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

October 27, 1999 (DCN: GEP2060499-AAIY)

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

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

TABLE OF CONTENTS—VOLUME IIA, APPENDIX A, CONTINUED

APPENDIX A—STANDARD OPERATING PROCEDURES (CONTINUED)

TABLE OF CONTENTS—VOLUME IIA (Continued)

TABLE OF CONTENTS—VOLUME IIA (Continued)

TABLE OF CONTENTS—VOLUME IIA (Continued)

APPENDIX A-62

STANDARD OPERATING PROCEDURES FOR BIOCHEMICAL OXYGEN DEMAND EPA METHOD 405.1

KEMRON
ENVIRONMENTAL SERVICES

Document Control #: 1014

STANDARD OPERATING PROCEDURES FOR BIOCHEMICAL OXYGEN DEMAND EPA Method 405.1 SOP K4051

Issue Date: 25 February 1998
Revision 7

Implementation Date: 25 March 1998

Last Review: 03 September 1999

KEMRON Environmental Services
109 Starlite Park
Marietta, OH 45750

Approved by:

Deanna I. Hesson, Wet Chemistry Supervisor — Date: 9/3/99

Dennis S. Tepe, Laboratory Manager — Date: 9/30/99

Daniel A. Musgrave, QA/QC Supervisor — Date: 10/1/99

David L. Bumgarner, Director, Analytical Services — Date: 10/1/99

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of the relative oxygen requirements of municipal and industrial waste waters, effluents, and polluted waters.

1.2 This method also includes carbonaceous, soluble, and ultimate BOD.

1.3 A sample of waste, appropriately diluted, is placed in an airtight bottle and incubated for 5 days at 20° C.

1.4 The dissolved oxygen (DO) is measured initially and after incubation. BOD is calculated from the difference between the two DO readings.

1.5 The Biochemical Oxygen Demand (BOD) test is an empirical bioassay-type procedure that determines the relative oxygen requirements of the sample. The test measures the oxygen utilized for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material (Nitrogenous demand).

1.6 BOD-SL is defined as soluble BOD. The sample is filtered before being analyzed.

1.7 BOD-UL is defined as ultimate BOD. The sample is incubated for twenty days instead of five days.

1.8 BOD-C = (Carbonaceous BOD): An inhibitor is added to inhibit the nitrogenous demand.

1.9 This method references EPA Method 405.1 and Standard Methods 5210B.

2.0 SAFETY PRECAUTIONS

2.1 Standard Laboratory safety procedures should be followed when working with unknown samples.

2.2 Lab coats and safety glasses with sideshields must be worn. Gloves are recommended since acid, base, and unknown samples are being analyzed.

2.3 Sulfuric acid and sodium hydroxide are used in this procedure and should be used with caution. Consult the MSDS for further information on the hazards and toxicity of these chemicals.

3.0 SAMPLE PRESERVATION AND STORAGE

3.1 Samples should be stored at 4° C for a period not exceeding 48 hours from time of collection before analysis is performed. Samples should be allowed to warm to 20° C before analysis. After analysis, samples are stored in a designated area in the archive room.

3.2 A minimum of 500 ml is required to insure sufficient volume for one analysis. If less than the recommended volume is available, the analysis will be performed on a lesser amount and the detection limit will be elevated proportionately.

4.0 METHOD PERFORMANCE

4.1 This method has a minimum reporting limit of 3 mg/L O_2 for an undiluted (200 ml) liquid sample..

4.2 The current MDL is 1.168 mg/L. This data is updated annually or when necessary.

4.3 The linear range of the method is 3 mg/L (full volume of sample) to approximately 22,000 (0.1 ml of sample). This range can be extended on the upper end by using less than 0.1 ml.

4.4 The current statistical limits are 74-128% for the LCS and MS. However the method set limits of 84 - 114% are used for the LCS. The relative percent difference for the duplicate is 18%. This data is updated annually.

5.0 INTERFERENCES & CORRECTIVE MEASURES

5.1 Samples containing caustic alkalinity or acidity must be neutralized.

5.2 Samples containing residual chlorine must be treated to destroy the residual chlorine.

5.3 Incubation must be done in the dark to prevent photosynthetic production of dissolved oxygen.

6.0 EQUIPMENT AND SUPPLIES

6.1 Dissolved Oxygen Meter with bottle probe and stirrer. YSI Model 58 or equivalent.

6.2 Incubator: thermostatically controlled at 20± 1°C, excluding all light.

6.3 300 ml incubation bottles with ground glass stoppers and plastic caps.

7.0 STANDARDS AND REAGENTS

NOTE: Discard any of the following reagents if there is any sign of biological growth in the bottle, or if 6 months old.

NOTE: All standards and reagents are prepared using class A volumetric flasks and pipets unless otherwise stated differently.

7.1 BOD LCS Stock Solution (10,000 ppm): Dissolve 7.5 g each of glutamic acid and glucose (or dextrose)(each dried at 103° C) in deionized water. Preserve with 10 ml sulfuric acid, and dilute to 1 liter. Discard after 6 months.

7.2 BOD Second Source Stock: purchased as 400 mg/L.

7.3 Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K2HPO4, 33.4 g $Na_2HPO_4(7H_2O)$, and 1.7 g NH_4Cl in deionized water and dilute to 1 liter. Confirm that the pH is 7.2. Discard after 6 months.

7.4 Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4(7H_2O)$ in deionized water and dilute to 1 liter. Discard after 6 months.

7.5 Calcium Chloride solution: Dissolve 27.5 g $CaCl_2$ in deionized water and dilute to 1 liter. Discard after 6 months.

7.6 Ferric chloride solution: Dissolve 0.25 g $FeCl_3(6H_2O)$ in deionized water and dilute to 1 liter. Discard after 6 months.

7.7 NaOH (5%): Dissolve 50 g NaOH in deionized water and dilute to 1 liter. Discard after 6 months.

7.8 H_2SO_4 (5%): Slowly add 50 ml H_2SO_4 deionized water and dilute to 1 liter. Discard after 6 months.

7.9 Acetic acid, glacial

7.10 Potassium Iodide (KI) pellets

7.11 Starch solution: Add a cold water suspension of 5 g soluble starch to about 800 ml boiling deionized water with stirring. Dilute to 1 liter and boil a few more minutes. Let settle overnight and decant the clear supernatant. Preserve with 1.3 g salicylic acid. Discard after 6 months.

7.12 Sodium sulfite solution: Dissolve about 0.5 g Na_2SO_3 in about 25-50 ml deionized water. **Make daily as necessary.**

7.13 Nitrification inhibitor: 2-chloro-6-(trichloro methyl) pyridine. (purchased from HACH or equivalent)

7.14 Polyseed: purchased commercial BOD seeding material

8.0 CALIBRATION PROCEDURES

8.1 Turn the meter on and allow to warm up for 30 minutes.

8.2 Blot the probe to remove any condensation.

8.3 Turn the knob on the meter to temperature and record the temperature in the calibration logbook.

8.4 Turn the knob to the 0.01 range.

8.5 Get the reading from the chart that corresponds to the temperature. Record this reading in the logbook.

8.6 Adjust the calibration knob to make the meter read the correct value.

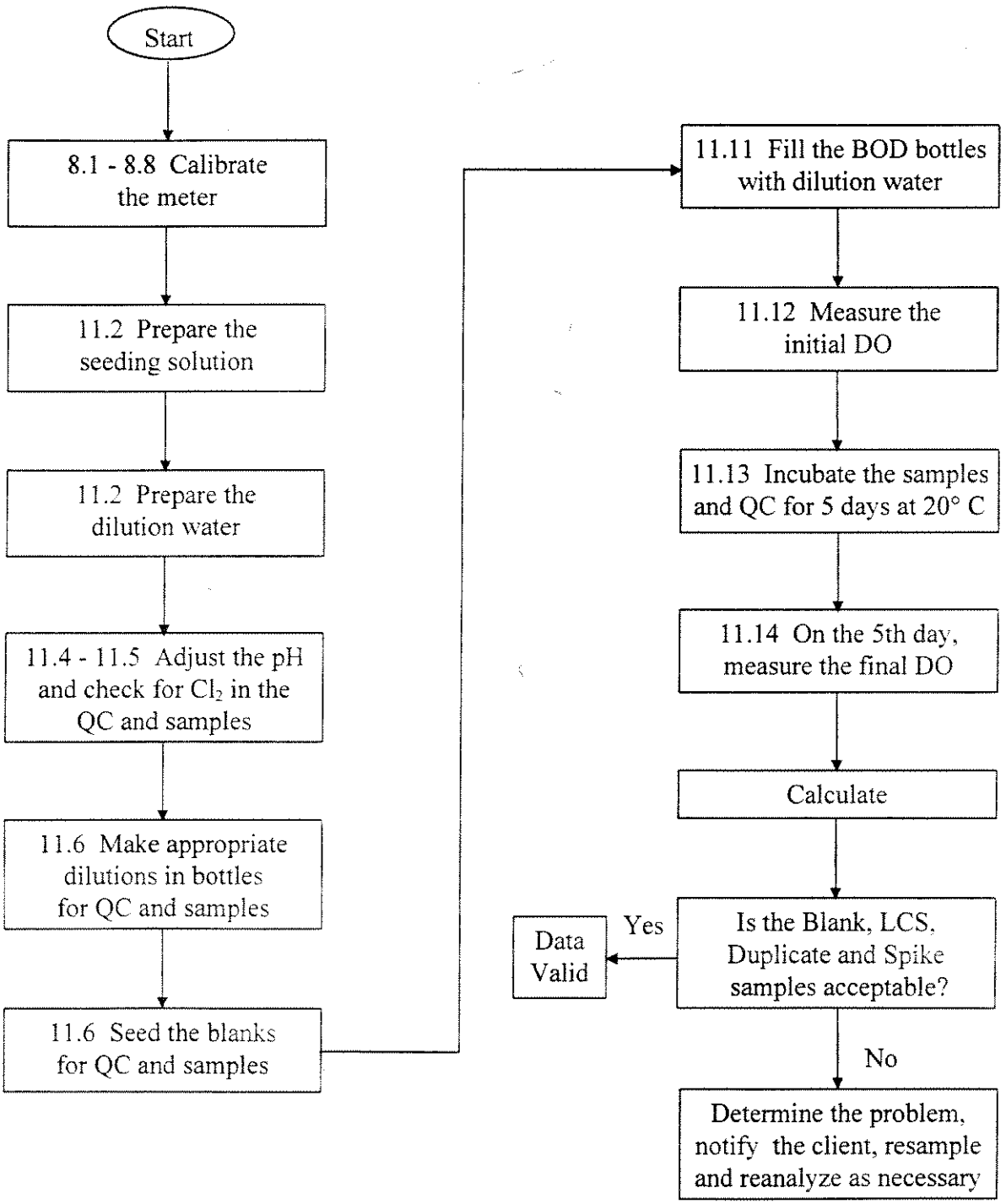
8.7 Record the size of the adjustment.

8.8 Turn the knob to %. If it isn't reading 99 - 101% , something is wrong. Check the membrane and recalibrate if necessary.

9.0 SAMPLE PREPARATION

Sample preparations are described in Section 11 to insure all steps are taken in the correct sequence.

10.0 DIAGRAM OR TABLES TO OUTLINE PROCEDURES



11.0 ANALYTICAL PROCEDURE

11.1 In a 14 gallon container, add 1 - 2 gallons deionized water. To this water add 53 ml each of phosphate buffer (7.3), $MgSO_4$ buffer (7.4), $CaCl_2$, buffer (7.5) and $FeCl_3$ buffer (7.6). Fill the container to 14 gallons with deionized water and mix well. Before this dilution water may be used, determine the DO uptake. Determine the initial DO of 300 ml of the dilution water. Incubate for 5 days and then determine the final DO. The DO uptake should be 0.2 mg/L or lower. If the DO uptake is above 0.2 the water should not be used.

11.2 Prepare seed by emptying the contents of one polyseed capsule into 450 ml deionized water. Stir the solution using a magnetic stir bar and stirrer. Stir continuously while bubbling in air for one hour. This seeding solution is stable for 6 hours. The amount of deionized water used may vary throughout the year.

11.3 Fill a 5 gallon cubitainer with previously tested dilution water (11.1) and aerate if necessary to bring the DO to 7 - 9.

11.4 SAMPLE PREPARATION: Warm sample to 20° C before beginning analysis. Record initial pH and adjust to pH 6.5 to 7.5 with NaOH (7.7) and/or H_2SO_4 (7.8) if necessary. Also adjust DO to 7-9 mg/L O by shaking or aerating.

11.5 CHLORINE CHECK: Pour 50 ml of the neutralized sample into a cup. Add 5 drops acetic acid (7.9), 2 or 3 KI pellets (7.10), and approximately 1 ml starch solution (7.11). A change to any shade of blue indicates the presence of residual chlorine. Add sodium sulfite solution (7.12) drop wise to any sample that shows a blue color until the sample returns to its original color. Add a proportional amount of the sodium sulfite solution to the sample that has been pH adjusted. Do not add an excess of sodium sulfite.

11.6 Determine the appropriate amounts of sample to be used based on the sample source or historical data. For a sample of unknown source use a range from 0.5 to 200 ml per 300 ml total volume. Measure the appropriate amounts of the sample into the 300 ml incubation bottles. Mark each bottle with the sample ID and the sample volume.

11.6.1 If Carbonaceous BOD (BOD-C) is to be determined, add 2 drops of nitrification inhibitor (7.13) using a dry dispenser bottle to each bottle. Two blanks containing the inhibitor are also analyzed with the samples.

11.6.2 If Soluble BOD (BOD-SL) is to be determined, filter the entire sample through a 934-AH glass fiber filter prior to making the appropriate dilutions.

11.7 Prepare two 10 ml blanks by pipeting 10 ml of the seed solution into two BOD bottles. This is best accomplished by using a 10 ml disposable pipet.

11.8 Prepare two 2 ml blanks by pipeting 2 ml of the seed solution into two BOD bottles. It is best to use a 5 ml disposable pipet and fill to the 4 ml mark and then dispense 2 ml into the two bottles.

11.9 Using a 5 ml pipet and filling to the 4 or 6 ml mark with the seed solution, dispense 2 ml of the solution into all of the BOD bottles containing QC and / or samples. Two or three bottles may be seeded at a time using this technique.

11.10 NOTE: Do not use a pipet larger than a 5 ml. The bran contained in the seed solution settles very rapidly and will result in inconsistent seeding and the results will also vary.

11.11 Fill each blank, QC sample, and sample BOD bottle with dilution water (11.3).

11.12 Measure and record the DO for each bottle. Add a few drops of the dilution water if necessary to eliminate all air bubbles when the stopper is placed in the bottle. Add plastic caps to prevent evaporation of the water seal.

11.13 Place the bottles in the 20° C incubator and incubate for 5 days, or 20 days if Ultimate BOD is being determined.

11.14 After the five (5) day incubation period (or 20 days), measure and record the final DO for each bottle.

12.0 DETAILS OF CALCULATIONS

12.1 The following calculation is used for the bottles that contain the highest volume of sample and meet the following criteria:

12.1.1 Final DO of at least 1 mg/L.

12.1.2 DO depletion of at least 2 mg/L.

12.1.3 Have no evidence of toxicity, or an obvious anomaly at the higher concentrations.

12.2 The following equations are used to calculate the BOD of one bottle.

12.2.1 (B1 - B2) * F = B

where:

B1 = initial DO of seeded blank
B2 = final DO of seeded blank
F = ration of seed in sample to seed in the blank in decimal form
example: 2 ml seed in blank and sample; F = 1
example: 10 ml seed in blank and 2 ml in the sample; F = 2/10 = 0.2

12.2.2 ((D1 - D2) - B)/(volume/300) = mg/L O

where:

D1 = initial DO of sample
D2 = final DO of sample
B = blank result (step 12.2.1)
300 = volume of BOD bottle
volume = ml of sample

12.3 Average the results of 1 - 3 bottles that meet the criteria and have the highest concentration of sample.

12.4 The following equation is used to calculate the LCS recovery:

A/B * 100 = % recovery

where:

A = the LCS result
B = the true LCS value

12.5 The following equation is used to calculate the duplicate RPD:

$$\frac{(A - B)}{(A + B)/2} * 100 = RPD$$

where:

A = the original sample result
B = the duplicate sample result

12.6 The following equation is used to calculate the spike recovery:

$$\frac{(A - B)}{C} * 100 = \% \text{ recovery}$$

where:

A = the combined sample and spike result
B = the original sample result
C = the true spike value

13.0 QUALITY CONTROL (QC) REQUIREMENTS

13.1 Seeded Control Blanks: Prepare as described in steps 11.7 and 11.8. The results should be below 2 mg/L.

13.2 LCS (200 mg/L): Add 10 ml of the stock solution (7.1) to 450 ml deionized water. Adjust the pH to 6.5 - 7.5 and dilute to 500 ml. Add 6.0 ml to two incubation bottles and treat exactly like the samples. The recovery must be within the method set limits of 84 - 114%. If these limits are exceeded the method will be examined for biases and out of control situations.

13.3 2nd Source Check (400 mg/L): Add 3 ml of this purchased standard (7.2) to two BOD bottles and analyze as described. This standard should be analyzed with each new batch of dilution water, or when another check of the method is needed.

13.4 Spike

13.4.1 If the sample being spiked is expected to have a BOD greater than 50 mg/L, spike with 200 mg/L. Add 6 ml of sample, and 6 ml of 200 mg/L LCS (13.2) and analyze like the samples.

13.4.2 If the sample being spiked is expected to have a BOD less than 50 mg/L, spike with 20 mg/L. Add 20 and 50 ml each of sample and 20 mg/L LCS (one-tenth dilution of 200 mg/L (13.2).

13.5 Duplicate: Choose any sample being run in the batch and use the same dilutions. The RPD should be less than the statistically determined RPD, or the run will need to be examined for biases.

13.6 Unseeded Blank: 300 ml of unseeded dilution water is analyzed exactly like the samples. The DO depletion should not be more than 0.2 mg/L.

13.7 A batch (workgroup) is defined as two seeded control blanks (13.1), LCS (13.2), Spike (13.4), duplicate (13.5), and up to 20 samples. A second check may also be included (13.3).

14.0 DATA REVIEW AND REPORTING REQUIREMENTS

14.1 BOD is reported in mg/L O using one significant digit for values <10, and 2 digits for values of 10 mg/L or greater.

14.2 The analyst, date and time are reported.

14.3 QA/QC data is entered onto special forms and reported to the client upon request.

14.4 Data review uses the attached checklist. All data is calculated and reviewed by the analyst. The supervisor (or designated person) performs a second review before entry into the LIMS system.

15.0 PREVENTATIVE MAINTENANCE

15.1 The probe membrane should be checked daily and if a tear or bubbles are observed, the membrane should be changed.

15.2 The membrane should be changed approximately monthly.

16.0 REFERENCES

16.1 "Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79/020, Method 405.1 (5 Days 20 degrees C), 1983

16.2 Standard Methods for the Examination of Water and Wastewater, 18th Edition, Method 5210B, 1992

Table 1
Wet Lab

Parameter: _____

Analyst/Date/Time: _____

SOP: K-_____ Revision: _____

Work Group(s): _____

Preservation Check: Yes _____ No _____

	Analyst	
Calibration/Linearity		
Second Source Check		
ICV/CCV (std)		
ICB/CCB		
Blank		
LCS		
MS/MSD		
Duplicate		
Record On ACS Benchsheet		
EXCEL QC Sheet		
QC Violation Sheet		
Signed Raw Data		
STD/LCS On Benchsheet		

Primary Reviewer Initials & Date Checked _____

Secondary Reviewer Initials & Date Checked _____

_____ • Check for compliance with Method and project-specific requirements
_____ • Check the completeness of the reported information
_____ • Check the information for the report narrative
_____ • Check the reasonableness of results

Supervisory Review Initials & Date Checked _____

Comments: _____

_____

√ - Checked & OK
NA - Not Applicable
DL - Diluted Out

APPENDIX A-63

STANDARD OPERATING PROCEDURES FOR ORGANIC CARBON, TOTAL (OXIDATION)

KEMRON
ENVIRONMENTAL SERVICES

Document Control #: EP 0924

STANDARD OPERATING PROCEDURES FOR ORGANIC CARBON, TOTAL (OXIDATION) SOP K4151

Issue Date: 21 May 1999
Revision 7

Implementation Date: 21 June 1998

Last Review: 21 May 1999

KEMRON Environmental Services
109 Starlite Park
Marietta, Ohio 45750

Approved by:

Deanna I. Hesson, Wet Chemistry Supervisor — 6/10/99 Date

Dennis S. Tepe, Laboratory Manager — 6/25/99 Date

Daniel A. Musgrave, QA/QC Supervisor — 6/25/99 Date

David L. Bumgarner, Director, Analytical Services — 6/25/99 Date

TABLE OF CONTENTS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for the determination of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. It also applicable for leachable organic carbon on a 1:10 soil to acid mixture.

1.2 This method references EPA Method 415.1 and SW846 Method 9060.

1.3 Total Organic Carbon is defined as all of the organic carbon present in the sample that can be determined by this method.

1.4 All analyses are performed within the ASTRO 2001 System 2 Analyzer.

1.5 The sample is acidified to a pH < 2, to convert all of the carbonates to dissolved CO_2. The sample is sparged and the off-gas is routed to the IR analyzer. This is the Total Inorganic Carbon.

1.6 The UV lamp and reactor heater are then turned on and a computer controlled amount of sodium persulfate is then added to the sample to oxidize the remaining organic carbon. The sample is again sparged and the off gases directed to the IR analyzer. This is the Total Organic Carbon.

1.7 To comply with SW846 Method 9060, each sample must be injected in quadruplicate.

1.7.1 The test code TOC-14 is used to show that one sample is injected four times and one average result is reported (1 sample * 4 injections).

1.7.2 The test code TOC-44 is used to show that the sample was sampled in the field in quadruplicate and each one is injected four times. This gives 16 results. The average of each bottle (four injections) is reported (4 samples * 4 injections).

1.8 Method 415.1 requires only one injection

1.8.1 The test code TOC is used to show that one sample gets one injection and one result (1 sample * 1 injection).

1.8.2 The test code TOC-4 is used to show that one sample was sampled in the field in quadruplicate. Each sample gets one result (4 samples * 1 injection).

2.0 SAFETY PRECAUTIONS

2.1 Standard laboratory safety procedures should be followed when working with unknown samples. Lab coats and safety glasses with sideshields are required.

2.2 When doing maintenance on the TOC instrument, the electricity should be turned off to prevent electrocution.

2.3 The following chemicals have the potential to be toxic or hazardous. Consult the MSDS for further information.

2.3.1 Sodium persulfate: This is a strong oxidizing agent and should not be stored near strong reducing agents.

2.3.2 Phosphoric acid: This is a strong and corrosive reagent.

3.0 SAMPLE PRESERVATION AND STORAGE

3.1 Samples should be collected in a glass container and preserved with sulfuric acid ($pH < 2$).

3.2 Samples should be kept refrigerated at 4° C until time of analysis, which is not to exceed 28 days from the time of collection. After analysis, samples are stored in a designated area in the archive room.

3.3 Samples should be kept from sunlight and atmospheric oxygen.

3.4 40 ml is required for Method 415.1

3.5 100 ml is required for Method 9060.

3.6 If less than the recommended volume is available the analysis will be performed on a dilution, and the reporting limit will be elevated proportionately.

4.0 METHOD PERFORMANCE

4.1 This method uses a reporting limit of 1 mg/L for an undiluted liquid sample. Upon request, a reporting limit of 0.5 mg/L can be reported. For leachable organic carbon, the reporting limit is 10 mg/kg.

4.2 The current MDL is 0.161 mg/L. This data is updated annually or more often if necessary.

4.3 The linear range of the method depends on the range selected. The overall range is 0.5 mg/L to about 60 mg/L.

4.4 The current statistical limits are 83 - 111% for the LCS, and the relative percent difference is 20%. This data is updated yearly. However, for method 9060, the method specified limits of 90 - 110% are used.

5.0 INTERFERENCES & CORRECTIVE MEASURES

5.1 Carbonate and bicarbonate carbon are removed by acidification (Total Inorganic Carbon).

5.2 Large particles that cannot enter the sipper tube cannot be analyzed. This can result in low recovery.

5.3 Filtration can result in low recovery (removal of carbon-containing particles) or high recovery (carbon from filter paper).

5.4 Very high chloride content results in low recovery. Adding mercuric nitrate to the sample reduces this interference.

6.0 EQUIPMENT AND SUPPLIES

6.1 TOC Analyzer. ASTRO MODEL 2001 system 2 with autosampler, computer, and printer

6.2 Several test tubes that can hold a volume of at least 20 mL

6.3 Mechanical shaker

6.4 All glassware is washed with soap and water as described in KEMRON SOP K0001.

7.0 STANDARDS AND REAGENTS

7.1 TOC Stock Standard Solution (1000 mg/L): purchased. Discard by manufacturer's printed expiration date.

7.2 TOC Stock LCS Solution (1000 mg/L): Add 1.240 g each of glucose and glutamic acid to deionized water. Mix well. Preserve with 5 mL of 1:1 sulfuric acid. Dilute to 1 liter. Discard after 6 months.

7.3 Sodium Persulfate Solution: Dissolve 714 g ultra pure sodium persulfate in deionized water and dilute to two liters. This solution should stir for as long as possible to allow oxidation of trace impurities (at least 48 hours). Discard after 6 months.

7.4 Phosphoric Acid: Dilute 118 mL of concentrated phosphoric acid to 1 liter with deionized water. Discard after 6 months.

7.5 Sulfuric Acid (20%): Add 200 ml concentrated sulfuric acid to 800 ml deionized water. Mix well.

8.0 CALIBRATION PROCEDURES

8.1 The instrument is calibrated daily. The calibration standard will be either a 50 or a 10 mg/L standard, depending on the range being used. The standard is run three times. The instrument will then average the peaks and use the calibration peak area as a scaling factor on the multi-point calibration from step 8.6.

8.2 Three ICV standards are analyzed at three levels daily as a check of the calibration. A CCV and CCB are also analyzed every 10 analysis.

8.3 A second source check is analyzed immediately following the calibration.

8.4 Semi-annually, a true vs. actual curve will be analyzed.

8.5 The following standards are analyzed for the semi-annually multi-point curve and the true vs. actual curve:

Standard	mls Used	Stock Used	Total Volume	Concentration mg/L
1	7	1000 ppm (7.1)	100	70
2	10	1000 ppm (7.1)	200	50
3	4	1000 ppm (7.1)	100	40
4	2	1000 ppm (7.1)	100	20
5	3	1000 ppm (7.1)	200	15
6	20	STD 2	100	10
7	10	STD 1	100	7
8	10	STD 2	100	5
9	20	STD 6	100	2
10	10	STD 6	100	1
11	5	STD 6	100	0.5
12	Blank			0.0

8.5.1 For the multi-point curve, analyze standards 2, 3, 4, 6 and 8 on the 50 mg/L range, and standards 6, 7, 8, 9, 10 and 11 on the 10 mg/L range.

8.5.2 For the actual vs. true curve, analyze 1, 2, 4, 6, 8 and 12 on the 50 mg/L range, and standards 5, 6, 8, 10, 11 and 12 on the 10 mg/L range.

8.6 To run the multi-point calibration, press Selection 6 for Multiple Point Calibration (at the main menu). Follow the instruction on the screen for entering and running standards. See page 70 of the Astro 2001 manual for more detailed instructions.

8.7 The run sequence as outlined in Section 11.3.18 should be followed.

9.0 SAMPLE PREPARATIONS

9.1 If the sample is a solid and leachable organic carbon is needed, a leachate of the solid will need prepared.

9.2 Add 10 ml of 20% sulfuric acid (7.5) to 10 g of soil. Mix well.

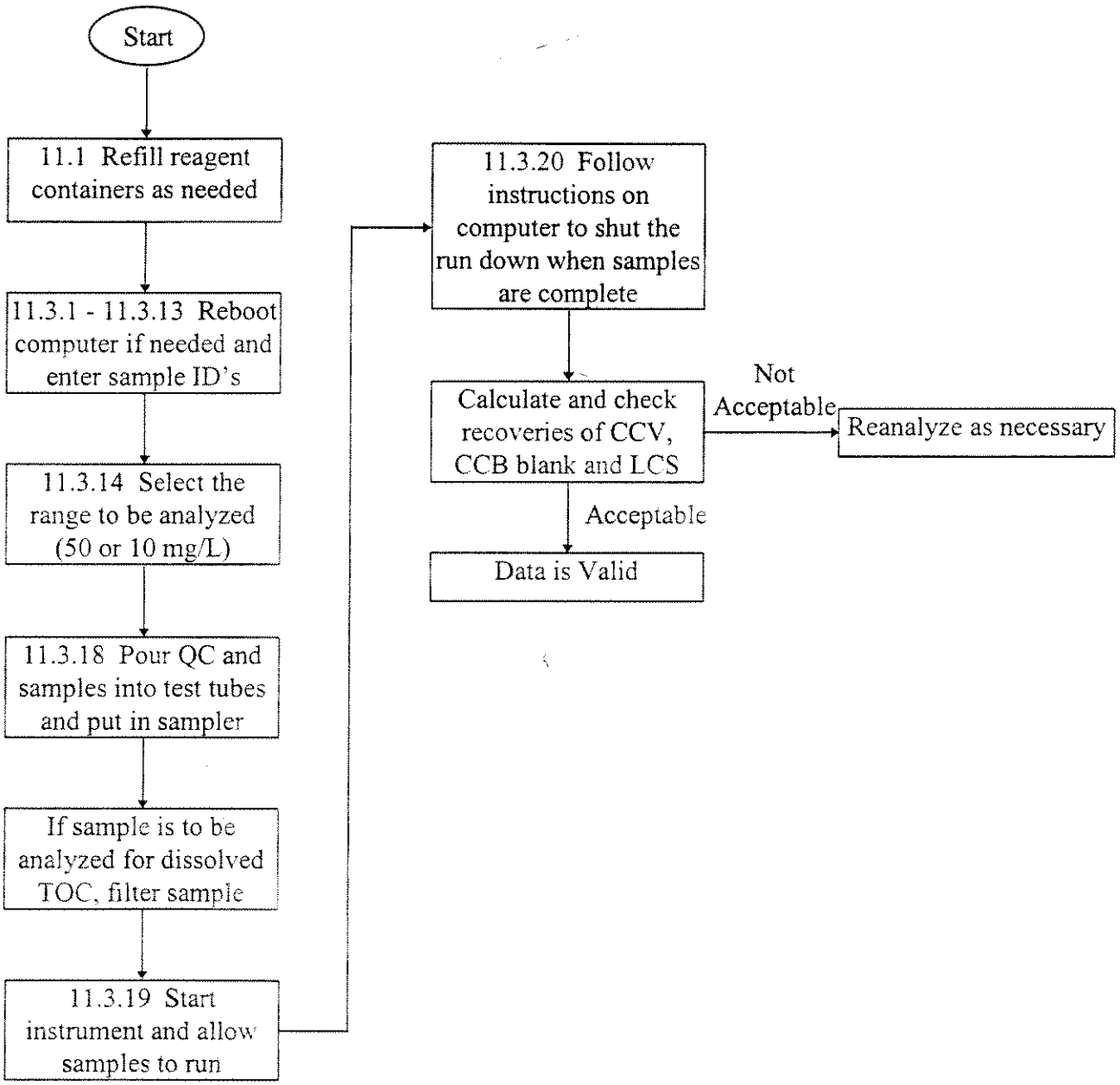
9.3 Add 90 ml of deionized water and shake on a mechanical shaker for 30 minutes.

9.4 Let the sample settle.

9.5 Decant the solution and analyze the solution for TOC. This is considered Leachable Organic Carbon.

9.6 If dissolved organic carbon is needed, filter the sample through a 0.45 um membrane filter (previously soaked in 1:1 nitric acid) and analyze as below. A filtered deionized water blank should also be analyzed.

10.0 DIAGRAM OR TABLE OR OUTLINE PROCEDURES



11.0 ANALYTICAL PROCEDURES

11.1 Fill reagent containers with the persulfate (7.3) and acid reagents(7.4), and also the deionized water container.

11.2 Make sure gas is on. The gas is left on at the tank at all times. The computer turns the gas on and off within the instrument.

11.3 The following directions apply only to the ASTRO 2001 System 2 TOC Analyzer.

11.3.1 Insert program disk into the disk drive. Check the date and time at this point.

11.3.2 At the A> prompt type CD ASTRO. At the A> prompt type 2001 and wait for further instructions.

11.3.3 Initialize pump? No (only answer yes if sample tube contains air or is contaminated). See page 28 of the manufacturer's manual.

11.3.4 Printer on-line? Yes (adjust printer if not on-line)

11.3.5 Distilled water blanks? No

11.3.6 Multiple calibrations: Yes (type in 3 for number of calibrations, and NO to "Enable Decisions?")

11.3.7 Previous data? Yes (this will keep the 10 previous results on the screen for reference). **At this time remove program disk and insert the data disk.**

11.3.8 At the Main menu several options are available. Refer to manual for instructions involving each option. Press 2 for Automatic run.

11.3.9 Press 8 for Menu

11.3.10 Press T for screen to enter sample ID's being run. Enter the sample ID's. Dilution factors can be typed in as a reference also, but the computer does not calculate the results using the dilution factors.

11.3.11 Press ESC to save the ID's

11.3.12 Press E to escape the sampler menu

11.3.13 Press 2 for TOC analysis

11.3.14 Select the appropriate range. Choose either 50 mg/L or 10 mg/L range.

11.3.15 Enter the value of the standard (50 or 10)

11.3.16 Enter number of samples to be run. **Do not count the three calibration standards.**

11.3.17 Enter beginning station number.

11.3.18 Place the standard in 3 test tubes and place in the first three stations to be used, followed by QC and samples as outlined below. Pour about 20 ml into each test tube.

NOTE: If method 415.1 is needed, each sample is injected once. If Method 9060 is required each sample must be injected in quadruplicate.

11.3.18.1. Three Calibration Standards (10 or 50 mg/L)

11.3.18.2 Low standard (1 or 10 mg/L)

11.3.18.3. Mid standard (5 or 25 mg/L)

11.3.18.4 High standard (10 or 50 mg/L):ICV

11.3.18.5 ICB

11.3.18.6 Blank

11.3.18.7 LCS

11.3.18.8 8 Samples

11.3.18.9 CCV

11.3.18.10 CCB

11.3.18.11 10 Samples

11.3.18.12 CCV

11.3.18.13 CCB

11.3.18.14 2 Samples

11.3.18.15 Duplicate (may be run anytime after the first sample)

11.3.18.16 Spike (may be run anytime after the first sample)

11.3.18.17 Continue with QC and samples for as many as needed. A CCV and CCB need analyzed every 10 samples.

11.3.18.18 End the run with a CCV and CCB.

11.3.19 Press enter and the instrument will begin the TOC analysis

11.3.20 When the run is complete, the prompt will ask if statistical data are desired. Enter No.

11.3.21 Press Q for quit

11.3.22 At this point the run is finished and the instrument may be left alone.

11.4 The TOC benchsheet should include the analyst, date, time, reference numbers for standards and LCS, the sample numbers and dilutions in the exact order that the samples are being run.

11.5 The computer printout should be signed by the analyst and all dilutions written in if they were not typed in.

12.0 DETAILS OF CALCULATIONS

12.1 The instrument calculates and prints out TOC in mg/L. These results do not take into account dilution factors.

12.2 To get the correct result, the following formula is used:

(instrument readout)/(dilution)= mg/L TOC

Readout = Answer obtained from instrument.

Dilution = Dilution of the sample in decimal form
(example: A 1/5 Dilution = 0.2)

12.3 If leachable organic carbon is needed, the formula is:

[(instrument readout)/(dilution)] * 10 = mg/kg LOC

where 10 is a factor to convert to mg/kg (10g/100 mL)

12.4 The following equation is used to calculate the LCS recovery:

A/B * 100 = % recovery

where:

A = the LCS result
B = the true LCS value

12.5 The following equation is used to calculate the spike recovery:

$$\frac{(A-B) * 100}{C} = \%\ \text{recovery}$$

where:

A = the combined sample and spike result
B = the original sample result
C = the true spike value

12.6 The following equation is used to calculate the duplicate RPD.

$$\frac{(A-B) * 100}{(A + B)/2} = \% \text{ recovery}$$

where:

A = the original sample result
B = the duplicate sample result

12.7 If Method 9060 is required, average the four results and report the average.

13.0 QUALITY CONTROL (QC) REQUIREMENTS

13.1 All standards are prepared using class A volumetric pipets and volumetric flasks.

13.2 Second Source Check: Prepare a 10 or 50 mg/L standard using the LCS stock (7.2). Dilute 2 ml of stock (7.2) to 200 ml deionized water to make a 10 mg/L standard. Dilute 10 ml of stock (7.2) to 200 ml to make a 50 mg/L standard. The result should be within ± 10% of true value, or the instrument will need recalibrated.

13.3 ICV (High Standard) (10 or 50 mg/L): Dilute 2 ml of the standard stock (7.1) to 200 ml to make a 10 mg/L standard, or dilute 10 ml of stock (7.1) to 200 ml to make a 50 mg/L standard. The result should be ± 10% of true value.

13.4 Mid-level Standard (5 or 25 mg/L): Dilute 1 ml of the standard stock (7.1 to 200 ml to make a 5 mg/L standard or dilute 5 ml of stock (7.1) to 200 ml to make a 25 mg/L standard.

13.5 Low-Level Standard (1 or 10 mg/L): Dilute 20 ml of the mid-level 5 mg/L standard to 100 ml to make a 1 mg/L standard, or dilute 1 ml of stock (7.1) to 100 ml to make a 10 mg/L standard.

13.6 Blank/ICB/CCB: Analyze deionized water exactly like the sample. The results should be less than or equal to the reporting limit, or the run will be examined and reanalyzed as necessary.

13.7 CCV: Analyze the high standard (10 or 50 mg/L) from step 13.3. The results should be within ± 15% of true value, or the affected samples will need reanalyzed.

13.8 Laboratory Control Sample (LCS)

13.8.1 High LCS (25 mg/L): Dilute 5 ml of LCS stock (7.2) to 200 ml with deionized water. Analyze exactly like the sample on the 50 mg/L range.

13.8.2 Low LCS (5 mg/L): Dilute 1 ml of LCS stock (7.2) to 200 ml and analyze on the 10 mg/L range.

13.8.3 For Method 415.1, the percent recovery should be within the statistically determined control limits.

13.8.4 For Method 9060, the recovery must be 90 - 110 %.

13.8.5 If the LCS recovery is not within the control limits, the run will be examined and reanalyzed as necessary.

13.9 Matrix Spike

13.9.1 High Spike (25 mg/L): Add 0.5 ml of LCS stock (7.2) to 20 ml of a sample, and analyze on the 50 mg/L range.

13.9.2 Low Spike (5 mg/L): Add 0.1 ml of LCS stock (7.2) to 20 ml of a sample and analyze on the 10 mg/L range.

13.9.3 The recovery should be within the statistically determined limits, or the run will be examined and reanalyzed as necessary.

13.10 Duplicate: Analyze any sample in the batch in duplicate at the same dilution. The RPD should be less than the statistically determined RPD, or the run will be examined and reanalyzed as necessary.

13.11 If method 9060 is required, run a spike duplicate instead of a duplicate.

13.12 A batch (workgroup) is defined as a blank (13.6), LCS (13.8.1 or 13.8.2), Spike (13.9.1 or 13.9.2), a duplicate (13.10) and up to 20 samples. Several batches may be run in sequence on any particular day. Each day a calibration is performed, and a second source check (13.2) and three standards (13.3, 13.4, 13.5) are analyzed.

14.0 DATA REVIEW AND REPORTING REQUIREMENTS

14.1 TOC is reported in mg/L TOC using one significant digit for values less than 10 mg/L and two significant digits for values of 10 mg/L or higher.

14.2 The analyst, date and time are reported.

14.3 QA/QC data is entered onto special forms and reported to the client upon request.

14.4 Data review uses the attached checklist (Table 1). All data is calculated and reviewed by the analyst. The supervisor (or designated person) performs a second review before entry into the LIMS system.

15.0 PREVENTATIVE MAINTENANCE

15.1 Daily

15.1.1 Check for leakage

15.1.2 Observe flow meter (200 cc/min at 11 psi)

15.1.3 Check reagents for sufficient volume

15.2 Yearly

15.2.1 Perform shutdown procedure (page 78 of manual)

15.3 As required

15.3.1 Replace septums if leakage occurs

15.3.2 Replenish reagents

15.3.3 Replenish gas

15.4 A quarterly maintenance is performed under contract by qualified ASTRO personnel.

16.0 REFERENCES

16.1 "Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79/020, Method 415.1 (Combustion or Oxidation), 1983.

16.2 SW846 Method 9060

16.3 ASTRO 2001 Systems 2 Instruction Manual

KEMRON
ENVIRONMENTAL SERVICES

METHOD VARIATION (MODIFICATION) APPROVAL FORM

PARAMETER: TOC

KEMRON SOP #: K4151

METHOD SOURCE AND #: SW9060

METHOD REQUIRES: ~~METH~~ REQUIRED TO REPORT BOTH THE AVERAGE AND THE RANGE OF Quadruplicate Analysis.

MODIFICATION REQUESTED: Just to Report THE AVERAGE per DLB in Dec 94.

RB.

APPROVED BY:

DLB: DLB

DAM: DAM

LSB: LSB 6/28/95

Figure 1
Wet Lab

Parameter: _____

Analyst/Date/Time: _____

SOP: K-_____ **Revision:** _____

Work Group(s): _____

Preservation Check: Yes _____ **No** _____

	Analyst	
Calibration/Linearity		
Second Source Check		
ICV/CCV (std)		
ICB/CCB		
Blank		
LCS		
MS/MSD		
Duplicate		
Record On ACS Benchsheet		
EXCEL QC Sheet		
QC Violation Sheet		
Signed Raw Data		
STD/LCS On Benchsheet		

Primary Reviewer Initials & Date Checked _____

Secondary Reviewer Initials & Date Checked _____

_____ • **Check for compliance with Method and project-specific requirements**
_____ • **Check the completeness of the reported information**
_____ • **Check the information for the report narrative**
_____ • **Check the reasonableness of results**

Supervisory Review Initials & Date Checked _____

Comments: _____

_____

_ - Checked & OK
NA - Not Applicable
DL - Diluted Out

APPENDIX A-64

STANDARD OPERATING PROCEDURE FOR TOC IN SEDIMENT AND SOIL—LLOYD KAHN

TITLE: TOC in Sediment and Soil - Lloyd Kahn			
Original Author: R. Smith		Revision Author: P. Rosiek	
Implementation Date: 6/2/99		Last Annual Review Date: 6/2/99	
File Information: L:\SOPs\Final\GAC\GAC76.ene-08/06/99 3:40 PM			
Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

1.0 SCOPE AND APPLICATION

1.1 This Standard Operating Procedure (SOP) is used to determine the concentration of total organic carbon in soil and sediment. The effective range of the Lloyd Kahn method is from 2000 to 800,000 mg/kg. The upper limit is based on 40 mg of sample and the lower limit on 1 g of sample and applying the respective calibration standards' masses. Results to the MDL may be reported at the client's request.

1.2 The sample results are reported on a dry weight basis by virtue of a preliminary drying step in section 10.4.

2.0 METHOD SUMMARY

2.1 The Lloyd Kahn method determines the concentration of Total Organic Carbon in a solid sample by pyrolyzing the sample in a stream of oxygen at approximately 900° C. The gas stream is then dried and analyzed for carbon dioxide by non-dispersive infrared detection. Inorganic carbon from carbonates and bicarbonates is removed prior to analysis by acid treatment of the sample.

2.2 The method uses dissolved KHP as calibration standard. This procedure is modified to use solid dextrose as calibration standards.

2.3 The method uses phosphoric acid to eliminate inorganic carbonates and bicarbonates. This procedure uses hydrochloric acid.

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.

4.0 REFERENCES

4.1 EPA attachment 6, Determination of Total Organic Carbon in Sediment, July 27, 1988, by Lloyd Kahn.

4.2 Shimadzu Manual for 5050A.

4.3 Use checklist number C-004 for analyst and peer review.

5.0 DEFINITIONS/ACRONYMS

5.1 **TC**: Total Carbon, **IC**: Inorganic Carbon.

5.2 **The following are possible remarks displayed when using the SSM-5000A:**

T: The peak is not completed within designated time period.

H: The peak height has exceeded full scale.

P: Measurement performed with the sample boat in an abnormal position.

B: Baseline not stable during measurement.

F: The temperature of the furnace exceeded the designated range during measurement.

5.3 **TC = TOC** based on Lloyd Kahn method.
5.4 **ASC Control Chart Database - Access ™** - database used for control charting by ASC. Control limits are tabulated by lab, method, and by matrix is the "Control Limit Summary".
5.5 **LCS/ICV** = Laboratory Control Sample/Initial Calibration Verification - A 2nd lot number (2nd source) of dextrose used to verify that the calibration curve is valid.

6.0 INTERFERENCES/POTENTIAL PROBLEMS

6.1 In many cases, the various components in a solid sample are not mixed together uniformly, as they are in liquid samples. For this reason, it is extremely important with solid samples to obtain an aliquot which is as representative as possible of the sampled material.
6.2 Volatile organics may be lost in the decarbonization step resulting in a low bias.
6.3 Bacterial decomposition and volatilization of the organic compounds are minimized by maintaining the sample at 2-6 C and analyzing within the specific hold time.
6.4 The combustion-oxidation reaction (TC measurement) and acidification reaction involving carbonate acid (IC measurement) are more efficient when the sample particles are smaller in size. Mix or breakup large chunks but do not grind.
6.5 Samples with high levels of carbonates such as sea sand and limestone are not appropriate for this method.

7.0 INSTRUMENTATION AND EQUIPMENT

7.1.1 Drying ovens, 103 – 105 C.
7.1.2 Analytical balance capable of weighting to 0.001 g
7.1.3 Shimadzu 5050A Total Organic Carbon Analyzer – resistance furnace, nondispersive infrared detector.
7.1.4 Ceramic Combustion Boats
7.1.5 Disposable pasteur pipets

8.0 REAGENTS AND MATERIALS

Table 8-1

SUMMARY OF STANDARD AND REAGENTS

Description	Source	Concentration
Concentrated Hydrochloric Acid (HCl)	Fisher or equivalent	38% HCl
Purified oxygen	Rodgers welding or equivalent	Carbon dioxide free containing < 1 mg/L hydrocarbons.
Dextrose-Anhydrous (D-Glucose) (2 lots required)	Fisher or equivalent	Neat
Tungsten oxide (wo)	Fisher or equivalent	Catalyst

Table 8-1

SUMMARY OF STANDARD AND REAGENTS

Description	Source	Concentration
Ultra pure Compressed Air CO_2 free containing < 1 mg/L hydrocarbons	Rogers Welding or equivalent	Neat

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

Table 8-2

STANDARD AND REAGENT PREPARATION

Stock	Standard Name	Amount of Stock Diluted to	Final Concentration
HCl, Concentrated (38%)	10% HCl	Slowly add 100 mL of concentrated HCl made up to 1000 mL with ASTM Type II water. Good for six months.	1:10 HCl
Dextrose 2nd Source	LCS/ICV 2nd Source	Weigh 40 mg into pretreated boat	400,000 mg/kg based on 40 mg
Dextrose same lot as calibration	CCV	Weigh 40 mg into pretreated boat	400,000 mg/kg based on 40 mg

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

9.0 PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Table 9-1

HOLDING TIMES

Matrix	Client/Project	Preparation (Days)	Analysis (Days)	Container Type and Preservative
Solid	Standard	NA	14	Glass, 2-6 C

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

10.0 PROCEDURE

10.1 Before instrument use check to make sure that the air flow is 500 mL/min with the flow meter.

10.2 Daily Instrument Calibration for TC Analysis as it appears on the instrument computer screen.

Table 10-1

GENERAL CONDITIONS

Description	Source
TC Catalyst	Normal Sens
Syringe Size	250 µL
Number of Washes	1
Unit of Concentration	%
Auto Ranging & Inj Vol	Auto Change
Auto Regeneration of IC	Off
Furnace on/off	SSM
Injection Speed	STD
ESU	Not Used
Bubble Removal	Off
Syringe Wash	STD
Cell Length	W-Short
TOC or SSM	SSM
Printer Device	Int New
Page Length	******
Calibration Curve Form	Least Squares
POC	Not Used
MEAS Interval (TC/NPOC)	0 Seconds
MEAS Interval (IC/POC)	0 Seconds

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

Daily Instrument Calibration For TC Analysis as it appears on the instrument computer screen

Table 10-2

CALIBRATION CONDITIONS

Amount Select	% Carbon	Amount	µg C (Carbon)
1 st STD Concentration	40%	80.0 mg (Dextrose)	32,000
2 nd STD Concentration	40%	40.0 mg (Dextrose)	16,000
3 rd STD Concentration	40%	20.0 mg (Dextrose)	8,000
4 th STD Concentration	40%	5.0 mg (Dextrose)	2,000
5 th STD Concentration	0	0.0 mg (empty boat)	0
Range x30			

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

10.2.1 Cleaning of Boats.
10.2.2 Scrape boats of all residue with spatula.
10.2.3 Put 10% HCl in beaker with boats and sonicate for 15-30 minutes.
10.2.4 Rinse boats again after sonication with ASTM Type II water.
10.2.5 Put in 180 C oven for 30 minutes.

10.3 Calibration for TC Analysis

10.3.1 Weigh 80 mg of Dextrose (Glucose) into a ceramic boat. [Note: The weighed sample is set on the bottom of the sample boat toward the front (TC furnace side).]
10.3.2 Place ceramic boat and contents in sample port of SSM-5050A.
10.3.3 Close sample port and press F1 key (next). Screen will display to press "start;" **do this.**
10.3.4 Instrument will now read "push sample boat to measuring;" **do this.**
10.3.5 When 80 mg std is completed; screen will read "completed". Pull sample boat to "cooling position." After 30 seconds, pull lever to "sample change position."
10.3.6 Press F1 (next); the instrument will automatically print out results.
10.3.7 Follow 10.3.2 – 10.3.6 for 2nd, 3rd, and 4th standard.
10.3.8 Calibration curve must be $r \geq 0.995$. Curve is good for 6 months.

10.4 Sample Analysis for TOC

10.4.1 Mix sample if necessary but do not grind.
10.4.2 Weigh up to 1.0 g of sample into ceramic boat. Record weight in mg. (Note: If samples are high in total carbon – a smaller amount is acceptable. Do not use less than 125 mg before consulting supervisor).
10.4.3 Add just enough drops of concentrated HCl to wet the sample. [Note: This is a pretreatment for removing IC. Inorganic carbon from carbonate and bicarbonates is removed by this acid treatment.]
10.4.3 Put ceramic boat and contents in drying oven at 103- 105 C for 10 minutes. [Note: Use tweezers.]
10.4.4 Place ceramic boat and contents in sample port of SSM-5050A.
10.4.5 Add a spatula-tip amount of WO catalyst.
10.4.6 Close sample port and press F1 key (next). Screen will display press "start"; **do this.**
10.4.7 Instrument will now read "push sample boat to measuring"; **do this**.
10.4.8 When sample is completed; screen will read "completed". Pull sample boat to cooling position, after 30 seconds, pull lever to "sample change position".
10.4.9 Press F1 (next) key; the instrument will automatically print out results.
10.4.10 Follow 10.4.1 – 10.4.8 for remaining analysis.
10.4.11 Analyze CCV, CCB, every 10 readings and at end of run batch.

10.5 Shut down of TOC Analyzer

10.5.1 Return to main menu.
10.5.2 Standby options.
10.5.3 Turn off instrument, **PRESS 1**, and then the **ENTER** key. Next, press the **STANDBY (F1)** key.
10.5.4 Screen will display "30 minute" countdown for cooling.
10.5.5 After cooling countdown turn off the monitor, the SSM500A and both oxygen tanks.

