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New England District
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Technical Support Services
General Electric (GE) Housatonic River Project
Pittsfield, Massachusetts

Contract No. DACW33-94-D-0009

Task Order No. 0032

QUALITY ASSURANCE PROJECT PLAN

Volume II
Appendix A

DCN: GEP2-100598-AADE

October 1998

WESTON SOLUTIONS

FINAL

QUALITY ASSURANCE PROJECT PLAN

GENERAL ELECTRIC (GE) HOUSATONIC RIVER PROJECT PITTSFIELD, MASSACHUSETTS

Volume II—Appendix A

Contract No. DACW33-94-D-0009
Task Order No.: 0032
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Prepared for

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TABLE OF CONTENTS

APPENDIX A—STANDARD OPERATING PROCEDURES

Appendix A-1—Standard Operating Procedure for Hardness, Total

Appendix A-2—Standard Operating Procedure for Total Dissolved Solids (Residue, Filtered)

Appendix A-3—Standard Operating Procedure for Total Suspended Solids (Residue, Non-Filtered

Appendix A-4—Standard Operating Procedure for Alkalinity as $CaCO_3$ (Titrimetric, pH 4.5)

Appendix A-5—Standard Operating Procedure for Total and Amenable Cyanide

Appendix A-6—Standard Operating Procedure for Ammonia-Nitrogen

Appendix A-7—Standard Operating Procedure for Total Kjeldahl Nitrogen

Appendix A-8—Standard Operating Procedure for Nitrate/Nitrite-N Method

Appendix A-9—Standard Operating Procedure for Nitrite-N

Appendix A-10—Standard Operating Procedure for Phosphate as P

Appendix A-11—Standard Operating Procedure for Orthophosphate as P

Appendix A-12—Standard Operating Procedure for Sulfide (Method 376.2/4500-S^2-D)

Appendix A-13—Standard Operating Procedure for Sulfide in Soil

Appendix A-14—Standard Operating Procedure for Biological Oxygen Demand

Appendix A-15—Standard Operating Procedure for Total Organic Carbon

Appendix A-16—Standard Operating Procedure for Total Organic Carbon in Sediment (Lloyd Kahn Method)

Appendix A-17—Standard Operating Procedure for Percent Solids

Appendix A-18—Standard Operating Procedure for Acid Digestion of Aqueous Samples for Total Metals

Appendix A-19—Standard Operating Procedure for Acid Digestion of Sediments, Sludges, and Soils for Total Metals

Appendix A-20—Standard Operating Procedure for Metals Analysis by ICP

Appendix A-21—Standard Operating Procedure for Mercury Preparation and Cold Vapor Analysis of Aqueous Samples

Appendix A-22—Standard Operating Procedure for Mercury Preparation and Cold Vapor Analysis of Soil Samples

Appendix A-23—Standard Operating Procedure for Organochlorine Pesticides by Gas Chromatography

TABLE OF CONTENTS
(Continued)

Appendix A-24—Standard Operating Procedure for Polychlorinated Biphenyls (PCB) Analysis

Appendix A-25—Standard Operating Procedure for Organophosphorus Pesticides by Capillary GC

Appendix A-26—Standard Operating Procedure for Chlorinated Herbicides by ECD

Appendix A-27—Standard Operating Procedure for Purge and Trap of Aqueous Samples

Appendix A-28—Standard Operating Procedure for Extractable Semivolatile Organic Compounds by GC/MS

Appendix A-29—Standard Operating Procedure for Extractable PAHs by GC/MS Selective Ion Monitoring

Appendix A-30—Standard Operating Procedure for Petroleum Hydrocarbons (by Infrared Spectrophotometry)

Appendix A-31—Standard Operating Procedure for Ignitability

Appendix A-32—Standard Operating Procedure for Reactivity (Cyanide/Sulfide)

Appendix A-33—Standard Operating Procedure for pH

Appendix A-34—Standard Operating Procedure for Volatile Organic Compounds by GC/MS

Appendix A-35—Standard Operating Procedure for Particle Size Analysis

Appendix A-36—Standard Operating Procedure for Polychlorinated Dibenzo Dioxin/Furans

Appendix A-37—Standard Operating Procedure for Polychlorinated Biphenyls and 1,2,4-TCB by GC-ECD (Modified EPA 8082)

Appendix A-38—Standard Operating Procedure for High Resolution Mass Spectrometry Modified Method 1668

Appendix A-39—Standard Operating Procedure for Chlorophyll-A

Appendix A-40—Standard Operating Procedure for Atterberg Limits (Liquid Limit, Plastic Limit, and Plasticity Index in Soil)

Appendix A-41—Standard Operating Procedure for Specific Gravity (for Use in Porosity Calculation)

APPENDIX A

STANDARD OPERATING PROCEDURES

APPENDIX A-21

STANDARD OPERATING PROCEDURE FOR MERCURY PREPARATION AND COLD VAPOR ANALYSIS OF AQUEOUS SAMPLES

Mercury Preparation and Cold Vapor Analysis Of Aqueous Samples By Method 7470A

Approvals and Signatures

QA Officer: Martha Roy Date: 3/10/97

Metals Section Head: Kristine L. Aubin Date: 03/10/97

1.0 Scope and Application

1.1 This SOP details the requirements of the mercury method 7470A used for water samples. All samples must be subjected to an appropriate dissolution step prior to analysis.

1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heating step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heating step is not necessary.

1.3 Using a 100 mL sample, a detection limit of 0.2 ug Hg/L can be achieved; concentrations below this level should be reported as < 0.2 ug/L.

2.0 Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption

spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduce and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 Sample Handling and Preservation

4.1 Aqueous Samples: Preserve by acidification with nitric acid to a pH of 2 or lower at the time of collection. Filter through an all glass apparatus before the acidification if only dissolved mercury is to be determined. For total mercury omit filtration.

