µL to 100 mL with acetone	0.1 – 1.0 µg/mL
10% HCl	HCl	10 mL to 100 mL ASTM Type II water	10 % (v/v)

Revision: 5	Status: Final	Method: SW-846, 3550B	Minor Revision Date: None

Table 8-3

AFCEE Pesticide Spike Mix

Compound	Spike Concentration (µg/mL)
alpha-BHC	0.1000
beta-BHC	0.1000
gamma-BHC	0.1000
delta-BHC	0.1000
Heptachlor	0.1000
Aldrin	0.1000
Heptachlor epoxide	0.1000
alpha-chlordane	0.1000
gamma-chlordane	0.1000
Endosulfan I	0.1000
4,4-DDE	0.1000
Dieldrin	0.1000
Endrin	0.1000
Endosulfan II	0.1000
4,4-DDD	0.1000
Endrin aldehyde	0.1000
4,4-DDT	0.1000
Endosulfan sulfate	0.1000
Toxaphene	5.000
Methoxychlor	1.000

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9.0 PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Table 9-1

HOLDING TIMES

Martrix	Client/ Project	Preparation (Days)	Analysis (Days)	Container Type and Preservative
Solid	Standard	14-day collection	40 days from extraction	4-, 8-, or 16-oz. glass jar. Store at 2-6 C.
Solid	NYSDEC	5 days from receipt (VSTR)	40 days from extraction	4-, 8-, or 16-oz. glass jar. Store at 2-6 C.

Revision: 5	Status: Final	Method: SW-846, 3550B	Minor Revision Date: None

10.0 PROCEDURE

10.1 Glassware Preparation

10.1.1 All glassware shall be immediately rinsed after use with the last solvent used, manually washed in hot soapy tap water using Sparkleen, or automatically washed using 2% Heikol-e.

10.1.2 At a minimum, manually washed glassware shall be tap water rinsed, followed by 3 rinses with ASTM Type II water.

10.1.3 If glassware still appears dirty, it shall be subjected to sonication, or cleaning with NOCHROMIX. Then it shall be rerun through the above cleaning procedure.

10.1.4 When washing glassware after extraction, do not combine glassware from high or medium level extracts with standard level glassware. The dishwasher can spread the contamination. Wash glassware by hand separately from standard level glassware or throw it away if it will not come clean.

10.2 Preventing Contamination

10.2.1 Before use, all glassware is solvent rinsed with acetone, followed by methylene chloride.

10.2.2 Sodium Sulfate (Na_2SO_4) is dried (recommended 120°C, overnight or longer).

10.2.3 Rinse dried Na_2SO_4 with methylene chloride before use.

10.3 Sample Setup

10.3.1 A batch of samples consists of a method blank, matrix spike (MS), matrix spike duplicate (MSD) and laboratory control sample (LCS) for every 20 or fewer samples. A laboratory control sample duplicate shall be used if insufficient sample is provided for an MSD. If both Pesticide and PCB extraction are required, allow three extra extraction setups for separate LCS, MS and MSD.

10.3.2 Each sample set up consists of one 400-mL beaker, one drying funnel, one 16-oz. Jar, and one spoonula. Set up the soil preparation logbook as follows.

10.3.2.1 Extraction date

10.3.2.2 Analyst name

10.3.2.3 Method/test (SOP numbers with revision number)

10.3.2.4 Job number

10.3.2.5 Sample number

10.3.2.6 Sample weight

10.3.2.7 Solvent used

10.3.2.8 Exchange solvent

10.3.2.9 Final volume

10.3.2.10 Date of concentration and analyst initials

10.3.2.11 Reference to balance calibration information and batch number.

10.4 Extraction

10.4.1 Weigh 25-35 g to the nearest 0.1 g of well-homogenized soil into a 400-mL beaker. Use sand for Method Blank and LCS. Record the weight to the nearest 0.1 g. Add 20-60 g sodium sulfate and mix with a spoonula until the sample is free-flowing.

10.4.2 Add 1.0 mL of 8081A Pesticide Surrogate/PCB Surrogate solution to each sample and QC sample (blank, MS, MSD, LCS) using a 1.0 mL syringe or volumetric pipette.

10.4.3 Pesticide Spiking Instructions:

10.4.3.1 If pesticide extraction is assigned to the sample do the following, otherwise proceed to PCB Spiking Instructions:

10.4.3.2 Add 1.0 mL of 8081A pesticide spike solution to the pesticide matrix spike, pesticide matrix spike duplicate and pesticide laboratory control sample (see Table 12-1).

10.4.4 PCB Spiking Instructions:

10.4.4.1 If PCB extraction is assigned to the sample a PCB MS, MSD, and LCS must be prepared. DO NOT spike the sample aliquot with both pesticide and PCB spikes.

10.4.4.2 Add 1.0 mL AR1660 PCB Spike to the PCB matrix spike, PCB matrix spike duplicate and PCB laboratory control sample (see Table 12-1).

10.4.3 Prepare a drying funnel by adding a plug of glass wool and approximately 15-20 g of sodium sulfate to the drying funnel. Rinse the funnel with methylene chloride and discard the rinse solvent.

10.4.4 Add 100 mL of 1:1 methylene chloride: acetone to each sample.

10.4.5 Place the bottom surface of the sonicator tip approximately 1/2 inch below the surface of the solvent but above the sediment layer. Do not use the microtip probe.

10.4.6 Sonicate for 3 minutes at an output of 10, the mode switch on Pulse and the duty cycle at 50%.

10.4.7 Decant the extract through the rinsed drying funnel into a labeled clean 16-oz. jar. Rinse down the drying funnel at a minimum after the first and final sonications.

10.4.8 Repeat the extraction two more times with (2) 100 mL volumes of 1:1 methylene chloride: acetone. Combine extracts.

10.4.9 Cover the 16-oz. jar with foil.

10.4.10 Clean the horn of the sonicator between samples rinsing with ASTM Type II water. Wipe the horn and rinse with acetone, then soapy H_2O, methylene chloride, and (Sparkleen or Alconox).

10.4.11 Rinse with ASTM Type II water and wipe the horn. Rinse with acetone, then methylene chloride.

10.5 K-D Concentration Procedure

10.5.1 Assemble a Kuderna-Danish (K-D) apparatus by attaching a 10-mL concentrator tube containing a boiling chip to a 500-mL evaporative flask.

10.5.2 Quantitatively transfer the extract to the K-D apparatus, rinsing the container with methylene chloride to complete the transfer.

10.5.3 Attach a 3-ball Snyder column and pre-wet with methylene chloride. Place on a hot water bath (80-90° C) so that the concentrator tube is partially immersed in the hot water and the lower rounded surface of the evaporative flask is bathed with hot water vapor. Expose as much surface area of the flask to the vapor as possible.

10.5.4 Adjust the vertical position of the apparatus and the water temperature to complete the concentration in 10-15 minutes.

10.5.5 Concentrate to an approximate volume of 4 mL. Allow the extract to cool and drain for at least 10 minutes. At no time should the extract be allowed to go to dryness throughout the concentration procedure. Should the extract go to dryness, restart the extraction from the beginning if sample is available. Otherwise, clearly note in extraction log and file a Corrective Action Form notifying the Project Manager and Supervisor.

10.6 K-D Solvent Exchange

10.6.1 After cooling, momentarily remove Snyder Column and add approximately 50 mL of hexane and a fresh boiling chip. Replace column and continue concentration.

10.6.2 Place the apparatus on the steam bath to complete the concentration in 5 to 10 minutes.

10.6.3 When the apparent volume of liquid reaches approximately 4 mL, remove the K-D apparatus from the bath and allow the K-D apparatus to drain and cool for approximately 10 min (or longer).Adjust the extract volume to 10 mL with hexane.

10.6.4 If during concentration, solvent vapor stops escaping from Snyder column before the final volume is reached, the extract contains large concentrations of higher boiling constituents. Concentration should be stopped and the extract brought to the next higher 5-mL level. Final volume must be noted in the soils preparation logbook.
10.6.5 If a significant amount of sediment appears in the concentrated extract, it should be centrifuged for 5 minutes. Decant the solvent into a 10-mL concentration tube and bring up to 10 mL final volume with hexane. Note this step in the logbook.
10.6.6 Transfer approximately 2 mL of extract into two, 1-mL screwtop vials with PFTE caps.

10.7 Turbovap Concentration Procedure (alternative to K-D procedure)
10.7.1 Quantitatively transfer sample from jar to Zymark Turbovap tube rinsing with 20-30 mL methylene chloride to complete the transfer.
10.7.2 Place in Turbovap, set at 38° C to 45° C with a gentle stream of nitrogen. Concentrate to 1 mL (or nearest 5 mL if evaporation/concentration can not be brought down to 1 mL).

10.8 Turbovap Solvent Exchange Procedure
10.8.1 Add a minimum of 10 mL hexane to sample in Turbovap tube.
10.8.2 Place in Turbovap, set at 38° C to 45° C with a gentle stream of nitrogen. Concentrate to 1 mL (or nearest 5 mL if evaporation/concentration can not be brought down to 1 mL).
10.8.3 Bring to 10 mL with Hexane. Record the final volume in the notebook.
10.8.4 Add approximately 1g activated copper to one of the 1-mL vials and vortex for 15 minutes. If no reaction, remove from vortex, if there is a reaction (dark or cloudy precipitate) vortex for an additional 15 minutes.
10.8.4.1 If sample is for pesticide only, stop and deliver entire batch of extracts to the instrument lab.
10.8.4.2 If samples are for PCB only, then add 250 µL of H_2O_4 to vial and vortex for 1 minute.
10.8.4.3 If samples are for pesticide and PCB, transfer one-half of the copper-treated extract into an additional screwtop vial and add 250 µL of H_2O_4 to the additional vial only. Vortex for 1 minute.
10.8.4.4 Deliver the entire batch of extracts to the instrument lab.

Instrument Maintenance

Table 10-1

ROUTINE MAINTENANCE PROCEDURES

Equipment/ Instrument	Symptom	Operation	Frequency
Sonicator	Not disrupting sample	Check power/ see Senior Scientist before adjusting	As necessary
Water Bath	Not heating	Replace coils	As necessary
Revision: 5	Status: Final	Method: SW-846, 3550B	Minor Revision Date: None

11.0 DATA REDUCTION/EVALUATION/REPORTING

NA

12.0 QUALITY CONTROL/QUALITY ASSURANCE/CORRECTIVE ACTION

Routine Quality Control Samples

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Preparation Instructions
Method Blank	One per 20 or fewer samples prepared in a batch	Approx. 30 g of sand
Pesticide Matrix Spike (MS)	One per 20 or fewer samples prepared in a batch	Add 1.0 mL of 8081A pesticide spike solution to 30 g Sample
Pesticide Matrix Spike Duplicate (MSD)	With every matrix spike for pesticide	Prepare as the matrix spike
Pesticide Laboratory Control Sample (LCS)	One per 20 or fewer samples prepared in a batch	Add 1.0 mL of a pesticide spike solution to 30 g sand
Surrogate	To each sample and QC sample (blank, MS, MSD, LCS)	Add 1.0 mL of 8081A pesticide/ PCB Surrogate solution
PCB Matrix Spike (MS)	One per 20 or fewer samples in a batch requiring PCB QC	1.0 mL AR1660 PCB Spike to 30 g sample
PCB Matrix Spike Duplicate (MSD)	With every PCB MS	Same as Matrix Spike
PCB Laboratory Control Sample (LCS)	One per 20 or fewer samples in a batch for PCB	1.0 mL AR1660 PCB Spike to 30 g sand

Revision: 5	Status: Final	Method: SW-846, 3550B	Minor Revision Date: None

13.0 SPECIAL PROJECTS REQUIREMENTS

13.1 Griffiss

13.1.1 When analyzing pesticide and PCB both pesticide MS/MSD and PCB MS/MSD must be extracted.

13.2 AFCEE - General Requirements

13.2.1 Batching

13.2.1.1 An AFCEE analytical batch is the environmental samples that are similar in composition (matrix) and are prepared at the same time and with the same **lot of reagents.**

13.2.1.2 A batch is not to exceed 20 samples. **The sample duplicate, MS, MSD are considered an**

13.2.2 Laboratory Control Sample
13.2.2.1 Laboratory Control Sample for solid must be prepared using **Ottawa sand** unless a variance was obtained.
13.2.2.2 The LCS must be prepared from second source materials
13.2.2.3 The LCS must contain all single component target analytes unless noted differently under specific method requirements or a variance was obtained (see Table 13-1).
13.2.2.4 The LCS must be spiked at a concentration ≤ midpoint of the calibration curve for each analyte unless a variance was obtained.
13.2.3 Matrix Spike/Matrix Spike Duplicate
13.2.3.1 The MS and MSD must be spiked at a concentration ≤ midpoint of the calibration curve for each analyte unless a variance was obtained.
13.2.3.2 AFCEE samples must be used for spiking.
13.2.3.3 If insufficient sample prevents use of Navy samples for MS/MSD, prepare a duplicate LCS.
13.2.3.4 Ottawa sand must be used as the solid matrix to prepare the solid LCS.
13.2.3.5 A batch is 20 environmental samples. These 20 samples *include* the MS/MSD or MS/MD.

13.3 U.S. Army Corps of Engineers (ACE)

Method Quantitation Limit (MQL) is between 3-10 times MDL. The low calibration standard concentration must be ≥3 times MDL. The Method Reporting Limit (MRL) may slide between two times the MDL and project specific or regulatory requirements. The MRL may be higher or lower than the MQL. Results below the MQL must be reported as estimated (J flagged).

14.0 SAMPLE DISPOSAL

See SOP A.10 for Waste Disposal.

15.0 EXAMPLE FORMS

NA

END OF SOP

APPENDIX A-49

STANDARD OPERATING PROCEDURE FOR PCB ANALYSIS BY METHOD 8082

TITLE: PCB Analysis by Method 8082			
Original Author: G. Rudz		Revision Author: G. Rudz	
Implementation Date: 3/3/98		Last Annual Review Date: 5/11/99	
File Information: \\LMSRV1\LABORATORY\SOPs\Final\GC\GC73.ene-08/19/99 4:25 PM			
Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

1.0 SCOPE AND APPLICATION

1.1 This Standard Operating Procedure (SOP) describes the procedure for identifying and quantifying polychlorinated biphenyl compounds in surface waters, groundwater, soils, sediments, and oils by a gas chromatographic procedure. This method may be expanded to include 19 PCB congeners.

2.0 METHOD SUMMARY

2.1 Extracts of water or soil samples (SOP EXT.4 or EXT.19) or dilutions of oils for PCB are analyzed on a gas chromatograph equipped with capillary columns and electron capture detectors. The GC is calibrated by injecting 5 levels of the analytes of interest and measuring response. An aliquot of a sample is injected into the GC and quantitative analysis is performed on the resulting chromatogram by comparing sample response to standard response. Qualitative Confirmation is accomplished by simultaneously injecting onto a second column.

2.2 The following deviations from the method are taken.

2.2.1 The target list of compounds usually reported by this method are listed in table 11-1. This SOP does not cover use of this method for specific PCB congeners.

2.2.2 Minor changes in chromatographic conditions may be used to optimize separation and sensitivity.

2.2.3 DCB is the primary surrogate, TCMX is a secondary surrogate.

2.2.4 Due to the likelihood that one or more surrogates may be interfered with, the following criteria are applied.

2.2.4.1 DCB in Laboratory Control Samples and method blanks must be recovered within in-house limits.

2.2.4.2 DCB recovery will be determined for all samples; if recovery is outside in-house limits, TCMX recoveries will be evaluated and reported.

2.2.4.3 Cases where both DCB and TCMX recoveries fail to meet criteria, and matrix effects are not evident, will require re-extraction and reanalysis of affected samples.

3.0 HEALTH AND SAFETY

3.1 All employees should protect themselves at a minimum with safety glasses, protective gloves, and a lab coat. For more information see the E & E, Inc., Analytical Services Center Chemical Hygiene Plan located in the QA Library Island shelf 2.

3.2 Pollution Prevention – Purchase chemicals based on expected usage, shelf life, and disposal cost. Prepare standard volumes on anticipated usage. Make appropriately sized dilutions and use serial dilutions where practical.

4.0 REFERENCES

4.1 Training SOP QA.5, A.23, and A.29.

4.2 Data Review SOP A.25.

4.3 Laboratory Quality Assurance Manual.

4.4 MDL SOP A.18.
4.5 Corrective Action Procedure, QA.1.
4.6 SW-846 3rd Edition, Update III, June 1997, Methods 8000B, 8082, 3660B, 3665A.
4.7 Use checklist C-055 for analyst and peer review.

5.0 DEFINITIONS/ACRONYMS

5.1 **MDL** - Method Detection Limit as determined by 40 CFR Part 136, Appendix B. Method detection limits must be determined yearly for both water and soil matrixes. See SOP A.18 for procedure.
5.2 **PQL** - Practical Quantitation Limit is the concentration above the MDL which can be reasonably obtained and is used as the limit of reporting (Table 1).
5.3 **TCMX** - Tetrachlorometaxylene.
5.4 **DCB** – Decachlorobiphenyl.

6.0 INTERFERENCES/POTENTIAL PROBLEMS

6.1 **Phthalates** may cause false positives. Care should be exercised to reduce exposure of samples to plastics.
6.2 Elemental Sulfur – if present in the samples, may cause interferences. Sulfur clean-up using mercury may be required. Refer to Section 10.5.4.
6.3 Heavy baseline and organics in samples may be cleaned up using acid-partitioning. Refer to Section 10.5.5.

7.0 INSTRUMENTATION AND EQUIPMENT

- Varian 3400 or Hewlett Packard 5890 equipped with electron capture detector and autosampler
- PE Nelson data system with TURBO*CHROM Software
- Restek RTX-5, 30 m column x 0.53mm 1.0 µm film (or equivalent)
- Restek RTX-35, 30 m column x 0.53mm 0.5 µm film (or equivalent)
- Volumetric Flasks, Fisher or equivalent
- Gastight Syringes, Krackler or equivalent
- Screwcap vials with Teflon-lined septa, Krackler or equivalent
- Disposable wiretrol pipettes, Krackler, Restek or equivalent

8.0 REAGENTS AND MATERIALS

Table 8-1

SUMMARY OF STANDARD AND REAGENTS

Description	Source	Concentration
AR1016/1260 MIX	Restek or equivalent	1000 µg/mL each
AR 1254 MIX	Restek or equivalent	1000 µg/mL
AR 1248 MIX	Restek or equivalent	1000 µg/mL
AR 1242 MIX	Restek or equivalent	1000 µg/mL
AR 1232 MIX	Restek or equivalent	1000 µg/mL

Table 8-1

SUMMARY OF STANDARD AND REAGENTS

Description	Source	Concentration
AR 1221 MIX	Restek or equivalent	1000 µg/mL
Pesticide Surrogate Mix	Restek or equivalent	2000 µg/mL TCMX and 2000 µg/mL DCB
Copper 30-40 Mesh	Supelco	Neat

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8.2 Standard Solution Preparation

8.2.1 All stock solutions commercially obtained shall be certified. Certificates are to be kept on file for all stocks received. All stocks and standards are to be stored at 2 - 6 C or lower.

8.2.2 Stock standards expire one year from the date opened, unless an earlier vendor supplied expiration date supercedes.

8.2.3 Working standards expire six months from date prepared unless expiration is superceded by stock expiration.

8.2.4 Unopened stock standards expire or per vendor-specified date if not provided (2) years from Date of Receipt.

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	Amount of Stock Diluted To	Final Concentration
Pest. Surr. Int.	Pesticide Surrogate Mix	250 µL to 50 mL Hexane	10 µg/mL
AR1660L	AR1016/1260 Mix Pest Surr. Int	2.5 µL plus 25 µL to 50 mL Hexane	See Table 8-3
AR1660ML	AR1016/1260 Mix Pest Surr. Int	5 µL plus 50 µL to 50 mL Hexane	See Table 8-3
AR1660M	AR1016/1260 Mix Pest Surr. Int	10 µL plus 100 µL to 50 mL Hexane	See Table 8-3
AR1660 MH	AR1016/1260 Mix Pest Surr. Int	20 µL plus 200 µL to 50 mL Hexane	See Table 8-3
AR1660H	AR1016/1260 Mix Pest Surr. Int	50 µL plus 500 µL to 50 mL Hexane	See Table 8-3
AR1254L	AR1254 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL Hexane	See Table 8-4
AR1254ML	AR1254 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL Hexane	See Table 8-4
AR1254M	AR1254 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL Hexane	See Table 8-4

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	Amount of Stock Diluted To	Final Concentration
AR1254MH	AR1254 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL Hexane	See Table 8-4
AR1254H	AR1254 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL Hexane	See Table 8-4
AR1221L	AR1221 Mix Pest Surr Int	5 µL plus 25 µL to 50 mL Hexane	See Table 8-5
AR1221ML	AR1221 Mix Pest Surr Int	10 µL plus 50 µL to 50 mL Hexane	See Table 8-5
AR1221M	AR1221 Mix Pest Surr Int	20 µL plus 100 µL to 50 mL Hexane	See Table 8-5
AR1221MH	AR1221 Mix Pest Surr Int	40 µL plus 200 µL to 50 mL Hexane	See Table 8-5
AR1221H	AR1221 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL Hexane	See Table 8-5
AR1232L	AR1232 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL Hexane	See Table 8-6
AR1232ML	AR1232 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL Hexane	See Table 8-6
AR1232M	AR1232 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL Hexane	See Table 8-6
AR1232MH	AR1232 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL Hexane	See Table 8-6
AR1232H	AR1232 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL Hexane	See Table 8-6
AR1242L	AR1242 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL Hexane	See Table 8-7
AR1242ML	AR1242 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL Hexane	See Table 8-7
AR1242M	AR1242 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL Hexane	See Table 8-7
AR1242MH	AR1242 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL Hexane	See Table 8-7
AR1242H	AR1242 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL Hexane	See Table 8-7
AR1248L	AR1248 Mix Pest Surr Int	2.5 µL plus 25 µL to 50 mL Hexane	See Table 8-8
AR1248ML	AR1248 Mix Pest Surr Int	5 µL plus 50 µL to 50 mL Hexane	See Table 8-8
AR1248M	AR1248 Mix Pest Surr Int	10 µL plus 100 µL to 50 mL Hexane	See Table 8-8

Table 8-2

STANDARD AND REAGENT PREPARATION

Standard Name	Stock	Amount of Stock Diluted To	Final Concentration
AR1248MH	AR1248 Mix Pest Surr Int	20 µL plus 200 µL to 50 mL Hexane	See Table 8-8
AR1248H	AR1248 Mix Pest Surr Int	50 µL plus 500 µL to 50 mL Hexane	See Table 8-8
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Table 8-3

COMPONENTS AND CALIBRATION CONCENTRATIONS OF AR 1660

Compound	µg/mL				
	AR1660L	AR1660ML	AR1660M	AR1660MH	AR1660H
TCMX	0.005	0.010	0.020	0.040	0.100
AR1016	0.050	0.100	0.200	0.400	1.000
AR1260	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100
Revision: 0	Status: Final	Method: 8082		Minor Revision Date: 8/19/99	

Table 8-4

AR1254 CALIBRATION LEVELS

Compound	µg/mL				
	AR1254L	AR1254ML	AR1254M	AR1254MH	AR1254H
TCMX	0.005	0.010	0.020	0.040	0.100
AR1254	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100
Revision: 0	Status: Final	Method: 8082		Minor Revision Date: 8/19/99	

Table 8-5

FINAL CONCENTRATIONS (µg/mL) OF AR1221 – 5-POINT CALIBRATON

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1221	0.100	0.200	0.400	0.800	1.000
DCB	0.005	0.010	0.020	0.040	0.100
Revision: 0	Status: Final	Method: 8082		Minor Revision Date: 8/19/99	

Table 8-6

FINAL CONCENTRATIONS (µg/mL) OF AR1232 - 5 POINT CALIBRATION

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1232	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

Table 8-7

FINAL CONCENTRATIONS (µg/mL) OF AR1242 - 5 POINT CALIBRATION

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1242	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

Table 8-8

FINAL CONCENTRATIONS (µg/mL) AR1248 - 5 POINT CALIBRATION

Compound	Level				
	Low	Med. Low	Med	Med High	High
TCMX	0.005	0.010	0.020	0.040	0.100
AR1248	0.050	0.100	0.200	0.400	1.000
DCB	0.005	0.010	0.020	0.040	0.100

Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

9.0 PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Holding Time

Table 9-1

HOLDING TIMES

Matrix	Client/Project	Preparation (Days)	Analysis (Days)	Container Type and Preservative
Water or Solid	Standard	Seven (7)for water; fourteen (14) for soil.	The PCB extracts from sample preparation are to be analyzed within 40 days from extraction date.	Extracts are stored in a secure area (Sample Custody) in a separate refrigerator from original samples at 2-5°C.
Water or Solid	NYSDEC	Five for water and soils from verified time of sample receipt.	The PCB extracts from sample preparation are to be analyzed within 40 days from extraction date.	Extracts are stored in a secure area (Sample Custody) in a separate refrigerator from original samples at 2-5°C.

Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

10.0 PROCEDURE

10.1 Apparatus Setup

10.1.1 The GC is equipped with two columns connected by a "Y" connector to one injection point and 2 electron capture detectors.

10.1.2 The carrier gas flow and temperature profile may vary somewhat to optimize analytical separation.

10.1.3 Recommended temperatures are set as follows: Injector = 200°C; Detector = 300°C Temperature program: Column Initial = 150°C. Initial Hold = 1.0 min. Column Rate = 5°C/min. Column Final = 280°C. Final Hold = minimum of 10 minutes and may be extended due to presence of late-eluting compounds in extracted samples.

10.1.4 The autosampler injects 2.0 µL of sample extract into each GC column. (i.e., 4 µL total injection).

10.1.5 Transfer of extracts to instrument autosampler vials shall be accomplished with disposable pipettes or graduated Wiretrol micropipettes.

10.2 Establishing Retention Time Windows

10.2.1 Make three injections of mid level Aroclor 1016/1260 standard over 72-hour period.

10.2.2 Calculate the multicomponent retention time windows based on five peaks of the Aroclor 1016/1260 mixture. The windows will apply to all multicomponents. Pattern recognition is still the primary means of identification.

10.2.3 The retention time window is defined as plus or minus 3 times the standard deviation from the retention time of the initial mid-level standards in the continuing calibration sequence. However, analyst experience should weigh heavily. Pattern recognition should primarily be used for multi-response products.

10.2.4 Retain this data so that it can be easily retrieved.

10.2.5 To facilitate analyte identification, the retention time windows are set as percentages (±% realtime of daily calibration) into the data system. These values are slightly wider than calculated windows.

10.3 Initial Calibration

10.3.1 Compound list and Quantitation Limits (Table 11.1).

10.3.2 Analyze an instrument blank (hexane) to verify the analytical system is clean (no target compounds are present greater than the quantitation limit) before Standards.

10.3.3 The initial calibration of PCBs is performed at the five levels identified with suffix L, ML, M, MH and H (see Tables 8.3 - 8.8.). See Table 10-1 for specific calibrations. Calibration standards are identified with a suffix L, ML, M MH, and H.

10.3.4 Each instrument is calibrated for all PCBs. Subsequent initial calibrations for PCBs only require five-point calibration for AR1660 and any suspected (based on-site history or screening) or spiked PCB. Should any additional PCB be detected, or suspected, calibration must be verified for that Aroclor. If not verified, new initial calibration must be done for that Aroclor.

10.3.5 Note: Hexane = Instrument blank

Table 10-1

INITIAL CALIBRATION SEQUENCE
HEXANE
AR1660L
AR1660ML
AR1660M
AR1660MH
AR1660H
AR1254L*
AR1254ML*
AR1254M*
AR1254MH*
AR1254H*
AR1221M*
AR1232M*
AR1242M*
AR1248M*

**See 10.3.4, Following 1660 calibration, the instrument is calibrated for any additional suspected or identified PCBs.*

10.3.6 Inject 2.0 µL per column (i.e., 4 µL total injection) of each calibration standard. Tabulate area responses against the mass injected. The results are used to prepare a calibration curve for each analyte.

10.3.7 If the linear correlation coefficient is ≥0.995, linear curve may be used for quantification.

10.3.8 If < 0.995, calculate the correlation coefficient of a second order curve. If the correlation coefficient is >0.995, use this second order curve for quantitation of the compound of interest. Additional concentration levels of standards are required for higher order curves. Refer to Method 8000 for guidance.

10.3.9 Alternatively, if the percent relative standard deviation is less than 20%, linearity through the origin is assumed and the mean calibration factor of the 5 point calibration curve can be used for quantitation of samples. The initial calibration may be acceptable if some analytes have an RSD greater than 20 percent so

long as the mean of all the RSD values is less than 20 percent. If these conditions are met, then the compounds individual mean response factor may be used. Average response factor is the preferred method of quantitation.

10.3.10 Calculate the ratio of the response to the amount injected, defined as the calibration factor (CF), for each analyte at each standard concentration.

$$Calibration\ Factor\ (CF) = \frac{Total\ Area\ of\ Peaks*}{Mass\ Injected\ (in\ nanograms)}$$

**Use the total area of the 5 largest peaks for quantitation. The number and specific peaks may need to be adjusted, depending if sample matrix interferences or pattern weathering exists (see Section 11.2).*

10.3.11 Calculate the % Relative Standard Deviation (%RSD) of the calibration factors for the 5-point initial calibration using the following equation:

$$\%RSD = \frac{S\tan dard\ Deviation}{Mean\ Calibration\ Factor} \bullet 100$$

10.3.12 Quantitation of samples must continue to be done using the procedure initially used.

10.3.13 When PCBs other than 1016 or 1260 are unexpectedly found at a given site, standard curves for those analytes must be run and checked against samples for pattern recognition. If positively identified, calibration must be established before samples can be quantified.

10.3.14 Following each initial calibration, analyze a reference standard from a second source to verify the curve. The curve is deemed acceptable provided the reference standard calibration is within 15% difference of the mean calibration factor or 15% of the theoretical concentration, dependent on which means of quantitation will be used for analysis.

10.4 Calibration Verification

10.4.1 The working calibration curve or calibration factor must be verified at the beginning of the analytical sequence, and if a lapse in time >12 hours, has occurred from last continuing standard.

10.4.2 An instrument blank (hexane) is run to verify that the analytical system is clean (no target compounds are present > PQL).

10.4.3 A calibration check standard equivalent to the mid-level calibration standard must be analyzed at the beginning of the analytical sequence and after no more than every twenty samples. Use AR1016/1260 mid-level (AR1660M).

10.4.4 The quantitation method used must be the same throughout the analytical run.

10.4.4.1 If the mean calibration factor is used for quantitation, then the calibration factor must be ≤ 15% difference (Section 10.4.6) from the mean calibration factor.

10.4.4.2 If the regression curve is used for quantitating, then the concentration of the calibration check standard must be ≤ 15% drift (Section 10.4.6) from the theoretical concentration (i.e. 85 – 115% recovery).

10.4.5 If any analyzed sample is found to have other PCBs and an initial five point calibration and/or continuing standard was not performed for that compound, the sample must be reanalyzed under an acceptable calibration.

10.4.6 Calculate % Drift and % Difference using the equations below.

When using a curve:

$$\%\,Drift = \frac{Calculated Concentration - Theoretical Concentration}{Theoretical Concentration} \bullet 100$$

When using mean calibration factor:

$$\%\,Difference = \frac{CF\ Verification\ \ Standard - \overline{CF}}{\overline{CF}} \bullet 100$$

10.5 Sample Analysis

10.5.1 Once a successful initial calibration is complete, the primary analytical daily or batch sequence may begin (See table 10-2).

Table 10-2

Daily Calibration Sequence

Instrument Blank
1660 M
1254 M or alternate PCB as needed.
1242 M or alternate PCB as needed.
Other PCB's as needed.
Samples not to exceed 20. Recommended – 10.
Aroclor 1660 M.
Samples, not to exceed 20, 10 recommended.
Alternate mid-level Aroclor.
Samples, not to exceed 20, 10 recommended.
Aroclor 1660 M.

10.5.2 After every 20 samples or less, a 1660 mid level standard is analyzed.
If any PCB is detected in a sample at a level which exceeds the linear range of the calibration curve, the sample must be diluted to within the calibrated range.

10.5.2.1 Instrument blanks (hexane) may be interspersed throughout the analytical run to check for carryover or when the system is run unattended (autosampler).

10.5.2 Additional instrument blanks may be run after suspect samples or before standards to help eliminate matrix carry over.

10.5.3 Peak detection is prevented by the presence of elemental sulfur. The samples are copper treated to remove sulfur.

10.5.4 The copper cleanup of sample extracts is as follows:
Transfer an aliquot (1.0 mL) of sample extract to a clean autosampler vial. Add 0.5 – 1.5 grams of copper. Tighten the top on the vial and agitate the sample for 30 seconds. Centrifuge the extract if needed. Transfer the extract to another vial, leaving behind all solid precipitate and liquid mercury. If the mercury appears shiny, analyze the extract. If the mercury turns black, repeat sulfur removal as necessary. ***CAUTION:*** Mercury is a highly toxic metal and therefore must be used with great care. Waste containing mercury should be segregated and disposed of properly. All clean-up must be done in a fume hood.

10.5.5 Samples exhibiting matrix interferences can be further cleaned up using sulfuric acid.
10.5.5.1 Transfer 0.5-1 mL of extract into a clean vial. Add approximately 0.5 mL of concentrated sulfuric acid.
10.5.5.2 Vortex 10 seconds. Let settle, transfer portion of hexane extract to either autosampler vial for analysis or additional treatment with sulfuric acid if still highly colored.

10.6 Confirmation Analysis
10.6.1 Confirmation is not required by Method 8082.
10.6.2 If required by the client, a PCB is confirmed as present if the recognizable pattern is present on the confirmation column.
10.6.3 The confirmation analysis is qualitative only.

Instrument Maintenance

Table 10-3

ROUTINE MAINTENANCE PROCEDURES

Equipment/ Instrument	Symptom	Operation	Frequency
V3400/HP5890	Retention time shift	Change septum	Daily (or as needed)
V3400/HP5890	High baseline	Bake out column, detector	As needed
V3400/HP5890	Non-linear calibration	Replace detector; replace column	As needed
Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

11.0 DATA REDUCTION/EVALUATION/REPORTING

11.1 If quantitating from a linear curve, the equation below is provided as a manual check.

$$\text{Concentration} = \text{mg/kg}, \mu\text{g/L} = \left[\frac{y-b}{m}\right]\frac{Vt}{S} \bullet Df$$

where:

y = Area of target analyte from initial curve,
b = Intercept (area),
m = Slope (area /[µg/mL]),
S = Mass of soil sample extracted in grams (g) or (volume of water sample extracted in liters L),
Vt = Final volume of the extract in milliliters (mL).
Df = Dilution factor. The dilution factor equals µL of extract used to make dilution + µL clean solvent used to make dilution divided by µL of extract used to make dilution.

11.2 Due to weathering effects or matrix interference, it is not always possible to quantitate samples using the same 5 peaks used in calibrating. All samples must be quantitated using a minimum of 3 peaks for each PCB and these same peaks from the calibration must be used to calculate concentrations. Peaks used for quantitation must be clearly identified on chromatograms of standards and samples.

Target Compounds and Reporting Limits

Table 11-1

TARGET COMPOUNDS/ANALYTES AND QUANTITATION LIMITS

Compound/Analyte	Type	PQL	
		Soil (µg/kg)	Water (µg/L)
Aroclor-1016	T	20	0.50
Aroclor-1221	T	40	1.0
Aroclor-1232	T	20	0.50
Aroclor-1242	T	20	0.50
Aroclor-1248	T	20	0.50
Aroclor-1254	T	20	0.50
Aroclor-1260	T	20	0.50
TCMX	Q	NA	NA
DCB	Q	NA	NA
Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

Key Type:

NA = Not applicable.
T = Compound/analyte is target compound routinely reported.
M = Compound/analyte is listed in the method but is not routinely reported by E & E.
C = Compound/analyte is specified by the client and can be analyzed under this method.
S = Compound/analyte is routinely used as a matrix spike (MS).
L = Compound/analyte is routinely used as a LCS spike (LCS).
Q = Compound/analyte is used as a surrogate spike (SUR).

Table 11-1.1

TARGET COMPOUNDS/ANALYTES AND QUANTITATION LIMITS (WIPES)

Compound/Analyte	Type	PQL
		µg /Wipe
Aroclor-1016	T	1.5
Aroclor-1221	T	3.0
Aroclor-1232	T	1.5
Aroclor-1242	T	1.5
Aroclor-1248	T	1.5
Aroclor-1254	T	1.5
Aroclor-1260	T	1.5
TCMX	Q	NA
DCB	Q	NA
Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

Key Type:

T = Compound/analyte is target compound routinely reported.
M = Compound/analyte is listed in the method but is not routinely reported by E & E.
C = Compound/analyte is specified by the client and can be analyzed under this method.
S = Compound/analyte is routinely used as a matrix spike.
L = Compound/analyte is routinely used as a LCS spike.
Q = Compound/analyte is used as a surrogate spike.

12.0 QUALITY CONTROL/QUALITY ASSURANCE/CORRECTIVE ACTION

12.1 Refer to the Quality Control Table below and the following sections for corrective actions.

12.2 Each sample is spiked with the surrogates DCB and TCMX. The DCB is the primary surrogate. Calculate its recovery. If peaks interfere with DCB, TCMX should be evaluated for acceptance. Proceed with corrective action when two surrogates are out of limits for a sample.

12.3 The sample is to be reextracted and reanalyzed unless it can be documented (chromatogram) that factors such as matrix effects are responsible. A corrective action report must be filed.

12.4 If any quality control criteria cannot be met, but the problem is correctable, the sample(s) affected must be reanalyzed.

12.5 Data that must be submitted with out of control events must be accompanied by a corrective action report.

12.6 If any criteria cannot be met, but the problem is correctable, the sample(s) affected must be reanalyzed.

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Acceptance Criteria	Corrective Action
Method Blank	1 per preparation batch of 20 or fewer samples.	PQL	Reanalyze samples having concentrations > Quantitation limits.
Matrix Spike (MS) Matrix Spike Duplicate (MSD)	1 per preparation batch of 20 or fewer samples.	Project requirements if specified	Project requirements if any, otherwise evaluate results in conjunction with other QC information to determine the effect of the matrix on the bias of the analysis. Comment in narrative if appropriate.
Laboratory Control Sample (LCS)	1 per extraction batch of 20 or fewer samples.	See control limit summary, 8082	Notify Project Manager immediately. Re-extract and reanalyze the entire batch.
LCS Duplicate	Client Specified	Client specified	Client specified

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Acceptance Criteria	Corrective Action
Surrogate (SUR)	Every sample, blanks and QC.	See Control Limit Summary, 8082. DCB must meet acceptance limits for method blanks and LCS samples. At least 1 surrogate must meet criteria in samples.	Re-extract batch for blank or LCS failure. Re-extract affected sample(s) unless matrix effect is evident from chromatogram.
Revision: 0	Status: Final	Method: 8082	Minor Revision Date: 8/19/99

Table 12-2

CONTROL CHARTED QUALITY CONTROL SAMPLES, (WIPES)

QC Type	Analytes Charted	Matrix Charted
MS/MSD	Per client	Soil, Water
LCS	Analytes per customer request	Soil, Water
Surrogate (SUR)	DCB	Soil, Water
Secondary Surrogate (SUR)	TCMX	Soil, Water
Revision: 0 Status: Final	Method: 8082	Minor Revision Date: 8/19/99

Table 12-2.1

CONTROL CHARTED QUALITY CONTROL SAMPLES, (WIPES)

QC Type	Analytes Charted	Matrix Charted
Surrogate	DCB	Wipe
Revision: 0 Status: Final	Method: 8082	Minor Revision Date: 8/19/99

Table 12-3

CRITERIA ASSIGNED TO ROUTINE QUALITY CONTROL SAMPLES (WIPES)

QC Type	Matrix	Analyte	Nominal Spike Amount	Recovery (%)	RPD	Source
Surrogate	Wipe	DCB	0.6 µg/wipe	50 – 150	NA	Laboratory
Revision: 0	Status: Final		Method: 8082		Minor Revision Date: 8/19/99	

13.0 SPECIAL PROJECT REQUIREMENTS

Client-Specific Quality Control Requirements

13.1 Navy

13.1.1 All blanks analyzed by the laboratory, including instrument and method blanks, are to considered acceptable if they contain no target analytes at or above the MDL.

13.1.2 A method blank, matrix spike/matrix spike duplicate (MS/MSD), and matrix-pecific laboratory control spike (LCS) are to be analyzed with every analytical batch.

13.1.3 All field sample analyses must be bracketed by acceptable calibration verification.

13.1.4 A matrix specific LCS must be included. When analyzing soil samples use sand and spike directly onto it. When analyzing water samples use organic-free reagent water and spike directly onto it.

13.1.5 The matrix-specific LCS must include all surrogates and at least two analytes from each class of compounds.

13.1.6 When analyzing Navy samples with other clients, the Navy samples must be spiked.

13.1.7 If insufficient sample prevents use of Navy samples for MS/MSD, a duplicate matrix specific LCS must be analyzed.

13.1.8 Matrix spikes must contain all targeted analytes. Spiking concentration must be > 10 times the MDL.

13.2 AFCEE

13.2.1 Second column must be fully calibrated and results quantitative.

13.2.2 LCS must contain all analytes listed in AFCEE.

13.3 U.S. Army Corps of Engineers (ACE)

Method Quantitation Limit (MQL) is between 3-10 times MDL. The low calibration standard concentration must be ≥3 times MDL. The Method Reporting Limit (MRL) may slide between two times the MDL and project specific or regulatory requirements. The MRL may be higher or lower than the MQL. Results below the MQL must be reported as estimated (J flagged).

14.0 SAMPLE DISPOSAL

14.1 See waste disposal SOP A.10.

15.0 EXAMPLE FORMS

NA

END OF SOP

APPENDIX A-50

STANDARD OPERATING PROCEDURE FOR GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B, 8021B, 8081A, 8082, AND 8151A, SW-846

QUANTERRA® STANDARD OPERATING PROCEDURE

TITLE: GAS CHROMATOGRAPHIC ANALYSIS BASED ON METHOD 8000B, 8021B, 8081A, 8082 and 8151A, SW-846,

WITH LAB SPECIFIC APPENDICES FOR 8141A & 8310

(SUPERSEDES: Revision 4)

Prepared by: Richard Burrows

Reviewed by: _____
Technology Standardization Committee

Reviewed by: _____
Director, Quality Assurance

Approved by: _____
Director, Environmental Health and Safety

Approved by: _____
Corporate Management

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1. SCOPE AND APPLICATION

This SOP describes procedures for analysis of organic analytes by Gas Chromatography (GC). The procedures are based on SW-846 methodology and are applicable for measurements made to comply with the Resource Conservation and Recovery Act (RCRA). Individual analytes and methods are described in the appendices.

2. SUMMARY OF METHOD

In general, semivolatile analytes in aqueous samples are prepared for analysis using continuous or separatory funnel liquid / liquid extraction or solid phase extraction (SOP # CORP-OP-0001) Solid samples are prepared using sonication, Soxhlet or pressurized fluid extraction (SOP # CORP-OP-0001). Volatile analytes are prepared for analysis using purge and trap methodology (Appendix A).

After the initial preparation step, the sample is introduced to the GC and concentrations of target analytes are measured by the detector response within a defined retention time window, relative to the response to standard concentrations. Internal or external standardization procedures are used as specified in the method appendices.

3. DEFINITIONS

Definitions of terms used in this SOP may be found in the glossary of the Quality Assurance Management Plan (QAMP).

4. INTERFERENCES

Contamination by carryover can occur when a low concentration sample is analyzed after a high concentration sample. In addition, some purge and trap autosamplers are susceptible to port specific contamination. Co-elution of target analytes with non-targets can occur, resulting in false positives or biased high results. In particular, this is a problem with non-selective detectors such as the Flame Ionization Detector (FID). See the appendices for interferences specific to individual tests and suggested corrective actions.

5. SAFETY

5.1. Procedures shall be carried out in a manner that protects the health and safety of all Quanterra® associates. The following requirements must be met:

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 become contaminated will be removed and discarded; other gloves will be cleaned immediately. Refer to the Quanterra® Chemical Hygiene plan for a complete description of personal protection equipment.

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 MSDS files maintained in the laboratory. Specific hazards are covered in the appendices.

5.1.1. Opened containers of neat standards will be handled in a fume hood.

5.2. Sample extracts and standards which are in a flammable solvent shall be stored in an explosion-proof refrigerator.

5.3. When using hydrogen gas as a carrier, all precautions listed in the CHP shall be observed.

5.4. Standard preparation and dilution shall be performed inside an operating fume hood.

6. EQUIPMENT AND SUPPLIES

An analytical system complete with a gas chromatograph is required. A data system capable of measuring peak area and/or height is required. Recommended equipment and supplies for individual methods are listed in each method appendix.

7. REAGENTS AND STANDARDS

7.1. Stock Standards

Stock standards are purchased as certified solutions or prepared from pure solutions. Stock standards for method 8021B are stored at -10 to -20°C. Other stock standard solutions are stored at ≤6°C. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

Semivolatile stock standard solutions must be replaced after one year. Stock standards of gases must be replaced at least every week, unless the acceptability of the standard is demonstrated (Less than 20% drift from the initial calibration is an acceptable demontration). Other volatile stock standards must be replaced every 6 months or sooner if comparison with check standards prepared from an independent source indicates a problem.

7.1.1. Expiration times for all standards are measured from the time the standard is prepared or from the time that the standard ampoule is opened, if the standard is supplied in a sealed ampoule. If a vendor supplied standard has an earlier expiration date then that date is used.

7.2. Calibration Standards

7.2.1. Volatile Calibration Standards

The procedure for preparation of volatile standards is given in Appendix A.

7.2.2. Semivolatile Calibration Standards

Semivolatile calibration standards are prepared as dilutions of the stock standards. Surrogates and internal standards are used as specified in the method appendices. Semivolatile calibration solutions must be refrigerated at ≤6°C and protected from light. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem.

7.3. Gases for carrier and make-up: Hydrogen, Helium, Nitrogen, Argon/Methane.

7.4. Quality control (QC) Standards

QC standards (matrix spiking and LCS standards) are prepared and stored in the same way as calibration standards. They must be made from a stock independent from the calibration standards.

8. SAMPLE PRESERVATION AND STORAGE

Semivolatile extracts must be refrigerated at ≤6°C and analyzed within 40 days of the end of the extraction. Volatile sample storage conditions and holding times are given in Appendix A.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

9.1.1. For the standard analyte list, the initial demonstration and method detection limit (MDL) studies described in section 13 must be acceptable before analysis of samples may begin.

9.1.2. For non-standard analytes, a MDL study must be performed and calibration curve generated before analyzing any samples, unless lesser requirements are previously agreed to with the client. In any event the minimum initial demonstration required is analysis of an extracted standard at the reporting limit and a single point calibration.

9.2. Batch Definition

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the Quanterra® QC Program document (QA-003) for further details of the batch definition.

9.2.1. Quality Control Batch

The batch is a set of up to 20 samples of the same matrix processed using the same procedures and reagents within the same time period. The Quality Control batch must contain a matrix spike / spike duplicate (MS/MSD), a Laboratory Control Sample (LCS), and a method blank. Laboratory generated QC samples (Blank, LCS, MS/MSD) do not count towards the maximum 20 samples in a batch. Field QC samples are included in the batch count. In some cases, at client request, the MS/MSD may be replaced with a matrix spike and sample duplicate. If insufficient sample is available for an MS/MSD a LCSD may be substituted.

9.3. Control Limits

In-house historical control limits must be determined for surrogates, matrix spikes, and laboratory control samples (LCS). These limits must be determined at least annually. The recovery limits are mean recovery +/- 3 standard deviations, unless that limit is tighter than the calibration criteria, in which case limits may be widened. Refer to policy QA-003 for more details.

9.3.1. These limits do not apply to dilutions (except for tests without a separate extraction), but surrogate and matrix spike recoveries will be reported unless the dilution is more than 5X.