10.6 Daily and Continuing Calibration

10.6.1 Check the instrument calibration daily by running the LCS/ICV. If the LCS/ICV is outside acceptance limits, prepare a new curve (see Section 10.3).
10.6.2 Run Sequence

- LCS/ICV

- Prep Blank (PBS)
- 8 more analyses
- CCV
- CCB
- 10 more analyses
- End with CCV
- End with CCB

Table 10-3

SPIKE AMOUNT

Amount of dextrose added to sample	Carbon (µg)	mg/kg of spike added to 1.0 g sample
10.0 mg	4000	4000
20.0 mg	8000	8000
30.0 mg	12000	12000
40.0 mg	16000	16000

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

Table 10-4

ROUTINE MAINTENANCE PROCEDURES

Equipment/ Instrument	Symptom	Operation	Frequency
Oxygen Tank	Pressure less than 500 psi	Change Tank	When Needed
Ceramic Boats	Poor baseline – Poor readings	Check port seal. Reclean boats. Check catalyst tube.	When Needed
SSM- 5050A	Abnormality in measurement sensitivity or repeatability.	Check for leaks – see manual for Figure 7.1.	When Needed
Compressed Air	Pressure less than 500 psi	Change tank	When needed
O-Rings	Gas leaks due to deformation or scratched "O" rings	Replace ring – see manual for figures 7.3 & 7.4.	When Needed

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

11.0 DATA REDUCTION/EVALUATION/REPORTING

11.1 Lloyd Kahn: TOC in Sediment and Soil TC = TOC

Table 11-1

TARGET COMPOUNDS/ANALYTES AND QUANTITATION LIMITS

Compound/Analyte	Type	PQL Sediment/Soil (Units)
Lloyd Kahn TOC	T	2000 mg/kg based on 1 g sample

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99

Key Type:

T = Compound/analyte is target analyte 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 s surrogate spike.

11.2 Method Calculations

11.2.1 The instrument parameters have been set up to print results in %C. This equation is a check on the instrument.

$$\%C = \frac{\text{Found } \mu g\, C}{\text{input sample size (mg)} \bullet 1000 \mu g / mg} \bullet 100\%$$

a.)

b.)

$$\text{Sample concentration} = \left(\frac{mg}{kg} TOC \right) = \frac{\%C}{100\%} \bullet \frac{1000\, mg}{1\, g} \bullet \frac{1000\, g}{kg}$$

If the input sample size is different from the basis sample size (e.g., if 40 mg is input for the ICV but it is desired to report to a 1-gram basis:

c.) Sample Concentration

$$\frac{\text{TOC mg}}{\text{kg}} = \frac{\%C}{100\%} \bullet \frac{\text{input sample (mg)}}{\text{actual (basis) sample size (g)}} \bullet \frac{1000\,\text{g}}{\text{kg}}$$

This equation reduces to equation (b) above when the input sample size is the same as the actual size.

d.)

$$\textit{Spike added concentration}\left(\frac{mg}{kg}\right) = \frac{\mu g\ C\ added\ from\ dextrose}{weight\,(g)\ of\ sample} = \frac{mg\ dextrose\ added \bullet 0.4 \bullet 1000\ g/kg}{weight\,(g)\ of\ sample}$$

12.0 QUALITY CONTROL/QUALITY ASSURANCE/CORRECTIVE ACTION

Routine Quality Control Samples

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Preparation Instructions	Acceptance Criteria	Corrective Action
LCS/ICV	Beginning of a batch	40 mg of 2nd source dextrose	See Control Limit Summary	Recalibrate with new multi-point curve
CCV	After every 10 samples and at the end of a batch	40 mg of calibration lot dextrose	80 - 120%	Recalibrate instrument. Repeat previous 10 analyses.
CCB	After every CCV	Empty boat with one drop conc. HCl	< 4000 mg/kg based on 1 g basis	Make sure boat is clean
PBS	After ICV	Empty boat with one crop conc. HCl	< 4000 mg/kg based on 1 g basis	Make sure boat is clean
Quadruplicate	1 per batch of 20 or fewer samples	Three additional aliquots of sample	Project requirements if specified or RSD ≤30%	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.
Matrix Spike	When requested by client	Aliquot of sample plus a known amount of 2nd source dextrose[1]	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.

Table 12-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Preparation Instructions	Acceptance Criteria	Corrective Action
				Comment in narrative if appropriate.
Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99	

[1]Spike with a known amount of dextrose to achieve a spike concentration within the calibration range. See Table 10-3.

Control Limits for Routine Quality Control Samples

Table 12-2

CONTROL LIMITS FOR ROUTINE QUALITY CONTROL SAMPLES

QC Type	Parameters Charted	Type of Samples Charted	Source of Limits	Frequency Updated
LCS/ICV	TOC	Solids	In-house	Annually
Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99	

Table 12-3

ACCEPTANCE CRITERIA FOR ROUTINE QUALITY CONTROL SAMPLES

QC Type	Parameter	Spike Amount	Recovery (%)	RSD
LCS/ICV	TOC	400,000 mg/kg	See Control Limit Summary	NA
Quadruplicate	TOC	NA	NA	30%
Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/6/99	

13.0 SPECIAL PROJECT REQUIREMENTS

Client-Specific Quality Control Requirements

13.1 Griffiss

13.1.1 Requires sample spikes at a frequency of 1 per 20 samples or fewer with 75 to 125% recovery.

13.1.2 A second aliquot of the sample is prepared and spiked with 40 mg of the 2nd source dextrose.

13.2 BCM Project. Use the following scheme at the appropriate step in the procedure.

13.2.1 Mix sample if necessary but do not grind.

13.2.2 Weigh 125 mg (a larger sample size. e.g., 250 mg may be used at the start if sample interferences such as tailing are absent) of as-received sample.

13.2.3 Acidify with just enough drops of concentrated HCl to wet the sample.
13.2.4 Place in 103 – 105 C oven for 10 minutes.
13.2.5 Add tungsten oxide (WO) ~~WO~~ catalyst (spatula tip amount).
13.2.6 Combust.
13.2.7 Correct for dry weight.
13.2.8 The quantitation limit for 125 mg sample size is 16,000 mg/kg. (The quantitation limit for 250 mg sample size is 8,000 mg/kg.)
13.2.9 The MDL for a 125 mg sample (dry weight adjusted) is 2860 mg/kg (for 250 mg sample, 1430 mg/kg).
13.2.10 If 125 mg sample was used, report values between the 3000 mg/kg (nominal MDL) and 16,000 mg/kg with a "J" flag. (If 250 mg sample was used, report values between 1500 mg/kg [nominal MDL] and 8,000 mg/kg with a "J" flag.)
13.2.11 If 125 mg sample was used, report values below 3000 mg/kg as "ND." (If 250 mg sample was used, report values below 1500 mg/kg as ND.)
13.2.12 Any values that are not detected at concentrations above 4000 mg/kg must be reanalyzed with a larger sample size.
13.2.13 One sample must be chosen as a matrix spike.
13.2.14 Use the BCM project-specific requirements in Table 13-1 to replace the similar quality control requirements given in Table 12-1.

~~**Table 12-1**~~
Table 13-1

ROUTINE QUALITY CONTROL SAMPLES

QC Type	Frequency	Preparation Instructions	Acceptance Criteria	Corrective Action
LCS/ICV	Beginning of a batch	40 mg of 2nd source dextrose	Client-specific 85-115%	Recalibrate with new multi-point curve.
Quadruplicate	1 per batch of 20 or fewer samples	Three additional aliquots of sample	Client-specific 20%	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.
Matrix Spike	When requested by client	Aliquot of sample plus a known amount of 2nd source dextrose[1]	Client specific 75-125%	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.

Revision: 3	Status: Final	Method: Lloyd Kahn	Minor Revision Date: 8/10/99

14.0 SAMPLE DISPOSAL

Residual sample and/or boats may be disposed of as nonhazardous solid waste.

15.0 EXAMPLE FORMS

NA

END OF SOP

APPENDIX A-65

STANDARD OPERATING PROCEDURE FOR TOTAL ORGANIC CARBON BY EPA METHOD 415.1/SW-846 METHOD 9060A

CEIMIC CORPORATION

Standard Operating Procedure

No. 9060

TITLE:

TOTAL ORGANIC CARBON BY EPA METHOD 415.1 / SW846 METHOD 9060A

FINAL

Approved By:

Eve Kump
QA/QC Officer

Harold Fatorelli
Laboratory Manager

Jeffrey D. Maymon
Laboratory Supervisor

DATE ISSUED
JAN 15 1999

Previous Revision Date: 3/10/97

Date Revised: 1/14/99

Control No.: _____

Note: This document may not be copied. Controlled copies of this document are available from the QA/QC Officer. The original is stamped with a red stamp.

CEIMIC CORPORATION

TITLE:

TOTAL ORGANIC CARBON BY EPA METHOD 415.1 / SW846 METHOD 9060A

1.0 SCOPE

This SOP applies to the analysis of Total Organic Carbon in soil and water samples by EPA Method 415.1 and SW846 Method 9060A.

2.0 REFERENCES

2.1 EPA Method 415.1 and SW846 Method 9060A.

3.0 TERMINOLOGY

3.1 Soluble, nonvolatile organic carbon: eg., natural sugars.

3.2 Soluble, volatile organic carbon: eg., mercaptans, alkanese, low molecular weight alcohols.

3.3 Insoluble, partially volatile carbon: eg., low molecular weight oils.

3.4 Insoluble, particulate carbonaceous materials: eg., cellulose fibers.

3.5 Soluble or insoluble carbonaceous materials absorbed or entrapped on insoluble inorganic suspended matter: eg., oily matter absorbed on silt particles. Carbonaceous analyzers are capable of measuring all forms of carbon in a sample. However, because of various properties of carbon-containing compounds in liquid samples, the manner of preliminary sample treatment as well as the instrument settings will determine which forms of carbon are actually measured.

4.0 METHOD SUMMARY

4.1 Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) by catalytic combustion. The CO_2 formed is then measured directly by an infrared detector. The amount of CO_2 in a sample is directly proportional to the concentration of carbonaceous material in the sample.

4.2 Carbonate and bicarbonate are inorganic forms of carbon and must be separated from the total organic carbon value. This separation ia accomplished by mathematical subtraction, or by removing the carbonate and bicarbonate by converting them to CO_2 with degassing prior to analysis.

4.3 All samples are to be analyzed in quadruplicate according to the method.

5.0 SIGNIFICANCE AND USE

This method applies to the analysis of Total Organic Carbon (TOC) in drinking, surface and saline water and industrial wastes, sediments and soils.

6.0 INTERFERENCES

6.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation.

6.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus, reproducibly by means of a microliter-type syringe. The opening of the syringe limit the maximum size of particle which may be included in the sample.

6.3 Removal of carbonate and bicarbonate by acidification an purging with nitrogen, or other inert gas can result in the loss of volatile organic substances.

7.0 APPARATUS

7.1 High Temperature TOC Analyzer (Dohrmann)

7.2 100 µl Syringe

7.3 Analytical Balance (0.0001 gm)

7.4 183 Boat Sampling Module

7.5 Hot Plate

8.0 REAGENTS AND MATERIALS

8.1 Deionized Water

8.2 Stock Solution = 1,000 mg/L carbon

(Primary Standard Grade) Potassium Hydrogen Phthalate 0.2128 g dissolved in 100 mls of DI water

8.3 Standard Solutions
Prepare standard solutions from the stock solution by dilution with DI water.

8.4 Blank Solution
Use the same DI water as was used to prepare the standard solutions.

9.0 HAZARDS AND PRECAUTIONS

All analysts must be familiar with Ceimic's Safety Manual and Chemical Hygiene Plan. Refer to the MSDS sheets located in the Ceimic Library in the bullpen prior to the use of any unfamiliar reagents.

10.0 SAMPLING AND SAMPLE PREPARATION

10.1 Sampling and storage of samples may be in glass or plastic bottles.

10.2 Samples must be acidified with H_2SO_4 to a pH <2 within 2 hours of sampling.

10.3 Samples should be kept cool at a temperature of 4°C and protected from sunlight and atmospheric oxygen.

10.4 Analysis must be performed on Aqueous samples within 28 days from sampling date.

10.5 Analysis must be performed on soil samples within 14 days from date of sampling.

11.0 PREPARATION OF APPARATUS

Refer to Section 12.0.

12.0 CALIBRATION AND STANDARDIZATION

12.1 Standard Run

12.1.1 Blank (DI H_2O)
Aqueous (less than 1.0 ppm) soil (less than 50 ppm)

12.1.2 Calibration standards
At least 3 standards will be used to construct the calibration curve.

12.1.3 Second source ICV to check against the calibration curve.

12.1.4 QC

Laboratory Control Sample

12.1.5 Sample

12.2 Calibration of Instrument

12.2.1 Blank (DI H_2O)
Aqueous (less than 1.0 ppm) soil (less than 50 ppm)

12.2.2 Standard run 3 times if recovery is 90-110% calibration update may be used for future analysis.

12.3 Standard Calibration Curve

12.3.1 A calibration curve with a minimum of 3 standards and a blank will be analyzed to demonstrate the instrument linearity and response. The concentration of the standards is summarized as follows:

Aqueous	Soil
Blank (D.I. H_20)	Blank (D.I. H_20)
10 ppm Std	1000 ppm Std
25 ppm Std	10000 ppm Std
50 ppm Std	20000 ppm Std

13.0 PROCEDURE

13.1 Start Up Procedure - Soils

13.1.1 Check O_2 line to make sure the air-flow and connections allow for soil analysis.

13.1.2 Turn the power on the Boat Sample Module.

13.1.3 Turn on the O_2 to the regulated pressure of 30 psi

13.1.4 Flip the Boat Gas Switch on, observe the brisk bubbling of the gas through the sparger when the hatch door is closed.

13.1.5 Check to ensure that the dispenser for the sparger is submerged in acidified water pH 2.

13.1.6 Check to ensure the mist trap is less than half filled with DI.

13.1.7 Monitor the baseline, verify that it is stable, it should be less than 1.

13.1.8 Advance the boat into the furnace and allow to bake until baseline is stable. This eliminates extraneous carbon from the boat.

13.1.9 Determine the value of a DI blank by injecting 40 µl of DI into the boat. It must be less than 50 mg/L.

13.1.10 Calibrate the analyzer by injecting 40 µl of 20,000 ppm standard into the boat.

13.1.11 Run three times then update the calibration factor.

13.1.12 This calibration factor can be used for future sample analysis if the recovery is 90-110% of its true value.

13.2 Testing Procedure - Soils

13.2.1 Homogenize the soil sample as well as possible.

13.2.2 Weigh 15-50 mgs of sample in the sample boat.

13.2.3 For TOC analysis, acidify the sample to pH 2 with a few drops of 1:1 H_3PO_4 or 1:1 HNO_3 as suggested by the manufacturer for 5 minutes to remove the inorganic carbon by heating on a hotplate. The manufacturer has recommended the use of either acid for removing inorganic carbon.

13.2.4 Transfer the sample into the Hatch port assembly.

13.2.5 Allow the baseline to stabilize.

13.2.6 Press start, enter the sample ID number and sample weight.

13.2.7 Wait for the inject now tune and advance the boat into the furnace.

13.2.8 Allow for the analysis to finish, retract the boat back to the hatch port and allow to cool for at least 30 seconds before introducing the next sample.

13.2.9 Soil samples require a quadruplicate analysis. Report the averaged result.

13.3 The Run Sequence for a Typical Analysis is:

13.3.1 DI water (Recovery less than 50 mg/Kg)

13.3.2 Calibration standards. The acceptance criteria is $r^2 >$, 0.995.

13.3.3 Second source ICV to check against the calibration curve. The % recovery must be within 90-110%.

13.3.4 QC soil (Recovery 80-120%)

13.3.5 Samples (in quadruplicate)

13.3.6 10,000 ppm Std (Recovery 90-110%) for every ten samples as CCV sample.

13.3.7 DI water (Recovery less than 50 mg/Kg) follows CCV sample as CCB sample.

13.4 Start Up Procedure - Water

13.4.1 Check O_2 line to make sure the air-flow and connections allow for water analysis.

13.4.2 Turn the O_2 to regulated pressure of 30 psi

13.4.3 Check the oxygen air-flow by pressing main 1. The air-flow should be about 200 $\pm$ 20 cc min.

13.4.4 Prime the IC chamber with acid by pressing main 251. The prime acid button may have to be pushed several times to completely prime the acid line.

13.4.5 Prime Sparagers A and B by pushing Sparage A and prime acid the same should be done for Sparager B.

13.4.6 Wait for the IR detector to stabilize, adjust to less than 1.

13.4.7 Press syringe - TOC mode.

13.4.8 Calibrate the analyzer using a 50 µl injection of an accurately prepared 50 ppm Std.

13.4.9 Run the Standard three times and if the recovery is 90-110%, this calibration factor update may be used for future analysis.

13.4.10 If the recovery is not 90-110% press calibrate 5 to update the calibration factor and repeat step #9.

13.4.11 Run a DI blank by injecting 50 µl of DI water. The value must be less than 1 mg/L.

13.5 Testing Procedure - Water

13.5.1 Sparge all aqueous samples before samples are analyzed.

13.5.2 Select Syringe - TOC mode.

13.5.3 Press Start, Type in the sample ID and press enter.

13.5.4 Inject 50 µl of DI water into the TC port when the inject tune goes off and the light flashes.

13.5.5 Upon completion of the TC analysis push yes, when the inject tune goes off and the light flashes inject 50 µl of DI water into the IC port.

13.5.6 Upon completion of analysis the IC will be subtracted from the TC to give you the TOC value.

13.5.7 Water samples require a quadruplicate analysis. Report both the average and the range.

13.6 The Run Sequence for a Typical Analysis is:

13.6.1 DI blank - 50 µl of DI water (must be less than 1.0 ppm)

13.6.2 Calibration standards. The acceptance criteria is $r^2 >$, 0.995.

13.6.3 QC Standard - 50 µl (Recovery 80-120%)

13.6.4 Samples - 50 µl (in quadruplicate)

13.6.5 Standard - 50 µl of 50 ppm (Recovery 90-110%) for every ten samples as CCV sample.

13.6.6 DI blank - 50 µl of DI water (must be less than 1.0 ppm) follows CCV sample as CCB sample.

14.0 QUALITY CONTROL

14.1 Method EPA 415.1, Method Blank

14.1.1 Must run one per twenty (20) samples or each batch whichever is more frequent.

14.1.2 Must be less than the method reporting limit (MRL).

14.1.3 If the blank result exceeds the MRL, correct the problem and reanalyze the blank.

14.2 Laboratory Control Sample

14.2.1 Run one per twenty (20) samples.

14.2.2 A 1 to 2 mg (120,000-240,000 mg/kg) ACS grade CaCO3 will be added to a second LCS to evaluate the inorganic carbon removal efficiency in the acid wash step for the soil sample.

14.2.3 Must be 80-120% recovery.

14.2.4 If the % recovery is not met, correct the problem and reanalyze the LCS sample. The LCS must be analyzed to be within control limits before sample analysis.

14.3 Duplicate Sample

14.3.1 Performed once per ten (10) samples.

14.3.2 Must agree to within 20% RPD.

14.3.3 Repeat once if not in control.

14.4 SW846 Method 9060, Method Blank

14.4.1 Must be run one per fifteen (15) samples.

14.4.2 Must be less than the method reporting limit.

14.4.3 If the blank result exceeds the MRL, correct the problem and reanalyze the blank.

14.5 Laboratory Control Sample

14.5.1 Run one per fifteen (15) samples.

14.5.2 Must be 90-120% recovery for aqueous and 69-130% recovery for soils.

14.5.3 If the % recovery is not met, correct the problem and reanalyze the LCS sample. The LCS must be analyzed to be within control limits before sample analysis.

14.6 Duplicate Sample

14.6.1 Performed once every ten (10) samples.

14.6.2 Must agree to within 20% RPD.

14.6.3 Repeat once if not in control.

15.0 CORRECTIVE ACTION PROCEDURES

All out of control situations must be recorded in the Corrective Action Logbook and documented returned to control.

16.0 CALCULATIONS

16.1 $$\% \text{ RPD} = \frac{X_1 - X_2}{(X_1 + X_2)/2} \times 100 = \pm 20\%$$

16.2 $$\text{Dry Weight Basis} = \frac{\text{TOC ppm in Sample}}{\text{Percent Solid of Sample}}$$

Ex. $\frac{3{,}779 \text{ ppm}}{0.846\% \text{ solid}} = 4{,}467 \text{ mg/Kg}$

17.0 REPORTING AND REVIEW

All data must be reviewed by a minimum of two (2) analysts proficient in the method and by the Lab Manager prior to release of the final report.

18.0 WASTE DISPOSAL

Follow SOP No. O32 for waste disposal procedures.

APPENDIX A-66

STANDARD OPERATING PROCEDURE FOR PARTICLE-SIZE ANALYSIS OF SOILS

REFERENCE NUMBER: ASTM D 422-98

TEST METHOD TITLE: **Test Method for Particle-Size Analysis of Soils**

TEST PROPERTY: grain size analysis

TEST SPECIMEN SIZE: passing #10 sieve: 115 g sandy soils, 65 g for silty or clayey soils
retained on #10 sieve see test standard (based on largest particle size)

NO. OF TEST SPECIMENS: 1 (representative sample obtained by quartering, mixing, or splitting)

TEST EQUIPMENT:
Stirring apparatus A
Hydrometer (ASTM)
Sedimentation Cylinder
Drying containers
Balance readable to 0.01 gram for material passing #10 sieve or 0.1% of mass for material retained on #10 sieve
Thermometer readable to 0.5 °C
Various sieves
250 mL beaker
Drying oven capable of maintaining a temperature of 110 ± 5 °C
Dispersing agent mixture (40 g/L of Sodium Hexametaphosphate solution)
Mechanical sieve shaker

STANDARD OPERATING PROCEDURES:

Sieve analysis of portion retained on #10 sieve

1. Separate the portion retained on #10 sieve into a series of fractions using various sieve sizes ranging from 3 inch to #10. Set up in mechanical shaker and shake for 10 minutes. Determine the mass retained on each sieve by weighing and recording mass to nearest 0.1 % of sample mass.

Hydrometer and sieve analysis of portion passing #10 sieve

2. Place appropriate size sample in a 250 mL beaker. Cover with 125 mL of dispersing agent mixture. Stir and allow to soak for at least 16 hours.

3. Disperse the solution further by using Stirring apparatus A. Add distilled water as needed to fill cup to the half. Stir 1 minute.

4. Immediately after dispersion, transfer slurry to a sedimentation cylinder. Add distilled water to 1000 mL point. Use rubber stopper over the open end and turn the cylinder upside down and back for a period of 1 minute (should be 60 turns per minute). Set the cylinder down and begin to take and record hydrometer readings at the following intervals: 1, 2, 4, 8, 15, 30, 60, 120, 240 and 1440 minutes. After each reading, the temperature of the solution should be recorded.

5. After the final hydrometer reading, transfer the suspension to a #200 sieve and wash with tap water until effluent water is clear. Transfer material to a container and dry in oven to constant mass at 110 ± 5 °C. After drying, sieve the remaining material in shaker using desired number of sieves for 10 minutes. Record mass retained on each fraction to nearest 0.01 g.

6. Calculations: use GLMS software to enter data and calculate % passing and retained for each sieve size and hydrometer readings.

7. Report: sample identification, sample description, percentage passing or retained on each sieve fraction (tabular and graphical).

APPENDIX A-67

STANDARD OPERATING PROCEDURE FOR DREDGING ELUTRIATE TEST

Soil Technology™, Inc.
Standard Operating Procedure
Dredging Elutriate Test

Apparatus and Materials

Decontaminated 20-liter glass carboy with rubber stopper and J-shaped glass tube
Compressed air source with DI water trap
Stainless steel bowls and spoons
Stainless steel or polycarbonate centrifuge bottles
Centrifuge
Refrigeration unit at 4°C for sample storage
Glass or polycarbonate filter units, if necessary
Filters (if necessary): 1 μm glass fiber in conjunction with glass prefilters for organics; 0.45 μm filters (type to be determined based on contaminants of concern) for inorganics

Sample Handling

Samples are logged in and the chain of custody form is signed upon receipt at STI. Sediment and site water samples should be kept in the cooler at 4°C until testing. Samples must be processed within the holding time specified by the client, preferably as soon as possible after they are received.

Procedure

1. Any equipment that will come into contact with the sediment or site water is decontaminated using a procedure specified or approved by the client, and chosen based on the contaminants of concern.
2. A slurry is prepared using site water and sediment at a concentration of 10 g/L (dry weight basis).
3. The slurry is combined and mixed in the glass carboy under atmospheric conditions for 5 minutes.
4. The slurry is vigorously aerated using a compressed air source passed through a DI water trap and the glass tubing for one hour.
5. The carboy is capped and the slurry is allowed to settle for one hour.
6. After settling the elutriate is removed from the carboy using the compressed air system and the J-shaped glass tubing, with care taken not to resuspend the settled material.
7. If samples are to be collected for dissolved inorganic concentrations, an aliquot of the elutriate is vacuum filtered through polycarbonate filter units using 0.45 μm membrane filters, decanted into proper containers, and preserved as necessary.
8. For dissolved organics, the elutriate may be centrifuged or filtered, depending on the needs of the project. For organic contaminants, it is recommended that the elutriate be centrifuged rather than filtered, because glass fiber filters have been found to adsorb organic compounds.
9. For filtering samples to be analyzed for organic compounds, an aliquot of the pore water is vacuum filtered through glass filter units using glass fiber prefilters and 1 μm glass fiber filters, decanted into proper containers and preserved as necessary.

10. For centrifuging samples for dissolved organics, stainless steel bottles are used. The time required for spinning is determined from application of Stoke's Law, using the desired particle size diameter:

$$t_{\min} = \frac{6.3 \times 10^{9} (n) \log(R/S)}{(N_m)^2 (D_u)^2 (\Delta S)}$$

where:

n = fluid viscosity (poise)
R = radius of rotation of top of sediment in tube (15.13 cm)
S = radius of rotation of surface of suspension (3.93 cm)
N_m = revolutions per minute
D_u = particle diameter (μm)
ΔS = difference in specific gravity between the fluid and the particles (e.g., assuming a particle specific gravity of 2.6 g/cm^3 and a water specific gravity of 1.02 g/cm^3, this difference would equal 1.58 g/cm^3)

11. For total organic and inorganic analyses, bulk elutriate supernatant will not be filtered or centrifuged, but will be decanted into proper containers and preserved as necessary.
12. Total suspended solids are measured on a subsample of the bulk elutriate sample using a 0.45 μm filter.
13. Samples are packed with ice in coolers, accompanied by a chain of custody. A signed chain of custody seal should be placed on two unhinged sides of the cooler. The cooler is shipped via overnight service as requested by the client.

Quality Control

If required by the project laboratory duplication can be performed as a quality control measure. For a laboratory duplicate, the entire elutriate test is conducted in duplicate and both sample sets are submitted to the laboratory for analysis.

APPENDIX A-68

STANDARD OPERATING PROCEDURE FOR SEDIMENT FRACTIONATION FOR CHEMICAL ANALYSIS

APPENDIX A

Soil Technology, Inc.
Standard Operating Procedure
Sediment Fractionation for Chemical Analysis
Housatonic River Project
October 1999

Scope and Application

This method is used to separate sediment samples while wet into three size fractions: >250 μm, 62.5-250 μm, and <62.5 μm. These fractions are separated by wet sieving the sediment to collect the two coarsest fractions on No. 60 (>250 μm) and No. 230 (>62.5 μm) sieves, and then centrifuging the final liquid fraction to obtain all material less than 62.5 μm. The separated fractions are then submitted to an analytical laboratory for analysis of PCBs and TOC.

Apparatus and Materials

Stainless steel sieves: No. 60 and 230
Stainless steel equipment: Pots, spoons, spatulas, tares, centrifuge bottles
Deionized water
Reagent-grade methane and hexane
Centrifuge

Sample Handling

Samples are logged in and the chain of custody form is signed upon sample receipt at STI. Sediment samples are kept in the cooler at 4°C until processing. Samples must be processed within the holding time specified by the client, preferably as soon as possible after they are received. Any materials that will come into contact with the sediment are decontaminated prior to use, as described in this SOP.

Cleaning and Decontamination of Equipment

All stainless steel equipment used for fractionation (sieves, pots, utensils, centrifuge bottles) are washed in a Liquinox/water solution. Equipment is then rinsed once with methanol, once with hexane, and three times with deionized (DI) water.

Sediment Fractionation

Set Up and Sieving

1. Record sample information on a clean bench sheet. Obtain weights and record the information for the following: a) empty pan for solids content, b) empty pan for +60 material, and c) empty pan for +230 material. Weigh the full jar of sample

and record the weight. Note whether 50 or 80 g of each fraction will be needed (50 g for PCBs and TOC, 80 g for PCB congeners also).

2. Empty the entire jar of sample into a pan and homogenize the sample. Place 50-100 g of representative material onto the empty tared pan for solids content, weigh, and record the weight. Place sample into the geotechnical oven for drying, or in a designated area for later placement into the oven.
3. Set up the sieves so they are placed over an 8 inch pot with the No. 60 sieve over the No. 230. Put a few spoonfuls of sediment onto the top sieve and begin washing with DI water. It may be necessary to prepare a slurry of the sediment with DI water to facilitate the initial washing process. To completely empty a jar, rinse it with DI water onto the top sieve.
4. When a sieve has sufficient material on it, wash the sediment until the water running under the sieve is clear. Then empty the material in that sieve into the designated pan for that size fraction.
5. Continue the above process until enough material is obtained for each size fraction. There must also be sufficient material in the <230 size fraction, which can be estimated once the centrifuging process has begun.
6. After sufficient material has been processed, weigh the empty jar or the jar and its remaining contents. Record the weight on the bench sheet. All sample removed from the jar must be sieved.

Centrifuging

1. The material passing through the No. 230 sieve must be centrifuged to obtain all solids in that size fraction. Decontaminate six centrifuge bottles, with matching weights in pairs. Make sure each bottle number is matched with its corresponding lid.
2. Fill the bottles to the shoulder with the <230 material. The weights of each matching pair after being filled must be within 1 g to balance the centrifuge while spinning. To match the weights, put the heaviest bottle on the scale and zero the weight. Then place the lighter bottle on the scale and add DI water until the weight is within (plus or minus) 1 g.
3. Wipe each bottle rim with a kimwipe to remove any sediment particles that may cause leaking. Place lid with O-ring onto bottle and screw cap on tightly.
4. Place bottles into centrifuge with matching pairs opposite each other. Centrifuge the bottles for 10 minutes at 6,500 rpm with the temperature at 15 °C.
5. After spinning, decant the supernatant, taking care not to disturb or pour out any solids. Refill the bottles and repeat the process until all material has been processed. For the final spin, consolidate the sediment into one bottle by consecutively rinsing all material from one bottle into the next. Record the empty weight (with lid and O-ring) from a sheet containing weights obtained previously for the bottle containing the consolidated sediment.

Sample Collection

1. For the +60 and +230 size fractions, decant all overlying water in each pan over its respective sieve and return any sample collected on the sieve to the pan. Weigh the pans and record the weights.
2. Thoroughly homogenize the sample in each pan so the solids content is representative of each sample. Place each sample into a 4 oz. amber jar, attach

labels to the samples, and record the date and time on the bench sheet. If there is more than about 200 g of sample, place a subsample in a jar to be archived.

3. Put samples in designated areas in the cooler.
4. For the <230 fraction, decant all supernatant from the bottle after its final centrifuge run. Weigh the sample bottle with lid and O-ring and record the weight. Using a stainless steel spatula, homogenize the sample in the centrifuge bottle and place in a sample jar as described above. If the sample weight is greater than about 200 g, put the sample into a decontaminated pan and homogenize. Place at least 50 g or more into one jar for analysis and archive the remaining sample. Attach labels to the jars and record the date and time.

Calculations

Percent solids and dry weight of total material fractionated are calculated as follows:

$$\text{Percent solids} = (S_{DS}/S_{WS}) \times 100$$

$$S_{WF} = (S_1 + S_2 + S_3 \ldots) - S_{WS}$$

$$S_{DF} = S_{WF} \times (\text{percent solids}/100)$$

where:

S_{DS} is dry weight of sediment removed for solids content determination
S_{WS} is wet weight of sediment removed for solids content determination
S_{WF} is wet weight of sediment fractionated
S_{DF} is dry weight of sediment fractionated
S_1 is wet weight of sediment removed from sample Jar 1.

Quality Control

If required by the project, quality control measures such as laboratory duplication or sample blanks can be performed. For a laboratory duplicate, a homogenized subsample of the original sample is processed in the same way as the original sample using separately decontaminated equipment. Both samples are submitted to the laboratory for analysis. For a sample blank, reagent-grade water is run through the process and then submitted to the laboratory for analysis.

APPENDIX A-69

STANDARD OPERATING PROCEDURE FOR PORE WATER EXTRACTION METHOD BY CENTRIFUGE

Soil Technology™, Inc.
Standard Operating Procedure
Pore Water Extraction Method by Centrifuge
October 1999

Apparatus and Materials

Nitrogen chamber, nitrogen supply, and oxygen meter for anaerobic processing
Stainless steel bowls and spoons
Stainless steel or polycarbonate centrifuge bottles
Centrifuge
Cooler at 4°C for sample storage
Glass or polycarbonate filter units
Filters: 1 μm glass fiber (Gelman A/E) in conjunction with glass prefilters (Whatman GF/D), 0.45 μm polycarbonate (Millipore Durapore), or 0.45 μm silver membrane (Osmonics)

Sample Handling

Samples are logged in and the chain of custody form is signed upon receipt at STI. Sediment samples should be kept in the cooler at 4°C until extraction. Samples must be processed within the holding time specified by the client, preferably as soon as possible after they are received. If samples are to be extracted anaerobically, then sample cores or containers must only be opened within the anaerobic chamber. Centrifuge bottles or analytical laboratory bottles must be purged with nitrogen before filling.

Procedure

1. Any equipment that will come into contact with the sediment is decontaminated using a procedure specified or approved by the client, and chosen based on the contaminants of concern.
2. For anaerobic extraction the nitrogen tank is turned on in the nitrogen chamber. The oxygen content is checked and work in the chamber does not proceed until the oxygen concentration is below 1 ppm.
3. Sediment is removed from the cores or containers and homogenized in a stainless steel bowl.
4. Sediment is loaded into stainless steel or polycarbonate centrifuge bottles and centrifuged at 6,500 rpm for 30 minutes. The centrifuge temperature should be set at 10°C. Pore water is then decanted from the bottles, taking care not to pour off any solids. For anaerobic processing this is done in the nitrogen chamber and bottles are first purged with nitrogen before fillling.
5. The extracted pore water may be either filtered or centrifuged to remove remaining particulates, depending upon the requirements of the project. For organic contaminants, it is recommended that the pore water be centrifuged rather than filtered, because glass fiber filters have been found to adsorb organic compounds.
6. For filtering samples to be analyzed for organic compounds, an aliquot of the pore water is vacuum filtered through glass filter units using glass fiber prefilters and 1 μm glass fiber filters. For inorganic substances, an aliquot of the pore water is vacuum filtered through polycarbonate filter units using either 0.45 μm polycarbonate or 0.45 μm silver membrane filters.

7. For centrifuging samples for organic compound analysis stainless steel bottles are used; for inorganic substances, polycarbonate bottles are used. The centrifuge temperature should be set at 10°C. For anaerobic processing, the bottles are purged with nitrogen prior to filling, and are filled inside the chamber. The time required for spinning is determined from application of Stoke's Law:

$$t_{\min} = \frac{6.3 \times 10^{9} (n) \log(R/S)}{(N_m)^2 (D_u)^2 (\Delta S)}$$

where:

n = fluid viscosity (poise)
R = radius of rotation of top of sediment in tube (15.13 cm)
S = radius of rotation of surface of suspension (3.93 cm)
N_m = revolutions per minute
D_u = particle diameter (μm)
ΔS = difference in specific gravity between the fluid and the particles (e.g., assuming a particle specific gravity of 2.6 g/cm^3 and a water specific gravity of 1.02 g/cm^3, this difference would equal 1.58 g/cm^3)

8. Sample bottles supplied by the laboratory are first purged with nitrogen if processing anaerobically, and then are filled with pore water and preserved if necessary. Samples are packed with ice in coolers, accompanied by a chain of custody. A signed chain of custody seal should be placed on two unhinged sides of the cooler. The cooler is shipped via overnight service as requested by the client.

Quality Control

If required by the project, quality control measures such as laboratory duplication or sample blanks can be performed. For a laboratory duplicate, a homogenized subsample of the original sample is extracted and filtered/centrifuged in the same way as the original sample using separately decontaminated equipment. Both samples are submitted to the laboratory for analysis. For a sample blank, reagent-grade water is centrifuged and filtered in the same way as the sediment and pore water samples, and submitted to the laboratory for analysis.

APPENDIX A-70

STANDARD OPERATING PROCEDURE FOR PORE WATER EXTRACTION METHOD FOR SANDY SEDIMENTS

Soil Technology™, Inc.
Standard Operating Procedure
Pore Water Extraction Method for Sandy Sediments
September 1999

Scope and Application

This method is used for extracting pore water from sediment that is too sandy to be extracted using the centrifuge method. This method uses a stainless steel thin-layer column apparatus for extraction. These columns were designed by the USACE to run leachate tests on sediment and have been used successfully for porewater extractions for the Asarco and Eagle Harbor Superfund sites in Washington State. The method was approved by both the USACE and EPA for those projects.

Apparatus and Materials

Nitrogen chamber, nitrogen supply, and oxygen meter for anaerobic processing
Thin-layer column with 100 μm porous disk (stainless steel)
Stainless steel bowls and spoons
Stainless steel or polycarbonate centrifuge bottles
Centrifuge
Cooler at 4°C for sample storage
Glass or polycarbonate filter units
Filters: 1 μm glass fiber (Gelman A/E) in conjunction with glass prefilters (Whatman GF/D), 0.45 μm polycarbonate (Millipore Durapore), or 0.45 μm silver membrane (Osmonics)

Sample Handling

Samples are logged in and the chain of custody form is signed upon receipt at STI. Sediment samples should be kept in the cooler at 4°C until extraction. Samples must be processed within the holding time specified by the client, preferably as soon as possible after they are received. If samples are to be extracted anaerobically, then sample cores or containers must only be opened within the anaerobic chamber. Centrifuge bottles or analytical laboratory bottles must be purged with nitrogen before filling.

Procedure

1. Any equipment that will come into contact with the sediment is decontaminated using a procedure specified or approved by the client, and chosen based on the contaminants of concern.
2. For anaerobic extraction the nitrogen tank is turned on in the nitrogen chamber. The oxygen content is checked and work in the chamber does not proceed until the oxygen concentration is below 1 ppm.
3. Sediment is removed from the cores or containers and homogenized in a stainless steel bowl.
4. Sediment is loaded into the thin-column on top of the porous disk and the top plate is attached. The tube through which nitrogen enters the chamber is directed through the top of the column while agitating the column with a rubber mallet.
5. The pore water is collected through stainless steel and teflon tubing at the bottom of the column.
6. The extracted pore water may be either filtered or centrifuged to remove particulates, depending upon the requirements of the project. For organic contaminants, it is recommended that the pore water be centrifuged rather than filtered, because glass fiber filters have been found to adsorb organic compounds.

7. For filtering samples to be analyzed for organic compounds, an aliquot of the pore water is vacuum filtered through glass filter units using glass fiber prefilters and 1 μm glass fiber filters. For inorganic substances, an aliquot of the pore water is vacuum filtered through polycarbonate filter units using either 0.45 μm polycarbonate or 0.45 μm silver membrane filters.
8. For centrifuging samples for organic compound analysis stainless steel bottles are used; for inorganic substances, polycarbonate bottles are used. The centrifuge temperature should be set at 10°C. For anaerobic processing, the bottles are purged with nitrogen prior to filling, and are filled inside the chamber. The time required for spinning is determined from application of Stoke's Law:

$$t_{\min} = \frac{6.3 \times 10^{9} (n) \log(R/S)}{(N_m)^2 (D_u)^2 (\Delta S)}$$

where:

n = fluid viscosity (poise)
R = radius of rotation of top of sediment in tube (15.13 cm)
S = radius of rotation of surface of suspension (3.93 cm)
N_m = revolutions per minute
D_u = particle diameter (μm)
ΔS = difference in specific gravity between the fluid and the particles (e.g., assuming a particle specific gravity of 2.6 g/cm^3 and a water specific gravity of 1.02 g/cm^3, this difference would equal 1.58 g/cm^3)

9. Sample bottles supplied by the laboratory are first purged with nitrogen if processing anaerobically, and then are filled with pore water and preserved if necessary. Samples are packed with ice in coolers, accompanied by a chain of custody. A signed chain of custody seal should be placed on two unhinged sides of the cooler. The cooler is shipped via overnight service as requested by the client.

Quality Control

If required by the project, quality control measures such as laboratory duplication or sample blanks can be performed. For a laboratory duplicate, a homogenized subsample of the original sample is extracted and filtered/centrifuged in the same way as the original sample using separately decontaminated equipment. Both samples are submitted to the laboratory for analysis. For a sample blank, reagent-grade water is passed through the thin-layer column and then centrifuged or filtered in the same way as the pore waters, and submitted to the laboratory for analysis.

APPENDIX A-71

STANDARD OPERATING PROCEDURE FOR SEDIMENT FRACTIONATION OF HOUSATONIC RIVER SUSPENDED SEDIMENT

Soil Technology™, Inc.
Sediment Fractionation of
Housatonic River Suspended Sediment
June 1999

Weston sampled suspended sediments from three stations in the Housatonic River during a storm flow event on May 19, 1999. The samples were identified as H2-ST000004-0-9419-1000F, H3-ST000007-0-9419-1000F, and H4-ST000009-0-9419-1000F. Samples were collected into mesh bags with a 5 μm screen size. Six to ten bags were used at each station to obtain a sufficient quantity of material for analysis. Soil Technology, Inc. (STI) received these samples on May 25, 1999.

Suspended material was carefully removed by STI from the bags by cutting them open and first collecting any material that could be scraped from the surface of the bags. The remaining material adhering to the surface of the bags was removed by rinsing with a squirt bottle containing carbon-filtered deionized water. All rinsewater was collected into a large stainless steel container. Approximately 10 L of rinsewater containing the suspended matter was collected in this way because of the large quantity of bags and the large surface area of each bag.

All equipment used for the fractionation was decontaminated using the following procedure:

1) Wash with liquinox/water
2) Rinse with tap water
3) Rinse with methanol
4) Rinse with hexane
5) Rinse with reagent-grade water

The following sections describe how each of the four size fractions were obtained from the suspended sediment. A wet weight of each size fraction was also measured. Table 1 presents the sampling date and wet weights for each size fraction for the three samples.

>250 μm: The material collected from the mesh bags (solids and rinsed material including rinsewater) was wet-sieved through a decontaminated stainless steel #60 sieve (250 μm mesh size) into a large stainless steel container using carbon-filtered deionized water. The material retained on the #60 sieve (>250 μm) was collected by inverting the screen over a second stainless steel pan and running water over the screen. This material was then centrifuged at 6500 rpm for 10 minutes in a stainless steel centrifuge bottle and the supernatant was decanted and discarded[1]. The remaining solids in the bottle were collected and submitted for TOC analysis.

>63 – 250 μm: The material passing through the #60 sieve was wet-sieved through a #230 sieve (63 μm mesh size). The material remaining on the sieve (>63 μm) was collected and centrifuged as described for the previous fraction and submitted for PCB and TOC analysis.

>10-63 μm: The material and rinse water that passed through the #230 and #60 sieves was centrifuged to separate the material greater than 10 μm and less than 10 μm[2]. The time required

[1] The proposed method called for settling the solids out for a certain time period and decanting the water from the top. However, this method left a very high water content in the small amount of material, so centrifuging was conducted to obtain a lower moisture content without losing any material.
[2] The proposed method called for sieving the material through a #850 sieve (10 μm mesh size). However, very little material was able to pass through the sieve, and it failed under vacuum pressure.

for spinning to separate these two fractions was determined using a method obtained from the U.S. Army Engineer Waterways Experiment Station which applies Stokes' Law (Jackson 1979; Svedberg and Nichols 1923), as follows:

$$t_{\min} = \frac{6.3x10^{9}(n)\log(R/S)}{(N_{\mathrm{m}})^{2}(D_{\mathrm{u}})^{2}(\Delta S)} \qquad (1)$$

where:

$t_{\min}$ = time (minutes)
n = fluid viscosity (0.01002 poise)
R = radius of rotation of top of sediment in tube (15.1 cm)
S = radius of rotation of surface of suspension (3.9 cm)
N_{m} = revolutions per minute (500 rpm)
D_{u}= particle diameter (10 μm)
ΔS= difference in specific gravity between the fluid and the particles (1.6 g/cm^3)

Based on the above equation, the material was centrifuged at 500 rpm for 55 seconds to settle out particles greater than 10 μm. Since each centrifuge bottle holds approximately 450 ml, and the centrifuge holds six bottles, four centrifuge runs were necessary to process the >10 L of material. After each centrifuge run, the supernatant was slowly decanted from each bottle into a clean stainless steel container, leaving the sediment and several centimeters of water in each bottle. More material was added to each bottle and centrifuged again until all the material was processed. After the last of the supernatant was decanted, a final centrifuge run was conducted at 6500 rpm for 30 minutes. The supernatant was discarded and the remaining solids (representing 10-63 μm) were collected and submitted to the laboratory for TOC and PCB analysis.

<10 μm: According to Equation 1, the supernatant decanted from the centrifuging in the previous step contained particles with a diameter less than 10 μm. This supernatant was centrifuged in decontaminated stainless steel bottles at 6,500 rpm for 30 minutes. As in the previous step, it took four centrifuge runs to process all the material (>10 L). After each centrifuge run, the supernatant was slowly decanted from each bottle into a clean stainless steel container, leaving the sediment and several centimeters of water in each bottle. After the final centrifuge run, all of the supernatant was decanted from each bottle and the remaining material was collected and submitted for PCB and TOC analysis.

APPENDIX A-72

STANDARD OPERATING PROCEDURE FOR SBLT LEACHING PROCEDURE

Time of contact

Contact time in a batch leach test, such as the SBLT, refers to the lapse time between introduction and removal of water. Experiments consistently demonstrate that a contact time of 24 hr is sufficient to achieve steady-state conditions for organics in leachate (Figure 9) (Environmental Laboratory 1987; Myers and Brannon 1988a; Myers and Brannon 1988b; Palermo et al. 1989; Brannon, Meyers, and Price 1990).

The kinetic behavior of metals is more complex than the behavior of organics (Brannon, Myers, and Price 1990). Metals generally show either no significant change in leachate concentrations over time or a peak in concentration following 1 day of contact. Either way, a contact time of 24 hr is appropriate.

Oxidation status of sediment

Development of the SBLT has also included batch testing of anaerobic and aerobic sediment. Leaching of aerobic, aged sediment has been used to simulate leaching of the surface crust in a CDF, and anaerobic leaching has been used to simulate leaching in the saturated-anaerobic zone of a CDF. Neither hydraulic nor mechanical dredging adds sufficient oxygen to overcome the sediment oxygen demand of polluted sediments. As a result, the dredged material in a CDF is anaerobic, except for a surface crust that develops as the CDF dewaters by evaporation and seepage. The oxidized crust may eventually be several feet thick, but, in general, never represents a significant portion of the vertical profile for the typically fine-grained material. The procedure below, therefore, describes the technique for anaerobic leaching. The technique for aerobic leaching is described in Environmental Laboratory (1987), Myers and Brannon (1988b), Palermo et al. (1989), and Brannon, Myers, and Price (1992). The aerobic leaching procedure may be necessary if the dredged material is to be applied in a thin layer as in, for example, land farming.

SBLT Test Procedure

The recommended procedure for anaerobic sequential batch leaching of sediments and dredged material is as follows:

a. *Step 1.* Load sediment into appropriate centrifuge tubes fitted with leakproof, airtight tops: 250 or 500 mL polycarbonate for metals and 450 mL stainless steel for organic contaminants. Add sufficient deoxygenated distilled-deionized water to each tube to bring final water-to-sediment ratio to 4:1. All operations should be conducted in a glove box under a nitrogen atmosphere.

b. *Step 2.* Place centrifuge tubes in a rotary tumbler such as described by Garrett et al. (1984) and turn at 40 rpm for 24 hr.

c. *Step 3.* Centrifuge for 30 min at 9,000 × g for metals and 6,500 × g for organics.

d. *Step 4.* Filter leachate through a 0.45-μm membrane filter for metals and a Whatman GD/F glass-fiber prefilter followed by a Gelman AE glass-fiber filter (1.0 μm nominal pore size) for organics.

e. *Step 5.* Set aside a small amount of leachate for analysis of pH and electrical conductivity. Acidify leachate with 1 mL of concentrated HCl or Ultrex nitric acid per liter of leachate for metals and organics, respectively. Store samples in the dark. Sample bottles should be cleaned to Environmental Protection Agency specifications or commercially purchased precleaned bottles should be used; polycarbonate for metals and glass for organics should be used. Bottles for organics should be filled to the top.

f. *Step 6.* Return to Step 2 after replacing leachate removed in Step 4 with fresh deoxygenated distilled-deionized water. Repeat the entire procedure to obtain a minimum of four complete sequential cycles.

Additional details are provided in Appendix A.

APPENDIX A-73

STANDARD OPERATING PROCEDURE FOR SAMPLE PREPARATION SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM A SOIL/SEDIMENT MATRIX USING SONICATION EXTRACTION

SOP No.	Revision No.	Date	Page
USP-SOP-3550	00	03/22/99	1 of 27

TITLE: Sample Preparation Semivolatile and Nonvolatile Organic Compounds from a Soil/Sediment Matrix Using Sonication Extraction

Updated by:	Signature:	Date
Nancy J. Walsh Organic Extractions	Nancy J Walsh	3/20/99

Approved by:	Signature:	Date
Linda S. Mackley, Section Manager, Organics Dept.	Linda S Mackley	3-19-99
Raymond J. Frederici Quality Manager	Ray J Fred	3-19-99

CONTROLLED DISTRIBUTION

COPY # : 008

ISSUED TO : Sharon Nordstrom - USACE
Re: Housatonic River Site Proj

Full Signature Approvals Are Kept on File with
Severn Trent Laboratories QA Standard Practice Records

1.0 SCOPE AND APPLICATION

To outline the extraction procedure of semivolatile and nonvolatile compounds[1] from soil and sediment matrices using SW-846 Methods 3500B, 3550A and 3550B. The compounds of interest are as listing in the analytical Standard Operating Procedure (SOP). On occasion, clients request slight modification of this standard operating procedures. These modifications are addressed on a case-by-case basis and would be written into a Quality Assurance Plan (QAP).

[1]BNAs, Pesticides, Pesticides/PCBs, PCBs, Organophosphorus Pesticides, and PAHs.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

Not applicable. Refer to the analytical SOP(s).

1.1.2 Reporting Limits

Not applicable. Refer to the analytical SOP(s).

1.2 Summary of Procedure

The following procedure is used for the sonication extraction of semivolatile and nonvolatile organics from soils and sediments for subsequent analysis. Approximately 30 grams of sample, or 10 grams depending on previous sample experience, is mixed with anhydrous sodium sulfate to form a free-flowing powder. This mixture is solvent extracted three times (using sonication) with DCM:acetone (1:1)(v:v). The combined extract is dried, concentrated, exchanged to another solvent if necessary, and adjusted to the appropriate final volume. The labeled extracts are stored in extraction batches at 4 +/- 2°C prior to analysis. Optional cleanup procedures may be performed upon request. The mandatory acid cleanup for PCB samples is described within this SOP. GPC, Florisil, and sulfur removal cleanup procedures are described in other SOPs (refer to the cleanup section of this SOP for specific references).

Sludge samples (water and suspended solids) with very low solid content may be prepared following the SOP on the Preparation of Semivolatile and Nonvolatile Organics from Waste Waters. Organic sludges and wastes, both single phase, are generally prepared following the SOP Preparation of Semivolatile and Nonvolatile Organics from Wastes and Oils. (See references in the appropriate SOP).

2.0 INTERFERENCES

2.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

2.2 Phthalate esters contaminate many types of products commonly found in the laboratory. **Plastics, in particular**, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic material.