Note: Preserve samples not preserved at the time of collection because of transport restrictions. Acidify with nitric acid to a pH <2 upon receipt in the laboratory.

4.2 The holding time for mercury analysis is 26 days from receipt of the sample.

5.0 Apparatus and Materials

5.1 Leeman Labs PS200 and PS200II with autosampler and personal computer (10/91), (3/96).

5.2 300 mL BOD Bottles

5.3 Hot Water Bath

6.0 Reagents and Standards

All prepared standards and reagents are assigned the expiration date provided by the vendor. This indicates a maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation is necessary. All standards and reagents are stored at room temperature. The preparation of all standards is recorded in the metals standard preparation notebook. Calibration standards are prepared fresh daily.

6.1 Concentrated Sulfuric Acid, Reagent Grade

6.2 Concentrated Nitric Acid, Reagent Grade

6.3 Concentrated Hydrochloric Acid, Reagent Grade

6.3.1 3 N HCL (for instrument rinsing)

Add 91.41 mL of Concentrated Hydrochloric Acid, bring to 1 liter with ASTM Type I Water.

6.4 10% Stannous Chloride (reducant added by the instrument)

Add 100 grams of Stannous Chloride to 1000 mLs 3 N HCl.

6.5 Hydroxylamine Hydrochloride Solution.

Dissolve 320 grams of Crystalline Hydroxylamine Hydrochloride in 2 liters of ASTM Type 1 Water.

6.6 Potassium Permanganate (5% solution, w/v):

Dissolve 100 grams Potassium Permanganate crystal in 2 liters of ASTM Type I Water.

6.7 Potassium Persulfate (5% solution, w/v):

Dissolve 100 grams Potassium Persulfate Crystal in 2 liters of ASTM Type 1 Water.

6.8 100 ppb Stock Mercury Solution (Diluted from 1000 ug/mL Hg Spex Plasma Standard) for Calibration Curve and Continuing Calibration Check Standards.

To make 10,000 ppb Hg intermediate, add 1 mL Spex Plasma Standard to approximately 80 mLs ASTM Type I and 0.15 mL concentrated HNO_3, bring to 100 mL. Add 10 mL of the 10,000 ppb Hg intermediate to approximately 800 mL ASTM Type I and 1.5 mL concentrated HNO_3, and bring to final volume of 1000 mL. The final solution is 100 ppb Hg. See Table in Section 7.1 for preparation of the calibration curve.

6.9 18 ppb Stock Mercury Solution for Initial Calibration Verification:

Dilute 1 mL 1000 ug/mL Hg Inorganic Ventures Standards and 0.15 mL HNO_3 to 100 mL with ASTM Type 1 water. From this intermediate take 1.8 mL, 1.5 mL HNO_3 and dilute to 1000 mL with ASTM Type 1 water. Final concentration is 18 ppb Hg.

6.10 Mixed Acids Solution (50% H_2SO_4, 25% HNO_3 and 25% H_2O).

With constant stirring slowly add 500 mLs concentrated HNO_3 and 1000 mL concentrated H_2SO_4 and 500 mL ASTM Type I.

6.11 Magnesium Perchlorate, desiccant. Drying reagent used in trap.

7.0 Preparation of Aqueous Samples

7.1 Transfer a 100 mL mixed portion of sample to a clean 300 mL BOD bottle.

Prepare a preparation blank consisting of 100 mL of ASTMType I water.

7.2 Duplicate analyses are used to check reproducibility and sample consistency.

Duplicate samples are prepared by taking two sample aliquots and placing them in two distinct bottles. One sample will be labeled with the laboratory number and the other will be labeled with the laboratory number and DP suffix. These bottles will be carried through the preparation and analysis procedures as two separate samples. Prepare duplicates at a frequency of 1 per 20 samples of the same matrix.

7.3 Matrix spike analysis are used to check for possible matrix interferences. They are prepared by taking two sample aliquots and placing them in two distinct bottles. One bottle will be labeled as the laboratory number and the other will be labeled with the laboratory number and MS suffix. The bottle labeled MS will be spiked with 1 mL (or otherwise noted) of 100 ppb Hg stock standard. These bottles will be carried through the preparation and analysis procedures as two separate samples. Prepare matrix spikes at a frequency of 1 per 20 samples of the same matrix.

Matrix Spikes - 100 ppb Hg stock is added to sample to raise final concentration by 1 ppb (i.e. 1.0 mL for 100 mL volume sample, 0.5 mL for 50 mL volume sample). A spike must be witnessed and documented by another analyst.

7.4 An aqueous laboratory control sample (LCS) is digested with every batch of 20 aqueous samples. 100 mL of ASTM Type 1 is spiked with 1.0 mL 1000 ppb mercury.

7.5 Add ten (10) mL of mixed acids to each sample bottle and swirled. Add potassium permanganate (15.0 mL).

7.6 Allow the samples to stand for 15 minutes to determine if the samples remain purple in color. Add additional $KmnO_4$ as required to maintain purple color. If extra $KMnO_4$ is needed to colorize samples, standards must also have extra permanganate to keep the same matrix.

7.7 Add eight (8) mL of potassium persulfate (5%w/v).

7.8 Heat the bottles containing aqueous samples are heated for two hours at 95 °C in a hot water bath. Samples are removed and allowed to cool to room temperature.

7.9 If samples are suspected to be high in organics they are aspirated utilizing the house air jet to eliminate possible interference by organics. This procedure takes

place under a hood, an aspirating tube with disposable tip is inserted into each sample bottle and allowed to bubble for 2 minutes.

7.10 Add six (6) mL of Hydroxylamine hydrochloride to each solution to reduce the excess permanganate. Use 8-10 mL of the mercury digestate for the initial analysis.

7.11 Dilutions can be performed if results of 100% analyses are above the highest calibration standard (10 ppb). Dilutions are prepared by taking an appropriate aliquot of the previously digested sample and adding an appropriate amount of matrix blank. The sample is then reanalyzed.