9.3.2. All surrogate, LCS, and MS recoveries (except for dilutions) must be entered into QuantIMS (when available) or other database so that accurate historical control limits can be generated. For tests without a separate extraction, surrogates and matrix spikes will be reported for all dilutions.

9.3.3. Refer to the QC Program document (QA-003) for further details of control limits.

9.4. Surrogates

All methods must use surrogates to the extent possible. Surrogate recoveries in samples and QC samples must be assessed to ensure that recoveries are within established limits. If any surrogates are outside limits, the following corrective actions must take place (except for dilutions):

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze the extract if either of the above checks reveal a problem.

- Reprepare and reanalyze the sample or flag the data as "Estimated Concentration" if neither of the above resolves the problem. Repreparation is not necessary is there is obvious chromatographic interference.
- The decision to reanalyze or flag the data should be made in consultation with the client. It is only necessary to reprepare / reanalyze a sample once to demonstrate that poor surrogate recovery is due to matrix effect, unless the analyst believes that the repeated out of control results are not due to matrix effect.

9.4.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in-control result is reported.

9.4.2. If the surrogates are out of control for the sample, matrix spike, and matrix spike duplicate, then matrix effect has been demonstrated for that sample and repreparation is not necessary. If the sample is out of control and the MS and/or MSD is in control, then repreparation or flagging of the data is required.

9.4.3. Refer to the Quanterra® QC Program document (QA-003) for further details of the corrective actions.

9.5. Method Blanks

For each batch of samples, analyze a method blank. The method blank consists of reagent water for aqueous semivolatiles samples, and sodium sulfate for semivolatiles soils tests (Refer to SOP No. CORP-OP-0001 for details). For low level volatiles, the method blank consists of reagent water. For medium level volatiles, the method blank consists of methanol as described in Appendix A. Surrogates are added and the method blank is carried through the entire analytical procedure. 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 5% of the measured concentration of that analyte in the associated samples, whichever is higher.

If the analyte is a common laboratory contaminant (methylene chloride, acetone, 2-butanone, phthalate esters) the data may be reported with qualifiers if the concentration of the analyte is less than five times the reporting limit. Such action must be taken in consultation with the client.

Re-extraction and reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples.

If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.5.1. Refer to the Quanterra® QC Program document (QA-003) for further details of the corrective actions.

9.6. Instrument Blanks

9.6.1. An instrument blank must be analyzed during any 12 hour period of analysis that does not contain a method blank.

9.6.2. An instrument blank consists of the appropriate solvent with internal standards added. If internal standards are not used the surrogates should be added.

9.6.3. Control criteria are the same as for the method blank, except that only reanalysis of affected samples would be required, not re-extraction.

9.7. Laboratory Control Samples (LCS)

For each batch of samples, analyze a LCS. The LCS contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The LCS may also contain the full set of analytes. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur. Corrective action will normally be repreparation and reanalysis of the batch; however, if the matrix spike and matrix spike duplicate are within limits, the batch may be acceptable.

9.7.1. Refer to the Quanterra® QC Program document (QA-003) for further details of the corrective action.

9.7.2. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.7.3. LCS compound lists are included in the appendices.

9.7.4. If full analyte spike lists are used at client request, it will be necessary to allow a percentage of the components to be outside control limits as this would be expected statistically. These requirements should be negotiated with the client.

9.8. Matrix Spikes

For each QC batch, analyze a matrix spike and matrix spike duplicate. Spiking compounds and levels are given in the appendices. Compare the percent recovery and relative percent difference (RPD) to those in the laboratory specific historically generated limits.

- 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.
- If the recovery for any component is outside QC limits for both the Matrix spike / spike duplicate and the LCS, the laboratory is out of control and corrective action must be taken. Corrective action will normally include repreparation and reanalysis of the batch.
- If a MS/MSD is not possible due to limited sample, then a LCS duplicate should be analyzed.
- The matrix spike / duplicate must be analyzed at the same dilution as the unspiked sample, unless the matrix spike components would then be above the calibration range.

9.8.1. If dual column analysis is used the choice of which result to report is made in the same way as for samples (Section 12.1.2) unless one column is out of control, in which case the in control result is reported.

9.9. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.10. Quanterra® QC Program

Further details of QC and corrective action guidelines are presented in the Quanterra® QC Program document (QA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION AND STANDARDIZATION

Internal or external calibration may be used. Internal calibration is recommended unless the sample matrix is likely to interfere with the quantitation of the internal standard. In either event prepare standards containing each analyte of interest at a minimum of five concentration levels. The low level standard should be at or below the reporting limit. The other standards define the working range of the detector. Recommended calibration levels are given in the appendices.

10.1. A new calibration curve must be generated after major changes to the system or when the continuing calibration criteria cannot be met. Major changes include new columns, changing PID lamps or FID jets or replacing the ECD detector. A new calibration is not required after clipping the column, replacing the septum or syringe, or other minor maintenance.

10.2. With the exception of 10.3 below, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points. Third order calibrations require at least seven points.

10.3. A level may be removed from the calibration if the reason can be clearly documented, for example a broken vial or no purge run. A minimum of five levels must remain in the calibration. The documentation must be retained with the initial calibration. Alternatively, if the analyst believes that a point on the curve is inaccurate, the point may be reanalyzed and the reanalysis used for the calibration. All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.4. External standard calibration

Quantitation by the external standard method assumes a proportional relationship between the calibration run and the analyte in the sample. To use this approach, introduce each calibration standard into the GC using the technique that will be used for samples. The ratio of the peak height or area response to the mass or concentration injected may be used to prepare a calibration curve.

$$Calibration\ Factor\ (CF) = \frac{Area\ or\ Height\ of\ Peak}{Mass\ Injected\ (ng)}$$

Some data systems may use the inverse of this formula. This is acceptable so long as the same formula is used for standards and samples. It is also possible to use the concentration of the standard rather than the mass injected. (This would require changes in the equations used to calculate the sample concentrations). Use of peak area or height must be consistent. However, if matrix interferences would make quantitation using peak area inaccurate for a particular sample, then peak height may be used as a substitute.

10.5. Internal standard calibration

10.5.1. The internal standard approach assumes that variations in instrument sensitivity, amount injected etc. can be corrected by determining the ratio of the response of the analyte to the response of an internal standard that has been added to the extract. To use this approach, select one or more internal standard(s) that are similar in analytical behavior to the compounds of interest. Recommended internal standards are given in the appendices. The analyst must demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. If the sample matrix interferes with quantitation of the internal standard, then the external standard

approach must be used instead. In this event use the response factors from the previous continuing calibration to quantitate the analytes in the sample with the interference (applies only to the sample with the interference).

10.5.2. Introduce each calibration standard into the GC using the technique that will be used for samples. Response factors (RF) for each compound are calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

Where:

A_s = Response for the analyte to be measured
A_{is} = Response for the internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of the analyte to be determined in the standard

10.6. Calibration curve fits

Average response factor, linear regression, or quadratic curves may be used to fit the data. Average response factor may be used if the average % RSD of the response factors or calibration factors of all the analytes in the calibration standard taken together is $\leq 20\%$. The average %RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes.

10.6.1. In general, for environmental analysis, average response factors are the most appropriate calibration model. Linear or curved regression fits should only be used if the analyst has reason to believe that the average RF model does not fit the normal concentration/response behavior of the detector.

10.6.2. Average response factor

The average response factor may be used if the average percent relative standard deviation (%RSD) of all the response factors taken together is $\leq 20\%$.

The equation for average response factor is:

$$\textit{Average response factor} = \overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n}$$

Where: n = Number of calibration levels

$\sum_{i=1}^{n} RF_i$ = Sum of response factors for each calibration level

10.6.3. Linear regression

The linear fit uses the following functions:

10.6.3.1. External Standard

$$y = ax + b$$

or

$$x = \frac{(y - b)}{a}$$

Where: y = Instrument response
x = Concentration
a = Slope
b = Intercept

10.6.3.2. Internal Standard

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$

Where: C_s = Concentration in the sample
A_s = Area of target peak in the sample
A_{is} = Area of internal standard in the sample
C_{is} = Concentration of the internal standard

10.6.4. Quadratic curve

The quadratic curve uses the following functions:

10.6.4.1. External standard

$$y = ax + cx^2 + b$$

Where c is the curvature

10.6.4.2. Internal Standard

$$y = a\left(\frac{A_s \times C_{is}}{A_{is}}\right) + c\left(\frac{A_s \times C_{is}}{A_{is}}\right)^2 + b$$

10.7. Evaluation of calibration curves

10.7.1. The percent relative standard error (%RSE) from the calibration curve is used to evaluate the initial calibration. This provides a measure of how much error is associated with using the calibration curve for quantitation.

10.7.2. The least squares regression line is calculated and used to calculate the predicted concentration for each level. The percent relative standard error is calculated as follows:

$$\%\ RSE = 100\% \times \sqrt{\frac{\sum_{i=1}^{N}\left[\frac{C_i - PC_i}{C_i}\right]^2}{(N-P)}}$$

Where:
N = Number of points in the curve
P = Number of parameters in the curve (= 1 for average response factor, 2 for linear, 3 for quadratic)
C_i = True concentration for level i
PC_i = Predicted concentration for level i

Note that when average response factors are used, %RSE is equivalent to %RSD.

10.8. The following requirements must be met for any calibration to be used:

- Response must increase with increasing concentration.
- If a curve is used, the intercept of the curve at zero response must be less than $\pm$ the reporting limit for the analyte.
- The average Relative Standard Error (RSD for average response factors) of the calibration points from the curve used must be $\leq 20\%$.
- Some data systems will not measure the %RSE from a linear or quadratic fit. For the linear case, the correlation coefficient may be used as an alternative to the %RSE, and must be greater than or equal to 0.990. For the quadratic case the Coefficient of Determination may be used, and must be greater or equal to 0.990.

Note: The Relative Standard Error (RSE) is superior to the Correlation Coefficient (r) and Coefficient of Determination (r^2) for testing the fit of a set of calibration points to a line. The lower points on a curve have little effect on r. As a result a curve may have a very good correlation coefficient (>0.995), while also having > 100% error at the low point.

10.9. Weighting of data points

10.9.1. In linear and quadratic calibration fits, the points at the lower end of the calibration curve have less absolute variance than points at the high concentration end of the curve. This can cause severe errors in quantitation at the low end of the calibration. However, in environmental analysis, accuracy at the low end of the curve is very important. For this reason it is preferable to increase the weighting of the lower concentration points. $1/Concentration^2$ weighting (often called $1/X^2$ weighting) will improve accuracy at the low end of the curve and should be used if the data system has this capability.

10.10. Non-standard analytes are sometimes requested. For these analytes, it may be acceptable to analyze a single standard at the reporting limit with each continuing calibration rather than a five point initial calibration. This action must be with client approval. If the analyte is detected in any of the samples, a five point initial calibration must be generated and the sample(s) reanalyzed for quantitation.

10.11. Calibration Verification

10.11.1. 12 hour Calibration

The working calibration curve or RF must be verified by the analysis of a mid point calibration standard at the beginning, after every 12 hours, and at the end of the analysis sequence. The center of each retention time window is updated with each 12 hour calibration.

10.11.2. Calibration Verification

It may be appropriate to analyze a mid point standard more frequently than every 12 hours. If these calibration verification standards are analyzed, requirements are the same as the 12 hour calibration with the exception that retention times are not updated.

10.11.3. Any individual compounds with %D $\leq$ 15% meet the calibration criteria. The calibration verification is also acceptable if the average of the %D for all the analytes is $\leq$ 15%. This average is calculated by summing all the absolute %D results in the calibration (including surrogates) and dividing by the number of analytes.

10.11.4. It is not necessary to run a calibration verification standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.11.5. Samples quantitated by external standard methods must be bracketed by calibration verification standards that meet the criteria listed above. Bracketing is not necessary for internal standard methods.

10.11.6. If the analyst notes that a CCV has failed and can document the reason for failure (e.g. no purge, broken vial, carryover from the previous sample etc.) then a second CCV may be analyzed without any adjustments to the instrument. If this CCV meets criteria then the preceding samples have been successfully bracketed. If adjustments to the instrument are performed before the repeat CCV then the preceding samples have not been successfully bracketed but analysis may continue.

10.11.7. In general, it is not advisable to analyze repeat CCVs on unattended runs. If repeat CCVs are analyzed then the first will serve as the bracketing standard for the preceding samples and the last will serve as the CCV for the following samples.

10.11.8. If highly contaminated samples are expected it is acceptable to analyze blanks or primers at any point in the run.

10.11.9. % Difference calculation

% Difference for internal and external methods is calculated as follows

Internal Standard:

$$\%D = \frac{RF_c - \overline{RF}}{\overline{RF}} \times 100$$

External standard:

$$\%D = \frac{CF_c - \overline{CF}}{\overline{CF}} \times 100$$

Where RF_c and CF_c are the response and calibration factors from the continuing calibration

$\overline{RF}$ and $\overline{CF}$ are the average response and calibration factors from the initial calibration

10.11.10.% Drift calculation

% Drift is used for comparing the continuing calibration to a linear or quadratic curve. The criteria for % drift are the same as for % difference

$$\%\ Drift = \frac{Calculated\ Conc. - Theoretical\ Conc.}{Theoretical\ Conc.} \times 100\%$$

10.11.11.Corrective Actions for Continuing Calibration

If the overall average %D of all analytes is greater than $\pm$ 15% corrective action must be taken. This may include clipping the column, changing the liner or other minor instrument adjustments, followed by reanalyzing the standard. If the overall average %D still varies by more than $\pm$ 15%, a new calibration curve must be prepared.

10.11.12.Corrective Action for Samples

For internal standard methods, any samples injected after a standard not meeting the calibration criteria must be reinjected.

For external standard methods, any samples injected after the last good continuing calibration standard must be reinjected.

If the average %D for all the analytes in the calibration is over 15%, but all of the analytes requested for a particular sample have %D $\leq$15%, then the analysis is acceptable for that sample.

11. PROCEDURE

11.1. Extraction

Extraction procedures are referenced in the appendices.

11.2. Cleanup

Cleanup procedures are referenced in the appendices.

11.3. Gas Chromatography

Chromatographic conditions for individual methods are presented in the appendices.

11.4. Sample Introduction

In general, volatiles analytes are introduced using purge and trap as described in Appendix A. Semivolatile analytes are introduced by direct injection of the extract. Samples, standards, and QC must be introduced using the same procedure.

11.5. Analytical Sequence

An analytical sequence starts with an initial calibration or a daily calibration. Refer to the individual method appendices for method specific details of daily calibrations and analytical sequences.

11.5.1. The daily calibration includes analysis of standards containing all single response analytes and updating the retention time windows.

11.5.2. If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration.

11.6. Retention Time Windows

11.6.1. Retention time windows must be specified for all analytes. *A Fixed retention time windows (-.05 minutes) will be used for all GC methods. Alternatively, if it is determined through calculation that wider limits are necessary, the limits will be developed as follows:* Make an injection of all analytes of interest each day over a three day period. Calculate the standard deviation of the three retention times for each analyte (relative retention times may also be used). For multiresponse analytes (e.g., Aroclors) use the retention time of major peaks. Plus or minus three times the standard deviation of the retention times of each analyte defines the retention time window.

11.6.2. The center of the retention time window is the retention time from the last of the three standards. The centers of the windows are updated with the mid point of the initial calibration and each 12 hour calibration. The widths of the windows will remain the same until new windows are generated following the installation of a new column.

11.6.3. *Where calculated limits are being used, if* the retention time window as calculated above is less than +/- 0.05 minutes, use +/- 0.05 minutes as the retention time window. This allows for slight variations in retention times caused by sample matrix.

11.6.4. *Where calculated limits are being used, t* he laboratory must calculate new retention time windows each time a new column is installed. The new windows must be generated within one week of the installation of the new column. Until these standards have been run on the new column, the retention time windows from the old column may be used, updated with the retention times from the new initial calibration.

11.6.5. Corrective Action for Retention Times

The retention times of all compounds in each continuing calibration must be within the retention time windows established by the 12 hour calibration. If this condition is not met, all samples analyzed after the last compliant standard must be reanalyzed unless the following conditions are met for any compound that elutes outside the retention time window:

The retention time of that compound in the standard must be within a retention time range equal to twice the original window.

No peak that would be reportable may be present on the sample chromatogram within an elution time range equal to three times the original retention time window.

11.7. Daily Retention Time Windows

The center of the retention time windows determined in section 11.6 are adjusted to the retention time of each analyte as determined in the 12 hour calibration standards. (See the method 8081A and 8082 appendices for exceptions for multi-response components.) The retention time windows must be updated at the beginning of each analytical sequence and with each 12 hour calibration, but not for any other calibration verification standards.

11.8. Percent Moisture

Analytical results may be reported as dry or wet weight, as required by the client. Percent moisture must be determined if results will be reported as dry weight. Refer to SOP CORP-OP-0001 for determination of percent moisture.

11.9. Procedural Variations

Procedural variations are allowed only if deemed necessary in the professional judgment of the supervisor 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 approved by a supervisor and QA/QC manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file. The nonconformance is also addressed in the case narrative. 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. Qualitative Identification

12.1.1. Tentative identification occurs when a peak is found within the retention time window for an analyte, at a concentration above the reporting limit, or above the MDL if J flags are required. Normally confirmation is required on a second column, but if the detector is sufficiently specific or if the sample matrix is well enough defined, single column analysis may be adequate. In some cases GC/MS confirmation may be required. Client specific requirements may also define the need for second column confirmation and / or GC/MS confirmation. Refer to the appendices for test specific requirements for confirmation. Identification is confirmed if a peak is also present in the retention time window for that analyte on the confirmatory column, at a concentration greater than the reporting limit (MDL if J flag confirmation required).

12.1.2. Dual column quantitation

For confirmed results, two approaches are available to the analyst;
A) The primary column approach
Or
B) The better result approach
Both are acceptable to avoid the reporting of erroneous or unconfirmed data.

12.1.2.1. Primary column approach:

The result from the primary column is normally reported. The result from the secondary column is reported if any of the following three bulleted possibilities are true.

- There is obvious chromatographic interference on the primary column
- The result on the primary column is > 40% greater than the result on the secondary column
- Continuing or bracketing standard fails on the primary column but is acceptable on the secondary column. (If the primary column result is > 40% higher than the secondary

and the primary column calibration fails, then the sample must be evaluated for reanalysis.)

12.1.2.2. Better result approach

The lower of the two results is normally reported. The lower result is considered better because the higher result is generally higher because of chromatographic interference. The higher result is reported if any of the following two bulleted possibilities are true.

- There is obvious chromatographic interference on the column with the lower result
- The continuing or bracketing calibration on the column with the lower result fails. (If the higher result is > 40% higher and the calibration on the column with the lower result fails, then the sample must be evaluated for reanalysis.)

12.1.3. If the Relative percent difference (RPD) between the response on the two columns is greater than 40%, or if the opinion of an experienced analyst is that the complexity of the matrix is resulting in false positives, the confirmation is suspect and the results are qualified. RPD is calculated using the following formula:

$$RPD = \frac{R_1 - R_2}{\frac{1}{2}(R_1 + R_2)} x\,100$$

Where R=Result

12.1.4. Multi-response Analytes

For multi-response analytes, the analyst should use the retention time window, but should rely primarily on pattern recognition. The pattern of peaks will normally serve as confirmation.

12.1.5. The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times.

12.2. Calibration Range

If concentrations of any analytes exceed the working range as defined by the calibration standards, then the sample must be diluted and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. It may be necessary to dilute samples due to matrix.

12.3. Dilutions

Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.3.1. Guidance for Dilutions Due to Matrix

If the sample is initially run at a dilution and only minor matrix peaks are, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgement is required to determine the most concentrated dilution that will not result in instrument contamination.

12.3.2. Reporting Dilutions

The most concentrated dilution with no target compounds above the calibration range will be reported. Other dilutions will only be reported at client request.

12.4. Interferences

If peak detection is prevented by interferences, further cleanup should be attempted. If no further cleanup is reasonable, then elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

12.5. Internal Standard Criteria for Continuing Calibration

If internal standard calibration is used, then the internal standard response in a continuing calibration standard must be within 50 to 150% of the response in the mid level of the initial calibration.

12.6. Calculations

Capabilities of individual data systems may require the use of different formulas than those presented here. When this is the case, the calculations used must be shown to be equivalent and must be documented in an appendix attached to this document.

12.6.1. External Standard Calculations

12.6.1.1. Aqueous samples

$$Concentration\ (mg/L) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times V_s)}$$

Where:

A_x = Response for the analyte in the sample
V_i = Volume of extract injected, µL
D_f = Dilution factor
V_t = Volume of total extract, µL
V_s = Volume of sample extracted or purged, mL
CF = Calibration factor, area or height/ng, Section 10.1

12.6.1.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times V_t \times D_f)}{(CF \times V_i \times W \times D)}$$

Where:

W = Weight of sample extracted or purged, g

$$D = \frac{100 - \%\ Moisture}{100}$$ (D = 1 if wet weight is required)

12.6.2. Internal Standard Calculations

12.6.2.1. Aqueous Samples

$$Concentration\ (mg/L) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times V_s)}$$

Where:

C_{is} = Amount of internal standard added, ng
A_{is} = Response of the internal standard
RF = Response factor for analyte

12.6.2.2. Non-aqueous Samples

$$Concentration\ (mg/kg) = \frac{(A_x \times C_{is} \times D_f)}{(A_{is} \times RF \times W \times D)}$$

12.6.3. Surrogate Recovery

Concentrations of surrogate compounds are calculated using the same equations as for the target compounds. The response factor from the initial calibration is used. Surrogate recovery is calculated using the following equation:

$$\%\ \text{Recovery} = \frac{Concentration\ (or\ amount)\ found}{Concentration\ (or\ amount)\ spiked} \times 100$$

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix B, and further defined in QA Policy #: QA-005.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.2. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in each appendix.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any

analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will 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

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, December 1996, Section 8000B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the Method Detection Limit. 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 to be up to 5 times the reporting limit in the blank following consultation with the client.

17.2. Modifications from Previous Revision

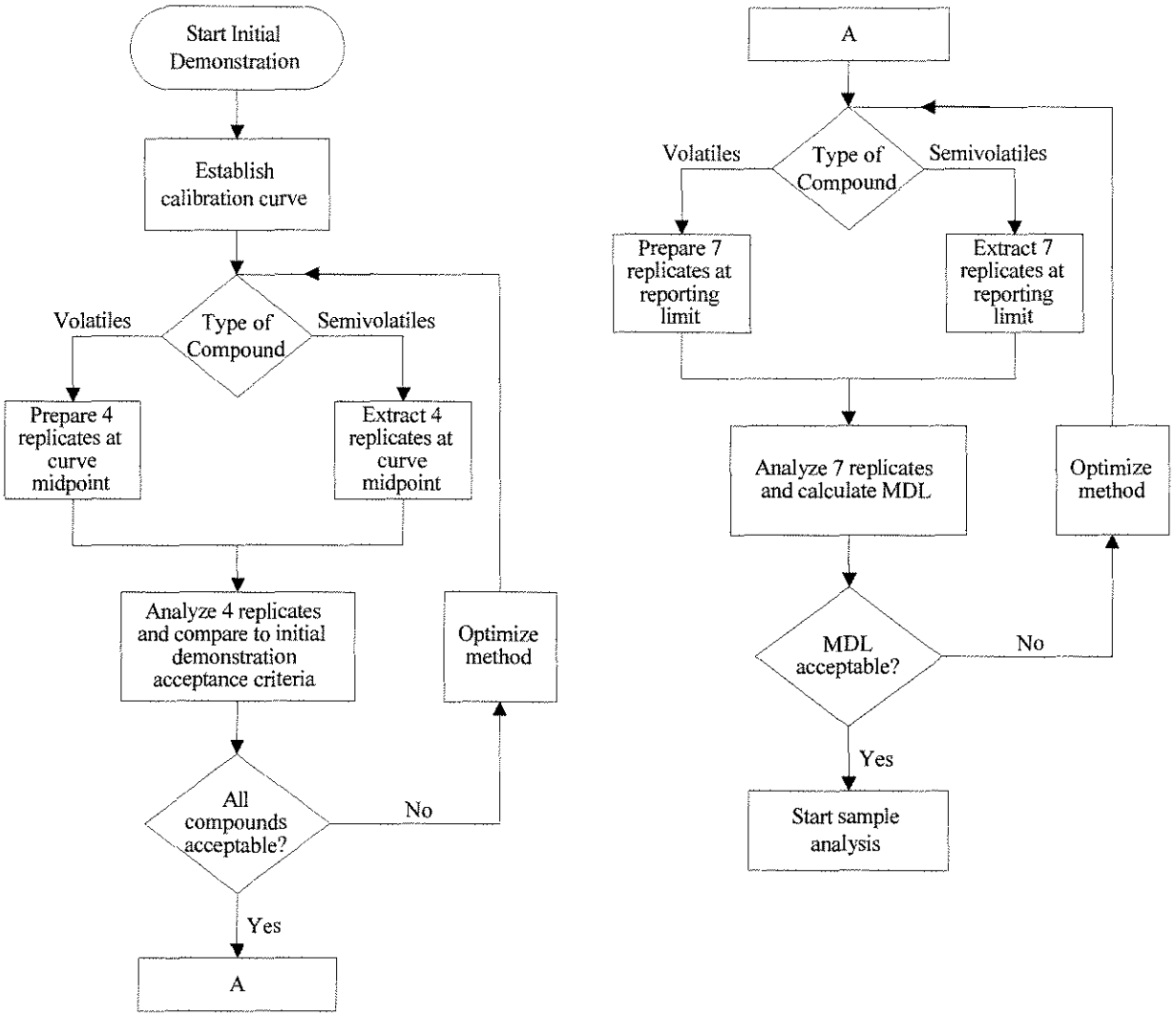
The calibration criteria in section 10.11 have been rewritten to improve consistency with SW-846 and to improve clarity.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

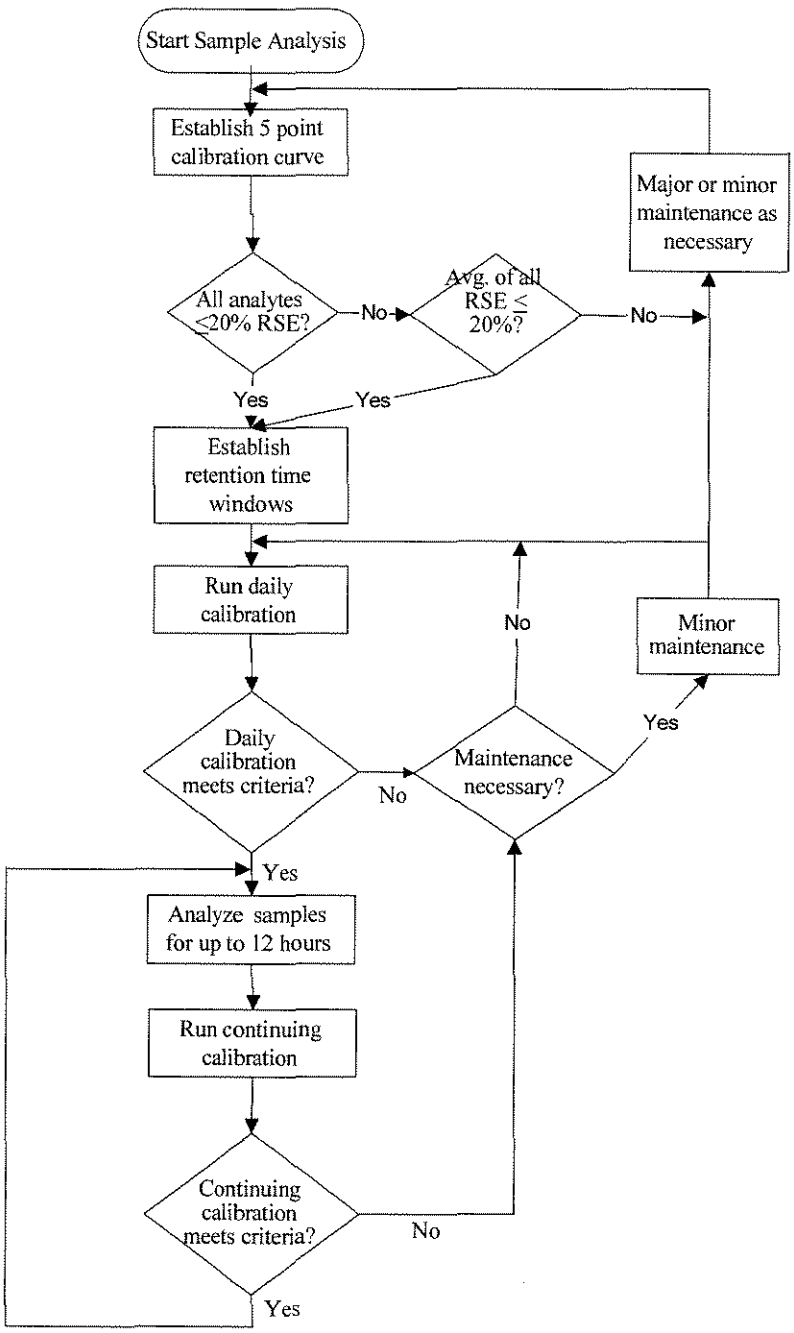
17.4. Flow Diagrams

17.4.1. Initial demonstration and MDL[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

17.4.2. Sample Analysis[1]



[1] This flow diagram is for guidance and cannot cover all eventualities. Consult the SOP text and a supervisor if in doubt.

1. SCOPE AND APPLICATION

1.1. This method describes sample preparation and extraction for the analysis of volatile organics by a purge and trap procedure, following method 8021B. However, where required by a client QAPP this section may also be used to analyze aromatic volatiles by discontinued methods 8020A and 8010B. All requirements of the 8000B section of this SOP must be met except when superseded by this Appendix. Refer to Table A-1 for the individual analytes normally determined by these procedures.

1.2. Compounds within the scope of this method have boiling points below 200°C and are soluble or slightly soluble in water. Classes of compounds best suited to purge-and-trap analysis include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3. Water samples and soils samples with low levels of contamination may be analyzed directly by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in soil may be determined by the medium level methanol extraction procedure.

1.4. This method also describes the preparation of water-miscible liquids, non-water-miscible liquids, solids, wastes, and soils/sediments for analysis by the purge-and-trap procedure.

2. SUMMARY OF METHOD

2.1. An inert gas is bubbled through the sample at ambient temperature or at 40 °C (40°C required for low level soils), and the volatile components are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. Analytes are detected using a photoionization Detector, an electrolytic conductivity detector or a combination of both.

2.2. For soil samples, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water. It is then analyzed by purge-and-trap GC following the normal water method. If very low detection limits are needed for soil samples then direct purge using sodium bisulfate preservation may be necessary.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this SOP.

4. INTERFERENCES

4.1. Refer to section 4 of the method 8000B part of this SOP for general information on chromatographic interferences.

4.2. Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.3. Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

4.4. Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the system may be required.

4.5. When utilizing an autosampler system which has multiple ports for sample analysis, it is likely that only a single stage or port may be contaminated by a highly concentrated sample. If a port is suspect, a water blank should be analyzed to verify lack of contamination. If the water blank and subsequent blanks on that port show contamination consistent with the concentrated sample, further maintenance is required. This may include replacing or cleaning the multi-port valve, transfer lines, etc.

4.6. A holding blank is kept in the sample refrigerator. This is analyzed and replaced every 14 days. If the holding blank does not meet the method blank criteria, the source of contamination must be found and corrected. Evaluation of all samples analyzed in the 14 day period prior to the analysis of the contaminated holding blank is required.

4.7. Acidification of samples may result in hydrolysis of 2-chloroethyl vinyl ether.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B section of this SOP for general safety requirements.

5.2. Often, purge vessels on purge-and-trap instrumentation are pressurized by the time analysis is completed. Therefore, vent the pressure prior to removal of these vessels to prevent the contents from spraying out.

5.3. The toxicity or carcinogenicity of each chemical used in this procedure has not been fully defined. Additional health and safety information can be obtained from the MSDS files maintained in the laboratory. The following specific hazards are known:

Methanol -- Flammable and toxic

5.4. Methanol shall not be used in a CaptAir hood.

6. EQUIPMENT AND SUPPLIES

6.1. Microsyringes -- 10µL, 25µL, 100µL, 250µL, 500µL, and 1000µL. These should be equipped with a 20 gauge (0.006" ID) needle. These will be used to measure and dispense methanolic solutions and aqueous samples.

6.2. Gas tight syringes -- 5 mL and 25 mL. Used for measuring sample volumes.

6.3. Purge and Trap Apparatus -- A device capable of extracting volatile compounds, trapping on a sorbent trap, and introducing onto a gas chromatograph.

6.4. Purge and Trap Autosampler -- In order to maintain high sample throughput, an autosampler is highly recommended.

6.5. Trap -- The trap used is dependent on the class of compound to be analyzed. Refer to Table A-2 for suggested traps for specific tests.

6.6. Purge Vessels -- These are dependent on the purge and trap unit/autosampler used. Both disposable culture tubes (needle sparge units) and specially designed vessels with fritted bottoms may be used. Follow the manufacturer's suggestions for configuration.

6.7. Columns - Refer to Table A-2 for details of columns.

6.8. Volumetric flasks, Class A: 5 mL to 250 mL

6.9. pH paper

6.10. Balance capable of weighing to 0.01g for samples.

7. REAGENTS AND SUPPLIES

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Organic Free Water

Organic free water is defined as water in which an interferent is not observed at the reporting limit of the compounds of interest. Suggested methods for generating organic free water include:

- Filtration through a carbon bed.
- Continuously sparging water with helium or nitrogen.
- Use of commercial water purification systems.

Other methods may be used, so long as the requirement that the water not show any interferences is met. The procedure used should be documented in a lab specific attachment.

7.3. Sodium Bisulfate

7.4. Methanol -- Purge and Trap Grade

7.5. Standards

Refer to tables A-5 and A-6 for details of surrogate, matrix spiking and internal standards. Calibration standard levels are not specified, since they may depend on the sensitivity and linear range of specific detectors. However, the low level standard must be equivalent to the reporting limits specified in Table A-1.

7.5.1. Volatile standards are prepared by injecting a measured volume of the stock standard into a syringe containing the appropriate volume of organic free water. The calibration standard is then loaded into the purge device.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1. Holding times for all volatile analysis are 14 days from sample collection.

1.2. Water samples are normally preserved at pH < 2 with 1:1 hydrochloric acid. If residual chlorine is present, 2 drops of 10% sodium thiosulfate are added.

8.3. Solid samples are field preserved with sodium bisulfate solution for low level analysis, or with methanol for medium level analysis. Soil samples can also be taken using the EnCore™ sampler and preserved in the lab within 48 hours of sampling. At specific client request, unpreserved soil samples may be accepted.

8.4. There are several methods of sampling soil. The recommended method, which provides the minimum of field difficulties, is to take a EnCore sample. (The 5 g or 25 g sampler can be used, depending on client preference). Following shipment back to the lab the soil is preserved in methanol. This is the medium level procedure. If very low detection limits are needed (< 50 µg/kg for

most analytes) then it will be necessary to use two additional 5 g EnCore samplers or to use field preservation.

8.5. Sample collection for medium level analysis using EnCore samplers.

8.5.1. Ship one 5 g (or 25 g) EnCore sampler per field sample position.

8.5.2. An additional bottle must be shipped for percent moisture determination.

8.5.3. When the samples are returned to the lab, extrude the (nominal) 5g (or 25 g) sample into a tared VOA vial containing 5 mL methanol (25 mL methanol for the 25 g sampler). Obtain the weight of the soil added to the vial and note on the label.

8.5.4. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.5.5. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.5.6. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.5.7. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.5.8. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.6. Sample collection for medium level analysis using field methanol preservation

8.6.1. Prepare a VOA vial by adding 5 mL purge and trap grade methanol. (If a 25 g sample is to be used, add 25 mL methanol to the VOA vial).

8.6.2. Seal the bottle and attach a label.

8.6.3. Weigh the bottle to the nearest 0.01g and note the weight on the label.

8.6.4. Ship with appropriate sampling instructions.

8.6.5. Each sample will require an additional bottle with no preservative for percent moisture determination.

8.6.6. At client request, the methanol addition and weighing may also be performed in the field.

8.6.7. When the samples are returned to the lab, obtain the weight of the soil added to the vial and note on the label.

8.6.8. Add the correct amount of surrogate spiking mixture. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.)

8.6.9. Add the correct amount of matrix spiking solution to the matrix spike and matrix spike duplicate samples. (Add 100 µL of 250 µg/mL solution for a nominal 25 g sample, 20µL for a nominal 5 g sample.) The addition of spike introduces a slight error, (0.4%) which can be neglected, into the calculations.

8.6.10. Prepare an LCS for each batch by adding the correct amount of matrix spiking solution to clean methanol. (100 µL of spike to 25 mL methanol or 20 µL spike to 5 mL methanol).

8.6.11. Shake the samples for two minutes to distribute the methanol throughout the soil.

8.6.12. Allow to settle, then remove a portion of methanol and store in a clean Teflon capped vial at 4+2°C until analysis.

8.7. Low level procedure

8.7.1. If low detection limits are required (typically < 50 µg/kg) sodium bisulfate preservation must be used. However, it is also necessary to take a sample for the medium level (methanol preserved) procedure, in case the concentration of analytes in the soil is above the calibration range of the low-level procedure.

8.7.2. A purge and trap autosampler capable of sampling from a sealed vial is required for analysis of samples collected using this method. (Varian Archon or O.I. 4552).

8.7.3. The soil sample is taken using a 5g EnCore sampling device and returned to the lab. It is recommended that two EnCore samplers be used for each field sample position, to allow for any reruns than may be necessary. A separate sample for % moisture determination is also necessary.

8.7.4. Prepare VOA vials by adding a magnetic stir bar, approximately 1 g of sodium bisulfate and 5 mL of reagent water.

8.7.5. Seal the vial and attach a label. The label must not cover the neck of the vial or the autosampler will malfunction.

8.7.6. Weigh the vial to the nearest 0.01g and note the weight on the label.

8.7.7. Extrude the soil sample from the EnCore sampler into the prepared VOA vial. Reweigh the vial to obtain the weight of soil and note on the label.

8.7.8. **Note:** Soils containing carbonates may effervesce when added to the sodium bisulfate solution. If this is the case at a specific site, add 5 mL of water instead, and freeze at $\geq$ -10°C until analysis.

8.7.9. Alternatively the sodium bisulfate preservation may be performed in the field. Ship at least two vials per sample. The field samplers must determine the weight of soil sampled. Each sample will require an additional bottle with no preservative for percent moisture determination, and an additional bottle preserved with methanol for the medium level procedure.

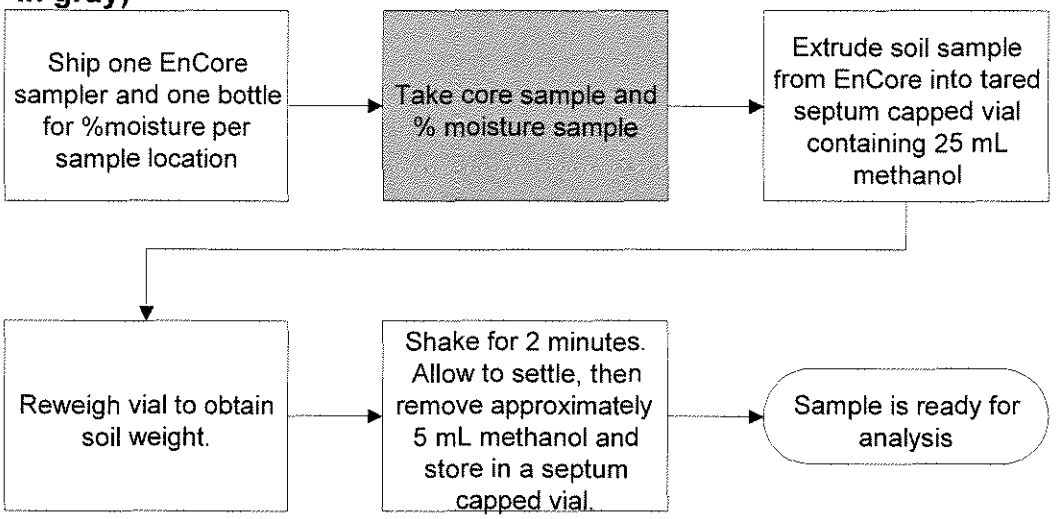
8.8. Aqueous samples are stored in glass containers with Teflon lined septa at 4°C +/- 2°C, with minimum headspace.

8.9. Medium level solid extracts are aliquoted into 2 - 5 mL glass vials with Teflon lined caps and stored at 4°C +/- 2°C. The extracts are stored with minimum headspace.

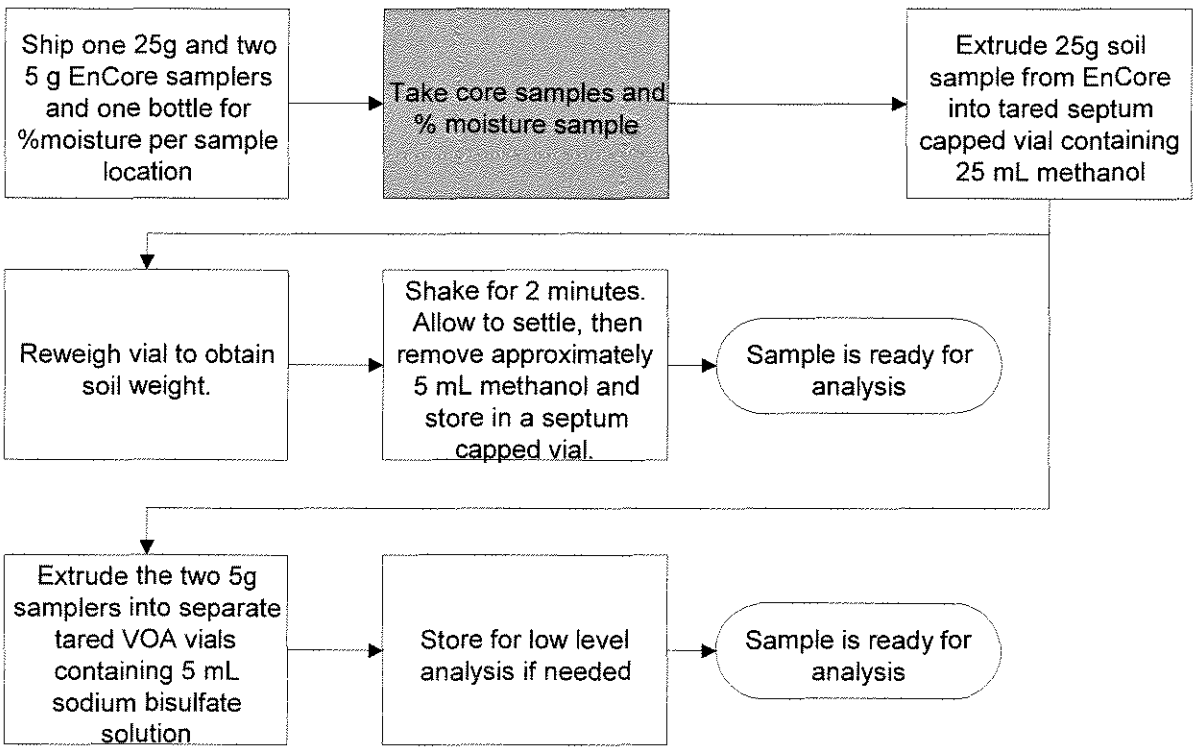
8.10. The maximum holding time is 14 days from sampling until the sample is analyzed. (Samples that are found to be unpreserved still have a 14 day holding time. However they should be analyzed as soon as possible. The lack of preservation should be addressed in the case narrative). Maximum holding time for the EnCore sampler (before the sample is added to methanol or sodium bisulfate) is 48 hours.

8.11. A holding blank is stored with the samples. This is analyzed and replaced if any of the trip blanks show any contamination. Otherwise it is replaced every 14 days.

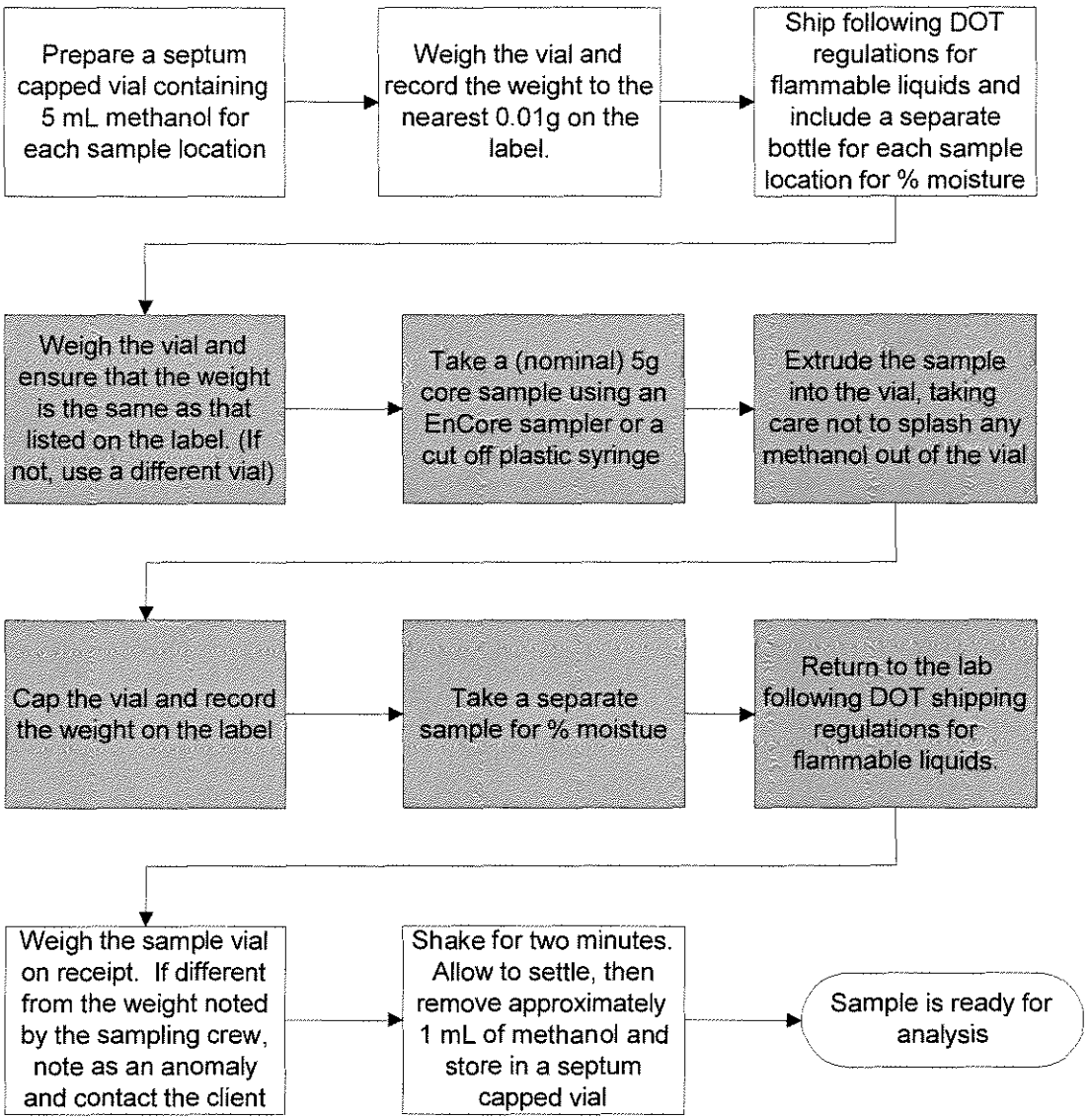
EnCore procedure when low level is not required (field steps in gray)



EnCore procedure when low level is required



Field methanol extraction procedure (field steps in gray)



9. QUALITY CONTROL

9.1. Refer to the method 8000B section of this SOP, section 9, for general quality control procedures, including batch definition, requirements for method blanks, LCS, matrix spikes, surrogates, and control limits.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to the method 8000B section of this SOP, section 10, for general calibration procedures.