2.3 Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.

2.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. These can appear as large, distinct peaks and/or elevated baselines. Occasionally matrix interferences may prevent the proper detection of surrogate and/or analytes, resulting in the reporting of low, or possibly high, surrogate and/or spike recoveries. The extent of matrix interferences will vary considerably from sample to sample, depending upon the nature of the site being sampled. Various cleanup procedures may be performed to remove heavy background or interferences, including GPC cleanup, Florisil cleanup, acid cleanup, and sulfur removal procedures.

3.0 SAFETY

3.1 Take careful note of those sections marked "***CAUTION***" and "***NOTE***".

3.2 As always, general laboratory safety practices should always be followed.

3.3 Refer to the specific Material Safety Data Sheets (MSDS) for the hazardous properties of any chemicals or reagents involved in this procedure.

3.4 Safety glasses and lab coats must be worn at all times during the extraction process. Nitrile or equivalent gloves are available and must be worn when handling acids, bases, or samples.

3.5 All extractions and handling of solvents should be performed under well-ventilated conditions of a fume hood.

3.6 DCM is considered a health hazard and possible carcinogen. It is harmful if swallowed or inhaled. The vapor is irritating, and thus should be used in a hood. It is readily absorbed through the skin and contact may be irritating.

3.7 All wastes, solvents, reagents, and samples in need of disposal should be placed in the appropriate waste containers. The analyst should consult their unit leader or safety officer if he/she is unclear on how to properly dispose of materials.

3.8 All samples should be handled with care due to the uncertainty of the properties and contents involved.

3.9 The sonicator is an electrical instrument with high voltage. If a sample is spilled into the components box, unplug it immediately and have it serviced prior to using.

4.0 EQUIPMENT AND SUPPLIES

4.1 Glassware

- 100 mL, 1000 mL, 2000 mL graduated cylinders
- 0.5 mL, 1.0 mL, 10 mL volumetric pipet, Class A
- 25 mL, 100 mL volumetric flask, Class A
- 500 uL, 1000 uL syringe
- 250 mL, 400 mL beakers
- 100 mm glass, powder funnels
- Buchner funnels
- 500 mL filtering, Erlenmeyer flasks
- 500 mL Kuderna-Danish flasks
- 10 mL receiver (concentrator tubes) with clips, standard and insulated
- 3 ball Snyder columns
- 250 mL Erlenmeyer flasks
- 16 X 125 screw-top test tubes with caps
- Transfer pipets
- Shallow Pyrex drying tray
- Vials, 1.5 - 2.0 mL, screw-capped, teflon-lined

4.2 Miscellaneous

- Ultrasonic Cell disrupter (Misonix Incorporated, Model XL2020 Sonicator, 550 Watts with pulsing capability, Dual Horn with No. 208, 3/4 in. solid extenders).
- Sonabox acoustical enclosure
- Balance (capable of weighing to 0.01 g)
- Teflon squeeze bottles
- Nitrogen evaporator
- Waterbath - heated, with concentric ring covers, capable of temperature control. Bath must be in a hood.
- Magnetic stir plate and stir bars
- Wide range pH paper 1 to 12
- #41 Whatman filter paper
- Mixing pan/aluminum foil
- Wooden spatulas
- Vacuum pump
- Boiling chips; soxhlet extracted
- Muffle furnace
- Desiccator
- Stainless steel spatula
- Centrifuge

5.0 REAGENTS AND STANDARDS

A label on any reagent bottle must contain the concentration of the reagent, name of the reagent, date prepared, expiration date and the analyst who prepared the reagent.

5.1 Reagents

5.1.1 Pesticide Grade Methylene Chloride (DCM)
Pesticide Grade Acetone
Pesticide Grade Hexane
Pesticide Grade Acetonitrile

5.1.2 Heat Purified Granular Sodium Sulfate

Purify by heating at 400°C for four hours in a shallow drying tray, cool in a desiccator, and store in a glass bottle.

- Life of Reagent: One year.
- Storage Requirements: Store in a glass container and keep dry (anhydrous).

5.1.3 Heat Purified Powdered Sodium Sulfate

Purify by heating at 400°C for four hours in a shallow drying tray, cool in a desiccator, and store in a glass bottle.

- Life of Reagent: One year.
- Storage Requirements: Store in a glass container and keep dry (anhydrous).

5.1.4 DCM:Acetone (1:1) (v:v)

Add 1000 mL pesticide grade DCM into 1000 mL pesticide grade acetone in a 2 Liter graduated cylinder. Pour into a 4-L solvent bottle and swirl to mix. Do not close the top on the bottle because the pressure will build and may cause it to explode.

- Hazardous Properties: Acetone is flammable. When not in use it should be stored in a flammable cabinet. Do not use near open flame or heat. DCM is an inhalation hazard. Use only in a well ventilated area. Harmful if swallowed.

- Life of Reagent: One year.
- Storage requirements: Store in a glass container with a teflon-lined cap. Store in a flammable cabinet.

5.1.5 Concentrated Sulfuric Acid

Purchased from a supplier

Hazardous Properties: Sulfuric Acid (H_2SO_4) is extremely corrosive and toxic to tissues. Vapors are also harmful.

- Life of Reagent: One year
- Storage Requirements: Store in glass container. The label on the bottle must contain concentration and name of reagent.

5.2 Quality Control (QC) Solutions

QC solutions must be stored in amber or foil-wrapped, glass containers that have Teflon-lined caps. the label on the container must contain the following information: Name of the solution, standard #, concentration of the components, date prepared, preparation analyst, and expiration date. All QC solutions are stored either in the standards refrigerator in the GC/MS lab, GC Extractables lab, or in the standards refrigerator located in the organic extraction lab. QC solutions are stored at 4 ± 2 °C.

Listed below are the various QC solutions and concentrations appropriate for extraction of BNAs, Pesticides, Pesticides/PCBs, PCBs, Organophosphorus Pesticides, and PAHs from soil/sediment matrices. Instructions detailing the preparation of these solutions are found in the corresponding analytical OPs.

5.2.1 Surrogate Spike Solutions

5.2.1.1 BNA Surrogate Spike Solution

The BNA Surrogate Spike Solution is purchased directly from a chemical vendor at the levels listed below. 500 uL of BNA Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
p-Terphenyl-d_4	100 ug/mL
Nitrobenzene-d_5	100 ug/mL
2-Fluorobiphenyl	100 ug/mL
1,2-Dichlorobenzene-d_4	100 ug/mL
Phenol-d_5	150 ug/mL
2-Fluorophenol	150 ug/mL
2,4,6-Tribromophenol	150 ug/mL
2-Chlorophenol-d_4	150 ug/mL

- Life of Reagent: 6 months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

5.2.1.2 Pesticide/PCB Surrogate Spike Solution

The surrogate used in the extraction of pesticides/PCBs from soil/sediments is a solution of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCMX) in acetone at the concentrations listed below. 1000 uL of Pesticide/PCB Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
DCB	0.4 ug/mL
TCMX	0.4 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.1.3 Organophosphorus Pesticide Surrogate Spike Solution

The surrogate solution used in the extraction of organophosphorus pesticides from soil/sediments is a solution of tributylphosphate and triphenyl phosphate in acetone. The GC Extractables department prepares all standard solutions. The desired concentration of each compound is 20 ug/mL; however, there may be slight variability between separate solutions. 1000 uL of Organophosphorus Pesticide Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
Tributylphosphate	~ 20 ug/mL
Triphenyl Phosphate	~20 ug/mL

- Life of Reagent: 6 months from the preparation date or as documented by the vendor, whichever comes first
- Storage Requirements: As stated in Section 5.2

5.2.1.4 PAH Surrogate Spike Solution

The surrogate used in the extraction of polynuclear aromatic hydrocarbons from soil/sediments is a solution of Decafluorobiphenyl and Benzo (e) pyrene in acetone at the concentrations listed below. The HPLC group prepares the working surrogate solution. 500 uL of PAH Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
Decafluorobiphenyl	100 ug/mL
Benzo (e) pyrene	5.0 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2 Spike Blank & Matrix Spike Solutions

5.2.2.1 BNA TCL Spike Solution

The BNA TCL Spike Solution is purchased directly from vendor at the levels listed below. 1000 uL of BNA TCL Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
Acid Compounds	100 ug/mL
Base/Neutral Compounds	100 ug/mL

- Life of reagent: Six months from the from the preparation date (as documented from the vendor).
- Storage: As stated in Section 5.2.

5.2.2.2 Pesticide (Full List) Spike Solution

The spike blank/matrix spike solution used in the extraction of pesticides or pesticides/PCB from soil/sediments is a solution of 20 pesticides in methanol at the following concentrations. 1000 uL of Pesticide (Full List) Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
gamma & alpha Chlordane	0.2 ug/mL
All other compounds	0.4 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2.3 PCB Spike Solution

The spike blank/matrix spike solution used in the extraction of PCBs from soil/sediments is a solution of Arochlor 1016 and Arochlor 1260 in methanol at the following concentrations. 1000 uL of PCB Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
AR1016	5.0 ug/mL
AR1260	5.0 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2.4 Organophosphorus Pesticide Spike Solution

The spike blank/matrix spike solution used in the extraction of organophosphorus pesticides from soil/sediments is a solution of 9 organophosphorus pesticides in methanol at the following concentrations. 1000 uL of Organophosphorus Pesticide Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
o,o,o-TEPA	20.0 ug/mL
Thionazin	20.0 ug/mL
Sulfotepp	20.0 ug/mL
Phorate	20.0 ug/mL
Dimethoate	20.0 ug/mL
Disulfoton	20.0 ug/mL
Methyl parathion	20.0 ug/mL
Ethyl parathion	20.0 ug/mL
Famphur	20.0 ug/mL

- Life of Reagent: 6 months from preparation date or as documented by the vendor, whichever comes first
- Storage Requirements: As stated in Section 5.2

5.2.2.5 PAH Spike Solution

The spike blank/matrix spike solution used in the extraction of polynuclear aromatic hydrocarbons from soil/sediments is a solution of 16 analytes in acetonitrile at the following concentrations. The HPLC group prepares the spike solution. 500 uL of PAH Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
Acenaphthene	8 ug/mL
Acenaphthylene	16 ug/mL
Anthracene	0.8 ug/mL
Benzo(a)anthracene	0.8 ug/mL
Benzo(a)pyrene	0.8 ug/mL
Benzo(b)fluoranthene	1.6 ug/mL
Benzo(ghi)perylene	1.6 ug/mL
Benzo(k)fluoranthene	0.8 ug/mL
Chrysene	0.8 ug/mL
Dibenzo(a,h)anthracene	1.6 ug/mL
Fluorene	1.6 mg/mL
Indeno(1,2,3-cd)pyrene	0.8 mg/mL
Naphthalene	8.0 mg/mL
Phenanthrene	0.8 mg/mL
Pyrene	0.8 mg/mL

- Life of Reagent: Same as the parent solution
- Storage Requirements: As stated in Section 5.2

6.0 CALIBRATION

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control

The following QC is performed with each organic extraction batch. An extraction batch contains samples of similar matrix that are logged in for the same test code. An extraction batch may contain no more than 20 samples.

7.1.1 Method Blank

The method blank is heat purified powdered sodium sulfate, which has been spiked with the appropriate surrogate (Sec 5.2.1), then taken through the entire extraction procedure and is used to monitor the introduction of artifacts into the process. This demonstrates that the materials used are free of interferences.

7.1.2 Blank Spike/Blank Spike Duplicate

The blank spike is heat purified powdered sodium sulfate which has been spiked with a predetermined quantity of spike solution (Sec 5.2.2)with the appropriate analytes of interest and the appropriate surrogate solution (Sec. 5.2.1).

7.1.3 Matrix Spike/Matrix Spike Duplicate

In matrix spike/matrix spike duplicate analysis, predetermined quantities of spike solutions of specified analytes (Sec 5.2.2) and surrogate (Sec. 5.2.1) are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected by the analysis. The relative percent difference between the samples is calculated and used to assess analytical precision.

7.1.4 Surrogate

A surrogate is an organic compound(s) which is similar to the analytes of interest in chemical composition, extraction and chromatography, but which is not normally found in environmental samples. The surrogate is added to **all** blanks, blank spikes, samples, and matrix spike samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

7.2 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Sample container, preservation technique and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract/client requests. In general, samples collected for soil/sediment extractions are collected in 8 oz. wide-mouth glass jars, with teflon-lined screw-cap lids. If a teflon-lined lid is not available, solvent-rinsed aluminum foil can be used as a liner.

Samples, sample extracts and standards are stored separately.

NOTE: If the sample matrix is highly acidic or basic, corrosion of the foil may occur and contaminate the sample.

Samples are stored at 4 $\pm$ 2° prior to extraction. Any samples received by the preparation group that do not comply must be noted. Deviations in results "could" be explained by the failure of sample collector/client/ custodian to comply to sample collection and storage requirements.

7.2.1 **SW-846 Holding Time**

14 days (vts) vts= verified time of sample collection

7.3 **Sample Preparation**

7.3.1 **Glassware Preparation**

7.3.1.1 All glassware (except Snyder columns, volumetric flasks, volumetric pipets, and syringes) must be washed thoroughly with warm soapy water, rinsed **five** times with hot tap water and rinsed **three** times with DI water. The stopcocks of the separatory funnels should be cleaned with a small brush. **It is absolutely mandatory that all glassware be scrupulously clean.** Failure to rinse well with water, may leave a soap film that is incompletely removed with solvent rinsing, and with subsequent extraction, "soap" peaks will appear in the chromatograms.

7.3.1.2 If glassware is very wet it may be towel dried. **All** Glassware should be rinsed with acetone, and the excess should be discarded into the appropriate waste container. This step is done to ensure that the glassware is dry. **If after rinsing once, the glassware still contains any water, repeat the acetone rinse.** At this point let the glassware dry before continuing to ensure that all of the water is gone. All glassware should then be rinsed with DCM using a Teflon squeeze bottle, and the excess discarded into the appropriate waste container. Repeat this step at least three times and allow the glassware to dry. Failure to remove all water prior to DCM rinsing prevents the DCM solvent from coming into contact with all surfaces on the glassware. The solvent rinse is then incomplete, and may leave contaminants on the glass, which are then co-extracted with the sample.

NOTE: DCM is considered a health hazard. It is harmful if swallowed or inhaled. The vapor is irritating and thus should be used in a hood. It is readily absorbed through the skin and contact may be irritating.

7.3.2 **Procedures for Return of Glassware to Dishroom**

Any glassware that has organic residue present, all K-D receivers, and all separatory funnels should be rinsed with acetone, or whatever other solvent which removes the residue, prior to return to the dishroom from the lab. Glassware in which the residue can not be removed should be segregated from other glassware being returned to the dishroom. Glassware should be carefully placed in a tub and placed on the "Dirty" side of the dish racks. In order to reduce glassware breakage, glassware should not be stacked in the tubs. Severely chipped glassware should be removed from service. Some items are repairable. Check with the unit leader as to what items get repaired.

7.4 Calibration/Standardization

Not Applicable.

7.5 Preventive Maintenance

7.5.1 Balance should be cleaned and checked for levelness prior to each use. Class "S" weights should be weighed and documented each day the balance is used. Consult your unit leader if the weights are out of acceptable limits. Do not use the balance until the situation is back in control.

7.5.2 The probe tips of the sonicator should be periodically examined for extensive wear. To assure optimum operation, periodically tune the generator in accordance to the instructions listed on page 13 of the Misonix XL2020 "Instruction Manual, SON-IM".

7.5.3 The K-D waterbath should contain DI water only. The water level should be checked prior to each use, and should not fall below the heating coils. If the heating coils do become exposed to the air while in use, they could burn-out and would require replacement. Keep the water level approximately one inch from the top of the bath edge.

7.5.4 The N-Evap waterbath should also contain DI water. The water level in the bath should be sufficient to cover 3/4 of the receivers when submerged.

7.5.5 The thermometer used in the extraction waterbaths are checked against a reference NIST thermometer on a yearly basis or sooner if necessary.

7.5.6 The desiccant used in the desiccator should be removed and dried in an oven at 130°C whenever the color indicates that it is saturated with moisture. This is usually indicated by a change of color from blue to purple/pink.

7.5.7 To avoid the breakage of sample extracts, the analyst needs to take care that the containers are properly balanced on the centrifuge. The container should fit snugly in the holder. Use a paper towel to cushion the centrifuge bottles if necessary.

7.6 Sample Analysis

7.6.1 Analytical (Preparation) Sequence

The following preparation sequence will be required of each extraction batch of at most, 20 samples:

Quality Control	Frequency
Method Blank (MB1)	1 per extraction batch of at most 20 samples
Blank Spike (MBIS)/BS Dup (MBIT)	1 set per extraction batch of at most 20 samples
Matrix Spike (MS)/MS Dup (MSD)	At least 1 set in 20 samples (may be requested by the client)
Surrogate	Every sample/blank/MBIS/MBIT/ MS/MSD

7.6.2 Extraction Process

Semivolatile and nonvolatile organics from soil matrix following SW 846 procedures are extracted using sonication extraction.

7.6.2.1 Sonication Extraction

NOTE: All soils and sediments receive total solids analysis on them by the metals department, so the extraction analyst should not have to perform this step. Results are available on LIMS.

7.6.2.1.1 Sample Homogenization

7.6.2.1.1.1 Prepare the mixing pan by completely covering the inside with aluminum foil. The dull side of the foil should be toward the sample. Complete the following steps as quickly as possible so as to avoid losses of the more volatile extractables. Transfer the entire contents of the sample container to the mixing pan. Mix the sample well. Using a wooden spatula or solvent-rinsed, stainless steel spatula, break up any chunks of soil material. The objective is to get as representative of a sample as possible. If objects such as rocks and plant material seem "foreign", they should not be used for the sample. However, sometimes material other than soil constitutes a large portion of the sample. These materials should be represented in the sample.

NOTE: If a soil or sediment sample contains more than 90% moisture, it is generally extracted using the separatory funnel method. Contact your unit leader immediately in this case.

7.6.2.1.1.2 Weigh out 30 grams of sample into a labeled 250 mL beaker. Repeat for each sample. Weigh out three, 30 g aliquots of the sample designated/chosen to have the MS and MSD. Label as the sample, sample MS, and sample MSD. Record the sample weights to the nearest 0.001 g in the extraction log book. Dispose of the aluminum foil and wooden spatulas into a lab waste container. Cover each sample with foil.

NOTE: If previous experience has shown very high concentrations and/or background, a 10 gram sample size can be used. It is advisable to weigh out samples with high moisture content into 400 mL beakers. This allows for additional sodium sulfate needed to dry the sample. It is extremely important to stir those types of samples very well and very often once the sodium sulfate has been added. The sodium sulfate / wet sample mixture has a tendency to solidify.

7.6.2.1.1.3 Add powdered sodium sulfate to each sample, MS and MSD and mix well using separate spatulas. Add sodium sulfate until the sample has a free-flowing consistency. Recover with foil. Make sure all glassware is appropriately labeled with the sample #.

7.6.2.1.2 pH Determination

Weigh out the pH sample aliquot at the time as the extraction aliquot is weighed out. Weigh out 50 g of sample into a 250 mL beaker for pH determination. Add 50 mL of deionized water. Add a Teflon-coated stir bar and cover tightly with aluminum foil. Stir for one hour on a magnetic stir plate. Determine the pH of the sample with wide range pH paper. Record the pH value in the extraction log book. If the pH of the sample is <5 or >11, notify the unit leader. If sample is limited, use 5 g of soil and 5 mL of reagent water for pH determination. Denote this in the extraction log book. Solid and liquid waste from pH determination should be placed in appropriate waste containers. No pH waste is to be put in the sink.

7.6.2.1.3 Add ~30 g of heat-purified, powdered sodium sulfate to each of three 250 mL beakers. Label the beakers as the method blank (MB1), blank spike (MB1S), and blank spike duplicate (MB1T).

NOTE: All spiking solutions MUST be at room temperature before use. Actual concentrations will change at colder temperatures. Furthermore, some components may come out of solution in the freezer. Warming to room temperatures reverses the process.

7.6.2.1.4 Add the appropriate amount of the appropriate surrogate solution (Sec. 5.2.1) to each sample, including the blank and the blank spikes.

7.6.2.1.5 Add the appropriate amount of the appropriate spiking solution (Sec. 5.2.2) to the blank spike, blank spike duplicate, matrix spike(s), and the matrix spike duplicate(s).

7.6.2.1.6 Add 100 mL of DCM:Acetone (1:1) extraction solvent to each sample. Wipe off the tip of the sonicator with a acetone-soaked paper towel. Repeat with another acetone-soaked paper towel and then rinse with acetone, into a waste beaker.

7.6.2.1.7 The sonicator processor output control should be set at 10 and the %duty cycle at 50. The unit should be set on "pulsed" operation.

7.6.2.1.8 Put the first sample into the sonabox acoustic enclosure and place the sonicator tip into the sample. Make sure the tip is below the solvent layer but not touching the sample. Turn the sonicator on. Start the sonication cycle and sonicate for three minutes. Open the sonabox acoustic enclosure, lift the tip out of the solvent, and touch the tip to the inside of the beaker above the solvent layer.

7.6.2.1.9 Label a collecting flask for each sample. Fold a 18.5 cm, Whatman #41, filter paper and place in a 100 mm glass funnel. Fill the funnel half full with heat-purified, granular, sodium sulfate. Place a prepared funnel on each collecting flask.

NOTE: Vacuum filtration apparatus (Buchner funnel, filtering flask, and vacuum pump) is available, but not normally used.

7.6.2.1.10 Decant the solvent layer of the sonicated sample through the prepared funnel and into the collecting flask. Add another 100 mL aliquot of DCM:Acetone (1:1) to the soil sample.

7.6.2.1.11 Repeat the extraction and decanting steps two more times. Combine the three solvent extracts in the same 500 mL collection flask.

7.6.2.1.12 After the final sonication, pour the entire sample into the funnel and rinse with the extraction solvent. Rinse the beaker with approximately 10 mLs of solvent, repeat twice. Add the solvent rinses to the funnel.

7.6.2.1.13 In between each sample, wipe and rinse the sonicator tip as described before.

The samples are now ready for concentration using the K-D apparatus. Proceed to section 7.6.2.2 for instructions.

7.6.2.2 Sample Concentration

All samples being concentrated must be recorded in the "Sample Concentration Log".

**Occassionally samples extracted from soil/sediments for subsequent BNA analysis and/or Pesticide/PCB analysis receive a gel permeation cleanup (GPC). These samples need to be identified prior to concentrating. Refer to the appropriate section of the SOP for BNA extraction via CLP Procedure for concentration of these "pre-GPC" BNA samples. Refer to the appropriate section of Cleanup for Pesticide/PCBs for concentration of these "pre-GPC" Pesticide/PCB samples.

7.6.2.2.1 Assemble a K-D concentrator by attaching a 10 mL concentrator tube to a 500 mL K-D flask. Add a couple of boiling chips. Transfer each extract to it's own K-D concentrator (making sure that each flask is appropriately labeled). Rinse the Erlenmeyer flask 3 times with DCM, adding each rinse to the K-D flask. Rinse down the joint with DCM and then attach a 3-ball Snyder column to each and place on the waterbath. The temperature control should be set to medium. This setting should correspond to 80-90°C. Concentration to < 10 mLs is usually completed in 60 - 90 minutes. The balls should chatter but the chambers should not flood.

7.6.2.2.2 Refer to appropriate test for further concentration instructions:

BNA When the apparent final volume reaches about 2-5 mL, remove from the bath. Allow to drain and cool for 10 minutes. Remove the Snyder column, rinsing the joint and flask with 1-2 mLs DCM. Allow to drain. Dry off the outside of the joint between the flask and receiver to remove the water. Pull the 2 pieces apart gently, in a twisting motion. Rinse off the joint with DCM into the receiver. Cover the receiver with a piece of aluminum foil. If the extracts are to sit overnight, they are to be stored at 4 +/- 2°C.

Proceed to section 7.6.2.3 for further concentration using nitrogen evaporation.

PCB, Pesticide/PCB, and Organophosphorus Pesticides When the apparent final volume reaches about ~5 mL, a solvent exchange is required. Add 50 mL of hexane to the K-D flask (through the Snyder column). Concentrate the extract by raising the temperature of the water bath, if necessary, to maintain proper distillation. The Snyder column may be wrapped with foil to aid proper evaporation. When the apparent volume reaches 3-5 mL, remove from the bath. Allow to drain and cool for 10 minutes. Remove the Snyder column, rinsing the joint and flask with 1-2 mLs hexane. Allow to drain. Dry off the outside of the joint between the flask and receiver to remove the water. Pull the 2 pieces apart gently, in a twisting motion. Rinse off the joint with hexane into the receiver.

Transfer the extract into a labeled, 16X125 test tube that has been previously marked at 10.0 mL. Rinse the receiver 3 times with hexane, transferring the rinsate each time to the 16X125 test tube. Refrigerated the extracts if they are not going to be immediately concentrated.

Proceed to section 7.6.2.3 for further concentration using nitrogen evaporation.

PAHs When the apparent final volume reaches about ~5 mL, a solvent exchange is required. Add 5 mL of acetonitrile to the K-D flask (through the Snyder column). Concentrate the extract by raising the temperature of the water bath, if necessary, to maintain proper distillation. The Snyder column may be wrapped with foil to aid proper evaporation. When the apparent volume reaches 3-5 mL, remove from the bath. Allow to drain and cool for 10 minutes. Remove the Snyder column, rinsing the joint and flask with 1-2 mLs acetonitrile. Allow to drain. Dry off the outside of the joint between the flask and receiver to remove the water. Pull the 2 pieces apart gently, in a twisting motion. Rinse off the joint with acetonitrile into the receiver.

Transfer the extract into a labeled, 16X125 test tube that has been previously marked at 5.0 mL. Rinse the receiver 3 times with acetonitrile, transferring the rinsate each time to the 16X125 test tube. Refrigerated the extracts if they are not going to be immediately concentrated.

Proceed to section 7.6.2.3 for further concentration using nitrogen evaporation.

7.6.2.3 Nitrogen Evaporation

7.6.2.3.1 For further concentration, place each receiver or test tube on the N-evap tray. The N-Evap outlet needles should be stored in a 600 mL beaker containing DCM:Acetone (1:1) mixture prior to each use. Wipe each outlet needle with a KimWipe and lock into place on the N-Evap. Lower the outlet tube into the receiver being careful not to touch the sides of the receiver. The outlet tube should remain above the surface of the extract. Open the valve of the nitrogen tank and adjust the pressure in order to achieve the appropriate nitrogen stream. The nitrogen stream should make a slight "dimple" in the surface of the extract. If the extract bubbles, the nitrogen stream is **not** gentle enough. Lower the entire N-Evap tray into the warm water bath to aid the evaporation process. Heat is not necessary and if used the temperature should not exceed 35 ° C.

7.6.2.3.2 Some soil extracts contain sediment after concentrating on the water bath. If this is the case, the extraction analyst will transfer the sample extract (including the sediment) from the receiver to a screw-top test tube. The sample extract is centrifuged and the supernatant is transferred back to the appropriate receiver. The residue that is left in the screw top test tube is washed with 1 mL of appropriate solvent (see corresponding test instructions below for final solvent) and centrifuged. The "wash" supernatant is added to the appropriate receiver and the sample is placed on the Nitrogen evaporator to be concentrated. All samples requiring this centrifuging step are documented in the comment section of the K-D logbook.

7.6.2.3.3 The extracts must never be allowed to go dry. While the extracts are concentrating, occasionally rinse down the sides of the receiver or test tube with appropriate solvent (see corresponding test instructions below).

7.6.2.3.4 Refer to appropriate test below for further concentration instructions:

BNA

a. Once the extracts reach ~0.5 mL, remove from the N-Vap. Label a 1.5- 2 mL screw capped vial with appropriate sample #. Transfer the 0.5 mL to the vial using a transfer pipet. Rinse the receiver well with a little (< 1/4 mL) DCM and add to the vial. Compare the sample volume in the vial to a pre-marked, 0.9 mL vial. Rinse receiver with a little more DCM (< 1/4 mL). Transfer to sample vial. Compare volume to the pre-marked 0.9 mL vial. Bring up sample volume (if necessary) to 0.9 mL with another DCM rinsate. The extraction analyst must rinse the receiver at least two times and stay at or below 0.9 mL. The use of a 500 uL syringe gives the analyst more control when adding the small-volume DCM rinses to the receiver. If the rinsates make the extract more than the 0.9 mL, the analyst may hold the vial under the stream of nitrogen momentarily to reduce the volume back down to 0.9 mL. The GC/MS analyst will bring the sample extract to exactly 1.0 mL prior to analysis. Seal vial with a teflon-lined screw-cap.

b. There will be samples that will not concentrate to a 1 mL final volume. In these cases, bring the sample up to the smallest final volume (increments of 1 mL)* that the sample and three rinses will transfer into. All changes in final volume must be documented in the extraction log book. Notify your unit leader.

* Volumetrically add the appropriate volume of DCM to a 16 X 125 screw top test tube and mark the meniscus using a fine-tipped marker. Discard the DCM into an appropriate waste vessel. Bring up sample to volume using this test tube.

c. All samples pertaining to one extraction batch are placed in a plastic vial holder and secured. A listing of the entire contents of the batch, including clients, sample #'s, batch number and date extracted, is to be placed WITH the set. To relinquish samples, the extraction analyst takes the sample extracts and the extraction log book to the sample extract refrigerator (located in the GC/MS Lab).

d. An analyst from the GC/MS BNA group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 +/- 2°C in the dark, until analysis.

PCBs, Pesticide/PCB, and Organophosphorus Pesticides

a. Concentrate the sample to the 10 mL mark. If the solvent goes below the 10 mL mark, bring up to 10 mL with hexane.

***PCBs** refer to mandatory sulfur acid cleanup (Sec. 7.6.2.4.5)

b. All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

c. To relinquish samples, the extraction analyst takes the sample extracts and the extraction log book to the sample cooler area (located in the GC Extractables Lab). An analyst from the GC Extractables group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 +/- 2°C in the dark, until analysis.

PAHs

a. Concentrate the sample to ~ 2 mL to remove any remaining DCM. Dilute the sample up to 5.0 mL with acetonitrile.

b. All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

c. To relinquish samples, the extraction analyst takes the sample extracts and the extraction log book to the sample cooler area (located in the GC Extractables Lab). An analyst from the HPLC group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 +/- 2°C in the dark, until analysis.

7.6.2.4 Screening and Cleanup

7.6.2.4.1 Samples are not pre-screened prior to extraction. Unless previous experience has proven high concentrations and/or background a 30 gram sample will be extracted.

7.6.2.4.2 Sludge samples are a mixture of water and suspended solid materials. If the percent moisture of a given sludge is greater than 90%, a 10 g or 30 g portion may be weighed and added to 1000 mL of reagent water. It is then extracted like a water matrix as described in the water extraction SOPs. Aqueous drum liquids may be prepared in the same manner. Despite the extraction method, sludges are generally reported on a dry weight basis and the total solids result must be entered into the spreadsheet.

7.6.2.4.3 Extract cleanup by Gel Permeation Chromatography (GPC)

7.6.2.4.3.1 Organophosphorus pesticide samples and PAH samples receive no cleanup procedures.

7.6.2.4.3.2 It is not mandatory BNA samples be subjected to further cleanup steps prior to analysis. However, if it is requested that the BNA sample set receives a GPC cleanup, refer to the appropriate section of the SOP for BNA extraction via CLP Procedure for the GPC procedures.

7.6.2.4.3.3 It is not mandatory that Pesticide/PCB samples be subjected to further cleanup steps prior to analysis. However, if it is requested that the Pesticide/PCB sample set receives a GPC cleanup, refer to the appropriate section of Cleanup for Pesticide/PCBs SOP for the GPC procedures.

7.6.2.4.4 It is not mandatory that Pesticide/PCB samples be subjected to further cleanup steps prior to analysis. However, if it is requested that the Pesticide/PCB set receives a Florisil cleanup, refer to the appropriate sections of Cleanup for Pesticide/PCBs SOP for Florisil procedures.

7.6.2.4.5 Mandatory Acid Cleanup for PCBs

If the sample is to be analyzed for **PCBs ONLY**, a mandatory sulfuric acid cleanup is performed. Add ~3-4 mL of concentrated H_2SO_4 to the extract (contained in a screw-top test tube). Shake vigorously for a least 1 minute. Centrifuge the hexane/acid for at least a couple minutes to ensure adequate separation. If the acid layer (the bottom layer) is dark in color, transfer the hexane layer (the top layer) to another screw-top test tube and repeat the acid cleanup. The acid cleanup should be repeated until the acid layer no longer turns dark in color. The hexane extract must always be immediately removed from the acid and transferred into another clean, labeled, screw-top test tube. Document acid cleanup in comment section of the extraction log book. Relinquish the samples as described in the nitrogen evaporation section.

7.7 Documentation

7.7.1 All extraction information must be carefully documented in the appropriate extraction log. Any additional sample or extraction information is recorded in the comment section of the extraction log. All problems and/or deviations from normal procedures must be documented in the extraction log. The unit leader should be notified and a Sample Discrepancy Report (SDR) may need to be initiated.

7.7.2 An extraction batch contains samples of similar matrix that are logged in for the same test code. Sometimes O608 samples are extracted in the same extraction batch as OPCB samples (see Sec. 8.1.5).

7.7.3 Different parameters are given different test codes for use with the LIMS system. The test code for PAHs is OHPAH. The test code for organophosphorus pesticides is O8141. The test code for PCBs is OPCB. The test code for Pesticides/PCB is O608. The test code for BNAs is O625. The O608 and O625 test codes have an analyte identifier, which refers to the letter appearing after the test code. Examples of different analyte identifiers appear below.

H=Hazardous Substance List
N= Appendix IX List
P=Priority Pollutant List
X= Special List

8.0 QUALITY CONTROL

The following QC is performed with each organic extraction batch. An extraction batch may contain no more than 20 samples.

8.1 QC Summary

8.1.1 Method Blank

The method blank is powdered sodium sulfate which has been spiked with the appropriate surrogate (Sec 5.2.1), then taken through the entire extraction procedure and is used to monitor the introduction of artifacts into the process. This demonstrates that the materials used are free of interferences.

8.1.2 Blank Spike/Blank Spike Duplicate

The blank spike/blank spike duplicate (BS/BSD) are powdered sodium sulfate which has been spiked with known concentration of matrix spike compounds (Sec 5.2.2) and appropriate surrogate solution (Sec. 5.2.1). These will be referred to as the MB1S and MB1T.

NOTE: BSDs are performed only until a minimum of 20 points are obtained to generated internal statistical limits.

8.1.3 Matrix Spike/Matrix Spike Duplicate

A known concentration of matrix spike compounds, which are selected analytes, and surrogate are added to aliquots of the sample matrix prior to extraction. These will be referred to as the MS/MSD.

8.1.4 **Surrogate**

A surrogate is an organic compound(s) which is similar to the analytes of interest in chemical composition, extraction and chromatography, but which is not normally found in environmental samples. The surrogate is added to **all** blanks, samples, and QC samples prior to extraction. Percent recoveries are calculated for each surrogate.

8.1.5 Sometimes O608 samples are extracted in the same extraction batch as OPCB samples. When this occurs, the QC includes one method blank (MB1), one spike blank and spike blank duplicate (MB1S/MB1T) for the pesticide compounds, one spike blank / spike blank duplicate (MB2S/MB2T) for PCB compounds, one matrix spike/ matrix spike duplicate for the pesticide compounds, and one matrix spike / matrix spike duplicate for PCB compounds.

8.2 **Corrective Actions**

8.2.1 The extraction analyst must perform the Quality Control described in Section 8.1. The extraction analyst will not know if all QC is in control until the GC/MS, GC/Extractable, or HPLC group analyzes the extracts and determine the results of the method blank, spikes, and surrogate recoveries. It is the responsibility of the analysis group to inform the Organic Extractions Department when a sample or set of samples requires re-extraction by documenting in the "BNA Re-extraction Log" or by initiating a Sample Discrepancy Report (SDR). Re-extractions are to be designated as R1 in the extraction process.

8.2.2 All problems and/or deviations from normal procedures must be documented in the extraction logbook. The unit leader should be notified and a Sample Discrepancy Report (SDR) may need to be initiated.

9.0 DATA ANALYSIS AND CALCULATIONS

Not Applicable.

10.0 WASTE MANAGEMENT AND POLLUTION CONTROL

Refer to the SOP entitled "Disposal of Laboratory Waste".

11.0 METHOD PERFORMANCE CRITERIA

Refer to the analytical SOP(s).

12.0 REFERENCES

Refer to Section 1.0.

13.0 ATTACHMENTS

Appendix A. Example: Extraction Logbook
Appendix B. Example: Extraction Flowcharts

Historical File: Revision 00: 03/17/99

Revision 00:

- Consolidation of extraction SOPs USP-OP-3550.BNA; -3550.OPP; -3550.PAH; -3550.PCB; -3550-PP.

U:\QC\SOP\SP\3550.DOC

Appendix A.

Example: Extraction Logbook

Extraction Date:_____
Test Code:_____
Solvent::_____
Solvent Dispenser Volume Checked (SW 3510/3550):_____

Severn Trent Laboratories Chicago
Organic Extraction Record
GC Extractables/HPLC

Page No.:_____
Batch No.:_____
Analyst Initials:_____
Balance ID No.:_____

Matrix:
a. Water
b. Soil
c. Other_____

Extraction Method:
a. SW-846 3510 (Sep Funnel)
b. SW-846 3550 (Sonication)
c. SW-846 3580 (Waste Dil.)
d. SW-846 3520 (Cont. Liq-Liq.)
e. Other_____

Method Extraction Times:
Start Time:_____
End Time:_____

	RFW #	Sample ID	pH	Initial Vol/Wt. (mLs/g)	Total Solids	Final Vol.[1] (mLs)	Clean-Up Absorbent	Multipliers		
								Surr.	Spike	Split
1	-MB1									
2	-MB1S									
3	-MB1T									
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										

[1]The extract volume is ~2.0 mL for Herbicides and 10 mL for TCLP Pesticides. The final volume documented for these extracts, 10 mLs and 100 mLs respectively, reflects the adjusted measures prepared by the instrumentation analysts. This process allows for the comparison of the extraction logbook to the extraction spreadsheet.

___ Insufficient Sample for MS/MSD ___ MS/MSD Not Requested (Limited Vol.) ___ MS/MSD Designated ___MS/MSD Chosen
___ Sample Container Shaken ___ Sample Container Shaken & Rinsed with Solvent ___ Sample Container Not Shaken Due To:_____

Comments:_____

Surrogate:_____ Volume:_____ Std. ID#:_____
SB/MS Solution:_____ Volume:_____ Std. ID#:_____
SB/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____

Reviewer Signature:_____ Date:_____

Extraction Custody Record

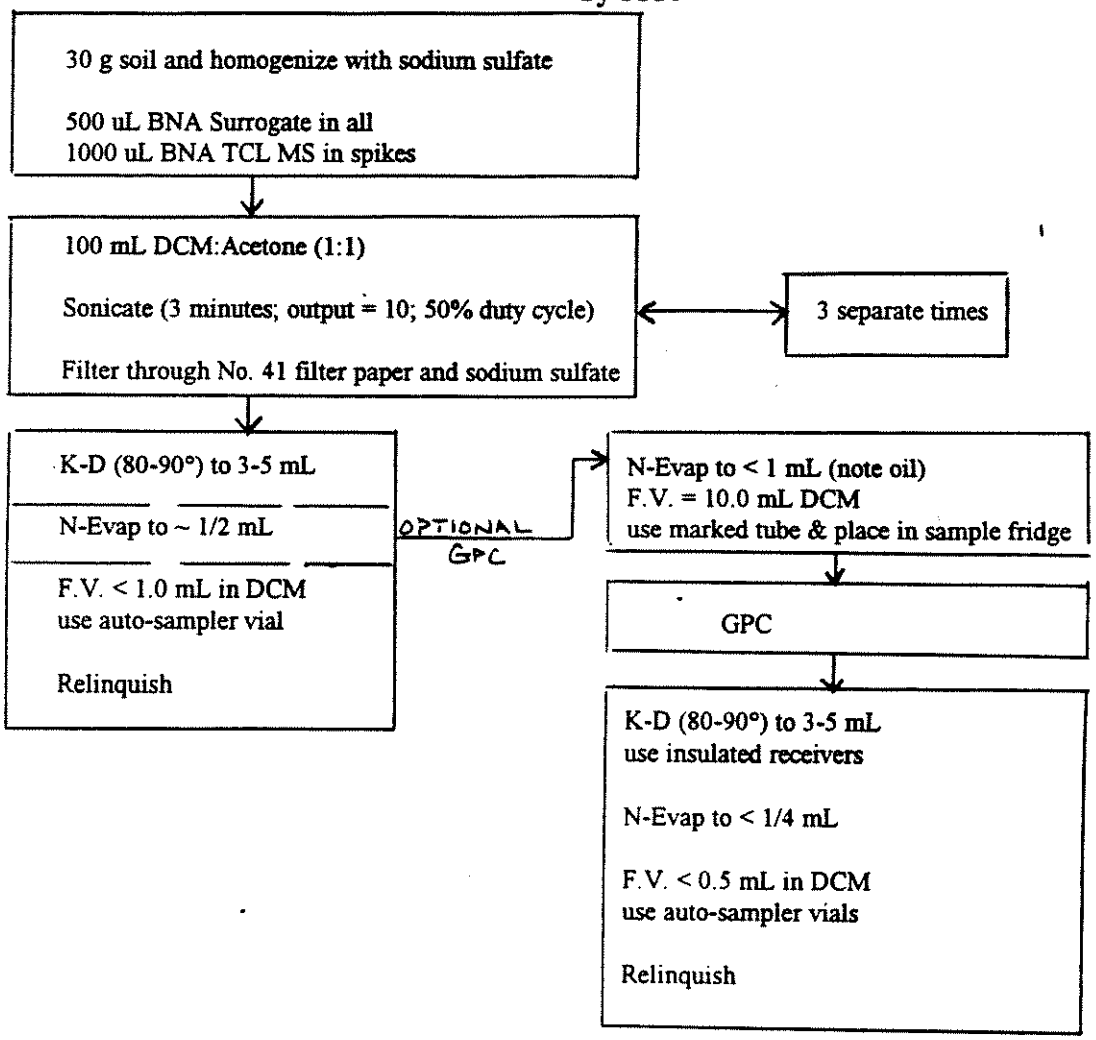
Extracts Transferred	Relinquished by	Date	Time	Received by	Date	Time	Reason for Transfer

Appendix B.

Example: Extraction Flowcharts

Soil Extraction by Method 3550					
Test Code	**Name**	**Analysis Methods**	**Final Volume**	**Final Solvent**	**Cleanups**
O625	Base Neutral Acids	8270B	1 mL	DCM	Optional GPC
O608	Pesticides Pesticide/PCB	8081A 8080, 8081	10 mL	Hexane	Optional GPC and/or optional Florisil
OPCB	Polychlorinated Biphenyls	8080,8081,8082	10 mL	Hexane	Mandatory Acid Optional GPC,Florisil
O8141	Organophosphorus Pesticides	8141	10 mL	Hexane	None
OHPAH	Polynuclear Aromatic Hydrocarbons	8310	5 mL	Acetonitrile	None

FLOWCHART FOR BNA SOIL (8270)
by 3550



FLOWCHART FOR PEST/PCB SOIL (8081/O608/OPCB)
by 3550

30 g soil and homogenize with sodium sulfate

1000 uL DCB/TCMX (0.4/0.4 ppm) in all
1000 uL Pest Full List MS (0.4 ppm) → in spikes
**or 1000 uL AR1660 (5.0 ppm) if OPCB →

↓

100 mL DCM:Acetone (1:1)

Sonicate (3 minutes; output = 10; 50% duty cycle) ↔ 3 separate times

Filter through No. 41 filter paper and sodium sulfate

↓

K-D (80-90°) to 3-5 mL → OPTIONAL GPC

50 mL Hexane exchange

K-D (90-100°) to 3-5 mL

N-Evap if needed

F.V. = 10 mL in Hexane → OPTIONAL FLORISIL

Acid Cleanup if OPCB

Relinquish

Optional GPC branch:

N-Evap to < 1 mL (note oil)
F.V. = 10.0 mL DCM
use marked tube & place in sample fridge

↓

GPC → GPC/AUTOVAP

↓

K-D (80-90°) to 3-5 mL

50 mL Hexane exchange

K-D (90-100°) to 3-5 mL

N-Evap; F.V. = 5.0 mL in Hexane
use marked tube → OPTIONAL FLORISIL

Acid Cleanup if OPCB

Relinquish

Florisil branch:

FLORISIL

↓

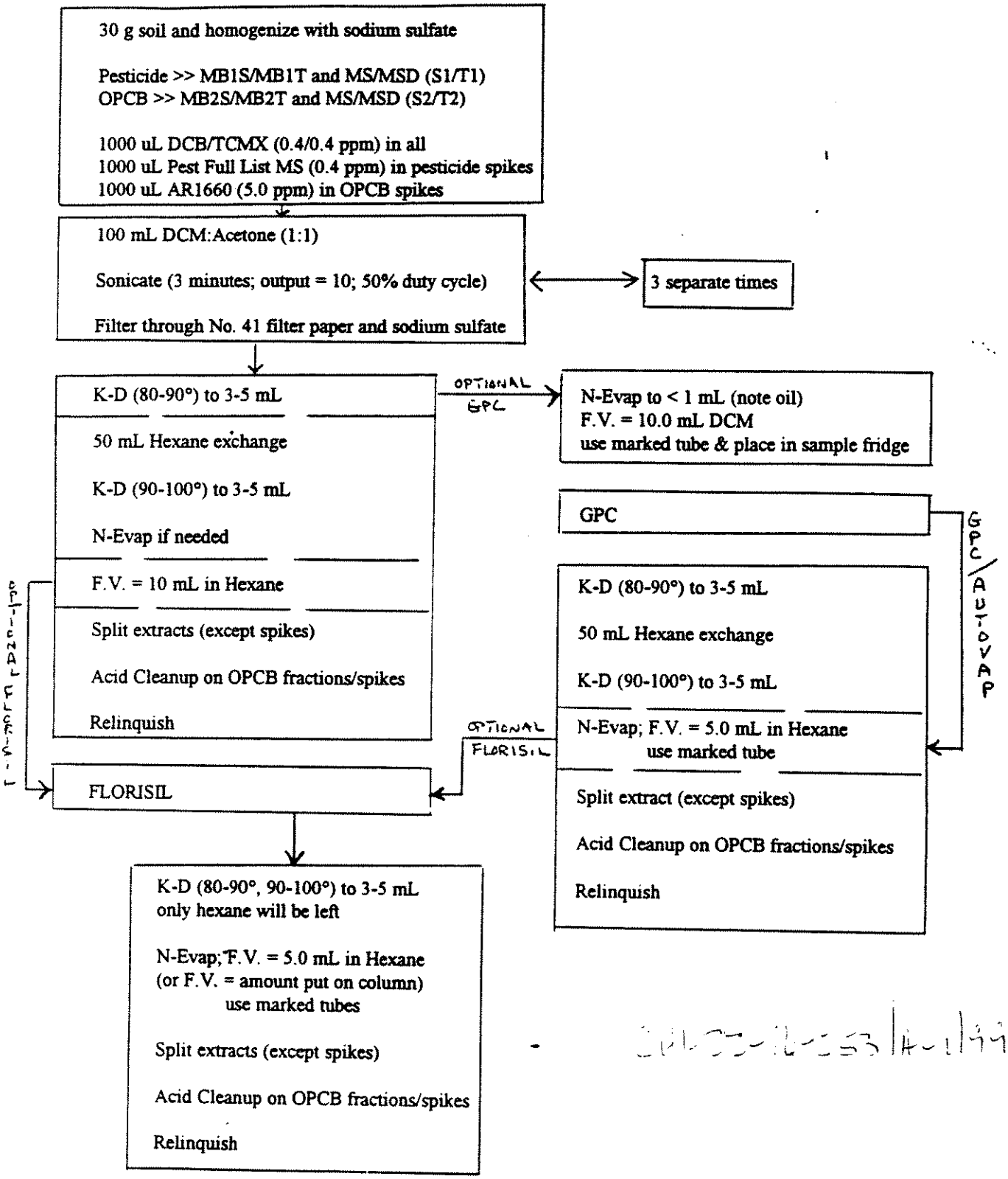
K-D (80-90°, 90-100°) to 3-5 mL
only hexane will be left

N-Evap; F.V. = 5.0 mL in Hexane
(or F.V. = amount put on column)
use marked tubes

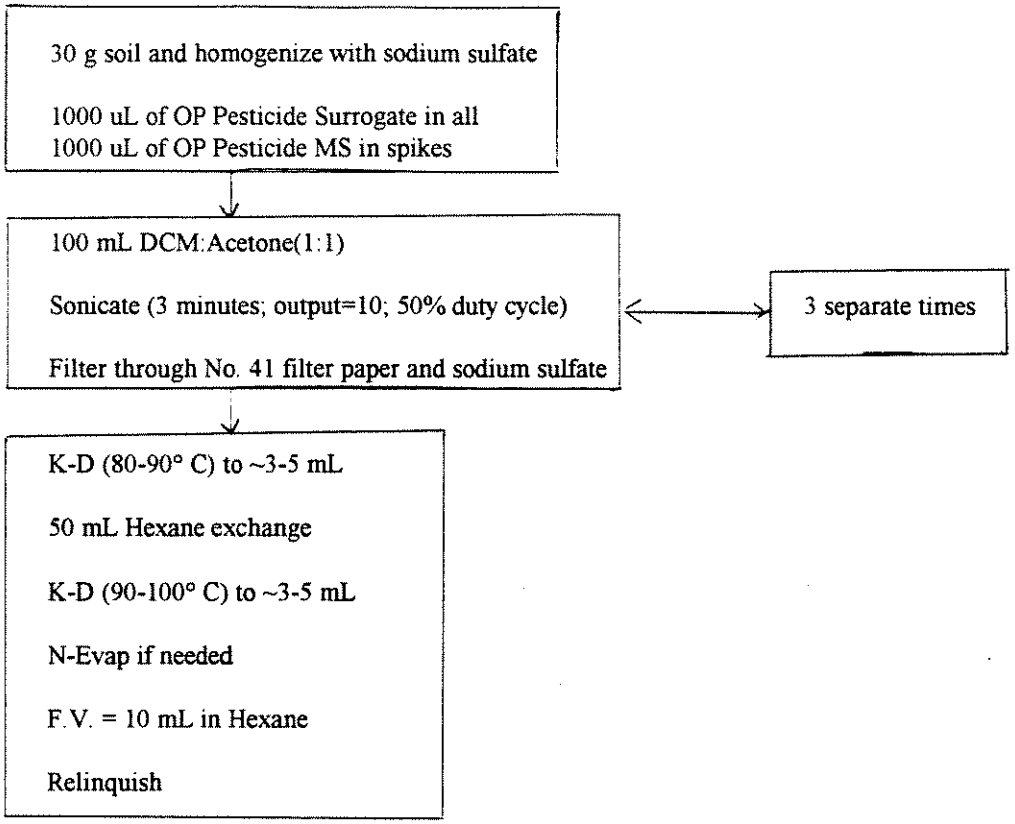
Acid Cleanup if OPCB

Relinquish

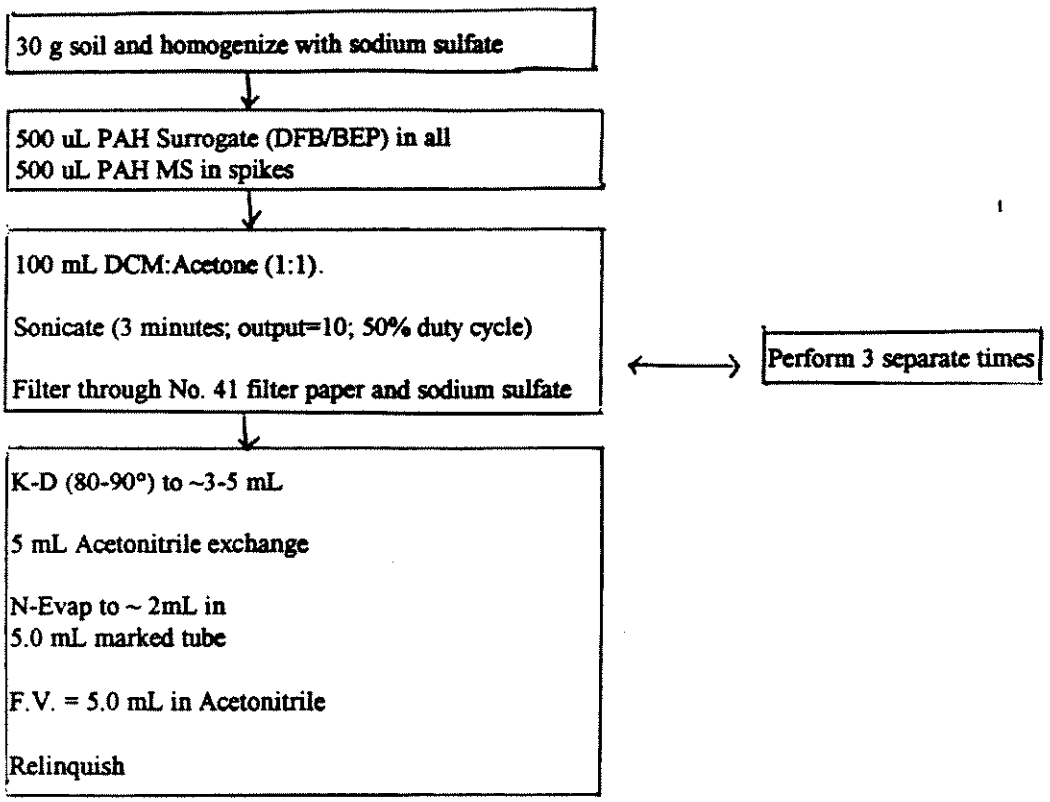
FLOWCHART FOR PEST/PCB SOIL (8081A/8082)
by 3550



FLOWCHART FOR ORGANOPHOSPHORUS PESTICIDE SOIL (8141) by 3550



FLOWCHART FOR PAH SOIL (8310)
by 3550



APPENDIX A-74

STANDARD OPERATING PROCEDURE FOR SAMPLE PREPARATION SEMIVOLATILE AND NONVOLATILE ORGANIC COMPOUNDS FROM A WASTEWATER OR LEACHATE MATRIX USING ACCELERATED CONTINUOUS LIQUID-LIQUID EXTRACTION

SOP No.	Revision No.	Date	Page
USP-SOP-3520	00	03/26/99	1 of 30

TITLE: Sample Preparation Semivolatile and Nonvolatile Organic Compounds from a Wastewater or Leachate Matrix Using Accelerated Continuous Liquid-Liquid Extraction

Updated by:	Signature:	Date
Nancy J. Walsh Analyst, Organic Extractions	Nancy J. Walsh	3/26/99
Daniel A. Knieriemen Unit Leader, Organic Extractions	Daniel A. Knieriemen	03/23/99

Approved by:	Signature:	Date
Linda S. Mackley, Section Manager, Organics Dept.	Linda S Mackley	3-23-99
Raymond J. Frederici Quality Manager	Raymond J. Frederici	3-29-99

CONTROLLED DISTRIBUTION

COPY # : DQR

ISSUED TO : Shawn Nordstrom - RAW
Re: Housatonic River Site Project

Full Signature Approvals Are Kept on File with
Severn Trent Laboratories QA Standard Practice Records

1.0 SCOPE AND APPLICATION

This Standard Operating Procedure (SOP) outlines the extraction procedure of semivolatile and nonvolatile organic compounds[1] from wastewater or leachate matrices using SW-846, Third Edition, Methods 1311, 3500B, and 3520C; and 40CFR, Part 136, Methods 608, 610, and 625 as references.