8.0 Calibration

8.1 Calibrate the instrument at the beginning of each analytical series. For every calibration, prepare a curve at the following concentrations 0.0 ug/L, 0.2 ug/L, 0.5 ug/L, 1.0 ug/L, 3.0 ug/L, and 5.0 ug/L from a 100 ug/L stock mercury standard. Transfer the mercury into clean 300 mL BOD bottles. Adjust the total volume up to 100 mL with ASTM Type 1 water. See the following table:

Standard ID	mL of 100 ppb Hg Stock Solution	mL of ASTM Type I water
0.0	0	100
0.2	0.2	99.8
0.5	0.5	99.5
1	1	99
5	5	95
10	10	90

8.2 Prepare independent check standards and calibration blanks at this time. The initial check standard is prepared using 10 mL of 18 ppb Hg stock which is brought to a volume of 100 mL with ASTM Type 1 water, followed by the reagents. Prepare the continuing calibration verification standard by diluting 3.0 mL of 100 ppb Hg to 100 mL with ASTM Type 1 water, followed by reagents.

8.3 Prepare calibration blanks using 100 mL of ASTM Type 1 water followed by the

reagents.

8.4 Prepare the CRA (0.2 ppb) by diluting 0.2 mLs of 100 ppb Hg stock to 100 mL with ASTM Type I water, followed by reagents.

8.5 Add the following reagents to the above bottles:

* 10 mL of mixed acids solution
* 15 mL of potassium permanganate (5% solution, w/v) solutions
* 8 mL of potassium persulfate (5% solution, w/v)

8.6 Heat standards and check standards for aqueous samples in 95°C water bath for two hours.

9.0 Cold Vapor Instrument Set-up

9.1 Wavelength setting 253.7 nm.
9.2 Replace drying tube with fresh Magnesium Perchlorate
9.3 Fill rinse bath 3/4 full with 3 N HC1
9.4 If instrument is on macro "OVERNITE" function, enter macro "WARMSTRT" sequence
9.5 If instrument is off, enter macro "COLDSTRT" sequence (WARMSTRT takes 10 minutes, COLDSTRT takes 2 1/2 hours)
9.6 Check zero detector for good peak and aperture for reading between ± 100, check 5v ref (@ 548000) and optics (within 10000)
9.7 Open folder, naming is as the date
9.8 Check to make sure XMIT function is "ON"
9.9 Make sure the stannous chloride reductant reservoir and the 3 N HCL reservoir are full.

10.0 Sample Analysis

10.1 Sample ID's and dilution factors are entered and autosampler set-up is programmed.

10.2 Autosampler calibration tubes and sample tubes are put in place (CRA and check standard are put in sequence of sample tubes)

10.3 Calibration and sampling is initiated using the macro "AQUCLP" sequence.

10.4 See Table 1 at the end of this SOP for analytical run sequence.

11.0 Calculation

Liquids

$$C_{(ug/L)} = \frac{ug}{L_{dig}} * \frac{V_{dig}}{V_{samp}}$$

Where:
ug/L_{dig} = Leeman result including all dilution factors
V_{dig} = final digestate volume in mLs (typically 100 mLs)
V_{samp} = sample volume in mLs (typically 100 mLs)

Example

$$25_{(ug/L)} = \frac{25\ ug}{L_{dig}} * \frac{100\ mL}{100\ mL}$$

12.0 Quality Control

12.1 The correlation coefficient of the calibration curve must be ≥ 0.995. If the correlation does not meet this criteria the run must be stopped, the instrument recalibrated, and the associated samples reanalyzed.

12.2 All sample results must be within the calibration range of the instrument. If not the sample must be diluted and reanalyzed.

12.3 A maximum of ten samples are run between each set of EPA check standards (ICV/CCV) and calibration blanks (ICB/CCB). The ICV/CCV results must be within 80-120% recovery of the true value. The ICB/CCB results must be less than the reporting limit of 0.2 ug/l. If any of these criteria are not met the run must be stopped, the instrument recalibrated, and the associated samples reanalyzed.

12.4 Preparation blanks are prepared and run at a frequency of 1 per 20 samples per matrix type. The preparation blank results must be less than the reporting limit of 0.2 ug/l. In addition the results cannot be less than the negative reporting limit. If

any of these criteria are not met the run must be stopped, the instrument recalibrated, and the associated samples reanalyzed.

12.5 Matrix Spike analysis and Replicate analysis will be performed per batch of 20 samples of the same matrix. The matrix spike analysis should be within 75-125% recovery. The replicate should have an RPD of <20%. All data will be flagged according to contract specifications.

Table 1: Typical Analytical Run Sequence For An SDG

Standard 0 ppb
Standard 0.2 ppb
Standard 0.5 ppb
Standard 1 ppb
Standard 5 ppb
Standard 10 ppb
ICV
ICB
CRA
CCV
CCB
Preparation Blank
Laboratory Control Sample
7 samples
CCV
CCB
9 samples
CCV
CCB
9 samples (includes MS/DP)
CCV
CCB

APPENDIX A-22

STANDARD OPERATING PROCEDURE FOR MERCURY PREPARATION AND COLD VAPOR ANALYSIS OF SOIL SAMPLES

Mercury Preparation and Cold Vapor Analysis Of Soil Samples By Method 7471A

Approvals and Signatures

QA Manager: Kym B. Watson Date: 9/5/97

Metals Section Manager: Will S. Ci Date: 9/5/97

Inorganic Lab Manager: Kristine Aulvin Date: 9/5/97

1.0 Scope and Application

1.1 This SOP details the requirements of the mercury method 7471A used for soil samples. All samples must be subjected to an appropriate dissolution step prior to analysis.

1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heating step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heating step is not necessary.