10.2. Gas Chromatograph Operating Conditions

Various column configurations are possible. If dual column confirmation is necessary, the sample may be split using a Y splitter at the injector end to direct the sample to two columns and two detectors. For simultaneous determination of aromatic and halogenated volatiles, a single column is used and the PID and ELCD detectors are connected in series.

10.2.1. Refer to Table A-2, A-3 and A-4 for GC operating conditions.

10.3. Initial Calibration

10.3.1. Refer to Section 10 of the 8000B section of this SOP for details of initial calibration criteria.

10.3.2. Low level soil samples must be purged at 40°C, therefore the calibration curve must also be purged at 40°C. In addition, the low level soil calibration solutions should contain approximately the same amount of sodium bisulfate as the samples.

10.3.3. The low level calibration must be at the reporting limit or below. The remaining standards encompass the working range of the detector.

10.3.4. Calibrate the instrument using the same volume that will be used during sample analysis.

10.4. Calibration Verification

10.4.1. A mid level calibration standard is used for the calibration verification. The gases have 20 % D criteria rather than the 15% used for other analytes.

10.4.2. A calibration verification run is performed after every 10 samples for this method.

10.4.3. Bracketing of samples with calibration verification runs is only necessary for external standard analysis.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a 12 hour calibration that meets % difference criteria from an existing initial calibration.

11.3. Confirmation

The PID and ELCD detectors are sufficiently selective that second column confirmation is not always necessary. Requirements for second column confirmation should be decided in consultation with the

client. If the PID and ELCD are used in series confirmatory information for many analytes can be gained by comparing the relative response from the two detectors.

11.4. Aqueous Sample Analysis (Purge and Trap units using sparge vessels)

11.4.1. Depending on the sensitivity of the instrument and capabilities of the purge and trap device, 5, 10, 20, or 25 mL sample volumes may be analyzed. A 5 mL sample volume is recommended.

11.4.2. Rinse a 5 mL (or 25 mL for larger sample volumes) gas-tight syringe with organic free water. Fill the syringe with the sample to be analyzed, and compress to volume.

11.4.3. Check and document the pH of the sample remaining in the VOA vial after loading the syringe.

11.4.4. This procedure invalidates the contents of the VOA vial for further analysis, unless an aliquot is transferred to a smaller VOA vial with no headspace (e.g., 20 mL) at the same time the analysis aliquot is removed.

11.4.5. Spike with the appropriate volume of surrogate/internal standard solution and spike solution (if required) through the barrel of the syringe. The method blank is spiked with surrogates only, the LCS and matrix spikes with the surrogate and matrix spiking solutions. Refer to Tables A-5 and A-6 for volumes and concentrations of spiking solutions.

11.4.6. Load onto the purge and trap device and start the run.

11.4.7. If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample has a high response for a compound, analysis should be followed by an organic free water blank. It is recognized that during automated unattended analysis, this may not occur. If any potential carryover hits are present in samples following highly contaminated samples, the sample must be reanalyzed to determine if any of these hits are a result of carryover or are actually present in the sample.

11.4.8. Dilutions may be made in gas tight syringes unless the volume of sample used is less than 5 µL, in which case dilution in volumetric flasks will be necessary.

11.4.8.1. Spike with the same volume of surrogate/internal standard solution as used for undiluted samples prior to loading onto the purge and trap device.

11.4.8.2. For Matrix spike / matrix spike duplicates where the sample requires dilution, the sample is spiked <u>after</u> the dilution is performed.

11.5. Aqueous and Soil Sample Analysis (Purge and Trap units that sample directly from the VOA vial)

11.5.1. Units which sample from the VOA vial should be equipped with a module which automatically adds surrogate and internal standard solution to the sample prior to purging the sample.

11.5.2. If the autosampler uses automatic IS/SS injection, no further preparation of the VOA vial is needed. Otherwise the internal and surrogate standards must be added to the vial. *Note:* Aqueous samples with high amounts of sediment present in the vial may not be suitable for analysis on this instrumentation, or they may need to analyzed as soils.

11.5.3. Sample remaining in the vial after sampling with one of these mechanisms is no longer valid for further analysis. A fresh VOA vial must be used for further sample analysis.

11.5.4. Check the pH of the sample remaining in the VOA vial after analysis is completed.

11.6. Low-Level Solids Analysis using discrete autosamplers

Note: This technique may seriously underestimate analyte concentration and must not be used except at specific client request for the purpose of comparability with previous data. It is no longer part of SW-846.

This method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples (e.g., heated). The calibration curve is also heated during analysis. Purge temperature is 40°C.

11.6.1. Do not discard any supernatant liquids. Mix the contents of the container with a narrow metal spatula.

11.6.2. Weigh out 5 g (or other appropriate aliquot) of sample into a disposable culture tube or other purge vessel. Record the weight to the nearest 0.1 g. If method sensitivity is demonstrated, a smaller aliquot may be used. Do not use aliquots less than 1.0 g. If the sample is contaminated with analytes such that a purge amount less than 1.0 g is appropriate, use the medium level method described in section 11.7.

11.6.3. Connect the purge vessel to the purge and trap device.

11.6.4. Rinse a 5 mL gas-tight syringe with organic free water, and fill. Compress to 5 mL. Add surrogate/internal standard (and matrix spike solutions if required.) (See Tables A-5, A-6, A-7 and A-8.) Add directly to the sample from 11.6.2.

11.6.5. The above steps should be performed rapidly and without interruption to avoid loss of volatile organics.

11.6.6. Add the heater jacket or other heating device and start the purge and trap unit.

11.6.7. Soil samples that have low IS recovery when analyzed (<50%) should be reanalyzed once to confirm matrix effect. If external standard calibration is used, samples with surrogate recovery below the control limit should be reanalyzed once to confirm matrix effect.

11.7. Methanol Extract Soils

11.7.1. Rinse a gas-tight syringe with organic free water. Fill the syringe with the same volume of organic free water as used in the calibrations. Add no more than 2% (v/v) (100 µL for a 5 mL purge) methanolic extract (from Section 8.5 or 8.6) to the syringe. Add internal standard (if used). Load the sample onto the purge and trap device and analyze as for aqueous samples. If less than 5µL of methanolic extract is to be added to the water, dilute the methanolic extract such that a volume greater than 5µL will be added to the water in the syringe.

12. DATA ANALYSIS AND CALCULATIONS

Refer to section 12 of the 8000B section of this SOP.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the 8000B section of this SOP are 70-130%, with %RSD $\leq$ 25% The spiking level should be 20 µg/L. These limits are for guidance, and certain "difficult" analytes may fall outside this range. Any outliers must be discussed with Quanterra's ® Director of Quality Assurance and/or Director of Technology before proceeding with sample analysis.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will 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, SW846, 3rd Edition, Final Update III, December 1996, Sections 5000, 5030B, 5035 and 8021B

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.2. Modifications from previous revision

17.2.1. No revisions were made to this appendix.

17.3. Facility Specific SOPs

Each facility shall attach a list of facility specific SOPs or approved attachments (if applicable) which are required to implement this SOP or which are used in conjunction with this SOP. If no facility specific SOPs or amendments are to be attached, a statement must be attached specifying that there are none.

17.4. Tables

Table A-1					
Standard Analyte List					
Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
Halogenated volatiles by 8021B	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chloroethane	70-00-3	1.0	1.0	50
	2-Chloroethyl vinyl ether	110-75-8	5.0	5.0	250
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	Dibromochloromethane	124-48-1	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-45-4	1.0	1.0	50
	cis-1,2 Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50
	Dichloromethane(DCM)	75-09-2	5.0	5.0	250
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
Additional halogenated volatiles	Benzyl Chloride	100-44-7	5.0	5.0	250
	Bromobenzene	108-86-1	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
BTEX by 8021B	Benzene	71-43-2	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50

Table A-1

Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	Chlorobenzene	108-90-7	1.0	1.0	50
	1,2-Dichlorobenzene	75-34-3	1.0	1.0	50
	1,3-Dichlorobenzene	107-06-2	1.0	1.0	50
	1,4-Dichlorobenzene	75-45-4	1.0	1.0	50
	Ethyl Benzene	100-41-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50
Additional aromatic and unsaturated volatiles	1,2,4 Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5 Trimethylbenzene	108-67-8	1.0	1.0	50
	Acetone	67-64-1	10	10	500
	MEK (2-butanone)	78-93-3	5.0	5.0	250
	MIBK (4-methyl-2-pentanone)	108-10-1	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	Styrene	100-42-5	1.0	1.0	50
	Methyl tert-butyl ether (MTBE)	1634-04-4	1.0	1.0	50
Combined halogenated and aromatic volatiles by 8021B	Benzene	71-43-2	1.0	1.0	50
	Bromobenzene	108-86-1	1.0	1.0	50
	Bromochloromethane	74-97-5	1.0	1.0	50
	Bromodichloromethane	75-27-4	1.0	1.0	50
	Bromoform	75-25-2	1.0	1.0	50
	Bromomethane	74-83-9	1.0	1.0	50
	n-butylbenzene	104-51-8	1.0	1.0	50
	sec-Butylbenzene	135-98-8	1.0	1.0	50
	tert-Butylbenzene	98-06-6	1.0	1.0	50
	Carbon Tetrachloride	56-23-5	1.0	1.0	50
	Chlorobenzene	108-90-7	1.0	1.0	50
	Chlorodibromomethane	124-48-1	1.0	1.0	50
	Chloroethane	75-00-3	1.0	1.0	50
	Chloroform	67-66-3	1.0	1.0	50
	Chloromethane	74-87-3	1.0	1.0	50
	2-Chlorotoluene	95-49-8	1.0	1.0	50
	4-Chlorotoluene	106-43-4	1.0	1.0	50
	1,2-Dibromo-3-Chloropropane(DBCP)	96-12-8	1.0	1.0	50
	1,2-Dibromoethane(EDB)	106-93-4	1.0	1.0	50
	Dibromomethane	74-95-3	1.0	1.0	50
	1,2-Dichlorobenzene	95-50-1	1.0	1.0	50
	1,3-Dichlorobenzene	541-73-1	1.0	1.0	50
	1,4-Dichlorobenzene	106-46-7	1.0	1.0	50
	Dichlorodifluoromethane	75-71-8	1.0	1.0	50
	1,1-Dichloroethane	75-34-3	1.0	1.0	50
	1,2-Dichloroethane	107-06-2	1.0	1.0	50
	1,1-Dichloroethene	75-35-4	1.0	1.0	50
	cis-1,2-Dichloroethene	156-59-4	1.0	1.0	50
	trans-1,2-Dichloroethene	156-60-5	1.0	1.0	50

Table A-1
Standard Analyte List

Test	Compound	CAS number	Reporting Limit, µg/L or µg/kg		
			Aqueous	Low Soil	Medium Soil
	1,2-Dichloropropane	78-87-5	1.0	1.0	50
	1,3-Dichloropropane	142-28-9	1.0	1.0	50
	2,2-Dichloropropane	590-20-7	1.0	1.0	50
	1,1-Dichloropropene	563-58-6	1.0	1.0	50
	cis-1,3-Dichloropropene	10061-01-5	1.0	1.0	50
	trans-1,3-Dichloropropene	10061-02-6	1.0	1.0	50
	Ethylbenzene	100-41-4	1.0	1.0	50
	Hexachlorobutadiene	87-68-3	1.0	1.0	50
	Isopropylbenzene	98-82-8	1.0	1.0	50
	p-Isopropyltoluene	99-87-6	1.0	1.0	50
	Methylene Chloride	75-09-2	5.0	5.0	250
	Naphthalene	91-20-3	2.0	2.0	250
	n-Propylbenzene	10306501	1.0	1.0	50
	Styrene	100-42-5	1.0	1.0	50
	1,1,1,2-Tetrachloroethane	630-20-6	1.0	1.0	50
	1,1,2,2-Tetrachloroethane	79-34-5	1.0	1.0	50
	Tetrachloroethene	127-18-4	1.0	1.0	50
	Toluene	108-88-3	1.0	1.0	50
	1,2,3-Trichlorobenzene	87-61-6	1.0	1.0	50
	1,2,4-Trichlorobenzene	120-82-1	1.0	1.0	50
	1,1,1-Trichloroethane	71-55-6	1.0	1.0	50
	1,1,2-Trichloroethane	79-00-5	1.0	1.0	50
	Trichloroethene	79-01-6	1.0	1.0	50
	Trichlorofluoromethane	75-69-4	1.0	1.0	50
	1,2,3-Trichloropropane	96-18-4	1.0	1.0	50
	1,2,4-Trimethylbenzene	95-63-6	1.0	1.0	50
	1,3,5-Trimethylbenzene	108-67-8	1.0	1.0	50
	Vinyl Chloride	75-01-4	1.0	1.0	50
	Xylenes (total)	1330-20-7	1.0	1.0	50

Table A-2
Recommended Conditions for Aromatic Volatiles

Parameter	**Recommended Conditions**
Temperature program	50°C, 1min, 10°C/min to 200°C,1min
Column 1	Rtx-502.2 or DB-502.2 60m x 0.53mm 3.0um
Column 2	Rtx-1 or DB-1 60m x 0.53mm 3.0 um
Carrier gas	Helium or hydrogen
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-3
Recommended Conditions for Method Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4 °C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-4
Recommended Conditions for Method Combined Aromatic and Halogenated Volatiles

Parameter	Recommended Conditions
Temperature program	35°C, 12 min, then 4 °C/min to 200°C, hold for 5 min
Column 1	DB-VRX or RTX-502.2 105m x 0.53 mm id df = 3.0um
Column 2	DB-1 or RTX-1 105m x 0.53 mm ID df = 3.0um
Column 3	Rtx - Volatiles 120m x 0.53mm ID df=2.0um
Carrier gas	Helium
Purge Flow / time	40 mL/min, 11 minutes
Desorb Temp / time	180°C, 2 minutes (220°C for Vocarb 3000)
Bake Time / temp	200°C, 12 minutes (230°C for Vocarb 3000)
Transfer line / valve temp	115°C

Table A-5
Surrogate and Internal Standard Concentrations

Standard	Components	Working Solution µg/mL	Spike amount µL (for 5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic volatiles IS/SS	4-Chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Halogenated volatiles IS/SS	4-chlorotoluene (SS) 1-Chloro-4-fluorobenzene (IS)	20 40	5	20 40
Combined Aromatic and halogenated volatiles IS/SS	Fluorobenzene (SS)	20	5	20
	1,4-Dichlorobutane (SS)	20	5	20
	1-Chloro-4-fluorobenzene (IS)	40	10	40

It may be necessary to select different surrogates in order to minimize sample interferences. 1-chloro-4-fluorobenzene and 4-chlorotoluene are fairly well resolved from analytes listed in this SOP. However 4-chlorotoluene may sometimes be requested as a target analyte. Other surrogates that may be considered, and issues associated with their use are:

Bromochloromethane: Elutes very close to chloroform and cis-1,2-dichloroethene on the 502.2 column. May be a target analyte.

1,2-Bromochloroethane:

1-Chloro-2-fluorobenzene: Elutes close to ethylbenzene on DB-1 or Rtx-1 and close to m,p-xylene on 502.2

a,a,a-Trifluorotoluene: Good for aromatic volatiles, coelutes or very close to trichloroethene

Bromofluorobenzene: Close to 1,1,2,2-trichloroethane and 1,2,3-trichloropropane on the 502.2 column. Good on DB-1 or Rtx-1.

2-Bromo-1-chloropropane: May coelute with 1,1,2-trichloroethane

Table A-6
Concentrations for LCS and MS/MSD compounds

Standard	Components	Working Solution µg/mL	Spike amount µL (5 mL purge)	Final concentration µg/L (µg/kg)
Aromatic	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
Halogenated	Chlorobenzene	20	5	20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20
Combination aromatic / halogenated	Benzene	20	5	20
	Toluene	20		20
	Chlorobenzene	20		20
	1,1-Dichloroethene	20		20
	Trichloroethene	20		20

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8081A is applied to the analysis of organochlorine pesticides by GC/ECD. This Appendix may also to be applied when discontinued SW-846 Method 8080A is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate Quanterra® sample extraction SOPs. (CORP-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

At client request, this method may also be used for the analysis of PCBs (Arochlors) in combination with pesticides, although these are normally analyzed following method 8082, as described in Appendix C of this SOP. In any event, if samples for PCB analysis do not need the acid clean up procedure, then the same injection may be used for method 8081B and 8082, assuming all calibration and QC requirements for both methods are met. Extracts that have been acid cleaned may not be analyzed for pesticides, since several of the pesticides will be degraded.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of organochlorine pesticides. The pesticides are injected onto the column and separated and detected by electron capture detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001. Use or hexane / acetone as the extraction solvent (rather than hexane / methylene chloride) will reduce the amount of interferences extracted.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

7.4. Column Degradation Evaluation Mix

A mid-level standard containing 4,4'-DDT and Endrin and not containing any of their breakdown products must be prepared for evaluation of degradation of these compounds by the GC column and injection port. This mix must be replaced after one year, or whenever corrective action to columns fails to eliminate the breakdown of the compounds, whichever is shorter. This solution also contains the surrogates. Refer to Table B-4 for details of the column degradation evaluation mix.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both columns. Closely eluting pairs are DDE and Dieldrin on the Rtx-5 or DB-5 column and Endosulfan II and DDD on the 1701 column.

10.3. Column Degradation Evaluation

Before any calibration runs, either initial or 12 hour, The column evaluation mix must be injected before each initial or daily calibration. The degradation of DDT and endrin must be calculated (see equations 9 and 10) and each shown to be less than 15% before calibration can proceed. This is only necessary if the target compound list includes DDT, Endrin, or any of their degradation products.

If the breakdown of DDT and/or endrin exceeds the limits given above, corrective action must be taken. This action may include:

- Replacement of the injection port liner or the glass wool.
- Cutting off a portion of the injection end of a capillary column.
- Replacing the GC column.

10.4. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.4.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.4.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4.3. The surrogate calibration curve is calculated from the Individual AB mix. Surrogates in the other calibration standards are used only as retention time markers. If there are resolution problems, then the A and B mixes may be analyzed separately.

10.4.4. For multi-component pesticides:

Single point calibration is used for multicomponent pesticides (typically toxaphene and technical chlordane). Two options are possible; the same quantitation option must be used for standards and samples. Refer to section 12.3 for guidance on which option to use.

10.4.5. For multicomponent analytes, the mid level standard must be analyzed as part of the initial calibration. This single point calibration is used to quantitate multicomponent analytes.

10.4.6. The analyst may include a full 5 point calibration for any of the multicomponent analytes with the initial calibration.

10.5. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.5.1. At a minimum, the 12 hour calibration includes analysis of the breakdown mix followed by mid level standards of any single and multicomponent analytes.

10.5.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.6. Continuing Calibration

The AB calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. The continuing calibration standard need not include multicomponent analytes. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.6.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Identification of Multicomponent Analytes

Retention time windows are also used for identification of multi-component analytes, but the "fingerprint" produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.3. Quantitation of Multicomponent Analytes

Use 3-10 major peaks or total area for quantitation as described in section 10.4.4, initial calibration of multicomponent analytes.

12.3.1. If there are no interfering peaks within the envelope of the multicomponent analyte, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.3.1.1. Multiple peak option

This option is particularly valuable if toxaphene is identified but interferences make quantitation based on total area difficult. Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per multi-peak pesticide, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

Chlordane may be quantitated either using the multiple peak option (12.3.1.1) total area option (12.3.1.2.) or by quantitation of the major components, α-chlordane, γ-chlordane and heptachlor.

12.3.1.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option

should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

12.4. Second column confirmation multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

12.6. Calculation of Column Degradation/% Breakdown (%B)

$$DDT\ \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100$$

where:
A_{DDD}, A_{DDE}, and A_{DDT} = the response of the peaks for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT in the column degradation evaluation mix.

$$Endrin\ \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100$$

where:
A_{EK}, A_{EA}, and A_E = the response of endrin ketone, endrin aldehyde, and endrin in the column degradation evaluation mix.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-7. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will 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

SW846, Update III, December 1996, Method 8081A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	waste
Aldrin	0.05	1.7	50
α-BHC	0.05	1.7	50
β-BHC	0.05	1.7	50
δ-BHC	0.05	1.7	50
γ-BHC (Lindane)	0.05	1.7	50
α-Chlordane	0.05	1.7	50
γ-Chlordane	0.05	1.7	50
Chlordane (technical)	0.5	17	500
4,4'-DDD	0.05	1.7	50
4,4'-DDE	0.05	1.7	50
4,4'-DDT	0.05	1.7	50
Dieldrin	0.05	1.7	50
Endosulfan I	0.05	1.7	50
Endosulfan II	0.05	1.7	50
Endosulfan Sulfate	0.05	1.7	50
Endrin	0.05	1.7	50
Endrin Aldehyde	0.05	1.7	50
Heptachlor	0.05	1.7	50
Heptachlor Epoxide	0.05	1.7	50
Methoxychlor	0.1	3.3	100
Toxaphene	2.0	67	2000
APPENDIX IX ADD ONs			
Diallate	1.0	33	1000
Isodrin	0.1	3.3	100
Chlorobenzillate	0.1	3.3	100
Kepone[1]	1.0	33	1000

[1] Kepone is sometimes requested for analysis by method 8081A. However kepone may produce peaks with broad tails that elute later than the standard by up to a minute (presumably due to hemi-acetal formation). As a result kepone analysis by 8081A is unreliable and not recommended. Analysis by method 8270C is a possible alternative.

Note: alpha chlordane, gamma chlordane, and endrin ketone are not required for some projects.

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	120°C for 1 min, 8.5°C/min to 285°C, , 6 min hold
Column 1	Rtx-CLPesticides 30m x 0.32mm id, 0.5µm
Column 2	Rtx-35 30m x 0.32 mm id, 0.5µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[2]
Individual Mix AB[1]						
Aldrin	5	10	25	50	100	200
g-BHC (Lindane)	5	10	25	50	100	200
Heptachlor	5	10	25	50	100	200
Methoxychlor	10	20	50	100	200	400
Dieldrin	5	10	25	50	100	200
Endosulfan I	5	10	25	50	100	200
Endosulfan II	5	10	25	50	100	200
4,4'-DDT	5	10	25	50	100	200
Endrin Aldehyde	5	10	25	50	100	200
Endrin Ketone	5	10	25	50	100	200
β-BHC	5	10	25	50	100	200
δ-BHC	5	10	25	50	100	200
α-BHC	5	10	25	50	100	200
4,4'-DDD	5	10	25	50	100	200
4,4'-DDE	5	10	25	50	100	200
Endosulfan Sulfate	5	10	25	50	100	200
Endrin	5	10	25	50	100	200
α-Chlordane [3]	5	10	25	50	100	200
γ-Chlordane [3]	5	10	25	50	100	200
Multicomponent Standards						
Chlordane (Technical)			250[4]			
Toxaphene			1000[5]			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Standards may be split into an A and B mix if resolution of all compounds on both columns is not obtained.

[2] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

[3] Compounds may be used in lieu of running a daily technical Chlordane standard for samples that are non-detect for technical Chlordane.

[4] This standard may be used for quantitation of technical chlordane between 50 and 1000 ng/mL. If the chlordane is more concentrated, the extract must be diluted and reanalyzed.

[5] This standard may be used for quantitation of toxaphene between 200 and 4000 ng/mL. If the toxaphene is more concentrated, the extract must be diluted and reanalyzed.

Table B-4	
Column Degradation Evaluation Mix ng/mL	
Component	Concentration
4,4'-DDT	25
Endrin	25
Tetrachloro-m-xylene (Surrogate)	20
Decachlorobiphenyl (Surrogate)	20

Table B-5			
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg			
	Aqueous	Soil	Waste
gamma BHC (Lindane)	0.20	6.67	200
Aldrin	0.20	6.67	200
Heptachlor	0.20	6.67	200
Dieldrin	0.50	16.7	500
Endrin	0.50	16.7	500
4,4DDT	0.50	16.7	500
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table B-6		
LCS/Matrix Spike and Surrogate Spike levels for TCLP µg/L or µg/kg		
	Aqueous	Waste
Heptachlor	5	500
Heptachlor epoxide	5	500
Lindane	5	500
Endrin	5	500
Methoxychlor	10	1000

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)	
Breakdown Mix	
Individual mix AB	All levels
Technical Chlordane	Level 3[1]
Toxaphene	Level 3[1]
Solvent blank	
Up to 20 samples unless 12 hours comes first)	
Solvent blank (optional)	
Individual mix AB	Mid level (Continuing calibration)
Samples	
After 12 hours:	
Breakdown mix	
Individual mix AB	
Any other single component analytes	
Any multicomponent analytes	

[1] A five point curve for any of the multicomponent analytes may be included
If Arochlors are included, a 5 point calibration for Arochlor 1016/1260 should be included with the initial calibration and a single point for the other Arochlors. The mid point 1016/1260 mix is included with the daily calibration (every 12 hours).

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB, and the breakdown mix must be run before the continuing calibration.

Table B-8

Performance limits, four replicate initial demonstration of capability

Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
Aldrin	46-112	21
alpha-BHC	51-122	24
beta-BHC	61-120	32
delta-BHC	49.5-118.5	36
gamma-BHC	57-116	23
Chlordane	44.8-108.6	20
4,4'-DDD	52-126	28
4,4'-DDE	46-120	27.5
4,4'-DDT	54-137	36
Dieldrin	42.5-124.5	38
Endosulfan I	43-141	24.5
Endosulfan II	78-171	61
Endosulfan Sulfate	62-132	27
Endrin	49-126	37
Heptachlor	57-100	20
Heptachlor Epoxide	43.5-131.5	25.4
Toxaphene	44.4-111.2	20

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8000B is applied to the analysis of polychlorinated biphenyls (PCB) by GC/ECD. This Appendix is to be applied when SW-846 Method 8082 is requested, and is applicable to extracts derived from any matrix which are prepared according to the appropriate Quanterra® sample extraction SOPs. (CORP-OP-0001). The PCBs are determined and quantitated as Arochlor mixes.

Table C-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

Note: SW-846 method 8082 provides incomplete guidance for determination of individual PCB congeners. This SOP does not include directions for congener specific analysis.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of PCBs. The PCBs are injected onto the column and separated and detected by electron capture detection. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups may be performed on the sample extracts, including florisil cleanup (Method 3620), Gel Permeation Chromatography (Method 3640), and Sulfur cleanup (Method 3660). These cleanup procedures are included in SOP # CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2. Aroclors have been classified as a potential carcinogen under OSHA. Concentrated solutions of Aroclors must be handled with extreme care to avoid excess exposure. Contaminated gloves and clothing must be removed immediately. Contaminated skin surfaces must be washed thoroughly.

5.3. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the manufacturer's general radioactive material license.

5.4. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Director, EH&S shall be immediately notified and a letter sent to the NRC or local state agency.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A ^{63}Ni electron capture detector is required.

6.2. Refer to Table C-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies. All standards for this method must be replaced

7.2. Refer to Table C-3 for details of calibration standards.

7.3. Surrogate Standards

Tetrachloro-m-xylene and decachlorobiphenyl are the surrogate standards. Other surrogates may be used at client request. Refer to Table C-4 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Initial Calibration

10.2.1. Refer to Table C-5 for the initial calibration analytical sequence.

10.2.2. The response for each Arochlor will be calculated by the procedures described in the general method for GC analysis, with the following modifications.

10.2.3. A five point calibration of the Arochlor 1016/1260 mix is generated with at least mid level single points for the other Aroclor mixes. The average response factor is used to quantitate Arochlors 1260 and 1016, other Arochlors are quantitated from the mid level single point.

10.2.4. The analyst may include a full 5 point calibration for any of the Arochlors with the initial calibration.

10.2.5. The high and low standards for the initial 5 point calibration of 1016 / 1260 define the acceptable quantitation range for the other Arochlors. If any Arochlor is determined above this concentration the extract must be diluted and reanalyzed.

10.2.6. If the analyst knows that a specific Arochlor is of interest for a particular project, that Arochlor may be used for the five point calibration rather than the 1016 / 1260 mix.

10.2.7. The surrogate calibration curve is calculated from the Aroclor 1016/1260 mix. Surrogates in the other calibration standards are used only as retention time markers.

10.2.8. Two options are possible for quantitation of Aroclors. The same quantitation option must be used for standards and samples.

10.2.8.1. Multiple peak option

Select 3-10 major peaks in the analyte pattern. Calculate the response using the total area or total height of these peaks. Alternatively, find the response of each of the 3-10 peaks per Aroclor, and use these responses independently, averaging the resultant concentrations found in samples for a final concentration result. When using this option, it is appropriate to remove peaks that appear to be coeluting with contaminant peaks from the quantitation. (i.e. peaks which are significantly larger than would be expected from the rest of the pattern.)

10.2.8.2. Total area option

The total area of the standards and samples may be used for quantitation of multicomponent analytes. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area. This option should not be used if there are significant interference peaks within the multicomponent pattern in the samples. The retention time window for total area measurement must contain at least 90% of the area of the analyte.

10.3. 12 hour Calibration

The 12 hour calibration verification must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration.

10.3.1. At a minimum, the 12 hour calibration includes analysis of the Arochlor 1260 / 1016 mix.

10.3.2. It is adequate to verify calibration with a mixture of Aroclors 1016 and 1260. If a specific Aroclor is expected, it should be included in the daily calibration check.

10.3.3. The retention time windows for any analytes included in the daily calibration are updated.

10.3.4. For this method samples must be bracketed with successful calibration verification runs.

10.4. Calibration verification

The Arochlor 1260/1016 calibration mix is analyzed as the calibration verification standard. This is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. (Depending on the type of samples, it may be advisable to analyze verifications more frequently in order to minimize reruns.).

10.4.1. A mid level standard is used for the calibration verification.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

Cleanup procedures are described in SOP No. CORP-OP-0001.

11.4. Suggested gas chromatographic conditions are given in Table C-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table C-5.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Identification of Arochlors

Retention time windows are used for identification of Arochlors, but the "fingerprint" produced by major peaks of those analytes in the standard is used in tandem with the retention times for identification. The ratios of the areas of the major peaks are also taken into consideration. Identification may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst's judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

A clearly identifiable Arochlor pattern serves as confirmation of single column GC analysis. However, if the pattern is not clear, or if no historical data for the site is available, then second column confirmation must be performed.

12.2. Quantitation of Arochlors

Use 3-10 major peaks or total area for quantitation

If the analyst believes that a combination of Aroclor 1254 and 1260, or a combination of 1242, 1248 and 1232 is present, then only the predominant Arochlor is quantitated and reported, but the suspicion of multiple Aroclors is discussed in the narrative. If well separated Aroclor patterns are present, then both Aroclors are quantitated and reported.

12.3. If there are no interfering peaks within the envelope of the Arochlor, the total area of the standards and samples may be used for quantitation. Any surrogate or extraneous peaks within the envelope must be subtracted from the total area.

12.4. Second column confirmation of Aroclors will only be performed when requested by the client, or if the pattern is not clear or there is no historical data leading to a suspicion that Arochlors may be present. The appearance of the multiple peaks in the sample usually serves as a confirmation of Aroclor presence.

12.5. Surrogate recovery results are calculated and reported for decachlorobiphenyl (DCB) unless it is determined that sample interference has adversely affected the quantitation of that surrogate. Tetrachloro-m-xylene (TCMX) recovery is reported in lieu of DCB in samples having the interference, and also may be used in samples in which DCB recovery is low. Corrective action is only necessary if DCB and TCMX are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are recovery of 70-130%. The spiking level should be equivalent to a mid level calibration.

13.2. Method detection limits (MDL) are determined for Arochlor 1016 and 1260. Arochlor 1016 represents an Arochlor consisting primarily of low chlorinated congeners while Arochlor 1260

represents an Arochlor consisting primarily of high chlorinated congeners. The same reporting limit is applied to all Arochlors, and must be supported by both MDLs.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will 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

SW846, Update III, December 1996, Method 8082

17. MISCELLANEOUS

17.1. Modifications from Reference Method

17.1.1. Method 8082 includes limited direction for congener specific quantitation. This is outside the scope of this SOP.

17.2. Modifications from Previous Revisions

No changes were made to this Appendix

17.3. Tables

Table C-1 Standard Analyte list and Reporting Limits			
	Reporting Limit, µg/L or µg/kg		
Compound	water	soil	waste
Aroclor-1016	1.0	33	1000
Aroclor-1221	1.0	33	1000
Aroclor-1232	1.0	33	1000
Aroclor 1242	1.0	33	1000
Aroclor-1248	1.0	33	1000
Aroclor-1254	1.0	33	1000
Aroclor-1260	1.0	33	1000

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.
Ground water	1000 mL	10 mL
Low-level Soil	30 g	10 mL
High-level soil / waste	1 g	10 mL

Table C-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	325°C
Temperature program	70°C for 0.5min, 30°C/min to 190°C, 2.5°C/min to 225, 18°C/min to 280°C, 3 min hold
Column 1	DB-5 or Rtx-5 30m x 0.32mm id, 0.5µm
Column 2	DB-1701 or Rtx 1701 30m x 0.32 mm id, 0.25µm
Column 3	DB-608, 30m X 0.32 mm, 0.25µm
Injection	1-2µL
Carrier gas	Helium or Hydrogen
Make up gas	Nitrogen
Y splitter	Restek or J&W or Supelco glass tee

Table C-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6[1]
Aroclor 1016/1260	100	200	500	1000	2000	4000
Aroclor 1242[2]			500			
Aroclor 1221 +1254[2]			500			
Aroclor 1232[2]			500			
Aroclor 1248[2]			500			
Surrogates are included with all the calibration mixes at the following levels:						
Tetrachloro-m-xylene	5	10	25	50	100	200
Decachlorobiphenyl	5	10	25	50	100	200

[1] Level 6 is optional and should only be used if linearity can be maintained on the instrument to this level.

[2] Aroclors may be quantitated within the range 100 to 2000 ng/mL (4000ng/mL if the level 6 1016/1260 standard is included). If the Aroclor is more concentrated, it must be reanalyzed at a dilution.

Table C-4			
LCS/Matrix Spike and Surrogate Spike levels for Aroclor analysis with Acid Cleanup µg/L or µg/kg			
	Aqueous	Soil	Waste
Aroclor 1016/1260	10	333	10,000
Tetrachloro-m-xylene (Surrogate)	0.20	6.67	200
Decachlorobiphenyl (Surrogate)	0.20	6.67	200

Table C-5
Suggested Analytical Sequence

Initial Calibration

Injection #		
1	Solvent blank (optional)	
2	Aroclor 1016/1260	Level 1
3	Aroclor 1016/1260	Level 2
4	Aroclor 1016/1260	Level 3
5	Aroclor 1016/1260	Level 4
6	Aroclor 1016/1260	Level 5
7	Aroclor 1232	Level 3
8	Aroclor 1242	Level 3
9	Aroclor 1248	Level 3
10	Aroclor 1221/1254	Level 3
11	Solvent blank	
12-31	Sample 1-20 (or as many samples as can be analyzed in 12 hours	
	Solvent blank (optional)	
32	Aroclor 1016/1260	Level 3

etc

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Aroclor 1260 / 1016 mix. Mid level standards of any other Aroclors expected to be present in the samples are also injected.

1. SCOPE AND APPLICATION

This method is applicable to the gas chromatographic determination of Chlorinated phenoxy acid herbicides in extracts prepared by SOP CORP-OP-0001. The herbicides listed in Table D1 are routinely analyzed. Other chlorinated acids may be analyzed by this method if the quality control criteria in section 9 and the initial demonstration of method performance in section 13 are met.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of phenoxy acid herbicides by gas chromatography. The herbicides, as their methyl esters, are injected onto the column, separated, and detected by electron capture detectors. Quantitation is by the external standard method.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for general information regarding chromatographic interferences.

4.2. Chlorinated acids and phenols cause the most direct interference with this method.

4.3. Sulfur may interfere and may be removed by the procedure described in SOP#CORP-OP-0001.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A Ni_{63} electron capture detector is required.

6.2. Refer to Table D2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to section 7 of the 8000B section of this SOP for general information on reagents and standards.

7.2. Refer to Table D-3 and D-4 for details of calibration and other standards.

8. SAMPLE PREPARATION, PRESERVATION AND STORAGE

Refer to section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

9.1. Refer to Section 9 of the 8000B section of this SOP for quality control requirements, including the initial demonstration of capability, definition of a batch, surrogate limits, method blanks, laboratory control samples (LCS), and matrix spikes (MS).

9.2. Refer to Table D-5 for minimum performance criteria for the initial demonstration of capability.

9.3. Refer to Table D-4 for the components and levels of the LCS and MS mixes.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Calibration standards are made up from the free acids, and then esterified using the same process as for samples (See SOP Corp-OP-0001)

10.3. The low level standard must be at or below the laboratory reporting limit. Other standards are chosen to bracket the expected range of concentrations found in samples, without saturating the detector or leading to excessive carryover.

10.4. Refer to Table D-2, for details of GC operating conditions.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP #CORP-OP-0001.

11.3. Cleanup

The alkaline hydrolysis and subsequent extraction of the basic solution described in the extraction procedure provides an effective cleanup.

11.4. Analytical Sequence

The analytical sequence starts with an initial calibration of at least five points, or a daily calibration that meets % difference criteria from an existing initial calibration.

11.4.1. The daily calibration must be analyzed at least once every 24 hours when samples are being analyzed. If there is a break in the analytical sequence of greater than 12 hours, then a new continuing calibration run must be analyzed before proceeding with the sequence. If more than 24 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a daily calibration.

11.4.2. The daily calibration consists of mid level standards of all analytes of interest. Retention time windows must be updated with the daily calibration.

11.4.3. After every 12 hours a continuing calibration is analyzed. The continuing calibration consists of mid level standards of all analytes of interest. Retention time windows are updated with continuing calibrations.

11.5. Gas Chromatography

Chromatographic conditions are listed in Table D-2.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. The herbicides are analyzed as their methyl esters, but reported as the free acid. For this reason it is necessary to correct the results for the molecular weight of the ester versus the free acid. This is

achieved through the concentrations of the calibration standards. For example the 20µg/L calibration standard for 2,4-D contains 21.3 µg/L of the methyl ester. No further correction is necessary.

13. METHOD PERFORMANCE

13.1. Multiple laboratory performance data has not been published by the EPA for this method. Table D-5 lists minimum performance standards required by Quanterra® for the four replicate initial demonstration or capability (required by Section 13.2 of the 8000B part of this SOP) for this method. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

This method does not contain any specific modifications that serve to minimize or prevent pollution.

15. WASTE MANAGEMENT

Waste generated in this procedure will 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

Method 8151A, SW-846, Update III, December 1996

17. MISCELLANEOUS

17.1. Modifications from Reference Method

Refer to the method 8000B section of this SOP for modifications from the reference method.

17.2. Modifications from Previous Revision

The calibration procedure has been changed to require esterification of the calibration standards

17.3. Tables

Table D-1					
Standard Analyte list					
Compound	CAS Number	Reporting Limit, µg/L or µg/kg			
		Aqueous	Soil	Waste	TCLP
2,4-D	94-75-7	4	80	4000	500
2,4-DB	94-82-6	4	80	4000	---
2,4,5-TP (Silvex)	93-72-1	1	20	1000	500
2,4,5-T	93-76-5	1	20	1000	---
Dalapon	75-99-0	2	40	2000	---
Dicamba	1918-00-9	2	40	2000	---
Dichloroprop	120-36-5	4	80	4000	---
Dinoseb	88-85-7	0.6	12	600	---
MCPA	94-74-6	400	8000	400,000	---
MCPP	93-65-2	400	8000	400,000	---

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.	Final Vol.	Dilution Factor
Ground water	1000 mL	10 mL	20
Low-level Soil without GPC	50 g	10 mL	20
High-level soil / waste	1 g	10 mL	20

Specific reporting limits are highly matrix dependent. The reporting limits listed above are provided for guidance only and may not always be achievable. For special projects, the extracts may be analyzed without any dilution, resulting in reporting limits 20 times lower than those in Table D-1.

Table D-2	
Instrumental Conditions	
PARAMETER	Recommended conditions
Injection port temp	220°C
Detector temp	325°C
Temperature program	80,2/30/170,0/1/180,1
Column 1	DB-5MS or RTX 5 30x0.32, 0.5um
Column 2	DB-1701 or Rtx-1701
Injection	1-2µL
Carrier gas	Helium / Hydrogen
Make up gas	Nitrogen

Recommended conditions should result in resolution of all analytes listed in Table D-1.

The reporting limits listed in Table D-1 will be achieved with these calibration levels and a 20 fold dilution of the sample extract. Lower reporting limits can be achieved with lesser dilutions of the sample extract.

Table D-3

LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg[1]

	Aqueous	Soil	Waste	TCLP
2,4-D	16	800	16000	6ug/L ; 120ug/kg
Silvex	4	200	4000	6ug/L ; 120ug/kg
2,4,5-T	4	200	4000	6ug/L ; 120ug/kg
2,4-DB	16	800	16000	---
Dalapon	8	400	8000	---
DCAA (surrogate)	16	800	16000	10ug/L;500ug/kg

[1] LCS, MS and SS spikes are as the free acid.

Table D-4

Performance limits, four replicate initial demonstration of capability

Compound	Initial demonstration, mean recovery limits	Initial demonstration, RSD limits
2,4-D	50-150	25
2,4-DB	50-150	25
2,4,5-TP (Silvex)	50-150	25
2,4,5-T	50-150	25
Dalapon	50-150	25
Dicamba	50-150	25
Dichloroprop	50-150	25
Dinoseb	25-120	40
MCPA	50-150	25
MCPP	50-150	25

PITTSBURGH SPECIFIC APPENDIX FOR THE ANALYSIS OF ORGANOPHOSPHOROUS PESTICIDES BY SW-846 METHOD 8141A

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

1. SCOPE AND APPLICATION

1.1. This SOP Appendix describes procedures to be used when SW-846 Method 8141 is applied to the analysis of organophosphorous pesticides by GC/FPD. This Appendix is applicable to extracts derived from any matrices which are prepared according to the appropriate Quanterra® sample extraction SOPs. (CORP-OP-0001)

1.2. Table B-1 lists compounds which are routinely determined by this method and their associated Reporting Limits (RL) for each matrix. RLs given are based on the low-level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

2.1. This method presents conditions for the analysis of prepared extracts of organophosphorous pesticides. The pesticides are injected onto the column and separated and detected by Flame Photometric detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

3.1. Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the flame photometric detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding sample/reagent contact with plastic materials.

4.3. Sulfur will interfere and can be removed using procedures described in SOP CORP-OP-0001.

4.4. Interferences extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups have not been determined for this method.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. A flame photometric detector is required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Triphenyl phosphate and Tributyl phosphate are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of GC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 using both columns.

10.3. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.3.1. Refer to Table B-7 for the initial calibration analytical sequence.

10.3.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.4.1. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.5. Continuing Calibration

The mid-level calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.5.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

No cleanup procedure has been determined.

11.4. Suggested gas chromatographic conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

12.1. Refer to the 8000B section of this SOP for identification and quantitation of single component analytes.

12.2. Surrogate recovery results are calculated and reported for Triphenyl phosphate and Tributylphosphate. Corrective action is only necessary if Triphenyl phosphate and Tributyl phosphate are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Current laboratory performance limits are listed in Tables B-5a and B-5b. The spiking level should be equivalent to a mid-level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will 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

SW846, Update III, December 1996, Method 8141A

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits

Compound	Reporting Limit, µg/L or µg/kg	
	water	soil
Dimethoate	1	33
Disulfoton	1	33
Famphur	1	33
Methyl parathion	1	33
O,O,O-Triethyl phosphorothioate	1	33
Parathion	1	33
Phorate	1	33
Tetraethyldithiopyrophosphate	1	33
Thionazin	1	33
Azinphos-methyl	1	33
Bolstar	1	33
Chlorpyrifos	1	33
Coumaphos	1	33
Demeton (total)	1	100
Demeton-O	1	33
Demeton-S	1	33
Diazinon	1	33
Dichlorvos	1	33
EPN	1	33
Ethoprop	1	33
Ethyl parathion	1	33
Fensulfothion	1	33
Fenthion	1	33
Malathion	1	33
Merphos	1	33
Mevinphos	1	33
Monocrotophos	1	33
Naled	1	33
Ronnel	1	33
Stirophos	1	33
Sulfotepp	1	33
Tokuthion	1	33
Trichloronate	1	33

Table B-2	
Parameter	**Recommended Conditions**
Injection port temp	220°C
Detector temp	250°C
Temperature program	110C for .5 min, 3.0°C/min to 250°C, , 2.84 min hold
Column 1	DB608 30m x 0.53mm id, 1µm
Column 2	DB1701 30m x 0.53 mm id, 1µm
Injection	2µL
Carrier gas	Helium
Make up gas	Helium

Table B-3					
Calibration Levels ng/mL					
	Level 1	Level 2	Level 3	Level 4	Level 5
Dimethoate	.2	.5	1.0	2.0	4.0
Disulfoton	.2	.5	1.0	2.0	4.0
Famphur	.2	.5	1.0	2.0	4.0
Methyl parathion	.2	.5	1.0	2.0	4.0
O,O,O-Triethyl phosphorothioate	.2	.5	1.0	2.0	4.0
Parathion	.2	.5	1.0	2.0	4.0
Phorate	.2	.5	1.0	2.0	4.0
Tetraethyldithiopyrophosphate	.2	.5	1.0	2.0	4.0
Thionazin	.2	.5	1.0	2.0	4.0
Tributyl phosphate	.2	.5	1.0	2.0	4.0
Triphenyl phosphate	.2	.5	1.0	2.0	4.0
Azinphos-methyl	.2	.5	1.0	2.0	4.0
Bolstar	.2	.5	1.0	2.0	4.0
Chlorpyrifos	.2	.5	1.0	2.0	4.0
Coumaphos	.2	.5	1.0	2.0	4.0
Demeton (total)	.2	.5	1.0	2.0	4.0
Demeton-O	.2	.5	1.0	2.0	4.0
Demeton-S	.2	.5	1.0	2.0	4.0
Diazinon	.2	.5	1.0	2.0	4.0
Dichlorvos	.2	.5	1.0	2.0	4.0
EPN	.2	.5	1.0	2.0	4.0
Ethoprop	.2	.5	1.0	2.0	4.0
Ethyl parathion	.2	.5	1.0	2.0	4.0
Fensulfothion	.2	.5	1.0	2.0	4.0
Fenthion	.2	.5	1.0	2.0	4.0
Malathion	.2	.5	1.0	2.0	4.0
Merphos	.2	.5	1.0	2.0	4.0
Mevinphos	.2	.5	1.0	2.0	4.0
Monocrotophos	.2	.5	1.0	2.0	4.0
Naled	.2	.5	1.0	2.0	4.0
Ronnel	.2	.5	1.0	2.0	4.0
Stirophos	.2	.5	1.0	2.0	4.0
Sulfotepp	.2	.5	1.0	2.0	4.0
Tetraethyl pyrophosphate	.2	.5	1.0	2.0	4.0
Tokuthion	.2	.5	1.0	2.0	4.0
Trichloronate	.2	.5	1.0	2.0	4.0

1 Standards may be split into multiple mixs if resolution of all compounds on both columns is not obtained.
Note: Component mixes of a CCAL should be run sequentially. The ccal evaluation is performed on the sum of the mixes, rather than by mix. Ie. the CCAL = sum of the component mixes.