[1]BNAs, Pesticides, Pesticides/PCBs, PCBs, Organophosphorus Pesticides, PAHs, and Diesel Range Organics (DRO) from waste water and TCLP Leachate samples.

On occasion, clients request slight modification of the standard operating procedures. These modifications are addressed on a case-by-case basis and would be written into a Quality Assurance Plan (QAP).

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be measured for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Not Applicable - refer to the analytical SOPs.

1.2 Summary of Method

The following procedure is used for the continuous liquid-liquid extraction of semivolatile and nonvolatile organics from wastewater and leachate matrices for subsequent analysis.

A measured volume of sample (usually 1 liter for waste waters and 100 mL for leachates) is extracted at an appropriate pH using Accelerated One-Step Continuous Liquid-Liquid Extraction (AOE) with DCM. The extract is concentrated, exchanged to another solvent if necessary, adjusted to the appropriate final volume, and stored at 4°C ± 2° C prior to analysis. Optional cleanup procedures may be performed upon request. The mandatory acid cleanup for PCB samples is described within this SOP. GPC, Florisil, sulfur removal cleanups, and silica gel cleanup are described in other SOPs (see the cleanup section of this SOP for references).

2.0 INTERFERENCES

- Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

- Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic material.

- Soap residue on glassware may cause degradation of certain analytes. This problem is especially pronounced with glassware that may be difficult to rinse. These items should be hand-rinsed very carefully to avoid this problem.

- Matrix interferences may be caused by contaminants that are co-extracted from the sample. These can appear as large, distinct peaks and/or elevated baselines. Occasionally matrix interferences may prevent the proper detection of surrogate and/or analytes, resulting in the reporting of low, or possibly high, surrogate and/or spike recoveries. The extent of matrix interferences will vary considerably from sample to sample, depending upon the nature of the site being sampled. Various cleanup procedures may be performed to remove heavy background or interferences, including GPC cleanup, florisil cleanup, acid cleanup, silica gel cleanup, and sulfur removal procedures.

3.0 SAFETY

- Take careful note of those sections marked "**CAUTION**" and "**NOTE**".

- As always, general laboratory safety practices should always be followed.

- Refer to the specific Material Safety Data Sheets (MSDS) for the hazardous properties of any chemicals or reagents involved in this procedure.

- Safety glasses and lab coats must be worn at all times during the extraction process. Nitrile or equivalent gloves are available and must be worn when handling acids, bases, or samples.

- All extractions and handling of solvents should be performed under well-ventilated conditions of a fume hood.

- DCM is considered a health hazard and possible carcinogen. It is harmful if swallowed or inhaled. The vapor is irritating, and thus should be used in a hood. It is readily absorbed through the skin and contact may be irritating.

- All glassware should be carefully inspected for any kind of crack or star prior to use. An imperfect separatory funnel could explode from the pressure that builds up when solvent is added. Dispose of imperfect glassware in an appropriate container. Some types of glassware are repairable.

- All wastes, solvents, reagents, and samples in need of disposal should be placed in the appropriate waste containers. The analyst should consult their unit leader or safety officer if he/she is unclear on how to properly dispose of materials.

- All samples should be handled with care due to the uncertainty of the properties and contents involved.

4.0 EQUIPMENT AND SUPPLIES

4.1 Glassware

- Corning Accelerated One-Step Extractor/Concentrator
  - Extractor body
  - Condenser
  - Snyder column with ball joint
  - 100 mL jacketed receiver
  - Teflon tube with Teflon-lined seals
  - coupler assembly with Teflon stopcock
  - hydrophobic membrane assembly
- 100 mL, 1000 mL graduated cylinder
- 1.0 mL, 10.0 mL, class A, volumetric pipet
- 2.0 mL disposable pipet
- 500 uL, 1000 uL syringe
- 16 X 125 test tubes with Teflon lined lids
- Glass stirring rods
- Shallow Pyrex drying tray
- Teflon squeeze bottles

4.2 Miscellaneous

- transfer pipets
- wide range pH paper 1 to 12
- Centrifuge
- Boiling Chips and boiling strands, Teflon, soxhlet-extracted using DCM
- Muffle furnace
- Desiccator
- Balance, top-loading, capable of weighing to 0.001g
- hot water circulator
- Nitrogen Evaporator - N-Evap by Organomation Associates, Inc.

5.0 REAGENTS AND STANDARDS

A label on any reagent bottle must contain the concentration of the reagent, name of the reagent, date prepared, expiration date and the analyst who prepared the reagent.

5.1 Reagents

5.1.1 Pesticide Grade Methylene Chloride (DCM)
Pesticide Grade Acetone
Pesticide Grade Hexane
Pesticide Grade Acetonitrile

5.1.2 Reagent Water

Defined as a water in which no interferent is observed at one-half the reporting limit of any target compounds when one liter of the reagent water is extracted and prepared by using the same procedure as for a water sample.

5.1.3 Concentrated Sulfuric Acid

Purchased from a supplier

- Hazardous Properties: Sulfuric Acid (H_2SO_4) is extremely corrosive and toxic to tissues. Vapors are also harmful.
- Life of Reagent: One year
- Storage Requirements: Store in glass container. The label on the bottle must contain concentration and name of reagent.

5.1.4 Sulfuric Acid (1:1)

Cautiously add 500 mL concentrated sulfuric acid to 500 mL reagent water. Because this is an exothermic reaction, prepare in Pyrex glassware and in a cold water bath.

- Hazardous Properties: Extremely corrosive and toxic to tissues. Vapors are also harmful.
- Life of Reagent: One year from preparation date
- Storage Requirements: Store in a glass bottle

5.1.5 10 N Sodium Hydroxide

Cautiously dissolve 200 grams of solid NaOH in reagent water and dilute to 500 mLs. Always prepare in Pyrex glassware due to the amount of heat given off by the reaction.

- Hazardous Properties: Toxic & Corrosive. Harmful if swallowed, inhaled or absorbed through the skin.
- Life of Reagent: One year from preparation date
- Storage Requirements: Store in a glass bottle.

5.2 Quality Control (QC) Solutions

QC solutions must be stored in amber or foil-wrapped, glass containers that have Teflon-lined caps. The label on the container must contain the following information: Name of the solution, the standard number, concentration of the components, date prepared, preparation analyst, and expiration date. All QC solutions are stored in the standards refrigerator in the GC/MS lab, GC Extractables lab, or in the standards refrigerator located in the organic extraction lab. QC solutions are stored at 4° C ± 2 °C.

Listed below are the various QC solutions and concentrations appropriate for extraction of BNAs, Pesticides, Pesticides/PCBs, PCBs, Organophosphorus Pesticides, PAHs, and diesel range organics (DRO) from waste water and TCLP Leachate samples.

5.2.1 Surrogate Spike Solutions

a. BNA Surrogate Spike Solution

The BNA Surrogate Spike Solution is purchased directly from a chemical vendor at the levels listed below. 500 uL of BNA Surrogate Spike Solution is added to all samples and blanks for both waste water and TCLP leachates.

Compound	Concentration
p-Terphenyl-d_4	100 ug/mL
Nitrobenzene-d_5	100 ug/mL
2-Fluorobiphenyl	100 ug/mL
1,2-Dichlorobenzene-d_4	100 ug/mL
Phenol-d_5	150 ug/mL
2-Fluorophenol	150 ug/mL
2,4,6-Tribromophenol	150 ug/mL
2-Chlorophenol-d_4	150 ug/mL

- Life of Reagent: 6 months from the preparation date (as documented from the vendor).
- Storage Requirements: As stated in Section 5.2

b. **Pesticide/PCB Surrogate Spike Solution**

The surrogate used in the extraction of pesticides/PCBs from **waste waters** is a solution of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCMX) in acetone at the concentrations listed below. 1000 uL of Pesticide/PCB Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
DCB	0.4 ug/mL
TCMX	0.4 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

c. **Pesticide/PCB Surrogate Spike Parent Solution**

The parent surrogate is used in the extraction of pesticides from **TCLP leachates** and is a solution of decachlorobiphenyl (DCB) and 2,4,5,6-tetrachloro-m-xylene (TCMX) in acetone at the concentrations listed below. 1000 uL of Pesticide/PCB Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
DCB	4.0 ug/mL
TCMX	4.0 ug/mL

- Life of Reagent: 6 months from date of preparation, not to exceed expiration date of standards
- Storage Requirements: As stated in Section 5.2

d. **Organophosphorus Pesticide Surrogate Spike Solution**

The surrogate solution used in the extraction of organophosphorus pesticides from waste waters is a solution of tributyl phosphate and triphenyl phosphate in acetone. The GC Extractables department prepares all standard solutions. The desired concentration of each compound is 20 ug/mL; however, there may be slight variability between separate solutions. 1000 uL of Organophosphorus Pesticide Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
Tributyl Phosphate	~ 20 ug/mL
Triphenyl Phosphate	~ 20 ug/mL

- Life of Reagent: 6 months from the preparation date or as documented by the vendor, whichever comes first
- Storage Requirements: As stated in Section 5.2

e. **PAH Surrogate Spike Solution**

The surrogate used in the extraction of polynuclear aromatic hydrocarbons from soil/sediments is a solution of decafluorobiphenyl (DFB) and Benzo (e) pyrene in acetone at the concentration listed below. The HPLC group prepares the working surrogate solution. 500 uL of PAH Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
Decafluorobiphenyl	100 ug/mL
Benzo (e) pyrene	5.0 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

f. **Diesel/DRO Surrogate Spike Solution**

The surrogate used in the extraction of diesel range organics (DRO) from waste waters is a solution of 2-fluorobiphenyl and o-terphenyl in acetone at the concentration listed below. The GC Extractables group prepares the working surrogate solution. 500 uL of Diesel/DRO Surrogate Spike Solution is added to all samples and blanks.

Compound	Concentration
2-fluorobiphenyl	200 ug/mL
o-terphenyl	200 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

5.2.2 Spike Blank & Matrix Spike Solutions

a. **BNA TCL Spike Solution**

The BNA TCL Spike Solution is purchased directly from vendor at the levels listed below. 1000 uL of BNA TCL Spike Solution is added to spike blanks and matrix spikes and their duplicates for both waste waters and TCLP leachates.

Compound	Concentration
Acid Compounds	100 ug/mL
Base/Neutral Compounds	100 ug/mL

- Life of reagent: Six months from the from the preparation date (as documented from the vendor).
- Storage: As stated in Section 5.2.

b. **Pesticide (Full List) Spike Solution**

The spike blank/matrix spike solution used in the extraction of pesticides or pesticides/PCB from waste waters is a solution of 20 pesticides in methanol at the following concentrations. 1000 uL of Pesticide (Full List) Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
gamma & alpha Chlordane	0.2 ug/mL
All other compounds	0.4 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

c. **TCLP Pesticide Spike Solution**

The spike blank/matrix spike solution used in the extraction of pesticides from **TCLP leachates** is a solution of 6 pesticides in methanol at the following concentrations. 1000 uL of TCLP Pesticide Spike Solution is added to the spike blank and matrix spike(s), **only those labeled with a "S".**

Compound	Concentration
Lindane	1.0 ug/mL
Heptachlor	1.0 ug/mL
Heptachlor Epoxide	1.0 ug/mL
gamma-Chlordane	1.0 ug/mL
Endrin	1.0 ug/mL
Methoxychlor	10.0 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

d. **Toxphene Spike Solution**

The spike blank/matrix spike solution used in the extraction of pesticides from **TCLP leachates** is a solution of toxaphene in methanol at the following concentration. 1000 uL of Toxaphene Spike Solution is added to the spike blank and matrix spike(s), **only those labeled with a "T".**

Compound	Concentration
Toxaphene	100 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

e. **PCB Spike Solution**

The spike blank/matrix spike solution used in the extraction of PCBs from waste waters is a solution of Arochlor 1016 and Arochlor 1260 in methanol at the following concentrations. 1000 uL of PCB Spike Solution is added to the spike blanks and matrix spikes and their duplicates.

Compound	Concentration
AR1016	5.0 ug/mL
AR1260	5.0 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

f. **Organophosphorus Pesticide Spike Solution**

The spike blank/matrix spike solution used in the extraction of organophosphorus pesticides from waste waters is a solution of 9 organophosphorus pesticides in methanol at the following concentrations. 1000 uL of Organophosphorus Pesticide Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
o,o,o-TEPA	20.0 ug/mL
Thionazin	20.0 ug/mL
Sulfotepp	20.0 ug/mL
Phorate	20.0 ug/mL
Dimethoate	20.0 ug/mL
Disulfoton	20.0 ug/mL
Methyl parathion	20.0 ug/mL
Ethyl parathion	20.0 ug/mL
Famphur	20.0 ug/mL

- Life of Reagent: 6 months from preparation date or as documented by the vendor, whichever comes first
- Storage Requirements: As stated in Section 5.2

g. **PAH Spike Solution**

The spike blank/matrix spike solution used in the extraction of polynuclear aromatic hydrocarbons from waste waters is a solution of 16 analytes in acetonitrile at the following concentrations. The HPLC group prepares the spike solution. 500 uL of PAH Spike Solution is added to spike blanks and matrix spikes and their duplicates.

Compound	Concentration
Acenaphthene	8 ug/mL
Acenaphthylene	16 ug/mL
Anthracene	0.8 ug/mL
Benzo(a)anthracene	0.8 ug/mL
Benzo(a)pyrene	0.8 ug/mL
Benzo(b)fluoranthene	1.6 ug/mL
Benzo(ghi)perylene	1.6 ug/mL
Benzo(k)fluoranthene	0.8 ug/mL
Chrysene	0.8 ug/mL
Dibenzo(a,h)anthracene	1.6 ug/mL
Fluorene	1.6 mg/mL
Indeno(1,2,3-cd)pyrene	0.8 mg/mL

Compound	Concentration
Naphthalene	8.0 mg/mL
Phenanthrene	0.8 mg/mL
Pyrene	0.8 mg/mL

- Life of Reagent: Same as the parent solution
- Storage Requirements: As stated in Section 5.2

h. Diesel/DRO Spike Solution

The spike blank/matrix spike solution used in the extraction of diesel range organics (DRO) from waste waters is a solution of diesel fuel #2 composite in methanol at the following concentration. 500 uL of Diesel/DRO Spike Solution is added to the spike blanks and matrix spikes and their duplicates.

Compound	Concentration
Diesel Fuel #2 Composite	4000 ug/mL

- Life of Reagent: Same as parent solution
- Storage Requirements: As stated in Section 5.2

6.0 CALIBRATION

Not Applicable.

7.0 PROCEDURE

7.1 Quality Control

The following QC is performed with each organic extraction batch. An extraction batch contains samples of similar matrix that are logged in for the same test code. An extraction batch may contain no more than 20 samples.

7.1.1 Method Blank

The method blank is reagent (Milli-Q) water, which has been spiked with the appropriate surrogate (Sec 5.2.1), then taken through the entire extraction procedure and is used to monitor the introduction of artifacts into the process. This demonstrates that the materials used are free of interferences.

7.1.2 Blank Spike/Blank Spike Duplicate

The blank spike is reagent (Milli-Q) water, which has been spiked with a predetermined quantity of spike solution (Sec 5.2.2)with the appropriate analytes of interest and the appropriate surrogate (Sec. 5.2.1).

7.1.3 Matrix Spike/Matrix Spike Duplicate

In matrix spike/matrix spike duplicate analysis, predetermined quantities of spike solutions of specified analytes (Sec 5.2.2) and appropriate surrogate (Sec. 5.2.1) are added to a sample matrix prior to sample extraction and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected by the analysis. The relative percent difference between the samples is calculated and used to assess analytical precision.

7.1.4 Surrogate

A surrogate is an organic compound(s) which is similar to the analytes of interest in chemical composition, extraction and chromatography, but which is not normally found in environmental samples. The surrogate is added to **all** blanks, blank spikes, samples, and matrix spike samples prior to extraction and analysis. Percent recoveries are calculated for each surrogate.

7.2 Sample Collection, Preservation and Handling

Sample container, preservation technique and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract/client requests. In general, water samples are collected in one-liter or 80 oz. narrow-mouth, amber, glass jars, with teflon-lined screw-cap lids. If a teflon-lined lid is not available, solvent-rinsed aluminum foil can be used as a liner.

Samples, sample extracts and standards are stored separately.

NOTE: If the sample matrix is highly acidic or basic, corrosion of the foil may occur and contaminate the sample.

Samples are stored at $4 \pm 2^{\circ}C$ prior to extraction. Any samples received by the preparation group that do not comply must be noted. Deviations in results "could" be explained by the failure of sample collector/client/ custodian to comply to sample collection and storage requirements.

7.2.1 SW-846 and 40 CFR Required Holding Time

Waste Waters
7 days from VTS (verified time of sampling)

TCLP Leachates
TCLP Extraction = 14 days from VTS (performed by Inorganic Prep Group)
Organic Extraction of TCLP Leachate = 7 days from the completion date of TCLP

7.3 Sample Preparation (Glassware Preparation)

7.3.1 All glassware (except Snyder columns, volumetric flasks, volumetric pipets, and syringes) must be washed thoroughly with warm soapy water, rinsed **five** times with hot tap water and rinsed **three** times with DI water. The stopcocks of the separatory funnels should be cleaned with a small brush. **It is absolutely mandatory that all glassware be scrupulously clean.** Failure to rinse well with water, may leave a soap film that is incompletely removed with solvent rinsing, and with subsequent extraction, "soap" peaks will appear in the chromatograms.

7.3.2 If glassware is very wet it may be towel dried. **All** Glassware should be rinsed with cleaning grade acetone, and the excess should be discarded into the appropriate waste container. This step is done to ensure that the glassware is dry. **If after rinsing once, the glassware still contains any water, repeat the acetone rinse.** At this point let the glassware dry before continuing to ensure that all of the water is gone. All glassware should then be rinsed with DCM using a Teflon squeeze bottle, and the excess discarded into the appropriate waste container. Repeat this step at least three times and allow the glassware to dry. Failure to remove all water prior to DCM rinsing prevents the DCM solvent from coming into contact with all surfaces on the glassware. The solvent rinse is then incomplete, and may leave contaminants on the glass, which are then co-extracted with the sample.

NOTE: DCM is considered a health hazard. It is harmful if swallowed or inhaled. The vapor is irritating and thus should be used in a hood. It is readily absorbed through the skin and contact may be irritating.

7.3.2 Procedures for Return of Glassware to Dishroom

Any glassware that has organic residue present, all K-D receivers, and all separatory funnels should be rinsed with cleaning grade acetone, or whatever other solvent which removes the residue, prior to return to the dishroom from the lab. Glassware in which the residue can not be removed should be segregated from other glassware being returned to the dishroom. Glassware should be carefully placed in a tub and placed on the "Dirty" side of the dish racks. In order to reduce glassware breakage, glassware should not be stacked in the tubs. Severely chipped glassware should be removed from service. Some items are repairable. Check with the unit leader as to what items get repaired.

7.4 Calibration/Standardization

Not Applicable.

7.5 Preventive Maintenance

7.5.1 Balance should be cleaned and checked for levelness prior to each use. Class "S" weights should be weighed and documented each day the balance is used. Consult your unit leader if the weights are out of acceptable limits. Do not use the balance until the situation is back in control.

7.5.2 The K-D waterbath should contain DI water only. The water level should be checked prior to each use, and should not fall below the heating coils. If the heating coils do become exposed to the air while in use, they could burn-out and would require replacement. Keep the water level approximately one inch from the top of the bath edge.

7.5.3 The N-Evap waterbath should also contain DI water. The water level in the bath should be sufficient to cover 3/4 of the receivers when submerged.

7.5.4 The thermometer used in the extraction waterbaths are checked against a reference NIST thermometer on a yearly basis or sooner if necessary.

7.5.5 The desiccant used in the desiccator should be removed and dried in an oven at 130°C whenever the color indicates that it is saturated with moisture. This is usually indicated by a change of color from blue to purple/pink.

7.5.6 To avoid the breakage of sample extracts, the analyst needs to take care that the containers are properly balanced on the centrifuge. The container should fit snugly in the holder. Use a paper towel to cushion the centrifuge bottles if necessary.

7.6 Extraction Process

The extraction of semivolatile and nonvolatile organic compounds from waste waters and the extraction of BNAs and Pesticide/PCBs from TCLP leachates following SW-846 or 40 CFR procedures may be extracted using the separatory funnel procedure (method 3510) or the Accelerated One-Step Continuous Liquid-Liquid Extraction (3520 modified).

The following procedure describes the Accelerated One-Step Continuous Liquid-Liquid Extraction (method 3520 modified).

7.6.1 Analytical (Preparation) Sequence

The following preparation sequence will be required of each extraction batch of at most, 20 samples:

Quality Control	Frequency
Method Blank (MB)	1 per extraction batch of at most 20 samples
Blank Spike (MBIS)/BS Dup (MBIT)	1 set per extraction batch of at most 20 samples
Matrix Spike (MS)/MS Dup (MSD)	At least 1 set in 20 samples (may be requested by the client)
Surrogate	Every sample/blank/MBIS/MBIT/ MS/MSD

7.6.2 Accelerated One-Step Continuous Liquid-Liquid Extraction Assembly

7.6.2.1 Severn Trent Laboratories (STL) Chicago uses the Accelerated One-Step Extractor/Concentrator by Corning.

7.6.2.2 Both continuous liquid-liquid extraction and concentration can be performed with this apparatus. After extraction is completed, the valve is closed and concentration is started with no apparatus change required between extraction and concentration.

Turn on the hot water circulators. Adjust to appropriate operating temperature (see Chart B).

7.6.2.3 Visually inspect all glassware for imperfections (especially the smooth surface of the flange at the bottom of the extractor body and flange of the extractor cup).

7.6.2.4 Secure the extractor body to your bench framework with a chain clamp fastened snugly around the body.

7.6.2.5 Place one of the 1.5" I.D. Viton O-rings under the flange of the extractor cup. (The second one is a spare).

7.6.2.6 Place the extractor cup into the bottom half of the coupler assembly.

7.6.2.7 Place one of the FOTOCERAM support disks in the support shelf in the top of the extractor cup.

7.6.2.8 Place a membrane-assembly on top of the membrane support disk in the top of the extractor cup. Please be sure that the recessed side of the membrane assembly is facing up. The hydrophobic membrane works best if heated briefly (10-15 minutes) in an oven (130 ° C) and stored in a desiccator prior to use.

7.6.2.9 Place the second FOTOCERAM support disk on top of the membrane assembly, inside the recessed portion of the membrane assembly.

7.6.2.10 Screw the top half of the coupler assembly onto the bottom half one or two turns. Slide the slot in the upper half of the coupler assembly onto the flange of the extractor body.

7.6.2.11 Rotate the extractor cup so that the bottom outlet tube is facing the direction of the Snyder column side arm for proper alignment.

7.6.2.12 While holding the bottom half of the coupler assembly and the extractor cup against the underside of the extractor body flange, rotate the upper half of the coupler assembly until the coupler is finger tight. (Continue to turn it 1/4 to 1/3 of a turn beyond the point where it does not turn freely).

7.6.2.13 Slip the split ferrule over the bead of the extractor cup outlet tube, insert the stopcock assembly into the outlet tube and tighten the split ferrule into the nut on the stopcock assembly finger tight.

7.6.2.14 At this point, turn on the hot water circulators. Check the water level and fill with DI water if necessary.

7.6.2.15 Install the 1.0" I.D. Viton O-ring onto the 35/25 ball joint of the Snyder column side-arm and loosely fasten the side arm to the 35/25 socket joint on the extractor body with the stainless-steel ball joint clamp.

7.6.2.16 Install the Teflon lined silicone washers and the plastic connecting caps onto the Teflon tubing (the Teflon should face outward). Verify that the Teflon lining is in good condition. With the body assembly and side-arm properly aligned, fasten one of the connecting caps to the threaded end of the Teflon stopcock assembly. Loosely fasten the other connecting cap to the tabulation at the bottom of the side arm.

7.6.2.17 Adjust the alignment of the side arm so that it hangs vertically and parallel to the extractor body. When it is properly aligned, tighten the connector cap and then the stainless-steel ball-joint clamp.

NOTE: Do not try to position the side arm after you have tightened the stainless-steel ball-joint clamp or glass breakage may result.

(Assembly instructions from Corning glassware.)

7.6.2.18 Add two Teflon boiling strands & a few Teflon boiling chips to the concentrator tube. Connect the 100 mL K-D concentrator tube to the bottom 24/40 joint of the Snyder column side-arm with the 24/40 taper-joint clamp. (It is best if this is done after the hot water recirculator has reached operating temperature. If the concentrator is connected while cold, the 24/40 taper joint may expand enough during heat-up of the water to cause the concentrator tube to fall away slightly from the bottom of the Snyder column side arm and loose excess solvent.)

7.6.2.19 Turn on the cold water condensers.

7.6.2.20 Pour 100 mL of DCM into the extractor body and then close the stopcock (only a very small amount of DCM drips into the receiver at this point). Adding the DCM first then closing the stopcock seems to relieve pressure which helps avoid leakage.

7.6.3 Extraction Process

7.6.3.1 Blank and Blank Spikes Water Preparation

Add 1.0 liter of Milli-Q water to three liquid-liquid extractors and label as MB1, MB1S, and MB1T.

*** BNA TCLP** Add 1.0 L of Milli-Q water to only two liquid-liquid extractors and label as MB1 and MB1S.

7.6.3.2 Sample Preparation

Prior to pouring water samples, sample containers should be inverted a few times to mix the sample. However, if there is a sediment layer present, consult your unit leader or section manager before mixing. Also, if the sample appears to have more than one phase, immediately contact your unit leader, section manager, or project manager. The client will need to be notified.

a. **Waste Waters**

If the container is of a 1-liter or 1-quart size pour the entire sample (unless instructed otherwise) into the graduated cylinder and measure the amount (instead of measuring out 1.0 liter). Rinse the sample container with some DCM and transfer it to the graduated cylinder. Pour the sample and rinse into labeled extractor.

If the container is of a 80 oz. size, measure 1.0 liter of each sample into a graduated cylinder and transfer to a labeled extractor. Measure out two additional aliquots (three total) of the sample chosen/designated to have a MS/MSD performed on it. Use 1.0 liter aliquots for MS/MSD if sample volume allows. Label as the sample, MS and MSD.

b. **TCLP Leachates**

Measure 900 mL of Milli-Q water into each sample extractor body. Measure 100 mL of each sample and add it to the labeled extractor body containing the water.

***BNA TCLP** Measure an additional 100 mL aliquot of those samples designated to have a matrix spike. Label the matrix spike with an "S".

***Pesticide TCLP** Measure two additional 100 mL aliquots of those samples designated to have a matrix spike. Label one matrix spike with an "S" and the other with a "T".

7.6.3.3 Check the pH by dipping a transfer pipet into the sample and touching it to wide-range pH paper. Record the pH in the extraction log.

7.6.3.4 Add the appropriate amount of the appropriate surrogate spike solution (Sec. 5.2.1) to every sample including the blank and blank spikes.

7.6.3.5 Add the appropriate amount of the appropriate spike solution (Sec. 5.2.2) to the matrix spike sample(s), the matrix spike duplicate sample(s), and the blank spike/blank spike duplicate.

***BNA TCLP** Blank spike duplicates and matrix spike duplicates are not performed.

***Pesticide TCLP** There are no blank spike duplicates or matrix spike duplicates. One matrix spike ("S") contains TCLP Pesticide Spike and one matrix spike ("T") contains Toxaphene Spike.

NOTE: All spiking solutions MUST be at room temperature before use. This includes stock solutions when preparing working spike solutions. Actual concentrations will change at colder temperatures. Furthermore, some components may come out of solution in the freezer. Warming to room temperature reverses the process.

7.6.3.6 Adjust the pH as required (refer to Chart in Appendix B for appropriate pH for each parameter). Use sulfuric acid (1:1) to acidify and NaOH (10N) to make basic. Record pH adjustments in the log book.

7.6.3.7 Verify that the hot water circulators are at the correct operating temperature (refer to Chart B for operating temperature for each parameter).

7.6.3.8 Open the stopcock to allow the DCM to run into the jacketed receiver. Record the start time in the extraction log book. Extract for the pre-determined time (refer to Chart B for extraction time for each parameter).

*BNAs The extraction is first performed for 5 1/2 hours at pH < 2. The pH of the sample is then adjusted to pH > 11 and extracted for another 5 1/2 hours.

7.6.4 Sample Concentration

Sample concentration is performed directly on the Accelerated One-Step Extraction (AOE) apparatus.

7.6.4.1 After the appropriate extraction time turn the stopcock to the closed position (record end time in the Extraction Log Book). This begins the concentration step.

7.6.4.2 **If the sample does not require a solvent exchange** (refer to Chart B for solvent exchange requirements), evaporate the DCM to ~ 5 mL and proceed to 7.6.4.3.

If the sample does require a solvent exchange (refer to Chart B for solvent exchange requirements), remove the Teflon tubing between the stopcock assembly and the Snyder column and screw in place a screw-top cap on the Snyder column opening. Evaporate the DCM to ~ 5mL.

Remove the previously placed screw-top cap and add the appropriate amount of exchange solvent (refer to Chart B for amount of exchange solvent) through the opening in the Snyder column. Replace the screw-top cap. Increase the temperature to 95 °C and evaporate to ~ 5 mL. Small quantities of exchange solvent may be added through that same opening to keep the evaporating extracts level. Even though the jacketed receivers have an unheated tip, the analyst should monitor the evaporation step closely.

7.6.4.3 Turn off the hot water circulators.

7.6.4.4 Let the extracts cool. Using a disposable pipet, transfer the extract from the receiver into a 16x125 test tube that has been previously marked at the appropriate volume**.

**All Pesticides/PCBs (including TCLP), Organophosphorus Pesticides require 10.0 mL marked test tube.
**PAHs and DROs require a 5.0 mL marked test tube.
**BNAs does not need to be marked.

7.6.4.5 Rinse the receiver well three times with small amounts of the appropriate solvent. Transfer the rinsates to the test tube. Cap and refrigerate if the extracts are not going to be concentrated immediately. The analyst who evaporated and transferred the extracts should initial and date in the comment section of the log book.

Proceed to 7.6.5 for further concentration by nitrogen evaporation.

7.6.5 Nitrogen Evaporation

7.6.5.1 For further concentration, place each receiver or test tube on the N-Evap tray. The N-Evap outlet needles should be stored in a 600 mL beaker containing DCM:Acetone (1:1) mixture prior to each use. Wipe each outlet needle with a KimWipe and lock into place on the N-Evap. Lower the outlet tube into the receiver being careful not to touch the sides of the receiver. The outlet tube should remain above the surface of the extract. Open the valve of the nitrogen tank and adjust the pressure in order to achieve the appropriate nitrogen stream. The nitrogen stream should make a slight "dimple" in the surface of the extract. If the extract bubbles, the nitrogen stream is **not** gentle enough. Lower the entire N-Evap tray into the warm water bath to aid the evaporation process. Heat is not necessary and if used the temperature should not exceed 35 ° C.

7.6.5.2 The extracts must never be allowed to go dry. While the extracts are concentrating, occasionally rinse down the sides of the receiver or test tube with appropriate solvent (see corresponding test instructions below).

7.6.5.3 Refer to appropriate test below for further concentration instructions.

a. BNA

a1. Once the extracts reach ~0.5 mL, remove from the N-Evap. Label a 1.5- 2 mL screw capped vial with appropriate sample #. Transfer the 0.5 mL to the vial using a transfer pipet. Rinse the receiver well with a little (< 1/4 mL) DCM and add to the vial. Compare the sample volume in the vial to a pre-marked, 0.9 mL vial. Rinse receiver with a little more DCM (< 1/4 mL). Transfer to sample vial. Compare volume to the pre-marked 0.9 mL vial. Bring up sample volume (if necessary) to 0.9 mL with another DCM rinsate. The extraction analyst must rinse the receiver at least two times and stay at or below 0.9 mL. The use of a 500 uL syringe gives the analyst more control when adding the small-volume DCM rinses to the receiver. If the rinsates make the extract more than the 0.9 mL, the analyst may hold the vial under the stream of nitorgen momentarily to reduce the volume back down to 0.9 mL. The GC/MS analyst will bring the sample extract to exactly 1.0 mL prior to analysis. Seal vial with a teflon-lined screw-cap.

There will be samples that will not concentrate to a 1 mL final volume. In these cases, bring the sample up to the smallest final volume (increments of 1 mL)* that the sample and three rinses will transfer into. All changes in final volume must be documented in the extraction log book. Notify your unit leader.

* Volumetrically add the appropriate volume of DCM to a 16 X 125 screw top test tube and mark the meniscus using a fine-tipped marker. Discard the DCM into an appropriate waste vessel. Bring up sample to volume using this test tube.

a2. All samples pertaining to one extraction batch are placed in a plastic vial holder and secured. A listing of the entire contents of the batch, including clients, sample #'s, batch number and date extracted, is to be placed WITH the set. To relinquish samples, the extraction analyst takes the sample extracts and the extraction log book to the sample extract refrigerator (located in the GC/MS Lab).

a3. An analyst from the GC/MS BNA group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 +/- 2°C in the dark, until analysis.

b. <u>PCBs, Pesticide/PCB, and Organophosphorus Pesticides</u>

b1. Concentrate the sample to 2-3 mL and bring up to the 10.0 mL mark with hexane.

***PCBs** refer to mandatory sulfur acid cleanup (Sec. 7.6.6.7)

***TCLP** The final volume is 100 mL, however, the GC/Extractables Group does the 1/10 dilution prior to analyzing.

b2. All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

b3. To relinquish samples, the extraction analyst takes the sample extracts and the extraction log book to the sample cooler area (located in the GC Extractables Lab). An analyst from the GC Extractables group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 +/- 2°C in the dark, until analysis.

c. <u>PAHs</u>

c1. Concentrate the sample to ~ 2 mL to remove any remaining DCM. Dilute the sample up to 5.0 mL with acetonitrile.

c2. All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

c3. To relinquish samples, the extraction analyst takes the sample extracts and the extraction log book to the sample cooler area (located in the GC Extractables Lab). An analyst from the HPLC group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 +/- 2°C in the dark, until analysis.

d. **Diesel/DRO**

d1. Concentrate the sample to the 5.0 mL mark. If the solvent goes below the 5.0 mL mark, bring up to 5.0 mL with DCM.

d2. All samples pertaining to one extraction batch are placed in a test tube rack. Each test tube should have the extraction batch number, sample #, and test code written on it.

d3. To relinquish samples, the extraction analyst takes the sample extracts and the extraction log book to the sample cooler area (located in the GC Extractables Lab). An analyst from the GC Extractables group must be present to receive the samples. Both analysts check for completeness and correctness of the information and sign in the appropriate spaces of the extraction log book. All extracts are to be kept at 4 +/- 2°C in the dark, until analysis.

7.6.6 **Screening and Cleanup**

7.6.6.1 Samples are not pre-screened prior to extraction. Unless previous experience has proven high concentrations and/or background a one-liter sample will be extracted. Some samples interfere with the hydrophobic membrane of the one-step liquid-liquid extraction that a lesser volume (usually 100 mL) diluted into 900 mL of Milli-Q water is used. Many times aqueous drum samples are handled in this manner. If the diluted sample still interferes with the hydrophobic membrane, separatory funnel extraction may have to be used.

7.6.6.2 Sludge samples are a mixture of water and suspended solid materials. If the percent moisture of a given sludge is greater than 90%, a 10 g or 30 g portion may be weighed and added to 1000 mL of reagent water. It is then extracted like a water matrix as described in this procedure. Despite the extraction method, sludges are generally reported on a dry weight basis and the total solids result must be entered into the spreadsheet.

7.6.6.3 Organophosphorus pesticide samples and PAH samples receive no cleanup procedures.

7.6.6.4 **Extract cleanup by Gel Permeation Chromatography (GPC)**

7.6.6.4.1 It is not mandatory BNA samples be subjected to further cleanup steps prior to analysis. However, if it is requested that the BNA sample set receives a GPC cleanup, refer to the appropriate section of the SOP for BNA extraction via CLP Procedure for the GPC procedures.

7.6.6.4.2 It is not mandatory that Pesticide/PCB samples be subjected to further cleanup steps prior to analysis. However, if it is requested that the Pesticide/PCB sample set receives a GPC cleanup, refer to the appropriate section of Cleanup for Pesticide/PCBs SOP for the GPC procedures.

7.6.6.5 It is not mandatory that Pesticide/PCB samples be subjected to further cleanup steps prior to analysis. However, if it is requested that the Pesticide/PCB set receives a Florisil cleanup, refer to the appropriate sections of Cleanup for Pesticide/PCBs SOP for Florisil procedures.

7.6.6.6 It is not mandatory that DRO sample be subjected to further cleanup procedures prior to analysis. However, if it is requested that the DRO set receives a Silica Gel cleanup, refer to the appropriate cleanup section in the Extraction of DRO from soil/sediments SOP.

7.6.6.7 Mandatory Acid Cleanup for PCBs

If the sample is to be analyzed for **PCBs ONLY**, a mandatory sulfuric acid cleanup is performed. Add ~3-4 mL of concentrated H_2SO_4 to the extract (contained in a screw-top test tube). Shake vigorously for a least 1 minute. Centrifuge the hexane/acid for at least a couple minutes to ensure adequate separation. If the acid layer (the bottom layer) is dark in color, transfer the hexane layer (the top layer) to another screw-top test tube and repeat the acid cleanup. The acid cleanup should be repeated until the acid layer no longer turns dark in color. The hexane extract must always be immediately removed from the acid and transferred into another clean, labeled, screw-top test tube. Document acid cleanup in comment section of the extraction log book. Relinquish the samples as described in the nitrogen evaporation section (Sec. 7.6.5.6b).

7.7 Documentation

7.7.1 All extraction information must be carefully documented in the appropriate extraction log. Any additional sample or extraction information is recorded in the comment section of the extraction log. All problems and/or deviations from normal procedures must be documented in the extraction log. The unit leader should be notified and a Sample Discrepancy Report (SDR) may need to be initiated.

7.7.2 An extraction batch contains samples of similar matrix that are logged in for the same test code. Sometimes O608 samples are extracted in the same extraction batch as OPCB samples (see Sec. 8.1.5).

7.7.3 Different parameters are given different test codes for use with the LIMS system. The test code for PAHs is OHPAH. The test code for Diesel/Diesel Range Organics is ODRO. The test code for organophosphorus pesticides is O8141. The test code for PCBs is OPCB. The test code for Pesticides/PCB is O608. The test code for BNAs is O625. The O608 and O625 test codes have an analyte identifier, which refers to the letter appearing after the test code. Examples of different analyte identifiers appear below.

A=608 List or 625 List
P=Priority Pollutant List
H=Hazardous Substance List
N= Appendix IX List
X= Special List
T= TCLP List

8.0 QUALITY CONTROL

The following QC is performed with each organic extraction batch. An extraction batch may contain no more than 20 samples.

8.1 QC Summary

8.1.1 Method Blank

The method blank is reagent water which has been spiked with the appropriate surrogate (Sec 5.2.1), then taken through the entire extraction procedure and is used to monitor the introduction of artifacts into the process. This demonstrates that the materials used are free of interferences.

8.1.2 Blank Spike/Blank Spike Duplicate

The blank spike/blank spike duplicate (BS/BSD) are reagent water which has been spiked with known concentration of matrix spike compounds (Sec 5.2.2) and appropriate surrogate solution (Sec. 5.2.1). These will be referred to as the MB1S and MB1T.

NOTE: BSDs are performed only until a minimum of 20 points are obtained to generated internal statistical limits.

8.1.3 Matrix Spike/Matrix Spike Duplicate

A known concentration of matrix spike compounds, which are selected analytes, and surrogate solution, are added to aliquots of the sample matrix prior to extraction. These will be referred to as the MS/MSD.

8.1.4 Surrogate

A surrogate is an organic compound(s) which is similar to the analytes of interest in chemical composition, extraction and chromatography, but which is not normally found in environmental samples. The surrogate is added to **all** blanks, samples, and QC samples prior to extraction. Percent recoveries are calculated for each surrogate.

8.1.5 Sometimes O608 samples are extracted in the same extraction batch as OPCB samples. When this occurs, the QC includes one method blank (MB1), one spike blank and spike blank duplicate (MB1S/MB1T) for the pesticide compounds, one spike blank / spike blank duplicate (MB2S/MB2T) for PCB compounds, one matrix spike/ matrix spike duplicate for the pesticide compounds, and one matrix spike / matrix spike duplicate for PCB compounds.

8.1.6 Spike blank duplicate and matrix spike duplicates are not performed for BNA TCLP.

8.1.7 Blank spike and matrix spike duplicates are not performed for Pesticide TCLP samples. However, an MB1S and MB1T along with a matrix spike ("S") and matrix spike ("T") are extracted and recorded. The TCLP Pesticide Spike and Toxaphene Spike need to remain separate from one another. The TCLP Pesticide Spike is added to "S" samples and the Toxaphene Spike is added to "T" samples.

8.2 Corrective Action

8.2.1 The extraction analyst must perform the Quality Control described in Section 7.1. The extraction analyst will not know if all QC is in control until the GC/MS, GC/Extractables, or HPLC group analyzes the extracts and determine the results of the method blank, spikes, and surrogate recoveries. It is the responsibility of the analysis group to inform the Organic Extractions Department by documenting in the "BNA Re-Extraction Log" or by initiating a Sample Discrepancy Report when a sample or set of samples requires re-extraction. Re-extractions are to be designated as R1 in the extraction process.

8.2.2 All problems and/or deviations from normal procedures must be documented in the extraction logbook. The unit leader should be notified and a Sample Discrepancy Report (SDR) may need to be initiated.

9.0 Data Analysis and Calculations

Not Applicable.

10.0 Waste Management and Pollution Control

Refer to the SOP entitled "Disposal of Laboratory Waste".

11.0 Method Performance Criteria

Refer to the analytical SOP(s).

12.0 References

Refer to Section 1.0

13.0 ATTACHMENTS

Figure 1: Example: Liquid-Liquid Extraction Apparatus
Appendix A. Example: Extraction Logbook.
Appendix B. Example: Extraction Flowcharts

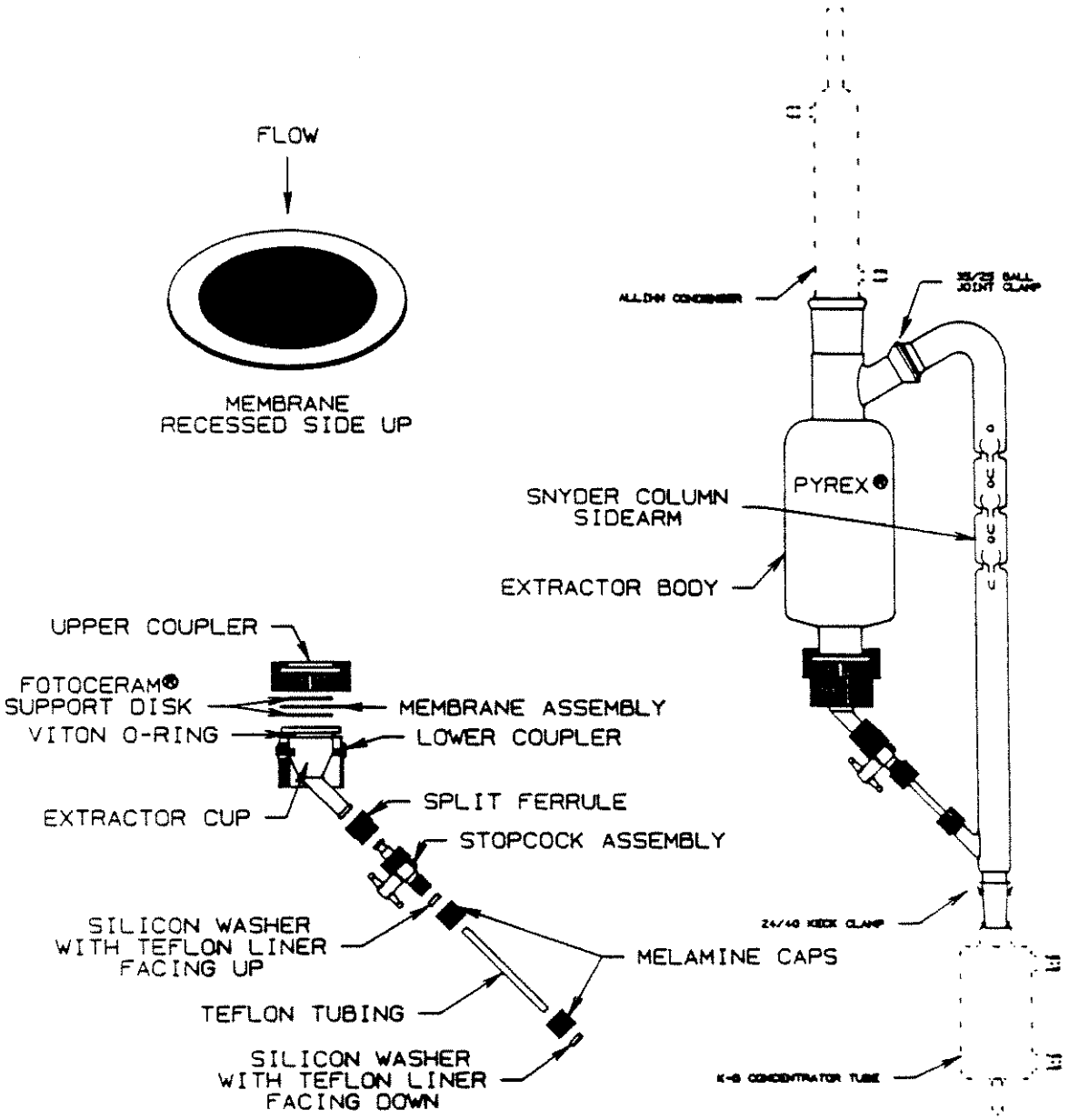
Historical File: Revision 00: 03/23/99

Revision 00:
• Combined SOPs: USP-SOP-3520.BNA, USP-SOP-3520.OPP, USP-SOP-3520.PAH, USP-SOP-3520.PP, USP-SOP-3520BT, USP-SOP-3520PHC, USP-SOP-3520PT

U:QC\SOP\SP\3520.DOC

Figure 1:

Example: Liquid-Liquid Extraction Apparatus


FLOW
MEMBRANE
RECESSED SIDE UP
ALLIHN CONDENSER
35/25 BALL JOINT CLAMP
PYREX®
SNYDER COLUMN SIDEARM
EXTRACTOR BODY
UPPER COUPLER
FOTOCERAM® SUPPORT DISK
MEMBRANE ASSEMBLY
VITON O-RING
LOWER COUPLER
EXTRACTOR CUP
SPLIT FERRULE
STOPCOCK ASSEMBLY
SILICON WASHER WITH TEFLON LINER FACING UP
MELAMINE CAPS
TEFLON TUBING
SILICON WASHER WITH TEFLON LINER FACING DOWN
24/40 KEECK CLAMP
K-D CONCENTRATOR TUBE

Appendix A.

Example: Extraction Logbook.

Extraction Date:_____
Test Code:_____
Solvent::_____
Solvent Dispenser Volume Checked:_____

Severn Trent Laboratories Chicago
Organic Extraction Record
GC/MS Semi-Volatiles

Page No.:_____
Batch No.:_____
Analyst Initials:_____
Balance ID No.:_____

Matrix:
a. Water
b. Soil
c. Other_____

Extraction Method:
a. SW-846 3510 (Sep Funnel)
b. SW-846 3550 (Sonication)
c. SW-846 3580 (Waste Dil.)
d. SW-846 3520 (Cont. Liq-Liq.)
e. Other_____

Method Extraction Times:
Start Time:_____
End Time:_____

	RFW #	Sample ID	pH[1]	Initial Vol/Wt. (mLs/g)	Total Solids	Final Vol.[2] (mLs)	Clean-Up Absorbent	Multipliers		
								Surr.	Spike	Split
1	-MB1									
2	-MB1S									
3	-MB1T									
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										

[1]Sample pH / Acid Adjusted pH / Base Adjusted pH

[2]The extract volume for BNAs is either ~0.5 mL or ~1.0 mL when the final volume is documented as 0.5 mL or 1.0 mL, respectively. The documented final volume reflects the adjusted measures prepared by the instrumentation analysts. This process allow for the comparison of the extraction logbook to the extraction spreadsheet. Any final volume greater than 1.0 mL is measured exactly by the extraction group.