1.3 Using 0.6 grams of sample a detection limit 0.04mg/kg as received can be achieved.

2.0 Summary of Method

2.1 The flameless AA procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration and recorded in the usual manner.

3.0 Sample Handling and Preservation

3.1 Soil Samples: A minimum sample volume of 5 grams of sample in pre-cleaned glass containers.

3.2 The holding time for mercury analysis is 26 days from receipt of the sample.

4.0 Apparatus and Materials

4.1 Leeman Labs PS200 and PS200II with autosampler and personal computer (10/91), (3/96).

4.2 300 mL BOD Bottles

4.3 Hot Water Bath

5.0 Reagents

5.1 Reagent Water, Reagent water will be interference free. The laboratory uses DI water.

5.2 Concentrated Nitric Acid, Reagent Grade

5.3 Concentrated Hydrochloric Acid, Reagent Grade

5.3.1 3 N HCL

Add 91.41 mL of Concentrated Hydrochloric Acid, bring to 1 liter with DI water.

5.3.2 Aqua Regia

Add three volumes of Concentrated Hydrochloric Acid to one volume of concentrated Nitric Acid.

5.4 Stannous Chloride (10% Solution):

Add 100 grams of Stannous Chloride to 1 liter of 3 N HCL.

5.5 Hydroxylamine Hydrochloride Solution.

Dissolve 320 grams of Crystalline Hydroxylamine Hydrochloride in 2 liters of DI water.

5.6 Potassium Permanganate (5% solution, w/v):

Dissolve 100 grams Potassium Permanganate crystal in 2 liters of DI water.

5.7 100 ppb Stock Mercury Solution (Diluted from 1000 ug/mL Hg Spex Plasma Standard) for Calibration Curve and Continuing Calibration Check Standards.

To make 10,000 ppb Hg intermediate, add 1 mL Spex Plasma Standard to approximately 80 mLs ASTM Type 1 water and 0.15 mL concentrated HNO_3, bring to 100 mL. Add 10 mL of the 10,000 ppb Hg intermediate to approximately 800 mL ASTM Type 1 water and 1.5 mL concentrated HNO_3, and bring to final volume of 1000 mL. The final solution is 100 ppb Hg. See Table in Section 7.1 for preparation of the calibration curve.

5.8 18 ppb Stock Mercury Solution for Initial Calibration Verification:

Dilute 1 mL 1000 ug/mL Hg Inorganic Ventures Standards and 0.15 mL HNO_3 to 100 mL with ASTM Type 1 water. From this intermediate take 1.8 mL, 1.5 mL HNO_3 and dilute to 1000 mL with ASTM Type 1 water. The final solution is 18 ppb Hg.

5.9 Magnesium Perchlorate, desiccant. Drying reagent used in trap.

5.10 Solid Laboratory Control Sample- Provided by EPA

6.0 Preparation of Soils & Sediments Samples

All prepared standards and reagents are assigned the expiration date provided by the vendor. This indicates a maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation is necessary. All standards and reagents are stored at room temperature. The preparation of all standards is recorded in the metals standard preparation notebook. Calibration standards are prepared fresh daily.

6.1 Weigh out in triplicate a representative 0.2 gram portion of wet sample (relatively void of stones) into a clean 300 mL BOD bottle. Larger sample sizes may be used when the sample contains a large amount of water.

Prepare a preparation blank that consists of 0.6 grams of DI water. A preparation blank is digested with every batch of 20 soil samples.

Prepare a solid laboratory control sample by weighing out 0.2 grams of the EPA provided solid laboratory control standard. A solid laboratory control sample is digested with every batch of 20 soil samples.

6.2 Duplicate analyses are used to check reproducibility and sample consistency. Duplicate samples are prepared by taking two sample aliquots and placing them in two distinct bottles. One sample will be labeled with the laboratory number and the other will be labeled with the laboratory number and DP suffix. These bottles will be carried through the preparation and analysis procedures as two separate samples. Prepare duplicates at a frequency of 1 per 20 samples of the same matrix.

6.3 Matrix spike analysis are used to check for possible matrix interferences. They are prepared by taking two sample aliquots and placing them in two distinct bottles. One bottle will be labeled as the laboratory number and the other will be labeled with the laboratory number and MS suffix. The bottle labeled MS will be spiked with 1 mL (or otherwise noted) of 100 ppb Hg stock standard. These bottles will be carried through the preparation and analysis procedures as two separate samples. Prepare matrix spikes at a frequency of 1 per 20 samples of the same matrix.

Matrix Spikes - 100 ppb Hg stock is added to sample to raise final concentration by 1 ppb (i.e. 1.0 mL for 100 mL volume sample, 0.5 mL for 50 mL volume sample). A spike must be witnessed and documented by another analyst.

6.4 Weigh in triplicate 0.2 gram portions of soil sample into a clean BOD bottle. Add 5 mL of DI water and 5 mL of Aqua Regia. Heat 2 minutes in a water bath at 95°C. Cool; then add 50 mL of DI water and 15 mL of potassium permanganate are added to each sample bottle. Mix thoroughly and allow the samples to stand for 15 minutes to determine if the samples remain purple in color. Add additional $KmnO_4$ as required to maintain purple color. If extra $KMnO_4$ is needed to colorize samples, standards must also have extra permanganate to keep the same matrix.

6.5 Heated for ½ hour at 95°C. Cool and add six mLs of Hydroxylamine Hydrochloride to reduce extra permanganate. An additional 50 mL of DI water is added.

6.6 If samples are suspected to be high in organics they are aspirated utilizing the house air jet to eliminate possible interference by organics. This procedure takes place under a hood, an aspirating tube with disposable tip is inserted into each sample bottle and allowed to bubble for 2 minutes.

6.7 Dilutions can be performed if results of 100% analyses are above the highest calibration standard (10 ppb). Dilutions are prepared by taking an appropriate aliquot of the previously digested sample and adding an appropriate amount of matrix blank. The sample is then reanalyzed.