Table B-5a

Aqueous LCS/Matrix Spike and Surrogate Spike levels µg/L

		LCS		MSD	
Compound	ug/L	LCL	UCL	LCL	UCL
Dimethoate	10	46	153	70	192
Disulfoton	10	17	185	36	130
Famphur	10	14	165	59	131
Methyl parathion	10	36	159	65	157
O,O,O-Triethyl phosphorothioate	10	65	141	60	172
Parathion	10	13	150	65	144
Phorate	10	35	152	54	154
Tetraethyldithiopyrophosphate	10	75	140	51	158
Thionazin	10	69	149	56	136
Tributyl phosphate	10	30	150	30	150
Triphenyl phosphate	10	25	152	25	152

Table B-5b

Soil LCS/Matrix Spike and Surrogate Spike levels µg/mg

		LCS		MSD	
Compound	ug/kg	LCL	UCL	LCL	UCL
Dimethoate	33	65	135	45	170
Disulfoton	33	66	133	26	136
Famphur	33	42	162	31	178
Methyl parathion	33	64	144	56	150
O,O,O-Triethyl phosphorothioate	33	58	131	48	130
Parathion	33	58	141	58	145
Phorate	33	71	135	51	140
Tetraethyldithiopyrophosphate	33	69	144	63	143
Thionazin	33	68	140	64	136
Tributyl phosphate	33	30	150	30	150
Triphenyl phosphate	33	20	151	20	151

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)
Calibration Mix A
Calibration Mix B
Calibration Mix C
Solvent blank
Up to 20 samples unless 12 hours comes first)
Solvent blank (optional)
Individual mix AB Mid level (Continuing calibration)
Samples
After 12 hours:

Calibration Check Mix

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix AB.

Tables B8 & B9 Laboratory Control Limits and Control Compound List (Quanterra Reference Data Summary) See Attachments: current print outs from LIMS system.

PITTSBURGH SPECIFIC APPENDIX FOR THE ANALYSIS OF PAHs by HPLC SW-846 METHOD 8310

Prepared by: _____

Reviewed by: _____
Technology Specialist

Approved by: _____
Quality Assurance Manager

Approved by: _____
Environmental, Health and Safety Coordinator

Approved by: _____
Laboratory Director

1. SCOPE AND APPLICATION

This SOP Appendix describes procedures to be used when SW-846 Method 8310 is applied to the analysis of Polynuclear Aromatic Hydrocarbons by HPLC. This Appendix is applicable to extracts derived from any matrix which are prepared according to the appropriate Quanterra® sample extraction SOPs. (CORP-OP-0001)

Table B-1 lists compounds which are routinely determined by this method and gives the Reporting Limits (RL) for each matrix. RLs given are based on the low level standard and the sample preparation concentration factors. Matrix interferences may result in higher RLs than those listed.

2. SUMMARY OF METHOD

This method presents conditions for the analysis of prepared extracts of Polynuclear Aromatic Hydrocarbons. The extracts are injected onto the column and separated and detected by ultraviolet(UV) and fluorescence detection. Quantitation may be by internal or external standard methods.

3. DEFINITIONS

Refer to the QAMP for definitions of terms used in this document.

4. INTERFERENCES

4.1. Refer to the method 8000B section of this SOP for information regarding chromatographic interferences.

4.2. Interferences in the HPLC analysis arise from many compounds amenable to HPLC that give a measurable response on the UV and fluorescence detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3. Interferences co-extracted from samples will vary considerably from source to source. The presence of interferences may raise quantitation limits for individual samples. Specific cleanups have not been determined for this method.

5. SAFETY

5.1. Refer to section 5 of the Method 8000B SOP for general safety requirements.

5.2.

6. EQUIPMENT AND SUPPLIES

6.1. Refer to Section 6 of the 8000B section of this SOP. UV and fluororescence detectors are required.

6.2. Refer to Table B-2 for analytical columns.

6.3. Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

7. REAGENTS AND STANDARDS

7.1. Refer to the method 8000B section of this SOP for general requirements for reagents and supplies.

7.2. Refer to Table B-3 for details of calibration standards.

7.3. Surrogate Standards

Benzo(e)pyrene and p-terphenyl are the surrogate standards. Refer to tables B-5 and B-6 for details of surrogate standards.

.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

Refer to Section 8 of the 8000B section of this SOP.

9. QUALITY CONTROL

Refer to Section 9 of the 8000B section of this SOP.

10. CALIBRATION AND STANDARDIZATION

10.1. Refer to Section 10 of the 8000B section of this SOP for general calibration requirements.

10.2. Refer to Table B-2 for details of HPLC operating conditions. The conditions listed should result in resolution of all analytes listed in Table B-1 on both detectors.

10.3. Initial Calibration

Refer to Section 10 of the 8000B section of this SOP for details of calibration procedures.

10.3.1. Refer to Table B-8 for the initial calibration analytical sequence.

10.3.2. The response for each single-peak analyte will be calculated by the procedures described in the general method for GC analysis.

10.4. 12 hour Calibration Verification

The 12 hour calibration verification sequence must be analyzed within 12 hours of the start of the initial calibration and at least once every 12 hours thereafter if samples are being analyzed. If more than 12 hours have elapsed since the injection of the last sample in the analytical sequence, a new analytical sequence must be started with a 12 hour calibration. A mid level calibration standard is used for the 12 hour calibration. Refer to the 8000B section of this SOP for acceptance criteria.

10.4.1. .

10.4.2. The retention time windows for any analytes included in the 12 hour calibration are updated.

10.5. Continuing Calibration

The mid-level calibration mix is analyzed as the continuing calibration standard. At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCS, and method blanks. If 12 hours elapse analyze the 12 hour standard sequence instead. If instrument drift is expected due to sample matrix or other factors, it may be advisable to analyze the continuing calibration standard more frequently.

10.5.1. A mid level calibration standard is used for the continuing calibration.

11. PROCEDURE

11.1. Refer to the method 8000B section of this SOP for general procedural requirements.

11.2. Extraction

The extraction procedure is described in SOP No. CORP-OP-0001.

11.3. Cleanup

No cleanup procedure has been determined.

11.4. Suggested HPLC conditions are given in Table B-2.

11.5. Allow extracts to warm to ambient temperature before injection.

11.6. The suggested analytical sequence is given in Table B-8.

12. DATA ANALYSIS AND CALCULATIONS

Both the fluorescence detector and the UV detector are used for qualitative determination and confirmation of the presence of target compounds, however each target compound is quantitated using only one detector. Table B-1 presents the detectors used for quantitating each compound.The MDL studies are performed on both detectors. The highest MDL will be used for reporting "J"-Values. In the instance where there is no detection of any compounds on the UV detector, the Flourescence Detector results will not be submitted.

12.1. Surrogate recovery results are calculated and reported for Benzo(e)pyrene and p-terphenyl. Corrective action is only necessary if Triphenyl phosphate and Tributyl phosphate are both outside of acceptance limits.

13. METHOD PERFORMANCE

13.1. Performance limits for the four replicate initial demonstration of capability required under Section 13.1 of the main body of this SOP are presented in Table B-7. The spiking level should be equivalent to a mid level calibration.

14. POLLUTION PREVENTION

Refer to section 14 of the 8000B section of this SOP.

15. WASTE MANAGEMENT

15.1. Waste generated in this procedure will 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

SW846, Update III, December 1996, Method 8310

17. MISCELLANEOUS

17.1. Modifications from Reference Method

None

17.2. Modifications from Previous Revisions

17.2.1. No revisions were made to this appendix.

17.3. Tables

Table B-1
Standard Analyte list and Reporting Limits and Detectors

Compound	Reporting Limit, µg/L or µg/kg		
	water	soil	Detectors
Carbazole	1.0	33	UV/Flourescence
Naphthalene	1.0	33	UV/Flourescence
Acenaphthene	1.0	33	UV/Flourescence
Acenaphthylene	1.0	33	UV
Anthracene	.2	6.7	UV/Flourescence
Benzo(a)anthracene	.2	6.7	UV/Flourescence
Benzo(b)fluoranthene	.2	6.7	UV/Flourescence
Benzo(k)fluoranthene	.2	6.7	UV/Flourescence
Benzo(g,h,i)perylene	.2	6.7	UV/Flourescence
Benzo(a)pyrene	.2	6.7	UV/Flourescence
Chrysene	.2	6.7	UV/Flourescence
Fluoranthene	.2	6.7	UV/Flourescence
Fluorene	.2	6.7	UV/Flourescence
Indeno(1,2,3-cd)pyrene	.2	6.7	UV/Flourescence
Pyrene	.2	6.7	UV/Flourescence
Phenanthrene	.2	6.7	UV/Flourescence
Dibenzo(a,h)anthracene	.2	6.7	UV/Flourescence
1-methylnaphthalene	1.0	33	UV/Flourescence
2-methylnaphthalene	1.0	33	UV/Flourescence

The following concentration factors are assumed in calculating the Reporting Limits:

	Extraction Vol.		Final Vol.
Ground water	1000 mL	1.0 mL	
Low-level Soil	30 g		1.0 mL
High-level soil / waste	1 g		1.0 mL

Table B-2	
Parameter	**Recommended Conditions**
Mobile phase program	Time 0min:solvent A 50% solvent B 50% flow 1.5 ml/min Time 7min:solvent A 65% solvent B 35% flow 1.5 ml/min Time 10min:solvent A 75% solvent B 25% flow 1.5 ml/min Time 15min:solvent A 85% solvent B 15% flow 1.5 ml/min Time 20min:solvent A 95% solvent B 5% flow 1.5 ml/min
Column 1	Hypersil PAH 150mm x 4.6mm ID
Injection	20µL
Solvent A	CH3CN
Solvent B	H2O

Table B-3						
Calibration Levels ng/mL						
	Level 1	Level 2	Level 3	Level 4	Level 5	
Individual Mix						
Carbazole	1	4	7.5	10	20	
Naphthalene	1	4	7.5	10	20	
Acenaphthene	1	4	7.5	10	20	
Acenaphthylene	1	4	7.5	10	20	
Anthracene	.2	.8	1.5	2	4	
Benzo(a)anthracene	.2	.8	1.5	2	4	
Benzo(b)fluoranthene	.2	.8	1.5	2	4	
Benzo(k)fluoranthene	.2	.8	1.5	2	4	
Benzo(g,h,i)perylene	.2	.8	1.5	2	4	
Benzo(a)pyrene	.2	.8	1.5	2	4	
Chrysene	.2	.8	1.5	2	4	
Fluoranthene	.2	.8	1.5	2	4	
Fluorene	.2	.8	1.5	2	4	
Indeno(1,2,3-cd)pyrene	.2	.8	1.5	2	4	
Pyrene	.2	.8	1.5	2	4	
Phenanthrene	.2	.8	1.5	2	4	
Dibenzo(a,h)anthracene	.2	.8	1.5	2	4	
1-methylnaphthalene	1	4	7.5	10	20	
2-methylnaphthalene	1	4	7.5	10	20	
p-terphenyl	1	4	7.5	10	20	
Benzo(e)pyrene	1	4	7.5	10	20	

Table B-5		
LCS/Matrix Spike and Surrogate Spike levels µg/L or µg/kg		
	Aqueous	Soil
Carbazole	6.25	208
Naphthalene	6.25	208
Acenaphthene	6.25	208
Acenaphthylene	6.25	208
Anthracene	1.25	41.7
Benzo(a)anthracene	1.25	41.7
Benzo(b)fluoranthene	1.25	41.7
Benzo(k)fluoranthene	1.25	41.7
Benzo(g,h,i)perylene	1.25	41.7
Benzo(a)pyrene	1.25	41.7
Chrysene	1.25	41.7
Fluoranthene	1.25	41.7
Fluorene	1.25	41.7
Indeno(1,2,3-cd)pyrene	1.25	41.7
Pyrene	1.25	41.7
Phenanthrene	1.25	41.7
Dibenzo(a,h)anthracene	1.25	41.7
1-methylnaphthalene	6.25	208
2-methylnaphthalene	6.25	208
p-terphenyl	10	333
Benzo(e)pyrene	10	333

Table B-7
Suggested Analytical Sequence

Initial Calibration

Solvent blank (optional)

Individual mix — All levels

Solvent blank
Up to 20 samples unless 12 hours comes first)
Solvent blank (optional)
Individual mix — Mid level (Continuing calibration)
Samples
After 12 hours:

Individual mix [1]

12 hour Calibration

At least every 12 hours, counting from the start of the initial calibration, or from the start of the last daily calibration, the retention time windows must be updated using the Individual mix ..

Tables B8 & B9 Laboratory Control Limits and Control Compound List (Quanterra Reference Data Summary) See Attachements: current print outs from LIMS system.

Table 8

Quanterra Control Limit Summary

Target Analyte List: All Analytes
Method: Hydrocarbons, Polynuclear Aromatic (HPLC - 8310)
Extraction: None specified.

Matrix: WATER
QC Program: STANDARD TEST SET
Location: Quanterra - Pittsburgh

Constituent List	Check List 3041			Spike List 3042		
Constituent	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	37	135	27	20	144	27
Acenaphthylene	42	132	20	22	147	20
Anthracene	60	118	20	29	147	20
Benzo(a)anthracene	62	133	20	57	135	20
Benzo(b)fluoranthene	68	133	50	64	133	20
Benzo(k)fluoranthene	67	122	26	64	122	20
Benzo(ghi)perylene	65	128	20	65	128	20
Benzo(a)pyrene	62	120	25	60	120	20
Chrysene	67	129	33	67	130	20
Dibenzo(a,h)anthracene	65	126	20	65	126	20
Fluoranthene	57	126	25	46	146	20
Fluorene	47	128	20	24	157	20
Indeno(1,2,3-cd)pyrene	71	124	33	52	128	20
Naphthalene	41	128	20	10	153	20
Phenanthrene	46	141	48	33	162	20
Pyrene	56	129	20	44	139	20

Table 9

Quanterra Control Limit Summary

Target Analyte List: All Analytes
Method: Hydrocarbons, Polynuclear Aromatic (HPLC - 8310)
Extraction: None specified.

Matrix: SOLID
QC Program: STANDARD TEST SET
Location: Quanterra - Pittsburgh

Constituent List	Check List 3041			Spike List 3042		
Constituent	**LCL**	**UCL**	**RPD**	**LCL**	**UCL**	**RPD**
Acenaphthene	19	122	27	19	144	27
Acenaphthylene	20	140	20	20	147	20
Anthracene	19	120	20	19	147	20
Benzo(a)anthracene	50	137	20	50	137	20
Benzo(b)fluoranthene	63	134	50	28	162	50
Benzo(k)fluoranthene	63	127	26	43	140	26
Benzo(ghi)perylene	56	134	20	56	134	20
Benzo(a)pyrene	63	121	25	32	126	25
Chrysene	55	135	33	38	128	33
Dibenzo(a,h)anthracene	65	124	20	38	173	28
Fluoranthene	28	141	25	28	114	25
Fluorene	22	134	20	22	157	20
Indeno(1,2,3-cd)pyrene	58	133	33	35	141	33
Naphthalene	15	118	20	10	153	20
Phenanthrene	20	138	48	20	140	48
Pyrene	49	124	20	44	139	20

APPENDIX A-51

STANDARD OPERATING PROCEDURE METHOD 8290 FOR SOLID SAMPLES

Paradigm Analytical Laboratories

Standard Operating Procedure

Method 8290 for Solid Samples

1. Purpose

To describe the procedures followed for the analysis of solid samples by USEPA Method 8290[1,5].

2. Scope & Application

Method 8290 is suitable for the analysis of the seventeen 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and total homologues (tetra- through octachlorinated congeners) in soil, sediment, solid wastes, paper products, pulp, ash, resins, polyurethane foam, wipe and filter. The methodology is based on the use of high-resolution gas chromatography (HRGC) combined with high-resolution mass spectrometry (HRMS) and is capable of achieving sub-parts per trillion detection limits.

3. Summary

Twenty grams (dry equivalent) of the homogenized solid sample are fortified with a known amount of nine carbon-13 labeled PCDD/F congeners (ES = Extraction Standards), extracted by Soxhlet-Dean Stark or by Method 3545 using toluene as the solvent. After the addition of 0.5 mL of purified tridecane, the dried toluene (sodium sulfate) is evaporated under vacuum until no traces of toluene are present. The residue is then fortified with another group of five labeled PCDD/F congeners (CS = Cleanup Standards) and divided into two equal portions. One half of the extract is archived at room temperature while the other half is subjected to a multi-chromatographic columns clean up procedure. The purified extract is transferred inside a 1-mL vial using methylene chloride and concentrated to dryness. The sample is reconstituted into the final extract using 20 µL of a nonane solution containing two additional labeled PCDD congeners (JS = Injection Standards). One µL of the final extract is injected into the injection port of a GC/MS system operating in the high-resolution mode. The GC column is a 60-m DB-5 or HP-5MS capable of 2,3,7,8-TCDD isomer specificity and is used to analyze the tetra- through octachlorinated PCDD/F congeners. The confirmation of 2,3,7,8-TCDF is conducted on a 30-m DB-225 capillary column capable of 2,3,7,8-TCDF isomer specificity. In all cases, the mass spectrometer operates in the high-resolution mode (10,000 resolving power; 5 percent crossing over). The results are reported in pg per gram or parts-per-trillion using the dry weight.

4. Procedure

Figure 1 is a schematic description of the procedures involved for the preparation of the final extract using the Soxhlet-Dean-Stark technique. Figure 2 is the corresponding diagram when Method 3545 is used for the extraction. Key steps are referred to the corresponding SOP. Figure 3 is the schematic for the analysis and reporting phases of the method. Tables 1 and 2 summarize the labeled compounds used throughout this procedure.

4.1 Definitions

- Congener: Any one particular member of the same chemical family (e.g., 135 PCDF congeners).
- Homologue: Group of structurally related chemicals that have the same number of chlorines.
- Isomer: Compounds that belong to the same homologue group (e.g., 22 TCDD isomers).
- Extraction Standards: Group of nine carbon-13 labeled PCDD/F congeners added to the sample before the extraction. The function of the ES is to provide both qualitative (identifying the PCDD/F congeners) and quantitative (determining the concentrations) information on the sample. The measurement of the recoveries of the ES provides information on the extraction and

fractionation efficiencies. Method 8290 call these "Internal Standards", while PAL has decided to adopt a more practical nomenclature.

- Cleanup Standards: A group of five labeled PCDD/F congeners that are added to the sample right after the extraction and before the fractionation. Their function is to measure the fractionation efficiencies independently of the extraction step. They are not required by Method 8290.
- Injection Standards: The two labeled PCDD congeners are added to the final extract just before GC/MS analysis. Their function is to measure the ES and CS recoveries. They are named "Recovery Standards" in Method 8290.
- EMPC: Term used to report the presence of a GC/MS signal that does not meet all the PCDD/F identification criteria. In particular, when the ion-abundance ratio of any unlabeled analyte falls outside the method's acceptable range, the associated peak can not be identified as a PCDD/F congener. PAL will report an Estimated Maximum Possible Concentration (EMPC) for that peak using the same formulae used to calculate the concentration of a detected analyte.

4.2 Equipment/Apparatus

- 12-L giant Soxhlet extractor (Ace Glass) with heat controller (GlasCol) and condenser for purification of supplies.
- Muffle furnace capable of temperatures of at least 500°C (Wilt, Model 210).
- Heavy-duty meat grinder (Berkel ES 22 or equivalent).
- Drying oven capable of at least 110°C (Fisher 106G) for moisture determinations only.
- Drying oven capable of at least 130°C (Fisher 825G) for supplies only.
- Dessicator all SS (Boekel).
- Top loading balance (0.01 g; Denver Instruments; XL-3100D).
- Aluminum weigh boats.
- Clean stainless steel forceps.
- Fume hood (Safeaire).
- Mortar and pestle.
- Certified and calibrated thermometer.
- Refrigerator (4° ± 2°C) and freezer (-20°C).
- Complete SDS assembly (500-mL RB flask, thimble holder, Dean-Stark, condenser, heater)
- Pre-Cleaned thimbles.
- 90-mm filter assembly with a 6- place vacuum manifold.
- Pre-cleaned glass wool.
- 2 µm x 90-mm GMF 150 filters.
- 90-mm 3M C-18 Empore™ membrane disks.
- 10- and 25-mL drying columns.
- 40-mL wide-mouth sample jars.
- 40-mL VOA vials.
- Complete Accelerated Solvent Extractor assembly (Dionex ASE 200).
- 1.9 mm filter disks.
- 2-liter separatory funnel.
- Glass funnels.
- 250-mL beakers.
- 90-mm filter set-up with a 1-liter vacuum container.
- 2-liter Erlenmeyer.
- Microextractor for isooctane liquid-liquid partitioning.
- Hot plates (Fisher).
- 10 µl – 1000 µl automated pipette (eppendorf).
- Class A disposable 5 mL pipette.
- 1.8 mL autosampler vials.
- Stainless steel spatula.
- Pasteur pipettes.

- Glass beads.
- Vacuum chamber (Labconco) complete with an oil-free vacuum pump (Leybold) properly vented, and gauges.
- Welch 2025 oil-free vacuum pump.
- Rotary evaporator (Buchi R) equipped with a condenser, steam duct, "catch" flask, condensate flask, glass stopcock to adjust vacuum, peer-shaped sample flask, and water bath with temperature control.
- Double focussing mass spectrometer (MicroMass AutoSpec Ultima) coupled to a HP 6890 gas chromatograph (EPC) with capillary split/splitless injection port
- Autosampler (CTC A200 SE).
- OPUS Mass Spectrometer data system (CPU, monitor, disk and tape drives).
- Laboratory Information Management System (Labvantage Systems).
- Centrifuge (Damon IEC HN-SII).
- Recirculator (Polyscience and Neslab CFT-300).
- UPS (Exide Electonics).
- Water purification system (Dracor).
- High-precision solvent delivery pumps (Fluid Metering; Model RHSY).

4.3 Reagents

- Optima™ , H_2SO_4
- Pre-cleaned Na_2SO_4.
- High Purity N_2 and He.
- Solvents: distilled-in-glass toluene, methylene chloride, hexane, acetone, isooctane and methanol.
- Purified tridecane (carbon treatment).
- Acid- and base-coated silica, alumina (acid and/or basic), and Florisil.
- Standards:
  - GC Performance: CIL R633 DB-225 Mixture (20-40 pg/µL)
  - GC Performance: CIL 31340-62 DB-5 Mixture (20-40 pg/µL)
  - Extraction Standards: CIL 31531-11 (1000 ng/mL; Table 1)
  - Cleanup Standards: CIL R681 (1000 ng/mL; Table 2)
  - Injection Standards: CIL R682 (500 ng/mL)
  - Matrix Spike or Lab Control Spike: CIL 29573-27 (2.5 ng/µL; Table 3)
  - ConCal: CIL CS-3 R685 (5.0 ng/mL)
  - Calibration Standards: CIL (Table 4)
    - ✓ CS-1 (0.5 ng/mL); R683
    - ✓ CS-2 (1.0 ng/mL); R684
    - ✓ CS-3 (5.0 ng/mL); R685
    - ✓ CS-4 (50 ng/mL); R686
    - ✓ CS-5 (100 ng/mL); R687
- Preparation of Standards:
  - All entries and calculation details are made with the help of the LIMS Standards Preparation Program.
  - Call the Standards Preparation Program.
  - Follow the directives and menu options as required.
  - When all information entry is completed, print the Summary page.
  - In the space provided on the Summary page, write the page number.
  - Insert the Summary page inside the Standards Preparation Logbook (e.g., S-01).
  - When adequate, attach the supplier's "Certificate of Analysis" correctly labeled to facilitate traceability.
  - Print the waterproof label containing:
    - **Solution identification number,**
    - **Nominal concentration,** and

- **Expiration date.**

➢ Apply label on the vials and with the help of a magic marker, place a mark indicating the meniscus.
➢ Keep all PCDD/F standard solutions at room temperature inside amber vials.
➢ Expiration dates (apply only for nominal concentrations ≥0.1 ng/µL):
  - **Primary Standard Solutions** (ampoule from commercial source) have no expiration date.
  - **Stock Standard Solutions** (obtained from dilution/mixing/opening Primary Standard Solutions): 3 years.
  - **Working Standard Solutions** (from Stock/Primary and used as such during sample processing): 1 year.
➢ Good practice: what is removed from the vial never returns to the vial.

4.4 Interferences

- The use of high purity reagents and solvents helps minimize interference problems. The use of distilled-in-glass solvents is highly recommended. Other precautions regarding cross-contamination consist of minimizing the use of re-usuable glassware, and effective glassware cleaning procedures.
- Co-extractants from the sample matrix are generally removed during the multi-chromatographic column procedure. The cleanup is designed to remove commonly encountered interferences (e.g., PCBs, DDT…). The resolution of the GC column and of the mass spectrometer provides additional tools in the elimination of interferences.
- Other types of materials have been found to interfere with the analysis, especially from a quantitative stand point. When operating, the analyst will evaluate the impact these interferences – named quantitative interferences[2,3] -- may have on the data, assign a data qualifier and present conclusions in the narrative or cover letter.

4.5 Safety

- The toxicity or carcinogenicity of each reagent used is not precisely defined. Each chemical compound should be treated as potential health hazard. Exposure to these chemicals must be kept to a minimum. Conducting some of the key operations inside a hood minimizes contamination of the laboratory. The effluent from the sample splitters for the GC should pass through an activated carbon trap. Use protective gears (throwaway gloves, lab coat, safety glasses) is required in the laboratory area.

4.6 Sample Preservation

- Storage and Holding Times: All solid samples (except for tissues) are stored at 4°C. Samples are extracted within 30 days from the collection time, and the extract analyzed within 45 days of the extraction. Following the delivery of the data package, the remainder of the solid sample is kept refrigerated for another 3 months, after which, the sample is moved into a room temperature storage awaiting final disposal.

- Sample Receipt:

  ➢ Upon delivery to the lab, all containers are checked for noticeable damage that may affect the integrity of the contents. Report problems to the Project Manager so that client can be informed.
  ➢ Open carefully the cooler and examine contents carefully for damage.
  ➢ Record on the COC and the Sample Receipt Checklist the temperature (e.g., from the trip thermometer).
  ➢ Sign, date and record the time on the COC.
  ➢ Remove and examine all the contents of the cooler.

- Verify that all the information on the COC matches the information on the sample bottle labels.
- When applicable, verify the information pertaining to the sample preservation.
- Sign the COC and complete the Sample Receipt Checklist (SRC).
- At this time, take the COC and the SRC to a login computer station to assign a laboratory project number, a laboratory sample identification number, and enter the information into the LIMS.
- Open a project folder to hold all the information generated for the project. This information becomes part of the Document Control section of the data package.
- When the data entry for login is completed, print the sample receipt summary and the labels.
- Apply the labels on the relevant sample containers and verify that the client sample identification number and the laboratory sample identification number coincide.
- Place all project-related documentation in the folder. This includes the COC, carrier air bill, SRC, and any other documents (e.g., cover letter) that arrived with the samples.
- Fax to the client the Sample Receipt Acknowledgment form.

- Sample Tracking and Storage

  - At data entry for login of the samples, a designated location is assigned to the project samples.
  - Once labeled, place the samples in the assigned location.
  - The normal locations are: (To locate the samples, check the location identifier in the LIMS.)

LIMS	Description	Storage
W2	Walk-in	Solids, Liquids
F1	Freezer	Tissues

- Review:

  - When a folder is completed and all the samples have been placed in their storage location, review the folder for completeness, correctness, and sensibility. If all is correct, the folder is placed into a queue awaiting completion of the analysis.

- Authorized Personnel

  - All employees associated with the Ultra-Trace Analysis Laboratory are permitted to access the samples in the storage areas.

- Sample Storage Temperature Recording

  - Place the calibrated thermometer and the supplied bottle inside the storage unit.
  - Attach the "Certificate of Calibration" to the storage unit specific logbook.
  - Record the temperature inside the logbook daily (except on Sundays; see Figure 4).
  - If the temperature deviates by more than 2 degrees, adjust the settings and document the action inside the logbook.
  - In case of prolonged downtime, use the back up generator or dry ice until power is restored or the unit is repaired.
  - One logbook per storage unit.
  - Place all non-biological samples in the refrigerators, while tissue samples are kept inside the freezers.
  - The samples from a given project are kept together by proper means.
  - Following the sample preparation /submission of the analytical report, keep the samples refrigerated for up to 30 d.
  - After such waiting period, immediately dispose of the biological samples while non-biological samples are stored at room temperature awaiting disposal.

- Samples that have been found to contain more than 0.7 ppb TEQ must be segregated and crushed inside a 55-gallon drum for special disposal or can be returned to the Client when such arrangements have been made at bidding time.

Note: Do not store standards and/or food with the samples.

4.7 Sample Handling

Solid samples are homogenized, and may require grinding following particle sizing. The procedures followed by PAL call for the use of 20 g of solid based on dry weight. Percent moisture are determined using a dedicated oven (i.e., this oven is never used for the treatment and the preparation of supplies or samples undergoing analysis). The aliquot used during this moisture determination is never analyzed. Finely divided solids (e.g., fly ash) are handled inside a hood or disposable plastic bag.

- Grinding

  - After donning the appropriate PPE, usually nitrile gloves, open the sample in the hood.
  - Remove any large objects such as rocks.
  - If necessary pass the sample through a series of sieves to help facilitate the partitioning of the various particle sizes.
  - Particles requiring grinding can in most instances be reduced by means of a mortar and pestle.
  - In some cases reducing the temperature of the sample will aide in the grinding process.
  - Some matrices such as certain papers, grains and amorphous solids need to be reduced using a Wiley Mill or other suitable mechanism. Reference the appropriate manufacturer documentation for specific equipment operational instructions.
  - After sufficient reduction in the gross particle size, recombine and mix the various fractions of the sample.

- Particle Sizing

  - Spread a piece of clean aluminum foil in an appropriately ventilated fume hood.
  - After donning the appropriate PPE, usually nitrile gloves, open the sample in the hood.
  - With the aide of forceps spread a representative portion of sample on the aluminum foil.
  - Estimate the size of the particles in the sample.
  - If the estimate determines that the average particle size is less than 1 mm, proceed with the sample extraction.
  - If the estimate determines that the average particle size is greater than 1 mm, then the sample must be ground.

- Moisture Determination

  - Label each weigh boat required with the unique sample ID number.
  - Thoroughly mix the sample, and if necessary grind the sample (SP-C-06) to ensure a fully homogenized sample.
  - Weigh out 10-20 g of sample into the appropriate weigh boat.
  - Record the weight taken and make note of any unique characteristics into the project notebook.
  - Dry in a 110°C $\pm$ 5°C for a minimum of twelve hours.
  - After the required drying time, remove the sample and allow cooling in a dessicator.
  - Reweigh the sample and record the dried weight into the project notebook.
  - Calculate the % solids as shown below.
  - Record the %solid value for future use.

$$\%solids = \frac{weight\ of\ sample\ after\ drying}{weight\ of\ sample\ before\ drying} \times 100\%$$

4.8 Quality Control

- Method 8290 contains a series of performance checks including verifying the calibration of the mass spectrometer response and the various analyte relative response factors. The calibration entails an initial calibration (ICal) using a set of five solutions whose validity is verified every 12 H during which samples are analyzed (continuing calibration, or ConCal). The latter is performed using the middle point solution (CS3) of the calibration curve. Additionally, the GC/MS operator is required to verify and document the performance of the GC and MS systems. In particular, the homologue retention time windows, the 10,000 resolving power of the MS, and the 2,3,7,8-TCDD (or 2,3,7,8-TCDF) isomer specificity (25 percent valley) are established and documented every 12 H during which samples are analyzed. Balance is calibrated using NIST weights.

- During the initial start-up, the laboratory performs a Method Detection Limit (as per the CFR methodology), and determines the precision and bias. An on-going precision and accuracy (OPR) determination is conducted every day for each matrix undergoing analysis. A Laboratory Method Blank is always prepared alongside any batch of samples. A batch of samples is defined by Method 8290 as no more than 20 samples. PAL uses a more stringent schedule.

- Initial Calibration

  - Table 4 summarizes the composition of the five calibration solutions.
  - Each calibration solution is analyzed once, and the relative response factors (RRF) for unlabeled and labeled analytes computed for each analytical run.
  - For each unlabeled and labeled compound, an average RRF is calculated along with the relative standard deviation (RSD).
  - An acceptable ICal must meet the following criteria:

    - ✓ The signal-to-noise ratio for all analytes must be at least 10:1.
    - ✓ The ion abundance ratio for all analytes must be within 15 percent of the theoretical ratio.
    - ✓ The RSD obtained from the mean RRFs must be within 20 percent for the unlabeled analytes, and 30 percent for the labeled standards.

- Continuing Calibration

  - The authenticity of the ICal is validated at the beginning and the end of every 12-H shift during which samples are analyzed.
  - This is accomplished by analyzing CS-3, or the middle point of the calibration curve.
  - A valid ConCal meets the following specifications:

    - ✓ The signal-to-noise ratio for all analytes must be at least 10:1.
    - ✓ The ion abundance ratio for all analytes must be within 15 percent of the theoretical ratio.
    - ✓ The RRFs must be within 20 percent of the RRF (ICal) for the unlabeled analytes.
    - ✓ The RRFs must be within 30 percent of the RRF (ICal) for the labeled analytes.
    - ✓ For situations where the back-end ConCal fails, follow the chart shown in Figure 5, which is representative of the provisions written in Method 8290 Section 8.3.2.4 (September 1994)[5].

- Instrumentation Performance Checks

  - Instrumentation performance is verified and documented every 12 hours during which samples are analyzed.
  - The mass spectrometer resolving power of 10,000 (or 100 ppm mass resolution) is established at the beginning and ending of every 12-H shift during which samples are analyzed.
  - Additionally, the GC column performance – RETCHECK -- allows the GC/MS operator to define the various homologue retention time windows. It is also used to demonstrate the isomer specificity of the analysis for 2,3,7,8-TCDD on the DB-5 column and for 2,3,7,8-

TCDF on the DB-225 column. A 25 percent valley between the close eluters for either analyte must be obtained before samples can be analyzed.

Note: Confirmation of 2,3,7,8-TCDF on the DB-225 column is completed when its concentration as determined on the DB-5 column is less than half the lowest calibration point (<0.25 pg/μL).

- Batch QC Samples

  - Laboratory Method Blank (LMB): Always processed alongside a batch of samples. Paradigm Analytical Labs defines a batch of samples as no more than 10 samples processed simultaneously (EPA defines a batch as made of 20 samples). The LMB is obtained following the exact same steps used to process field samples with the exception of the actual matrix. Generally, soil is replaced by sand, effluent by DI water, Method 23 resin by XAD-2 resin from the same batch used to prepare the air sampling modules sent to the field, and biological tissues by vegetable oil.

    Acceptable method blank shows (Figure 6):

    a) Recoveries of the extraction standards within the specification of the method,

    b) Detection limits that are within a factor of five from the MDL, and

    c) No target analytes at concentrations exceeding the guidelines presented in Figure 6 when analyzing samples showing high levels of PCDD/Fs (i.e., more than 100 times the method calibration lower limit). Otherwise, the level of the specific target analyte should not exceed 50 percent of the lower limit of the calibration curve.

    An invalid LMB requires a re-extraction of the affected samples.

  - On-Going Precision and Recovery Sample (OPR): In addition to the initial demonstration of system's performance, an On-Going Precision and Recovery sample is processed daily for batches of samples of a given matrix and for a given core methodology. The OPR is fortified with the collection of seventeen 2,3,7,8-substituted PCDD/Fs at levels corresponding to the core method's quantitation limit. (OPR is synonymous with Lab Control Spike or LCS.)

    Acceptable performance is determined by:

    ✓ Recoveries of the isotopically-labeled extraction standards to fall within the 40 to 135 percent range for the tetra- through octachlorinated congeners, while

    ✓ Recoveries (accuracy) of the unlabeled compounds should be 100 ± 35 percent when spiked at the method quantitation limit and ± 30 percent when spiked above 20 times the method quantitation limit, and

    ✓ When duplicate OPR are required, the relative percent difference (RPD) of the unlabeled analytes concentrations should be within 30 percent when spiked at the method quantitation limit and ± 25 percent when spiked above 20 times the method quantitation limit.

  - Matrix Spike (MS): When requested, a matrix spike (MS) and matrix spike duplicate (MSD) samples are analyzed by subjecting another aliquot of the designated field sample to the same procedures as the regular sample but with the addition of the collection of the seventeen 2,3,7,8-substituted PCDD/F congeners (200 ppt for solid and 200 ppq for aqueous matrices).

Acceptable performance is determined by:

- ✓ Recoveries of the isotopically-labeled extraction standards to fall within the 40 to 135 percent range for the tetra- through octachlorinated congeners, while
- ✓ Recoveries (accuracy) of the unlabeled compounds should be 100 ± 30 percent assuming no "significant" amounts of endogenous analytes are present in the sample.
- ✓ When duplicate MS/MSD are required, the relative percent difference (RPD) of the unlabeled analytes concentrations should be within 20 percent.

➢ Duplicate Analyses: When requested, a second aliquot of the field sample is analyzed following the same procedures.

Acceptable performance is determined by:

- ✓ Recoveries of the isotopically-labeled extraction standards to fall within the 40 to 135 percent range for the tetra- through octachlorinated congeners, while
- ✓ The relative percent difference (RPD) of the unlabeled analytes concentrations should be within 25 percent provided the analyte levels are within the calibration range.

♦ Quality Control Charts: Quality control charts are designed to detect trends and deviations from normal performance. A variety of charts are developed and analyzed on a regular basis to ensure adequate system performance. Whenever possible, lower and upper control and warning limits are defined to help with the management of the laboratory operations. Such information can be reviewed as part of a laboratory audit.

➢ Examples of charts that can be monitored include:

- ✓ Lab Method Blank for background contamination (e.g., OCDD levels in LMB vs time).
- ✓ Daily OPR results for analyte and labeled compounds recoveries.
- ✓ LMB recoveries of the extraction and cleanup standards.
- ✓ ConCal RRF deviations.
- ✓ GC column resolution.
- ✓ Certain MS parameters (e.g., air ratio to He, amplitude of PFK reference peaks, repeller...).

4.9 Analytical Procedures

♦ Solid samples are processed as shown on Figures 1, 2, and 3. Two separate extraction procedures are currently available for solid samples (SDS and 3545). Each of the key steps in the procedure is described in the SOPs referred on the diagram. Documentation of the completion of each of the key step (e.g., spiking, extraction, concentration, fractionation, dates, initials of the chemist...) is recorded on the Sample Tracking & Management Forms (Figures 1, 2, 3, 7,8,9). The documentation also includes a Communication (Figure 9) sheet where the chemist notes any relevant observations made about the samples, and the handling of the sample. Batches of solvents, reagents, GC columns and the likes are recorded on the aforementioned forms.

- Sample Fortification

At the extraction stage:

- Aliquot 1 mL of acetone to each autosampler vial; equal in number to samples requiring spiking.
- To each vial, add 40 µl of Extraction Standards (0.1 ng/µl). It is advisable to have a 'witness' present so that double spiking or omissions can be avoided.
- Cap the vial and vortex. Vortexing will ensure that the concentrated standard cocktail in n-nonane is thoroughly mixed into solution.
- Pour the acetone solution into the sample. Holding the upside down, rinse the vial with a small quantity of acetone.
- For water samples, cap the container and shake vigorously.

At the cleanup stage:

- To each labeled archive test tube, add 40 µl of Clean-Up Standards (0.1ng/µl). As stated above, it is advisable to have a second person observe this procedure as to avoid double spiking of a sample extract, and omissions.

At the analysis stage:

- Before GC/MS analysis, add to each **labeled** autosampler vial 20 µL of the Injection Standards nonane solution.
- Vortex each vial and allow to sit.
- Wash the walls of the vial again by rotating the vial slowly in a horizontal disposition. This ensures that all vial surfaces come in contact with the standard.

- Soxhlet Dean-Stark Extraction:

  - Pre-Soxhlet the unit before using it for samples.
  - To that effect, assemble the SDS without the condenser.
  - Add a couple of Teflon™ chips inside the 500-mL round-bottom flask.
  - Add 300 mL of toluene through the DS section.
  - Assemble the condenser and insulate the "vapor pathway".
  - Turn on the water recirculator, which is set between 4° and 7°C.
  - Turn on the heating mantle to position "9" for toluene.
  - Allow the reflux to go on for at least three hours.
  - Turn off the heating element, and allow the unit to cool down.
  - Transfer the toluene inside a labeled bottle container (for washing dirty glassware).
  - Add a couple of fresh Teflon™ chips.
  - Add 350 mL of toluene and **0.5 mL of purified tridecane**.
  - Adapt the thimble holder and insert the thimble containing the **fortified** sample using a clean SS spatula. Use 20 g dry-weight equivalent.
  - Assemble the DS and condenser components.
  - Cap the opened extremity of the condenser with foil.
  - Turn on the water recirculator (set between 4° and 7°C) and heater (position "9") for toluene.
  - Insulate the "vapor pathway".
  - Allow the extraction to continue for 16 to 18 H.
  - During the extraction, verify that the solvent siphons normally.
  - Drain the water as appropriate to prevent water from returning to the boiling flask.
  - At the end of the reflux cycle time, proceed with the sample concentration as described below.
  - **Do not turn off the heater.**
  - Drain the toluene present in the DS side arm directly inside the labeled bottle container (for washing dirty glassware).

- Continue to drain the toluene until approximately 20 mL of toluene remains inside the RB flask.
- Turn off the heater when the toluene reaches the 20-mL mark. **Do not go to "near dryness".**
- The toluene inside the thimble holder is removed and disposed off.
- Remove the heating mantle and allow the flask to cool down.
- The sample is now ready for the vacuum concentrator (SP-N-01).

- Method 3545 Extraction:

  - Fill all solvent reservoirs with appropriate solvent.
  - Ensure that the purging gas cylinder (N_2) has a minimum of 500 psi pressure.
  - Load a disposable 1.9 mm filter into each cell to be used and top with 2-4 g of clean sand.
  - Transfer 20 g dry wt. equivalent of sample to an extraction cell and fill any remaining headspace with clean sand.
  - Using a spatula, mix as thoroughly as possible the sand into the sample.
  - Spike each extraction cell with the appropriate extraction standards.
  - Replace the tops onto the extraction cells and load onto the ASE.
  - Ensure that the correct number of collection vials is also loaded.
  - Add 0.5 mL of tridecane to each collection vial.
  - Begin the extraction process according to the manufacturer recommendations.
  - Extractor conditions:

Oven Temp.:	200°C (for toluene)
Pressure:	2000psi
Static Time:	10 min.
Flush Vol.:	60%
N_2 Purge:	70 sec.
Static Cycles:	2

These conditions have been optimized and all MDL studies and subsequent sample extractions have utilized the above conditions.

  - Allow all extracts to cool prior to drying with sodium sulfate and concentration.

- Sample Extract Concentration

  - The rotary evaporator is equipped with a condenser, steam duct, "catch" flask, condensate flask, glass stopcock to adjust vacuum, peer-shaped sample flask, and water bath with temperature control.
  - All glassware must be cleaned between samples:
    - ✓ **Rinse the steam duct with acetone using squeeze bottle while rotating the unit.**
    - ✓ **The "catch" and pear-shaped flasks must be replaced by clean ones between samples.**
  - Water chiller providing water for the rotary evaporator condenser at 5°C.
  - An oil-free vacuum pump properly vented with gauge.
  - Set the water bath temperature to 40°C making sure enough DI water is present.
  - Allow cold water to circulate inside the condenser.
  - Turn the vacuum pump into the "on" position.
  - Make sure the glass stopcock is in the open position.
  - Attach the sample and "catch" flasks assembly onto the steam duct.
  - Hold the assembly or place the clamp to insure the assembly does not fall inside the water bath.
  - Close the glass stopcock.
  - Monitor the pressure gauge.
  - Normally with solvents such as toluene and methylene chloride, the reading should be in the 300 to 700 mm Hg range.
  - The solvent starts evaporating and condensation becomes visible.

- Maintain steady evaporation rate and make sure no bumping is occuring.
- If bumping happens, reduce the pressure to less than 300 mm Hg on the vacuum pump or using the glass stopcock.
- When bumping occurs, contact laboratory manager to discuss viable options to address sample integrity.
- Once the level of solvent is low enough (0.5 to 2 mL), reduce the rotation (position 1-2) and re-establish atmospheric pressure by opening fully the glass stopcock and switching off the pump (that is if you don't have a need for it). Switch off the rotation.
- Remove the glass assembly (i.e., the "catch" and the pear-shaped flasks).
- Turn off water heater and cooling water.
- Rinse the steam duct (vide supra) and wash glassware.
- Note: Normally, 0.5 mL tridecane remains. **However, to ensure complete solvent exchange before the sample cleanup, it is necessary to complete the solvent concentration and exchange using the vacuum concentrator (see below).**

- When using the vacuum chamber, place the 500-mL round-bottom flask on a cork ring, the sample bottle, 100-mL jar, 1-mL vial inside the vacuum chamber.
- Turn the vacuum pump into the "on" position.
- Follow the program shown in Table 5.

◆ Sample Fractionation

- Prepare an Acid/Base Silica Column (25-mL pipet):

From bottom:
- glasswool
- 1 g SiO_2,
- 4 g NaOH-coated,
- 1 g SiO_2,
- 8 g H_2SO_4-coated,
- 2 g SiO_2,
- 4 g Na_2SO_4.

All solvents are stored inside dedicated bottles with Teflon™ connections to the columns. An hexane-dedicated pump is used for the elution of the tandem columns. Do not use the hexane pump to deliver other solvent systems. When a single pump is used to deliver 2% MC/hexane and straight MC, always flush the line with the eluant before allowing the eluant to reach the column.

- The acid/base-modified silica column is washed with hexane,
- Sample loaded with two 1-mL rinses of hexane and
- Eluted with 100 mL hexane directly into a pre-washed Florisil column.

- Florisil column cleanup (1.5-1.6 g, 10-mL pipet, directly from the supplier's jar, no activation, reseal jar):

- Pre-elute column with MC.
- Then with hexane/MC (98:2).
- The column is ready for the tandem set up.
- Once the 100 mL hexane from the tandem columns has eluted off,
- Remove the silica column and connect the Florisil to the 2% MC/hexane bottle delivery line.
- Elute with about 20 mL hexane/MC (98:2).
- This fraction goes to waste.
- Elute with about 35 mL MC.
- Collect MC eluate.

- Concentrate the MC eluate.
- Transfer using MC inside an autosampler vial
- Concentrate to dryness

♦ Sample Analysis by HRGC/HRMS

- HRGC/HRMS instrument setup

➢ The GC temperature/pressure/flow program is stored on the instrument as [vg.opus$instrument]DEFAULT.
➢ The MS experiment is stored on the instrument as [vg.opus$experiment]M23_DB5 (Table 6).

- HRGC/HRMS pre-sample analysis checks

➢ Perform any daily PM (see SOP PM-02).
➢ Tune the MS resolution to 100 ppm (or 10,000 resolving power using the 10% valley definition).
➢ Acquire location data to calibrate the MS and print a copy of function one's MS resolution.
➢ Inject the retention time windowing mix for the column in use. Then evaluate switching times for accuracy and make any corrections, reanalysis maybe required for a large correction. If the switching times are off by a considerable amount, the reason for the change should be found, then a survey scan should be analyzed to find the new switching times. This injection is also used to verify that there is less then 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 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 CS3 may be analyzed to verify continuing calibration. If the curve or the CS3 passes method requirements sample analysis may begin.

- HRGC/HRMS sample analysis

➢ Reconstitution of a sample is accomplished by adding nonane containing the injection standards, capping the vial, and mixing well with a vortex (see SOP SP-S-01).
➢ Samples are injected under conditions identical to that used to establish calibration.

- HRGC/HRMS post-sample analysis checks

➢ A "back-end" CS3 must be injected within 12 H from the front end CS3 or the CS3 in the curve. This standard is used to verify sufficient stability of the calibration after sample analysis. It has requirements set by the method. Depending on the back-end CS3 results, different calibration files maybe required to quantitate the samples (see SOP RP-G-03). These results also may require a new initial calibration.
➢ A "back-end" print out of the MS resolution must also be performed.

- HRGC/HRMS sample package assembly and QC data filing

➢ The QC 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 and the front/back end CS3s.
➢ Each samples hardcopy should include the quant report, totals pages, deviations, chromatograms, and report forms.