___ Insufficient Sample for MS/MSD ___ MS/MSD Not Requested (Limited Vol.) ___ MS/MSD Designated ___ MS/MSD Chosen
___ Sample Container Shaken ___ Sample Container Shaken & Rinsed with Solvent ___ Sample Container Not Shaken Due To:_____

Comments:_____

Surrogate:_____ Volume:_____ Std. ID#:_____
SB/MS Solution:_____ Volume:_____ Std. ID#:_____
SB/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____

Reviewer Signature:_____ Date:_____

Extraction Custody Record

Extracts Transferred	Relinquished by	Date	Time	Received by	Date	Time	Reason for Transfer

Extraction Date:_____
Test Code:_____
Solvent::_____
Solvent Dispenser Volume Checked (SW 3510/3550):_____

Severn Trent Laboratories Chicago
Organic Extraction Record
GC Extractables/HPLC

Page No.:_____
Batch No.:_____
Analyst Initials:_____
Balance ID No.:_____

Matrix:
a. Water
b. Soil
c. Other_____

Extraction Method:
a. SW-846 3510 (Sep Funnel)
b. SW-846 3550 (Sonication)
c. SW-846 3580 (Waste Dil.)
d. SW-846 3520 (Cont. Liq-Liq.)
e. Other_____

Method Extraction Times:
Start Time:_____
End Time:_____

	RFW #	Sample ID	pH	Initial Vol/Wt. (mLs/g)	Total Solids	Final Vol.[1] (mLs)	Clean-Up Absorbent	Multipliers		
								Surr.	Spike	Split
1	-MB1									
2	-MB1S									
3	-MB1T									
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										

[1]The extract volume is ~2.0 mL for Herbicides and 10 mL for TCLP Pesticides. The final volume documented for these extracts, 10 mLs and 100 mLs respectively, reflects the adjusted measures prepared by the instrumentation analysts. This process allows for the comparison of the extraction logbook to the extraction spreadsheet.

___ Insufficient Sample for MS/MSD ___ MS/MSD Not Requested (Limited Vol.) ___ MS/MSD Designated ___MS/MSD Chosen
___ Sample Container Shaken ___ Sample Container Shaken & Rinsed with Solvent ___ Sample Container Not Shaken Due To:_____

Comments:_____

Surrogate:_____ Volume:_____ Std. ID#:_____
SB/MS Solution:_____ Volume:_____ Std. ID#:_____
SB/MS Solution:_____ Volume:_____ Std. ID#:_____

Analyst Signature:_____ Date:_____

Reviewer Signature:_____ Date:_____

Extraction Custody Record

Extracts Transferred	Relinquished by	Date	Time	Received by	Date	Time	Reason for Transfer

Appendix B.

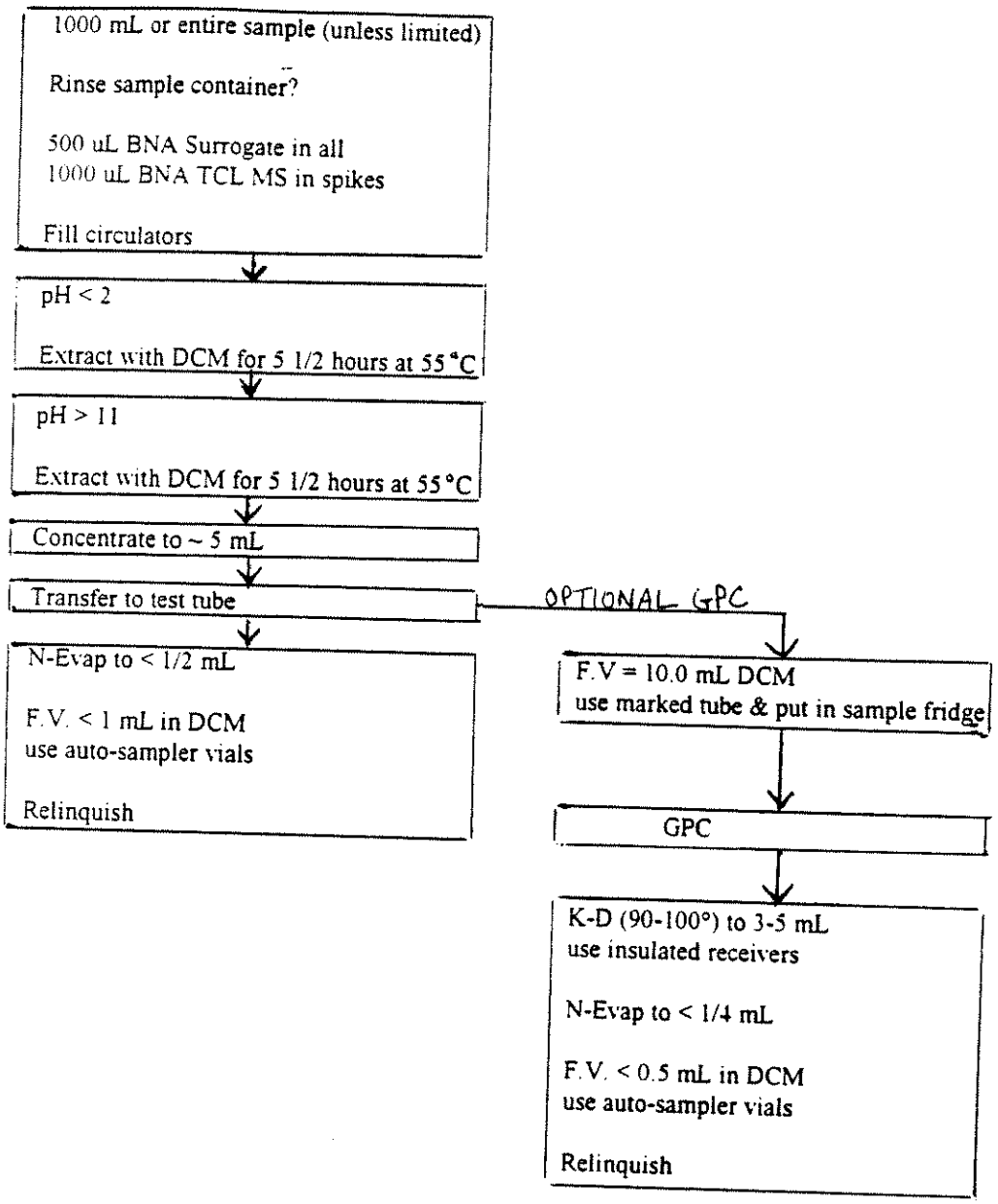
Example: Extraction Flowcharts

Water Extraction by Method 3520 and 40 CFR					
Test Code	**Name**	**Analysis Methods**	**Final Volume**	**Final Solvent**	**Cleanups**
O625A	Base Neutral Acids	625	1 mL	DCM	None Required
O625 (H,N,P,X)	Base Neutral Acids	8270B	1 mL	DCM	Optional GPC
O625T	TCLP Base Neutral Acid	8270B	1 mL	DCM	None Required
O608A	Pesticides/PCB	608	10 mL	Hexane	None Required
O608 (H,N,P,X)	Pesticides Pesticide/PCB	8081A 8080, 8081	10 mL	Hexane	Optional GPC and/or optional Florisil
O608T	TCLP Pesticides	8081	100 mL	Hexane	None
OPCB	Polychlorinated Biphenyls	8080,8081,8082	10 mL	Hexane	Mandatory Acid Optional GPC,Florisil
O8141	Organophosphorus Pesticides	8141	10 mL	Hexane	None
OHPAH	Polynuclear Aromatic Hydrocarbons	8310, 610	5 mL	Acetonitrile	None
ODRO	Diesel Range Organics	8015 CA Method	5 mL	DCM	Optional Silica Gel

ACCELERATED ONE-STEP EXTRACTION
SW846 AND 40 CFR

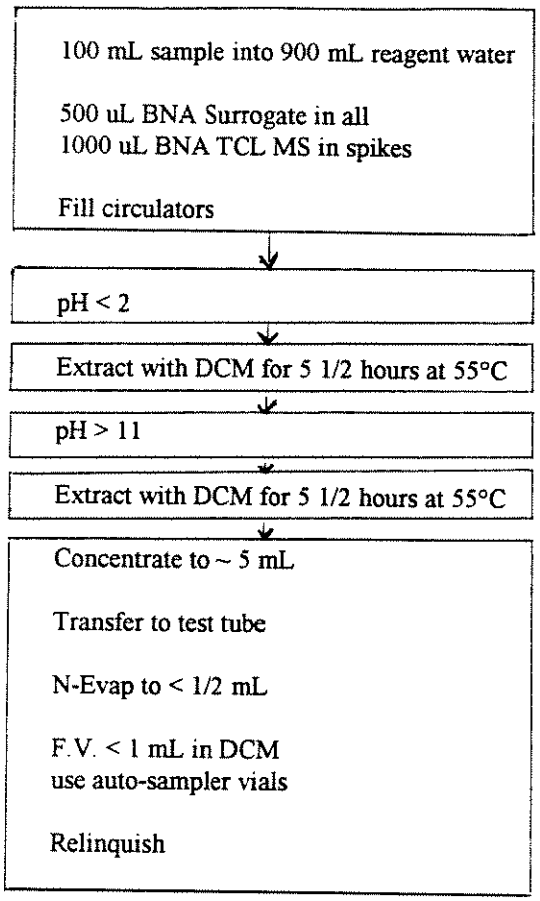
Parameter	Initial pH	Secondary pH	Operating Temperature (°C)	Process Time (Hours / pH)	Exchange Solvent	Exchange Temperature (°C)
O625 (A,H,N,P,T,X)	< 2	> 11	55	5 1/2	N/A	N/A
O608 (A,H,N,P,T,X)	5-9	N/A	70	6 1/2	Hexane (50 mL)	95
OPCB	5-9	N/A	70	6 1/2	Hexane (50 mL)	95
O8141	As Received	N/A	65	6	Hexane (50 mL)	95
OHPAH	As Received	N/A	65	6	Acetonitrile (5 mL)	95
ODRO	5-9	N/A	55	6	N/A	N/A

FLOWCHART FOR BNA WATER (8270/625)
by 3520

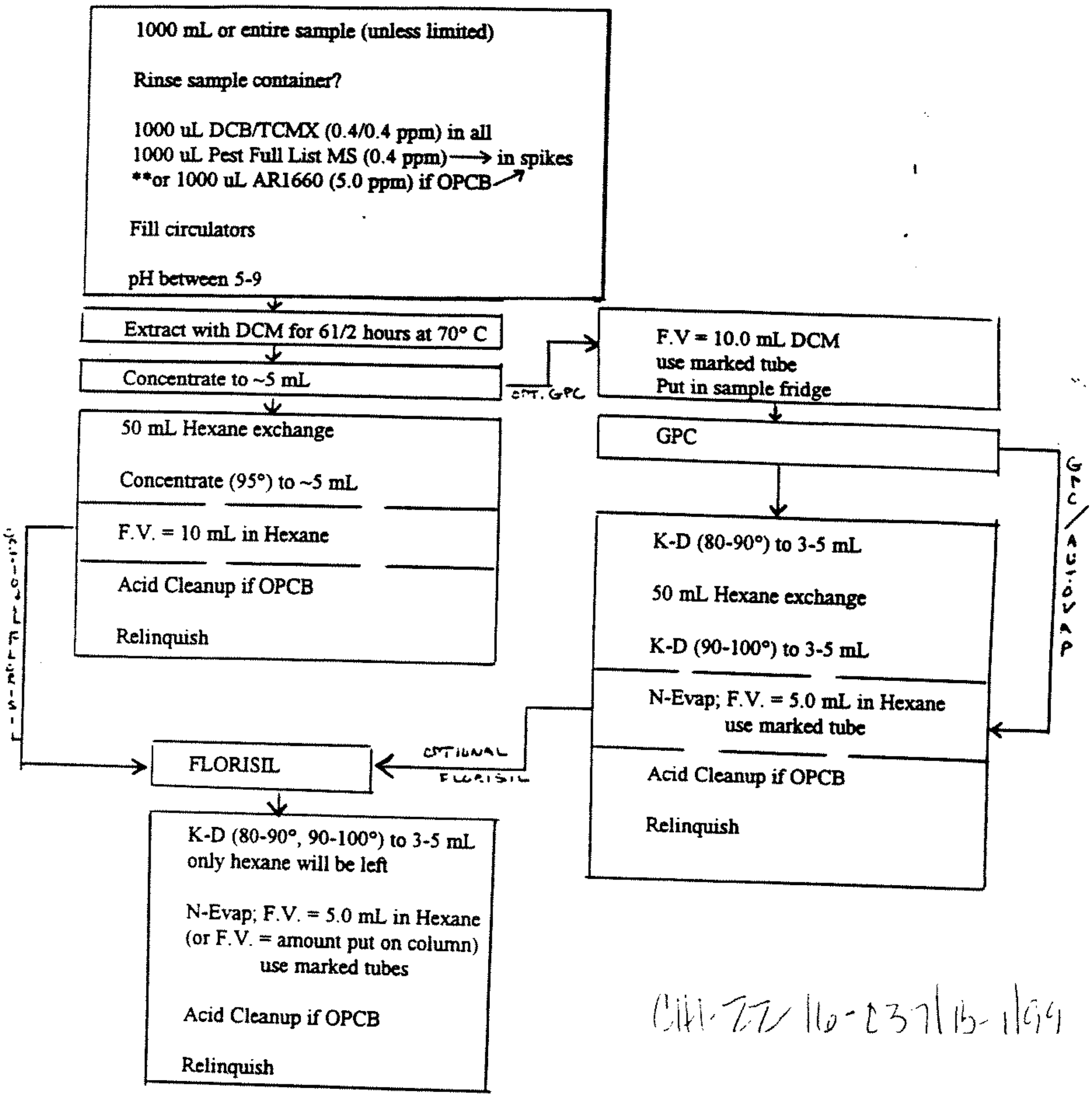


LHL-22-16-041/C-9/99

FLOWCHART FOR BNA TCLP WATER (8270)
by 3520

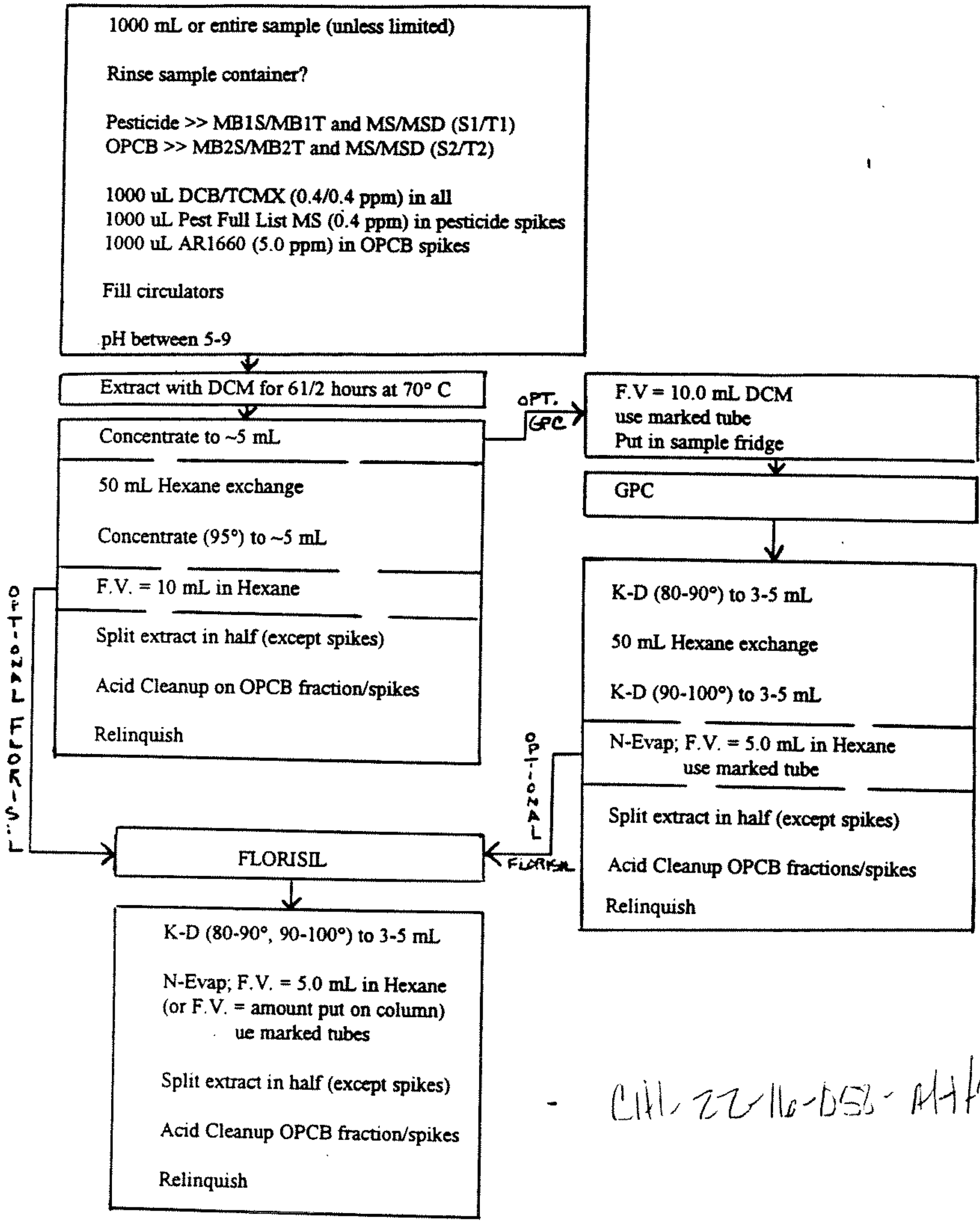


FLOWCHART FOR PEST/PCB WATER (8080/8081/608/OPCB)
by 3520



CHI-ZZ/16-237/15-1/94

FLOWCHART FOR PEST/PCB WATER (8081A/8082) by 3520



FLOWCHART FOR PEST/PCB TCLP
by 3520

100 mL sample into 900 mL reagent water

1000 uL DCB/TCMX (4.0/4.0 ppm)
1000 uL Pest TCLP MS in "S"
1000 uL Toxaphene MS in "T"

Fill circulators

pH between 5-9

↓

Extract with DCM for 61/2 hours at 70° C

↓

Concentrate to ~5 mL

50 mL Hexane exchange

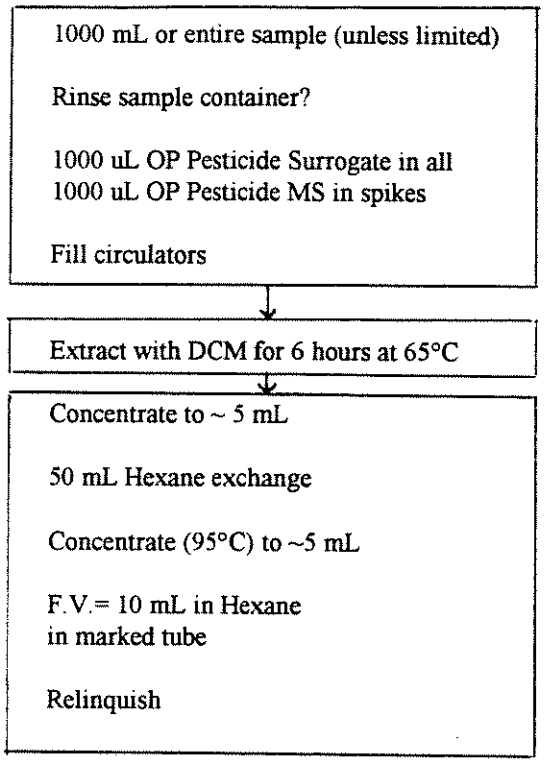
Concentrate (95°) to ~5 mL

F.V. = 10 mL in Hexane
in marked tube

Relinquish

LLL-22-16-C39 | B-1 | 09

FLOWCHART FOR ORGANOPHOSPHORUS PESTICIDES WATER (8141) by 3520



FLOWCHART FOR PAH WATER (8310/610)
by 3520

1000 mL or entire sample (unless limited)

Rinse sample container?

500 uL PAH Surrogate (DFB/BEP) in all
500 uL PAH Full List MS in spikes

Fill circulators

pH as received

↓

Extract with DCM for 6 hours at 65° C

↓

Concentrate to ~5 mL

5 mL Acetonitrile exchange

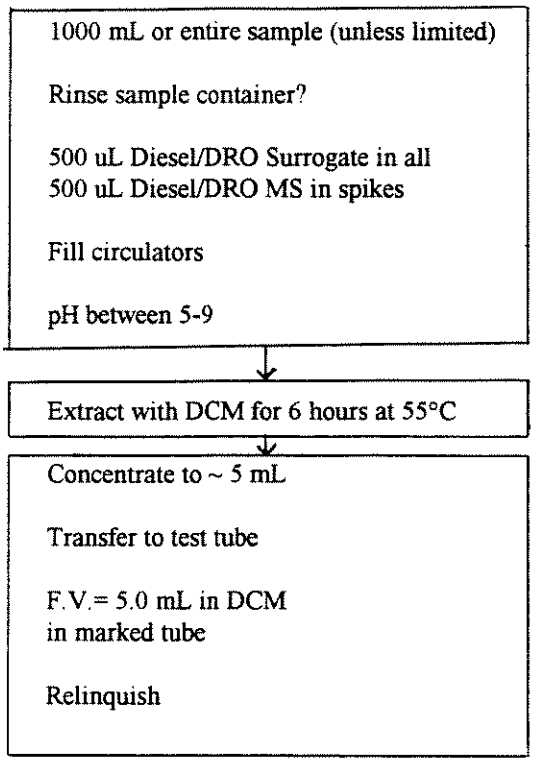
Concentrate (95°) to ~5 mL

F.V. = 5.0 mL in Acetonitrile
use marked tube

Relinquish

CHL 33-16-1521(H-1)99

FLOWCHART FOR DIESEL/DRO WATER (8015,CA)
by 3520



APPENDIX A-75

STANDARD OPERATING PROCEDURE FOR GAS CHROMATOGRAPHY - SEMIVOLATILES ANALYSIS OF PCBS BY SW-846 METHOD 8082

SOP No.	Revision No.	Date	Page
UGE-SOP-8082	01	03/01/99	1 of 26

TITLE: Gas Chromatography - Semi-Volatiles Analysis of PCBs by SW-846 Method 8082

Updated by:	Signature:	Date
Patti J. Anderson Unit Leader, Pesticides/PCBs	Patti Anderson	3/1/99

Approved by:	Signature:	Date
Linda S. Mackley Section Manager, Organics Dept.	Linda S Mackley	3-1-99
Raymond J. Frederici Quality Manager	Ray J Fred	3-1-99

CONTROLLED DISTRIBUTION

COPY # : 008

ISSUED TO : Shannon Nordstrom - RAW
Re: Housatonic River Site Project

Full Signature Approvals Are Kept on File with
Severn Trent Laboratory QA Standard Practice Records

Severn Trent Laboratories Chicago
STANDARD OPERATING PRACTICE (SOP) CHANGE FORM

Original SOP Number/Revision #: UGE-SOP-CA DRO, CA GRO, 8081A, 8082, 8151A, 8150
Last Mod ID (circle): NA / _____

SOP Title: Analysis of GC Extractable
Affected SOP Section Number(s): 6.0 Calibration
Effective Date: 2 July 1999

CONTROLLED DISTRIBUTION

COPY # :
ISSUED TO :

Full Signature Approvals Are Kept on File with Severn Trent Laboratory Standard Practice Records

Revision Number with Mod ID: (various)

The following SOP change is in effect as of the stated date. This form will remain attached to the referenced SOP until such a time that the SOP is updated, approved, and redistributed, at which time it will become part of the historical SOP record. **Append this form to the front of the SOP copy.**

1. Reason for SOP Change: Further clarification of initial five-point calibration and points associated with linear and non-linear regression curves.

2. Summary of Procedure Change (circle to indicate if there are attachments to this form: No / Yes: # pages attached = 1)

Initiated/Reviewed By: Name/Date 7/1/99

Initiated/Reviewed By: Name/Date

Approval Signature/Date: Section Manager

Approval Signature/Date: QA Manager or Designee 7-6-99

GC and GC/MS Calibration – Evaluation and Acceptance Criteria

- Run several calibration standards at various concentrations. The concentrations must cover the range of quantitation for all analytes. The lowest point of the calibration curve must be at, or below, the reporting limit
- All analytes must contain at a minimum 5 calibration points for Linear regressions, linear curves, or average response factors
- Analytes using second order fits must have a minimum of 6 calibration points on a curve
- Analytes using 3rd order curves must have a minimum of 7 calibration points
- Calibration levels deemed to be statistical or visual outliers shall be dropped from the curve and replaced by a similar concentration standard. The standard shall be dropped in its entirety, not on a per analyte basis
- Using "priori" knowledge some compounds ranges may be shortened (i.e. not as low a reporting limit or not as high a range.)
- The laboratory will initially evaluate all compounds using the "grand mean RSD" criteria as an indicator of minimum calibration acceptance. If no %RSD for any given compound is above 20%RSD for GC or 15% RSD for GC/MS tests, the calibration is deemed to have met minimum calibration criteria and the analyst will then evaluate each compound to determine the best calibration fit. Using the grand mean RSD approach should be deemed **minimum** calibration acceptance criteria. It should be used as a last resort in determining whether a compound's calibration will be used. Even when the grand mean RSD indicates minimum acceptance has been met, the analyst must use his discretion when quantifying analytes that met only the minimum standard. Quantitation for said compounds may be biased and should be used with caution.
- Curves analyzed at different dates (i.e. appix compounds analyzed at different dates that the HSL calibrations) should not be taken into account when calculating the "grand mean RSD". If the grand mean RSD is below 20% RSD for GC and 15%RSD for GC/MS, the calibration is deemed to have met minimum calibration criteria and the analyst will then evaluate each compound to determine the best calibration fit.
- Having determined that the calibration meets minimum requirements, the laboratory will evaluate each compound to determine the best calibration fit using statistical and visual evaluation of the curve.
- Citing priori knowledge the laboratory may decide to "keep" calibrations for several compounds despite exceeding the statistical threshold allowed by the method. The compounds that fall in this category are known poor performers as indicated by the method or as indicated from historical performance data (e.g. Appendix IX compounds). These compounds will be listed in the SOP as possibly trouble analytes. Quantitation for said compounds may be biased and should be used with caution.

1.0 SCOPE / APPLICATION

This method is used to determine the concentrations of polychlorinated biphenyls (PCBs) as Aroclors in assorted matrices by SW-846 Methods 8000B & 8082.

On occasion, clients request modifications of this standard operating procedure (SOP). These modifications are addressed on a case-by-case basis and would be written into a Quality Assurance Plan (QAP) and addressed in the case narrative.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be measured for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. Because of the high level of quantitative error associated with determinations at the level of the MDL, the laboratories endeavor to keep reporting limits higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the IDL or MDL are special circumstances not to be confused with the previous statement.

Table 1 provides a list of compounds analyzed by this method and their reporting limits.

1.2 Summary of Method

This method provides the gas chromatographic (GC) conditions and necessary standardization procedures for the detection of parts per billion (ppb) levels of Aroclors. Prior to this method, the appropriate extraction must be performed depending upon the sample matrix.

2.0 INTERFERENCES

2.1 Phthalates

Interference's by phthalate esters can pose a problem in PCB analysis. These compounds generally appear in the chromatogram as large late-eluting peaks. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interference's from phthalates can best be minimized by avoiding contact with any plastic materials.

2.2 Co-extractions

Co-extracted interferences will vary considerably from sample to sample. Clean-ups are available to help eliminate or lessen interferences. All extracts analyzed for PCBs routinely receive a sulfuric acid cleanup. Additionally, florisil clean-ups, sulfur clean-ups, and GPC clean-ups may be performed (Refer to SOP on cleanup procedures).

3.0 SAFETY

Care should always be taken when working with samples of unknown composition. For specific hazards associated with the solvents used or any of the standard materials, see the specific MSDS.

4.0 EQUIPMENT AND SUPPLIES

4.1 Gas Chromatographs

Gas Chromatographs are equipped with dual electron capture detectors (Ni_{63}). Each GC has an autosampler associated with it and a Perkin Elmer DCI 2000 data collection system in conjunction with a Perkin Elmer LIMS.

4.2 Column - Megabor

- RTX-5, 0.53 mm from Restek, 30 m length, temperature limits of -20°C to 260°C < 310°C, and 0.5 - 1.0 micron film thickness (or equivalent).
- RTX-35 cross bonded, 65% dimethyl-35%diphenyl-polysiloxane, 30 m length, 0.53 I.D., film thickness of 0.5 micron, maximum temperature of 290°C (or equivalent).
- Guard Column - Phenyl-methyl deactivated 5 meter, 0.53 mm I.D. (or equivalent).

*Similar columns can be used if all QC criteria can be met.

5.0 REAGENTS AND STANDARDS

A label on any reagent bottle must contain the concentration of the reagent, name of the reagent, date prepared, expiration date and the analyst who prepared the reagent. Standard labels will additionally contain the standard log number for that particular standard.

All standards and spikes must be stored at 4± 2°C in glass bottles with Teflon-lined lids. The standard log number must also be indicated on the bottle label.

5.1 Solvents

Hexane, Acetone, Isooctane, Toluene.....Pesticide quality or better.

5.2 Intermediate Standards

All standards will be obtained with A2LA, or EPA certification. If unavailable they will be verified against an alternate source. Aroclor standards are purchased as solutions at a level of ~5000 ug/mL. Appropriate dilutions are prepared such that the intermediate standards are at a level of 5.0 ug/mL in Hexane for all Aroclors (1016, 1221, 1232, 1242, 1248, 1254 and 1260). Aroclor 1016 and 1260 are added together into the same intermediate solution and is referred to as AR1660.

The surrogate compounds (TCX and DCB) are purchased as a solution at a level of ~200 ug/mL. The surrogate compounds are added to the intermediate standard, prior to volumetrically adjusting the final volume, such that the concentrations of the surrogates in the intermediate standard are at 2.0 ug/mL in Hexane. Intermediate standard solutions must be replaced 6 months from the date of preparation.

5.3 Calibration Standards

A standard containing a mixture of Aroclor 1016 and Aroclor 1260 (AR1660) will include many of the peaks represented in the other five Aroclor mixtures. As a result, a multi-point initial calibration employing a mixture of Aroclors 1016 and 1260 at five concentrations should be sufficient to demonstrate the linearity of the detector response without the necessity of performing initial calibrations for each of the seven Aroclors. In addition, such a mixture can be used as a standard to demonstrate that a sample does not contain peaks that represent any one of the Aroclors. Working calibration standards are prepared in Hexane from the intermediate solutions. At least 5 levels of AR1660 are required, however, generally 6 levels are prepared. Concentrations range from 0.025 ng/uL to 1.00 ng/uL. The five concentration levels are prepared through dilutions of the intermediate standards with hexane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.4 Surrogates

The analyst must monitor the performance of the extraction, clean-up (when used), analytical system and the effectiveness of the method for each sample matrix by spiking each sample, matrix spike, blank spike and method blank with the surrogates. The surrogates used are Decachlorobiphenyl (DCB) and 2,4,5,6-Tetrachloro-m-xylene (TCX).

6.0 CALIBRATION

Before any instrument is used as a measurement device, the instrument response to known reference materials must be determined. The manner in which various instruments are calibrated depends on the particular type of instrument and its intended use. All sample measurements must be made within the calibration range of the instrument. Preparation of all reference materials used for calibration must be documented.

Calibration pertains to both primary and secondary columns. Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.4.1. Prepare calibration standards using the procedures indicated in Section 5.3.

Calibration Controls	Sequence	Control Limit
Initial Calibration Standards	5 pt. curve of AR1660 prior to samples	$\leq$ 20% RSD (alternatively if the correlation coefficient is >0.99, linear regression may be used).
Continuing Cal. Verif	after initial calibration, every 10 samples*	$\pm$ 15% Pred. Resp.
Retention Time Windows		3 X RSD

* The CCV is required at least once per 20 samples; however, it is strongly recommended that it be analyzed after every 10 samples, to reduce the number of reanalyses if the CCV is out of control.

6.1 External Standard Calibration

6.1.1 Prepare calibration standards as described in section 5.3. Because of the sensitivity of the electron capture detector, the injection port and column should always be cleaned prior to performing the initial calibration. When PCBs are to be quantitatively determined as Aroclors, the initial calibration consists of two parts.

6.1.1.1 As noted in section 5.3, a standard containing a mixture of Aroclor 1016 and Aroclor 1260 will include many of the peaks represented in the other five Aroclor mixtures. Thus, such a standard may be used to demonstrate the linearity of the detector and that a sample does not contain peaks that represent any one of the Aroclors. This standard can also be used to determine the concentrations of either Aroclor 1016 or Aroclor 1260, should they be present in a sample.

Therefore, an initial five-point calibration is performed using the mixture of Aroclors 1016 and 1260 described in section 5.3.

6.1.1.2 Standards of the other five Aroclors are necessary for the pattern recognition. These standards are also used to determine a single-point calibration factor for each Aroclor, assuming that the AR1660 mixture has been used to describe the detector response. The standards for these five Aroclors should be analyzed before the analysis of any samples, and may be analyzed before or after the analysis of the five AR1660 standards.

6.1.1.3 In situations where only a few Aroclors are of interest for a specific project, the analyst may employ a five-point initial calibration of each of the Aroclors of interest and not use the AR1660 mixture, or the pattern recognition standards described above. However, this would be an exception and would be written into a Quality Assurance Plan.

6.1.2 Record the peak area (or height) for each characteristic Aroclor peak to be used for quantitation. A minimum of 3 peaks must be chosen for each Aroclor, and preferably 5 peaks. The peaks must be characteristic of the Aroclor in question. Choose peaks in the Aroclor standards that are at least 25% of the height of the largest Aroclor peak. For each Aroclor, the set of 3 to 5 peaks should include at least one peak that is unique to that Aroclor. Use at least five peaks for the AR1660 mixture, none of which should be found in both of these Aroclors.

6.1.3 Calculate the calibration factor (CF) for each characteristic Aroclor peak in each of the initial calibration standards using the equation below:

$$\text{calibration factor (CF)} = \frac{\text{Peak Area (or Height) in the Standard}}{\text{Total Mass of the Standard Injected (in nanograms)}}$$

Five sets of calibration factors will be generated for the AR1660 mixture, each set consisting of the calibration factors for each of the five (or more) peaks chosen for this mixture. The single standard for each of the other Aroclors will generate at least three calibration factors, one for each selected peak.

6.2 **Retention Time Windows** - Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for the misidentification of PCBs as Aroclors. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

6.2.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all standard mixtures throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

6.2.2 Record the retention time for three to five major peaks for each Aroclor to three decimal places. Calculate the mean and the standard deviation of the three absolute retention times.

6.2.3 If the standard deviation of the retention times for a target compound is 0.000 (no difference between the three retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes.

6.2.4 The width of the retention time window is defined as plus or minus three times the standard deviation of the absolute retention times. If the default standard deviation is employed, the width of the window will be 0.03 minutes.

6.2.5 Establish the center of the retention time windows from the calibration verification at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration. Retention time windows can be updated every 12 hours. However, they are usually only updated at the onset of a continuing calibration sequence or after maintenance has been performed.

6.2.6 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory and available for review.

7.0 PROCEDURE

7.1 Quality Control Checks

The following quality control samples are prepared with each batch of samples.

Quality Controls	Frequency	Control Limit
Prep. Blank (PB)	1 in 20 samples	< reporting limit
Blank Spike (BS)	1 in 20 samples	See Sec. 8.1.9
BS Duplicate (BSD)	1 in 20 samples	See Sec. 8.1.9
Matrix Spike (MS)	1 in 20 samples	See Sec. 8.1.9
MS Duplicate (MSD)	1 in 20 samples	See Sec. 8.1.9
Surrogate	every sample	At least 1 within statistical limits.

7.2 Sample Preservation and Storage

All samples should be collected in a glass container with a Teflon-lined lid. If the lid does not have a Teflon liner, aluminum foil should be placed between the jar and lid (dull side facing sample). All samples should be refrigerated up until extraction.

7.2.1 Hold Time Prior to Extraction

Matrix	SW-846
Soil/Sediment	14 days (VTS)
Water	7 days (VTS)
Waste/Oil	14 days (VTS)

VTS = verified time of sampling

7.2.2 After the samples have been extracted the extracts must remain refrigerated at 4 ± 2°C prior to analysis. The extract must be analyzed within 40 days after extraction.

7.3 Sample Preparation

7.3.1 Extraction Procedure

The matrix determines which extraction procedure to follow. Waters are extracted following the separatory funnel method; soils are by sonication; and wastes and oils are by dilution. Refer to the specific SOPs for the extraction procedures.

7.3.2 Clean-up Procedure

Various clean-up procedures are available if interferences are present. Florisil, mercury, copper, GPC, and acid clean-ups are most commonly used. Refer to the specific SOP for details.

7.4 Calibration / Standardization

7.4.1 GC Conditions

Carrier Gas (Helium)	3 - 10 mL/min
Make up Gas (Nitrogen)	> 60 mL/min
Column Temp Program	140 - 285°C (based on elution profile)
Ramp	3 - 5°C/min
Injector Temp	200°C
Detector Temp	300°C

NOTES:
Subject to change based on instrument performance.
The oven temperature and carrier gas flow may vary slightly between instruments and columns.

7.4.2 Verification of Calibration Curve

Verify calibration each 12-hour shift by injecting calibration verification standards prior to conducting any sample analyses. A calibration standard must also be injected at intervals of not less than once every twenty samples (after every 10 samples is recommended to minimize the number of samples requiring re-injection when QC limits are exceeded) and at the end of the analysis sequence. For Aroclor analyses, the calibration verification standard should be a mixture of AR1660. The calibration verification process does not require analysis of the other Aroclor standards used for pattern recognition, but the analyst may wish to include a standard for one of these Aroclor after the AR1660 mixture used for calibration verification throughout the analytical sequence.

7.4.2.1 The calibration factor for each analyte calculated from the calibration verification standard (CCV) must not exceed a difference of more than ±15% when compared to the mean calibration factor from the initial calibration curve.

$$\% \text{ Difference} = \frac{\text{Mean CF} - \text{CF of CCV}}{\text{Mean CF}} \times 100$$

7.4.2.2 If this criterion is exceeded for any calibration factor, inspect the GC to determine the cause and perform whatever maintenance is necessary before verifying calibration and proceeding with sample analysis. If routine maintenance does not return the instrument performance to meet the QC requirements based on the last initial calibration, then a new initial calibration must be performed.

7.5 Qualitative identification - qualitative identifications of target analytes are made by examination of the sample chromatograms versus the standard chromatograms from the initial calibration. If the responses in the sample chromatogram exceed the calibration range of the system, dilute the extract and reanalyze. Peak height measurements are recommended over peak area when overlapping peaks cause errors in area integration.

7.5.1. Each sample analysis must be bracketed with an acceptable initial calibration, verification standard(s) (each 12 hour shift), or calibration standards interspersed within the samples. When a calibration verification standard fails to meet the QC criteria, all samples that were injected after the last standard than last met the QC criteria must be re-injected.

7.5.2 Sample injections may continue for as long as the calibration verification standards and standards interspersed with the samples meet instrument QC requirements. The sequence ends when the set of samples has been injected or when qualitative or quantitative QC criteria are exceeded.

7.5.3 Use the calibration standards analyzed during the sequence to evaluate retention time stability. If any of the standards fall outside their daily retention time windows, the system is out of control. Determine the cause of the problem and correct it.

7.5.4 The identification of Aroclors using this method is based on agreement between the retention times of peaks in the sample chromatogram with the retention time windows established through the analysis of standards of the target analytes. Tentative identification of an analyte occurs when a peak from a sample extract falls within the established retention time window for a specific target analyte. Each tentative identification must be confirmed: using a second GC column of dissimilar stationary phase, based on a clearly identifiable Aroclor pattern, or using another technique such as GC/MS.

7.5.5 Since the calibration standards are analyzed on both columns, the results for both columns must meet the calibration acceptance criteria. If the retention times of the peaks on both columns fall within the retention time windows on the respective columns, then the target analyte identification has been confirmed.

7.6 Quantitation of PCBs as Aroclors - The quantitation of PCB residues as Aroclors is accomplished by comparison of the sample chromatogram to that of the most similar Aroclor standard. A choice must be made as to which Aroclor is most similar to that of the residue and whether that standard is truly representative of the PCBs in the sample.

7.6.1 Use the individual Aroclor standards (not the AR1660 mixtures) to determine the pattern of peaks on Aroclors 1221, 1232, 1242, 1248, and 1254. The patterns for Aroclors 1016 and 1260 will be evident in the mixed calibration standards.

7.6.2 Once the Aroclor pattern has been identified, compare the responses of 3 to 5 peaks observed in the sample extract. The amount of Aroclor is calculated using the individual calibration factor for each of the 3 to 5 characteristic peaks chosen in section 6.1 and the calibration model (linear or non-linear) established from the multi-point calibration of the AR1660 mixture. A concentration is determined using each of the characteristic peaks and then those 3 to 5 concentrations are averaged to determine the concentration of that Aroclor.

7.6.3 Weathering of PCBs in the environment and changes resulting form waste treatment processed may alter the PCBs to the point that the pattern of a specific Aroclor is no longer recognizable. Samples containing more than one Aroclor present similar problems. The quantitation of Aroclors may be performed by measuring the total area of the PCB pattern and quantitating on the basis of the Aroclor standard that is most similar to the sample. Any peaks that are not identifiable as PCBs of the basis of retention times should be subtracted from t he total area. When quantitation is performed in this manner, the problems should be fully described for the data user and the specific procedures employed by the analyst should be thoroughly documented.

7.6.4 Manual Integration Policy

In each case where manual integrations have taken place, the operator must identify, initial and date the changes on the hardcopy. The following guidelines apply :

- Manual integrations should be consistent between all files integrated.
- Manual integrations should not be performed to meet QC criteria.
- Excessive manual integrations may reflect an instrumental or methodological problem that should be addressed.

Manual integrations are most often performed for the following reasons.

- Assignment of correct peak that was mis-identified by the system.
- Incomplete auto-integration due to high level of target detected.
- Incomplete auto-integration due to background interference.
- Incorrect auto-integration due to co-elution or near co-elution of compounds.
- Missed peaks.

All integrations are reviewed by the analyst. All chromatograms and reports are printed after any integrations take place and are routinely included in the data packages.

Manual integrations may be documented in the narrative if so required, however, references to this SOP will be used for explanations, and any further documentation beyond initials and dates will not be done.

7.7 Preventive Maintenance

7.7.1 The septa should be changed between each analyses sequence. The number of injections made plays a part in how frequently they should be changed. Generally, not more than 100-125 injections should be made without changing the septum.

7.7.2 The laboratory is equipped with a gas generation system, which includes nitrogen and hydrogen. Helium is supplied by tanks, oxy-trap should be changed every other tank.

7.7.3 The entire system should be periodically checked for leaks and frayed wires.

7.7.4 Leak tests must be performed every six months on every electron capture detector.

7.7.5 Suggested Maintenance

When any calibration, QC sample or analytical sample is outside the acceptance criteria, one or more of the following actions may be necessary.

- Inspect injection end of column for particulates and/or cracks.

- Check press connectors.
- Condition of the column - upper end of column temperature 285°C for 1 - 2 hours.
- Remove 1-6 inches from the injector and guard column.
- Make sure septum doesn't need to be changed.

7.7.6 Refer to the instrument manuals if problems are encountered which can not be solved by routine maintenance.

7.8 Gas Chromatographic Analysis

7.8.1 Column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column may need to be primed or deactivated by injecting a PCB standard mixture approximately 20 times more concentrated than the mid-level standard. Inject this prior to beginning initial or daily calibration. This is accomplished using the highest level of the calibration standards.

7.8.2 Direct Injection - For a capillary column, inject 1 - 2 uL of the sample extract using a solvent flush technique equipped with the autosampler.

7.8.3 If the response of a sample exceeds the linear range of the system dilute the extract and reanalyze. Over lapping peaks are not always evident when peaks are off scale. The computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.8.4 If peak detection is prevented by the presence of interferences, further clean-up may be required.

7.8.5 Standards must be injected at the intervals no more than every 20 samples; however, it is recommended that no more than 10 samples be analyzed between CCVs. The calibration factor for each CCV must not exceed a 15% difference when compared to the initial calibration. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary. The instrument must be within control before proceeding with sample analysis. All samples that were injected after the last in control CCV must be re-injected. If routine maintenance does not return the instrument back into control based on the last initial calibration, verify that proper maintenance has been performed and if still out of control start a new initial calibration.

8.0 QUALITY CONTROL

8.1 QC Summary

For each analytical batch (20 samples), a method blank, blank spike (BS)(also referred to as LCS), blank spike duplicate (BSD), matrix spike and matrix spike duplicate must be analyzed. The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps. Also, every sample must be spiked with the surrogates TCX and DCB. These results are tabulated by the QA/QC to generate in-house control limits.

8.1.1 The method blanks will be examined to determine if contamination is being introduced in the laboratory.

8.1.2 The BS will be examined to determine both precision and accuracy.

8.1.3 Accuracy will be measured by the percent recovery (%R) of the BS. The recovery must be in range, as determined by statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.4 Precision will be measured by the reproducibility of both BSs and will be calculated as Relative Percent Difference (RPD). Results must agree within statistical control limits in order to be considered acceptable.

8.1.5 Surrogate compounds will be added to every sample to measure performance of the analysis. Results must agree within statistical control limits in order to be considered acceptable. However, if DCB recovery is low or compounds interfere with DCB, then the TCX should be evaluated for acceptance. Proceed with correction action when both surrogates are outside of control limits.

8.1.6 Each time an analytical sequence is started, the first Aroclor 1660 must be evaluated to determine if the chromatographic system is operating properly. The analyst should consider:

- Do the peaks look normal?
- Is the response obtained comparable to the response from previous calibrations?

Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc.

8.1.7 Required Instrument QC

8.1.7.1 Section 6.0 requires that the %RSD be < or = 20% when comparing calibration factors to determine if the initial calibration curve is linear.

8.1.7.2 Section 6.0 sets a limit of ±15% difference when comparing the continuing response of AR1660 versus the initial response. If the limit is exceeded, corrective action must be taken to correct the problem or the sequence must be started over. All samples following the last standard that was in control must be reanalyzed.

8.1.7.3 Section 6.2 requires the establishment of retention time windows.

8.1.7.4 Section 7.4.2 sets a limit of ±15% difference when comparing the initial response of the initial linearity to any succeeding standards analyzed during an analytical sequence.

8.1.7.5 Section 7.5.5 requires that all succeeding standards in an analytical sequence must fall within the daily retention time window established by the first standard of the sequence.

8.1.8 For every batch of samples (20 samples = a batch) the analyst must perform a matrix spike, matrix spike duplicate, method blank, and blank spike. Also, every sample, and QC sample must be spiked with the surrogates.

8.1.8.1 The desired concentrations of the spikes used are as follows:

Compound	Water (ug/mL)	Soil/Sediment (ug/mL)	Waste/Oil (ug/mL)
AR1660	5.0	5.0	5.0
Tetrachloro-m-xylene	0.40	0.40	0.40
Decachlorobiphenyl	0.40	0.40	0.40

*Surrogates are prepared in a separate solutions from the matrix spike compounds. Refer to the SOP for the preparation of standards and QC solutions.

8.1.9 Limits used for spike recoveries are in-house statistically generated control limits, or limits which have been specifically assigned by the client. If statistical data is not available due to lack of data points, default limits of 50-150% are used until enough data points are available. Refer to the backlog for the requested control limits (see also the QAP, when appropriate).

8.1.10 If a recovery is outside of its control limits, the result should first be examined for any possible calculation errors. If that isn't the problem, then the sample should be re-injected. If after re-injecting the sample it is still out of control, and the BS are within control, the out of control recovery may be attributed to the matrix.

8.2 Corrective Actions

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources when determining the action to be taken. The out of control situation may or may not be caused by more than one problem. The analyst should seek the help of his/her immediate supervisor, QA personnel, or other experienced staff if he/she are uncertain of the cause

of the out of control situation and the required corrective action. The analysis must not be resumed until the source of the problem and an in control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, QA personnel or the lab managers approval.

Listed below are steps to be taken when an out of control situation occurs. The analyst **MUST**:

- demonstrate that all the problems creating the out of control situation were addressed
- document the problem and the action which was taken to correct the problem on a corrective action report form
- document on the corrective action report that an in control situation has been achieved
- receive approval (signature) of the section manager, QA personnel, or the laboratory manager prior to the release of any analytical data associated with the problem

Whenever a problem exists, such as insufficient sample to run matrix spikes and matrix spike duplicates, a Sample Discrepancy Report (SDR) is written. It is filed with the report discussing the actions taken to correct and document the problem. The analyst and their section manager decide what to do with this problem, whether it is analytical, sampling, or matrix interference.

Listed below are some suggested courses of action that may be taken to correct out of control situations that may occur with the procedure.

8.2.1 Calibration Factors

Correct the problem, re-run the calibration curve and determine new response factor.

8.2.2 Initial Calibration Verification

Repeat the standard to verify proper preparation. If still non-compliant, prepare a new standard from the original stock, recalibrate with a new standard curve, or prepare new stock and/or working standards.

8.2.3 Blank Spike

The recoveries for the spiked compounds must be within statistical (or otherwise specified) limits. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, then reanalyze the blank spike to determine if instrumental conditions or analytical preparation was the cause. If the blank spike is still non-compliant notify the Project Manager using an SDR, to determine if re-extraction is required of all associated samples. Unless otherwise directed, samples will not be extracted outside the hold time and the data will be submitted with the appropriate narration.

8.2.4 Blank Spike Duplicate

The BS Duplicate must meet all control limits as BS in addition to limits set for precision (same corrective action as BS).

8.2.5 Method Blank (MB1)

The method blank should not contain any target compounds at or above the reporting limit. If non-compliant, then the method blank should be reanalyzed to determine if instrument contamination was the cause. If the method blank is still non-compliant and the samples are within the extraction holding time, then request re-extraction using an SDR and reanalyze all associated samples containing target compounds at <10x amount found in the method blank. If a sample contains target compounds at ≥ 10x amount found in the method blank, or if target compounds are not detected in the sample, then that sample does not require re-extraction and the results may be reported without qualification. If the samples our outside the extraction holding time, then contact the project manager using an SDR. Unless directed otherwise, samples will not be extracted outside the holding time and the data will be submitted with appropriate narration.

8.2.6 Matrix Spike

The recoveries for the spiked compounds should be within statistical. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, and the associated blank spikes are within advisory limits, then sample matrix effects are the most likely cause.

8.2.7 Matrix Spike Duplicate

See Matrix Spike for recoveries. RPDs should be within statistical limits. If non-compliant, check calculations for documentable errors. Check unspiked sample results and surrogate recoveries for indications of matrix effects. If significant differences exist between the MS and MSD, reanalysis of the sample spikes may be necessary.

8.2.8 Surrogate Spike

At least one recovery for the surrogate(s) should be within control limits. If non-compliant, check calculations and spike preparation for documentable errors. If no errors are found, and the surrogate recoveries in the method blank and blank spikes are within the advisory limits, then sample matrix effects are the most likely cause. Any samples with both surrogate recoveries outside statistical limits with, no visible chromatographic cause, should be reanalyzed to determine if an injection error was the cause for the out of control recovery. If the surrogate recoveries in the associated method blank and blank spike are not within advisory limits, and the samples are within the extraction holding time, then re-extract and reanalyze all associated samples. If the samples are outside the extraction holding time, then contact the project manager using and SDR. Unless

otherwise directed, samples will not be re-extracted out of hold time and data will be submitted with appropriate narration.

8.2.9 Continuing Calibration Verification (CCV)

The response factors of the initial calibration check standard should not vary from the response factors of the corresponding standard from the calibration curve by more than ± 15% on both columns. If any of the target compounds fail the criteria, then the standard is considered to be non-compliant. If the standard is non-compliant, then reanalyze the standard. If the standard is still non-compliant, remove 6-12 inches from the guard column and condition the column for 1-2 hours. If the standard is still non-compliant, then prepare a new standard. If the new standard is non-compliant, then recalibrate the instrument with a new curve. All target compounds which fail the criteria should be narrated as showing increased sensitivity, and how this might bias data. Notify the project manager of any non-compliance using the SDR. Unless directed otherwise, samples will not be analyzed outside of holding time and the data will be submitted with appropriate narration.