7.0 Calibration

7.1 Prepare an analytical calibration at the following concentrations: 0.0 ug/L, 0.2 ug/L, 0.5 ug/L, 1.0 ug/L, 5.0 ug/L, and 10.0 ug/L from a 100 ug/L stock mercury standard. Transfer the mercury into clean 300 mL BOD bottles. Adjust the total volume up to 10 mL with DI water. See the following table:

Standard ID	mL of 100 ppb Hg Stock Solution	mL of ASTM Type I water
0.0	0	10
0.2	0.2	9.8

Standard ID	mL of 100 ppb Hg Stock Solution	mL of ASTM Type I water
0.5	0.5	9.5
1	1	9
5	5	5
10	10	--

7.3 Prepare independent check standard (ICV). The initial check standard is prepared using 10 mL of 18 ppb Hg stock which is brought to a volume of 100 mL with DI water, followed by the reagents. Prepare a continuing calibration verification standard (CCV) by diluting 5 mL of 100 ppb Hg to 100 mL with DI water, followed by reagents.

7.2 Add 5 mL of Aqua Regia to calibration and check standards and heat in a hot water bath at 95°C for 2 minutes. Remove from heat and allow to cool. Add 50 mL of Nanopure water and 15 mL of potassium permanganate, mixed and then heated for ½ hour at 95°C. Cool and add six mLs of Hydroxylamine Hydrochloride to reduce extra permanganate. An additional 50 mL of DI water is added.

8.0 Cold Vapor Instrument Set-up

8.1 Wavelength setting 253.7 nm.
8.2 Replace drying tube with fresh Magnesium Perchlorate
8.3 Fill rinse bath 3/4 full with 3 N HC1
8.4 If instrument is on macro "OVERNITE" function, enter macro "WARMSTRT" sequence
8.5 If instrument is off, enter macro "COLDSTRT" sequence (WARMSTRT takes 10 minutes, COLDSTRT takes 2 1/2 hours)
8.6 Check zero detector for good peak and aperture for reading between ± 100, check 5v ref (@ 548000) and optics (within 10000)
8.7 Open folder, naming is as the date
8.8 Check to make sure XMIT function is "ON"
8.9 Make sure stannous chloride reductant reservoir is full

9.0 Sample Analysis

9.1 Sample ID's and dilution factors are entered and autosampler set-up is programmed.

9.2 Autosampler calibration tubes and sample tubes are put in place (CRA and check standard are put in sequence of sample tubes)

9.3 Calibration and sampling is initiated using the macro "AQUCLP" sequence.

9.4 See Table 1 at the end of this SOP for analytical run sequence.

10.0 Calculation

Solids

$$C_{(mg/Kg\ drywt.)} = \frac{ug}{L_{dig}} * \frac{V_{dig}}{g_{samp}} * \frac{100}{\%\ solids}$$

Where:
ug/L_{dig} = Leeman result including all dilution factors
V_{dig} = final distillate volume in Liters
g_{samp} = sample weight in grams
% Solids = Percent solids to nearest 0.1%

Example

$$9.5_{mg/Kg\ drywt.} = \frac{15\ ug}{L_{dig}} * \frac{0.1\ L}{0.2\ g} * \frac{100}{78.8}$$

11.0 Quality Control

11.1 The correlation coefficient of the calibration curve must be ≥0.995. If the correlation does not meet this criteria the run must be stopped, the instrument recalibrated, and the associated samples reanalyzed.

11.2 All sample results must be within the calibration range of the instrument. If not the sample must be diluted and reanalyzed.

11.3 A maximum of ten samples are run between each set of EPA check standards (ICV/CCV) and calibration blanks (ICB/CCB). The ICV/CCV results must be within 80-120% recovery of the true value. The ICB/CCB results must be less than the reporting limit of 0.2 ug/l. If any of these criteria are not met the run must be stopped, the instrument recalibrated, and the associated samples reanalyzed.

11.4 Preparation blanks are prepared and run at a frequency of 1 per 20 samples per matrix type. The preparation blank results must be less than the reporting limit of 0.2 ug/l. In addition the results cannot be less than the negative reporting limit. If any of these criteria are not met the run must be stopped, the instrument recalibrated, and the associated samples reanalyzed.

11.5 Matrix Spike analysis and Replicate analysis will be performed per batch of 20 samples of the same matrix. The matrix spike analysis should be within 75-125% recovery. The replicate should have an RPD of <20%. All data will be flagged according to contract specifications.

11.6 A Solid Laboratory Control Sample (LCSS) must be analyzed with each batch of 20 soil samples. The solid LCS is purchased from an independent vendor and must be within the supplied control limits. If the Solid LCS is not within the control limits the associated samples must be reprepared and reanalyzed.

Table 1: Typical Analytical Run Sequence For An SDG

Standard 0 ppb
Standard 0.2 ppb
Standard 0.5 ppb
Standard 1 ppb
Standard 5 ppb
Standard 10 ppb
ICV
ICB
CRA
CCV
CCB
Preparation Blank
Laboratory Control Sample
7 samples
CCV
CCB
9 samples
CCV
CCB
9 samples (includes MS/DP)
CCV
CCB

APPENDIX A-23

STANDARD OPERATING PROCEDURE FOR ORGANOCHLORINE PESTICIDES BY GAS CHROMATOGRAPHY

Organochlorine Pesticides by Gas Chromatography
Method:8081A

Approvals and Signatures

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1.0 Scope and Application

1.1 This method is used to determine the concentration of various organochlorine pesticides (not PCBs) in extracts from solid and liquid matrices, using fused silica open-tubular, capillary columns with electron capture detectors (ECD). A compound list and reporting limits are presented in Section 13.0. Spikes (Matrix Spikes/Spike Duplicates/LCS) must be prepared specifically for this method (i.e. without added PCBs). A split portion of the 8081A extract taken prior to method specific cleanup steps can be processed for PCBs using the cleanup and analysis procedures of method 8082 .