4.10Data Validation

- Data Review

  - Use the check list shown in Figure 7 when conducting the validation of the data.
  - When MS/MSD and/or duplicate analyses have been requested, verify that the results are within the acceptable performance criteria outlined in the Quality Control section of this document.
  - Data qualifiers are used whenever deviations or analytical difficulties are encountered. Data that do not meet the QA/QC specifications need to be reviewed on a case-by-case basis before rejecting the data. An assessment of the impact on the data is discussed in the cover letter or narrative. When data is rejected, mark across the data set "Rejected" and provide the reason for the rejection. Also, state the corrective action(s) taken to remedy this situation. Generally, rejected data will require a re-extraction and analysis of the sample (if ample sample is available). Typical data qualifiers are:

    - ✓ "B" for any analyte found in the LMB at levels exceeding the recommended value.
    - ✓ "V" to validate results from samples showing recoveries of less than 40 percent.
    - ✓ "R" to reject the data for a particular congener due to low recoveries of the associated extraction/cleanup standard.
    - ✓ "D" to indicate the presence of a possible chlrorinated diphenylether.
    - ✓ "E" to indicate that the analyte concentration exceeded the upper range of the calibration curve.
    - ✓ "Q" to indicate the presence of a quantitative interferrence.[2,3]

4.11Calculations

- Relative Response Factors: For each calibration solution (ICal or ConCal), the analyte relative response factor is calculated according to the formulae shown below.

$$RRF_a = \frac{A_a \times Q_{es}}{A_{es} \times Q_a}$$

Where RRF_a represents the relative response factor of the analyte "a"

A_a represents the summed area of the two ions monitored for analyte "a",
A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,
Q_a represents the absolute amount or concentration of the analyte "a" in the solution, and
Q_{es} represents the absolute amount or concentration of the extraction standard in the solution.

- Analyte Concentration: The concentration of each of the 17 2,3,7,8-substituted PCDD/F congeners is obtained according the formulae below.

$$C_a = \frac{A_a \times Q_{es}}{A_{es} \times \underline{RRF_a} \times W}$$

Where C_a represents the concentration of the analyte "a" in the sample,

A_a represents the summed area of the two ions monitored for analyte "a",
A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,

Q_{es} represents the amount of the extraction standard added to the sample before the extraction,
W is the dry weight of the solid sample, and
$\underline{RRF}_a$ is the average of the five RRFs obtained for analyte "a" during the ICal.

- Labeled Compounds Recovery: The recoveries of the extraction (or cleanup) standards are obtained using the following expression.

$$\text{"Percent Recovery"} = \frac{A_{es} \times Q_{js}}{Q_{es} \times A_{js} \times \underline{RRF}_{es}} \times 100$$

Where "Percent Recovery" is the extraction standard recovery expressed in percent,

A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,
A_{js} represents the summed area of the two ions monitored for the labeled injection standard,
Q_{es} represents the amount of the extraction standard added to the sample before the extraction,
Q_{js} represents the amount of the injection standard added to the sample before GC/MS analysis,
$\underline{RRF}_{es}$ is the average of the five RRFs obtained for the extraction standard during the ICal.

Note: The same formulae can be applied for the computation of the cleanup standard recoveries (CS). In this case, replace "es" by "cs" in the above equation.

- Detection Limit: The detection for each of the 17 2,3,7,8-substituted PCDD/F congeners is obtained according the formulae below.

$$DL_a = 2.5 \times \frac{A_a \times Q_{es}}{A_{es} \times \underline{RRF}_a \times W}$$

Where DL_a represents the detection limit for analyte "a" in the sample,

A_a is the summed area for the noise measured for the two ions monitored for analyte "a",
A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,
Q_{es} represents the amount of the extraction standard added to the sample before the extraction,
W is the dry weight of the solid sample, and
$\underline{RRF}_a$ is the average of the five RRFs obtained for analyte "a" during the Ical.

- Relative Percent Difference (RPD): Difference expressed as a percentage of the mean.

$$RPD = \frac{|X_1 - X_2|}{(X_1 + X_2)/2}$$

where X_1 and X_2 are the duplicate results for a particular analyte.

4.12References

1. Y. Tondeur and W.F. Beckert; "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by High-

Resolution Gas Chromatography / High-Resolution Mass Spectrometry", USEPA, EMSL-LV.

2. Yves Tondeur, Philip W. Albro, J. Ronald Hass, Donald J. Harvan, and J. L. Schroeder, "Matrix Effect in Determination of 2,3,7,8- Tetrachlorodibenzo-p-Dioxin by Mass Spectrometry." *Anal. Chem. 56:1344-1347, 1984.*

3. Yves Tondeur, W. J. Niederhut, J. Campana and S. R. Missler; "A Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated-p-Dioxins in Environmental Samples." *Bio. Med. and Environ. Mass Spectr. 14, 449-456, 1987.*

4. *Paradigm Analytical Labs Standard Operating Procedures for the Measurement of PCDD/Fs in Environmental Samples by Isotope-Dilution HRGC/HRMS: see Figure 11 for a complete listing.*

5. *Method 8290, PCDD/Ss by HRGC/HRMS; Revision 0, September 1994; SW-846.*

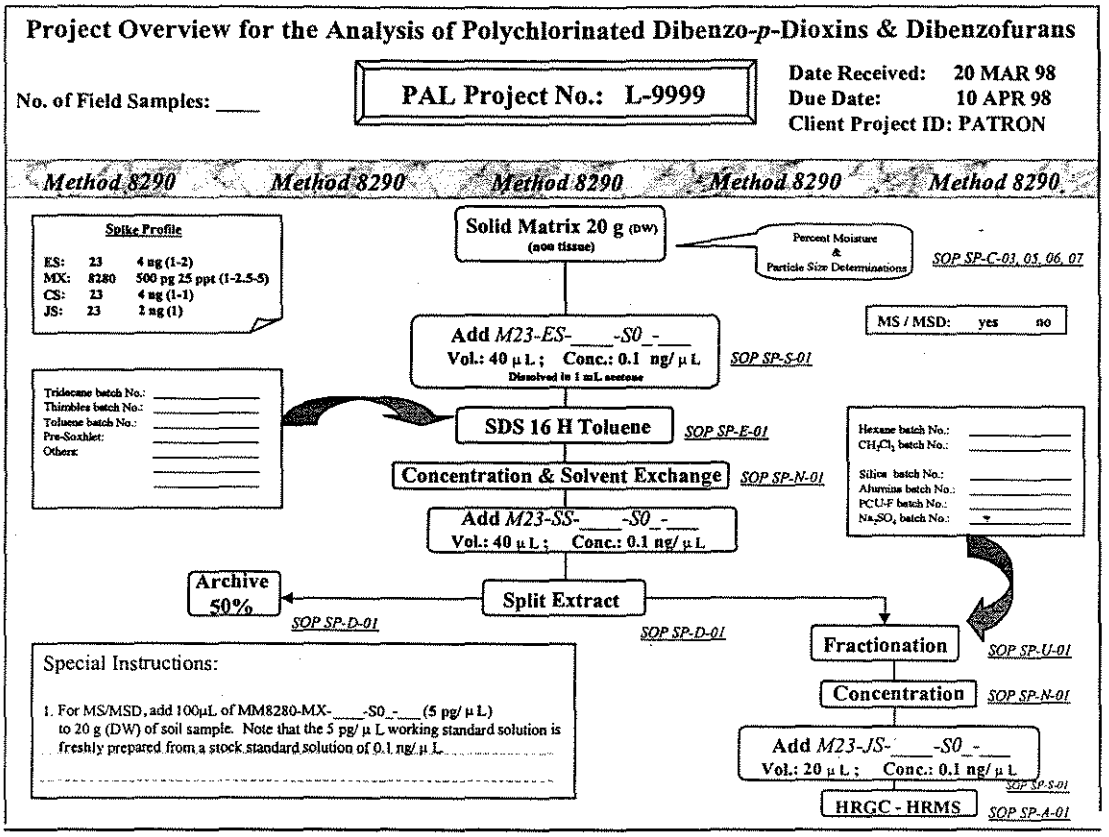


Figure 1: Schematic representation of Method 8290 for solids using the SDS extraction technique.

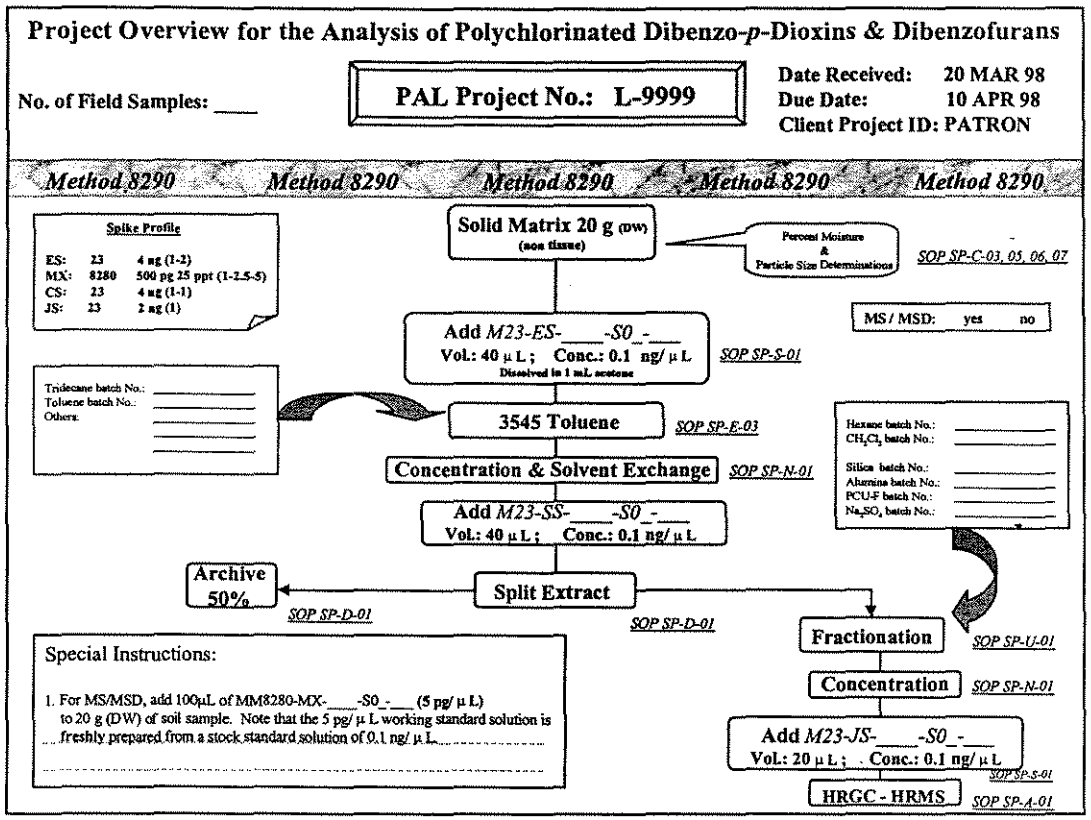


Figure 2: Schematic representation of Method 8290 for solids using Method 3545 extraction technique.

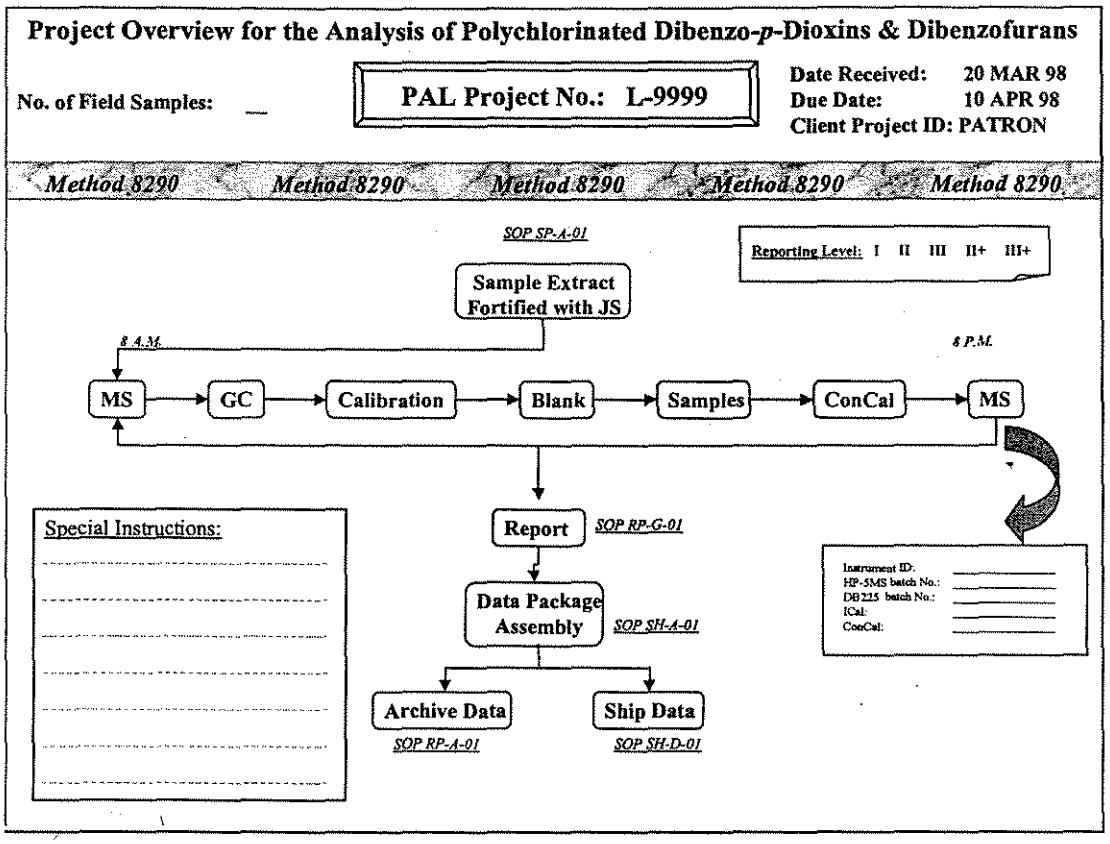


Figure 3: Schematic representation of the analysis and reporting phases of Method 8290.

Sample Storage F 1 Temperature					Logbook No. 1 Page_____
Date	**°C**	**Corrective Action**	**Date**	**°C**	**Corrective Action**

Figure 4: Sample storage temperature tracking.

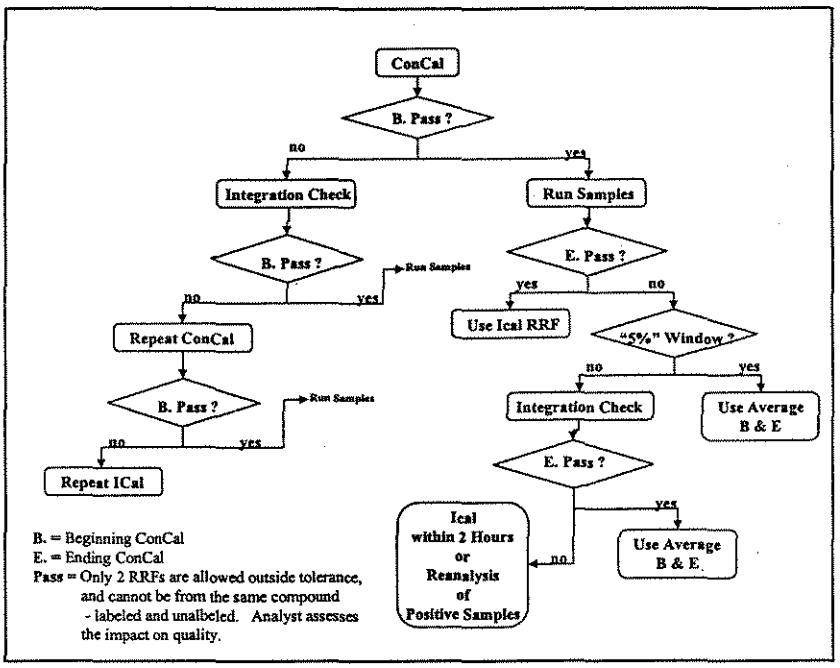


Figure 5: Decision flow chart for handling ConCals.

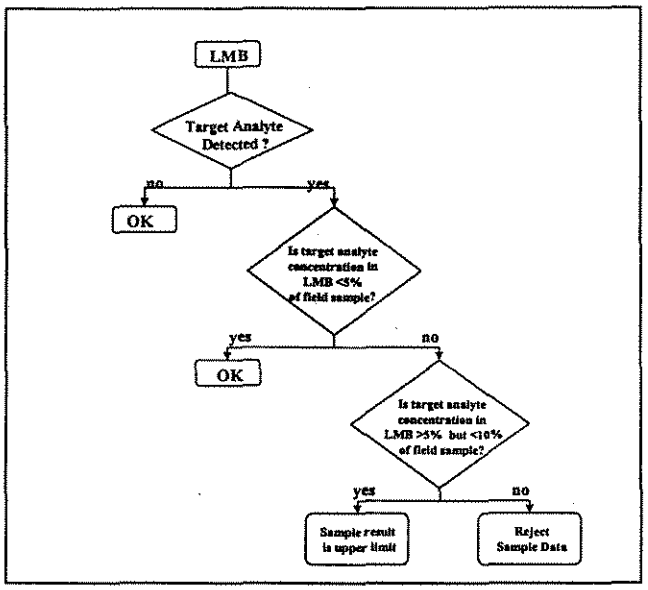


Figure 6: Decision chart for handling background levels of PCDD/Fs in the LMB.

Prepared by Yves Tondeur
Signature:

Approved by Greg Dickinson
Signature:

No.: REF-21

PAL Project No.: _____

Paradigm Analytical Labs
Data Review Check List

Item	Initials
1. Initial Data Package Components (Section 2): Project Overview & Sample Tracking/Management Forms	
➢ COC	
➢ Correspondence	
➢ Login information	
➢ Injection Log	
2. Initial Data Package Components (Section 3): Analytical Results	
➢ Two-page Summary Topsheet	
➢ Raw data containing the retention times, areas, signal-to-noise ratios, totals, ion ratios…	
➢ Raw data showing all relevant selected ion current profiles (i.e., chromatograms).	
3. Project Overview	
➢ Check and read the communication page.	
➢ Read any correspondence accompanying this project.	
➢ Verify that the COC is present and signed.	
➢ Verify that the login report is present and signed.	
➢ Verify that the SRC is present and signed.	
➢ Verify that the number of samples is consistent with client's request, COC, correspondence.	
➢ Verify that the method information is correct.	
➢ Verify that all relevant entries have been made on the laboratory tracking forms)including page No.).	
➢ Review spiking information.	
➢ Verify sample preparation information.	
➢ Look for any special instructions.	
4. Sample Results & Overview	
➢ Injection Log must be present for each PAL project.	
➢ Have at hands the MS and GC performance checks associated with this analytical run.	
➢ Have at hands the associated ConCals (begin and end).	
➢ Raw data including SICPs and totals list, areas, S/N, retention times, and summary QUAN reports.	
➢ TCDF confirmation data if necessary.	
5. Data Review	
• From the injection log, verify the time and date for the various system performance checks (12-H).	
➢ Verify that the OPR passed, MS/MSD and/or Duplicates as appropriate	
• Verify that system performance checks passed (MS, GC, Calibrations).	
➢ 100 ppm in mass for the resolution at m/z 317.	
➢ <25% valley for 2,3,7,8-TCDD (and/or 2,3,7,8-TCDF).	
➢ Deviations for ConCal are <20% for unlabeled (beginning) or <25% for unlabeled (ending).	
➢ Deviations for ConCal are <30% for labeled (beginning) or <35% for labeled (ending).	
➢ See SOP RP-G-03 for handling deviations.	
➢ Verify that all ion-abundance ratios passed.	
➢ All of the above apply to confirmation analyses as well.	
• For each samples, and starting with the LMB, and check the following:	
➢ Verify client, laboratory and sample information (matrix, weight, volume, file name, ICal, ConCal and RetCheck file names, dates…).	
➢ Verify the name of the client.	
➢ Verify the PAL Project No.	
➢ Verify the method's name.	

➢ Verify holding times (extraction 30 days from collection; 45 d from extraction for analysis).	
➢ Check recoveries of the ES, SS, and CS (40 to 135 percent).	
➢ Review the SICPs from the LMB to validate the LMB (i.e., absence of signals).	
➢ Examine the QC check ion SICPs for the presence of quantitative interferences (QI).	
➢ Examine the PCDPE SICPs for the presence of "ethers" as potential interferences.	
➢ Assess the impact of these "ethers" or QI on the data.	
➢ Perform a manual calculation of at least one specific analyte concentration.	
➢ Perform a manual calculation of at least one labeled standard recovery (e.g., ES).	
➢ Occasionally, perform a manual calculation for a total homologue group.	
➢ Examine the SICPs for the presence of saturated peaks.	
➢ Verify that the chlorine-37 correction is applied to 2,3,7,8-TCDD.	
➢ Verify that the 2,3,7,8-TCDF result originates from the confirmation analysis.	
➢ Perform a general overview of the SICPs and look for inconsistencies between the SICPs and the tabulated results, between the samples themselves, and observations noted by the lab staff.	
6. Initial and date the topsheets.	

Notes to be used for the Cover Letter or Narrative

Figure 7: Check list for data validation.

Sample Tracking for the Analysis of Polychlorinated Dibenzo-*p*-Dioxins & Dibenzofurans

No. of Field Samples:
Page 1 of ___

PAL Project No.: L-9999

Date Received: 20 MAR 98
Due Date: 10 APR 98
Client Project ID: PATRON

		Method 8290 S				*Method 8290 S*				*Method 8290 S*				*Method 8290 S*			
Lab Sample ID	Client Sample ID	Jar Weight Before	Jar Weight After	Moisture Percent	Sample Weight Wet (g)	ES	MX	SDS	Conc. S.Ex.	CS	Split Arch.	FCU	Conc.	JS	TCDF	Misc.
L-9999-0	Lab Method Blank															
L-9999-1	8030974															
L-9999-3	8030975															
L-9999-4	8030977															
L-9999-5	8030978															
L-9999-6	8030979															
L-9999-7	8030980															
L-9999-8	8030982															
L-9999-9	8030983															

Figure 8: Sampling Tracking & Management Form (Method 8290; SDS extraction).

Sample Tracking for the Analysis of Polychlorinated Dibenzo-*p*-Dioxins & Dibenzofurans

No. of Field Samples:
Page 1 of ___

PAL Project No.: L-9999

Date Received: 20 MAR 98
Due Date: 10 APR 98
Client Project ID: PATRON

		Method 8290 S				*Method 8290 S*				*Method 8290 S*				*Method 8290 S*			
Lab Sample ID	Client Sample ID	Jar Weight Before	Jar Weight After	Moisture Percent	Sample Weight Wet (g)	ES	MX	3545	Conc. S.Ex.	CS	Split Arch.	FCU	Conc.	JS	TCDF	Misc.
L-9999-0	Lab Method Blank															
L-9999-1	8830974															
L-9999-3	8830975															
L-9999-4	8830977															
L-9999-5	8830978															
L-9999-6	8830979															
L-9999-7	8830980															
L-9999-8	8830982															
L-9999-9	8830983															

Figure 9: Sampling Tracking & Management Form (Method 8290; M3545 extraction).

Communication Exchanges Form for the Analysis of PCDD/PCDFs

No. of Field Samples: ____
Page __ of __

PAL Project No.: L-9999

Date Received: 20 MAR 98
Due Date: 10 APR 98
Client Project ID: PATRON

Method 8290	*Method 8290*	*Method 8290*	*Method 8290*	*Method 8290*

Figure 10: Communication Exchanges Form (Method 8290).

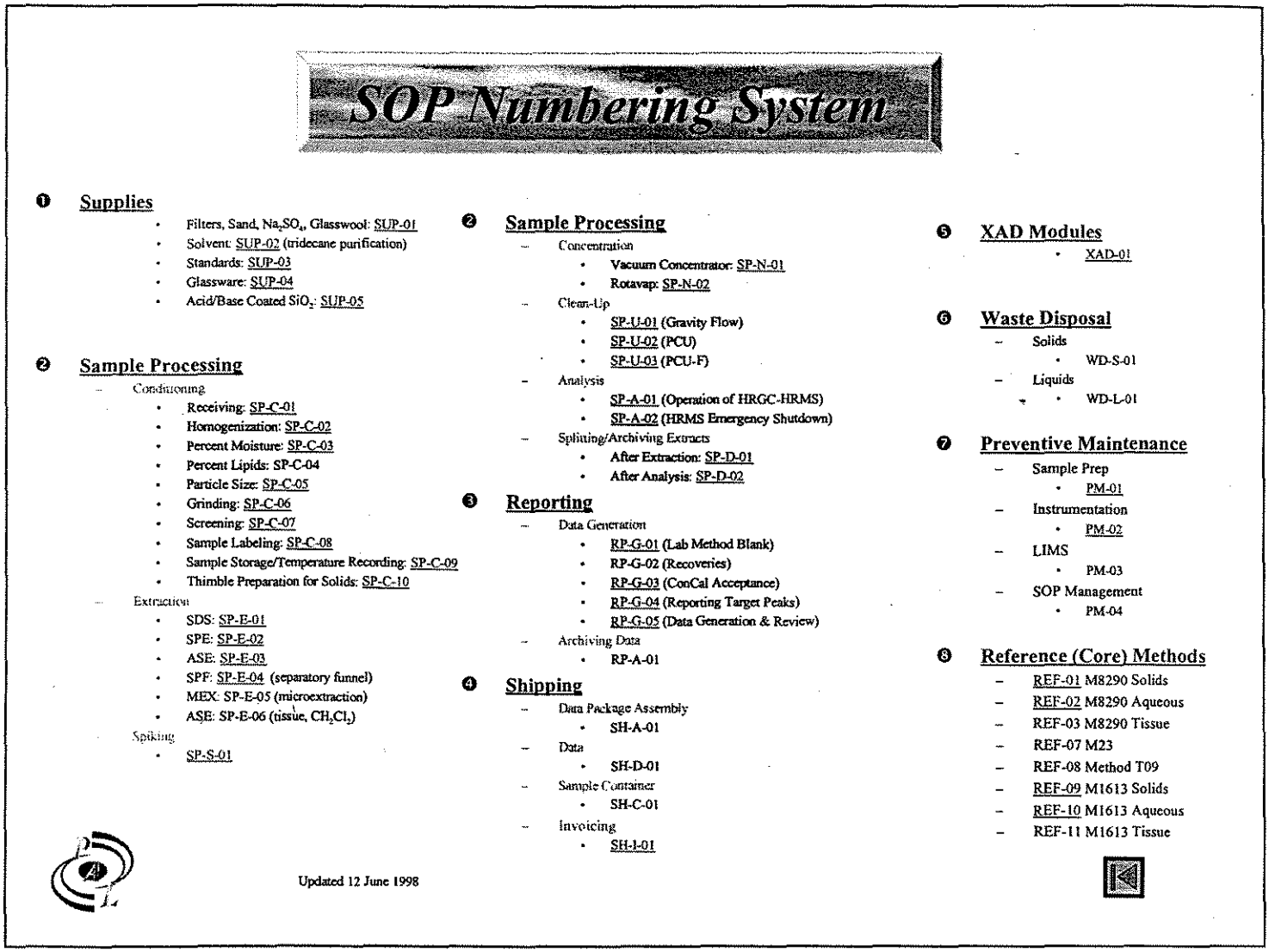


Figure 11: Paradigm Analytical Labs Standard Operating Procedures for the Measurement of PCDD/Fs in Environmental Samples by Isotope-Dilution HRGC/HRMS

Table 1: List and concentrations of the Extraction Standards used during the sample fortification step.

$^{13}C_{12}$-2,3,7,8-TCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,7,8-PeCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,6,7,8-HxCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,6,7,8-HpCDD	100 pg / µL
$^{13}C_{12}$ -OCDD	200 pg / µL
$^{13}C_{12}$ -2,3,7,8-TCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,7,8-PeCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,6,7,8-HxCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,6,7,8-HpCDF	100 pg / µL

Table 2: List and concentrations of the Cleanup Standards used during the sample fortification step.

$^{37}Cl_4$-2,3,7,8-TCDD	100 pg / µL
$^{13}C_{12}$ -2,3,4,7,8-PeCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,7,8-HxCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,7,8-HxCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,7,8,9-HpCDF	100 pg / µL

Table 3: Composition of the Matrix Spike solution.

Unlabeled Analyte	Concentration in pg / µL
2,3,7,8-TCDD	5
2,3,7,8-TCDF	5
1,2,3,7,8-PeCDD	12.5
1,2,3,7,8-PeCDF	12.5
2,3,4,7,8-PeCDF	12.5
1,2,3,4,7,8-HxCDD	12.5
1,2,3,6,7,8-HxCDD	12.5
1,2,3,7,8,9-HxCDD	12.5
1,2,3,4,7,8-HxCDF	12.5
1,2,3,6,7,8-HxCDF	12.5
1,2,3,7,8,9-HxCDF	12.5
2,3,4,6,7,8-HxCDF	12.5
1,2,3,4,6,7,8-HpCDD	12.5
1,2,3,4,6,7,8-HpCDF	12.5
1,2,3,4,7,8,9-HpCDF	12.5
OCDD	25
OCDF	25

Table 4: Initial Calibration Solutions (concentrations are in pg/µL)

Analyte	CS-1	CS-2	CS-3	CS-4	CS-5
Unlabeled					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD	2.5	5	25	250	500
1,2,3,7,8-PeCDF	2.5	5	25	250	500
2,3,4,7,8-PeCDF	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5.0	10	50	500	1000
OCDF	5.0	10	50	500	1000
Extraction Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Cleanup Standards					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	5	50	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
Injection Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

Table 5: Vacuum Chamber Program for 5-mL Tridecane Sample Extracts (solvent exchange procedure)

Pressure	Time	Note
0" – 15" Hg	Start	Open the valve slowly and allow pressure to reach 15" Hg.
16" – 20" Hg	2 min / mark	Allow pressure to gradually reach 20" Hg with a two-minute hold at 16, 17, 18, 19 and 20"Hg.
21" – 25" Hg	3 min / ½ mark	Allow pressure to gradually reach 25" Hg with a three-minute hold at 21, 21.5, 22, 22.5, 23, 23.5, 24, 24.5 and 25"Hg.
26" – 30" Hg	5 min / ½ mark	Allow pressure to gradually reach 30" Hg with a five-minute hold at 26, 26.5, 27, 27.5, 28, 28.5, 29, 29.5, and 30"Hg.
10 T – 5 T	***Read pump gauge***	At this point, you can monitor the pressure from the pump gauge rather than the chamber pressure gauge. Typically, between 10 and 5 Torr, you need to proceed cautiously in a stepwise manner as described above (i.e., 5 min at 10 T, 5 min at 9 T, 5 min at 8 T, 5 min at 7 T, 5 min at 6 T, and 5 min at 5 T.)
5 T – 1 T	***Read pump gauge***	Again, by opening and closing the pump valve, allow the pressure to reach 4 T, 3 T, 2 T, and 1 T. Here, the stepping down can take place at a slightly higher pace. Bumping has been observed down to 1.2 T if pumping is too fast. When opening the pump valve, do it slowly by watching the gauge.
1T – 0.75 T	***Read pump gauge***	Once you reach 1 T, you can keep the pump valve fully opened and pump continuously until the pressure drops below 0.5 T. The sample is ready for the next step.

Table 6: 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

APPENDIX A-52

STANDARD OPERATING PROCEDURE METHOD 8290 FOR AQUEOUS SAMPLES

Paradigm Analytical Laboratories

Standard Operating Procedure

Method 8290 for Aqueous Samples

1. Purpose

To describe the procedures followed for the analysis of aqueous samples by USEPA Method 8290[1,5].

2. Scope & Application

Method 8290 is suitable for the analysis of the seventeen 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and total homologues (tetra- through octachlorinated congeners) in aqueous matrices (e.g., water, non-SDWA drinking water, non-NPDES industrial waste waters and effluents, surface and ground waters). The methodology is based on the use of high-resolution gas chromatography (HRGC) combined with high-resolution mass spectrometry (HRMS) and is capable of achieving low parts per quadrillion detection limits.

3. Summary

One liter of the water sample is fortified with a known amount of nine carbon-13 labeled PCDD/F congeners (ES = Extraction Standards). The extraction is a function of the presence or not of visible particulates. Generally, a water sample containing visible particulates is subjected to a double extraction procedure. The filter and catches are extracted either by Soxhlet-Dean Stark or by Method 3545 using toluene as the solvent. The filtrate is extracted using liquid-liquid partitioning with an organic solvent (methylene chloride for separatory funnel extraction or isooctane for microextraction). Samples freed of visible particulates are extracted directly by liquid-liquid partitioning using an organic solvent as described previously. Alternate extraction procedures consist of solid phase extraction (SPE) using either C_{18} disk or carbon adsorption diffusion techniques followed by a toluene Method 3545 extraction of the sample after filtration (i.e., the solid phase material, and filter catches).

After the addition of 0.5 mL of purified tridecane, the dried toluene (sodium sulfate) is evaporated under vacuum until no traces of toluene are present. The dried methylene chloride (or isooctane) is evaporated under vacuum until no traces of methylene chloride subsist. The two residues are combined before the addition of another group of five labeled PCDD/F congeners (CS = Cleanup Standards). For aqueous samples, no splitting and archiving of half the extract is taking place. The entire fortified extraction residue is subjected to a multi-chromatographic columns clean up procedure. The purified extract is transferred inside a 1-mL vial using methylene chloride and concentrated to dryness. The sample is reconstituted into the final extract using 20 µL of a nonane solution containing two additional labeled PCDD congeners (JS = Injection Standards). One µL of the final extract is injected into the injection port of a GC/MS system operating in the high-resolution mode. The GC column is a 60-m DB-5 or HP-5MS capable of 2,3,7,8-TCDD isomer specificity and is used to analyze the tetra- through octachlorinated PCDD/F congeners. The confirmation of 2,3,7,8-TCDF is conducted on a 30-m DB-225 capillary column capable of 2,3,7,8-TCDF isomer specificity. In all cases, the mass spectrometer operates in the high-resolution mode (10,000 resolving power; 5 percent crossing over). The results are reported in ng per liter or parts-per-trillion (ppt).

4. Procedure

Four options are available for processing aqueous matrices. The first two involve organic solvent partitioning, while the last two are solid phase extractions followed by toluene extraction of the solid phase material. Figure 1 is a schematic description of the procedures involved for the extraction and fractionation of aqueous matrices using the liquid-liquid partitioning (methylene chloride) technique on the filtrate and Method 3545 toluene extraction of the filter and particulates. Figure 2 is the corresponding diagram when for aqueous matrices are extracted using the liquid-liquid partitioning (isooctane) microextraction technique on the filtrate and Method 3545 toluene extraction of the filter

and particulates. Figure 3 corresponds to the solid phase approach that entails C_{18}-disk solid phase extraction technique on the water sample followed by Method 3545 toluene extraction of the filter and particulates. Finally, Figure 4 shows the solid phase Carbon Adsorption Diffusion alternative followed by Method 3545 extraction with toluene on the filter, the solid phase material, and the solid catches. Key steps are referred to the corresponding SOP. Figure 5 is the schematic for the analysis and reporting phases of the method. Tables 1 and 2 summarize the labeled compounds used throughout this procedure.

4.1 Definitions

- Congener: Any one particular member of the same chemical family (e.g., 135 PCDF congeners).
- Homologue: Group of structurally related chemicals that have the same number of chlorines.
- Isomer: Compounds that belong to the same homologue group (e.g., 22 TCDD isomers).
- Extraction Standards: Group of nine carbon-13 labeled PCDD/F congeners added to the sample before the extraction. The function of the ES is to provide both qualitative (identifying the PCDD/F congeners) and quantitative (determining the concentrations) information on the sample. The measurement of the recoveries of the ES provides information on the extraction and fractionation efficiencies. Method 8290 call these "Internal Standards", while PAL has decided to adopt a more practical nomenclature.
- Cleanup Standards: A group of five labeled PCDD/F congeners that are added to the sample right after the extraction and before the fractionation. Their function is to measure the fractionation efficiencies independently of the extraction step. They are not required by Method 8290.
- Injection Standards: The two labeled PCDD congeners are added to the final extract just before GC/MS analysis. Their function is to measure the ES and CS recoveries. They are named "Recovery Standards" in Method 8290.
- EMPC: Term used to report the presence of a GC/MS signal that does not meet all the PCDD/F identification criteria. In particular, when the ion-abundance ratio of any unlabeled analyte falls outside the method's acceptable range, the associated peak can not be identified as a PCDD/F congener. PAL will report an Estimated Maximum Possible Concentration (EMPC) for that peak using the same formulae used to calculate the concentration of a detected analyte.

4.2 Equipment/Apparatus

- 12-L giant Soxhlet extractor (Ace Glass) with heat controller (GlasCol) and condenser for purification of supplies.
- Muffle furnace capable of temperatures of at least 500°C (Wilt, Model 210).
- Heavy-duty meat grinder (Berkel ES 22 or equivalent).
- Drying oven capable of at least 110°C (Fisher 106G) for moisture determinations only.
- Drying oven capable of at least 130°C (Fisher 825G) for supplies only.
- Dessicator all SS (Boekel).
- Top loading balance (0.01 g; Denver Instruments; XL-3100D).
- Aluminum weigh boats.
- Clean stainless steel forceps.
- Fume hood (Safeaire).
- Mortar and pestle.
- Certified and calibrated thermometer.
- Refrigerator ($4° \pm 2°C$) and freezer (-20°C).
- Complete SDS assembly (500-mL RB flask, thimble holder, Dean-Stark, condenser, heater)
- Pre-Cleaned thimbles.
- 90-mm filter assembly with a 6- place vacuum manifold.
- Pre-cleaned glass wool.
- 2 µm x 90-mm GMF 150 filters.
- 90-mm 3M C-18 Empore™ membrane disks.
- 10- and 25-mL drying columns.

- 40-mL wide-mouth sample jars.
- 40-mL VOA vials.
- Complete Accelerated Solvent Extractor assembly (Dionex ASE 200).
- 1.9 mm filter disks.
- 2-liter separatory funnel.
- Glass funnels.
- 250-mL beakers.
- 90-mm filter set-up with a 1-liter vacuum container.
- 2-liter Erlenmeyer.
- Microextractor for isooctane liquid-liquid partitioning.
- Hot plates (Fisher).
- 10 µl – 1000 µl automated pipette (eppendorf).
- Class A disposable 5 mL pipette.
- 1.8 mL autosampler vials.
- Stainless steel spatula.
- Pasteur pipettes.
- Glass beads.
- Vacuum chamber (Labconco) complete with an oil-free vacuum pump (Leybold) properly vented, and gauges.
- Welch 2025 oil-free vacuum pump.
- Rotary evaporator (Buchi R) equipped with a condenser, steam duct, "catch" flask, condensate flask, glass stopcock to adjust vacuum, peer-shaped sample flask, and water bath with temperature control.
- Double focussing mass spectrometer (MicroMass AutoSpec Ultima) coupled to a HP 6890 gas chromatograph (EPC) with capillary split/splitless injection port
- Autosampler (CTC A200 SE).
- OPUS Mass Spectrometer data system (CPU, monitor, disk and tape drives).
- Laboratory Information Management System (Labvantage Systems).
- Centrifuge (Damon IEC HN-SII).
- Recirculator (Polyscience and Neslab CFT-300).
- UPS (Exide Electonics).
- Water purification system (Dracor).
- High-precision solvent delivery pumps (Fluid Metering; Model RHSY).

4.3 Reagents

- Optima™, H_2SO_4
- Pre-cleaned Na_2SO_4.
- High Purity N_2 and He.
- Solvents: distilled-in-glass toluene, methylene chloride, hexane, acetone, isooctane and methanol.
- Purified tridecane (carbon treatment).
- Acid- and base-coated silica, alumina (acid and/or basic), and Florisil.
- Standards:
  - GC Performance: CIL R633 DB-225 Mixture (20-40 pg/µL)
  - GC Performance: CIL 31340-62 DB-5 Mixture (20-40 pg/µL)
  - Extraction Standards: CIL 31531-11 (1000 ng/mL; Table 1)
  - Cleanup Standards: CIL R681 (1000 ng/mL; Table 2)
  - Injection Standards: CIL R682 (500 ng/mL)
  - Matrix Spike or Lab Control Spike: CIL 29573-27 (2.5 ng/µL; Table 3)
  - ConCal: CIL CS-3 R685 (5.0 ng/mL)

- Calibration Standards: CIL (Table 4)
  - ✓ CS-1 (0.5 ng/mL); R683
  - ✓ CS-2 (1.0 ng/mL); R684
  - ✓ CS-3 (5.0 ng/mL); R685
  - ✓ CS-4 (50 ng/mL); R686
  - ✓ CS-5 (100 ng/mL); R687

- Preparation of Standards:

  - All entries and calculation details are made with the help of the LIMS Standards Preparation Program.
  - Call the Standards Preparation Program.
  - Follow the directives and menu options as required.
  - When all information entry is completed, print the Summary page.
  - In the space provided on the Summary page, write the page number.
  - Insert the Summary page inside the Standards Preparation Logbook (e.g., S-01).
  - When adequate, attach the supplier's "Certificate of Analysis" correctly labeled to facilitate traceability.
  - Print the waterproof label containing:
    - **Solution identification number,**
    - **Nominal concentration,** and
    - **Expiration date.**
  - Apply label on the vials and with the help of a magic marker, place a mark indicating the meniscus.
  - Keep all PCDD/F standard solutions at room temperature inside amber vials.
  - Expiration dates (apply only for nominal concentrations $\geq$0.1 ng/µL):
    - **Primary Standard Solutions** (ampoule from commercial source) have no expiration date.
    - **Stock Standard Solutions** (obtained from dilution/mixing/opening Primary Standard Solutions): 3 years.
    - **Working Standard Solutions** (from Stock/Primary and used as such during sample processing): 1 year.
  - Good practice: what is removed from the vial never returns to the vial.

4.4 Interferences

- The use of high purity reagents and solvents helps minimize interference problems. The use of distilled-in-glass solvents is highly recommended. Other precautions regarding cross-contamination consist of minimizing the use of re-usuable glassware, and effective glassware cleaning procedures.
- Co-extractants from the sample matrix are generally removed during the multi-chromatographic column procedure. The cleanup is designed to remove commonly encountered interferences (e.g., PCBs, DDT…). The resolution of the GC column and of the mass spectrometer provides additional tools in the elimination of interferences.
- Other types of materials have been found to interfere with the analysis, especially from a quantitative stand point. When operating, the analyst will evaluate the impact these interferences – named quantitative interferences[2,3] -- may have on the data, assign a data qualifier and present conclusions in the narrative or cover letter.

4.5 Safety

- The toxicity or carcinogenicity of each reagent used is not precisely defined. Each chemical compound should be treated as potential health hazard. Exposure to these chemicals must be kept to a minimum. Conducting some of the key operations inside a hood minimizes contamination of the laboratory. The effluent from the sample splitters for the GC should pass through an activated

carbon trap. Use protective gears (throwaway gloves, lab coat, safety glasses) is required in the laboratory area.

4.6 Sample Preservation

- Storage and Holding Times: All water samples are stored at 4°C. Samples are extracted within 30 days from the collection time, and the extract analyzed within 45 days of the extraction. Following the delivery of the data package, the backup sample (if any) is kept refrigerated for another 3 months, after which, the sample is moved into a room temperature storage awaiting final disposal.

- Sample Receipt:

  - Upon delivery to the lab, all containers are checked for noticeable damage that may affect the integrity of the contents. Report problems to the Project Manager so that client can be informed.
  - Open carefully the cooler and examine contents carefully for damage.
  - Record on the COC and the Sample Receipt Checklist the temperature (e.g., from the trip thermometer).
  - Sign, date and record the time on the COC.
  - Remove and examine all the contents of the cooler.
  - Verify that all the information on the COC matches the information on the sample bottle labels.
  - When applicable, verify the information pertaining to the sample preservation.
  - Sign the COC and complete the Sample Receipt Checklist (SRC).
  - At this time, take the COC and the SRC to a login computer station to assign a laboratory project number, a laboratory sample identification number, and enter the information into the LIMS.
  - Open a project folder to hold all the information generated for the project. This information becomes part of the Document Control section of the data package.
  - When the data entry for login is completed, print the sample receipt summary and the labels.
  - Apply the labels on the relevant sample containers and verify that the client sample identification number and the laboratory sample identification number coincide.
  - Place all project-related documentation in the folder. This includes the COC, carrier air bill, SRC, and any other documents (e.g., cover letter) that arrived with the samples.
  - Fax to the client the Sample Receipt Acknowledgment form.

- Sample Tracking and Storage

  - At data entry for login of the samples, a designated location is assigned to the project samples.
  - Once labeled, place the samples in the assigned location.
  - The normal locations are: (To locate the samples, check the location identifier in the LIMS.)

LIMS	Description	Storage
W2	Walk-in	Solids, Liquids
F1	Freezer	Tissues

- Review:

  - When a folder is completed and all the samples have been placed in their storage location, review the folder for completeness, correctness, and sensibility. If all is correct, the folder is placed into a queue awaiting completion of the analysis.

- Authorized Personnel

  - All employees associated with the Ultra-Trace Analysis Laboratory are permitted to access the samples in the storage areas.

- Sample Storage Temperature Recording

  - Place the calibrated thermometer and the supplied bottle inside the storage unit.
  - Attach the "Certificate of Calibration" to the storage unit specific logbook.
  - Record the temperature inside the logbook daily (except on Sundays; see Figure 6).
  - If the temperature deviates by more than 2 degrees, adjust the settings and document the action inside the logbook.
  - In case of prolonged downtime, use the back up generator or dry ice until power is restored or the unit is repaired.
  - One logbook per storage unit.
  - Place all non-biological samples in the refrigerators, while tissue samples are kept inside the freezers.
  - The samples from a given project are kept together by proper means.
  - Following the sample preparation /submission of the analytical report, keep the samples refrigerated for up to 30 d.
  - After such waiting period, immediately dispose of the biological samples while non-biological samples are stored at room temperature awaiting disposal.
  - Samples that have been found to contain more than 0.7 ppb TEQ must be segregated and crushed inside a 55-gallon drum for special disposal or can be returned to the Client when such arrangements have been made at bidding time.

Note: Do not store standards and/or food with the samples.

4.7 Sample Handling

Aqueous samples -- typically 1 L -- are allowed to come to room temperature. The chemist places a mark on the bottle indicating the level of the water inside the bottle. This will be used for determining the amount of water that is analyzed. The chemist also looks for the presence of particulates. Samples containing more than one percent solids are treated as solid matrices after filtration through a 0.45 μm filter.

4.8 Quality Control

- Method 8290 contains a series of performance checks including verifying the calibration of the mass spectrometer response and the various analyte relative response factors. The calibration entails an initial calibration (ICal) using a set of five solutions whose validity is verified every 12 H during which samples are analyzed (continuing calibration, or ConCal). The latter is performed using the middle point solution (CS3) of the calibration curve. Additionally, the GC/MS operator is required to verify and document the performance of the GC and MS systems. In particular, the homologue retention time windows, the 10,000 resolving power of the MS, and the 2,3,7,8-TCDD (or 2,3,7,8-TCDF) isomer specificity (25 percent valley) are established and documented every 12 H during which samples are analyzed. Balance is calibrated using NIST weights.

- During the initial start-up, the laboratory performs a Method Detection Limit (as per the CFR methodology), and determines the precision and bias. An on-going precision and accuracy (OPR) determination is conducted every day for each matrix undergoing analysis. A Laboratory Method Blank is always prepared alongside any batch of samples. A batch of samples is defined by Method 8290 as no more than 20 samples. PAL uses a more stringent schedule.

- Initial Calibration

  - Table 4 summarizes the composition of the five calibration solutions.
  - Each calibration solution is analyzed once, and the relative response factors (RRF) for unlabeled and labeled analytes computed for each analytical run.
  - For each unlabeled and labeled compound, an average RRF is calculated along with the relative standard deviation (RSD).
  - An acceptable ICal must meet the following criteria:

    - ✓ The signal-to-noise ratio for all analytes must be at least 10:1.
    - ✓ The ion abundance ratio for all analytes must be within 15 percent of the theoretical ratio.
    - ✓ The RSD obtained from the mean RRFs must be within 20 percent for the unlabeled analytes, and 30 percent for the labeled standards.