8.2.10 Retention Time Windows

Evaluate the data for usability based on a comparison with the standards run during the analytical sequence. Also, consider the retention times for the surrogates and spiked compounds analyzed before and after the sample in question.

8.2.10.1 For external standard calibration, it is required that a 5 point linearity must be run initially (Section 6.11). If the %RSD of the calibration factors is >20% for the 5 point, linear regression may be used to quantitate samples. Prior to running a new calibration, or preparing new standards, ensure proper maintenance has been performed.

8.2.10.2 The working calibration curve should be verified at the beginning of every analytical sequence. When the beginning AR1660 is not within ±15% of what the predicted response is, first try re-injecting the standard and see if it was a bad injection. Perhaps the column needs to be examined for a dirty inlet and cracks. Check press connector for a proper seal and ensure there are no leaks. If CFs are out high and inlet has been checked, condition column at an elevated temperature (no higher than 280-300 degrees). Baking the detector at 350 degrees for an hour or two may also be helpful. See section 7.7 for more details.

8.2.10.3 Initial retention time windows must be established following the procedure described in section 6.2. Daily windows are then established as in section 6.2.5 at the beginning of each analytical sequence. If a continuing standard is outside of their daily windows, corrective actions must be taken before continuing. Check the septa first and make sure it is tight before any other possibilities are investigated. Check the press connectors, discoloration of the guard column or check the carrier gas and its connection to the instrument for possible leaks.

Perhaps baking the detector at 350°C for about an hour or two will help.

8.2.10.4 If through out the analytical sequence any CFs for any of the CCVs exceeds the 15% difference limit, corrective action must take place. First, try re-injecting the standard. If that does not make a difference, refer to Section 7.7 for recommended maintenance. If the CF's are still unacceptable, a new analytical sequence should be started. All samples that were injected after the standard that last met QC criteria must be re-injected.

IF AT ANY TIME THE ANALYST IS UNCERTAIN AS TO WHAT ACTIONS TO TAKE OR HOW TO PERFORM SUGGESTED MAINTENANCE, PLEASE SEE YOUR SECTION MANAGER OR UNIT LEADER. IF SOMETHING UNUSUAL IS HAPPENING THAT IS NOT DESCRIBED IN THIS SECTION, SEE YOUR SECTION MANAGER OR UNIT LEADER. COSTLY (AS IN MONEY AND TIME) DAMAGE CAN RESULT TO THE INSTRUMENT, DETECTOR, OR COLUMN IF MAINTENANCE IS NOT PERFORMED CORRECTLY.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Concentration (ppb) = $\dfrac{[(A_1)(V_t)(Df)]}{[(V_i)(V_s)(D)][CF]}$

Where:
A_1 = response for the analyte in the sample (area or height)
V_i = volume of extract injected (mL).
Df = dilution factor (if applicable)
V_t = volume of total extract (mL).
V_s = volume/weight of sample extracted
D = (100 - % Moisture) / 100
CF = Average calibration factor from the initial calibration curve

Toxaphene and Technical Chlordane are all multi-response compounds. Peak shape and pattern are evaluated more so than just retention times when calculating the concentrations of these analytes.

9.2 %RSD = $\dfrac{\text{Standard Deviation}}{\text{Mean}} \times 100$

Where,
Standard Deviation = $\left| \dfrac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1} \right|^{1/2}$

Where,
x_1 = each individual value used to calculate the mean
x = the mean of n values
n = the total number of values

9.3 % Difference = $\frac{\text{Avg. CF - CF}}{\text{Avg. CF}} \times 100$

Where:
Avg CF = Average CF from initial linearity
CF = CF from the analysis of the verification standard

9.4 Surrogate Percent Recovery = $\frac{Q_d}{Q_a} \times 100$

Where:
Q_d = Quantity determined by analysis
Q_a = Quantity added to sample/blank

9.5 Spike Recovery = $\frac{SR}{SA} \times 100$

Where:
SR = Spike result
SA = Spike added

9.6 Accuracy: $\%R = \frac{(A_T - A_0)}{A_F} \times 100$

Where:
A_T = Total amount recovered in fortified sample
A_0 = Amount recovered in unfortified sample
A_F = Amount added to sample

9.7 Precision: $\%D = \frac{|B_1 - B_2|}{\text{Mean of } B_1 \text{ \& } B_2} \times 100$

Where:
B_1 = %Recovery MS (or BS)
B_2 = %Recovered MSD (or BS)

9.8 % Moisture = 100 - % Total Solids*

*% Total Solids are performed by the Metals Department - refer to SP No. USP-SOP-2540G.

9.9 Instrument Run-Logs

The analysis of samples and standards is documented within each instrument-specific run log, and must be completed for each day's analysis (Appendix A).

9.10 Traceability of Standards

When a run log is set up for each instrument, all initial standards are noted in the logbook with the logbook #'s for each standard. This allows for traceability of the original standard. It is assumed that if no further notations are made in the run log concerning the standard identification, book #'s of the initial standards used will be the same standard throughout the analytical sequence.

9.11 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review form (Appendix B). Upon the first 100% review, the review form is initialed and dated as reviewed. The package, with its review sheet, comments and any corrective action reports is submitted to the unit leader, section manager, or peer reviewer for a second review. Once again, the review form is initialed and dated by the second reviewer.

The completed data review form remains on file with the original data.

10.0 WASTE MANAGEMENT AND POLLUTION PREVISION

Refer to the SOP entitled "Disposal of Laboratory Waste".

11.0 METHOD PERFORMANCE CRITERIA

Refer to the SOP entitled "Laboratory Training: Skills and Mechanisms".

12.0 REFERENCES

Refer to Section 1.0

13.0 ATTACHMENTS

Table 1: Target Compounds and Reporting Limits
Table 2: Working Standard Solutions and Desired Concentrations
Table 3: Example: Analytical Sequence

Appendix A: Example: Analysis Run Log
Appendix B: Example: Data Review Form

Historical File: Revision 00: 02/16/98
Revision 01: 02/26/99

Reason for Change; Revision 01:

- Surrogate concentration changed to 0.04 ug/mL from 0.02 ug/mL.
- Add Precision/Accuracy calculations.
- Annual Review.

U:\QC\SOP\UGE\8082.DOC

Table 1

Target Compounds and Reporting Limits

Severn Trent Laboratories Chicago
PCB Reporting Limit Summary
Analytical Method: SW-846 8082

Parameter	Reporting Limits	
	Waters ug/L	Soils ug/kg
Aroclor 1016	0.25	8.33
Aroclor 1221	0.25	8.33
Aroclor 1232	0.25	8.33
Aroclor 1242	0.25	8.33
Aroclor 1248	0.25	8.33
Aroclor 1254	0.25	8.33
Aroclor 1260	0.25	8.33
Surrogates:		
DCB		
TCX		

Table 2

Individual Solutions

Compound	Approximate Concentrations (ng/uL)					
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Aroclor-1016	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1221	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1232	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1242	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1248	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1254	0.025	0.040	0.250	0.500	0.750	1.00
Aroclor-1260	0.025	0.040	0.250	0.500	0.750	1.00

These Individual Solutions must all have DCB and TCX in them. Aroclor 1016 and 1260 are prepared in the same solution and are referred to as AR1660. Unless otherwise specified, only AR1660 needs to be run at at least 5 levels to establish linearity. A single point standard is required for the other Aroclors, at the mid-level range (0.50 ng/uL).

Table 3:

Example: Analytical Sequence

Quantitation & Confirmation of Aroclors	
1. AR 1660-1	1. AR 1660-1
2. AR 1660-2	2. AR 1660-2
3. AR 1660-3	3. AR 1660-3
4. AR 1660-4	4. AR 1660-4
5. AR 1660-5	5. AR 1660-5
6. AR 1660-6	6. AR 1660-6
7. AR 1221-4	7. AR 1221-4
8. AR 1232-4	8. AR 1232-4
9. AR 1242-4	9. AR 1242-4
10. AR 1248-4	10. AR 1248-4
11. AR 1254-4	11. AR 1254-4
12-21 samples	12-21 samples
22. AR 1660-4	22. AR 1660-4
23-32 samples	23-32 samples
33. AR1660-4	33. AR1660-4

NOTE: AR1660 linearity is sufficient for initial calibration of all Aroclors since they include all congeners present in the different regulated Aroclors.

Appendix A.

Example: Analysis RunLog

Severn Trent Laboratories Chicago
GC/ECD Analysis Log

Page #: _____

GC Conditions: Initial Initial Hold Rate Final Final Hold
Temperature Prog. (1/2): _____ _____ _____ _____ _____

Analyst:_____			Instrument ID#: XX		Date:_____	
Sample File ID#	Rep#	Method	Sample Description	D.F.	Injection Date/Time	Comments

Reviewer's Signature:_____ Date:_____

Appendix B.

Example: Data Review Form

Severn Trent Laboratories Chicago
GC/HPLC Data Review Checklist

Client: _____ **RFW#:** _____ **Test:** _____

Reviewer(1): _____ **Date:** _____

Reviewer(2): _____ **Date:** _____

Prior to Updating Results Review List: _____
Instr.: _____

Reviewer 1	Reviewer 2	
____	____	All required holding times were met.
____	____	Method has been calibrated.
____	____	Chromatograms are scaled properly and chromatography is good.
____	____	All peaks are labeled properly (peakmet if necessary)
____	____	All initial linearities are within control limits.
____	____	All continuing standards are within control limits.
____	____	All retention times are within their windows.
____	____	All method blanks are clean.

Comments: _____

Updating Results

____	____	All reported data is circled, and those not required have been crossed out.
____	____	All reports have been signed/initialed and dated.
____	____	All results on summary and Form 1 match report.
____	____	Initial and date Chromatogram (if written on)

Comments: _____

FORM1/Associated Data

____	____	Client information has been checked: correct list, reporting limits and special requirements (i.e., no "J" values).
____	____	Check all header information for correctness (RFW #, sample size, dilution factor, matrix..).
____	____	Check values reported. If an "E" is present, there must be another dilution; if a value is reported review the chromatogram; if a "J" is reported, review the chromatogram; if an "I" is reported there must be another dilution run.
____	____	Check that all RFW#s on chromatograms match quant report and data on quant report is correct.
____	____	Check that samples were reviewed under the correct list.
____	____	Check that surrogates and spike recoveries are correct.

Comments: _____

Severn Trent Laboratories Chicago
GC/HPLC Data Review Checklist

QC Data Review

Reviewer 1	Reviewer 2	
____	____	All surrogate recoveries are within control limits. If not, samples have been reanalyzed.
____	____	All blank spike/blank spike duplicate recoveries are within control limits as well as %RPD's (Form 3).
____	____	All matrix spike and matrix spike duplicates recoveries are within control limits, if not, they have been reanalyzed.
____	____	Newchron has correct sample data and analysis dates, all blanks and spike blanks are present.
____	____	Corrective action report has been completed.

Comments:_____

Note: Anything out of the ordinary must be commented on and be approved by the Unit Leader/Section Manager for inclusion in the Case Narrative.

____ RG LabChron/Report Review Initial/Date _____

Comments:_____

APPENDIX A-76

STANDARD OPERATING PROCEDURE FOR TOTAL ORGANIC CARBON/TOTAL CARBON/TOTAL INORGANIC CARBON IN SOIL, SLUDGE, AND SEDIMENT

SOP No.	Revision No.	Date	Page
UWC-SOP-KAHN	01	09/17/99	1 of 15

TITLE: WET CHEMISTRY
Total Organic Carbon / Total Carbon / Total Inorganic Carbon in Soil, Sludge, and Sediment

Updated by:	Signature:	Date
Diane L. Harper Section Manager, Wet Chemistry	Diane L Harper	9/20/99

Approved by:	Signature:	Date
Diane L. Harper Section Manager, Wet Chemistry	Diane L Harper	9/20/99
Raymond J. Frederici Quality Manager		9-28-99

CONTROLLED DISTRIBUTION

COPY # : 005

ISSUED TO : Sharon Nordstrom - NUS
NUS Housatonic River Site Proj

Full Signature Approvals Are Kept on File with
Severn Trent Laboratories QA Standard Practice Records

1.0 SCOPE / APPLICATION

This Standard Operating Procedure (SOP) describes a method for the determination of Total Organic (TOC), Inorganic Carbon, and Total Carbon in soil, sediment, and sludge samples. This SOP was written using the following references:

- *Standard Methods for the Examination of Water and Wastes,* 18th Edition, 1989, Method 5310C.
- *Methods for Chemical Analysis of Water and Wastes,* March 1983 Revision, Method 415.1.
- "Determination of Total Organic Carbon in Sediment", July 27, 1988, Lloyd Kahn, USEPA Region II.
- "Instructions for Installation and Operation of the 183 Boat Module with the Phoenix 8000." Tekmar-Dohrmann, Brian Wallace, Application Chemist.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

An MDL is analyzed by the injection of 20 uLs of Stock Standard II (Rgt. 5.4), for a concentration of 40 ug C. A sample MDL is calculated from this by assuming a sample size of 0.050 grams, which results in a "true value" of the MDL of 800 mg/kg.

1.1.2 Reporting Limits

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. Because of the high level of quantitative error associated with determinations at the level of the MDL, the laboratory endeavors to keep reporting limits higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported.

The low standard of the calibration curve is 20 ug of carbon. Sample reporting limits will vary with sample size, but are based on a detectable mass of 20 ug carbon.

1.2 Summary of Method

Samples are oxidized in a quartz combustion tube in an oxygen atmosphere at 800°C. The CO_2 produced is carried in the gas stream to a non-dispersive infrared detector that is specifically tuned to the absorptive wavelength of CO_2. The instrument microprocessor calculates the peak areas of each sample and compares them to the peak areas of the calibration standards in memory.

When only organic carbon (TOC) is required, pre-treatment with nitric acid followed by air drying eliminates interference from inorganic carbon. Total carbon is obtained by burning the sample without pre-treatment. Inorganic carbon requires analyzing a sample both with and without pre-treatment and is calculated as the difference between total and organic carbon.

2.0 INTERFERENCES

- Inorganic carbon is removed prior to oxidation in the instrument for TOC.
- Volatile organics may be lost in the decarbonation step resulting in a low bias.
- Bacterial decomposition and volatilization of organics are minimized by maintaining the samples at 4 ± 2°C and analyzing within 14 days of collection.

Gas flow is critical to successful operation and calibration of this instrument. Watch for the following:

- The tank regulator should be set between 20 and 30 psi, and tank pressure must be >500 psi. The regulator can be adjusted daily to achieve an in-control ICV. See below.
- The extension kit essentially dilutes the gas flow from 200 mL/min to 600 mL/min, which prevents the sensitive IR detector from being overwhelmed by up to 800 ug of carbon, theoretically.
- The check valve in line after the combustion tube fails periodically and must be replaced when initial symptoms of failure are detected. The main symptom is steam backing out of the boat inlet port when the hatch is open. When the valve fails, the cobalt can violently eject through the open hatch. The check valve also gets very hot. Always keep new valves in stock.
- If bubbling through the mist trap is low or non-existent while the hatch is closed, check all seals, especially the hatch seal, which is the most likely seal to be loose.

3.0 SAFETY

- Fully fastened lab coat, safety glasses and latex gloves must be worn.
- Immediately clean up any materials spilled on the floor, in hoods or on bench tops.
- Be sure all chemical containers are clean and properly labeled.
- Discard all damaged or broken glassware immediately.

4.0 EQUIPMENT AND SUPPLIES

- Dohrmann Phoenix 8000 Total Carbon Analyzer, with sludge and sediment sample accessory 183 Boat Module and carbon range extension kit.
- Analytical balance capable of weighing 0.01 mg.

5.0 REAGENTS AND STANDARDS

5.1 Phosphoric acid, H_3PO_4 (50%)

Add 50 mL of DI water to 50 mL of phosphoric acid.

- Life of Reagents: one year
- Storage Requirements: none

5.2 Nitric Acid, HNO_3
Sulfuric Acid, H_2SO_4

Purchased from a vendor.

- Life of Reagents: three years
- Storage Requirements: none

5.3 Stock Carbon Standard I (2000 mg/L as C)

Weigh 0.425 g of anhydrous potassium hydrogen phthalate (KHP) acid ($KHC_8H_4O_4$). Transfer to a 100 mL volumetric flask. Dissolve in carbon dioxide free water, acidify with 100 uL of H_2SO_4 and dilute to volume.

- Life of Reagent: one month
- Storage Requirements: refrigerate at $4 \pm 2°C$

5.4 Stock Carbon Standard II (2000 mg/L as C)

Weigh 0.425 g of anhydrous potassium hydrogen phthalate (KHP) acid ($KHC_8H_4O_4$) from an alternate manufacturer. Transfer to a 100 mL volumetric flask. Dissolve in carbon dioxide free water, acidify with 100 uL of H_2SO_4 and dilute to volume.

- Life of Reagent: one month
- Storage Requirements: refrigerate at $4 \pm 2°C$

5.5 Soil Standard

Purchased from ERA.

- Life of Reagent: see manufacturer's label.
- Storage Requirements: refrigerate at 4 ± 2°C

6.0 CALIBRATION (NON-DAILY)

6.1 Calibration Curve

A multi-point calibration curve will be prepared and analyzed monthly according to the following table.

Volume of Stock Std. I (uLs)	ug Carbon
0	0
10	20
20	40
40	80
50	100
60	120
100	200
150	300
200	400

NOTE: The curve is verified daily with the ICV/CCVs. The life of the curve can be extended by adjusting the gas flow at the oxygen tank regulator. If the ICV is low (<85% recovery), the gas flow can be turned down by ~3 or 4 psi. If the ICV is too high (>115% recovery) the flow can be turned up a few psi, as long as it is in the 20-30 psi range.

Inject the known amount (see above) of Stock Std. I into the boat through the injection port. (The empty pre-burned boat, with only the quartz wool is used for the blank.) Click "Start" and wait for software to prompt the user with the statement "Push Boat in Now". Push boat into furnace. Click "OK". After peak reaches its height and it is descending, move boat from furnace to cooling area. Allow 30 seconds to cool. Curve screen will appear after each analysis. Click "OK" once the screen appears. Continue the procedure with all the above standard concentrations.

When the curve screen appears, select the standards to be used in curve by clicking on each concentration. Click on "Recalc" to receive r^2 value. Take the square-root of the r^2 value to determine the r value, which must be ≥ 0.995. Click on "Print" then "OK" to accept the calibration. Make sure to note the "r" value on the instrument print-out.

7.0 PROCEDURE

7.1 Quality Control Checks

Quality Controls	Description	Frequency	Control Limits
Calibration Curve	See Section 6.1	Monthly	$r \geq 0.995$
Init. Cal. Verif. (ICV)	50 uL Stock II (100 ug C)	Daily, 1st reading	85 – 115 %
Init. Cal. Blank (ICB) / Preparation blank	50 uL DI water	After ICV	< Rpt. Limit
Laboratory Control Standards (LCS)	~ 0.020 g Solid TOC Std.	1 in 20 or fewer samples	*statistical accuracy limits
Matrix Duplicate TOC/TOC2	~ 0.010-0.050 g	All samples	*statistical precision limits
Matrix Quadruplicate	~ 0.010-0.050 g	1 in 20 or fewer samples	*statistical precision limits
Cont. Cal. Verif. (CCV)	50 uL Stock II (100 ug C)	Every 10 samples	85 – 115 %
Cont. Cal. Blank (CCB)	50 uL DI water	After every CCV	< Rpt. Limit

*Statistical precision and accuracy limits must be established annually by at least 15 analyses of a solid TOC standard obtained from a vendor.

7.2 Sample Preservation and Storage

Samples are collected in glass containers, filled to volume and kept tightly capped, as volatile organics may be lost otherwise. There is no regulatory holding time for this test; however, the laboratory employs a 14 day holding time with samples maintained at 4 ± 2°C before analysis.

7.3 Sample Preparation

7.3.1 Total Organic Carbon (TOC)

Total Organic Carbon (TOC): For total organic carbon, a small amount of each sample must be pretreated with nitric acid. For convenience this can be done in the top or bottom of a small petri dish. After effervescence is complete, air dry or dry on a low setting on a hot plate. Samples can be stored in a desiccator overnight. Grind as possible to ensure homogeneity. Continue with Section 7.6.

7.3.2 Total Carbon (TC)

Analyze untreated air-dried sample, as above, for total carbon (TC). Continue with Section 7.6. Inorganic carbon (TIC) may be determined by difference.

7.4 Calibration / Standardization

7.4.1 Start-Up Operation

To access computer software, double click on TOC/TALK 3.0 icon within the Phoenix Soils window. Click on "set up", go to "instrument", then press "ready". Wait for initialization of instrument. Double click "Run" to open the analysis screen. In "Sample/Setup", the Method ID should always be "BOAT".

Turn on the furnace. Allow ~ 1 hour to for the furnace to reach the operating temperature (800°C). The green ready light will come on when the set temperature has been achieved.

Open the valve on the O_2 tank. The gas pressure should be about 20 to 30 psi. Turn on the Boat Gas. Fill the mist trap to just above the injection septum with 50% phosphoric acid.

Place a small piece of quartz wool in the sample boat.

Slide the boat into the furnace to bake off accumulated impurities. After the peak reaches its height and it's descending, move the boat from the furnace to the cooling area. Allow 30 seconds to cool.

7.4.2 Instrument Calibration

Click on "Setup" > "Calibration" > "Set Active" > "TC Curve". SoilCurve should be selected for range 0.002-0.1ppm. Click "OK". Click "Sample Setup". Change Sample Type to TC Standard. Click "OK" if range is 0.002 - 0.1ppm and select Standard ID needed. Click "Exit" > "Save/Use".

7.4.3 Initial and Continuing Calibration Verification

Click "Setup" > "Instrument". Select the option to automatically print the data when the analysis is done. Click "OK". Go to "Sample/Setup". Type in "Sample ID" and Change Sample Type to Cal. Verification. In Cal. Verification screen, select verification/ID needed and click "OK". Click "Save/Use".

Move the boat to the injection port. Inject the ICV/CCV.

Click "Start". Wait for the software to prompt the user with the statement "Push Boat in Now". Push the boat into the furnace. Click "OK". Once the peak reaches its height and it's descending, remove the boat from the furnace to the cooling area.

The data will automatically print out. Results will be in ugs (micrograms) of Carbon (even though the software says ppm as well as ug C).

7.4.4 Initial and Continuing Verification Blanks.

Click "Sample/Setup". Type in Sample ID. Change Sample Type to SAMPLE. Inject DI water. Proceed to Section 7.6.

7.5 Preventive Maintenance

The analyst(s) performs the daily, weekly, and monthly preventive maintenance checks as defined in each instruments maintenance logbook (Appendix A).

7.6 Sample Analysis

7.6.1 Remove the platinum boat from the top loading hatch on the furnace module. (Note: this is also the cooling area). Place the platinum boat in a container on the pan of an analytical balance and tare it. Place approximately 10-50 mg of sample in the boat. Amount weighed is at discretion of analyst. (Note: Use less sample for samples containing high amounts of humus; use more sample for sandy samples). Record the weight to the nearest 0.01 mg (0.00001 grams).

7.6.2 Open the hatch and load the boat into the holder. Close the hatch. Make sure the seal is tight to ensure proper gas flow.

7.6.3 Click "Sample/Setup". Type sample ID and change Sample type to SAMPLE. Click "Save/Use".

7.7 Documentation

7.7.1 Data Cover Page

The analysis of samples and standards is documented by the instrument print-out and with a data cover page that provides standard curve data, standard traceability, and QC levels. An example of this cover page is in Appendix B.

7.7.2 Traceability of Standards

Upon receipt, each chemical is recorded in a bound chemical receipt log book and is issued a unique source ID#. The manufacturer, lot #, date received, expiration date, and the initials of the recording analyst are documented in the log book. When a standard is prepared at the laboratory, the Source ID#, weight of the chemical, the type and volume of solvent, concentration, date of preparation, date of expiration, preservative if applicable, and the analyst's initials are recorded in the Standards Preparation Log. Each standard is given a unique ID# that is the book#-page#-line# where the preparation information is recorded. The traceability of the standard(s) to each analysis is documented in the data cover page.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews to ensure that all required QC samples are present and for proper laboratory documentation practices. The logbook is signed by both the analyst and peer reviewer.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 The method blank and Laboratory Control Standard (LCS) will be included in each laboratory lot of 20 or fewer samples.

8.1.2 The method blank will be examined to determine if contamination is being introduced in the laboratory.

8.1.3 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.4 Precision can be measured by the reproducibility of two LCS's -- when required/requested -- and will be calculated as relative percent difference (%RPD). Results must agree within in-house control limits or statistical control limits in order to be considered acceptable.

8.1.5 All analyses are done in duplicate and one sample per 20 or fewer samples in an analytical batch is done in quadruplicate. Results must agree within the in-house precision/accuracy limits or statistical control limits in order to be considered acceptable.

8.2 Corrective Actions

When an out of control situation occurs, the analysts must use their best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the section manager, QA personnel or the laboratory manager.

Listed below are steps to be taken when an out of control situation occurs. The analyst must:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on a corrective action report form;
- document on the corrective action report that an in control status has been achieved; and
- receive approval (signature) of the section manager, QA personnel, or the laboratory manager prior to the release of any analytical data associated with the problem.

The following are suggested actions to specific out of control situations:

8.2.1 Calibration Curve

- reanalyze the standard curve;
- prepare new stock and/or working standards; and
- check reagents/solutions and prepare fresh if necessary.

8.2.2 Initial Calibration Verification (ICV)

- repeat ICV to verify proper preparation;
- prepare new ICV from original stock;
- check for instrument base-line drift;
- restandardize with existing standards, reanalyze;
- check reagents/solutions and prepare fresh if necessary; and
- prepare new stock and/or working standards and recalibrate.

8.2.3 Initial Calibration Blank (ICB)

- prepare a new ICB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability; and
- determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).

8.2.4 Laboratory Control Standards (LCS)

- reanalyze LCS to verify that an out of control situation exists; and
- determine the source of error within the preparation procedure, correct the problem and repeat the sample set. (Sources of contamination could be either the reagents, the LCS, or the preparation area.)

Precision (if LCS Duplicate is Required): LCS1 and LCS2 must meet the control limits of $\leq$ 20% RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your section manager for proper corrective action.

8.2.5 Preparation Blank (PB)

- reanalyze PB to verify contamination at a level > Reporting Limit;
- determine the source of contamination and correct the problem; and
- all samples whose concentration is <10 times the PB level must be reprocessed and reanalyzed; any sample which is >10 times the PB level need not be reanalyzed. However, a corrective action report must be filled out and approval obtained.

8.2.6 Matrix Duplicate (DUP)

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the ± Reporting Limit rule applies;
- if the reanalysis is within the control limits, the second value is reported; and
- if the reanalysis is still outside of the control limits, the data must be flagged with a "*" and a CAR must be written and then approved by your section manager.

8.2.7 Continuing Calibration Verification (CCV)

- repeat CCV to verify proper preparation;
- prepare new CCV from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control CCV;
- never dispose of any samples until you are sure that all QC are within their designated control limits.

8.2.8 Continuing Calibration Blank (CCB)

- prepare a new CCB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contamination are two common sources); and
- never dispose of any samples until you are sure that all QC are within their designated control limits.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Sample Concentration

$$\text{TOC(mg/kg) or TC (mg/kg)} = \frac{\text{mg C}}{\text{wt. of sample (g)}}$$

An Excel spreadsheet is available for this calculation, and must be included in the raw data (Appendix C). Most analysis is done in duplicate or quadruplicate and the average is reported. Do not correct for % solids since the samples are dried prior to analysis.

9.2 Total Inorganic Carbon

Total Inorganic Carbon (TIC) = TC - TOC

10.0 Waste Management and Pollution Control

Refer to the SOP entitled "Disposal of Laboratory Waste".

11.0 Method Performance Criteria

Refer to the SOP entitled "Laboratory Training: Skills and Mechanisms".

12.0 References

Refer to Section 1.0

13.0 Attachments

Appendix A: Example: Maintenance Logbook
Appendix B: Example: Data Cover Page
Appendix C: Example: Excel Calculation Page

Historical Record: Revision 00: 3/12/99
Revision 01: 9/17/99

Reason for Change: Revision 01:

- Updated Section 7.4.1; Start-up Operation.

U:\QC\SOP\WC\KAHN.DOC

Appendix A.

Example: Maintenance Logbook

STL Chicago
TOC Maintenance Logbook
Instrument No. 3 (Phoenix 8000)

Page No.__________

Date of Maintenance:______________________ Analyst:______________________

Check O_2 Supply: ______________________

Check Carrier Flow (~200 cc/min): ______________

Check Acid Persulfate Levels:______________

Check Calibration / Level:______________

Correlation Coefficient: ______________

System Status:______________

Comments: ____

Date of Maintenance:______________________ Analyst:______________________

Check O_2 Supply: ______________________

Check Carrier Flow (~200 cc/min): ______________

Check Acid Persulfate Levels:______________

Check Calibration / Level:______________

Correlation Coefficient: ______________

System Status:______________

Comments: ____

Date of Maintenance:______________________ Analyst:______________________

Check O_2 Supply: ______________________

Check Carrier Flow (~200 cc/min): ______________

Check Acid Persulfate Levels:______________

Check Calibration / Level:______________

Correlation Coefficient: ______________

System Status:______________

Comments: ____

Reviewer Signature:______________________________ Date:______________

Appendix B.

Example: Data Cover Page

Severn Trent Laboratories Chicago
Total Organic/Inorganic Carbon

Method:

Prep. Batch: _____
File: _____

EPA 415.1 _____
EPA 415.1, mod. for IC _____
SW 846 9060 _____
Lloyd Kahn _____

Instrument: Phoenix 8000 TOC 4

Matrix: _____ soil _____ water

Standard Curve:

Soils ug C	Waters ug C / 4 mL	measured, ug C
0	0	_____
20	4	_____
40	20	_____
80	40	_____
100	60	_____
120	80	_____
160	120	_____
200	160	_____

Corr. Coeff.: _____
y-intercept: _____
slope: _____

Calculations:

soils: $mg/kg = \frac{\text{ug C from instrument}}{\text{grams sample}}$

Soils are air dried, so do not correct for % solids.

waters: mg/L = mg/L X dilution

Standards Traceability:

Stock I : Calibration and Curve : _____
Stock II: LCS, ICV, CCV, Matrix spikes _____
Solid LCS : _____

Spiking Levels:

LCS	_____ ug C	_____ mg/L
ICV	_____ ug C	_____ mg/L
CCV	_____ ug C	_____ mg/L
MS/MSD		_____ mg/L

Analyst: _____ **Date of analysis:** _____

Reviewer: _____ **Date:** _____

Appendix C.

Example: Excel Calculation Page

Severn Trent Laboratories Chicago
Total Organic Carbon Calculation Worksheet

Prep Batch:	
Date of Analysis:	

Method:	Lloyd Kahn
Instrument:	Phoenix - TOC4

Note: Soil samples are air dried prior to analysis so no correction for % Soilds is required.

	Sample ID	µg C (from Instr.)	Sample Amount (g)	Result (mg/kg)	Calc. Detection Limit (20 mg/kg)	Comments
1				#DIV/0!	#DIV/0!	
2				#DIV/0!	#DIV/0!	
3				#DIV/0!	#DIV/0!	
4				#DIV/0!	#DIV/0!	
5				#DIV/0!	#DIV/0!	
6				#DIV/0!	#DIV/0!	
7				#DIV/0!	#DIV/0!	
8				#DIV/0!	#DIV/0!	
9				#DIV/0!	#DIV/0!	
10				#DIV/0!	#DIV/0!	
11				#DIV/0!	#DIV/0!	
12				#DIV/0!	#DIV/0!	
13				#DIV/0!	#DIV/0!	
14				#DIV/0!	#DIV/0!	
15				#DIV/0!	#DIV/0!	
16				#DIV/0!	#DIV/0!	
17				#DIV/0!	#DIV/0!	
18				#DIV/0!	#DIV/0!	
19				#DIV/0!	#DIV/0!	
20				#DIV/0!	#DIV/0!	
21				#DIV/0!	#DIV/0!	
22				#DIV/0!	#DIV/0!	
23				#DIV/0!	#DIV/0!	
24				#DIV/0!	#DIV/0!	
25				#DIV/0!	#DIV/0!	
26				#DIV/0!	#DIV/0!	
27				#DIV/0!	#DIV/0!	
28				#DIV/0!	#DIV/0!	
29				#DIV/0!	#DIV/0!	
30				#DIV/0!	#DIV/0!	
31				#DIV/0!	#DIV/0!	
32				#DIV/0!	#DIV/0!	
33				#DIV/0!	#DIV/0!	
34				#DIV/0!	#DIV/0!	
35				#DIV/0!	#DIV/0!	
36				#DIV/0!	#DIV/0!	
37				#DIV/0!	#DIV/0!	
38				#DIV/0!	#DIV/0!	
39				#DIV/0!	#DIV/0!	
40				#DIV/0!	#DIV/0!	

Severn Trent Laboratories Chicago
Total Organic Carbon Calculation Worksheet

	RFW #	µg C (from Instr.)	Sample Amount (g)	Result (mg/kg)	Calc. Detection Limit (20 mg/kg)	Comments
41				#DIV/0!	#DIV/0!	
42				#DIV/0!	#DIV/0!	
43				#DIV/0!	#DIV/0!	
44				#DIV/0!	#DIV/0!	
45				#DIV/0!	#DIV/0!	
46				#DIV/0!	#DIV/0!	
47				#DIV/0!	#DIV/0!	
48				#DIV/0!	#DIV/0!	
49				#DIV/0!	#DIV/0!	
50				#DIV/0!	#DIV/0!	
51				#DIV/0!	#DIV/0!	
52				#DIV/0!	#DIV/0!	
53				#DIV/0!	#DIV/0!	
54				#DIV/0!	#DIV/0!	
55				#DIV/0!	#DIV/0!	
56				#DIV/0!	#DIV/0!	
57				#DIV/0!	#DIV/0!	
58				#DIV/0!	#DIV/0!	
59				#DIV/0!	#DIV/0!	
60				#DIV/0!	#DIV/0!	
61				#DIV/0!	#DIV/0!	
62				#DIV/0!	#DIV/0!	
63				#DIV/0!	#DIV/0!	
64				#DIV/0!	#DIV/0!	
65				#DIV/0!	#DIV/0!	
66				#DIV/0!	#DIV/0!	
67				#DIV/0!	#DIV/0!	
68				#DIV/0!	#DIV/0!	
69				#DIV/0!	#DIV/0!	
70				#DIV/0!	#DIV/0!	
71				#DIV/0!	#DIV/0!	
72				#DIV/0!	#DIV/0!	
73				#DIV/0!	#DIV/0!	
74				#DIV/0!	#DIV/0!	
75				#DIV/0!	#DIV/0!	
76				#DIV/0!	#DIV/0!	
77				#DIV/0!	#DIV/0!	
78				#DIV/0!	#DIV/0!	
79				#DIV/0!	#DIV/0!	
80				#DIV/0!	#DIV/0!	
81				#DIV/0!	#DIV/0!	
82				#DIV/0!	#DIV/0!	
83				#DIV/0!	#DIV/0!	
84				#DIV/0!	#DIV/0!	
85				#DIV/0!	#DIV/0!	
86				#DIV/0!	#DIV/0!	

Date Entered By: _____ Date: _____

APPENDIX A-77

STANDARD OPERATING PROCEDURE FOR TOTAL ORGANIC CARBON/TOTAL INORGANIC (DISSOLVED) CARBON

SOP No.	Revision No.	Date	Page
UWC-SOP-415.1	03	06/25/99	1 of 15

TITLE: Wet Chemistry
Total Organic Carbon / Total Inorganic (Dissolved) Carbon

Updated by:	Signature:	Date
Diane L. Harper Section Manager, Wet Chemistry	Diane L Harper	6/24/99

Approved by:	Signature:	Date
Diane L. Harper Section Manager, Wet Chemistry	Diane L Harper	6/24/99
Raymond J. Frederici Quality Manager	Ray J Fred	6-24-99

CONTROLLED DISTRIBUTION

COPY # : 030

ISSUED TO : Shawn Nordstrom - USACE
U.S. Housatonic River Site Project

Full Signature Approvals Are Kept on File with
Severn Trent Laboratory QA Standard Practice Records

1.0 SCOPE / APPLICATION

This Standard Operating Procedures is used to quantitatively determine the Total Organic Carbon and Total Inorganic (Dissolved) Carbon (TIC/DIC) content in water matrices using UV/persulfate oxidation and non-dispersive IR detection. Total Carbon and Inorganic Carbon may also be measured by setting up the instrument differently.

This SOP was written using EPA Method 415.1 and SW 846 Method 9060 as references. The analyst also must use the individual instrument Operations Manuals as references.

1.1 Method Sensitivity

1.1.1 Method Detection Limits

The method detection limit (MDL) is the lowest concentration that can be measured for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to Appendix B of 40 CFR 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants". MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually.

1.1.2 Reporting Limits

Waters.....1.0 mg/L

Reporting Limits are defined as the lowest concentration of an analyte determined by a given method in a given matrix that the laboratory feels can be reported with acceptable quantitative error or client requirements, values specified by the EPA methods or other project and client requirements. Because of the high level of quantitative error associated with determinations at the level of the MDL, the laboratories endeavor to keep reporting limits higher than the MDL. Wherever possible, reporting is limited to values approximately 3-5x the respective MDL to ensure confidence in the value reported. Client specific requests for reporting to the IDL or MDL are special circumstances not to be confused with the previous statement.

1.2 Summary of Method

The measurement of Total Organic Carbon (TOC) indicates the presence of organically bound carbon. Organic chemicals are of a primary environmental concern because of their wide spread industrial and agricultural uses. TOC analysis provides the basic screening measurement to warrant subsequent specific analyses if high TOC levels are found.

Inorganic carbon, in the form of carbonates and bicarbonates, present in a liquid sample is removed by acidifying the sample and sparging with oxygen to remove carbon dioxide. The remaining organic carbon is oxidized to carbon dioxide by acidified persulfate in the presence of ultraviolet light. This carbon dioxide is carried to an infrared analyzer. A microprocessor calculates the area of the peaks produced by the analyzer, compares them to the peak area of the calibration standards stored in the memory, and prints out a calibrated organic carbon value in mg/L. TIC/DIC values are determined via calculation

1.2.1 Theory of Operation

Liquid samples are introduced through a sipper probe on an automatic analyzer. Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC) are each determined on the same sample. In the TOC mode, acid and persulfate are automatically loaded into the reactor and sparged. The inorganic carbonates are converted to CO_2 and measured by a Non-Dispersive Infrared Analyzer (NDIR) as TIC. The ultra-violet source is then activated and sodium persulfate is added to the elevated temperature reactor module to convert the organic carbon to carbon dioxide which is measured by the NDIR and is directly proportional to the total organic carbon in the sample. Spent sample and reagents are purged from the unit and the next sample is then analyzed after an automatic system wash.

2.0 INTERFERENCES

2.1 Persulfate oxidation is slowed in samples containing significant concentrations of chloride by the preferential oxidation of chloride. At a concentration of 0.1% chloride, oxidation of organic matter may be inhibited completely.

2.2 To obtain TOC results, carbonates and bicarbonates, positive interferences, must be completely removed by acidification and sparging of a clean gas (O_2 or N_2) to remove CO_2.

2.3 Excessive acidification of sample, producing a reduction in pH of the persulfate solution to 1 or less, can result in sluggish and incomplete oxidation of organic carbon.

2.4 The intensity of the ultraviolet light reading the sample matrix may be reduced by highly turbid samples, resulting in sluggish or incomplete oxidation.

2.5 Large organic particles or very large or complex organic molecules may be oxidized slowly because persulfate oxidation is rate limited.

2.6 Improper sample handling and treatment is a likely source of contamination.

3.0 SAFETY

As always, general laboratory safety practices should always be followed. Waste samples should be handled with care due to the uncertainty of the properties and contents involved. Refer to the specific MSDS for the hazardous properties of any chemical or reagent involved in this procedure.

4.0 EQUIPMENT AND SUPPLIES

- Astro System 2 Model 2001 Automated Laboratory Organic Carbon Analyzer or the Dohrmann Phoenix TOC Analyzer.
- 20x150mm test tubes are used in the Astro autosampler and VOA vials, with or without septa are used in the Phoenix sampler.

5.0 REAGENTS AND STANDARDS

All standards and reagents are prepared with Type II Deionized Water, unless otherwise specified. All standards and reagents are prepared in Class A volumetric glassware and stored at 4 $\pm$ 2°C when required.

5.1 Stock Organic Carbon Standard I (2000 mg/L)

Prepare a 2000 mg/L standard by weighing 425 mg of reagent grade potassium hydrogen phthalate dried to a constant weight, and transferring quantitatively with reagent water to a 100 mL Class A volumetric flask, dissolve and add 0.1 mL of concentrated nitric acid and dilute to volume with DI Water.

- Life of Reagent: one month
- Storage Requirements: glass amber bottle

5.2 Stock Carbon Standard II (2000 mg/L)

Prepare as Reagent 8.1 **EXCEPT** prepare from an alternate source.

5.3 Sodium Persulfate for use in the Astro 2001

Prepare by dissolving 357 g of reagent sodium persulfate in 1-liter of Milli-Q water.

- Life of Reagent: one year
- Storage Requirements: none

5.4 Sodium Persulfate for use in the Phoenix 8000

Prepare by dissolving 25 grams of sodium persulfate in 213 mL of Milli-Q water and adding 9 mL of 85% (concentrated) phosphoric acid. Double or triple the preparation as required.

- Life of Reagent: one year
- Storage Requirements: none

5.5 0.1 M Phosphoric Acid for use in the Astro 2001

Prepare by adding 118 mLs concentrated phosphoric acid to 500 mLs Milli-Q water in a 1.0 liter volumetric flask. Dilute to volume with Milli-Q water.

- Life of Reagent: one year
- Storage Requirements: none

5.6 21% Acid Reagent for use in the Phoenix 8000

Add 37 mL of 85% (concentrated) phosphoric acid to 188 mL of Milli-Q water. Double or triple the preparation as needed.

- Life of Reagent: one year
- Storage Requirements: none

5.7 TIC Standard I (2000 ppm)

In a 1.0 L volumetric flask, dissolve 17.6667 g sodium carbonate in freshly boiled and cooled milli-Q water.

- Life of Reagent: one month
- Storage Requirements: glass amber bottle

5.8 TIC Standard II (1000 ppm)

In a 100 mL volumetric flask, dissolve 0.35 g sodium bicarbonate and 0.4418 g sodium carbonate in freshly boiled and cooled milli-Q water.

- Life of Reagent: one month
- Storage Requirements: glass amber bottle

6.0 CALIBRATION

Instrument calibration consists of two types: Initial Calibration and Continuing Calibration.

6.1.1 Initial Calibration

Establishes the calibration range of the instrument and determines the instrument response over that range.

TOC analyzers will be calibrated prior to each day of use. The laboratory analyzers have the option of a single concentration calibration standard or a multiple point curve calibration. If the latter is used the linearity must be confirmed by running a daily linear range curve with a blank and five (5) concentrations which cover the anticipated range of measurement. One of the calibration standards will be at the desired detection limit. The requirement for an acceptable initial calibration will be a correlation coefficient equal to or greater than 0.995.

If the correlation coefficient criteria of 0.995 is not met, the instrument will be recalibrated prior to analysis of samples. Calibration data, to include the correlation coefficient, will be entered into the TOC bench cover sheet kept with the sample data to maintain a permanent record of instrument calibrations.

Before sample analysis, an Initial Calibration Verification (ICV) Standard is analyzed. The response calculated as percent recovery of this standard must be within $\pm$ 15% of the true value or the instrument is recalibrated.

6.1.2 Continuing Calibration

Used within an analytical sequence to verify stable calibration throughout the sequence, and/or to demonstrate that instrument response did not drift during a period of non-use of the instrument.

A Continuing Calibration Verification standard (CCV) and Blank (CCB) will be analyzed at a frequency of every ten sample and at the end of the analysis sequence. The response, calculated as a percent recovery of the true value, must be $\pm$ 15% of the true value. The response of the blank must be less than the detection limit.

7.0 PROCEDURE

7.1 Quality Control Checks

Calibration Controls	Sequence	Control Limit
Single Cal. Standard (10 or 20 mg/L, specify in data)	prior to samples	
Standards (Curve)	prior to samples	y-int. < Reporting Limit
Corr. Coeff.	prior to samples	$\geq$ 0.995
Init./Cont. Cal. Ver. (ICV/CCV)	every 10 samples	85 - 115%
Init./Cont. Cal. Blk. (ICB/CCB)	every 10 samples	< Reporting Limit

Quality Controls	Frequency	Control Limit
Prep Blank (PB)	1 in 20 samples	< Reporting Limit
Lab Control Std. (LCS)	1 in 20 samples	*80-120%
**LCS Duplicate	1 in 20 samples	*80 - 120%
***Matrix Spike (MS/MSD)	1 in 20 samples	*75 - 125%

*In-house statistical limits or individual QAPP limits may be required rather than those in the table. Refer to the paper work accompanying a project's in-house chain-of-custody for appropriate limits to use for each sample.
**The reading of a second LCS is optional and specifically not needed for some clients. Refer to the paper work accompanying a project's in-house chain-of-custody for appropriate QC requirements.
***When analyzing quads according to SW-846 9060, a matrix spike and matrix spike duplicate must be analyzed on 1 in 10 samples.

7.2 Sample Preservation and Storage

Holding time, preservation techniques and sample container may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client request. Listed below are the holding times, and the references which include container and preservation requirements for compliance with the Clean Water Act (CWA).

Regulation	Holding Time	Reference
CWA	28 days	40CFR, Pt. 136.3

7.3 Sample Preparation

The pH of every sample is checked with pH indicator paper prior to analysis to ensure proper preservation. If the pH of a sample is not <2, three drops of concentrated phosphoric acid are added to the sample after it has been poured into an auto sampler tube for analysis.

Care is taken not to mix or shake the TOC sample container in order to prevent loss of volatile organic carbon compounds. If a sample contains sediment, the liquid portion is decanted into a clean beaker. The beaker contents are mixed thoroughly, pH adjusted if necessary, poured into sample vials or tubes, and arranged on the auto sampler.

If the sample appears dirty or has a strong odor, the sample usually contains a high amount of TOC and is thus diluted prior to its initial analysis to avoid overloading the infrared analyzer or clogging instrument tubing. All dilutions must be preserved with concentrated phosphoric acid. Should a diluted sample display a TOC result below the reporting limit, the sample is reanalyzed at a lower dilution or at full strength.

All TOC water samples are analyzed in replicate (415.1) or quadruplicate (9060).

Samples that contain gross solids or insoluble matter, homogenize until satisfactory replication is obtained. It may be necessary to decant some groundwater samples that contain unwanted sediments. Mix well before decanting.

7.4 Calibration / Standardization

7.4.1 Standard Curve Preparation

Prepare the following Standard Curve on a daily basis.

Stock Organic Standard I (Standard 8.1)	Volume of Standard (use eppendorf pipettes)
0 mg/L	200 mLs DI Water
1 mg/L	100 uL diluted to 200 mLs DI Water
5 mg/L	500 uL " "
10 mg/L	1000 uL " "
15 mg/L	1500 uL " "
20 mg/L	2000 uL " "

NOTE: For TIC/DIC, prepare the curve using the same volume of standard as TOC but use the TIC Standard I.

7.4.2 Matrix Spike Preparation

Dilute 0.5 mLs of Stock Organic Carbon Standard II (Std. 8.2) to 100 mLs of sample.
Concentration: 10 mg/L.

For TIC/DIC: Dilute 1.0 mL TIC Standards II to 100 mLs sample.
Concentration: 10 mg/L

7.4.3 ICV/CCV Solution Preparation

Dilute 1 mL of Stock Organic Carbon Standard II (Std. 8.2) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water acidified with phosphoric acid.
Concentration: 10 mg/L.

For TIC/DIC: Dilute 2 mLs of TIC Standard II into a 200 mLs volumetric flask. Dilute to volume with milli-Q water.
Concentration: 10 mg/L.

7.4.4 CCB Solution Preparation -- For TOC/TIC/DIC

Milli-Q water acidified with phosphoric acid.

7.4.5 LCS Preparation

Dilute 0.5 mL of Stock Organic Carbon Standard II (Std. 8.2) into a 200 mL volumetric flask. Dilute to volume with Milli-Q water, acidified with phosphoric acid.
Concentration: 5 mg/L

For TIC/DIC: Dilute 1.0 mL of TIC Standard II into a 200 mL volumetric flask. Dilute to volume with Milli-Q water.
Concentration: 5 mg/L

7.5 Preventive Maintenance

Follow the individual instrument manuals recommendations for preventive maintenance. Make sure that the laboratory maintenance manual is maintained for each instrument on each day of operation.

7.6 Sample Analysis

Sample Size.....10 mL per injection

Follow the individual analyzer manuals for instructions for setting up the computer and operating the instrument. Both of the laboratory's TOC analyzers are PC driven. Analysis of each injection requires approximately 6-10 minutes, depending on the concentration of TOC in the sample.

All standards, blanks and quality control samples are analyzed in duplicate.

7.7 Documentation

7.7.1 Instrument Print-out

The analysis of samples and standards is documented within the instrument print-out.

7.7.2 Traceability of Standards

Upon receipt, each chemical is recorded in a bound chemical receipt log book and is issued a unique source ID#. The manufacturer, lot #, date received, expiration date, and the initials of the recording analyst are documented in the log book. When a standard is prepared at the laboratory, the Source ID# and weight of the chemical, the type and volume of solvent, concentration, date of preparation, date of expiration, preservative if applicable, and the analyst's initials are recorded in the Standards Preparation Log. Each standard is given a unique ID# that is the book#-page#-line# where the preparation information is recorded. The traceability of the standard(s) to each analysis is documented in the analysis logbook.

7.7.3 Data Review

Analytical data goes through a 200% review cycle. The analyst and a trained data reviewer perform the reviews according to the criteria established on the data review form. Upon the first 100% review, the review form is initialed and dated as reviewed. The package, with its review sheet, comments and any corrective action reports is submitted to the section manager or peer reviewer for a second review. Once again, the review form is initialed and dated by the second reviewer.
The completed data review form remains on file with the original data.

8.0 QUALITY CONTROL

8.1 QC Summary

8.1.1 One method blank and one or two Lab Control Standards (LCS) will be included in each laboratory lot of 20 samples. Regardless of the matrix being processed, the LCS and method blanks will be in an aqueous media.

8.1.2 The method blank will be examined to determine if contamination is being introduced in the laboratory.

8.1.3 The LCS's will be examined to determine both precision and accuracy.

8.1.4 Accuracy will be measured by the percent recovery (%R) of the LCS. The recovery must be in range, as determined by in-house control limits or statistical analysis, in order to be considered acceptable. Additionally, %R will be plotted on control charts to monitor method accuracy.

8.1.5 Precision will be measured by the reproducibility of both injections for each analysis, but will only be statistically generated for LCS data. Results must agree within in-house control limits or statistical control limits in order to be considered acceptable.

8.1.6 One matrix spike, read in duplicate is performed per matrix per 20 sample analytical set. Results must agree within the in-house precision/accuracy limits or statistical control limits in order to be considered acceptable.

8.2 Corrective Action

When an out of control situation occurs, the analysts must use his/her best analytical judgment and available resources to determine the corrective action to be taken. The out of control situation may be caused by more than one variable. The analyst should seek the assistance of his/her immediate supervisor, QA personnel, or other experienced staff if he/she is uncertain of the cause of the out of control situation. The test must not be resumed until the source of the problem and an in-control status is attained. All samples associated with the out of control situation should be reanalyzed. Out of control data must never be released without approval of the supervisor, QA personnel or the lab manager.