2.0 Summary of Method

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Liquid samples are extracted at a neutral pH with methylene chloride using either method 3510 (separatory funnel), method 3520 (continuous liquid-liquid extractor) or other appropriate technique.

2.3 Solid samples are extracted with hexane-acetone (1:1) using method 3540 (Soxhlet), method 3541 (automated Soxhlet), method 3545 (pressurized fluid extraction), method 3550 (ultrasonic extraction), method 8081A-82:EXB (Modified 3550 tissuemizer method for biota with cleanups) or some other appropriate technique.

2.4 A variety of cleanup steps may be applied to the extract, depending on the nature of the matrix interferences and the target analytes. Suggested cleanups include silica gel (method 3630), gel permeation (method 3640) and sulfur (method 3660).

2.5 After cleanup, the extract is analyzed by injecting a 2ul sample into a gas chromatograph with a narrow or wide-bore fused silica capillary column and electron capture detector. The gas chromatograph is set up with two columns of different polarity: One used for quantitation, the second for confirmation.

2.6 Endrin and DDT breakdowns must be less than 15% and must be evaluated every 12 hours.

2.7 The GC is calibrated using five point calibration curves for all single-component pesticides. Single point calibrations near the mid-point of the expected calibration range are used for all multi-component compounds.

2.8 Although method 8081A suggests all target analytes be injected every twelve hours at alternating high and low concentrations for calibration verification, a mid-point standard will be used. Response factors must be ≤ 15%. Response factors can be higher than 15% for non-detects.

2.9 Interferences

2.9.1 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the ECD will respond. Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

2.9.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations.

2.9.3 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples.

3.0 Sample Preparation

3.1 Samples are prepared following appropriate extraction procedures as outlined in the summary of method.

4.0 Apparatus and Materials

4.1 Gas Chromatograph

An analytical system equipped with a packed or split/splitless injection port, two electron capture detectors, and an autosampler.

4.2 Data System

The data system must be capable of handling a minimum of 200 chromatographic peaks per detector. Fison's Vax based Multichrom software version 2.0 or higher will be used for acquisition and raw data handling in this analysisForms generation will be through Thru-put Target and Quick Forms software.

4.3 Fused Silica Capillary Columns

A two column system provides simultaneous primary and confirmation analyses. Capillary columns which may be used include the following:

4.3.1 RTX-5, 95% dimethyl - 5% diphenyl polysiloxane (or equivalent).

4.3.2 RTX-1, 100% dimethylpolysiloxane (or equivalent).

4.3.3 RTX-35, 65% dimethyl - 35% diphenylpolysiloxane (or equivalent).

4.3.4 RTX-1701, 14% cyanopropylphenyl - 86% methylpolysiloxane (or equivalent).

4.3.5 DB-17MS, 50% dimethyl - 50% diphenylpolysiloxane (or equivalent).

4.3.6 RTX-CLPesticides proprietary (or equivalent)

5.0 Reagents and Standards

5.1 Solvents

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

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

5.2 Standards. Formulation of standards is located in Standards Formulation Notebook under Method 8081A.

5.2.1 Standards for this method are purchased from Restek. The stock standards are:

Pesticide Surrogate Spike Mix - Restek Catalog No. 32000

Compound	Concentration (ug/mL)
Tetrachloro-m-xylene (TCX)	200
Decachlorobiphenyl (DCB)	200

Breakdown Check Standard - Ultra-Scientific

Compound	Concentration (ug/mL)	Catalog No.
4,4'-DDT	100	PP-180
Endrin	100	PP-230

Multicomponent Standards

Compound	Concentration (ug/mL)	Catalog No.
Toxaphene	1000	32005

Chlordane	1000	32021

Pesticide Standard Mix A - Catalog No. 32003

Compound	Concentration (ug/mL)
alpha-BHC	8
gamma-BHC	8
Heptachlor	8
Endosulfan I	8
Dieldrin	16
Endrin	16
4,4'-DDD	16
4,4'-DDT	16
Methoxychlor	80
tetrachloro-m-xylene	8
Decachlorobiphenyl	16

Pesticide Standard Mix B - Catalog No. 32004

Compound	Concentration (ug/mL)
beta-BHC	8
delta-BHC	8
Aldrin	8
Heptachlor Epoxide (isomer B)	8
gamma-Chlordane	8
alpha-Chlordane	8
4,4'-DDE	16

Compound	Concentration (ug/mL)
Endosulfan II	16
Endrin Aldehyde	16
Endosulfan Sulfate	16
Endrin Ketone	16
tetrachloro-m-xylene	8
Decachlorobiphenyl	16

Note: Careful attention should be paid to the expiration date of these stocks. Each stock should have the expiration date clearly labeled on the vial. This expiration date must also be noted on each standard vial and standard notebook entry for all subsequent standards prepared from this stock.

5.2.2 Working Standard Concentrations - Working standards must be prepared every 6 months. Store all standards in refrigerator at 4 ± 2°C.