- Continuing Calibration

  - The authenticity of the ICal is validated at the beginning and the end of every 12-H shift during which samples are analyzed.
  - This is accomplished by analyzing CS-3, or the middle point of the calibration curve.
  - A valid ConCal meets the following specifications:

    - ✓ The signal-to-noise ratio for all analytes must be at least 10:1.
    - ✓ The ion abundance ratio for all analytes must be within 15 percent of the theoretical ratio.
    - ✓ The RRFs must be within 20 percent of the RRF (ICal) for the unlabeled analytes.
    - ✓ The RRFs must be within 30 percent of the RRF (ICal) for the labeled analytes.
    - ✓ For situations where the back-end ConCal fails, follow the chart shown in Figure 7, which is representative of the provisions written in Method 8290 Section 8.3.2.4 (September 1994)[5].

- Instrumentation Performance Checks

  - Instrumentation performance is verified and documented every 12 hours during which samples are analyzed.
  - The mass spectrometer resolving power of 10,000 (or 100 ppm mass resolution) is established at the beginning and ending of every 12-H shift during which samples are analyzed.
  - Additionally, the GC column performance – RETCHECK -- allows the GC/MS operator to define the various homologue retention time windows. It is also used to demonstrate the isomer specificity of the analysis for 2,3,7,8-TCDD on the DB-5 column and for 2,3,7,8-TCDF on the DB-225 column. A 25 percent valley between the close eluters for either analyte must be obtained before samples can be analyzed.

    Note: Confirmation of 2,3,7,8-TCDF on the DB-225 column is completed when its concentration as determined on the DB-5 column is less than half the lowest calibration point (<0.25 pg/μL).

- Batch QC Samples

  - Laboratory Method Blank (LMB): Always processed alongside a batch of samples. Paradigm Analytical Labs defines a batch of samples as no more than 10 samples processed simultaneously (EPA defines a batch as made of 20 samples). The LMB is obtained following the exact same steps used to process field samples with the exception of the actual matrix. Generally, soil is replaced by sand, effluent by DI water, Method 23 resin by XAD-2 resin from the same batch used to prepare the air sampling modules sent to the field, and biological tissues by vegetable oil.

Acceptable method blank shows (Figure 8):

a) Recoveries of the extraction standards within the specification of the method,

b) Detection limits that are within a factor of five from the MDL, and

c) No target analytes at concentrations exceeding the guidelines presented in Figure 8 when analyzing samples showing high levels of PCDD/Fs (i.e., more than 100 times the method calibration lower limit). Otherwise, the level of the specific target analyte should not exceed 50 percent of the lower limit of the calibration curve.

An invalid LMB requires a re-extraction of the affected samples.

- On-Going Precision and Recovery Sample (OPR): In addition to the initial demonstration of system's performance, an On-Going Precision and Recovery sample is processed daily for batches of samples of a given matrix and for a given core methodology. The OPR is fortified with the collection of seventeen 2,3,7,8-substituted PCDD/Fs at levels corresponding to the core method's quantitation limit. (OPR is synonymous with Lab Control Spike or LCS.)

  Acceptable performance is determined by:

  - ✓ Recoveries of the isotopically-labeled extraction standards to fall within the 40 to 135 percent range for the tetra- through octachlorinated congeners, while
  - ✓ Recoveries (accuracy) of the unlabeled compounds should be 100 $\pm$ 35 percent when spiked at the method quantitation limit and $\pm$ 30 percent when spiked above 20 times the method quantitation limit, and
  - ✓ When duplicate OPR are required, the relative percent difference (RPD) of the unlabeled analytes concentrations should be within 30 percent when spiked at the method quantitation limit and $\pm$ 25 percent when spiked above 20 times the method quantitation limit.

- Matrix Spike (MS): When requested, a matrix spike (MS) and matrix spike duplicate (MSD) samples are analyzed by subjecting another aliquot of the designated field sample to the same procedures as the regular sample but with the addition of the collection of the seventeen 2,3,7,8-substituted PCDD/F congeners (200 ppt for solid and 200 ppq for aqueous matrices).

  Acceptable performance is determined by:

  - ✓ Recoveries of the isotopically-labeled extraction standards to fall within the 40 to 135 percent range for the tetra- through octachlorinated congeners, while
  - ✓ Recoveries (accuracy) of the unlabeled compounds should be 100 $\pm$ 30 percent assuming no "significant" amounts of endogenous analytes are present in the sample.
  - ✓ When duplicate MS/MSD are required, the relative percent difference (RPD) of the unlabeled analytes concentrations should be within 20 percent.

- Duplicate Analyses: When requested, a second aliquot of the field sample is analyzed following the same procedures.

  Acceptable performance is determined by:

  - ✓ Recoveries of the isotopically-labeled extraction standards to fall within the 40 to 135 percent range for the tetra- through octachlorinated congeners, while

- ✓ The relative percent difference (RPD) of the unlabeled analytes concentrations should be within 25 percent provided the analyte levels are within the calibration range.

- Quality Control Charts: Quality control charts are designed to detect trends and deviations from normal performance. A variety of charts are developed and analyzed on a regular basis to ensure adequate system performance. Whenever possible, lower and upper control and warning limits are defined to help with the management of the laboratory operations. Such information can be reviewed as part of a laboratory audit.

  - Examples of charts that can be monitored include:
    - ✓ Lab Method Blank for background contamination (e.g., OCDD levels in LMB vs time).
    - ✓ Daily OPR results for analyte and labeled compounds recoveries.
    - ✓ LMB recoveries of the extraction and cleanup standards.
    - ✓ ConCal RRF deviations.
    - ✓ GC column resolution.
    - ✓ Certain MS parameters (e.g., air ratio to He, amplitude of PFK reference peaks, repeller…).

4.9 Analytical Procedures

- Aqueous samples are processed as shown on Figures 1, 2, 3 , 4 and 5. Four separate extraction procedures are currently available for aqueous samples. Each of the key steps in the procedure is described in the SOPs referred to on the diagram. Documentation of the completion of each of the key step (e.g., spiking, extraction, concentration, fractionation, dates, initials of the chemist…) is recorded on the Sample Tracking & Management Forms (Figures 1, 2, 3, 4, 5, 10, 11, 12, 13, and 14). The documentation also includes a Communication (Figure 13) sheet where the chemist notes any relevant observations made about the samples, and the handling of the sample. Batches of solvents, reagents, GC columns and the likes are recorded on the aforementioned forms.

- Sample Fortification

  At the extraction stage:

  - Aliquot 1 mL of acetone to each autosampler vial; equal in number to samples requiring spiking.
  - To each vial, add 40 µl of Extraction Standards (0.1 ng/µl). It is advisable to have a 'witness' present so that double spiking or omissions can be avoided.
  - Cap the vial and vortex. Vortexing will ensure that the concentrated standard cocktail in n-nonane is thoroughly mixed into solution.
  - Pour the acetone solution into the sample. Holding the upside down, rinse the vial with a small quantity of acetone.
  - For water samples, cap the container and shake vigorously.

  Note: For the isooctane liquid-liquid micro-extraction option, it is not necessary to spike the water with acetone.

  At the cleanup stage:

  - To each labeled archive test tube, add 40 µl of Clean-Up Standards (0.1ng/µl). As stated above, it is advisable to have a second person observe this procedure as to avoid double spiking of a sample extract, and omissions.

At the analysis stage:

- Before GC/MS analysis, add to each **labeled** autosampler vial 20 µL of the Injection Standards nonane solution.
- Vortex each vial and allow to sit.
- Wash the walls of the vial again by rotating the vial slowly in a horizontal disposition. This ensures that all vial surfaces come in contact with the standard.

- Sample Conditioning:

  - Mark the level of sample on the outside of the sample container for future volume determination.
  - Test the pH of the sample and adjust to less than pH 2 with H_2SO_4.
  - Add the extraction standards to the sample, shake vigorously and allow to sit for 1 H.
  - For the isooctane liquid-liquid microextraction option, do not add the ES in acetone. Just add the 20 µL of the nonane solution directly to the water.
  - If visible particulates are present,

    - ✓ Quantitatively transfer the sample to the vacuum assembly reservoir and filter through a 90-mm GMF 150 filter, collecting the filtrate for extraction. The filter is saved and extracted by Method 3545 or by Soxhlet Dean-Stark.

- Separatory Funnel Liquid-Liquid Extraction:

  - Prepare drying funnels by packing the neck of the funnel with glass wool.
  - Add approximately 10-15 g of Na_2SO_4 on top of the glass wool and position over an appropriately labeled collection beaker.
  - Add 0.5 mL of tridecane inside the beaker to act as a 'keeper'.
  - Transfer the filtrate to the separatory funnel and add 60 mL of dichloromethane.
  - Rinse the vacuum flask, then the sample container with solvent prior to adding it to the separatory funnel.
  - Shake for at least 2 min, periodically purging the separatory of any built-up pressure.
  - Allow the sample-solvent solution to settle out and form a distinct interface.
  - Drain the solvent through the salt funnel and collect.
  - Repeat the extraction twice more, collecting all the solvent into the same beaker.
  - Concentrate the sample in the vacuum concentrator (SP-N-01).
  - Prepare a 25-mL salt column as above and dry the toluene from the Method 3545 extraction.
  - If necessary, decant the water present before adding the toluene to the drying column.
  - Concentrate this sample fraction in the vacuum concentrator (SP-N-01).
  - **Combine the two extracts** (SP-D-01) and clean up the combined extract (SP-U-03) in preparation for analysis.

- Isooctane Liquid-Liquid Microextraction:

  - When new, preclean the assembly by microextraction (1 L of DI water for 60 min using isooctane).
  - Discard the isooctane and the water.
  - Rinse the inside of the column with several mL of DI water, followed by several mL of hexane, followed by DI water.
  - Tip the column to draw out most of the water.
  - Between samples, rinse the unit with several mL water, followed by hexane, and again water.
  - With the unit precleaned, add a few mL of DI water inside the column, and 1 to 1.5 mL of isooctane.
  - Transfer the water sample or, as appropriate, the filtrate inside the Erlenmeyer.
  - Add a few glass beads as boiling chips.

- Adapt the Erlenmeyer flask to the column.
- Cover the top of the column with clean foil.
- Allow cooling water to circulate through the condenser.
- Start heating by turning the knob to position "9".
- Once the water starts boiling, make note of the time and allow the heat to continue for another 60 minutes.
- Note that the water vapor should not rise by more than 75 percent of the height of the column.
- After 60 min, turn off the heat and allow the system to cool down.
- Slowly drain the majority of the water to waste, and
- Do not allow the isooctane to move inside the return inner glass tubing,
- Capture the rest of the water and the isooctane layer directly inside a disposable and labeled centrifuge tube.
- Tip the column to draw out most of the isooctane/water.
- Rinse the inside of the column with several mL of hexane (5 mL); drain directly inside the tube.
- Tip the column to draw out most of the hexane/water.
- Allow the two layers (aqueous/organic) to separate.
- Using a pipette, draw the organic layer and transfer to a Pasteur pipette containing glasswool and sodium sulfate.
- Rinse the sodium sulfate with another 5 mL of hexane, which were added to the original centrifuge tube.
- Care must be taken to ensure that **NO water is added to the sodium sulfate**.
- Collect inside a labeled wide-mouth jar.
- Add the CS as specified on the paper work.
- **Do not add tridecane.**
- Concentrate to near dryness under vacuum.
- Transfer inside an autosampler vial using 1-2 mL of methylene chloride.
- Concentrate to dryness.
- The extract is ready for HRGC/HRMS analysis.

◆ Solid Phase C_{18} Extraction:

Preparation:

- Prepare drying columns by packing the neck of the column with glass wool.
- Add approximately 10-15 g of Na_2SO_4 on top of the glass wool and position over an appropriately labeled collection jar.
- Add 0.5 mL of tridecane inside the jar to act as a 'keeper'.
- Mark the level of sample on the outside of the sample container for future volume determination.
- **Add 5 mL methanol.**
- Test the pH of the sample and adjust too less than pH 2 with H_2SO_4. Use a minimum of 5 mL conc. Acid and water (1:1).
- Add Extraction Standards to the sample, shake vigorously and allow to sit for 1 H **with occasional shakings**.

Filtration:

- Assemble the vacuum apparatus by first placing the C_{18} onto the fritted support covered by the pre-filter.
- Place the reservoir carefully over the filters and clamp in place.
- Pre-condition the filters with **50 mL** of methanol. Let soak for 2 min. Vacuum off all but 1 mL of the methanol.
- Add 50 mL of DI water to the reservoir and vacuum through the filters to rinse out the methanol.

- Add a second 50 mL of DI water and vacuum through the filters; **DO NOT GO TO DRYNESS**.
- Quantitatively transfer the sample to the vacuum assembly reservoir and filter at a rate not to exceed 50 mL per minute.
- Rinse the sample container and the reservoir with small washes using DI water.
- Vacuum to dryness and continue pulling vacuum for a minimum of **20 minutes**.

Extraction:

- Remove the filter assembly from the manifold and place a 40-mL VOA vial into the manifold.
- Replace the filter assembly onto the manifold ensuring that the filter spout is inside the VOA vial.
- With the vacuum on, add approximately 1-2-mL of methanol to displace any remaining water.
- Add 2 x 10 mL of toluene to the reservoir, collecting the solvents into the VOA vial.
- Disassemble the vacuum apparatus.
- The pre-filter is saved and extracted by Method 3545 (SP-E-03).
- Discard the C_{18} disk.
- Dry the toluene/methanol extract through a salt column.
- Concentrate the sample in the vacuum concentrator (SP-N-01).
- Prepare a 25-mL salt column as above and dry the toluene from the Method 3545 extraction.
- If necessary, decant the water present before adding the toluene to the drying column.
- Concentrate this sample fraction.
- **Combine the two extracts.**

◆ Solid Phase Extraction by Carbon Adsorption Diffusion:

Preparation of the Carbon/Celite Tea Bag:

- Prepare a number of tea bags (2.5 cm x 2.5 cm) and insert 100 mg of carbon/Celite
- Soxhlet enough tea bags to fill the thimble holder using toluene for 16 H.
- Drain the toluene, and dry inside the vacuum chamber.
- Store in a clean, labeled glass container.

Procedure:

- Keep the water inside the original bottle.
- Make a mark on the bottle to measure the volume of its contents later.
- Verify solid contents is less than 1 percent. If more than 1 percent, treat the water as a solid sample (SOP SP-E-03).
- Measure the pH.
- Add 5 mL methanol.
- Add 5 mL conc. H_2SO_4 – H_2O (1:1).
- Add 20 of ES in 1 mL of **ethanol**.
- Add a tea bag containing the carbon/Celite.
- Cap the bottle, shake, and stir for 60 min using a Teflon™ stirring bar.
- Let the water settle for a few minutes allowing all particulates to decant.
- Gently filter the supernatant through a glassfiber filter (GMF 150 filter).
- Transfer the sediment last and retrieve the tea bag.
- Determine the volume of the sample by adding DI water and using a volumetric cylinder.
- Perform a M3545 extraction using toluene at 200°C and 2000 psi (SOP SP-E-03).
- Add 20 uL of CS.
- **Add 0.5 mL of tridecane.**

- Dry the toluene using a sodium sulfate column (do not transfer water to the column) and collecting the solvent inside a jar.
- Concentrate to near dryness ensuring that no traces of toluene are present.
- Transfer the tridecane residue inside a 10-mL tube, and adjust the volume to 7 mL using hexane.
- Archive 50% and transfer 3.5 mL to the cleanup procedure (PCU-F) and analysis by HRGC/HRMS.

- Soxhlet Dean-Stark Extraction:

  - Pre-Soxhlet the unit before using it for samples.
  - To that effect, assemble the SDS without the condenser.
  - Add a couple of Teflon™ chips inside the 500-mL round-bottom flask.
  - Add 300 mL of toluene through the DS section.
  - Assemble the condenser and insulate the "vapor pathway".
  - Turn on the water recirculator, which is set between 4° and 7°C.
  - Turn on the heating mantle to position "9" for toluene.
  - Allow the reflux to go on for at least three hours.
  - Turn off the heating element, and allow the unit to cool down.
  - Transfer the toluene inside a labeled bottle container (for washing dirty glassware).
  - Add a couple of fresh Teflon™ chips.
  - Add 350 mL of toluene and **0.5 mL of purified tridecane**.
  - Adapt the thimble holder and insert the thimble containing the **fortified** sample using a clean SS spatula. Use 20 g dry-weight equivalent.
  - Assemble the DS and condenser components.
  - Cap the opened extremity of the condenser with foil.
  - Turn on the water recirculator (set between 4° and 7°C) and heater (position "9") for toluene.
  - Insulate the "vapor pathway".
  - Allow the extraction to continue for 16 to 18 H.
  - During the extraction, verify that the solvent siphons normally.
  - Drain the water as appropriate to prevent water from returning to the boiling flask.
  - At the end of the reflux cycle time, proceed with the sample concentration as described below.
  - **Do not turn off the heater.**
  - Drain the toluene present in the DS side arm directly inside the labeled bottle container (for washing dirty glassware).
  - Continue to drain the toluene until approximately 20 mL of toluene remains inside the RB flask.
  - Turn off the heater when the toluene reaches the 20-mL mark. **Do not go to "near dryness".**
  - The toluene inside the thimble holder is removed and disposed off.
  - Remove the heating mantle and allow the flask to cool down.
  - The sample is now ready for the vacuum concentrator (SP-N-01).

- Method 3545 Extraction:

  - Fill all solvent reservoirs with appropriate solvent.
  - Ensure that the purging gas cylinder (N_2) has a minimum of 500 psi pressure.
  - Load a disposable 1.9 mm filter into each cell to be used and top with 2-4 g of clean sand.
  - Transfer 20 g dry wt. equivalent of sample to an extraction cell and fill any remaining headspace with clean sand.
  - Using a spatula, mix as thoroughly as possible the sand into the sample.
  - Spike each extraction cell with the appropriate extraction standards.
  - Replace the tops onto the extraction cells and load onto the ASE.
  - Ensure that the correct number of collection vials is also loaded.
  - Add 0.5 mL of tridecane to each collection vial.
  - Begin the extraction process according to the manufacturer recommendations.
  - Extractor conditions:

Oven Temp.:	200°C (for toluene)
Pressure:	2000psi
Static Time:	10 min.
Flush Vol.:	60%
N_2 Purge:	70 sec.
Static Cycles:	2

These conditions have been optimized and all MDL studies and subsequent sample extractions have utilized the above conditions.

- Allow all extracts to cool prior to drying with sodium sulfate and concentration.

- Sample Extract Concentration

  - The rotary evaporator is equipped with a condenser, steam duct, "catch" flask, condensate flask, glass stopcock to adjust vacuum, peer-shaped sample flask, and water bath with temperature control.
  - All glassware must be cleaned between samples:
    - ✓ **Rinse the steam duct with acetone using squeeze bottle while rotating the unit.**
    - ✓ **The "catch" and pear-shaped flasks must be replaced by clean ones between samples.**
  - Water chiller providing water for the rotary evaporator condenser at 5°C.
  - An oil-free vacuum pump properly vented with gauge.
  - Set the water bath temperature to 40°C making sure enough DI water is present.
  - Allow cold water to circulate inside the condenser.
  - Turn the vacuum pump into the "on" position.
  - Make sure the glass stopcock is in the open position.
  - Attach the sample and "catch" flasks assembly onto the steam duct.
  - Hold the assembly or place the clamp to insure the assembly does not fall inside the water bath.
  - Close the glass stopcock.
  - Monitor the pressure gauge.
  - Normally with solvents such as toluene and methylene chloride, the reading should be in the 300 to 700 mm Hg range.
  - The solvent starts evaporating and condensation becomes visible.
  - Maintain steady evaporation rate and make sure no bumping is occuring.
  - If bumping happens, reduce the pressure to less than 300 mm Hg on the vacuum pump or using the glass stopcock.
  - When bumping occurs, contact laboratory manager to discuss viable options to address sample integrity.
  - Once the level of solvent is low enough (0.5 to 2 mL), reduce the rotation (position 1-2) and re-establish atmospheric pressure by opening fully the glass stopcock and switching off the pump (that is if you don't have a need for it). Switch off the rotation.
  - Remove the glass assembly (i.e., the "catch" and the pear-shaped flasks).
  - Turn off water heater and cooling water.
  - Rinse the steam duct (vide supra) and wash glassware.
  - Note: Normally, 0.5 mL tridecane remains. **However, to ensure complete solvent exchange before the sample cleanup, it is necessary to complete the solvent concentration and exchange using the vacuum concentrator (see below).**

- When using the vacuum chamber, place the 500-mL round-bottom flask on a cork ring, the sample bottle, 100-mL jar, 1-mL vial inside the vacuum chamber.
- Turn the vacuum pump into the "on" position.
- Follow the program shown in Table 5.

- Sample Fractionation

  - Prepare an Acid/Base Silica Column (25-mL pipet):

From bottom:
- glasswool
- 1 g SiO_2,
- 4 g NaOH-coated,
- 1 g SiO_2,
- 8 g H_2SO_4-coated,
- 2 g SiO_2,
- 4 g Na_2SO_4.

All solvents are stored inside dedicated bottles with Teflon™ connections to the columns. An hexane-dedicated pump is used for the elution of the tandem columns. Do not use the hexane pump to deliver other solvent systems. When a single pump is used to deliver 2% MC/hexane and straight MC, always flush the line with the eluant before allowing the eluant to reach the column.

- The acid/base-modified silica column is washed with hexane,
- Sample loaded with two 1-mL rinses of hexane and
- Eluted with 100 mL hexane directly into a pre-washed Florisil column.

  - Florisil column cleanup (1.5-1.6 g, 10-mL pipet, directly from the supplier's jar, no activation, reseal jar):

- Pre-elute column with MC.
- Then with hexane/MC (98:2).
- The column is ready for the tandem set up.
- Once the 100 mL hexane from the tandem columns has eluted off,
- Remove the silica column and connect the Florisil to the 2% MC/hexane bottle delivery line.
- Elute with about 20 mL hexane/MC (98:2).
- This fraction goes to waste.
- Elute with about 35 mL MC.
- Collect MC eluate.
- Concentrate the MC eluate.
- Transfer using MC inside an autosampler vial
- Concentrate to dryness

- Sample Analysis by HRGC/HRMS

  - HRGC/HRMS instrument setup

  - The GC temperature/pressure/flow program is stored on the instrument as [vg.opus$instrument]DEFAULT.
  - The MS experiment is stored on the instrument as [vg.opus$experiment]M23_DB5 (Table 6).

  - HRGC/HRMS pre-sample analysis checks

  - Perform any daily PM (see SOP PM-02).
  - Tune the MS resolution to 100 ppm (or 10,000 resolving power using the 10% valley definition).
  - Acquire location data to calibrate the MS and print a copy of function one's MS resolution.
  - Inject the retention time windowing mix for the column in use. Then evaluate switching times for accuracy and make any corrections, reanalysis maybe required for a large correction. If the switching times are off by a considerable amount, the reason for the change should be found, then

a survey scan should be analyzed to find the new switching times. This injection is also used to verify that there is less then 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 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 CS3 may be analyzed to verify continuing calibration. If the curve or the CS3 passes method requirements sample analysis may begin.

- HRGC/HRMS sample analysis

- Reconstitution of a sample is accomplished by adding nonane containing the injection standards, capping the vial, and mixing well with a vortex (see SOP SP-S-01).
- Samples are injected under conditions identical to that used to establish calibration.

- HRGC/HRMS post-sample analysis checks

- A "back-end" CS3 must be injected within 12 H from the front end CS3 or the CS3 in the curve. This standard is used to verify sufficient stability of the calibration after sample analysis. It has requirements set by the method. Depending on the back-end CS3 results, different calibration files maybe required to quantitate the samples (see SOP RP-G-03). These results also may require a new initial calibration.
- A "back-end" print out of the MS resolution must also be performed.

- HRGC/HRMS sample package assembly and QC data filing

- The QC 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 and the front/back end CS3s.
- Each samples hardcopy should include the quant report, totals pages, deviations, chromatograms, and report forms.

4.10Data Validation

- Data Review

  - Use the check list shown in Figure 9 when conducting the validation of the data.
  - When MS/MSD and/or duplicate analyses have been requested, verify that the results are within the acceptable performance criteria outlined in the Quality Control section of this document.
  - Data qualifiers are used whenever deviations or analytical difficulties are encountered. Data that do not meet the QA/QC specifications need to be reviewed on a case-by-case basis before rejecting the data. An assessment of the impact on the data is discussed in the cover letter or narrative. When data is rejected, mark across the data set "Rejected" and provide the reason for the rejection. Also, state the corrective action(s) taken to remedy this situation. Generally, rejected data will require a re-extraction and analysis of the sample (if ample sample is available). Typical data qualifiers are:

    - ✓ "B" for any analyte found in the LMB at levels exceeding the recommended value.
    - ✓ "V" to validate results from samples showing recoveries of less than 40 percent.
    - ✓ "R" to reject the data for a particular congener due to low recoveries of the associated extraction/cleanup standard.
    - ✓ "D" to indicate the presence of a possible chlrorinated diphenylether.
    - ✓ "E" to indicate that the analyte concentration exceeded the upper range of the calibration curve.

✓ "Q" to indicate the presence of a quantitative interferrence.[2,3]

4.11 Calculations

- Relative Response Factors: For each calibration solution (ICal or ConCal), the analyte relative response factor is calculated according to the formulae shown below.

$$RRF_a = \frac{A_a \times Q_{es}}{A_{es} \times Q_a}$$

Where RRF_a represents the relative response factor of the analyte "a"

A_a represents the summed area of the two ions monitored for analyte "a",
A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,
Q_a represents the absolute amount or concentration of the analyte "a" in the solution, and
Q_{es} represents the absolute amount or concentration of the extraction standard in the solution.

- Analyte Concentration: The concentration of each of the 17 2,3,7,8-substituted PCDD/F congeners is obtained according the formulae below.

$$C_a = \frac{A_a \times Q_{es}}{A_{es} \times \underline{RRF}_a \times w}$$

Where C_a represents the concentration of the analyte "a" in the sample,

A_a represents the summed area of the two ions monitored for analyte "a",
A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,
Q_{es} represents the amount of the extraction standard added to the sample before the extraction,
w is the volume of water expressed in mL, and
$\underline{RRF}_a$ is the average of the five RRFs obtained for analyte "a" during the ICal.

- Labeled Compounds Recovery: The recoveries of the extraction (or cleanup) standards are obtained using the following expression.

$$\text{"Percent Recovery"} = \frac{A_{es} \times Q_{js}}{Q_{es} \times A_{js} \times \underline{RRF}_{es}} \times 100$$

Where "Percent Recovery" is the extraction standard recovery expressed in percent,

A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,
A_{js} represents the summed area of the two ions monitored for the labeled injection standard,
Q_{es} represents the amount of the extraction standard added to the sample before the extraction,
Q_{js} represents the amount of the injection standard added to the sample before GC/MS analysis,
$\underline{RRF}_{es}$ is the average of the five RRFs obtained for the extraction standard during the ICal.

Note: The same formulae can be applied for the computation of the cleanup standard recoveries (CS). In this case, replace "es" by "cs" in the above equation.

- Detection Limit: The detection for each of the 17 2,3,7,8-substituted PCDD/F congeners is obtained according the formulae below.

$$DL_a = 2.5 \times \frac{A_a \times Q_{es}}{A_{es} \times \underline{RRF_a} \times w}$$

Where DL_a represents the detection limit for analyte "a" in the sample,

A_a is the summed area for the noise measured for the two ions monitored for analyte "a",
A_{es} represents the summed area of the two ions monitored for the labeled extraction standard,
Q_{es} represents the amount of the extraction standard added to the sample before the extraction,
w is the volume of water expressed in mL, and
$\underline{RRF_a}$ is the average of the five RRFs obtained for analyte "a" during the Ical.

- Relative Percent Difference (RPD): Difference expressed as a percentage of the mean.

$$RPD = \frac{|X_1 - X_2|}{(X_1 + X_2)/2}$$

where X_1 and X_2 are the duplicate results for a particular analyte.

4.12References

1. Y. Tondeur and W.F. Beckert; "Method 8290: Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by High-Resolution Gas Chromatography / High-Resolution Mass Spectrometry", USEPA, EMSL-LV.

2. Yves Tondeur, Philip W. Albro, J. Ronald Hass, Donald J. Harvan, and J. L. Schroeder, "Matrix Effect in Determination of 2,3,7,8- Tetrachlorodibenzo-p-Dioxin by Mass Spectrometry." *Anal. Chem. 56:1344-1347, 1984.*

3. Yves Tondeur, W. J. Niederhut, J. Campana and S. R. Missler; "A Hybrid HRGC/MS/MS Method for the Characterization of Tetrachlorinated-p-Dioxins in Environmental Samples." *Bio. Med. and Environ. Mass Spectr. 14, 449-456, 1987.*

4. *Paradigm Analytical Labs Standard Operating Procedures for the Measurement of PCDD/Fs in Environmental Samples by Isotope-Dilution HRGC/HRMS: see Figure 14 for a complete listing.*

5. *Method 8290, PCDD/Ss by HRGC/HRMS; Revision 0, September 1994; SW-846.*

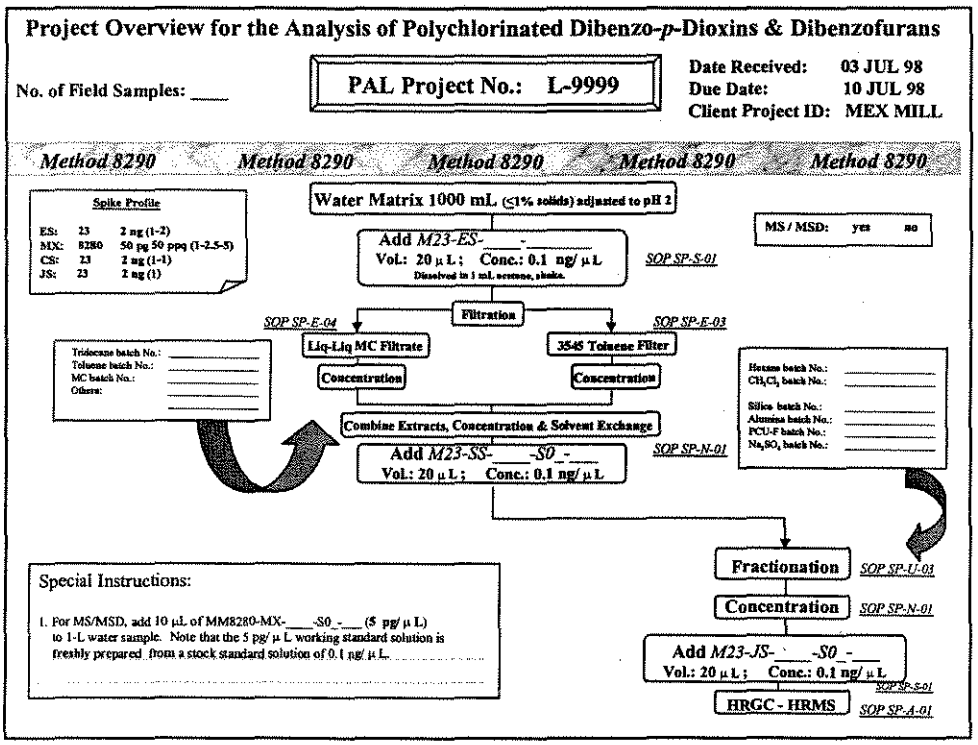


Figure 1: Schematic representation of Method 8290 for aqueous matrices using the liquid-liquid partitioning (methylene chloride) technique on the filtrate and Method 3545 toluene extraction of the filter and particulates.

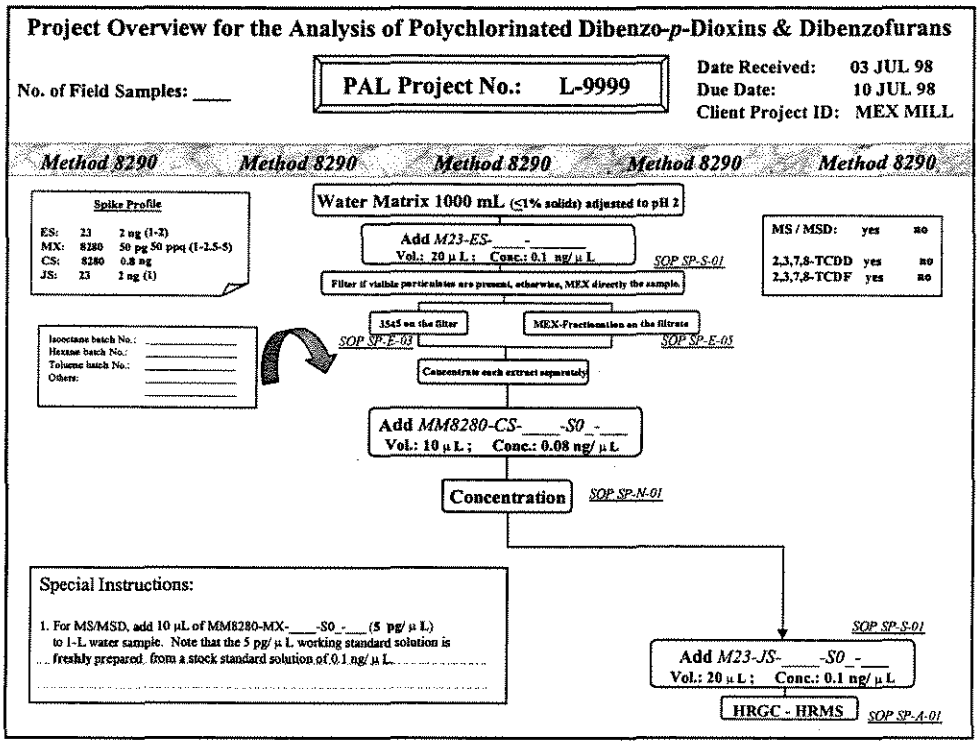


Figure 2: Schematic representation of Method 8290 for aqueous matrices using the liquid-liquid partitioning (isooctane) microextraction technique on the filtrate and Method 3545 toluene extraction of the filter and particulates.

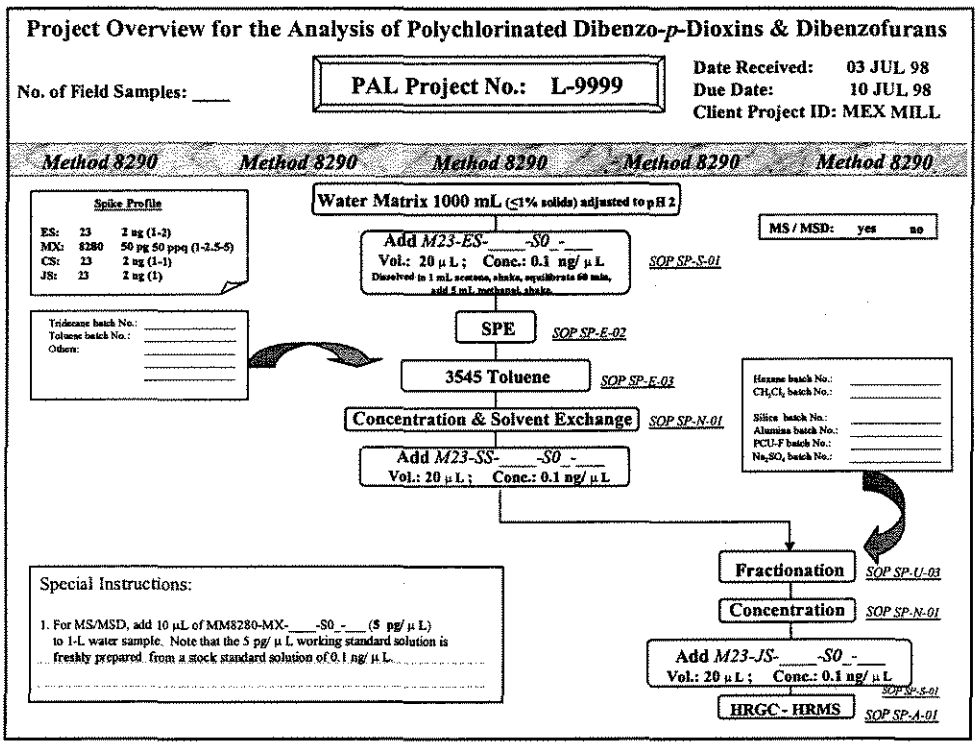


Figure 3: Schematic representation of Method 8290 for aqueous matrices using the C_{18}-disk solid phase extraction technique on the water sample followed by Method 3545 toluene extraction of the filter and particulates.

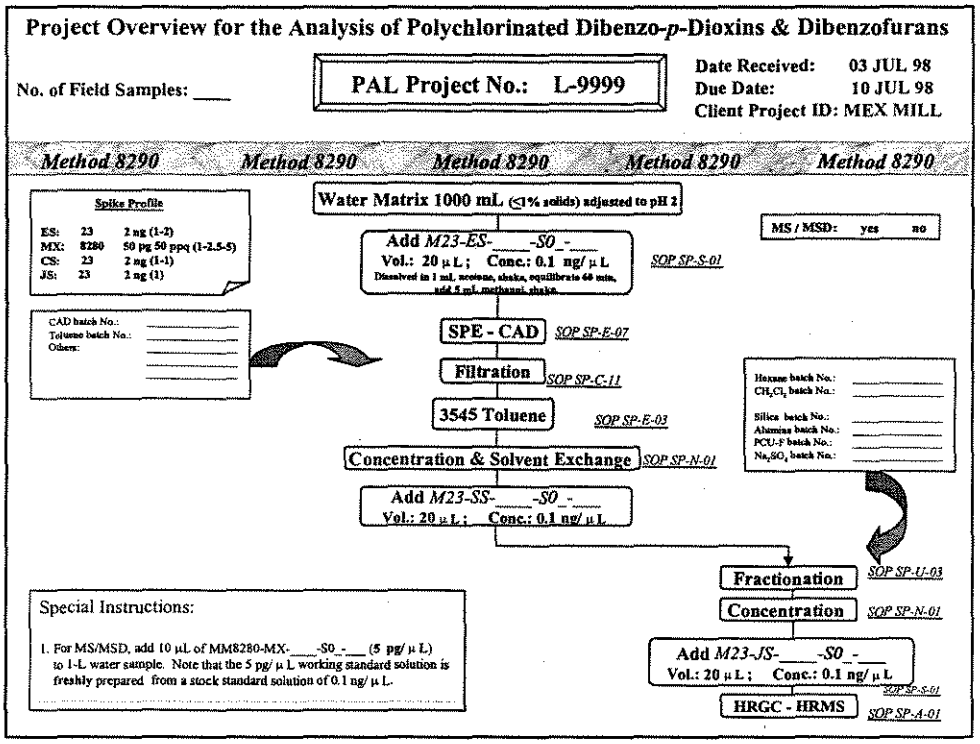


Figure 4: Schematic representation of Method 8290 for aqueous matrices using the Carbon Adsorption Diffusion solid phase extraction technique on the water sample followed by Method 3545 toluene extraction of the filter, solid phase material and particulates.

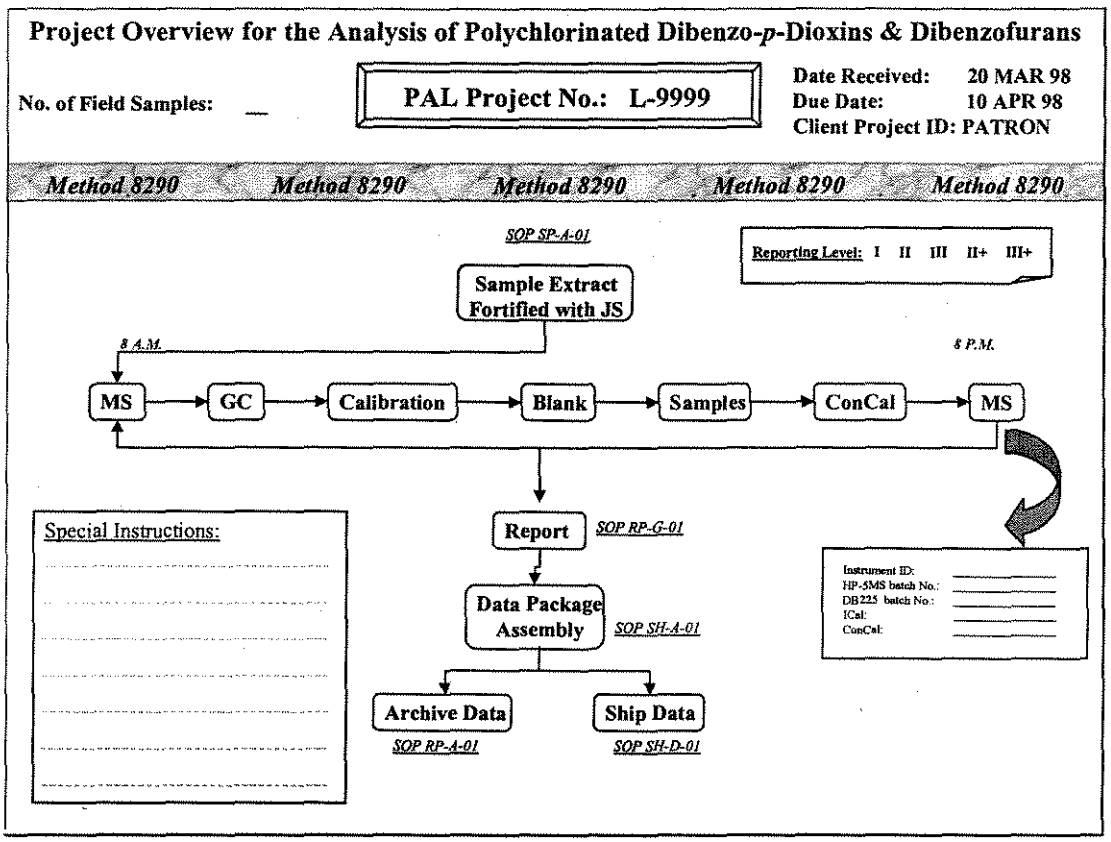


Figure 5: Schematic representation of the analysis and reporting phases of Method 8290.

Sample Storage F 1 Temperature					Logbook No. 1 Page____
Date	**°C**	**Corrective Action**	**Date**	**°C**	**Corrective Action**

Figure 6: Sample storage temperature tracking.

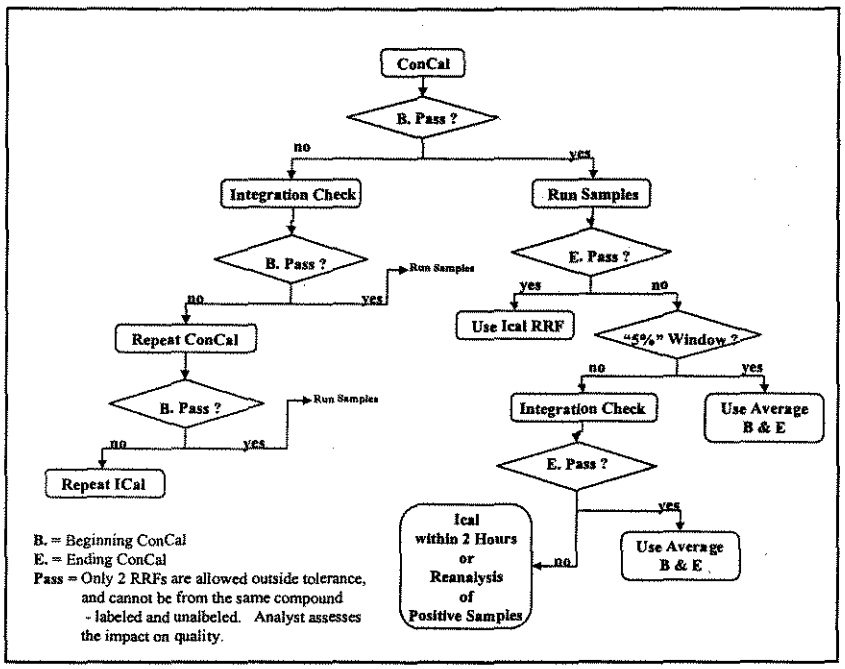


Figure 7: Decision flow chart for handling ConCals.

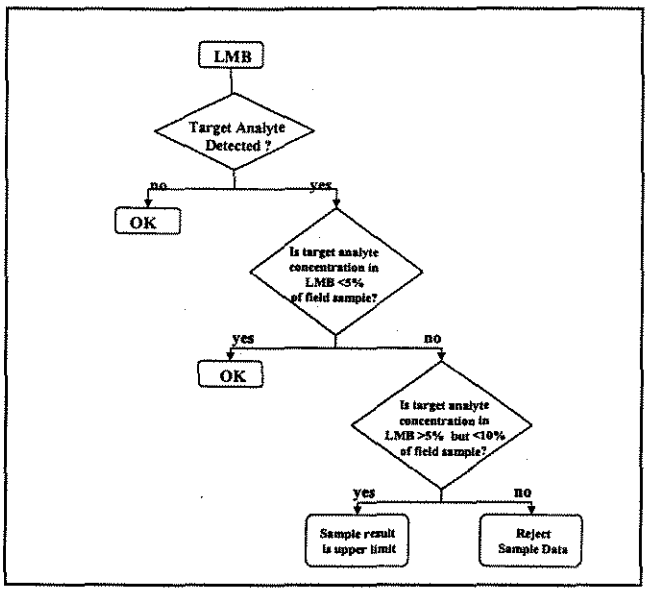


Figure 8: Decision chart for handling background levels of PCDD/Fs in the LMB.

PAL Project No.: _____

Paradigm Analytical Labs
Data Review Check List

Item	Initials
1. Initial Data Package Components (Section 2): Project Overview & Sample Tracking/Management Forms	
➢ COC	
➢ Correspondence	
➢ Login information	
➢ Injection Log	
2. Initial Data Package Components (Section 3): Analytical Results	
➢ Two-page Summary Topsheet	
➢ Raw data containing the retention times, areas, signal-to-noise ratios, totals, ion ratios…	
➢ Raw data showing all relevant selected ion current profiles (i.e., chromatograms).	
3. Project Overview	
➢ Check and read the communication page.	
➢ Read any correspondence accompanying this project.	
➢ Verify that the COC is present and signed.	
➢ Verify that the login report is present and signed.	
➢ Verify that the SRC is present and signed.	
➢ Verify that the number of samples is consistent with client's request, COC, correspondence.	
➢ Verify that the method information is correct.	
➢ Verify that all relevant entries have been made on the laboratory tracking forms)including page No.).	
➢ Review spiking information.	
➢ Verify sample preparation information.	
➢ Look for any special instructions.	
4. Sample Results & Overview	
➢ Injection Log must be present for each PAL project.	
➢ Have at hands the MS and GC performance checks associated with this analytical run.	
➢ Have at hands the associated ConCals (begin and end).	
➢ Raw data including SICPs and totals list, areas, S/N, retention times, and summary QUAN reports.	
➢ TCDF confirmation data if necessary.	
5. Data Review	
• From the injection log, verify the time and date for the various system performance checks (12-H).	
➢ Verify that the OPR passed, MS/MSD and/or Duplicates as appropriate	
• Verify that system performance checks passed (MS, GC, Calibrations).	
➢ 100 ppm in mass for the resolution at m/z 317.	
➢ <25% valley for 2,3,7,8-TCDD (and/or 2,3,7,8-TCDF).	
➢ Deviations for ConCal are <20% for unlabeled (beginning) or <25% for unlabeled (ending).	
➢ Deviations for ConCal are <30% for labeled (beginning) or <35% for labeled (ending).	
➢ See SOP RP-G-03 for handling deviations.	
➢ Verify that all ion-abundance ratios passed.	
➢ All of the above apply to confirmation analyses as well.	
• For each samples, and starting with the LMB, and check the following:	
➢ Verify client, laboratory and sample information (matrix, weight, volume, file name, ICal, ConCal and RetCheck file names, dates…).	
➢ Verify the name of the client.	
➢ Verify the PAL Project No.	
➢ Verify the method's name.	