Listed below are steps to be taken when an out of control situation occurs. The analyst must:

- demonstrate that all the problems creating the out of control situation were addressed;
- document the problem and the action which was taken to correct the problem on a corrective action report form;
- document on the corrective action report that an in control has been achieved; and
- receive approval (signature) of the Section Manager, QA personnel, or the Laboratory Manager prior to the release of any analytical data associated with the problem.

Suggested Actions to specific out of control situations:

8.2.1 Calibration Curve

- reanalyze the standard curve;
- prepare new stock and/or working standards;
- check reagents/solutions and prepare fresh if necessary.

8.2.2 Initial Calibration Verification (ICV)

- repeat ICV to verify proper preparation;
- prepare new ICV from original stock;
- check for instrument base-line drift;
- restandardize with existing standards, reanalyze;
- check reagents/solutions and prepare fresh if necessary;
- prepare new stock and/or working standards and recalibrate;

8.2.3 Initial Calibration Blank (ICB)

- prepare a new ICB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze. (Carry over from a previous analysis or reagent contamination are two common sources).

8.2.4 Laboratory Control Standards (LCS)

If either LCS1 or LCS2 exceeds acceptance limits:

- reanalyze LCS to verify that an out of control situation exists;
- determine the source of error within the preparation procedure, correct the problem and repeat the sample set. Sources of contamination could be either the reagents, the LCS stock solution, or the preparation area.

NOTE: When LCSs are high, any samples that are less than the reporting limit may be reported.

Precision: LCS1 and LCS2 must meet the control limits of $\leq$ 20% RPD. If this criteria is not met, and both LCS's meet the % Recovery control limits, then see your Section Manager for proper corrective action.

8.2.5 Preparation Blank (PB)

- reanalyze PB to verify contamination at a level > Reporting Limit;
- determine the source of contamination and correct the problem;
- all samples whose concentration is <10 times the PB level must be reprocessed and reanalyzed; any sample which is >10 times the PB level need not be reanalyzed. However, a corrective action report must be filled out and approval obtained.

8.2.6 Sample Replicates

- the sample must be reprocessed and reanalyzed unless the sample concentration is <5 times the Reporting Limit, then the $\pm$ Reporting Limit rule applies;
- if the reanalysis is within the control limits, the second value is reported;
- a CAR must be written and then approved by your section manager.

8.2.7 Matrix Spike (MS)

- the sample must then be reprocessed and reanalyzed unless the sample concentration exceeds the spike concentration by a factor of 4 times;
- the original spike results must be entered onto the spreadsheet with the "S" code even though the control limits were exceeded;
- the reanalysis result must be entered onto the spreadsheet using the "T" code regardless of whether it is within the control limits. A CAR must be written and then approved by your Section Manager.

8.2.8 Continuing Calibration Verification (CCV)

- repeat CCV to verify proper preparation;
- prepare new CCV from original stock;
- check for instrument base-line drift;
- check reagents/solutions and prepare fresh if necessary;
- recalibrate with a new standard curve and repeat all samples since the previous in control CCV;
- never dispose of any samples until you are sure that all QC are within their designated control limits.

8.2.9 Continuing Calibration Blank (CCB)

- prepare a new CCB to verify proper preparation;
- verify that the instrument base-line is stable and/or perform necessary maintenance, cleaning, etc... to achieve stability;
- determine the source of contamination by the process of elimination, correct the problem and reanalyze all the samples since the previous in control CCB. (Carry over from a previous analysis or reagent contamination are two common sources).
- never dispose of any samples until you are sure that all QC are within their designated control limits.

9.0 DATA ANALYSIS AND CALCULATIONS

9.1 Sample Results

mg/L values are read directly from the instrument printer and entered on the TOC Lotus Spreadsheet.

*Typically, the individual results of the replicate or quadruplicate analysis of samples are reported to the clients. Some clients prefer to have the mean of the readings reported. The mean is given directly in the Phoenix print-out, but must be manually calculated from the Astro print-out. The replicate results must meet the laboratory precision requirements. The high and low results obtained from quadruplicate analysis must meet the laboratory precision requirements.

9.1.1 For TIC (DIC) mg/L values will be entered on a standard LOTUS spreadsheet and the calibration curve will be used to calculate the results.

9.2 Accuracy

9.2.1 ICV/CCV, LCS % Recoveries

$$\%R = \frac{\text{avg. observed concentration}}{\text{actual concentration}} \times 100$$

9.2.2 Matrix Spike % Recovery

$$\%R = \frac{\text{(spike sample result) - (unspiked sample result)}}{\text{spike concentration}}$$

9.3 Precision

Matrix Duplicate and LCS Duplicate Relative Percent Difference (RPD):

$$RPD = \frac{|\text{orig. sample value - dup. sample value}|}{[(\text{orig. sample value} + \text{dup. sample value})/2]} \times 100$$

*For calculating duplicates and matrix spikes, the original sample value is the average of the replicate/quadruplicate results of the sample.

9.4 Reporting Results

Without rounding, enter the raw data on the appropriate Lotus spreadsheet. Save the worksheet and print file, then print, review and approve the spreadsheet, using the appropriate data checklist. Have the raw data and spreadsheet approved and signed by a designated reviewer before the print file is transferred to LIMS.

10.0 Waste Management and Pollution Control

Refer to the SOP entitled "Laboratory Waste Disposal Procedures".

11.0 Method Performance Criteria

Refer to the SOP entitled "Laboratory Training: Skills and Mechanisms".

12.0 References

Refer to Section 1.

13.0 Attachments

None.

Historical File:
Revision 00: 01/08/93
Revision 01: 11/09/93
Revision 02: 05/08/98
Revision 03: 06/25/99

Reasons for Change, Revision 03:

- Change in company name in the headers, footers and text (where applicable) from RECRA to STL resulting from the January acquisition of our laboratory by Severn Trent Laboratories.
- No text changes.

U:\QC\SOP\WC\4151.DOC

APPENDIX A-78

STANDARD OPERATING PROCEDURE FOR METHOD 8270C DETERMINATION OF EXTRACTABLE SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROSCOPY

STANDARD OPERATING PROCEDURE METHOD 8270C
DETERMINATION OF EXTRACTABLE SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

Approvals and Signatures

Laboratory Director: _____ Date: 12-2-98

QA Officer: _____ Date: 12-2-98

Organics Laboratory Manager: _____ Date: 12/2/98

1.0 SCOPE AND APPLICATION

1.1 This SOP is based on Method 8270C (USEPA Test Methods for Evaluating Solid Waste, Dec. 1996). The analytical method that follows is designed to analyze sample extracts prepared from a variety of sample matrices. Sample matrices include; water, soil, sediment, solid waste, tissues, and air sampling media. Compounds analyzed by this method can be found in Table 1.

1.2 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography.

1.3 This method involves solvent extraction of the matrix sample, characterization to determine the appropriate analytical protocol to be used followed by appropriate cleanup procedure and GC/MS analysis to determine the semivolatile organic compounds present in the sample.

1.4 Problems have been associated with the following compounds analyzed by this method:

1.4.1 Dichlorobenzidine and 4-chloroaniline can be subject to oxidative losses during solvent concentration.

1.4.2 Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reactions in acetone solution, and photochemical decomposition.

1.4.3 N-nitrosodiphenylamine decomposes in the gas chromatograph inlet forming diphenylamine and, consequently, may be detected as diphenylamine.

2.0 SUMMARY OF METHOD

2.1 A one liter aliquot of a liquid sample or a 30 g aliquot of a soil sample (or 1g of soil for medium level) is spiked with a surrogate compound mixture and then extracted with methylene chloride. The final extract is concentrated to 500 uL. A 2.0 uL aliquot of the concentrated final extract is injected into the gas chromatograph, where it is volatilized in the injection port and swept onto the chromatographic column. A temperature program is used to separate the semivolatile compounds, and they are carried on the gas stream into the ion source of a mass spectrometer. The end of the column is positioned so the eluting compounds are ionized immediately. The ionized molecules are focused and separated according to their mass/charge (m/z) by the quadrupole analyzer. The signal is amplified by an electron multiplier and interpreted by the mass spectrometer data system to produce a total ion chromatogram and mass spectra for every data point on the chromatogram. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard with a five point calibration curve.

2.2 The mass spectrometer is calibrated to recognize m/z values in the range of 35-500 amu with a scan rate not to exceed one second. Instrument performance is verified by the injection of Decafluorotriphenylphosphine (DFTPP). The ion abundances must meet the criteria shown in Table 2 before analyses can proceed. If the criteria are met, the instrument then must demonstrate acceptable chemical calibration and linearity by the injection of 5 concentrations of a standard mix containing the analytes of interest, as well as the internal standards. If the sensitivity (relative response factor, RRF) and linearity (relative standard deviation, %RSD) criteria shown in Table 3 are met the analysis may proceed. All analyses must occur within 12 hours of the injection of the passing DFTPP. Another analytical sequence may be started by analysis of a passing DFTPP followed by a continuing calibration standard. This standard must meet the sensitivity (RRF) and linearity (difference from the initial calibration , %D) criteria shown in Table 3 before analysis of samples may proceed.

2.3 Analysis: 40 days from extraction. Analyze all samples within 40 days of extraction. Note that extraction holding times for waters are 7 days from collection. Extraction holding time for soil samples is 14 days from collection.

3.0 DEFINITIONS

3.1 INTERNAL STANDARD (IS)

Non-target analyte compounds that are similar to the target analytes but are not expected to be found in environmental media (generally, isotopically labeled target analytes are used for this purpose) and are added to every standard, quality control sample, and field sample at a known concentration prior to analysis. IS responses are used as the basis for quantitation of target analytes.

3.2 SURROGATE ANALYTE (SS)

Non-target analyte compounds that are similar in composition and behavior to the target analytes but are not expected to be found in environmental media (often, isotopically labeled target analytes are used for this purpose) and are added to every standard, quality control sample, and field sample at a known concentration prior to preparation and/or analysis. Surrogate responses are used to evaluate the accuracy of the laboratory's performance of the analytical method in a specific sample matrix.

3.3 STOCK STANDARD SOLUTION

A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.4 PRIMARY DILUTION STANDARD SOLUTION

A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.5 CALIBRATION STANDARD (CAL)

A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.6 INITIAL CALIBRATION VERIFICATION (ICV)

An analytical standard solution containing all target analytes, surrogate and internal standard compounds that are prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The purpose of the ICV is to verify that the initial calibration is in control.

3.7 CONTINUING CALIBRATION VERIFICATION (CCV)

An analytical standard solution containing all target analytes, surrogate and internal standard compounds that is used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 METHOD BLANK (SBLK, similarly known as the LABORATORY REAGENT BLANK)

An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The SBLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.9

3.10 LABORATORY CONTROL SAMPLE (LCS)

The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. Its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements. When the results of the matrix spike analysis indicates a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

3.11 LABORATORY FORTIFIED SAMPLE MATRIX/SAMPLE MATRIX DUPLICATE (MS/MSD)

An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS/MSD is analyzed exactly like a sample. Its purpose is used to evaluate the accuracy and precision of the laboratory performance of the analytical method in a specific sample matrix.

3.12 SYSTEM PERFORMANCE CHECK COMPOUNDS (SPCCs)

Selective analytes from the compound list that are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. These compounds are identified in Table 3 (SPCC).

3.13 CALIBRATION CHECK COMPOUNDS (CCCs)

Selective analytes from the compound list that are used to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. These compounds are identified in Table 3 (CCC).

4.0 INTERFERENCES

4.1 Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts and/or elevated baselines in the extracted ion current profiles (EICPs). All of these materials routinely must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

4.2 Interferences from carryover contamination must be evaluated in samples subsequent to the analysis of extracts containing high-concentrations of target and non-target constituents.

4.3 Carryover contamination may be eliminated by ensuring that enough time has been allowed at elevated oven temperatures in order to permit elution of all sample constituents.

4.4 Sample syringe should be adequately flushed with solvent between injections in order to remove all traces of the prior sample.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these reagents should be reduced to the lowest possible level. A reference file of data handling sheets is available to all personnel involved in these analyses. Specifically, concentrated sulfuric acid presents some hazards and is moderately toxic and extremely irritating to skin and mucous membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing, and observe proper mixing when working with these reagents.

6.0 EQUIPMENT AND SUPPLIES

6.1 Instrumentation

- 6.1.1 SVOA Autosampler: HP 7673A™, CTC A200S™, or equivalent liquid sample sampler.
- 6.1.2 Gas Chromatograph: Hewlett-Packard™ 5890 GC
- 6.1.3 Mass Spectrometer: Hewlett-Packard™ 5971 and 5972 MSDs
- 6.1.4 Data System: Hewlett-Packard Chem server™, Target 3.1 software used for data processing
- 6.1.5 Balance: Capable of weighing to 0.1 mg (Neat standard preparation).

6.2 Supplies

- 6.2.1 Syringes: Micro syringes; 10 uL, 25 uL, 50 uL, 100uL, 1000uL.
- 6.2.2 Vials: 2 mL Autosampler vials with 200 uL inserts, PFTE crimp top. 4 mL sample vials with PFTE lined screw top caps.
- 6.2.3 Primary Column: Restek™ RTx-5 30m x 0.25mm ID x .25 um film thickness, or equivalent
- 6.2.4 Guard Column: Restek™ Deactivated 5m x 0.25 mm ID, or equivalent
- 6.2.5 Column unions: Restek Press-Tights™, or equivalent
- 6.2.6 Injection port liners: Single goose neck, borosilicate glass. Restek™ part number 20799, or equivalent
- 6.2.7 Injection port septa: HP™, 11 mm Thermo Red, or equivalent

7.0 REAGENTS AND STANDARDS

7.1 Pesticides grade Methylene Chloride (CH_2Cl_2), Hexane, Acetone, and Methanol.

7.2 Stock Standards are commercially prepared and certified solutions that contain mixes of the target analytes, generally at concentrations of 2-5 mg/mL. Commercial standards arrive as ampulized materials with vendor certifications and expiration dates.

7.3 *Primary Dilution standards*. *Stock standards* are used to prepare intermediate concentration, combined mix standards, that are easily diluted for use as working standards. For this method the primary dilution standard is combination of stock standards that comprise a calibration mix (CAL MIX) at a concentration of 166.67 ng/uL in methylene chloride. The calibration mix includes all target compounds and the *surrogate* compounds. The ampulized stocks and the primary dilution standard are stored at 4°C. Neat and ampulized material may be stored for 1 year (unless superceded by manufactures expiration date), diluted material may be stored for six months (unless standard degradation is apparent). Corrective action for degraded standards is reformulation with new or fresh

material.

7.4 *Calibration* or *working standards* are prepared by diluting the CAL MIX, in methylene chloride, into the final working concentrations that constitute the calibration range of the method (20, 50, 80, 120, 160 ng/ per 2 uL injection). Working standards are prepared at a final volume of 100 uL, and are therefore only good for one day.

7.5 *Internal standard* spiking solution contains the compounds that will be used as internal standards used for final compound concentration calculation. The spiking solution is prepared by diluting a commercially prepared mix (i.e. Restek™ Internal Standard Mix) in methylene chloride, to a concentration of 500ng/uL. This solution is good for 6 months, and stored at 4°C. Each 100 uL aliquot of sample, standard, and blank is spiked with 4 uL for a final extract concentration of 20 ng/uL (40 ng on column, 2 uL injection).

7.6 Initial Calibration Verification (ICV). The ICV mix is an independent source calibration mix (separate vendor or separate lot) used to confirm the accuracy and precision of the initial calibration. The solution is prepared from ampulized stock materials that are combined to include all target compounds and surrogates. The ICV stock is diluted with methylene chloride to a final concentration of 25 ng/uL. This represents a mid point of the calibrated range and is prepared by adding 4 uL of the ISTD mix to 100 uL of the 25ng/uL ICV solution (50 ng on column per 2 uL injection).

7.7 *Tune verification*, or DFTPP mix. A 25ng/uL solution is prepared from ampulized stock material that contains DFTPP, Benzidine, Pentachlorophenol, and DDT. A 2 uL aliquot of this mixture is analyzed at the onset of every analytical sequence to verify compliance with mass spectral acceptance criteria and chromatographic tailing performance.

7.8 *Surrogate, Matrix, and LCS* spiking solutions. These solutions are spiked into samples prior to extraction and concentration. Refer to the appropriated Extraction Procedure SOP for guidelines in the preparation and use of these solutions.

7.9 Additional solutions may be prepared from neats or ampulized material in order to satisfy specific project objectives. These solution are to be prepared in accordance with the guidelines of the method.

8.0 SAMPLE COLLECTION,PRESERVATION, AND STORAGE

8.1 Refer to the Extraction Procedure SOP for information on the Collection, Preservation and Storage of samples prior to the extraction process.

8.2 Sample extract handling. Extracts are collected and stored in 2-4mL amber sample vials with PFTE lined screw caps. Extracts are stored, away from light, at -10°C until sample analysis. Sample extracts are considered viable for 40 days from sample extraction.

8.3 Sample extracts are pre-screened prior to analysis, refer to the Sample Extract Screening Procedure SOP.

9.0 QUALITY CONTROL CRITERIA

9.1 DFTPP acquisition. Prior to the analysis of any calibration curve, calibration verification, samples, or blanks, it is necessary to confirm that instrumentation meets the tuning acceptance criteria (see Table 2). Analyze 2 uL of the Tune Verification Mix and generate to the Tune Verification report. Evaluation of the DFTPP spectra is carried out by the data processing system and includes the summation of three scans (apex scan, scan prior, and scan preceding) with background subtraction of a scan prior to the peak. If the acceptance criteria are met then instrument calibration or calibration verification may proceed. If the acceptance criteria is not met, re-analyze the solution. If tuning criteria can not be met then sample analysis is prohibited. Corrective action; re-tune the mass spectrometer either through automated routines or manually. Re-analyze tune mix to verify compliance with the acceptance criteria. Note: all subsequent standards, samples, blanks, and QC samples associated with a passing DFTPP must be acquired using identical instrument and tune conditions. Evaluate column performance and injection port inertness probes for tailing

(Pentachlorophenol and Benzidine), none should be visible.

9.2 Initial Calibration. Prior to the analysis of samples it is necessary to calibrate the instrumentation using five concentrations levels that define the linear range of the analysis (20, 50, 80, 120, 160 ng/ 2 uL injection). Initial calibration is required whenever calibration verification fails or instrumental conditions have been significantly modified through maintenance or repair. The initial calibration must include all compounds of interest, as specified by the project objectives and/or the methodology, at each of the concentration levels. Acceptance criteria for the initial calibration are defined in Table 3. Additionally all Calibration Check Compounds (CCC) and System Performance Check Compounds (SPCC) compounds must pass the 30%RSD and 0.050 minimum RF criteria respectively. All target compounds (with the exception of the CCCs) have a maximum 15 %RSD limit. Alternative calibration evaluation options are presented in Method 8000 and may be used but must be utilized for all subsequent calculations and calibrations. (Note: Utilization of the mean RRF to validate calibrations is the preferred option). Failure to meet the criteria requires re-calibration. Corrective action, such as instrument maintenance, cleaning, and column replacement, may be necessary in order to achieve valid calibration.

9.3 Initial Calibration Verification is performed to confirm the accuracy of the initial calibration using an independent calibration source. The ICV must agree with the calibration, using the criteria set forth in the evaluation of the continuing calibration verification (see Table 3). Failure to meet the acceptance criteria will require evaluation of the initial calibration, and formulation of both the ICV standard and calibration standards. Re-calibration is required if corrective actions do not resolve the discrepancy. The ICV is prepared at a concentration of 25ng/uL (50ng on column/2 uL injection).

9.4 If time remains in the 12 hour analytical sequence after successful calibration, samples may be analyzed.

9.5 Continuing calibration verification occurs each 12 hour analytical shift after DFTPP tune verification. The standard is prepared from the calibration mix (CAL MIX) at a concentration of 25 ng/uL (50 ng on column/2 uL injection). The standard is acquired and evaluated for compliance to calibration verification criteria (see Table 3). The CCC and SPCC compounds must not exceed the acceptance criteria of 20%RSD and 0.050 minimum RF respectively. If the CCV fails to meet these criteria the system is considered out of control and corrective action must be taken. All other target compounds must also meet the 20%RSD criteria. See method 8000 for specific options in evaluating linearity.

9.6 Each analytical sequence in which samples are analyzed should contain an extraction or method blank to check for contamination within the analytical system. Target compound detection in blanks must not exceed the reporting limit of the method (with the exception of the Phthalate compounds which may be present at 5X their reporting limit). Blank contamination should be investigated back to the extraction process in order to eliminate continued sample contamination.

9.7 Internal standard response, based on the area of the quantitation ion, must be tracked. Limits for internal standard response may not exceed –50% to +100% of those in the most recent calibration standard. Internal standard area response failures in blanks require reanalysis. Internal standard area response failures in samples may require re-analysis in the absence of interfering matrix affects.

9.8 Surrogate recoveries must fall within the specified QC limits as seen in Table 4. Current limits are set using the OLM03 recovery limits for both water and soil. Control charted data will be used when data is available. Provision is made for failing recovery for one Acid and one Base Neutral, as long as the recovery exceeds 10%. Samples failing to meet the recovery criteria must be reanalyzed and/or re-extracted.

9.9 Laboratory Control Spikes (LCS) extracted with each batch of samples should meet the acceptance criteria as defined in Update III, Dec. 1996 of SW-846. Failure to meet the acceptance criteria requires investigation of the overall extraction process, the impact upon sample data validity, and instrument calibration. Failure to meet the acceptance criteria may necessitate re-extraction of the entire sample batch.

9.10 Determine Instrument detection limits (IDLs) annually in accordance with the method described in 40 CFR, Part 136, Appendix B. Typical values for these analytes are in the range of 1-3 ug/L, the IDL must be less than the CRQL's shown in Table 1 as per section 8.09.2.01.5 of the NJIFB.

9.11 Reporting Limits = 10 and 25 ug/L or 330 or 800 ug/Kg (See Table 1). The 8270C method reporting limits are presented in Table 1. If a medium level extraction is performed, the base reporting limits will be 10000 and 25000 ug/Kg. For all soils.

10.0 CALIBRATION AND STANDARDIZATION

10.1 DFTPP The criteria shown in Table 2 must be met before analysis of calibration standards can begin.

10.2 Initial calibration involves acquisition of five calibration points at concentrations of 20, 50, 80, 120, 160 ng/ 2 uL injection. Analysis must fall within the 12 hour analytical shift as delimited by the passing DFTPP analysis. Concentrations of organic compounds will be determined by GC/MS using an internal standard and fixed response model. Calibration standards contain all Target Compound List (TCL) compounds for the method including surrogate compounds. A relative response factor for each compound within the calibration standard is calculated with the following equation:

$$RRF = \frac{A_x * C_{is}}{A_s * C_x}$$

where:
A_x = Area of characteristic ion for the compound to be measured
A_{is} = Area of the characteristic ion for the associated internal standard
C_{is} = Concentration of the internal standard (ng/uL)
C_x = Concentration of the compound to be measured (ng/uL)

(A list of characteristic ion used for quantitation can be found in Tables 6 and 7. Target Compound and Internal Standard assignments can be found in Table 8)

10.3 Relative response factors are calculated for all compounds in the calibration standards. Using the relative response factors, a percent relative standard deviation (%RSD) is calculated for each mean with the following equation:

$$\%\ RSD = \frac{SD}{x} * 100$$

where:
SD = Standard deviation of initial relative response factors (per compound)
x = Mean of initial relative response factors (per compound)

10.4 System performance check compounds (SPCC) must meet the minimum response factor shown in Table 3. The %RSD for all target compounds must be ≤ 15%. Calibration check compounds (CCC) must have an RSD ≤ 30%. Alternatively, if the average of all RSD values for all analytes is ≤ 15% (with the exception of the CCC compounds) the calibration may still be acceptable (Update III SW-846, Third Edition, Method 8000B, Section 7.5.1.2.1). Refer to Method 8000 for other linearity evaluation options.

10.5 Continuing calibration verification (CCV) is performed after successful DFTPP tune validation at the beginning of the analytical shift. The CCV must contain all target compounds and surrogates as calibrated in the initial calibration. The concentration of the CCV is 50ng/ 2 uL injection. The RF for each compound is calculated using the same formula as in 10.2. The SPCC compounds must meet the minimum response factor criteria (0.050 RF) as shown in Table 3. All target and CCC compounds must have a %D ≤ 20 as compared to the average relative response of the initial calibration as

$$\% \ Difference = \frac{RRF_i - RRF_c}{RRF_i} * 100$$

calculated below:
where:
RRF_i = average relative response factor from initial calibration
RRF_c = relative response factor from current calibration check std.

10.6 Note: Target software methods list CCV criteria for non-CCC target compounds at 25%D. This is to differentiate between the CCC 20%D criterion and the criterion for evaluating other target compounds with linearity options from Method 8000 (in general non-CCC targets will be assessed using the mean %D).

11.0 PROCEDURE

11.1 Samples are prepared for analysis by spiking a 100 uL aliquot of sample extract with 4 uL of the internal standard spiking solution in a 1 mL autosampler vials containing an insert. Autosampler vials are labeled with the corresponding laboratory ID number and sealed with a PTFE lined crimp top cap. Alternative extract volumes may be used (e.g. 50 uL extract) if spiked with the appropriate volume of internal standard Sample dilutions (based upon extract screen results) may be prepared by diluting an appropriate volume of sample extract with Methylene Chloride. Serial dilutions may be required if relative volumes needed for a single dilution step exceed the accuracy of the pipettes (for example: a sample requires a 0.1% analysis in order to have target constituents within the upper half of the calibrated range. Preparation of a 100 uL aliquot in an autosampler vial would require 0.1 uL of sample extract. Microliter pipettes are graduated to 0.2 uL. Therefore it would become necessary to perform a serial dilution of 1:100 (1.0%) and a 10:100 (10%) for a final extract concentration of 0.1%).

11.2 Chromatographic analysis and mass spectral detection of samples. Samples are injected (2 uL aliquot) into the gas chromatograph where the target constituents are separated and eluted from the chromatographic column into the mass spectrometer. Typical operating parameters can be found below. Sample acquisitions are collected, processed, and stored by the data processing system. Automated data processing routines generate final results and print reports.

Initial temperature: 35°C for 2 mins
Ramp 1: 14°C/min to 320°C for 4.6 mins
MS : 35-500 m/z Scan mode

11.3 Analytes are identified by comparison of their mass spectrum (after background subtraction) to a reference spectrum generated by a user-created data base. The GC retention time for each analyte should agree within ±0.5 minutes of the retention time found in the midpoint calibration standard for that analyte.

11.4 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree to within 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.5 Identification of target compounds by mass spectral means requires expert judgement when components are not resolved from interfering peaks or background (non-target constituents). When chromatographic peaks or EICPs indicate contribution from interfering analytes it may become necessary to examine spectra over the entire peak and use selective background subtraction in order to positively identify target analytes and account for extraneous ions. Analysts and Data reviewers should document the rationale used with poorly resolved or troublesome identifications in the narrative.

11.6 Identification of some isomers, due to the similarity of their spectra, is only possible when they have sufficiently different retention times. Acceptable resolution is achieved if the height of the valley between the two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs

11.7 Common laboratory contaminates will appear from time to time in samples and blanks. Common contaminates in semi-volatile analyses include phthalates. Subtraction for blank contaminates is not permitted.

12.0 CALCULATIONS

12.1 Recovery calculations for quality control spikes (surrogates, matrix and matrix spike duplicates, and laboratory control spikes LCS). Individual component recoveries are calculated with the following equation:

$$Surrogate\ Recovery\ (\%) = \frac{SR}{SA} * 100$$

where:
SR = Spike Result
SA = Spike Added (concentration)

$$MS\ Recovery\ (\%) = \frac{SSR\ -\ SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

Recovery criteria for surrogates can be found in Table 4. Matrix, matrix duplicate recovery criteria can be found in Table 5.

12.2 Relative percent difference (RPD) of the concentrations measured for the matrix spike/ matrix spike duplicates, or for duplicate analyses of unspiked samples. The RPD is calculated according to the following equation:

$$\%\ RPD = \frac{|D_1\ -\ D_2|}{\frac{D_1\ +\ D_2}{2}} * 100$$

where:
RPD = Relative Percent Difference
D_1 = First Sample Value
D_2 = Second Sample Value (duplicate)

Minimum RPD criteria for matrix and matrix spike duplicates can be found in Table 5.

12.3 Concentrations of Unknowns: Chromatographic peaks not identified by the automated search routines as non-target compounds are evaluated as tentatively identified compounds. These shall not include: 1) Peaks < 10% of the nearest internal standard; 2) peaks eluting earlier than 30 seconds before the first target analyte; 3) VOA or SVOA target analytes or standards. Up to 20 of the highest tentatively identified compounds (TIC's) are reported. These peaks are quantitated using total peak area and an assumed response factor of 1.0. Concentrations of TIC's and alkanes are calculated using the following formulas:

$$C_{(x)} = \frac{Amt_{(IS)} * H_{(x)} * V_{(t)}}{H_{(IS)} * V_{(o)} * V_{(i)}} * DF$$

Water

$C_{(x)}$= Concentration of Unknown (ug/L).
$Am_{(IS)}$= Amount of internal standard (ng).
DF = Dilution Factor
$H_{(x)}$ = Peak area of Unknown

$H_{(IS)}$= Peak height area of associated internal standard
$V_{(t)}$ = Volume of final extract (uL)

$$C_{(x)} = \frac{Amt_{(IS)} * H_{(x)} * V_{(t)} * GPC * DF * 10^3 g/Kg}{H_{(IS)} * W_{(s)} * \frac{100 - M}{100} * V_{(i)} * 10^3 ng/ug}$$

Soil

$C_{(x)}$ = Concentration of compound (ug/Kg)
$Am_{(IS)}$ = Amount of associated internal standard (ng)
DF = Dilution Factor.
$H_{(IS)}$ = Peak area of associated internal standard.
$H_{(x)}$ = Peak area of Unknown.
$V_{(t)}$ = Volume of final extract (uL)
$V_{(I)}$ = Volume injected (uL)
$W_{(s)}$= Weight of sample (g)
GPC= GPC dilution factor (usually=2)
M= % Moisture

12.4 Identified target compounds are quantitated by the internal standard method. Each compound has a designated internal standard and characteristic ions. Calculation of a TCL compound concentration performed with the following fraction and matrix specific equations:

$$C_{(x)} = \frac{A_{(x)} * Amt_{(IS)} * V_{(t)}}{A_{(IS)} * RRF * V_{(o)} * V_{(i)}} * DF$$

Waters
$C_{(x)}$ = Concentration of compound (ug/L)
$Am_{(IS)}$ = Amount of associated internal standard (ng)
DF = Dilution Factor.
$A_{(IS)}$ = Area of quantitation ion for associated internal standard.
$A_{(x)}$ = Area of quantitation ion for compound.

RRF = Relative Response Factor from calibration standard.
$V_{(t)}$ = Volume of final extract (uL)
$V_{(o)}$ = Sample volume (mL)
$V_{(i)}$ = Volume injected (uL)

$$C_{(x)} = \frac{A_{(x)} * Amt_{(IS)} * V_{(t)} * GPC * 10^3 g/Kg}{A_{(IS)} * RRF * W_{(s)} * \frac{100 - M}{100} * V_{(i)} * 10^3 ng/ug} * DF$$

Soil
$C_{(x)}$ = Concentration of compound (ug/Kg)
$Am_{(IS)}$ = Amount of associated internal standard (ng)
DF = Dilution Factor.
$A_{(IS)}$ = Area of quantitation ion for associated internal standard.
$A_{(x)}$ = Area of quantitation ion for compound.
RRF = Relative Response Factor from calibration standard.
$V_{(t)}$ = Volume of final extract (uL)
$V_{(i)}$ = Volume injected (uL)
$W_{(s)}$= Weight of sample (g)
GPC= GPC dilution factor (usually=2)
M= % Moisture

12.5 Calculation of a sample concentration using a secondary ions is done by calculating a new relative response factor, RRF[1], for the secondary ion from the check standard (substitute area of secondary ion where area of primary ion is in the equation for RRF). Secondary ion calculation is used when the primary ion shows matrix interferences in its spectra. In instances where secondary ion calculations are necessary, the narrative will state which samples were affected by interferences and required secondary ion calculations, and show the calculated results. The forms and documentation for the affected samples will reflect primary ion calculations.TCL compounds are verified in Target Review by a data analyst. Each chromatographic peak identified as a TCL is checked for retention time fit as compared to the continuing calibration standard and its mass spectra is verified using the guidelines below. Misassignments and interferences that are detected here are corrected. If manual integration is required, "Snap to Data" should be used whenever the peak is baseline resolved for each ion. Surrogates and internal standards should not be manually integrated without the supervision of the Laboratory Section Head or Laboratory Director. Integrations must be reviewed and initialed and dated on the quantitation report next to the "M" qualifier by a second party. A signal integration printout must be submitted for each compound that is manually integrated for any standard, blank, or sample. This is done in target review, use print signals command.

12.6 Data reporting will include the following qualifiers:

12.6.1 A = The TIC is a suspected aldol-condensation product
12.6.2 B = Analyte is found in the associated method blank as well as the sample
12.6.3 D = Compound is identified in an analysis at a secondary dilution factor
12.6.4 E = Compound quantitation is above the instrument's calibration range for this analysis
12.6.5 J = Indicates an estimated quantitation value
12.6.6 U = Compound was analyzed for but not detected
12.6.7 X = The reported compound is a suspected laboratory contaminant
12.6.8 Y = an additional qualifier which will be defined at the time of use by the data reviewer
12.6.9 Z = The reported result is based on the combined responses from coeluting compounds

13.0 METHOD PERFORMANCE

13.1 Annually laboratory accuracy and precision data are obtained for the method analytes using laboratory control spikes. Seven replicates at a concentration 3-5 times the expected MDL are used. Method detection limit studies were analyzed for each matrix type and each extraction procedure used. MDLs were derived from these data using the calculation below:

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

Where:

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

14.0 POLLUTION PREVENTION

14.1 Limited quantities of solvents are utilized in the analytical areas and are maintained in covered, closed, or sealed vessels. Primarily, solvent use is restricted to the fume hood.

15.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data assessment criteria and corrective action for out of control data is summarized in Table 9

16.0 CONTIGENCIES FOR HANDLING OUT-OF-CONTROL OF UNACCEPTABLE DATA

16.1 Data that fails to meet minimum acceptance criteria will be annotated (flagged) with qualifiers and/or appropriate narrative comments defining the nature of the outage. Data qualifiers can be found in Appendix A. If applicable, a Corrective Action Reports will be initiated in order to provide for investigation and follow-up.

17.0 WASTE MANAGMENT

17.1 Solvents and extracts used in the analytical procedure must be handled as hazardous waste and disposed of properly. Labeled containers for waste solvent and old vials are located in the semi-volatile prep lab fume hood. All waste material that is associated with sample analysis (rinse vials,

waste vials, cleaning solvents, and spill containment materials must be disposed of in the appropriate container. Notify Hazardous Waste Coordinator or manager if container removal is necessary.

18.0 REFERENCES

18.1 "Test Methods for Evaluating Solid Waste", USEPA Method 8270C revision 3, Dec. 1996.
18.2 "Test Methods for Evaluating Solid Waste", USEPA Method 8000B revision 3, Dec. 1996.

Appendix A:

Verification of Mass Spectra

Sample results are verified by their mass spectra. Mass spectra are visually verified by a laboratory staff member experienced in mass spectral interpretation. The following guidelines are used when evaluating mass spectra:

- All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) are to be present in the sample spectrum.
- The relative intensities of these ions are to agree within plus or minus 20% between the standard and sample spectra.
- Ions greater than 10% in the sample spectrum are considered and accounted for by the analyst making the comparison.

For target analytes (TCL) the laboratory uses the spectra generated from the working calibration standard as the primary spectral reference. The National Bureau of Standards (NBS) spectral library is the primary reference for non-target analytes (TIC).

Guidelines for Making Tentative Identification

- Relative intensities of major ions in the reference spectrum should be present in the sample spectrum.
- The relative intensities of the major ions should agree within ± 20%.
- Molecular ions present in the reference spectrum should be present in the sample spectrum.
- Ions present in the sample spectrum but not in the reference spectrum should be evaluated for possible background contamination or presence of co-eluting compounds.
- Ions present in the reference spectrum but not in the sample spectrum should be evaluated to determine if background contamination or coeluting compounds are responsible for the discrepancy. Data system library reduction programs can sometimes create these discrepancies.
- If in the technical judgement of the mass spectral interpretation specialist no valid tentative identification can be made, the compound should be reported as unknown. Additional classification of the compound should be given if possible (i.e. unknown aromatic).

The laboratory commonly uses spectral subtraction to resolve interferences arising from closely eluting compounds. The laboratory has a system of independent review and evaluation of spectral analysis. Any decisions made by the primary reviewer as to the identification and confirmation of mass spectra will be independently reviewed by a secondary data reviewer. Any points of discrepancy are discussed and a resolution reached before submission of the final data package to the client.

Reporting Qualifiers

A = The TIC is a suspected aldol-condensation product
B = Analyte is found in the associated method blank as well as the sample
D = Compound is identified in an analysis at a secondary dilution factor
E = Compound quantitation is above the instrument's calibration range for this analysis
J = Indicates an estimated quantitation value
U = Compound was analyzed for but not detected
X = The reported compound is a suspected laboratory contaminant
Y = an additional qualifier which will be defined at the time of use by the data reviewer
Z = The reported result is based on the combined responses from coeluting compounds

Appendix B: Filenaming

The GC/MS filename is designated at the time of acquisition and will follow the file through to archiving. The filenames presently carry information about the type of sample acquired so that a standard can be distinguished from a blank or sample merely by its filename. The following general rules are followed when naming a file on the GC/MS system.

I. First Character
The first character in a filename is an instrument identifier: The HP5971 instruments are named P, Q, and R.

II. Last Character
The last character designates the type of analysis: S: Semivolatiles

III. Interior Characters
A.Performance Standards (DFTPP)

- The second and third characters are the curve designator: AA-ZZ
- The fourth, fifth, and sixth characters are a sequence number which resets every calibration curve: 001-999.
- The next to last character is the type of standard being analyzed: P: performance standard (DFTPP)

Some examples:
RRG005PS (5th DFTPP for BNA curve RG on 5971R).
RRD001PS (1st DFTPP for BNA curve RD on 5971R).

B. Calibration Standards

- The second and third characters are the curve designator: AA-ZZ
- The fourth, fifth, and sixth characters are the nominal concentration of the standard: 001-999
- The next character is used to designate check standards as related to curves: A-Z
- The next to last character indicates what type of standard is being analyzed:
  B: BNA HSLs
  C: Pesticide/PCB
  Q: QC samples (LFBs)
- Multiple injections of check standards are designated by a number after the character.

Some examples:
QDX050BS (50 ng standard in BNA curve DX on 5971Q).
RDX050BBS (50 ng check std. "B" in BNA curve DX on 5971R).
RDX050B2BS (Second injection of above example).
QFD100CCS (100 ng pest/PCB std. for BNA window "C" of curve FD on 5971Q)

C. Blanks

- Semivolatile Method Blanks
  * The second character is a B.

* The third, fourth, fifth, and sixth characters are the extraction date in the form mmdd: 0101-1231

* The seventh and eighth characters are the method blank name as designated on the extraction sheet: A1-Z9

Some examples:
QB0914Z1S (Method Blank named SBLKZ1 extracted on 9/14/94 analyzed on 5971Q)
RB0829X8S (Method Blank named SBLKX8 extracted on 8/29/94 analyzed on 5971R)

D. Samples

➢ The second through seventh characters are the sample number.

➢ The eighth character is a (1) D if a dilution is necessary for analysis; (2) E if the sample is a methanol extract for volatile analysis; (3) R if the sample is a re-extract for volatile or semivolatile analyses.

Some examples:
Q112097S (Lab No. 112097 analyzed for BNA on 5971Q).
R121191DS (Lab No. 121191 analyzed at a dilution for BNAs on 5971R).

E. Matrix Spikes and Duplicates

➢ The six digit sample number is followed by:
MS: Matrix Spikes
MD: Matrix Spike Duplicates
Rn: n=1-9 for Replicates
Dn: n=1-9 for Dilutions (billable items--not to be confused with dilutions as determined by screening results)
D1-D9 should only be used if they have been logged in and appear on the worksheets, otherwise the previous use of "D" for dilution is adequate.

Some examples:
Q112934MSS (Lab No. 112934MS analyzed for BNA matrix spike on 5971Q).
Q112934MSDS (Lab No. 112934MS analyzed for BNA matrix spike on 5971Q analyzed at a dilution, as indicated by screening results).
R120954MDS (Lab No. 120954MD analyzed for BNA matrix spike duplicate on 5971R).

F. Re-extracts and Reinjects

➢ These characters appear just before the terminal S, V or Q. BNA re-extracts are designated as R1-R9 and reinjects are designated as I1-I9.

➢ "E"s , "R"s and "D"s always precede "I"s in a filename.

Some examples:
Q120986E2S(re-extract of Sample No. 120986 analyzed for BNA on 5971Q)
Q120986E2I2S (2nd injection of re-extract of Sample No. 120986 analyzed for BNA on 5971Q)

Appendix C: Data Acquisition Sequence

1. Tuning

- At the Top Level select Tune.
- Go into Files and select Load Tune Values from dftpp.u and click OK.
- Under Execute, select Profile Scan.
- An MS source pressure error may occur the first two times the profile scan performed. Execute Profile Scan two or three times. The peak width (PW) should be 0.5 ± 0.02. If the widths are too large or too small on the third attempt, select Repeat Profile (under Execute). Stop when peakwidths are in the desired range. Now select Profile Scan. Continue selecting Profile Scan until the desired range PW has again been obtained. It may be necessary to recalibrate the peak widths in order to achieve 0.5 ± 0.02 width.
- At the Edit Parameters menu, select MS Acq Parms.
- Click on Electron Multiplier.
- At Acquisition control, click on Repeat Scan. Allow scanning to continue until the abundance value for mass 69 stabilizes. Adjust the EM up or down to get the abundance of mass 69 to be 250,000 ± 10,000. Press OK. To adjust abundance, use the mouse to drag the blackbar or type in new numbers in the box to the left of the scroll bar for the multiplier potential.
- Press OK at the bottom of the MS Acq Parms window.
- Select Profile Scan. If these actions do not produce the desired abundance of mass 69, go back to MS Acq Parms and repeat. If peak widths, mass calibration or other lens settings need to be adjusted, consult a senior analyst for help. These values should be correct before the final setting of the multiplier voltage.
- When peak widths and abundances are at the desired levels, go under Files, exit, and save to the proper file:

  chem/config/dvc/ms5971-1/dftpp.u for instrument Q
  chem/config/dvc/ms5971-2/dftpp.u for instrument R
  chem/config/dvc/ms5971-1/dftpp.u for instrument P

  Answer the questions: Do you want to overwrite the last one? Yes. Do you want to save to source? No.

- Make sure the correct tune file (dftpp.u, NOT atune.u) is loaded when a new batch is created.

2. Creating a Batch

- From the Top Level select Create Batch.
- Name the batch

Character	Describes	Acceptable Characters
1st	the instrument	P, Q, R
2nd, 3rd	the curve designator	AA through ZZ
4th	the check standard which will be run under the current batch	A-Z; do not use for a curve (to find the check standard from the previous batch look at the run logbook

Note: The system will append ".b" to the batch name so it does not need to be typed in. Designate the method by appending "____method" where "method" may be OLM, LC, 524.2, etc.

Some examples:
QADD_OLM.b (batch for check standard D with method OLM on instrument Q).

- Click at OK.
- Select the instrument for Data directory (P.i, Q.i, ...or R.i).
- Click at OK.
- Select method for Batch Directory: e.g., dftpp.m and SV_OLM.m for semivolatiles, according to the following steps.
- Click at Parent Directory until you get to the top of the directory. The top of the directory will be /chem/inst.i or /chem/inst.i/inst.p
- Copy the method files, e.g., SV_OLM.m, dftpp.m, and BAKE.m from the previous batch for this method.
- Select Exit.

3. Acquisition

- To perform a single analysis, select Manual Injection from the Run Control menus.
- To perform multiple analyses using an autosampler, create a sequence as described in above.

1.Entering Sample Information
It is important to enter all acquisitions and sample information correctly. This is done through the Sample Information panels accessed by selecting either Manual Injection or Edit Sample Info..... from the Sequence menus.

Data File Name - type the file name as described above.

Sample Info- Lab Number, SDG Number, Case number, SMO number.

Misc. Info.- enter related information here, eg. Dilution, sample weight or volume, % moisture.

Dilution Factor - If you have diluted the samples and system monitoring compounds, the dilution factor must be typed in and for semivolatiles or volatiles methanol extracts the surrogates box must be selected.

Analyst -2 or 3 character associate ID of analyst who introduced the sample or set-up the autosampler.

Inj. Date - do not use: this will be filled in by the system.

Sample Type - Choose
Sample; Calib. Sample; Continuing Calib.; QC Control Sample:

Method Blank, Matrix Spike, Matrix Spike Duplicate
For QC samples that are spiked, select the appropriate spike list (Water Msd.spk or SoilMsd.spk)
Volume of spike solution is from the extraction log, in uL (usually 500).
Calibration Level - 1 to 5, corresponding to the five points of the curve.

Sample matrix - Liquid or Solid

Concentration Parameters: check or type in the following values:

For Semivolatile soils, enter the pH from the extraction log or worksheet. For Semivolatile waters, enter 0.0 for the pH. Check the correct concentration level (low, medium, or high).

The following variables apply to semivolatiles:

	Waters	Soils (low and medium)
Uf	1.000	1.000
Vt	1000.000	500.000
Vo	enter the value in mL from the extraction log	NA
Vi	2.000	2.000
Ws	NA	Enter the value in g. from the extraction log
M	NA	Enter the % moisture (100 - % solid) from the % Solids worksheet
GPC	NA	2.0

Fraction - Semivolatile

Column parms - do not change unless a different phase or diameter column has been installed.

Sample Prep parms - Extraction information

- Date - Date of extraction
- Operator - person who extracted the sample
- Method
  - continuous liquid/liquid for (BNA) waters
  - sonication for (BNA) soils
  - purge and trap (VOA)
- Sample Cleanup - for soil BNA samples, check GPC

Surrogate/ISTD Parms- Enter the volume of surrogate solution added from the extraction log (BNA; in uL)

- Report recovery - select Concentration

Sample ID Info

- Quality base report - Don't modify
- Client Name - 6 letter code from worksheet
- Date received - the date we received the sample in-house
- Sample location - (if available)
- Sample date - date of sample and time (if available)

Laboratory ID - lab number

Lab Prep Batch - For BNA's, the date the sample went through extraction(MM-DD) and the two-letter blank designator (letter, number).

Client ID- Client number (field sample number)

Client Sample Group- SDG Number

Tabular Report Parms- This menu allows you to set the parameters for a tabular report.

- Print Tabular Report- Select
- Format- Select 2 (for more information about format 1 and format 2 refer to the *Chemsystem User's Guide*.
- Report undetected target compound -select
- Print Library Search Compound Tabular Report- Select (this will print a mass spectrum library search for unknowns).
- Report Header - "SEMIVOLATILE QUANTITATION REPORT"
- Report Comment - Leave this field blank
- Print Internal Standard Monitor Report - Select
- Print Sample Report - Do not select
- Tentative ID Sample Report - Do not select
- Print Initial Cal Report Cal Level - Do not change the numbers; do not select
- Summary Report Format - Do not change the numbers
- Select OK

Graphic Report Parameters: Select the following:

- Print Graphic Report
- Select Non-Cal Format
- Choose Tune Target for bfb or dftpp
- Choose 8.tat for all others
- Select Cal Format
- Choose Tune Target for bfb or dftpp
- Choose 8.tat for all others
- Full Page Chromatogram
- Select Labeling - "STDS. ONLY"
- Number of Pages to Plot = 1
- Chromatogram Start Time - 0.0
- Do not select Display Integration Labels
- Select Display Peak Retention Times
- Do not select Print Cal Curves
- Select OK

If you are entering sample information for a sequence, enter the above selections in the method under Default Sample before loading the method and creating the sequence.

When you are finished modifying the sample table for all of the samples in the sequence, select OK. At the

Top Level Menu, save the sequence. The computer will show the file name seq.s. Press OK.

4. Acquisition within a Batch

- From Top Level, go into Batch and select Existing Batch. Check path name listed as Dir:. It should read: /chem/instrument name.i/yesterday's batch.b
  For example: /chem/P.i/PACG.b

- Click on Parent to return to Dir: /chem/instrument name.i

- Choose today's batch.b and click at OK. Verify that the window shows the correct Current Batch Directory.

- Select Load Target Method under Method.

- At Save Current Method select No unless it is desired to keep changes made to the current method. Tune methods should always be saved. Make sure that tunes are saved as bfb.u or dftpp.u, not atune.u.

- Choose Manual Injection under Run Control.

- Check or enter the relevant sample information as described above.
  There is a second layer of windows available, under the buttons, with box outlines. Open these and fill in the necessary information as needed.

- If you are ready to make an acquisition, Click at Run Method. On the semivolatile systems, Run Method or Start Sequence (see below) will start the autosampler.

5. Creating and Running a Sequence

From the Top Level, under Method, select Edit Target Method. Enter any sample information that is common to all samples in the batch (e.g., operator, lab prep batch) and as much other information as is helpful to decrease typing for each individual sample (e.g., header info, sample ID info). Select OK, then Save Current Method.

- Go to Sequence menus.

- Pull down "Edit Sequence Parameters". Check that the current batch is listed. If so, Click OK. If not re-select the existing batch.
- Pull down "Edit Sequence Table". Type in the method name(s), the vial numbers (make sure that vials are correctly loaded in the autosampler; they must be in the correct tray position when the 7673A autosampler is being used), and one injection/vial. Click OK.

- Pull down "Edit Sample Info.....". Type in all sample information, file names, and appropriate acquisition information. Click OK when done. Entering sample information is described in detail above.

- Save and Load the sequence.

- Go to Run Control menus.

- Go to Run Control
  Pull down "Run Sequence"

Click on "Start Sequence". The instrument will begin automatic operation. If it necessary to pause or stop the sequence, pull down on Run Control and click the appropriate box.