Breakdown Check Standard (BCS)

Compound	Concentration (ug/L)
4,4'-DDT	100
Endrin	100
Tetrachloro-m-xylene	20
Decachlorobiphenyl	20

Instrument Blank (PIBLK)

Compound	Concentration (ug/L)
Tetrachloro-m-xylene (TCX)	20
Decachlorobiphenyl (DCB)	20

Pesticide Standard Mix A - Five Point Calibration Curve (ug/L)

Compound	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Tetrachloro-m-xylene (TCX)	5.0	10	20	40	80
alpha-BHC	5.0	10	20	40	80
gamma-BHC	5.0	10	20	40	80
Heptachlor	5.0	10	20	40	80
Endosulfan I	5.0	10	20	40	80
Dieldrin	10	20	40	80	160
Endrin	10	20	40	80	160
4,4'-DDD	10	20	40	80	160
4,4'-DDT	10	20	40	80	160
Methoxychlor	50	100	200	400	800
Decachlorobiphenyl (DCB)	10	20	40	80	160

Pesticide Standard Mix B- Five Point Calibration Curve (ug/L)

Compound	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Tetrachloro-m-xylene (TCX)	5.0	10	20	40	80
beta-BHC	5.0	10	20	40	80
delta-BHC	5.0	10	20	40	80
Aldrin	5.0	10	20	40	80
Heptachlor Epoxide	5.0	10	20	40	80
gamma-Chlordane	5.0	10	20	40	80
alpha-Chlordane	5.0	10	20	40	80
4,4'-DDE	10	20	40	80	160

Compound	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Endosulfan II	10	20	40	80	160
Endrin Aldehyde	10	20	40	80	160
Endosulfan Sulfate	10	20	40	80	160
Endrin Ketone	10	20	40	80	160
Decachlorobiphenyl (DCB)	10	20	40	80	160

5.2.3 All standards should be stored in Teflon-lined screw cap vials. They should be protected from light and stored in a refrigerator at 4 ± 2°C.

5.2.4 Standard solutions must be replaced six months after preparation, or sooner if the stock standard expiration date is exceeded or if comparison with quality control standards indicates a problem.

6.0 Instrument Set-Up

6.1 GC Configuration

A five meter deactivated guard column is installed into the injection port. The guard column is connected to the two analytical columns by means of a glass "Y". The two analytical columns are installed into independent electron capture detectors (ECDs).

6.2 Operating Conditions

The following operating conditions are used as guidelines to starting an analytical method. Conditions may vary in order to meet the resolution and linearity requirements of the method.

Initial Temperature: 130 °C
Time 1: 1 minute
Rate: 6 °/min
Final Temperature: 270 °C

Time 2: 5 minutes
Injection Port Temperature: 225 °C
Detector Temperature: 310 °C
Injection Volume: 2 uL*
Carrier Gas Flow: 10 mL/min Hydrogen
ECD Make-up Gas: 60 mL/min % Nitrogen

* A 2 uL injection is used for the analysis. It is assumed that there is a 50:50 split to both columns. Therefore, a one uL injection volume is used for quantitation.

7.0 Initial Calibration

7.1 Initial Calibration Analytical Run Sequence

Injection #	Lab Description
1	PIBLK
2	BCS
3	INDA-1
4	INDA-2
5	INDA-3
6	INDA-4
7	INDA-5
8	INDB-1
9	INDB-2
10	INDB-3
11	INDB-4
12	INDB-5
13	Toxaphene 500 ppb
14	T-Chlordane 400 ppb

Injection #	Lab Description
15	ICV A
16	ICV B

7.2 Initial Calibration Quality Control Requirements

7.2.1 Instrument Blank (PIBLK)

- Target analytes must not be present at or above the reporting limit (i.e. the level of the low standards).
- The retention time of each of the surrogates must fall within the established retention time windows.

7.2.2 Breakdown Check Standard (BCS)

The BCS standard is used to check the percent breakdown of 4,4'-DDT and Endrin.

The percent breakdown of 4,4'-DDT and Endrin must each be ≤ 15.0%.

$$\%\ 4,4'\text{-DDT Breakdown} = \frac{\text{peak response (4,4'-DDE + 4,4'-DDD) *100}}{\text{peak response (4,4'-DDE + 4,4'-DDD + 4,4'-DDT)}}$$

$$\%\ \text{Endrin Breakdown} = \frac{\text{peak response (Endrin Aldehyde + Endrin Ketone) *100}}{\text{peak response (Endrin Aldehyde + Endrin Ketone + Endrin)}}$$

The retention time of each analyte in the BCS must fall within the established retention time windows.

7.2.3 ICVA and ICVB Check Standards -Mid Point Standard independent from the calibration curve.

- The concentrations of the analytes in the ICV standard must be ± 15% Drift on the quantitation and confirmation column.

$$\% \ Drift = \frac{| \ conc. \ (nominal) - conc. \ (calculated) \ |}{conc. \ (nominal)} * 100$$

The retention time of each major target analyte peak and surrogate must fall within ± 0.05 minutes of the initial curve except decachlorobiphenyl which must be within ± 0.10 minutes.

7.3 QC Non-compliance

If any of the quality control requirements stated above are not met, GC maintenance must be performed and re-calibration is required.

8.0 Continuing Calibration

8.1 Continuing Calibration Analytical Run Sequence

Laboratory Description
Initial Calibration
ICV
10 samples
PIBLK
BCS
INDA-3
INDB-3
Toxaphene (if required)
Technical Chlordane (if required)
10 samples
PIBLK
BCS

INDA-3
INDB-3
Toxaphene (if required)
Technical Chlordane (if required)

- **If Toxaphene and Technical Chlordane are target compounds they must be including in the calibration verification and analyzed every 10 samples.**

- The breakdown check standard (BCS) is analyzed every 10 sample injections. The midpoint pesticide standards, INDA-3 and INDB-3, must be analyzed every 10 sample injections.

- If the GC has been left idle for more than 8 hours, the following standards must be run and pass all QC criteria before sample analysis can begin.

  PIBLK
  BCS
  INDA-3
  INDB-3

- When sample analysis is completed, the analytical sequence must end with a passing pesticide standard INDA-3 or INDB-3.

- The previous samples will not be re-run if compounds in the INDA and INB are greater than 15% and there are no targets compounds in the samples analyzed.