➢ Verify holding times (extraction 30 days from collection; 45 d from extraction for analysis).	
➢ Check recoveries of the ES, SS, and CS (40 to 135 percent).	
➢ Review the SICPs from the LMB to validate the LMB (i.e., absence of signals).	
➢ Examine the QC check ion SICPs for the presence of quantitative interferences (QI).	
➢ Examine the PCDPE SICPs for the presence of "ethers" as potential interferences.	
➢ Assess the impact of these "ethers" or QI on the data.	
➢ Perform a manual calculation of at least one specific analyte concentration.	
➢ Perform a manual calculation of at least one labeled standard recovery (e.g., ES).	
➢ Occasionally, perform a manual calculation for a total homologue group.	
➢ Examine the SICPs for the presence of saturated peaks.	
➢ Verify that the chlorine-37 correction is applied to 2,3,7,8-TCDD.	
➢ Verify that the 2,3,7,8-TCDF result originates from the confirmation analysis.	
➢ Perform a general overview of the SICPs and look for inconsistencies between the SICPs and the tabulated results, between the samples themselves, and observations noted by the lab staff.	
6. Initial and date the topsheets.	

Notes to be used for the Cover Letter or Narrative

Figure 9: Check list for data validation.

Sample Tracking for the Analysis of Polychlorinated Dibenzo-*p*-Dioxins & Dibenzofurans

No. of Field Samples: ____
Page __ of __

PAL Project No.: L-9999

Date Received: 03 JUL 98
Due Date: 10 JUL 98
Client Project ID: MEX MILL

			Method 8290 W														
Lab Sample ID	Client Sample ID	Observations	Volume (mL)	pH	ES	MX	Filter	Liq-Liq	3545	Combine	Conc. S.Ex.	CS	Split Arch.	PCU	Conc.	JS	TCDF
L-1033-0	LMB																
L-1033-1	W-1																
L-1033-2	W-2																
L-1033-3	W-3																

Figure 10: Sampling Tracking & Management Form (Method 8290; liquid-liquid partitioning with methylene chloride extraction).

Sample Tracking for the Analysis of Polychlorinated Dibenzo-*p*-Dioxins & Dibenzofurans

No. of Field Samples: ____
Page __ of __

PAL Project No.: L-9999

Date Received: 03 JUL 98
Due Date: 10 JUL 98
Client Project ID: MEX MILL

Method 8290		*Method 8290*		*Method 8290*				*Method 8290*					*Method 8290*		
Lab Sample ID	Client Sample ID	Observations Solids ?	Volume (mL)	pH	ES	MX	Filtration	MEX	3545	Conc.	CS	PCU	JS	TCDF	
L-9999-0	MDL-1														
L-9999-1	MDL-2														
L-9999-2	MDL-3														
L-9999-3	MDL-4														
L-9999-4	MDL-5														
L-9999-5	MDL-6														
L-9999-6	MDL-7														

Figure 11: Sampling Tracking & Management Form (Method 8290; liquid-liquid partitioning with isooctane microextraction).

Sample Tracking for the Analysis of Polychlorinated Dibenzo-*p*-Dioxins & Dibenzofurans

No. of Field Samples: ____
Page __ of __

PAL Project No.: L-9999

Date Received: 03 JUL 98
Due Date: 10 JUL 98
Client Project ID: MEX MILL

				Method 8290 W															
Lab Sample ID	Client Sample ID	Observations	Volume (mL)	pH	pH 2	ES	MX	SPE	3545	Conc. S.Ex.	CS	Split Arch.	PCU	Conc.	JS	TCDF	Misc.
L-9999-0	CAD-5																
L-9999-1	CAD-6																

Figure 12: Sampling Tracking & Management Form (Method 8290; SPE C_{18}).

Sample Tracking for the Analysis of Polychlorinated Dibenzo-*p*-Dioxins & Dibenzofurans

No. of Field Samples: ____
Page __ of __

PAL Project No.: L-9999

Date Received: 03 JUL 98
Due Date: 10 JUL 98
Client Project ID:

			Method 8290 W		*Method 8290 W*		*Method 8290 W*			*Method 8290 W*			*Method 8290 W*			
Lab Sample ID	Client Sample ID	Observations	Volume (mL)	pH	pH 2	ES	MX	CAD SPE	3545	Conc. S.Ex.	CS	Split Arch.	PCU	Conc.	JS	TCDF	Misc.
L-9999-0	CAD-5																
L-9999-1	CAD-6																

Figure 13: Sampling Tracking & Management Form (Method 8290; SPE Carbon Adsorption Diffusion).

Communication Exchanges Form for the Analysis of PCDD/PCDFs

No. of Field Samples: ____
Page __ of __

PAL Project No.: L-9999

Date Received: 20 MAR 98
Due Date: 10 APR 98
Client Project ID: PATRON

Method 8290	*Method 8290*	*Method 8290*	*Method 8290*	*Method 8290*

Figure 13: Communication Exchanges Form (Method 8290).

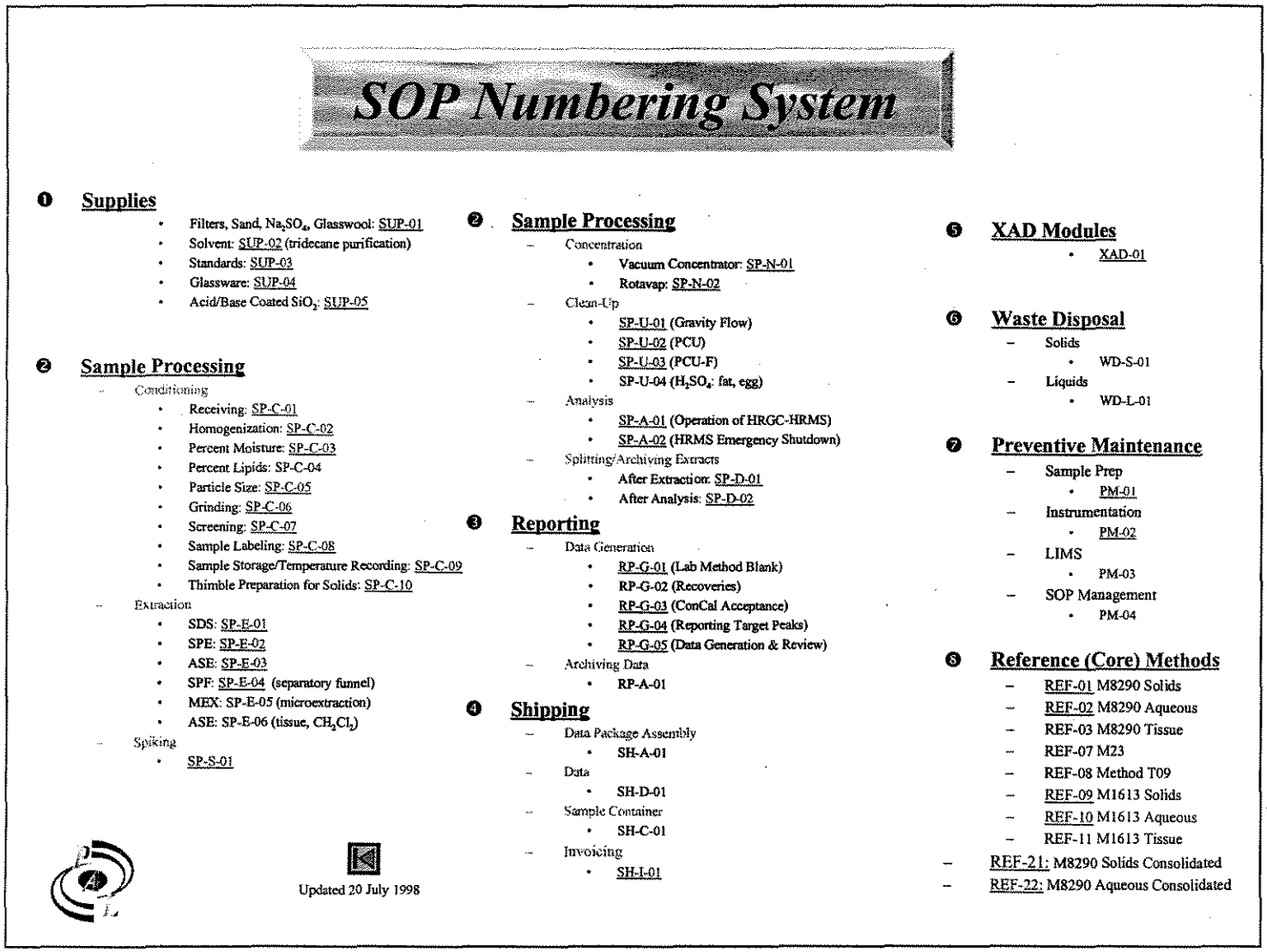


Figure 14: Paradigm Analytical Labs Standard Operating Procedures for the Measurement of PCDD/Fs in Environmental Samples by Isotope-Dilution HRGC/HRMS

Table 1: List and concentrations of the Extraction Standards used during the sample fortification step.

$^{13}C_{12}$-2,3,7,8-TCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,7,8-PeCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,6,7,8-HxCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,6,7,8-HpCDD	100 pg / µL
$^{13}C_{12}$ -OCDD	200 pg / µL
$^{13}C_{12}$ -2,3,7,8-TCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,7,8-PeCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,6,7,8-HxCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,6,7,8-HpCDF	100 pg / µL

Table 2: List and concentrations of the Cleanup Standards used during the sample fortification step.

$^{37}Cl_4$-2,3,7,8-TCDD	100 pg / µL
$^{13}C_{12}$ -2,3,4,7,8-PeCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,7,8-HxCDD	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,7,8-HxCDF	100 pg / µL
$^{13}C_{12}$ -1,2,3,4,7,8,9-HpCDF	100 pg / µL

Table 3: Composition of the Matrix Spike solution.

Unlabeled Analyte	Concentration in pg / µL
2,3,7,8-TCDD	5
2,3,7,8-TCDF	5
1,2,3,7,8-PeCDD	12.5
1,2,3,7,8-PeCDF	12.5
2,3,4,7,8-PeCDF	12.5
1,2,3,4,7,8-HxCDD	12.5
1,2,3,6,7,8-HxCDD	12.5
1,2,3,7,8,9-HxCDD	12.5
1,2,3,4,7,8-HxCDF	12.5
1,2,3,6,7,8-HxCDF	12.5
1,2,3,7,8,9-HxCDF	12.5
2,3,4,6,7,8-HxCDF	12.5
1,2,3,4,6,7,8-HpCDD	12.5
1,2,3,4,6,7,8-HpCDF	12.5
1,2,3,4,7,8,9-HpCDF	12.5
OCDD	25
OCDF	25

Table 4: Initial Calibration Solutions (concentrations are in pg/µL)

Analyte	CS-1	CS-2	CS-3	CS-4	CS-5
Unlabeled					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD	2.5	5	25	250	500
1,2,3,7,8-PeCDF	2.5	5	25	250	500
2,3,4,7,8-PeCDF	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5.0	10	50	500	1000
OCDF	5.0	10	50	500	1000
Extraction Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Cleanup Standards					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	5	50	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
Injection Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

Table 5: Vacuum Chamber Program for 5-mL Tridecane Sample Extracts (solvent exchange procedure)

Pressure	Time	Note
0'' – 15" Hg	Start	Open the valve slowly and allow pressure to reach 15'' Hg.
16" – 20" Hg	2 min / mark	Allow pressure to gradually reach 20" Hg with a two-minute hold at 16, 17, 18, 19 and 20"Hg.
21" – 25" Hg	3 min / ½ mark	Allow pressure to gradually reach 25" Hg with a three-minute hold at 21, 21.5, 22, 22.5, 23, 23.5, 24, 24.5 and 25"Hg.
26" – 30'' Hg	5 min / ½ mark	Allow pressure to gradually reach 30" Hg with a five-minute hold at 26, 26.5, 27, 27.5, 28, 28.5, 29, 29.5, and 30"Hg.
10 T – 5 T	***Read pump gauge***	At this point, you can monitor the pressure from the pump gauge rather than the chamber pressure gauge. Typically, between 10 and 5 Torr, you need to proceed cautiously in a stepwise manner as described above (i.e., 5 min at 10 T, 5 min at 9 T, 5 min at 8 T, 5 min at 7 T, 5 min at 6 T, and 5 min at 5 T.)
5 T – 1 T	***Read pump gauge***	Again, by opening and closing the pump valve, allow the pressure to reach 4 T, 3 T, 2 T, and 1 T. Here, the stepping down can take place at a slightly higher pace. Bumping has been observed down to 1.2 T if pumping is too fast. When opening the pump valve, do it slowly by watching the gauge.
1T – 0.75 T	***Read pump gauge***	Once you reach 1 T, you can keep the pump valve fully opened and pump continuously until the pressure drops below 0.5 T. The sample is ready for the next step.

Table 6: 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

APPENDIX A-53

STANDARD OPERATING PROCEDURE FOR SAMPLE RECEIPT AND SAMPLE LOGIN AT THE PITTSFIELD MOBILE LABORATORY

STANDARD OPERATING PROCEDURE FOR SAMPLE RECEIPT AND SAMPLE LOGIN AT THE PITTSFIELD MOBILE LABORATORY

Written by:

Lonnie Fallin, East Coast Operations Manager
ONSITE Environmental Laboratories, Inc.

Approved by:

Sharon Nordstrom, Project Manager
Roy F. Weston, Inc.

Approved by:

Marie Wojtas, Chemst
USACE

1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of the samples have not been precisely defined. Samples should be treated as dangerous, and handled with appropriate protective apparatus such as gloves, safety glasses and lab coats.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the steps involved in receiving samples from Weston at the Pittsfield Mobile Lab site.

3.0 LOGIN PROCEDURE

3.1 Samples are either hand delivered to the lab trailer, or picked up from the Weston field trailer by an ONSITE technician.

3.2 Upon receipt of the cooler, the cooler is checked for intact custody seals. If seals are not present, or seals are broken, Weston is notified immediately and the problem is noted on the chain of custody. The chain of custody is then signed in the appropriate location, and the pink copy is left with Weston for their records.

3.3 When the cooler is opened, either after Weston personnel have dropped it off or it is returned to the lab, a visual inspection is done to insure that there are no broken samples and that ice (either cube or blue-ice) is present in the cooler. Then the temperature of the cooler is taken and recorded on the chain of custody. The temperature should be < 10 °C. If it is higher, Weston personnel must be notified immediately and corrective action taken. Corrective actions can include, but are not limited to: not analyzing samples and waiting for resampling; qualifying data generated from samples; or just noting on chain of custody and case narrative.

3.4 Once temperature is taken, samples are removed from the cooler and compared to the chain of custody. If any samples are missing or mis-identified it is noted on the chain of custody and Weston is notified immediately. In the case of missing samples, Weston may elect to bring the sample over or have ONSITE cross it off the chain of custody and initial and date the cross off. In most cases, mis-identified samples are corrected and initialed on the chain of custody and analyzed normally. The major exception to this is when several samples are mis-identified, leading to confusion as to which sample is which. When this happens, Weston personnel must either resubmit samples or come to the trailer and, using other records, correctly identify the samples.

3.5 Once samples are verified against the chain of custody, then they are also given a unique ONSITE number. The number given is sequential and in the following format:

Pyydd-nn

where P = Pittsfield
yy = year
dd = day of lab operation
nn = sequential number

i.e. Weston sample MW101 is also given the ONSITE ID P9804-01, while MW102 is given P9804-02.

The ONSITE number is written in the comment section of the chain of custody, on the sample container and on the sample container lid.

3.6 Samples are also recorded in a sample receipt log. The log contains the Weston ID, the ONSITE ID, matrix, chain of custody ID and date received. Since only PCBs are being analyzed at this lab, no analysis type column is included.

3.7 Samples are then set up for analysis.

3.8 When the final report is generated, the gold copy of the chain of custody is included.

APPENDIX A-54

STANDARD OPERATING PROCEDURE FOR STANDARD TEST METHOD FOR SPECIFIC GRAVITY OF SOILS

GZA GeoEnvironmental, Inc. **SOP # GT5.0**

Standard Operating Procedure

Standard Test Method for Specific Gravity of Soils

Copy #: 2

Date: By:2/9/00 *Reviewed by Lab Supervisor:* MW *Date:* 2-9-00

Revision #: 1 *Reviewed by QA Officer:* DMS *Date:* 2/9/00

1. Scope and Application

   1.1 This test method covers the determination of the specific gravity of soils that pass the 4.75-mm (No. 4) sieve, by means of a pycnometer. When the soil contains particles larger than the 4.75-mm sieve, Test Method C 127 shall be used for the material retained on the 4.75-mm sieve and this test method shall be used for the material passing the 4.75-mm sieve.

   1.2 Two procedures for performing the specific gravity are provided as follows:

      1.2.1 Method A - Procedure for Oven-Dry Specimens.

      1.2.2 Method B - Procedure for Moist Specimens. The procedure to be used shall be specified by the requesting authority. For specimens of organic soils and highly plastic, fine grained soils, Procedure B shall be the preferred method.

2. Method Summary

   2.1 Related Standard Operating Procedures

3. Sample Preservation, Containers, Handling, and Storage

   Preservation: Non-Applicable

   Containers: Jars, Glass or Plastic (4-32oz), Plastic Sample Bags (5 gallon), 5 gallon buckets

   Storage: Samples are stored in Laboratory until project is complete, data is sent, and no additional testing required

4. Interference and Potential Problems

- Sample size is sometimes compromised due to limited amount of material to perform analysis.
- Organic matter can float causing inaccurate meniscus readings.
- Error in recording of weights during any step of this analysis.
- Error in calculating data.

5. Definitions

5.1 Specific Gravity: The ratio of the mass of a unit volume of a material at a stated temperature to the mass of the same volume of gas-free distilled water at a stated temperature.

6. Equipment and Apparatus

6.1 Pyncometer - The pycnometer shall be one of the following

6.1.1 Volumetric Flask, having a capacity of at least 100 mL.

6.1.2 Stoppered Bottle, having a capacity of at least 50mL. The stopper shall be of the same material, and shall permit the emission of air and surplus water when it is put in place.

6.2 Balance - Meeting the requirements of Specification D 4753 and readable, without estimation, to at least 0.1% of the specimen mass.

6.3 Drying Oven - Thermostatically-controlled oven, capable of maintaining a uniform temperature of 110± 5°C (230± 9°F) throughout the drying chamber.

6.4 Thermometer, capable of measuring the temperature range within which the test is being performed, graduated in a 0.5°C (1.0°F) division scale.

6.5 Entrapped Air Removal Apparatus - To remove entrapped air, use one or a combination of the following:

6.5.1 Hot Plate or Bunsen Burner, capable of maintaining a temperature adequate to boil water.

6.5.2 Vacuum System, a vacuum pump or water aspirator, capable of producing a partial vacuum of 26 in Hg.

6.6 Miscellaneous Equipment, specimen dishes and insulated gloves.

7. Reagents

- distilled and/or demineralized water,

8. Health and Safety Issues

Safety glasses, Long pants, socks, gloves and lab coats must be worn when handling samples with known contaminants.

The Laboratory Manager ensures that health and safety procedures are discussed with each new employee by the H&S representative prior to beginning work in the laboratory.

The chemical hygiene plan and the Hazardous Materials Handling and Disposal SOP should be reviewed by each employee. Copies of both plans are kept in the laboratory.

Use caution when dealing with any heated oven zones. Wear heat protection gloves.

9. Procedures

9.1 Login:

Samples are logged in as follows:

- Each sample is given a unique laboratory identification number.
- This number must be sequential beginning with number one.
- In the case of ongoing project refer to next Lab No. in numerical sequence.
- Last Lab No. can be found in log book in laboratory.
- This log must be updated each time a new sample is logged in.

9.2 Identify Sample for testing, check soils laboratory testing assignment sheet.

9.3 Specific Gravity test is assigned if an "X" is marked under Gs column of Identification tests and sample information (Boring/Test Pit No., Depth,) coincides with sample information on sample container.

9.4 Sample Preparation & Procedure:

- Take entire sample and screen through a #4 Sieve. After screening, take all minus #4 material, mix thoroughly and take a representative portion (approximately 30- 50 grams dry weight).

Note: Representative portion is obtained by either decanting through a sample splitter or using the Quartering method.

- Put sample into a calibrated 500ml pycometer using funnel and add distilled or demineralized water to below measured line on pycnometer.

- Place pycnometer in a warm temperature bath (30-38°C) and connect vacuum line using rubber stoppered bottle cap to top of pycnometer.

- Apply vacuum (minimum 26 reading on vacuum gage) to sample and allow all entrapped air to escape. Apply vacuum for at least 30 minutes.

- Shake pycnometer slightly with hand and determine visually that no additional air is present in sample. If air is present continue vacuum until such time that shaking pycnometer produces no entrapped air.

- Remove vacuum from open end of pycnometer and take pycnometer out of warn temperature bath.

- With an eyedropper adjust water level to desired line on pycnometer.

- Wipe outside of pycnometer clean with paper towel to remove any moisture and or other particles.

- Record weight of pyncometer (wt. Of Bottle+Water+Soil in gms) under Determination No. 1.

- Immediately after recording weight, insert thermometer and record temperature (Temperature, T. in °C) to the nearest .1°C, again under Determination No.1.

- Repeat prior step up to 3 times at various temperature readings, if meniscus is hard to read 4 determinations may be required.

- Weigh rectangular pan (capable of containing approximately 800 grams of material) and record as Wt. Dish in gms.

- Take pycnometer and agitate by turning and swirling in a circular motion with hand.

- Begin decanting soil/water mix pycnometer into rectangular pan.

- Take squirt bottle and rinse inside of pycnometer to get remaining particles into suspension and again decant into pan.

- Repeat prior step until no visual soil remaining in pycnometer.

- Place pan and soil in oven and dry for not less than 16hrs @ 110°C ±5°C.

  Note: Due to large amount of water sample may need additional drying rime.

- Remove pan from water and allow to cool.

- After cooling weigh pan and record under Wt. Of dish & dry soil.

9.5 Status Check on Data:

Status is obtained from the soils laboratory testing assignment sheet as follows:

- Test assigned is clearly designated with an X in appropriate column (Step 9.3).
- If one quarter of X is shaded, sample has been prepared

- If one half of X is shaded, sample has been run,
- If three quarters of X is shaded, test has been calculated,
- Finally if entire X is shaded in pencil, test has been Reduced and Reviewed and can be sent as final data.

9.6 **Data Reduction:** All data upon conclusion is then hand calculated, and input on to a Microsoft Excel spreadsheet and furnished along with raw data to lab director or supervisor for data review.

9.7 **Data Review:**

- Check calculation for weight of soil in gms.
- Check specific gravity value versus soil description
- After the specific gravity determination have been verified, cross examine Job Name, sample Identification, soil classification and any other pertinent information.

9.8 **Data Report:**

Final data is sent as follows:

- Identification of the sample (material) being tested such as boring number, sample number, test number, etc.
- Specific gravity at 20°C to the nearest 0.01.

10 Calculations

10.1 Formula:

$$Gs=\frac{GtWs}{Ws-W1+W2}$$

where:

Gs= Specific Gravity

Gt= Density of water at given temperature (see Table 1 ASTM D854)

Ws= Weight of Soil in gms

W1= Weight of pycnometer, Water & Soil in gms

W2= Weight of Bottle & Water in gms (see calibration folder for pycnometer used)

10.2 Verification of calculations

- Review all determinations to insure the Gs values are all similar

- Check soil description and any other test data associated with sample to see if Gs correlates with other test values

11. Calibration:

- Oven temperature is recorded daily and calibrated every four months (SOP SA-Draft)
- Balances are checked daily with S class weights and kept in Log Book in lab by Scale (SOP SA 3.0).
- Pycnometer are calculate annually. (SOP Draft)

12. QC Limits

Non-Applicable

13. Corrective Action Procedures

Corrective actions are taken as follows:

13.1.1 Any suspect or questionable data during test is to be reported to Supervisor immediately on finding.

13.1.2 Supervisor will review data and check any calculations for error.

13.1.3 If there is a calculation error that is made, correction will be noted and test will continue.

13.1.4 If error can not be retrieved, then Supervisor instructs technician to retrieve any unused portion of Sample.

13.1.5 When unused sample is retrieved Supervisor determines if there is enough material and is so instructs technician to re-run entire test. If there is not enough material to re-run test Supervisor relays that information to Project Manager or Client, at this stage it is determined whether more sample can be obtained to run analysis or test is canceled.

13.1.6 Supervisor or lab technician appointed by Supervisor, must weigh and calculate all oven-dried samples every morning. This is a routine check of testing to determine any errors in recording of weights during test.

13.1.7 When an error occurs during 13.1.6 the following measure is taken: first re-weigh sample & container and check against recorded weight. If weight doesn't check then re-record new weight and re-calculate to see if new data correlates with all other data. If weight checks, then remove oven-dried material and weigh container and repeat prior step. If correction is made test can continue or be reduced and reviewed. If correction is not made then refer to 13.1.5 for corrective action.

13.1.8 Oven-dried samples are not disposed of until Supervisor has checked all data calculations and determines data is valid.

13.1.9 During data review if there are any errors or questionable data Lab Director notifies Supervisor and Supervisor retrieves test sample. If checking test sample by weighing or sieving corrects error than test is reduced again and sent through for review. If checking test sample does not correct mistake then refer to 13.1.5.

13.1.10 Any corrections made to data sheet are done by putting a line through error and recording new data and initialing by individual. If more than one mistake is made and there is no room on data sheet to put correction, a line will be placed through error, a new data sheet will be stapled to original data and a brief explanation as to why sheet is stapled and then new data recorded on stapled sheet and initialed by individual.

13.1.11 Any changes deviance's or unusual measures taken during recording of data shall have an asterisk placed next to unusual data and a brief yet detailed description of what data represents and why its represented in this manner followed by initials of individual taking these actions.

14. Document Description and Example Forms

See Attached Forms

15. Miscellaneous Notes

None

16. References

ASTM D853 Standard Test Method for Specific Gravity of Soils

17. Confidentiality Statement

APPENDIX A-55

STANDARD OPERATING PROCEDURE FOR LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX OF SOILS

GZA GeoEnvironmental, Inc. **SOP # GT6.0**

Standard Operating Procedure for Liquid Limit, Plastic Limit, and Plasticity Index of Soils

Copy #: 2

Date: By:2/9/00 *Reviewed by Lab Supervisor:* MM *Date:* 2-5-00

Revision #: / *Reviewed by QA Officer:* [signature] *Date:* 2/9/00

1. Scope and Application

1.1 This test method covers the determination of the liquid limit, plastic limit, and the plasticity index of soils.

1.2 Since the test described herein is performed only on that portion of a soil which passes the 425-μm (No. 40) sieve, the relative contribution of this portion of the soil to the properties of the sample as a whole must be considered when using these tests to evaluate properties of a soil.

2. Method Summary

2.1 Method Overview

2.1.1 The sample is processed to remove any material retained on a 425μm (No. 40) sieve. The liquid limit is determined by performing trials in which a portion of the sample is spread in a brass cup, divided in two by a grooving tool, and then allowed to flow together from the shocks caused by repeatedly dropping the cup in a standard mechanical device. The multipoint liquid limit, Method A, requires three or more trials over a range of water contents to be performed and the data from the trials plotted or calculated to make a relationship from which the liquid limit is determined.

2.1.2 The plastic limit is determined by alternately pressing together and rolling into a 3.2-mm (1/8-in.) diameter thread a small portion of plastic soil until its water content is reduced to a point at which the thread crumbles and can no longer be pressed together and rerolled. The water content of the soil at this point is reported as the plastic limit.

2.1.3 The plasticity index is calculated as the difference between the liquid limit and the plastic limit.

2.2 Related Standard Operating Procedures

- GT - 4.0 Water Content Determination SOP
- SA - 3.0 Balance Calibration SOP
- GT - 1.0 Grain Size Analysis SOP

3. Sample Preservation, Containers, Handling, and Storage

Preservation: Non-Applicable

Containers: Jars, Glass or Plastic (4-32oz), Plastic Sample Bags (5 gallon), 5 gallon buckets

Storage: Samples are stored in Laboratory until project is complete, data is sent, and no additional testing required

4. Interference and Potential Problems

- Sample size is sometimes compromised due to limited amount of material to perform analysis.
- Error in recording of weights during any step of this analysis.
- Error in calculating data.
- Spillage of sample due to small sample containers.

5. Definitions:

- Liquid Limit: LL, W_L - (a) The water content corresponding to the arbitrary limit between the liquid and plastic state of consistency of a soil. (b) The water content at which a part of soil, cut by a groove of standard dimensions, will flow together for a distance of ½ in. (12.7 mm) under the impact of 25 blows in a standard liquid limit apparatus.
- Plastic Limit, W_p, PL, - (a) The water content corresponding to an arbitrary limit between the plastic and the semisolid states of consistency of a soil. (b) Water content at which a soil will just begin to crumble when rolled into a thread approximately 1/8 in. (3.2 mm) in diameter.
- Plasticity Index, I_p, PI, - Numerical difference between the liquid limit and the plastic limit.
- Plasticity - The property of a soil or rock which allows it to be deformed beyond the point of recovery without cracking or appreciable volume change.

6. Equipment and Apparatus

- Liquid Limit Device - A mechanical device consisting of a brass cup suspended from a carriage designed to control its drop onto a hard rubber base. The device may be operated by either a hand crank or electric motor.

- Base - A hard rubber base having a D Durometer hardness of 80 to 90, and a resilience such that an 8-mm (5/16-in.) diameter polished steel ball, when dropped from a height of 25 cm (9.84 in.) will have an average rebound of at least 77% but no more than 90%.

- Rubber Feet - supporting the base, designed to provide isolation of the base from the work surface, and having an A Durometer hardness no greater than 60 as measured on the finished feet attached to the base.

- Cam - designed to raise the cup smoothly and continuously to its maximum height, over a distance of at least 180° of cam rotation, without developing an upward or downward velocity of the cup when the cam follower leaves the cam.

- Carriage - constructed in a way that allows convenient but secure adjustment of the height of drop of the cup to 10mm (0.394 in.), and designed such that the cup and cup hanger assembly is only attached to the carriage by means of a removable pin.

- Motor Drive (Optional) - As an alternative to the hand crank, the device may be equipped with a motor to turn the cam. Such a motor must turn the cam at 2±0.1 revolutions per second and must be isolated from the rest of the device by rubber mounts or in some other way that prevents vibration from the motor being transmitted to the rest of the apparatus. It must be equipped with an ON-OFF switch and a means of conveniently positioning the cam for height of drop adjustments. The results obtained using a motor-driven device must not differ from those obtained using a manually operated device.

- Flat Grooving Tool - A tool made of plastic or noncorroding-metal. The design of the tool may vary as long as the essential dimensions are maintained. The tool may, but need not, incorporate the gage for adjusting the height of drop of the liquid limit device.

- Gage - A metal gage block for adjusting the height of drop of the cup. The design of the tool may vary provided the gage will rest securely on the base without being susceptible to rocking, and the edge which contacts the cup during adjustment is straight, at least 10 mm (3/8 in.) wide, and without bevel or radius.

- Containers - Small corrosion-resistant containers for water content specimens. Aluminum or stainless steel cans 2.5 cm (1 in.) high by 5 cm (2 in.) in diameter are appropriate.

- Balance - conforming to Specification D 4753, Class GP1.

- Storage Container - A container in which to store the prepared soil specimen that will not contaminate the specimen in any way, and will prevent moisture loss. A

porcelain, glass, or plastic dish about 11. 4 cm (41/2 in.) in diameter and a plastic bag large enough to enclose the dish and be folded over is adequate.

- Ground Glass Plate - A ground glass plate at least 30 cm (12 in.) square by 1 cm (3/8 in.) thick for rolling plastic limit threads.

- Spatula - A spatula or pill knife having a blade about 2 cm (3/4 in.) wide, and about 10 to 13 cm (3 to 4 in.) long.

- Sieve - A 20.3-cm (8-in.) diameter, 425-μm (No. 40.) sieve conforming to the requirements of Specification E 11 and having a rim at least 5 cm (2 in.) above the mesh. A 2-mm (No. 10) sieve meeting the same requirements may also be needed.

- Wash Bottle - or similar container for adding controlled amounts of water to soil and washing fines from coarse particles.

- Drying Oven - thermostatically controlled, preferably of the forced-draft type, capable of continuously maintaining a temperature of 110 ± 5°C (230± 9°F) throughout the drying chamber.

- Washing Pan - round, flat-bottomed, at least 7.6 cm (3 in.) deep, and slightly larger at the bottom than a 20.3-cm (8-in.) diameter sieve.

7. Reagents

7.1 Purity of Water - Where distilled water is referred to in this test method, either distilled or demineralized water may be used.

8. Health and Safety Issues

Safety glasses, Long pants, socks, gloves and lab coats must be worn when handling samples with known contaminants.

The Laboratory Manager ensures that health and safety procedures are discussed with each new employee by the H&S representative prior to beginning work in the laboratory.

The chemical hygiene plan and the Hazardous Materials Handling and Disposal SOP should be reviewed by each employee. Copies of both plans are kept in the laboratory.

Use caution when dealing with any heated oven zones. Wear heat protection gloves.

9.1 **Procedures**

Login:

Samples are logged in as follows:

- Each sample is given a unique laboratory identification number.

- This number must be sequential beginning with number one.
- In the case of ongoing project refer to next Lab No. in numerical sequence.
- Last Lab No. can be found in log book in laboratory.
- This log must be updated each time a new sample is logged in.

9.2 **Identify Sample for Testing:** Check soils laboratory testing assignment sheet.

9.3 **Liquid & Plastic Limit:** is assigned if X is marked under LL & PL%.

9.4 **Sample Preparation:**

9.4.1 For Granular Soils material is processed by removing any material retained on a 425 µm (No. 40) sieve. This will be accomplished by air-drying sample, then take mortar and pestle and grind material to break dry soil clods.

NOTE: Pulverize the sample using rubber tipped pestle in a manner that does not cause breakdown of individual grains.

9.4.2 Take ground material, place into No. 40 Sieve and shake by hand allowing material to pass through sieve and into rectangular pan.

9.4.3 Repeat step 9.4.1 and step 9.4.2 until all visual material (- No. 40 Sieve) has passed through sieve.

9.4.4 Wash all retained material with distilled or demineriliz ed water over No. 40 Sieve into rectangular pan with processed soil to insure all material has passed through sieve.

9.4.5 Discard any retained material at this point.

9.4.6 Take material in pan and add distilled or demineriliz ed water to material slowly, mixing soil/water to a uniform state with gloved hand until soil is around its liquid limit.

NOTE: Refer to definition section for liquid limit (Sample is around the liquid limit when water content will result in closure of the groove @ 25 blows.)

9.4.7 Take approximately 200 grams of processed soil and place in a plastic bag.

9.4.8 Place plastic bag in 8oz. Drillers jar, fill out Raw data sheet with sample information, and adhere white tape to jar.

9.4.9 Write Job No. and Test No. on white tape on jar, cap and allow to cure for not less than 16hrs.

9.5 **Plastic Limit**

9.5.1 Mixed cured material with either gloved hands or spatula.

9.5.2 Take approximately 20-25 grams of material and put on ground glass plate.

9.5.3 Put remaining material in porcelain cup for liquid limit.

9.5.4 Take soil from glass plate and reduce water content by blotting with paper towel in a manner that does not leave any paper towel matter in soil.

9.5.5 Take approximately 2 grams of material and roll with palm of hand with just enough pressure to allow sample to roll into uniform thread of 1/8 in. in thickness.

NOTE: Refer to Liquid limit cupholder as guide for 1/8 in. diameter.

9.5.6 Rework thread and repeat step 9.5.5 until sample exhibits cracking and crumbling. (Refer to Figure 8 ASTM D4318 for visual example.)

9.5.7 Weigh sample container and record under container weight on plastic limit portion of raw data sheet.

9.5.8 Take crumbled thread place in weighed container and cover assuring moisture is not lost.

9.5.9 Repeat steps 9.5.5, 9.5.6 and 9.5.8 until there is not less than 6 grams of crumbled soil in container.

9.5.10 Weigh container and crumbled soil and record under weight of container and wet soil of plastic limit portion of raw data sheet.

9.5.11 Repeat steps 9.5.5 through 9.5.10 2-3 times for plastic limit test.

9.5.12 Place container on container sheet in a row and leave until liquid limit is complete.

9.6 **Liquid Limit**

9.6.1 Take spatula and mix material in porcelain cup thoroughly.

9.6.2 Scoop some material with spatula and spread onto liquid limit cup assuring that no air bubbles are present.

9.6.3 Visually inspect grooving tool for groove height and thickness by alignment with "MASTER" grooving tool.

NOTE: Master grooving tool has been calibrated with calipers and dimensions recorded to insure proper tolerance levels for length and thickness.

9.6.4 If 9.6.3 checks than place a check under grooving tool checked, and record grooving tool ID Number (I.D. # commonly identified by date placed in service.)

9.6.5 If 9.6.3 does not check then destroy grooving tool and get another one and re-inspect until specification for grooving tool is met.

9.6.6 Take Crank from liquid limit device raise cup until just about ready to drop.

9.6.7 Place reverse end of grooving tool under cup and check cup height.

NOTE: Reverse end of grooving tool has prescribed cup height in cm.

9.6.8 Verify cup height for proper drop if height is either to low or to high, adjust by loosening screws that hold cup to shaft at top of device and moving further if too low or closer if too high, then tighten screws and check height again. If unsure notify Supervisor to verify cup height.

9.6.9 When 9.6.6 through 9.6.8 have been complete put check mark under height of cup checked.

9.6.10 Take grooving tool and form groove in soil pat by drawing tool, beveled edge forward through the soil on a line from highest point to lowest point on cup. (Refer to Figure 6 ASTM D4318 for visual example.)

9.6.11 Lift and drop cup at a rate of 2 blows per second until 2 halves of soil have closed ½ in. (See Figure 7 ASTM D4318 for visual example.)

9.6.12 Record number of blows under liquid limit portion of test.

9.6.13 Weigh and record container under container weight under liquid limit portion of test.

9.6.14 With spatula take closed portion of sample in liquid limit cup by scooping and placing in container.

9.6.15 Weigh and record under sample wet weight & container under liquid limit portion of test.

9.6.16 Return the unused portion in liquid cup back to remaining sample in porcelain cup.

9.6.17 Wash and dry liquid cup making sure no water or soil remains on or under cup and base contact with cup is clean.

9.6.18 If soil is at water content < 30 blows pat dry with paper towel and repeat 9.6.10 through 9.6.17.

9.6.19 If soil is > 35 blows add distilled or deminerilized water and repeat 9.6.10 through 9.6.17.

9.6.20 Repeat steps 9.6.10 through 9.6.19 not less than 3 times. (NOTE: Liquid limit points should be recorded between 25-35 blows, 20-30 blows & 15-25 blows as a guide.)

9.6.21 Take liquid limit containers place them on container tray in a row with plastic limit container.

9.6.22 Put tray in oven at 110°C ±5° and leave in oven for not less than 16hrs.

9.6.23 Remove tray from oven after at least 16hrs and allow to cool.

9.6.24 Weigh and record containers under weight of dry soil & container.

9.6.25 Calculate water content for each container to the nearest .1%. (Refer to calculation section.)

9.6.26 Check plastic limit water contents to verify that they are within 2%. If not, repeat plastic limit.

9.6.27 Average the plastic limit values and record under plastic limit on raw data sheet to the nearest percent.

9.6.28 Plot the relationship of water content verse number of blows on the semi log graph on raw data sheet.

9.6.29 Draw the best straight line through points on graph.

9.6.30 Take water content where line intersects 25 blows and report under liquid limit on Raw data sheet to the nearest percent.

9.6.31 Subtract plastic limit from liquid limit and record under plasticity index on Raw data sheet.

9.7 **Status Check on Data:**

Status is obtained from the soils laboratory testing assignment sheet as follows:

- Test assigned is clearly designated with an X in appropriate column (Step 9.3).
- If one quarter of X is shaded, sample has been prepared
- If one half of X is shaded, sample has been run,
- If three quarters of X is shaded, test has been calculated,
- Finally if entire X is shaded in pencil, test has been Reduced and Reviewed and can be sent as final data.

9.8 **Data Reduction:** All data upon conclusion is then hand calculated, and input on to a Microsoft Excel spreadsheet and furnished along with raw data to lab director or supervisor for data review.

9.9 **Data Reduction:**

- Check calculation for moisture content.
- Verify liquid and plastic limit are recorded correctly.
- After moisture content values have been verified, cross examine Job Name, Sample Identification, soil classification and any other pertinent information.

9.10 **Data Review:**

- Check at least one Plastic Limit Calculation
- Check Liquid Limit point @ or around 25 blow
- Check Plasticity Index Calculation

9.11 **Data Report:**

Final data is sent as follows:

- Liquid Limit Value
- Plastic Limit Value
- Moisture Content if desired or applicable
- Soil Classification
- Identification of the sample (material) being tested, such as boring number, sample number & test number.
- Summary data sheet with moisture content in Percent.
- Percent Solids, if required.

10. Calculations

10.1 $W=\{(Mcws-Mcs)/(Mcs-Mc)\} \times 100 = \frac{Mw}{Ms} \times 100$

where:

w=water content, %

Mcws= mass of container and wet specimen

Mw= mass of water (Mw=Mcws-Mcs)

Mcs= mass of container and oven dry specimen

Mc= mass of container

PL= Average of 2 or 3 determinations reported to nearest percent

LL= W@ 25 blows determined from plot of data points on semi-log graph

PI= LL-PL

where

LL= Liquid Limit

PL= Plastic Limit

PI= Plasticity Index

11. Calibration

- Oven temperature is recorded daily and calibrated every four months (SOP SA-Draft)
- Thermometers are calibrated quarterly, cross measuring temperature with thermometer of higher degree of accuracy (SOP SA-13).
- Balances are checked daily with S class weights and kept in Log Book in lab by Scale (SOP SA 3.0).
- Atterberg Limit device calibrated every 4 months SOPSA-Draft

12. QC Limits

Not Applicable

13. Corrective Action Procedures

Corrective actions are taken as follows:

13.1.1 Any suspect or questionable data during test is to be reported to Supervisor immediately on finding.

13.1.2 Supervisor will review data and check any calculations for error.

13.1.3 If there is a calculation error that is made, correction will be noted and test will continue.

13.1.4 If error can not be retrieved, then Supervisor instructs technician to retrieve any unused portion of Sample.

13.1.5 When unused sample is retrieved Supervisor determines if there is enough material and is so instructs technician to re-run entire test. If there is not enough material to re-run test Supervisor relays that information to Project Manager or Client, at this stage it is determined whether more sample can be obtained to run analysis or test is canceled.

13.1.6 Supervisor or lab technician appointed by Supervisor, must weigh and calculate all oven-dried samples every morning. This is a routine check of testing to determine any errors in recording of weights during test.

13.1.7 When an error occurs during 13.1.6 the following measure is taken: first re-weigh sample & container and check against recorded weight. If weight doesn't check then re-record new weight and re-calculate to see if new data correlates with all other data. If weight checks, then remove oven-dried material and weigh container and repeat prior step. If correction is made test can continue or be reduced and reviewed. If correction is not made then refer to 13.1.5 for corrective action.

13.1.8 Oven-dried samples are not disposed of until Supervisor has checked all data calculations and determines data is valid.

13.1.9 During data review if there are any errors or questionable data Lab Director notifies Supervisor and Supervisor retrieves test sample. If checking test sample by weighing or sieving corrects error than test is reduced again and sent through for review. If checking test sample does not correct mistake then refer to 13.1.5.

13.1.10 Any corrections made to data sheet are done by putting a line through error and recording new data and initialing by individual. If more than one mistake is made and there is no room on data sheet to put correction, a line will be placed through error, a new data sheet will be stapled to original data and a brief explanation as to why sheet is stapled and then new data recorded on stapled sheet and initialed by individual.

13.1.11 Any changes deviance's or unusual measures taken during recording of data shall have an asterisk placed next to unusual data and a brief yet detailed description of what data represents and why its represented in this manner followed by initials of individual taking these actions.

14. Document Description and Example Forms

See Attached.

15. Miscellaneous Notes

    - Samples with less cohesion may not behave in a manner that allows rolling to 1/8 in. thread for plastic limits, and may not sustain 25 blows in liquid limit cup.

16. References

    ASTM D4318 - Standard for Liquid Limit, Plastic Limit, and Plasticity Index of Soils

    ASTM D653 - Definitions & Terminology

    ASTM D2216 - Standard Moisture Content of Soil & Rock

17. Confidentiality Statement

    - **This SOP document has been developed and copyrighted by GZA. It is intended for internal (GZA) personnel and government agencies specifically. In addition, the document is not to be released externally for any other purpose without consent of GZA.**

APPENDIX A-56

STANDARD OPERATING PROCEDURE FOR LABORATORY DETERMINATION OF WATER (MOISTURE) CONTENT OF SOIL AND ROCK

GZA GeoEnvironmental, Inc. **SOP # -GT8.0**

Standard Operating Procedure for

Laboratory Determination of Water (Moisture) Content of

Soil and Rock

Copy #: 2

Date: By: 2/9/00 *Reviewed by Lab Supervisor:* MM *Date:* 2-9-00

Revision #: 1 *Reviewed by QA Officer:* DJS *Date:* 2/9/00

1. Scope and Application

   1.1 This test method covers the laboratory determination of the water (moisture) content of soil, rock, and similar materials by mass. For simplicity, the word "material" hereinafter also refers to either soil or rock, whichever is most applicable.

   1.2 The water content of a material is defined by this standard as the ratio, expressed as a percentage, of the mass of "pore" or "free" water in a given mass of material to the mass of the solid material.

2. Method Summary

   2.1 Related Standard Operating Procedures

   2.2 A test specimen is dried in an oven to a constant mass. The loss of mass due to drying is considered to be water. The water content is calculated using the mass of water and the mass of the dry specimen.

3. Sample Preservation, Containers, Handling, and Storage

   Preservation: Non-Applicable

   Containers: Jars, Glass or Plastic (4-32oz), Plastic Sample Bags (5 gallon), 5 gallon buckets

   Storage: Samples are stored in Laboratory until project is complete, data is sent, and no additional testing required

4. Interference and Potential Problems

    - Sample size is sometimes compromised due to limited amount of material to perform analysis.
    - Error in recording of weights during any step of this analysis.
    - Error in calculating data.

5. Definitions

    - Water Content: The ratio of the mass of water contained in the pore spaces of soil or rock material, to the solid mass of particles in that material, expressed as a percentage.

6. Equipment and Apparatus

    - Drying Oven - thermostatically-controlled, preferably of the forced-draft type, capable of maintaining a uniform temperature of 110 ± 5°C throughout the drying chamber.
    - Balances - All balances must meet the requirements of Specification D 4753 and this Section. A Class GPI balance of 0.01g readability is required for specimens having a mass of up too 200g (excluding mass of specimen container) and a Class GP2 balance of 0.1g readability is required for specimens having a mass over 200g.
    - Specimen Containers - Suitable containers made of material resistant to corrosion and change in mass upon repeated heating, cooling, exposure to materials of varying pH, and cleaning. One container is needed for each water content determination.
    - Container Handling Apparatus - gloves, tongs, or suitable holder for moving and handling hot containers after drying.
    - Miscellaneous - knives, spatulas, scoops, quartering cloth, sample splitters, etc. as required.

7. Reagents

    Non-Applicable

8. Health and Safety Issues

Safety glasses, Long pants, socks, gloves and lab coats must be worn when handling samples with known contaminants.

The Laboratory Manager ensures that health and safety procedures are discussed with each new employee by the H&S representative prior to beginning work in the laboratory.

The chemical hygiene plan and the Hazardous Materials Handling and Disposal SOP should be reviewed by each employee. Copies of both plans are kept in the laboratory.

Use caution when dealing with any heated oven zones. Wear heat protection gloves.