TABLES:

Table 1. Analytes and Reporting Limits

Analyte	CAS No.	Reporting Limits Water (ug/L)	Reporting Limits Low Level Soil (ug/Kg)	Reporting Limits Medium Level Soil (ug/Kg)
Acenaphthene	83-32-9	10	330	10000
Acenaphthylene	208-96-8	10	330	10000
Anthracene	120-12-7	10	330	10000
Benzo(a)anthracene	56-55-3	10	330	10000
Benzo(b)fluoranthene	205-99-2	10	330	10000
Benzo(k)fluoranthene	207-08-9	10	330	10000
Benzo(g,h,i)perylene	191-24-2	10	330	10000
Benzo(a)pyrene	50-32-8	10	330	10000
4-Bromophenyl-phenylether	101-55-3	10	330	10000
Butylbenzylphthalate	85-68-7	10	330	10000
Carbazole	86-74-8	10	330	10000
4-Chloroaniline	106-47-8	10	330	10000
bis(2-Chloroethoxy)methane	111-91-1	10	330	10000
bis(2-Chloroethyl)ether	111-44-4	10	330	10000
4-Chloro-3-methylphenol	59-50-7	10	330	10000
2-Chloronaphthalene	91-58-7	10	330	10000
2-Chlorophenol	95-57-8	10	330	10000
4-Chlorophenyl-phenylether	7005-72-3	10	330	10000
2,2'-oxybis(1-Chloropropane)	108-60-1	10	330	10000
Chrysene	218-01-9	10	330	10000
Dibenzofuran	132-64-9	10	330	10000
Dibenz(a,h)anthracene	53-70-3	10	330	10000
Di-n-butylphthalate	84-74-2	10	330	10000
1,2-Dichlorobenzene	95-50-1	10	330	10000

Analyte	CAS No.	Reporting Limits Water (ug/L)	Reporting Limits Low Level Soil (ug/Kg)	Reporting Limits Medium Level Soil (ug/Kg)
1,3-Dichlorobenzene	541-73-1	10	330	10000
1,4-Dichlorobenzene	106-46-7	10	330	10000
3,3'-Dichlorobenzidine	91-94-1	10	330	10000
2,4-Dichlorophenol	120-83-2	10	330	10000
Diethylphthalate	84-66-2	10	330	10000
2,4-Dimethylphenol	105-67-9	10	330	10000
Dimethylphthalate	131-11-3	10	330	10000
2,4-Dinitrophenol	51-28-5	25	800	25000
2,4-Dinitrotoluene	121-14-2	10	330	10000
2,6-Dinitrotoluene	606-20-2	10	330	10000
4,6-Dinitro-2-methylphenol	534-52-1	25	800	25000
Di-n-octylphthalate	117-84-0	10	330	10000
bis(2-Ethylhexyl)phthalate	117-81-7	10	330	10000
Fluoranthene	206-44-0	10	330	10000
Fluorene	86-73-7	10	330	10000
Hexachlorobenzene	118-74-1	10	330	10000
Hexachlorobutadiene	87-68-3	10	330	10000
Hexachlorocyclopentadiene	77-47-4	10	330	10000
Hexachloroethane	67-72-1	10	330	10000
Indeno(1,2,3-cd)pyrene	193-39-5	10	330	10000
Isophorone	78-59-1	10	330	10000
2-Methylnaphthalene	91-57-6	10	330	10000
2-Methylphenol	95-48-7	10	330	10000
4-Methylphenol	106-44-5	10	330	10000
Naphthalene	91-20-3	10	330	10000
2-Nitroaniline	88-74-4	25	800	25000

Analyte	CAS No.	Reporting Limits Water (ug/L)	Reporting Limits Low Level Soil (ug/Kg)	Reporting Limits Medium Level Soil (ug/Kg)
3-Nitroaniline	99-09-2	25	800	25000
4-Nitroaniline	100-01-6	25	800	25000
Nitrobenzene	98-95-3	10	330	10000
2-Nitrophenol	88-75-5	10	330	10000
4-Nitrophenol	100-02-7	25	800	25000
N-Nitrosodiphenylamine	86-30-6	10	330	10000
N-Nitroso-di-n-propylamine	621-64-7	10	330	10000
Pentachlorophenol	87-86-5	25	800	25000
Phenanthrene	85-01-8	10	330	10000
Phenol	108-95-2	10	330	10000
Pyrene	129-00-0	10	330	10000
1,2,4-Trichlorobenzene	120-82-1	10	330	10000
2,4,5-Trichlorophenol	95-95-4	25	800	25000
2,4,6-Trichlorophenol	88-06-2	10	330	10000

Table 2. DFTPP Criteria

Mass	Ion Abundance Criteria
51	30.0-60.0 percent of mass 198
68	less than 2.0 percent of mass 69
69	Present
70	less than 2.0 percent of mass 69
127	40.0-60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0-9.0 percent of mass 198
275	10.0-30.0 percent of mass 198
365	Greater than 1.0 percent of mass 198
441	Present, but less than mass 443
442	>40.0 of mass 198
443	17.0-23.0 percent of mass 442

Table 3 Initial, Continuing, and Minimum Response Factor Criteria

Analyte	Minimum RF	Maximum %RSD	Maximum %D
Pyridine	0.010	15	20
N-Nitrosodimethylamine	0.010	15	20
2-Fluorophenol (surr)	0.600	15	20
Phenol-d5 (surr)	0.800	15	20
Aniline	0.010	15	20
Phenol (CCC)	0.800	30	20
bis(2-Chloroethyl)Ether	0.700	15	20
2-Chlorophenol-d4 (surr)	0.800	15	20
2-Chlorophenol	0.800	15	20
1,3-Dichlorobenzene	0.600	15	20
1,4-Dichlorobenzene (CCC)	0.500	30	20
1,2-Dichlorobenzene-d4 (surr)	0.400	15	20
Benzyl Alcohol	0.010	15	20
1,2-Dichlorobenzene	0.400	15	20
2-Methylphenol	0.700	15	20
2,2'-oxybis(1-Chloropropane	0.010	15	20
4-Methylphenol	0.600	15	20
N-Nitroso-di-n-propylamine (SPCC)	0.050	15	20
Hexachloroethane	0.300	15	20
Nitrobenzene-d5 (surr)	0.200	15	20
Nitrobenzene	0.200	15	20
Isophorone	0.400	15	20
2-Nitrophenol (CCC)	0.100	30	20
2,4-Dimethylphenol	0.200	15	20
bis(2-Chloroethoxy)methane	0.300	15	20
Benzoic Acid	0.010	15	20
2,4-Dichlorophenol (CCC)	0.200	30	20
1,2,4-Trichlorobenzene	0.200	15	20
Naphthalene	0.700	15	20
4-Chloroaniline	0.010	15	20
Hexachlorobutadiene (CCC)	0.010	30	20
4-Chloro-3-methylphenol	0.010	15	20
2-Methylnaphthalene	0.010	15	20
Hexachlorocyclopentadiene (SPCC)	0.050	15	20

2,4,6-Trichlorophenol (CCC)	0.200	30	20
2,4,5-Trichlorophenol	0.200	15	20
2-Fluorobiphenyl (surr)	0.700	15	20
2-Chloronaphthalene	0.800	15	20
2-Nitroaniline	0.010	15	20
Dimethylphthalate	0.010	15	20
Acenaphthylene	0.900	15	20
2,6-Dinitrotoluene	0.200	15	20
3-Nitroaniline	0.010	15	20
Acenaphthene	0.900	15	20
2,4-Dinitrophenol (SPCC)	0.050	15	20
Dibenzofuran	0.800	15	20
4-Nitrophenol (SPCC)	0.010	15	20
2,4-Dinitrotoluene	0.200	15	20
Diethylphthalate	0.010	15	20
Fluorene	0.900	15	20
4-Chlorophenyl-phenylether	0.400	15	20
4-Nitroaniline	0.010	15	20
4,6-Dinitro-2-methylphenol	0.010	15	20
N-nitrosodiphenylamine (CCC)	0.010	30	20
Azobenzene	0.010	15	20
2,4,6-Tribromophenol (surr)	0.010	15	20
4-Bromophenyl-phenylether	0.100	15	20
Hexachlorobenzene	0.100	15	20
Pentachlorophenol (CCC)	0.050	30	20
Phenanthrene	0.700	15	20
Anthracene	0.700	15	20
Carbazole	0.010	15	20
Di-n-butylphthalate	0.010	15	20
Fluoranthene (CCC)	0.600	30	20
Benzidine	0.010	15	20
Pyrene	0.600	15	20
Terphenyl-d14 (surr)	0.500	15	20
Butylbenzylphthalate	0.010	15	20
Benzo(a)anthracene	0.800	15	20
3,3'-Dichlorobenzidine	0.010	15	20
Chrysene	0.700	15	20
bis(2-Ethylhexyl)phthalate	0.010	15	20
Di-n-octylphthalate (CCC)	0.010	30	20

Benzo(b)fluoranthene	0.700	15	20
Benzo(k)fluoranthene	0.700	15	20
Benzo(a)pyrene	0.700	15	20
Indeno(1,2,3-cd)pyrene	0.500	15	20
Dibenz(a,h)anthracene	0.400	15	20
Benzo(g,h,i)perylene	0.500	15	20

Table 4. Surrogate Recoveries

Surrogate Recovery Requirements		
Compound	**Water (% Recovery)**	**Soil (% Recovery)**
2-Fluorophenol	21-110	25-121
Phenol-d5	10-110	24-113
2,4,6-Tribromophenol	10-123	19-122
Nitrobenzene-d5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
Terphenyl-d14	33-141	18-137
2-Chlorophenol-d4	33-110	20-130
1,2-Dichlorobenzene-d4	16-110	20-130

Note: Recoveries for 2-Chlorophenol-d4 and 1,2-Dichlorobenzene-d4 are advisory only.

Table 5. Matrix Spike Recoveries

Matrix Spike Recovery Requirements				
Compound	**% Recovery Water**	**% RPD Water**	**% Recovery Soil**	**% RPD Soil**
Phenol	12-110	42	26-90	35
2-Chlorophenol	27-123	40	25-102	50
1,4-Dichlorobenzene	36-97	28	28-104	27
N-Nitroso-di-n-propylamine	41-116	38	41-126	38
1,2,4-Trichlorobenzene	39-98	28	38-107	23
4-Chloro-3-methylphenol	23-97	42	26-103	33
Acenaphthene	46-118	31	31-137	19
4-Nitrophenol	10-80	50	11-114	50
2,4-Dinitrotoluene	24-96	38	28-89	47
Pentachlorophenol	9-103	50	17-109	47
Pyrene	26-127	31	35-142	36

The Relative Percent Difference (%RPD) between matrix spike and matrix spike duplicate analysis is calculated with Recovery limits (shown in Table 5), spike limits are advisory only.

Table 6: Characteristic Ions For Semivolatile Target Compounds And Surrogates

Parameter	Primary Quantitation Ion	Secondary Ion (s)
Phenol	94	65, 66
bis(2-Chloroethyl)ether	93	63, 95
2-Chlorophenol	128	64, 130
1,3-Dichlorobenzene	146	148, 113
1,4-Dichlorobenzene	146	148, 113
1,2-Dichlorobenzene	146	148, 113
2-Methylphenol	108	107
2,2'-oxybis(l-Chloropropane)	45	77, 79
4-Methylphenol	108	107
N-Nitroso-di-n-propylamine	70	42, 101, 130
Hexachloroethane	117	201, 199
Nitrobenzene	77	123, 65
Isophorone	82	95, 138
2-Nitrophenol	139	65, 109
2,4-Dimethylphenol	107	121, 122
bis(2-Chloroethoxy)methane	93	95, 123
2,4-Dichlorophenol	162	164, 98
1,2,4-Trichlorobenzene	180	182, 145
Naphthalene	128	129, 127
4-Chloroaniline	127	129
Hexachlorobutadiene	225	223, 227
4-Chloro-3-methylphenol	107	144, 142
2-Methylnaphthalene	142	141
Hexachlorocyclopentadiene	237	235, 272

Parameter	Primary Quantitation Ion	Secondary Ion (s)
2,4,6-Trichlorophenol	196	198, 200
2,4,5-Trichlorophenol	196	198, 200
2-Chloronaphthalene	162	164, 127
2-Nitroaniline	65	92, 138
Dimethyl phthalate	163	194, 164
Acenaphthylene	152	151, 153
3-Nitroaniline	138	108, 92
Acenaphthene	153	152, 154
2,4-Dinitrophenol	184	63, 154
4-Nitrophenol	109	139, 65
Dibenzofuran	168	139
2,4-Dinitrotoluene	165	63, 182
2,6-Dinitrotoluene	165	89, 121
Diethylphthalate	149	177, 150
4-Chlorophenyl-phenylether	204	206, 141
Fluorene	166	165, 167
4-Nitroaniline	138	92, 108
4,6-Dinitro-2-methylphenol	198	182, 77
N-Nitrosodiphenylamine	169	168, 167
4-Bromophenyl-phenylether	248	250, 141
Hexachlorobenzene	284	142, 249
Pentachlorophenol	266	264, 268
Phenanthrene	178	179, 176
Anthracene	178	179, 176
Carbazole	167	166, 139
Di-n-butylphthalate	149	150, 104

Parameter	Primary Quantitation Ion	Secondary Ion (s)
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206
3,3'-Dichlorobenzidine	252	254, 126
Benzo(a)anthracene	228	229, 226
bis(2-Ethylhexyl)phthalate	149	167, 279
Chrysene	228	226, 229
Di-n-Octyl phthalate	149	--
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(a)pyrene	252	253, 125
Indeno(1,2,3-cd)pyrene	276	138, 227
Dibenzo(a,h)anthracene	278	139, 279
Benzo(g,h,i)perylene	276	138, 277
Phenol-d(5)	99	42, 71
2-Fluorophenol	112	64
2,4,6-Tribromophenol	330	332, 141
Nitrobenzene-d(5)	82	128, 54
2-Fluorobiphenyl	172	171
Terphenyl-d(14)	244	122, 212
2-Chlorophenol-d(4)	132	68, 134
1,2-Dichlorobenzene-d(4)	152	115, 150

Table 7: Characteristic Ions For Internal Standards For Semivolatile Compounds

Internal Standard	Primary Quantitation Ion	Secondary Ions
1,4-Dichlorobenzene-d(4)	152	115
Naphthalene-d(8)	136	68
Acenaphthene-d(10)	164	162,160
Phenanthrene-d(10)	188	94,80
Chrysene-d(12)	240	120,236
Perylene-d(12)	264	260,265

Table 8. Semivolatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

1,4-Dichlorobenzene-d(4)	Naphthalene-d(8)	Acenaphthene-d(10)
Phenol	Nitrobenzene	Hexachlorocyclopentadiene
bis (2-Chloroethyl) ether	Isophorone	2,4,6-Trichlorophenol
2-Chlorophenol	2-Nitrophenol	2,4,5-Trichlorophenol
1,3-Dichlorobenzene	2,4-Dimethylphenol	2-Chloronaphthalene
1,4-Dichlorobenzene	bis(2-Chloroethoxy)methane	2-Nitroaniline
1,2-Dichlorobenzene	2,4-Dichlorophenol	Dimethylphthalate
2-Methylphenol	1,2,4-Trichlorobenzene	Acenaphthylene
2,2'-oxybis-(1Chloropropane)	Naphthalene	3-Nitroaniline
4-Methylphenol	4-Chloroanaline	Acenaphthene
N-Nitroso-Di-n-propylamine	Hexachlorobutadiene	2,4-Dinitrophenol
Hexachloroethane	4-Chloro-3-methylphenol	4-Nitrophenol
2-Fluorophenol (surr)	2-Methylnapthalene	Dibenzofuran

1,4-Dichlorobenzene-d(4)	**Naphthalene-d(8)**	**Acenaphthene-d(10)**
Phenol-d(5)(surr)	Nitrobenzene-d(5) (surr)	2,4-Dinitrotoluene
2-Chlorophenol-d(4) (surr)		2,6-Dinitrotoluene
1,2-Dichlorobenzene-d(4) (surr)		Diethylphthalate
		4-Chlorophenylphenylether
		Fluorene
		4-Nitroaniline
		2-Fluorobiphenol (surr)

Phenanthrene-d(12)	**Chrysene-d(12)**	**Perylene-d(12)**
4,6-Dinoitro-2-methylphenol	Pyrene	Di-n-octylphthalate
N-nitroso-di-phenylamine	Butylbenzyl phthalate	Benzo(b)fluoranthene
4-Bromophenyl phenolether	3,3'-Dichlorobenzidine	Benzo(k)fluor anthene
Hexachlorobenzene	Benzo(a) anthracene	Benzo(a)pyrene
Pentachlorophenol	bis(2-ethyl-hexyl)phthalate	Indeno(1,2,3-cd)-pyrene
Carbazole	Chrysene	Benzo(g,h,i)-perylene
Phenanthrene	Terphenyl-d(14)(surr)	Dibenzo(a,h)-anthracene
Anthracene		
Di-n-butylphthalate		
Fluoranthene		
2,4,6-Tribromophenyl(surr)		

surr = surrogate compound

Table 9 Semi-volatile Corrective Action Summary

Quality Control Criteria	Frequency	Acceptance	Corrective Action
DFTPP	Initially and for every 12 hour analytical batch	Per Method Table 2	Re-tune Re-shoot
ICAL 20,50,80,120,160 ng on Column (2 uL inj)	As required	CCCs <30%RSD non-CCCs <15%RSD SPCC> 0.050 RRF	Verify Formulation Mix new Standards Re-analyze Re-calibrate
ICV 50 ng on Column (2 uL inj)	Every ICAL for verification	CCCs <20%D non-CCCs<20%D SPCC> 0.050 RRF	Verify Formulation Mix new Standards Re-analyze Re-calibrate
CCV 50 ng on Column (2 uL inj)	Each subsequent analytical batch	CCCs <20%D non-CCCs<20%D SPCC> 0.050 RRF	Verify Formulation Mix new Standards Re-analyze Re-calibrate
Method Blanks	Each Extraction batch	Free of contaminates to the reporting limit. 5XRL for Phthalates	Must meet criteria, re-analyze to confirm. Re-extract entire batch if necessary
LCS	Each Extraction batch	As per QC limits Table 5	Evaluate outages and impact on sample data. Re-extract batch if necessary
Samples	Within 12 hour analytical batch	As per Method; ISTD Rec., SSTD Rec. and Target concentrations (Section 9)	Dilute, re-analyze to confirm, and/or re-extract.
Duplicates	As required	None specified	NA
MS/MSD	As required	As per QC limits Table 5	Re-analyze to confirm QC outages.

APPENDIX A-79

STANDARD OPERATING PROCEDURE FOR PCBS BY METHOD 8082 IN LARGE VOLUME WATER

PACIFIC ANALYTICAL, INC.

Method for PCBs BY METHOD 8082 in large Volume Water
March 1999

Targets and Estimated Detection Limits: (Units = uG/kG)

PCB Congeners	0.5 nG/kG

SUMMARY OF METHOD:

Samples are spiked with 100 uL of a 1 uG/mL solution of labeled PCB congeners containing one homolog of each congener type. Sample aliquots are serially extracted in 4 liter sample bottles using 15:85 methylene chloride/hexane. Sample extracts are exchanged to hexane and processed thru sulfuric acid and acidified silica gel for cleanup. Extracts are taken to a final volume of 100 uL and analyzed by SIM GC/MS.

Reagents and Consumables:

a. Petroleum Ether - distilled in glass.
b. Surrogates - Cambridge Isotopes Part # EC-4189 containing
   4-Monochlorobiphenyl-$^{13}C_{12}$ (3),
   4,4'-Dichlorobiphenyl-$^{13}C_{12}$ (15),
   2,4,4'-Trichlorobiphenyl-$^{13}C_{12}$ (28),
   2,2',5,5'-tetrachlorobiphenyl-$^{13}C_{12}$ (52),
   2,3',4,4',5-Pentachlorobiphenyl-$^{13}C_{12}$ (118),
   2,2',4,4',5,5'-Hexachlorobiphenyl-$^{13}C_{12}$ (153),
   2,2',3,4,4',5,5'-Heptachlorobiphenyl-$^{13}C_{12}$ (180),
   2,2',3,3',4,4',5,5'-Octachlorobiphenyl-$^{13}C_{12}$ (194),
   2,2',3,3',4,5,5',6,6'-Nonochlorobiphenyl-$^{13}C_{12}$ (208),
   Decachlorobiphenyl-$^{13}C_{12}$ (209)
   at a concentration of 1 uG/mL.
c. 1.5 mL autosampler vials with crimp tops
d. Anydrous sodium sulfate baked at 400 deg C in muffle furnace.

Apparatus and Equipment:

a. 500 mL Boiling Flask with 24/40 joint
b. 400 nL beakers
c. Snyder Column with 24/40 joint
d. Powder funnel, 100 mm glass
e. Concentric Ring Boiling Bath
f. Nitrogen Blowdown device
g. Kuderna Danish Apparatus
h. Concentrated Sulfuric Acid
i. Shaker table.
j. 1mL syringe
k. 10 uL syringe
l. Analytical balance - capable of weighing 0.1 mG
m. Column - 30 meter X 0.25 mm I.D. DB-608 and RTX-1701

n. Gas Chromatograph - equiped with splitless injection for capillary chromatography capable of being heated to 300 deg C. GC capable of programed oven temperature ramps from 30 deg C to 310 deg C at a rate of 1 to 30 deg C/minute. Electron Capture Detector
o. Autosampler (Optional) - capable of injection of 1 uL +/- 0.05 uL sample into a splitless injection port.

Large Volume Aqueous Extraction:

1. Samples are collected into multiple 4 liter bottles. Spike each bottle with the surrogate solution so that a total of 100uL of the 1 ppm surrogate spike solution has been added to all the bottles of any one sample. (Example: if there are four 4 liter bottles, spike each with 25 uL of surrogate to yeild 4 X 25 uL = 100 uL). Place 20 mL of 15:85 methylene chloride/hexane into a 4 liter sample bottle containing the sample.

2. Shake for 2 minutes and let settle for 10 minutes.

3. Decant off the solvent and about 100 mL of water into a separatory funnel. Let settle and add the water back to the bottle. Drain the solvent into a 500 mL boiling flask.

4. Repeat step 2 thru 3 twice more, adding the solvent to the same boiling flask.

5. Repeat steps 2 thru 4 for each bottle of sample, adding the solvent to the same 500 mL boiling flask.

6. Attach a snyder column to the boiling flask containing the extract. Place on a steam bath and concentrate to about 100 mL. Remove and let cool.

7. Add 50 mL of concentrated sulfuric acid to the boiling flask and place on a shaker table over night.

8. Pour contents of boiling flask into a 500 mL separatory funnel. Rinse with flask over with about 10 mL of petroleum ether. Drain off lower sulfuric acid layer and discard. Rinse with 100 mL of distilled water. Rinse with 100 mL of 6N NaOH. Rinse with 100 mL of distilled water. Discard each rinse.

9. Drain the petroleum ether layer in the separatory funnel thru anydrous sodium sulfate into a clean 500 mL boiling flask. Rinse with 10 mL of petroleum ether.

10. Attach a snyder column to the boiling flask containing the extract. Place on a steam bath and concentrate to about 2 mL.

Let cool and transfer to a 3 dram vial with a few petroleum ether rinses. Using a stream of nitrogen, evaporate to 1 mL.

11. Use the same acidified silica gel specified for dioxin clean up in Method 1613.

Take a pasteur pipet and plug the tip with a small amount of glass wool using the glass wool puller.
Place a inch bed of the acidified silica gel in the column. Place the 1/2 mL extract from the autosampler vial onto the column. Collect into a 3 dram vial. Rinse the autosampler vial onto the column with 1 mL of hexane after the solvent has eluted to the top of the bed. Let the 1 mL rinse elute to the top of the bed. Continue to elute with 10 mL of petroleum ether. Using a stream of nitrogen, evaporate to 100 uL.

12. Place the 0.1 mL extract into a micro insert in an autosampler vial. Make sure and rinse the autosampler vial and insert before use.

QA/QC:

Ongoing Precision and Recovery: Prepare two 12 liter aliquots of reagent water to be used for OPR and OPR duplicate. Spike with 100 uL of a solution containing 1.0 uG/mL of each of the 52 targeted PCB congernes.

Lab blanks: Perform 2 lab blanks per set of 20 samples or per day whichever is the most frequent.

APPENDIX A-80

STANDARD OPERATING PROCEDURE FOR CHEMICAL OXYGEN DEMAND METHOD 410.1

Chemical Oxygen Demand
Method 410.1

Approvals and Signatures

QA Officer: Martha Roy Date: 9/25/96

Wet Chemistry Section Head: David E. Meadows Date: 9/25/96

1.0 Scope and Application

1.1 The Chemical Oxygen Demand (COD) method determines the quantity of oxygen, required to oxidize the organic matter in a waste sample, under specific conditions of oxidizing agent, temperature, and time.

1.2 Since the test utilizes a specific chemical oxidation the result has no definite relationship to the Biochemical Oxygen Demand (BOD) of the waste or to the Total Organic Carbon (TOC) level. The test result should be considered as an independent measurement of organic matter in the sample, rather than as a substitute for the BOD or TOC test.

1.3 The procedure for soil samples has been adopted from the "Procedures For Handling and Chemical Analysis of Sediment and Water Samples by Russell H. Plumb, May 1981."

1.4 Reporting Limit: 0.5 mg/L for liquids
900 mg/Kg for soil and sediment samples on an "as received" basis.

2.0 Summary of Method

2.1 Organic and oxidizable inorganic substances in the sample are oxidized by potassium dichromate in 50% sulfuric acid solution at reflux temperature. Silver sulfate is used as a catalyst and mercuric sulfate is added to remove chloride interference. The excess dichromate is titrated with standard ferrous ammonium sulfate, using orthophenanthroline ferrous complex as an indicator.

3.0 Sample Handling and Preservation

3.1 A minimum sample volume of 100 mLs must be collected in preserved plastic or glass containers. Liquid samples are preserved to pH < 2 with H_2SO_4 and maintained at 4 °C. Soil samples are not preserved, but are kept at 4 ± 2°C until analysis.

3.2 Holding time is 28 days from sample collection.

4.0 Reagents

4.1 $HgSO_4$ Powdered

4.2 Potassium Dichromate Solution (0.25N):

12.259 gram $K_2Cr_2O_7$ (Dried 2 hours at 105°C) plus DIH_2O to 1 liter.

4.3 Sulfuric Acid/Silver Sulfate Reagent:

Add 23.5 gram Ag_2SO_4 to a new 2.5 liter bottle of concentrated H_2SO_4. Add a stirbar and mix for about 30 minutes until Ag_2SO_4 is completely dissolved.

4.4 F.A.S. Titrant (0.05N):

Dissolve 41.05 gram $FE(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in approximately 1 liter DIH_2O. Add 40 ml concentrated H_2SO_4 and bring to 2 liter. This solution must be standardized daily (See 5.5) Standardization is recorded on the benchsheet.

4.5 Foreign Indicator:

1.48 gram 1-10 (orth.)phenanthroline monohydrate, 0.7 gram $FeSO_4 \cdot 7H_2O$ in 100 ml DIH_2O.

5.0 Procedure

5.1 All glassware must be thoroughly rinsed with 10% HCl and DIH_2O prior to use.

5.2 Pipette 20 mL liquid sample or 0.5 to 1.0 gram of soil with 20 mL boiled water in reflux flask. Add 0.4 gram $HgSO_4$ powder (2 scoops) and 5 mL concentrated

H_2SO_4 swirl to dissolve. Slowly add, with swirling, 5 mL 0.25 N potassium dichromate solution. Keep flask contents cool by swirling under cold running water or in an ice bath. Slowly add 30 mL H_2SO_4/Ag_2SO_4 to reflux flask, swirling to mix thoroughly. Add several boiling stones to flask, and connect to reflux condenser.

5.3 Each analysis batch shall consist of a "titration blank", a preparation blank and an LCS, and up to 9 samples.

5.4 Reflux for two hours. Do not begin timing until all flasks are boiling. Following reflux, cool for 30 minutes. Rinse each condenser with approximately 25 mL DIH_2O. The final volume in each reflux flask should be similar (it is not necessary that they be exactly the same).

5.5 Before titrating samples, the FAS titrant must be standardized. Pipette 5 mL 0.25 N Potassium Dichromate into clean flask. Add 60 mL 30% H_2SO_4 and 3 drops Foreign indicator. Titrate with FAS, recording volume required to go from blue-green to reddish-brown.

5.6 When flasks have cooled to room temperature, add 8-10 drops Foreign indicator and titrate with 0.05 N FAS. Indicator color will progress through green to a teal blue to blue. The endpoint is a reddish brown and is usually reached 1-2 drops after the blue color.

6.0 Calculation

6.1 Normality of FAS Titrant:

$$Normality = \frac{mL\ K\ Dichromate * 0.25}{mL\ FAS}$$

6.2 COD

$$Result = (A - B) * DF * Factor$$

Where: Result = mg/L or mg/Kg
A= mLs FAS to Titrate Blank
B= mLs FAS to Titrate Sample
DF= Addition Dilution Factor

Factor:

$$Factor = \frac{(N\ FAS) * 8000}{sample\ amount}$$

Sample amount= mL or gram

7.0 Quality Control

7.1 A prep blank and laboratory control sample (LCS) are analyzed with each reflux batch. The blank must be less than the reporting limit of 5.0 mg/L. The LCS must have a recovery between 90-110%.

7.2 A replicate and matrix spike are analyzed with every batch. The replicate analysis should have an RPD <20%. The matrix spike recovery should be between 75-125%. If two batches are analyzed in one shift, only one set of QC is prepared (ie one replicate and matrix spike).

COD Worksheet

F-0013

Analyst:_____ **Date :**_____ **Time :**_____

KHP Stock Lot #:_____ FAS Titrant Lot #:_____ LCS Lot #:_____

Standardization of FAS Titrant

1. Normality of K2Cr2O7: _____
2. Volume of K2Cr2O7: _____
3. mls of FAS: _____
4. Normality of FAS = (N K2Cr2O7)(Volume K2Cr2O7) = _____
   mls FAS
5. Factor = (N FAS) (8000) = _____
   mls sample
6. COD = (Blank - Net mls FAS) (Factor) = mg/l

Sample ID	mls Sample	mls K2Cr2O7	pH <2.0	FAS Titrant: Final mls	FAS Titrant: Initial mls	FAS Titrant: Net mls	Blank - Net mls	Additional Factors	COD: mg/l

Reviewed By:_____
Date:

APPENDIX A-81

STANDARD OPERATING PROCEDURE FOR DETERMINATION OF TOTAL ORGANIC CARBON IN SOIL AND SEDIMENT SAMPLES BY CHEMICAL OXIDATION AND DETECTION BY A THERMAL CONDUCTIVITY DETECTOR

STANDARD OPERATING PROCEDURE FOR
DETERMINATION TOTAL ORGANIC CARBON IN SOIL AND SEDIMENT SAMPLES BY CHEMICAL OXIDATION AND DETECTION BY A THERMAL CONDUCTIVITY DETECTOR (TCD)
(Modified Lloyd Kahn Method)

Written by:

Kjestine Allen, Mobile Lab Manager
ONSITE Environmental Laboratories, Inc.

Approved by:

Sharon Nordstrom, Project Manager
Roy F. Weston, Inc.

Approved by:

Marie Wojtas, Chemist
USACE

1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat each chemical as a potential health hazard and minimize potential exposure. Handle stock standard solutions containing these compounds in a fume hood. Wear personal protective equipment such as lab coats, gloves and safety glasses while performing this analysis.

1.2 All reagents and standards used for analysis must be accompanied to the laboratory by manufacturer's Material Data Safety (MSD) Sheets. MSD Sheets are kept on file in the laboratory in binders labeled MSDS on a bookshelf in the data processing area, and are available to all laboratory personnel. As part of the training process, analysts make themselves familiar with the contents of the MSD Sheets.

1.3 Secure all compressed gas cylinders with chains or straps. Train analysts in tank changing procedures.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the technique of determining Total Organic Carbon using a thermal conductivity detector (TCD). This method is based on a modified Lloyd Kahn Method. This method is applicable to soil and sediment samples collected along the GE Housatonic River Site.

3.0 SUMMARY OF METHOD

3.1 Approximately twenty (20) grams of soil are treated with phosphoric acid and allowed to stabilize in a controlled temperature environment. A portion, 25mg of the soil is placed in a tin sample introduction cup and analyzed for total organic carbon using a C.E. Instruments NC 2500 Elemental G.C.-T.C.D. analyzer.

4.0 INTERFERENCE'S

4.1 During the decarbonation and drying steps some of the volatile organics may be lost resulting in a low bias.

4.2 Analyzing within the holding time, and analyzing the sample immediately after preparation will help to minimize the loss of VOCs and bacterial decomposition of the organic compounds.

5.0 APPARATUS AND MATERIALS

5.1 C.E. Instruments NC 2500 Elemental Analyzer

5.2 Metler/Toledo AT21 analytical balance, capable of weighing to 0.001mg.

5.3 Data system

5.3.1 One Pentium computer with enough memory to run Excel and process raw data from the NC 2500.

5.3.2 Eager 200 data elemental software system

5.4 Microsyringes - Hamilton 10-, and 50-µL

5.5 VWR low/high temperature heat box

5.6 Disposable Pasteur pipettes, pipette bulbs, tweezers and spatulas

5.7 Class A Volumetric glassware - 10 mL and 100 mL

5.8 C.E. Elantech, tin capsules 5x9mm

5.9 Class A Graduated Cylinders, 10 mL, 50 mL, 100 mL

5.10 Certified weights, 10 mg - 50 mg.

6.0 REAGENTS AND STANDARDS

6.1 Water (VWR) - Purified DI water

6.2 Phosphoric Acid (VWR) - High Purity

6.3 Sucrose (J.T.Baker) - Ultra Pure

6.4 Sulfanilammide (C.E. Elantech)

6.5 Soil Standard (Environmental Resource Association)

6.6 Sea Sand (EM Science)

7.0 CALIBRATION PROCEDURE

7.1 Calibration Curve Preparation for TOC: Analyze a 5-point initial calibration curve for TOC. The range for the curve is approximately 1,500 ppm - 115,000 ppm. The standard curve concentrations are listed below.

41.84% Sulfanilammide	mg Carbon	ppm
0.10mg -0mg, + 0.1mg	0.042	1,680
1.50mg +/- 0.2mg	0.630	25,200
3.00mg +/- 0.2mg	1.255	50,400
5.00mg +/- 0.2mg	2.100	84,000
7.00mg -0.1mg, +0mg	2.930	117,200

7.2 Curve acceptance criteria for TOC:

The curve is analyzed, and the software (Eager 200) automatically calculates the curve using a linear regression. In order for the curve to be acceptable, the correlation coefficient must be 0.995 or higher.

8.0 QUALITY CONTROL

8.1 Before analysis of samples can proceed, calibration verification must occur.

8.1.1 Perform midpoint continuing calibration checks. The midpoint calibration standard in this case is the midpoint TOC standard. The TOC standard is analyzed and must be within ±15% of the initial calibration for analysis to continue.

$$\%\,\mathrm{Diff} = \frac{\mathrm{CF} - \overline{\mathrm{CF}}_y}{\mathrm{CF}} x100$$

This calibration verification occurs before samples are analyzed. A closing TOC standard is also analyzed after the last sample and must fall within the ± 15% window for results to be considered valid.

8.2 A Laboratory control spike (LCS) will be run every 20 samples in quadruplicate. This LCS will be a midpoint standard of 30% sucrose.

8.3 A matrix spike (MS) and a matrix spike duplicate (MSD) will be run every 20 samples in triplicate. The MS and MSD will be spiked with a midpoint standard of 30% sucrose and performed on a sample randomly picked from the 20 sample batch.

8.4 A method blank will be run at the beginning and end of every 20 sample batch, and must be clean of all target compounds before analysis may continue.

9.0 INSTRUMENT CONDITIONS AND SAMPLE ANALYSIS

9.1 Instrument Conditions:

9.1.2 NC 2500 Conditions

Combustion Chamber Temp:	1020 degrees C
Reduction Chamber Temp:	700 degrees C
Sample Weight:	25mg
Oxygen Injection Time:	45 seconds
Helium Flow:	100ml/minute
Total Run Time:	220 seconds

9.2 Sample Preparation:

9.2.1 Approximately 30 grams of soil is weighed into an aluminum weighing dish and placed in a oven at 75 degrees C for 12 hours. An aliquot of the dried sample is treated with 1:19 phosphoric acid solution until all signs of effervescence are gone. The sample is placed back in the oven at 75 degrees C for one hour.

9.2.2. Ideally, samples will be analyzed immediately after preparation. Holding time for samples is 28 days.

9.2.4 Load approximately 25mg of treated sample into the tin capsule and analyze according to manufacturer's recommendations. Samples are analyzed in triplicate and an average concentration is taken. All samples and QC that are analyzed are recorded in the TOC run log.

9.5 Quantitative analysis of results

9.5.1 Quantitative results are calculated using a calibration factor from the initial calibration. This is done by the software (Eager 200). Results are given in percent Carbon. Final concentration is calculated in the following manner:

$$mgC = \frac{(\%C)(W)}{100}$$

$$ppt = \frac{mgC}{(Wt)(Wd)}$$

$$ppm = (ppt)(1000)$$

where:
%C = Result taken from instrument readout.
W = Sample weight in mg
Wt = Sample weight in g
Wd = Dry weight of sample

Dry weight is calculated the following manner:

$$\% \text{ solids} = \frac{((\text{wet wt.})-(\text{tin wt.}))}{((\text{dry wt.})-(\text{tin wt.}))} \times 100$$

10.0 ACCEPTANCE OF DATA AND METHOD PERFORMANCE

10.1 All initial calibration data must be within compliance's listed in Sec. 7.0.

10.2 All continuing calibration results must be within compliance's listed in Sec. 8.1.

10.3 An independent check standard is run with each set. Recoveries must be within ±15% of the true value..

10.4 LCS recoveries must be within 75-125% of spiked value. LCS concentrations falling outside this window are noted to the client and the sample batch will be reanalyzed.

10.5 Matrix spike recoveries must be within 75-125% of spiked value. Concentrations outside this window are noted to the client. No corrective action is taken.

11.0 REFERENCES

1. Lloyd Kahn Quality Assurance Specialist, US EPA Region II, Determination of TOC in Sediment, July 27, 1988.

STANDARD OPERATING PROCEDURE FOR
DETERMINATION TOTAL ORGANIC CARBON IN SOIL AND SEDIMENT SAMPLES BY CHEMICAL OXIDATION AND DETECTION BY A THERMAL CONDUCTIVITY DETECTOR (TCD)
(Modified Lloyd Kahn Method)

Written by:

Kjestine Allen, Mobile Lab Manager
ONSITE Environmental Laboratories, Inc.

Approved by:

Sharon Nordstrom, Project Manager
Roy F. Weston, Inc.

Approved by:

Marie Wojtas, Chemist
USACE

1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat each chemical as a potential health hazard and minimize potential exposure. Handle stock standard solutions containing these compounds in a fume hood. Wear personal protective equipment such as lab coats, gloves and safety glasses while performing this analysis.

1.2 All reagents and standards used for analysis must be accompanied to the laboratory by manufacturer's Material Data Safety (MSD) Sheets. MSD Sheets are kept on file in the laboratory in binders labeled MSDS on a bookshelf in the data processing area, and are available to all laboratory personnel. As part of the training process, analysts make themselves familiar with the contents of the MSD Sheets.

1.3 Secure all compressed gas cylinders with chains or straps. Train analysts in tank changing procedures.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the technique of determining Total Organic Carbon using a thermal conductivity detector (TCD). This method is based on a modified Lloyd Kahn Method. This method is applicable to soil and sediment samples collected at the GE Housatonic River Site.

3.0 SUMMARY OF METHOD

3.1 Approximately twenty (20) grams of soil are treated with phosphoric acid and allowed to stabilize in a controlled temperature environment. A portion, 25mg of the soil is placed in a tin sample introduction cup and analyzed for total organic carbon using a C.E. Instruments NC 2500 Elemental G.C.-T.C.D. analyzer.

4.0 INTERFERENCE'S

4.1 During the decarbonation and drying steps some of the volatile organics may be lost resulting in a low bias.

4.2 Analyzing within the holding time, and analyzing the sample immediately after preparation will help to minimize the loss of VOCs and bacterial decomposition of the organic compounds.

5.0 APPARATUS AND MATERIALS

5.1 C.E. Instruments NC 2500 Elemental Analyzer

5.2 Metler/Toledo AT21 analytical balance, capable of weighing to 0.001mg.

5.3 Data system

5.3.1 One Pentium computer with enough memory to run Excel and process raw data from the NC 2500.

5.3.2 Eager 200 data elemental software system

5.4 Microsyringes - Hamilton 10-, and 50-µL

5.5 VWR low/high temperature heat box

5.6 Disposable Pasteur pipettes, pipette bulbs, tweezers and spatulas

5.7 Class A Volumetric glassware - 10 mL and 100 mL

5.8 C.E. Elantech, tin capsules 5x9mm

5.9 Class A Graduated Cylinders, 10 mL, 50 mL, 100 mL

5.10 Certified weights, 10 mg - 100 mg.

6.0 REAGENTS AND STANDARDS

6.1 Water (VWR) - Purified DI water

6.2 Phosphoric Acid (VWR) - High Purity

6.3 Sucrose (J.T.Baker) - Ultra Pure

6.4 Sulfanilammide (C.E. Elantech)

6.5 Soil Standard (Environmental Resource Association)

6.6 Sea Sand (EM Science)

7.0 CALIBRATION PROCEDURE

7.1 Calibration Curve Preparation for TOC: Analyze a 5-point initial calibration curve for TOC. The range for the curve is approximately 1,500 ppm - 115,000 ppm. The standard curve concentrations are listed below.

41.84% Sulfanilammide	mg Carbon	ppm
0.10mg -0mg, + 0.1mg	0.042	1,680
1.50mg +/- 0.2mg	0.630	25,200
3.00mg +/- 0.2mg	1.255	50,400
5.00mg +/- 0.2mg	2.100	84,000
7.00mg -0.1mg, +0mg	2.930	117,200

7.2 Curve acceptance criteria for TOC:

The curve is analyzed, and the software (Eager 200) automatically calculates the curve using a linear regression. In order for the curve to be acceptable, the correlation coefficient must be 0.995 or higher.

8.0 QUALITY CONTROL

8.1 Before analysis of samples can proceed, calibration verification must occur.

8.1.1 Perform midpoint continuing calibration checks. The midpoint calibration standard in this case is the midpoint TOC standard. The TOC standard is analyzed and must be within ±25% of the initial calibration for analysis to continue.

$$\%\,\mathrm{Diff} = \frac{\mathrm{CF} - \overline{\mathrm{CF}}_y}{\mathrm{CF}} x100$$

This calibration verification occurs before samples are analyzed. A closing TOC standard is also analyzed after the last sample and must fall within the ± 25% window for results to be considered valid.

8.2 A Laboratory control spike (LCS) will be run every 20 samples in quadruplicate. This LCS will be a midpoint standard of 10% sucrose.

8.3 A matrix spike (MS) and a matrix spike duplicate (MSD) will be run every 20 samples in triplicate. The MS and MSD will be spiked with a midpoint standard of 10% sucrose and performed on a sample randomly picked from the 20 sample batch.

8.4 A method blank will be run at the beginning and end of every 20 sample batch, and must be clean of all target compounds before analysis may continue.

9.0 INSTRUMENT CONDITIONS AND SAMPLE ANALYSIS

9.1 Instrument Conditions:

9.1.2 NC 2500 Conditions

Combustion Chamber Temp:	1020 degrees C
Reduction Chamber Temp:	700 degrees C
Sample Weight:	25mg
Oxygen Injection Time:	45 seconds
Helium Flow:	100ml/minute
Total Run Time:	220 seconds

9.2 Sample Preparation:

9.2.1 Treat approximately 20 grams with 4mls of 1:19 phosphoric acid solution. Add phosphoric acid until all signs of effervescence are gone. Place sample in the oven at 75 degrees C for six hours.

9.2.2. Ideally, samples will be analyzed immediately after preparation. Holding time for samples is 28 days.

9.2.4 Load approximately 25mg of treated sample into the tin capsule and analyze according to manufacturer's recommendations. Samples are analyzed in triplicate and an average concentration is taken. All samples and QC that are analyzed are recorded in the TOC run log.

9.5 Quantitative analysis of results

9.5.1 Quantitative results are calculated using a calibration factor from the initial calibration. This is done by the software (Eager 200). Results are given in percent Carbon. Final concentration is calculated in the following manner:

$$mgC = \frac{(\%C)(W)}{100}$$

$$ppt = \frac{mgC}{(Wt)(Wd)}$$

$$ppm = (ppt)(1000)$$

where:

%C = Result taken from instrument readout.
W = Sample weight in mg
Wt = Sample weight in g
Wd = Dry weight of sample

Dry weight is calculated the following manner:

$$\% \text{ solids} = \frac{((\text{wet wt.})-(\text{tin wt.}))}{((\text{dry wt.})-(\text{tin wt.}))} \times 100$$

10.0 ACCEPTANCE OF DATA AND METHOD PERFORMANCE

10.1 All initial calibration data must be within compliance's listed in Sec. 7.0.

10.2 All continuing calibration results must be within compliance's listed in Sec. 8.1.

10.3 An independent check standard is run with each set. Recoveries must be within ±25% of the true value..

10.4 LCS recoveries must be within 75-125% of spiked value. LCS concentrations falling outside this window are noted to the client and the sample batch will be reanalyzed.

10.5 Matrix spike recoveries must be within 75-125% of spiked value. Concentrations outside this window are noted to the client. No corrective action is taken.

11.0 REFERENCES

1. Lloyd Kahn Quality Assurance Specialist, US EPA Region II, Determination of TOC in Sediment, July 27, 1988.

STANDARD OPERATING PROCEDURE FOR
DETERMINATION TOTAL ORGANIC CARBON IN SOIL AND SEDIMENT SAMPLES BY CHEMICAL OXIDATION AND DETECTION BY A THERMAL CONDUCTIVITY DETECTOR (TCD)
(Modified Lloyd Kahn Method)

Written by: Kathleen N. Campbell
Kathleen Campbell, Mobile Lab Manager
ONSITE Environmental Laboratories, Inc.

Approved by:
Sharon Nordstrom, Project Manager
Roy F. Weston, Inc.

Approved by: Marie Wojtas
Marie Wojtas, Chemist
USACE

1.0 HEALTH AND SAFETY

1.1 The toxicity and carcinogenicity of chemicals used in this method have not been precisely defined. Treat each chemical as a potential health hazard and minimize potential exposure. Handle stock standard solutions containing these compounds in a fume hood. Wear personal protective equipment such as lab coats, gloves and safety glasses while performing this analysis.

1.2 All reagents and standards used for analysis must be accompanied to the laboratory by manufacturer's Material Data Safety (MSD) Sheets. MSD Sheets are kept on file in the laboratory in binders labeled MSDS on a bookshelf in the data processing area, and are available to all laboratory personnel. As part of the training process, analysts make themselves familiar with the contents of the MSD Sheets.

1.3 Secure all compressed gas cylinders with chains or straps. Train analysts in tank changing procedures.

2.0 SCOPE AND APPLICATION

2.1 The purpose of this SOP is to outline, in detail, the technique of determining Total Organic Carbon using a thermal conductivity detector (TCD). This method is based on a modified Lloyd Kahn Method. This method is applicable to soil and sediment samples collected along the GE Housatonic River Site.

3.0 SUMMARY OF METHOD

3.1 Approximately twenty (20) grams of soil are treated with phosphoric acid and allowed to stabilize in a controlled temperature environment. A portion, 25mg of the soil is placed in a tin sample introduction cup and analyzed for total organic carbon using a C.E. Instruments NC 2500 Elemental G.C.-T.C.D. analyzer.

4.0 INTERFERENCE'S

4.1 During the decarbonation and drying steps some of the volatile organics may be lost resulting in a low bias.

4.2 Analyzing within the holding time, and analyzing the sample immediately after preparation will help to minimize the loss of VOCs and bacterial decomposition of the organic compounds.

5.0 APPARATUS AND MATERIALS

5.1 C.E. Instruments NC 2500 Elemental Analyzer

5.2 Metler/Toledo AT21 analytical balance, capable of weighing to 0.001mg.

5.3 Data system

5.3.1 One Pentium computer with enough memory to run Excel and process raw data from the NC 2500.

5.3.2 Eager 200 data elemental software system

5.4 Microsyringes - Hamilton 10-, and 50-µL

5.5 VWR low/high temperature heat box

5.6 Disposable Pasteur pipettes, pipette bulbs, tweezers and spatulas

5.7 Class A Volumetric glassware - 10 mL and 100 mL

5.8 C.E. Elantech, tin capsules 5x9mm

5.9 Class A Graduated Cylinders, 10 mL, 50 mL, 100 mL

5.10 Class A calibration weights, 10 mg - 50 mg.

6.0 REAGENTS AND STANDARDS

6.1 Water (VWR) - Purified DI water

6.2 Phosphoric Acid (VWR) - High Purity

6.3 Sucrose (J.T.Baker) - Ultra Pure

6.4 Sulfanilammide (C.E. Elantech)

6.5 Soil Standard (Environmental Resource Association)

6.6 Sea Sand (EM Science)

7.0 CALIBRATION PROCEDURE

7.1 Calibration Curve Preparation for TOC: Analyze a 5-point initial calibration curve for TOC. The range for the curve is approximately 1,500 ppm - 115,000 ppm. The standard curve concentrations are listed below.

41.84% Sulfanilammide	mg Carbon	ppm
0.10mg -0mg, + 0.1mg	0.042	1,680
1.50mg +/- 0.2mg	0.630	25,200
3.00mg +/- 0.2mg	1.255	50,400
5.00mg +/- 0.2mg	2.100	84,000
7.00mg -0.1mg, +0mg	2.930	117,200

7.2 Curve acceptance criteria for TOC:

The curve is analyzed, and the software (Eager 200) automatically calculates the curve using a linear regression. In order for the curve to be acceptable, the correlation coefficient must be 0.995 or higher.

8.0 QUALITY CONTROL

8.1 Before analysis of samples can proceed, calibration verification must occur.

8.1.1 Perform midpoint continuing calibration checks. The midpoint calibration standard in this case is the midpoint TOC standard. The TOC standard is analyzed and must be within ±15% of the initial calibration for analysis to continue.

$$\%\,\text{Diff} = \frac{\text{CF} - \overline{\text{CF}_y}}{\text{CF}} x100$$

This calibration verification occurs before samples are analyzed. A closing TOC standard is also analyzed after the last sample and must fall within the ± 15% window for results to be considered valid.

8.2 A Laboratory control spike (LCS) will be run every 20 samples in quadruplicate. This LCS will be a midpoint standard of 30% sucrose.

8.3 A matrix spike (MS) and a matrix spike duplicate (MSD) will be run every 20 samples in triplicate. The MS and MSD will be spiked with a midpoint standard of 30% sucrose and performed on a sample randomly picked from the 20 sample batch.

8.4 A method blank will be run at the beginning and end of every 20 sample batch, and must be clean of all target compounds before analysis may continue.

9.0 INSTRUMENT CONDITIONS AND SAMPLE ANALYSIS

9.1 Instrument Conditions:

9.1.2 NC 2500 Conditions

Combustion Chamber Temp:	1020 degrees C
Reduction Chamber Temp:	700 degrees C
Sample Weight:	25mg
Oxygen Injection Time:	45 seconds
Helium Flow:	100 mL/minute
Total Run Time:	220 seconds

9.2 Sample Preparation:

9.2.1 Approximately 30 grams of soil is weighed into an aluminum weighing dish and placed in a oven at 75 degrees C for 12 hours. An aliquot of the dried sample is treated with 1:19 phosphoric acid solution until all signs of effervescence are gone. The sample is placed back in the oven at 75 degrees C for one hour.

9.2.2. Ideally, samples will be analyzed immediately after preparation. Holding time for samples is 28 days.

9.2.4 Load approximately 25mg of treated sample into the tin capsule and analyze according to manufacturer's recommendations. Samples are analyzed in triplicate and an average concentration is taken. All samples and QC that are analyzed are recorded in the TOC run log.

9.5 Quantitative analysis of results

9.5.1 Quantitative results are calculated using a calibration factor from the initial calibration. This is done by the software (Eager 200). Results are given in percent Carbon. Final concentration is calculated in the following manner:

$$mgC = \frac{(\%C)(W)}{100}$$

$$ppt = \frac{mgC}{(Wt)(Wd)}$$

$$ppm = (ppt)(1000)$$

where:

%C = Result taken from instrument readout.
W = Sample weight in mg
Wt = Sample weight in g
Wd = Dry weight of sample
ppt = Parts per thousand

Dry weight is calculated the following manner:

$$\% \text{ solids} = \frac{((\text{wet wt.})-(\text{tin wt.}))}{((\text{dry wt.})-(\text{tin wt.}))} \times 100$$

9.5.2 For each sample the software (Eager 200) calculates the %RSD of the triplicate analyses. If a sample has varying results and a %RSD > 30% it is reanalyzed. If the %RSD remains > 30%, the sample is said to exhibit a matrix effect. Both the original and reanalyzed results will be submitted. However, if a sample has a %RSD > 30% with only one outlying point that point is disregarded in the final calculation.

10.0 ACCEPTANCE OF DATA AND METHOD PERFORMANCE

10.1 All initial calibration data must be within compliance's listed in Sec. 7.0.

10.2 All continuing calibration results must be within compliance's listed in Sec. 8.1.

10.3 An independent check standard is run with each set. Recoveries must be within ±15% of the true value.

10.4 LCS recoveries must be within 75-125% of spiked value. LCS concentrations falling outside this window are noted to the client and the sample batch will be reanalyzed.

10.5 Matrix spike recoveries must be within 75-125% of spiked value. Concentrations outside this window are noted to the client. No corrective action is taken.

11.0 REFERENCES

1. Lloyd Kahn Quality Assurance Specialist, US EPA Region II, Determination of TOC in Sediment, July 27, 1988.