9. Procedures

9.1 **Login:**

Samples are logged in as follows:

- Each sample is given a unique laboratory identification number.
- This number must be sequential beginning with number one.
- In the case of ongoing project refer to next Lab No. in numerical sequence.
- Last Lab No. can be found in log book in laboratory.
- This log must be updated each time a new sample is logged in.

9.2 **Identify Sample for Testing:** Check soils laboratory testing assignment sheet.

9.3 **Water Content:** is assigned if X is marked under water content%.

9.4 **Sample Preparation:**

- Take entire sample and mix with hands and or spatula, until mixed thoroughly.
- Take container and record weight under container weight.
- Take a representative portion of sample (not less than 20 g) and place in container.
- Place container and soil on balance and record weight under Wet Sample & Container
- Put this sample in Oven and let dry for not less than 16hrs at 110°C ±5°.
- Remove sample after 16hrs or longer allow to cool.
- Place container on balance and record weight under Dry Sample & Container.
- Calculate moisture content in Percent. (Refer to Section 10)

9.5 **Status Check on Data:**

Status is obtained from the soils laboratory testing assignment sheet as follows:

- Test assigned is clearly designated with an X in appropriate column (Step 9.3).

- If one quarter of X is shaded, sample has been prepared
- If one half of X is shaded, sample has been run,
- If three quarters of X is shaded, test has been calculated,
- Finally if entire X is shaded in pencil, test has been Reduced and Reviewed and can be sent as final data.

9.6 **Data Reduction:** All data upon conclusion is then hand calculated, and input on to a Microsoft Excel spreadsheet and furnished along with raw data to lab director or supervisor for data review.

9.7 **Data Review:**

Data Review is done as follows:

- Check calculation for moisture content.
- After moisture content values have been verified, cross examine Job Name, Sample Identification, soil classification and any other pertinent information.

9.8 **Data Report:**

Final data is sent as follows:

- Identification of the sample (material) being tested, such as boring number, sample number & test number.
- Summary data sheet with moisture content in Percent.
- Percent Solids, if required.

10. Calculations

10.1 $W=\{(Mcws-Mcs)/(Mcs-Mc)\} \times 100 = \frac{Mw}{Ms} x100$

where:

w=water content, %

Mcws= mass of container and wet specimen

Mw= mass of water (Mw=Mcws-Mcs)

Mcs= mass of container and oven dry specimen

Mc= mass of container

10.2 Verification of calculations

- Calculations are verified via cross reference of hand calculation versus computer generated results.

11. Calibration

- Oven temperature is recorded daily and calibrated every four months (SOP SA-Draft)

- Balances are checked daily with S class weights and kept in Log Book in lab by Scale (SOP SA 3.0).

12. QC Limits

Non-Applicable

13. Corrective Action Procedures

Corrective actions are taken as follows:

13.1.1 Any suspect or questionable data during test is to be reported to Supervisor immediately on finding.

13.1.2 Supervisor will review data and check any calculations for error.

13.1.3 If there is a calculation error that is made, correction will be noted and test will continue.

13.1.4 If error can not be retrieved, then Supervisor instructs technician to retrieve any unused portion of Sample.

13.1.5 When unused sample is retrieved Supervisor determines if there is enough material and is so instructs technician to re-run entire test. If there is not enough material to re-run test Supervisor relays that information to Project Manager or Client, at this stage it is determined whether more sample can be obtained to run analysis or test is canceled.

13.1.6 Supervisor or lab technician appointed by Supervisor, must weigh and calculate all oven-dried samples every morning. This is a routine check of testing to determine any errors in recording of weights during test.

13.1.7 When an error occurs during 13.1.6 the following measure is taken: first re-weigh sample & container and check against recorded weight. If weight doesn't check then re-record new weight and re-calculate to see if new data correlates with all other data. If weight checks, then remove oven-dried material and weigh container and repeat prior step. If correction is made test can

continue or be reduced and reviewed. If correction is not made then refer to 13.1.5 for corrective action.

13.1.8 Oven-dried samples are not disposed of until Supervisor has checked all data calculations and determines data is valid.

13.1.9 During data review if there are any errors or questionable data Lab Director notifies Supervisor and Supervisor retrieves test sample. If checking test sample by weighing or sieving corrects error than test is reduced again and sent through for review. If checking test sample does not correct mistake then refer to 13.1.5.

13.1.10 Any corrections made to data sheet are done by putting a line through error and recording new data and initialing by individual. If more than one mistake is made and there is no room on data sheet to put correction, a line will be placed through error, a new data sheet will be stapled to original data and a brief explanation as to why sheet is stapled and then new data recorded on stapled sheet and initialed by individual.

13.1.11 Any changes deviance's or unusual measures taken during recording of data shall have an asterisk placed next to unusual data and a brief yet detailed description of what data represents and why its represented in this manner followed by initials of individual taking these actions.

14. Document Description and Example Forms

14.1 See attached forms

15. Miscellaneous Notes

None

16. References

ASTM D2216: Laboratory Determination of Water (Moisture) Content of Soil and Rock

17. Confidentiality Statement

APPENDIX A-57

STANDARD OPERATING PROCEDURE FOR DETERMINATION OF DRY WEIGHT OF SOLID SAMPLES

GZA GEOENVIRONMENTAL, INC.

SOP #: GT-2.0

Copy # 2

STANDARD OPERATING PROCEDURE
DETERMINATION OF DRY WEIGHT OF SOLID SAMPLES

Date: 8/24/99 By: MCM
Revision # 0 Date: 8/99

Reviewed by Lab Supervisor: MCM Date: 2-9-00
Reviewed by Lab Manager: [illegible] Date: 2/9/00

1.0 Scope and Application

Solid samples received at a natural moisture content must be oven-dried to determine the actual percentage of solid material. This percentage is reported as a descriptive characteristic of the sample and is used as a determination of a soil constant.

2.0 Method Summary

Between 10-50 grams of the solid material is weighed out into an aluminum weighing dish and is oven-dried for at least 16 hours at 110 degrees C (+/- 5 ºC).

See SOP # SA - 3.0 for information about the calibration and accuracy checks for the balance. (refer to calibration information affixed to the balance for last date of factory recalibration).

3.0 Sample Preservation, Containers, Handling, and Storage

Sample Preservation: Soil samples are not chemically preserved.

Containers: Soil samples are received in glass containers, plastic bags, shelby tubes, etc.

Handling: The soil samples should be handled with care. This includes wearing glasses, gloves and lab coats.

Storage: Samples are stored prior to analysis in their original containers in the GeoTech laboratory.

4.0 Interference and Potential Problems

Samples that are not handled properly may spill during transfer to the drying oven or while in the oven when moved by other analysts.

Use the top shelf of the oven to minimize contanmination caused by "fallout" from other samples or analyses being performed in the same oven.

5.0 Definitions

Dry weight: The weight of the solid sample after drying for 18 hours at 110 C.

Wet weight: The weight of the solid sample as received.

Percent Solid: The weight of the solid sample after drying for 18 hours at 110 C divided by the weight of the sample as received multiplied by 100 to convert to percent value.

6.0 Equipment/Apparatus

Aluminum Weighing Dish

Top Loading Balance: Mettler PM600, Mettler PM2000.

7.0 Reagents

Not applicable

8.0 Health and Safety

Safety glasses are to be worn in the laboratory at all times. Long pants and socks, gloves and lab coats must be worn when handling samples and extracts and when working in the laboratory.

The Laboratory Manager ensures that health and safety procedures are discussed with each new employee by the H&S representative prior to beginning work in the laboratory.

All samples are to be treated as though they are hazardous.

The chemical hygiene plan and the Hazardous Materials Handling and Disposal SOP should be reviewed by each employee. Copies of both plans are kept in the laboratory.

Use caution when dealing with any heated oven zones. Wear heat protection gloves.

9.0 Procedures

9.1 Weighing out the samples

- Measure the tare weight (~1.00g) of an aluminum weighing dish (Fisher Brand, catalogue # 08-732) size 57mm on the balance. Record the value on the % solid summary sheet.
- Cross reference the weighing dish number with the sample on the summary sheet.
- Mix the sample well.

  Note: It is very important that the sample is mixed well to ensure a representative aliquot is taken.

- Using a spatula weigh out between 10-50 grams of the homogenized sample and record this weight on the Summary Sheet. Once recorded, remove the dish from the balance and place upon a metal tray. If necessary, place another dish on the balance and continue weighing samples.

Note: It is very important that the spatula be rinsed in a jar of DI water between each sample to eliminate cross contamination.

- Once all dry weight samples have been weighed, place the metal tray in the oven.

  All laboratory samples should be placed on the top shelf of the oven. The samples must remain in the oven for at least sixteen hours.

- Record the temperature of the oven on the log sheet. A new sheet is to be used every month.

  This oven (Shel-Lab Model # 1280236) is set to 110 degrees C +/- 5 degrees C. If the oven is not within these limits, fill out a corrective action form, and notify your Laboratory Supervisor.

9.2 Weighing the dried samples

- At the end of the drying period, take the samples to the organic laboratory and let them cool for 5 minutes, but not more than fifteen minutes, before weighing.

- Place each sample on the balance and record the weight on the Summary Sheet

9.3 Calculating the percent solid

- Calculate the percent solid content using the formula below and record.

- Submit the completed Summary Sheet to the lab supervisor for review.

10.0 Calculations

Percent Solid = (B/A)*100

B = weight of dried soil (16 hours at 110C)

A = weight of wet soil (as received)

11.0 Data Validation

Summary Sheets with dry weight information are given to the supervisor for review

The Finalized Summary sheet with the raw data is placed into the "to-be-filed" bin and filed under the GTEL Project Number.

12.0 QC Limits

Not Applicable

13.0 Corrective Action Procedures

If there is not enough soil to perform a % solid test, see the Lab Supervisor

If there are any recurring issues, fill out a corrective action form to ensure action is taken.

If there is no room in the oven or the temperature is not correct, inform your laboratory supervisor.

If the percent solid results is greater than 100%, the test must be performed again.

14.0 Documentation Description and Example Forms

% Solid Summary Sheet: A sample of the GTEL summary sheet is attached..

15.0 Miscellaneous Notes

Associated SOPs:

SOP # SA-3.0: Calibration and Accuracy of Balances

16.0 References

ASTM D 2216 Standard Test Method for the Determination of Water (Moisture) Content of Soil and Rock," Annual Book of ASTM Standards, Vol 04.08 Construction.

APPENDIX A-58

STANDARD OPERATING PROCEDURE FOR THE GRAIN SIZE ANALYSIS ASTM TEST METHOD D-422

GZA GeoEnvironmental, Inc. **SOP GT-1.0**

Standard Operating Procedure for the GRAIN SIZE ANALYSIS

ASTM TEST METHOD D-422

Copy # 2

Date: By: MCM. 8/99 *Reviewed by Lab Supervisor:* MCM *Date:* 2/9/00

Revision #: 1 *Reviewed by QA Officer:* [signature] *Date:* 2/9/00

1. Scope and Application

This test method covers the quantitative determination of the distribution of particle size in soils. Soils larger than the 75um (#200 sieve) which consist of sand and gravel sizes are determined by the sieving, and the particle sizes smaller than 75um (#200 sieve) are determined by a sedimentation process using the hydrometer.

2. Method Summary

2.1 Method Overview

During sample preparation ASTM Test method D421-85 is used as a guide for dry preparation of samples. Remove soil samples from sample containers, spread out on plastic sheeting, labeled and a small representative portion is removed for percent solids. Samples then air dry with the aid of fans, for a period of not less than 16hrs. After drying samples are then gravel sieved to remove all particles greater than 4.75um (#4 sieve). A representative portion of - #4 sieve is taken and used for the hydrometer portion of test. In addition another portion of - #4 sieve is used to determine the hygroscopic moisture. Hydrometer readings are recorded in the conventional manner (typically 7-10 readings over 22-26 hr. time interval along with several temperature readings). After completion of hydrometer analysis sample is washed through #200 sieve and all retained material is put in oven to dry for sieve analysis of sand sized particles. This data will be used to determine the calculated percent finer for all sieve and hydrometer readings. Particle sizes ranging from coarse gravel (>19.0mm) to clay sized particles (<2micron). Calculations are predicated on hygroscopic moisture, percent solids and assumed specific gravity (Gs for hydrometer portion only).

2.2 Related Standard Operating Procedures

- GT-2.0 Percent Solids SOP
- SA-3.0 Balance Calibration

3. Sample Preservation, Containers, Handling, and Storage

Preservation: Non-Applicable

Containers: Jars, Glass or Plastic (4-32oz), Plastic Sample Bags (5 gallon), 5 gallon buckets

Storage: Samples are stored in Laboratory until project is complete, data is sent, and no additional testing required

4. Interference and Potential Problems:

- Sample size is sometimes compromised due to limited amount of material to perform analysis.
- Organic matter can float causing inaccurate Hydrometer readings.
- 1000ml Cylinders can crack (glass) during hydrometer portion of test.
- Error in recording of weights during any step of this analysis.
- Error in calculating data.

5. Definitions

- **Gradation** - The proportions by mass of soul or fragmented rock distributed in specified particle-size ranges.
- **Grain Size Analysis** - The process of determining grain-size distribution.
- **Gravel** - Rounded or semi-rounded particles of rock that will pass a 3 in. (76.2 mm) and be retained on a No. 4 (4.75μm) U.S. standard sieve.
- **Sand** - Particles of rock that will pass the No. 4 (4.75μm) U.S. standard sieve.
- **Silt** - Material passing the no. 200 (75 μm) U.S. standard sieve that is non-plastic or very slightly plastic and that exhibits little or no strength when air-dried.
- **Clay** - Fine-grained soil or the fine grained portion of soil that can be made to exhibit plasticity (putty-like properties) within a range of water contents, and that exhibits considerable strength when air-dry. The term has been used to designate the percentage finer than 0.002mm.
- **Organic** - Soil with a high organic content. (In general, organic soils are very compressible and have poor load sustaining properties.

6. Equipment and Apparatus

- Electric fans (for Sample drying)
- 5 gallon carboys & Squirt bottles (for DI or Demineralized Water)

- Balance sensitive to 0.01 grams.
- Mixer and dispersion cup
- 1000ml Cylinder for hydrometer analysis
- Thermometer accurate to 1.0 F
- Oven with temperature range of 110± 5°C.
- Sieves (2in,1in,3/4in,1/2in,#4,#10,#20,#40,#60,#100&#200 mesh)
- Hydrometer bulb (ASTM soil test hydrometer 151H)
- Clock with capability to read to seconds
- Spatulas and soil pans for mixing and sieving of soil
- Sieve Shaker for thorough sieving of sand sized particles
- Stirring rod for agitation of sample in hydrometer analysis

7. Reagents:

- Sodium Metaphosphate as dispersing agent,
- distilled and/or demineralized water,
- alconox and dish soaps as cleaning agents for apparatus

8. Health and Safety Issues

Safety glasses, Long pants, socks, gloves and lab coats must be worn when handling samples with known contaminants.

The Laboratory Manager ensures that health and safety procedures are discussed with each new employee by the H&S representative prior to beginning work in the laboratory.

The chemical hygiene plan and the Hazardous Materials Handling and Disposal SOP should be reviewed by each employee. Copies of both plans are kept in the laboratory.

Use caution when dealing with any heated oven zones. Wear heat protection gloves.

9. Procedures

9.1 **Login:**

Samples are logged in as follows:

- Each sample is given a unique laboratory identification number.
- This number must be sequential beginning with number one.
- In the case of ongoing project refer to next Lab No. in numerical sequence.
- Last Lab No. can be found in log book in laboratory.
- This log must be updated each time a new sample is logged in.

9.2 **Identify Sample for Testing:**
Check soils laboratory testing assignment sheet.

9.3 **Sieve or Sieve Hydrometer:** is assigned if an X is marked under Sieve-200% (for sieve) or Sieve-200% and Hyd-2m% for Sieve Hydrometer.

9.4 **Sample Wet Preparation:**

- Take entire sample record weight under "total sample wet weight"
- Sieve sample through a nest of gravel sieves (3in,2in,1in,3/4in,1/2in, #4sieve).
- Record cumulative weight retained on each sieve.
- Take a representative portion of -#4 sieve (approximately 250-500 grams) and place in a pre weighed pan and record weight (wet weight of soil & container)
- Oven-dry for hygroscopic moisture.

9.5 **Hydrometer Test:**

- Take approximately 50gms (Clay) to 100gms (Sandy) of -#4sieve material and combine in a 250mls container with 125 mls of 4% dispersing agent (Metaphosphate).
- Allow this solution to soak for not less than 16hrs.
- After soaking period is complete decant solution into stir cup using distilled water in squirt bottle , place cup into stirrer and allow to stir for at least one minute.
- Take squirt bottle with DI water and decant into a 1000, cylinder and fill remainder of cylinder with DI until 1000 mls is in cylinder.
- Agitate with stirring rod for one minute in an up-down and stirring fashion to get all material into suspension.
- After agitation, start clock, take hydrometer bulb and start to record settlement versus time specified on raw data sheet (1,2,4,8,16,32,64,120,...aprox.1400 minutes).
- During this phase of tests also record as many temperature readings as feasible coinciding with settlement readings.
- After final hydrometer reading is recorded re-agitate sample and wash through a 200 sieve.
- Take all retained material and place in a pan , put pan in oven to dry.
- After drying has occurred sieve through sand sized sieves and record weight in same manner as wash sieve.

9.6 **Wash Sieve:**

- Remove sample from oven, record weight (Dry weight of soil & container)
- Wash through a 200 sieve to remove any fine (Silt or Clay) fraction,
- Return to oven and allow to dry not less than 2 hours
- Take out of oven and pour sample into tared pan and record weight (pre-sieve weight).
- Take sample and pour into top of stacked sand sieves (#10,#20,#40,#60,100,#200) put into sieve shaker
- Shake for two minutes.
- Record cumulative weight of material passing #200 to sample and record weight (post sieve).
- Check pre-sieve weight divided by post sieve weight (must be within 5%) to insure proper recovery of soil is recorded.
- Using information contained from hygroscopic moisture calculate total sample dry weight, split sample dry weight, and percent finer by weight

9.7 **Status Check on Data:**

Status is obtained from the soils laboratory testing assignment sheet as follows:

- Test assigned is clearly designated with an X in appropriate column (Step 9.3).
- If one quarter of X is shaded, sample has been prepared
- If one half of X is shaded, sample has been run,
- If three quarters of X is shaded, test has been calculated,
- Finally if entire X is shaded in pencil, test has been Reduced and Reviewed and can be sent as final data.

9.8 **Data Reduction:** All data upon conclusion of test is then inputed into computer program (written and verified by GZA personnel) and computer generated plots are to be furnished along with raw data to lab director or supervisor for data review.

9.9 **Data Review:**

Data Review is done as follows:

- Check calculation for hygroscopic moisture.
- Check calculation for total sample dry weight.
- Check calculation for split sample dry weight.
- Check calculation for dry weight of soil in cylinder.
- Check Gs (specific gravity).
- Check at least one but not limited to one Hydrometer reading.
- After 5.6.1 through 5.6.6 have been verified, cross examine Job Name, sample Identification, soil classification and any other pertinent information on computer plots versus login identification to insure final data is furnished correctly.

9.10 **Data Report:**

Final data is sent as follows:

- Plotted results of % finer versus grain diameter (mm)
- Tabulated results, if required
- % Solids, if required
- Summary data sheet, if required

10. Calculations - Calculations for percent solids, hygroscopic moisture, total sample dry weight, split sample dry weight, particle size retained and finer by weight (both sieve and hydrometer portion) and dry weight of soil in suspension.

10.1 Formula

10.1.1 Percent Solids (PS):

PS= (Dry weight of soil & pan-pan weight)/(wet weight of soil & pan-pan weight) x 100.

10.1.2 Hygroscopic moisture (HM):

HM= (Wet weight of soil & pan - Dry weight of soil & pan)/ (Dry weight of soil & pan-pan weight) x 100

10.1.3 Total Sample Dry Weight (TSDW):

TSDW= (Total sample wet weight - weight retained on #4 sieve)/ $1+\left(\frac{HM}{100}\right)$ (Weight retained on # 4 sieve)

10.1.4 Split Sample Dry Weight (Sieve Analysis Only) (SSDW):

SSDW = (Dry weight of soil & pan-pan weight)

10.1.4.1 Split Sample Dry Weight (Sieve & Hydrometer) (SSDW):

SSDW= (Weight of wet soil in hydrometer)/ (1+HM)

10.1.5 Dry Weight of Soil in Suspension (DWSS):

DWSS= (SSDW - weight of soil retained on #200 sieve)

10.1.6 Total Weight of Gravel Retained in Percent (TWGR):

TWGR= (weight of gravel retained on sieve)/(TSDW) x 100

10.1.7 Total Weight of Gravel Finer in Percent (TWGF):

$$TWGF = 1 - \left(\frac{TWGR}{100}\right) \times 100$$

10.1.8 Split (sand portion)Sample Weight Retained in Percent (SSWR):

$$SSWR = \left(\frac{weight\ retained\ on\ sieve}{SSDW}\right) \times 100$$

10.1.9 Split (sand portion) Sample Weight Finer in Percent (SSWF):

$$SSWF = 1 - \left(\frac{SSWR}{100}\right) \times 100$$

10.1.10 Total Sample Sand & Gravel Finer by Weight in Percent (TSSGFW):

$$TSSGFW = \left(\frac{SSWF}{100}\right) \times TWGF$$

10.1.11 Hydrometer Weight Retained in Percent (HWR):

$$HWR = \left[\left(\frac{GS}{1 - GS} \right) \times 100 \div DWSS \right] \times (\text{Hydrometer Reading} - \text{Control Reading})$$

(Note: Control Reading = 4% Dispersing Agent in 1000 mls Distilled Water)

10.1.12 Entire Sample Weight Finer in Percent (ESWF):

$$ESWF = \left(\frac{TSSGFW}{100} \right) \times HWR$$

10.1.13 Diameter Size of Fine Particles (silt or clay) (DSFP):

$$DSFP = K\sqrt{L/T}$$ where K= constant depending on the temperature of the suspension and specific gravity of the soil particles.
T= time in minutes.
L= distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. This distance is known as effective depth.

10.2 Verification of calculations

- Calculations are verified via cross reference of hand calculation versus computer generated results.

11. Calibration

- Oven temperature is recorded daily and calibrated every four months (SOP SA-Draft)
- Thermometers are calibrated quarterly, cross measuring temperature with thermometer of higher degree of accuracy (SOP SA-13).
- Balances are checked daily with S class weights and kept in Log Book in lab by Scale (SOP SA 3.0).
- Sieves are calibrated bi-annually (SOP SA-Draft)
- Hydrometers are calibrated annually (SOP SA-Draft)

12. QC Limits

Non-Applicable

13. Corrective Action Procedures

Corrective actions are taken as follows:

13.1.1 Any suspect or questionable data during test is to be reported to Supervisor immediately on finding.

13.1.2 Supervisor will review data and check any calculations for error.

13.1.3 If there is a calculation error that is made, correction will be noted and test will continue.

13.1.4 If there is a procedural error whether it be in Sieving, Menisus Correction or Recording of invalid weight, Supervisor will re-trace procedural steps of sample in question. If error is recovered and corrected test will continue.

13.1.5 If error can not be retrieved, then Supervisor instructs technician to retrieve any unused portion of Sample.

13.1.6 When unused sample is retrieved Supervisor determines if there is enough material and is so instructs technician to re-run entire test. If there is not enough material to re-run test Supervisor relays that information to Project Manager or Client, at this stage it is determined whether more sample can be obtained to run analysis or test is canceled.

13.1.7 Supervisor or lab technician appointed by Supervisor, must weigh and calculate all oven-dried samples every morning. This is a routine check of testing to determine any errors in recording of weights during test.

13.1.8 When an error occurs during 13.1.7 the following measure is taken: first re-weigh sample & container and check against recorded weight. If weight doesn't check then re-record new weight and re-calculate to see if new data correlates with all other data. If weight checks, then remove oven-dried material and weigh container and repeat prior step. If correction is made test can continue or be reduced and reviewed. If correction is not made then refer to 13.1.6 for corrective action.

13.1.9 Oven-dried samples are not disposed of until Supervisor has checked all data calculations and determines data is valid.

13.1.10 During data review if there are any errors or questionable data Lab Director notifies Supervisor and Supervisor retrieves test sample. If checking test sample by weighing or sieving corrects error than test is reduced again and sent through for review. If checking test sample does not correct mistake then refer to 13.1.6.

13.1.11 Any corrections made to data sheet are done by putting a line through error and recording new data and initialing by individual. If more than one mistake is made and there is no room on data sheet to put correction, a line will be placed through error, a new data sheet will be stapled to original data and a brief explanation as to why sheet is stapled and then new data recorded on stapled sheet and initialed by individual.

13.1.12 Any changes deviance's or unusual measures taken during recording of data shall have an asterisk placed next to unusual data and a brief yet detailed description of what data represents and why its represented in this manner followed by initials of individual taking these actions.

14. Document Description and Example Forms

14.1 See attached Forms

15. Miscellaneous Notes

15.1 Hydrometer portion of analysis is performed on #4 Sieve

15.2 Stirring rod (Army Corps Manual Appendix V Figure 7 page V-16) was used to agitate soil in cylinder during hydrometer analysis.

16. References

16.1 ASTM D421 - Dry Preparation of Soil Samples for Particle Size Analysis and Determination of Soil Constants

16.2 ASTM D422 - Particle Size Analysis of Soils

16.3 Army Corps Manual EM1110 Appendix V - Combined Analysis

16.4 AASHTO-R18 - Establishing and Implementing A Quality System for Construction and Materials Testing Laboratory

17. Confidentiality Statement

- **This SOP document has been developed and copyrighted by GZA. It is intended for internal (GZA) personnel and government agencies specifically. In addition, the document is not to be released externally for any other purpose without consent of GZA.**

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APPENDIX A-59

STANDARD OPERATING PROCEDURE FOR TOTAL UNIT WEIGHT (BULK DENSITY)

GZA GeoEnvironmental, Inc. **SOP # GT3.0**

Standard Operating Procedure for

Total Unit Weight (Bulk Density)

Copy #: 2

Date: By: 2-8-00 *Reviewed by Lab Supervisor:* MM *Date:* 2-9-00

Revision #: 1 *Reviewed by QA Officer:* MS *Date:* 2/9/00

1. Scope and Application

   1.1 This test method covers the determination of total unit weight of samples in containers that are uniform in dimensions

   1.2 This test method provides the total unit weight of soil/rock per volume.

2. Method Summary

   2.1 Related Standard Operating Procedures-None

3. Sample Preservation, Containers, Handling, and Storage

   Preservation: Non-Applicable

   Containers: Cylindrical molds graduated cylinders and shelby tubes.

   Storage: Samples are stored in Laboratory until project is complete, data is sent, and no additional testing required

4. Interference and Potential Problems-Loss of sample during weighing and measuring dimensions.

5. Definitions

   - Bulk Density-The total mass (solids plus water) per total volume.

6. Equipment and Apparatus

   - Sample Extruder - capable of extruding the soil core from the sampling tube in the same direction of travel in which the sample entered the tube, at a uniform rate, and with negligible disturbance of the sample. Conditions at the time of sample removal may dictate the direction of removal, but the principal concern is to keep the degree of disturbance negligible.

- Balance - The balance used to weigh specimens shall determine the mass of the specimen to within 0.1% of its total mass.

- Miscellaneous equipment measuring tape or calipers to record accurate dimensions of sample and or molds. Also pipe cutter able to cut shelby tube to approximate length of sample.

7. Reagents

Non-Applicable

8. Health and Safety Issues

Safety glasses, Long pants, socks, gloves and lab coats must be worn when handling samples with known contaminants.

The Laboratory Manager ensures that health and safety procedures are discussed with each new employee by the H&S representative prior to beginning work in the laboratory.

The chemical hygiene plan and the Hazardous Materials Handling and Disposal SOP should be reviewed by each employee. Copies of both plans are kept in the laboratory.

Use caution when dealing with any heated oven zones. Wear heat protection gloves.

9. Procedures

9.1 **Procedures**

Login:

Samples are logged in as follows:

- Each sample is given a unique laboratory identification number.
- This number must be sequential beginning with number one.
- In the case of ongoing project refer to next Lab No. in numerical sequence.
- Last Lab No. can be found in log book in laboratory.
- This log must be updated each time a new sample is logged in.

9.2 Identify Sample for Testing: Check soils laboratory testing assignment

9.3 Total Unit Weight: is assigned if X is marked under total unit wt.(pcf)

9.4 Undisturbed Specimen Sample Setup:

9.4.1 Take undisturbed Specimen, place in vice and remove plastic and determine where top of sample is (this is done by using a tape measure and placing in tube until resistance occurs from the wax cap sealing the sample.

9.4.2 Mark outside of tube with marker as to where wax is in relationship to the top of tube.

9.4.3 With pipe cutter remove top portion of tube then pull wax plug out and visually determine where top of sample begins.

9.4.4 Remove wax plug from bottom of tube and again determine where bottom of sample ends.

9.4.5 With marker again mark outside of tube where the top of sample begins and the bottom of sample ends.

9.4.6 Take calipers or measuring tape record length to the nearest .001" under Initial Length (L_o)

9.4.7 Again with calipers, record diameter of the inner wall of shelby tube then nearest .001 under Initial Diameter (D_o).

9.4.8 Calculate Volume and record under V_o on Raw data sheet. (Refer to calculation section for formula.)

9.4.9 Weigh Sample and container on scale and record under sample & container wt.

9.4.10 Extrude sample from shelby tube and re-weigh tube and record under weight of tube.

9.4.11 Subtract value recorded in 9.4.10 from value in 9.4.9 and record under total sample weight .

9.4.12 Calculate total unit weight in pounds per cubic foot and record under total unit weight. (Refer to calculation section for formula.)

9.5 **Status Check on Data:**

Status is obtained from the soils laboratory testing assignment sheet as follows:

- Test assigned is clearly designated with an X in appropriate column (Step 9.3).
- If one quarter of X is shaded, sample has been prepared
- If one half of X is shaded, sample has been run,
- If three quarters of X is shaded, test has been calculated,
- Finally if entire X is shaded in pencil, test has been Reduced and Reviewed and can be sent as final data.

9.6 **Data Reduction:** All data upon conclusion of test is then inputed into computer spreadsheet and computer generated summary sheets are to be furnished along with raw data to lab director or supervisor for data review.

9.9 **Data Review:**

Data Review is done as follows:

- Check calculation for total sample weight.
- Check calculation for volume of sample.
- Check calculation for Total Unit weight.

- After Data Review completed, cross examine Job Name, sample Identification, soil classification and any other pertinent information on computer plots versus login identification to insure final data is furnished correctly.

10. Calculations -, Volume, Total Unit Weight,

10.1.1 Volume

$$V\ (ft^3) = \left[\frac{\Pi D^2}{4}(L_o)\right] \div 1728$$

$\Pi = 3.14$

D = Diameter

1728 - Conversion of in^3 to ft^3 (i.e. 12x12x12)

L_o = Initial Length

10.1.2 Total Unit Weight (Bulk Density)

$$\text{Total Unit WT (pcf)} = \left[\frac{WT\ of\ Wet\ Sample}{V}\right] \div 453.59\ \text{gms}$$

Where V = Volume in ft^3

453.59 = conversion of gms to pounds $\left(\frac{1lb.}{453.59gms}\right)$

11. Calibration

- Balances are checked daily with S class weights and kept in Log Book in lab by Scale (SOP SA 3.0).

12. QC Limits

Non-Applicable

13. Corrective Action Procedures

Corrective actions are taken as follows:

13.1.1 Any suspect or questionable data during test is to be reported to Supervisor immediately on finding.

13.1.2 Supervisor will review data and check any calculations for error.

13.1.3 If there is a calculation error that is made, correction will be noted and test will continue.

13.1.4 If error can not be retrieved, then Supervisor instructs technician to retrieve any unused portion of Sample.

13.1.5 When unused sample is retrieved Supervisor determines if there is enough material and is so instructs technician to re-run entire test. If there is not enough material to re-run test Supervisor relays that information to Project Manager or Client, at this stage it is determined whether more sample can be obtained to run analysis or test is canceled.

13.1.6 During data review if there are any errors or questionable data Lab Director notifies Supervisor and Supervisor retrieves test sample. If checking test sample by weighing corrects error than test is reduced again and sent through for review. If checking test sample does not correct mistake then refer to 13.1.5.

13.1.7 Any corrections made to data sheet are done by putting a line through error and recording new data and initialing by individual. If more than one mistake is made and there is no room on data sheet to put correction, a line will be placed through error, a new data sheet will be stapled to original data and a brief explanation as to why sheet is stapled and then new data recorded on stapled sheet and initialed by individual.

13.1.8 Any changes deviance's or unusual measures taken during recording of data shall have an asterisk placed next to unusual data and a brief yet detailed description of what data represents and why its represented in this manner followed by initials of individual taking these actions.

14. Document Description and Example Forms

14.1 See attached forms

15. Miscellaneous Notes

None

16. References

ASTM D1587 - Thin Walled Tube Geotechnical Sampling of Soils

APPENDIX A-60

STANDARD OPERATING PROCEDURE FOR Pb^{210} DATING DIGESTION AND ANALYSIS

Battelle
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Marine Sciences Laboratory

EFFECTIVE DATE: 2-09-2000

Battelle Pacific Northwest National Laboratories
Marine Sciences Laboratory

STANDARD OPERATING PROCEDURE
MSL-C-012-00 (new number)
MSL-M-006-00 (old number)

Pb^{210} Dating Digestion and Analysis

Approvals:		
AUTHOR: Linda Bingler	Linda S. Bingler	2-9-00
	Signature	Date
TECHNICAL REVIEWER: Eric Crecelius	E A Crecelius	2-9-00
	Signature	Date
QA OFFICER: Deborah Coffey	Deborah Coffey	2-09-2000
	Signature	Date
TECHNICAL GROUP MANAGER: Eric Crecelius	E A Crecelius	2-9-00
	Signature	Date

Pb^{210} DATING DIGESTION AND ANALYSIS
SOP MSL-M-6

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the preparation of sediment samples and the analysis of those samples for Pb^{210} concentrations.

2.0 SUMMARY OF METHOD

2.1 Samples are acid-digested, filtered, and the filtrate evaporated to remove any remaining acid. A plating solution is added to the evaporated filtrate which is spontaneously plated onto silver discs and counted using a Si(Li) alpha particle spectrometer. A Po^{208} spike is used to correct for plating and counting efficiency.

3.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

3.1 Frozen or dried sediment samples are stored in acid-cleaned plastic jars.

4.0 DEFINITIONS

4.1 Plating - the process of creating a smooth, flat piece of any material, thin or of uniform thickness.

5.0 INTERFERENCES

5.1 Organic material which is not completely removed during the digestion step can interfere with the plating process.

5.2 Nitric acid must be removed from the sample filtrate to assure adequate plating of Po^{208} on the silver disk.

6.0 RESPONSIBLE STAFF

6.1 Researcher/Technician.

7.0 APPARATUS AND REAGENTS

7.1 Analytical balance capable of accurate weighing to 0.01 g $\pm$ 3%.

7.2 Graduated cylinder, 25 ml and 250 ml.

7.3 Assorted automatic pipettes.

7.4 Hot plate.

7.5 Fleakers (brand name of a combination flask-beaker), 250 ml.

7.6 Filtration apparatus - fleakers, 500 ml, funnels, Whatman filters #41.

7.7 Silver disks.

7.8 Hydrochloric acid, concentrated (instra-pure for trace metals analysis).

8.14 Place each disc in a plastic bag. The data sheet should accompany the digested samples from this point. The samples are now ready for analysis.

9.0 ANALYSIS

9.1 Count samples using a Si(Li) alpha particle spectrometer and record on data sheet (Exhibit 1).

10.0 QUALITY CONTROL

10.1 One procedural blanks should be run with each batch of samples or as specified by the sponsor. The procedural blank consists of reagents and is processed as a sample.

10.2 One standard reference material should be analyzed with each batch of samples or as specified by the sponsor.

11.0 CALCULATIONS

11.1 Blank correction

$$A_{208} - (B_R + B_A) = C_{208}$$
$$A_{210} - (B_R + B_A) = C_{210}$$

where,

- A_{208} = Po^{208} count
- A_{210} = Po^{210} count
- B_R = reagent blank count
- B_A = air blank count
- C_{208} = reagent and air blank corrected Po^{208} count
- C_{210} = reagent and air blank corrected Po^{210} count

11.2 Decay correction

11.2.1 The Δ_T is the difference in time from when the disk was plated to when the disk was counted. Record the Δ_T factor for the time decay of Po^{210} (sister tracer to Pb^{210}) from the Po^{210} chart (Exhibit 2). To calculate the Δ_T factor for Po^{210} as they appear on the chart, use the following equations:

$$Po^{210}\ \Delta_T \text{ factor} = e^{-\lambda \Delta_T}$$

$$Po^{210}\ \Delta_T \text{ factor} = e^{-.005\ \Delta_T}$$

$$(Po^{210}\ \Delta_T \text{ factor})\ (C_{210}) = D_{210}$$

where,

- $\lambda = \frac{\ln 2}{t^1/_2} = 0.005$
- $t^1/_2$ = half life = 138 days for Po^{210}
- Δ_T = plate time - count time in activity (A_T)

ΔT Factors for Po^{210}

ΔT	Factor	ΔT	Factor	ΔT	Factor
0	1.00	64	1.38	130	1.92
2	1.01	66	1.39	132	1.94
4	1.02	68	1.41	134	1.96
6	1.03	70	1.42	136	1.98
8	1.04	72	1.44	138	2.00
10	1.05	74	1.45	140	2.02
12	1.06	76	1.46	142	2.04
14	1.07	78	1.48	144	2.06
16	1.08	80	1.49	146	2.08
18	1.09	82	1.51	148	2.10
20	1.11	84	1.52	150	2.12
22	1.12	86	1.54	152	2.15
24	1.13	88	1.56	154	2.17
26	1.14	90	1.57	156	2.19
28	1.15	92	1.59	158	2.21
30	1.16	94	1.60	160	2.23
32	1.17	96	1.62	162	2.26
34	1.19	98	1.64	164	2.28
36	1.20	100	1.65	166	2.30
38	1.21	102	1.67	168	2.33
40	1.22	104	1.69	170	2.35
42	1.23	106	1.70	172	2.37
44	1.25	108	1.72	174	2.40
46	1.26	110	1.74	176	2.42
48	1.27	112	1.76	178	2.45
50	1.28	114	1.77	180	2.47
52	1.29	116	1.79	182	2.49
54	1.31	118	1.81	184	2.52
56	1.32	120	1.83	186	2.55
58	1.34	122	1.85	188	2.57
60	1.35	124	1.86	190	2.60
62	1.37	126	1.88	192	2.62
		128	1.90	194	2.65

APPENDIX A-61

STANDARD OPERATING PROCEDURE FOR ANALYSES OF CS^{137} AND OTHER GAMMA-EMITTING ISOTOPES BY GAMMA COUNTING

Battelle
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Marine Sciences Laboratory

EFFECTIVE DATE: 2-09-2000

Battelle Pacific Northwest National Laboratories
Marine Sciences Laboratory

STANDARD OPERATING PROCEDURE
MSL-C-013-01

Analyses of ^{137}Cs and Other Gamma Emitting Isotopes by Gamma Counting

---

Approvals:		
AUTHOR: Linda Bingler	Linda S. Bingler	2-9-00
	Signature	Date
TECHNICAL REVIEWER: Eric Crecelius	Eq Crecelius	2-9-00
	Signature	Date
QA OFFICER: Deborah Coffey	Deborah Coffey	2-9-2000
	Signature	Date
TECHNICAL GROUP MANAGER: Eric Crecelius	Eq Crecelius	2-9-00
	Signature	Date

Analyses of ^{137}Cs and Other Gamma Emitting Isotopes by Gamma Counting

1.0 SCOPE AND APPLICATION

This method is used to measure the activity of ^{137}Cs and other gamma emitting isotopes (e.g., ^{7}Be and ^{40}K) in sediment. ^{137}Cs will be used as the example throughout this procedure, but the other isotopes can be easily substituted in the procedure and calculations. The activity of ^{137}Cs is used to provide a means of determining the age of a sediment layer. During the last 50 years, ^{137}Cs has been entering the oceans as a result of atmospheric testing of nuclear weapons. The major input occurred between 1957 and 1965, producing a maximum of ^{137}Cs activity in the ocean surface water in approximately 1965. Since then, the ^{137}Cs level in surface water has decreased slowly due to mixing with the deep ocean and radioactive decay. Marine sediments in contact with seawater exchange stable Cs and ^{137}Cs, thus, the levels of ^{137}Cs in the seawater and the sediments are related. Once these sediments are removed from interaction with seawater through burial, the ^{137}Cs activity changes only due to decay, which is predictable, and possibly by mixing as a result of bioturbation or other sediment perturbation. If the sediment remains relatively intact as sedimentation occurs over time, the levels of ^{137}Cs buried reflect the relative amounts of ^{137}Cs that were deposited. In this way, the subsurface maximum observed in a core from these undisturbed sediments can be assigned a year of 1965, as described above. This procedure replaces MSL-M-008-00 ^{137}Cs Analyses by Gamma Counting.

2.0 DEFINITIONS

GeLi - Germanium, Lithium crystal used to detect gamma rays.

dpm/g - disintegrations per minute per gram, units of measurement.

^{7}Be – Beryllium, isotope mass 7; 0.487 meV

^{137}Cs - Cesium, isotope mass 137; 0.66164 meV.

^{40}K - Potassium, isotope mass 40; 1.461 meV.

3.0 RESPONSIBLE STAFF

- Technician - sample digestion
- Analyst- sample analysis, calculations
- MSL QA Officer or Representative- data verification

4.0 SUMMARY OF METHOD

^{137}Cs, ^{7}Be and ^{40}K are measured directly in either wet or dry sediment by measuring the gamma rays emitted using a GeLi detector.

Typical detection limit for the method is 0.01-0.1 disintegrations per minute per gram. This corresponds to a sample weight of no less than 50 grams dry.

5.0 PROCEDURE

5.1 Sample Collection, Preservation and Handling

Samples can be held either wet or dry and do not require any special storage conditions.

5.2 Potential Interferences

5.2.1 Other gamma rays may interfere with ^{137}Cs counting of samples. This can be evaluated by analyzing standard reference materials to assess the accuracy of the method.

5.2.2 ^{40}K may be monitored for a number of reasons: 1.) to monitor system performance; and 2.) because the source of ^{40}K is crustal material, the activity present in a sediment core should only change due to changes in the types of crustal material present. Monitoring this isotope is a good indication of changes in type of material present in the core and aid in data interpretation.

5.3 Apparatus and Reagents

GeLi detector
Counter; Canberra, Series 35

5.4 Precautions

5.4.1 The detector must be kept cold at all times. This is done by keeping the detector in a Dewar flask filled with liquid nitrogen.

5.4.2 In case of power failure for the high voltage bias power supply, the voltage on the bias power supply **must** be turned down before resetting the power interrupt relay. Then the bias voltage must be increased gradually to 3500 volts at the rate of 100 volts per second. If in doubt, contact an experienced operator or contact facilities personnel.

5.5 Sample Preparation

Samples can be analyzed either wet or dry. It is important that the sample be placed in a container of the same geometry as the calibration standard.

5.6 Calibration

5.6.1 Setting Channels - Three ranges are set for analysis of ^{137}Cs; the range containing the left blank, the actual ^{137}Cs peak and the right blank. Because there is significant background noise, these background counts must be subtracted from the ^{137}Cs counts to obtain an accurate quantitation. The ^{137}Cs range should contain between 10 and 20 channels. The number of channels in the left and right blank ranges must add up to the number of ^{137}Cs channels being counted.

5.6.2 Calibrating to a known standard - The detector is calibrated by placing a standard of known activity on the detector for a known period of time. It is important that the standard be placed in a similar container and that the container be placed in the same position on the detector as the samples. Both the integration and area are recorded for all three channels. The integration is the non-background corrected number of counts measured. The area value is the system background corrected measurement. Generally, the integrations are used and manually corrected for the background integrations recorded for the left and right blank ranges being measured. The number of disintegrations per count is then calculated (Section 6.1) and used to calculate the activity of the unknowns (Section 6.2).

5.7 Analysis

The sample is placed in front or on top of the detector, depending on the configuration of the system. The sample should be placed in exactly the same position as the standard and this position should remain constant for all samples in that batch. Samples are generally counted for 24 hours, however, a shorter counting period can be used depending on the amount of sample available and the activity of the sample. After the prescribed counting period the sample integration and area counts are recorded for both the left and right background ranges and the actual ^{137}Cs peak range as well as the counting time in seconds. As described above, the integrations are generally used for all calculations. Section 6.0 describes these calculations.

5.8 Analysis of Sample Dry Weight.

The dry weight of the entire sample analyzed must be determined to calculate the final activity of the sample. Generally, the entire sample used for measurement is weighed either prior or after counting. If the sample is analyzed wet, the wet weight of the sample analyzed should be measured and either a subset or the entire sample can be dried to determine the percent moisture. Percent moisture is determined following MSL-C-003, Percent Dry Weight and Homogenizing Dry Sediment, Soil, and Tissue.

6.0 CALCULATIONS

The following calculations use ^{137}Cs as the example. If calculations for other isotopes (e.g., ^{7}Be and ^{40}K) are desired, the correct half life and standard activity will need to be substituted in the algorithms given below.

6.1 Standard Calibration (disintegrations/count)

$$A_t = A_i * e^{-\lambda t}$$

Where: $\lambda = \ln 2 / t_{1/2}$ [$t_{1/2}$ (half life) for ^{137}Cs = 30.7 years]
A_i = Initial Standard Activity (in Ci)
A_t = Activity at time t
t = time in years since initial activity determined

To convert from Ci (microcuries) to dps (disintegrations per second):

$$3.7 \times 10^{10} \text{ dps} = 1 \text{ curie}$$

$$\text{STD (disintegrations/count)} = A_t * (10^{-6} \text{ Ci/Ci}) * 3.7\ 10^{10} \text{ dps/Ci} * t_c / C_{std}$$

where: t_c = time standard counted in seconds
C_{STD} = Counts recorded for standard (integrations)

6.2 Sample Calculation

$$A_s = C_s / t_c / W_s * STD$$

Where: A_s = Sample activity in disintegrations per minute per gram
t_c = time standard counted in minutes
C_s = Net sample counts recorded (^{137}Cs integrations - sum of left and right blank integrations)
W_s = Sample dry weight in grams

6.3 Detection Limit (DL)

The detection limit is defined as 3 times the square root of the background counts.

7.0 QUALITY CONTROL

7.1 Instrument calibrations must be performed (Section 5.6.2) at a minimum of once per 10 samples or when the system changes or maintenance occurs. During calibration, range settings should be checked to make sure no system drift has occurred. If the ^{137}Cs peak has drifted outside of the set range, this range should be re-set and the new channel range should be recorded. If range settings continue to drift after each calibration there may be problems with the system and facilities should be notified to initiate instrument repair.

7.2 Quality assurance data must be composed of a minimum of 1 blank, 1 replicate and 1 standard reference material (SRM). These quality control samples should be analyzed at a minimum of once per batch. A batch, if not otherwise specified, consists of ≤20 samples.

7.3 Data quality objectives (DQOs) for this method are as follows (unless project specific DQOs are established):

Accuracy	SRMs	% Difference ≤30%
Precision	Replicates	Relative percent difference (RPD) ≤25%
Interference	Blank	< Detection Limit

8.0 SAFETY

Appropriate protective clothing such as gloves and safety glasses should be worn when handling liquid nitrogen to protect against the low temperatures and the potential of frostbite.

9.0 TRAINING

Before operating the instrument, the analyst should read this procedure and go through the steps in the procedure with an experienced operator. Monitoring of SRM results will be performed to determine if adequate training has occurred and thereafter to monitor proficiency over time. Training will be documented in accordance with the procedure, MSL-A-006, Marine Sciences Laboratory Training.

10. REFERENCES

MSL-A-006 Marine Sciences Laboratory Training
MSL-C-003 Percent Dry Weight and Homogenizing Dry Sediment, Soil, and Tissue