8.2 Continuing Calibration Quality Control Requirements

8.2.1 Instrument Blanks (PIBLK) (See Section 7.2.1)

8.2.2 Breakdown Check Standard (BCS) (See Section 7.2.2)

8.2.3 INDA-3 and INDB-3 Check Standards - Mid Point Calibration Standard - For continuing calibration.

- The concentrations of the analytes in the continuing calibration check standard must be ≤ 15% D on the quantitation column and the confirmation column. Calculate the % drift (%D) using the following formula:

- The retention time of each target analyte and surrogate must fall within ± 0.05 minutes of the initial curve except decachlorobiphenyl which must be within ± 0.10 minutes.

8.3 QC Non-Compliance

- If the concentration of the analytes in the continuing calibration check standard are > 15% D on the quantitation column, use the approach described in Section 7 of method 8000B and calculate the average percent difference across all analytes. If the average of the %D is within ±15%, then the calibration has been verified. The average must include all analytes in the calibration, regardlss of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the ±15% limit.

- If any of the quality control requirements stated above are not met, standards may be injected a second time. If they fail again, GC maintenance must be performed and re-calibration is required. All samples must be bracketed with passing check standards.

9.0 Sample Extract Preservation and Holding Times

9.1 Sample extracts are preserved in a refrigerator at 4 ± 2°C.

9.2 Analysis of sample extracts must be performed within 40 days from the start of sample extraction.

10.0 Retention Time Windows

The procedure recommended in SW-846 for the determination of retention time windows is as follows:

- Make three injections of all single component standard mixtures and multiresponse products (i.e. PCBs) throughout the course of a 72 hour period. Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the

standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples. The retention time window is defined as ± 3 times the standard deviation of the absolute retention times for each standard. The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed.

- It is the laboratories experience that the SW-846 procedure results in retention time windows that are very tight and that favor false negatives. This would result in analytes that are present in the sample to not be reported. SW-846 is a guidance document that encourages modifications based on laboratory expertise. For this reason the laboratory has taken a more conservative approach to the establishment of retention time windows.

- Each analytical sequence is thoroughly reviewed and a retention time of ± 0.05 minutes from the initial curve (except decachlorobiphenyl which must be within ± 0.10 minutes) is used identification purposes. In addition, the laboratory will look at the retention time shift of the surrogates in each sample to see if further compensation of the retention time window is necessary. This routine, while more time consuming than the SW-846 approach prevents the laboratory from reporting false negatives.

11.0 Sample Quantitation

11.1 A linear curve is used for quantitation of analytes

$$y = a_o + (1/a_1) * x$$

Where:
y =concentration
x =peak height or area
a_o =intercept
$(1/a_1)$ =slope

11.2 Quantitate multi-component compounds (i.e. Toxaphene) by comparing the responses of 3-5 major peaks in each appropriate standard with the peaks obtained from the sample extract. The amount of the multi-component compound is calculated using an individual response factor for each of the major peaks. The results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the standards that are at least 25% of the height of the largest peak. Late

eluting peaks are generally the most stable in the environment.

11.3 From injected sample extract concentration the sample concentrations are calculated as follows:

Water

$$Sample\ conc\ \frac{(ug)}{(L)} = extract\ conc\ \frac{(ug)}{(L)} * \frac{ext\ vol.\ (L)}{spl.\ vol.\ (L)} * D.F.$$

Soil/Tissue

$$Sample\ conc\ \frac{(ug)}{(Kg)} = extract\ conc\ \frac{(ug)}{(L)} * \frac{ext\ vol.\ (L)}{spl.\ wt.\ (Kg)} * \frac{100}{\%Solids} * S.F. * GPC * D.F.$$

S.F. = Splitting Factor, to account for extract split for 8081 and 8082 (Factor should be 2)
GPC= GPC Factor, should be 2
D.F. = Dilution Factor

11.4 Method 8000B requires that if the RPD value between the quantitation column result and the confirmation column result are <40% the higher result is reported, if the RPD is >40% and no anomalies are noted report the higher result. This process would be time consuming and could not be coded electronically on the instruments and in the reporting systems. Therefore, ITS will use the following quantitation rules for reporting. Data users will be alerting to column disparity by the use of the "P" flag which is explained in Section 14.0.

11.4.1 If no peak is present on the quantitation column then report the value as non detect.

11.4.2 If a peak is present on the quantitation column and no peak is present on the confirmation column then report the value as non detect.

11.4.3 If a peak is present on the quantitation column and on the confirmation column, and if the confirmation column meets all quantitation column

requirements report the lower value.

11.4.4 If a peak is present on the quantitation column and on the confirmation column, and if the confirmation column does not meet all quantitation column requirements report result from the quantitation column.

11.4.5 If the results between the two columns differ by more than 25% flag the result with a "P".

12.0 Quality Control (QC)

12.1 Surrogate Compounds Spike Analysis

All samples and blanks are fortified with surrogates prior to extraction. They are used to monitor the preparation and analysis of samples.

12.1.1 Surrogate Recovery Limits - Limits from control charted data

Compound	Water Recovery Limit (%)	Soil /Tissue Recovery Limit (%)
Tetrachloro-m-xylene (TCX)	30-140*	36-132
Decachlorobiphenyl (DCB)	30-140*	30-140*

*- Control charted limits came out very wide. Therefore the laboratory has defaulted to limits of 30-140. Limits listed for tissue are advisory at this time and will be updated when sufficient data points become available.

Individual component recoveries are calculated with the following equation:

$$Surrogate\ Recovery\ (\%) = \frac{SR}{SA} * 100$$

where:
SR = Spike Result
SA = Spike Added (concentration)

Note - If recovery of any surrogate compound is outside of these limits, the deviation will be investigated and the sample analysis thoroughly reviewed. Corrective action is reanalysis of the sample extract. If the surrogate is still out of recovery limits re-extraction may be required.

12.1.2 All surrogate retention times should fall within the established retention time windows.

12.2 Method Blank Analysis

Method blanks are required at a frequency of one per extraction batch, Sample Delivery Group (SDG) or for every 20 samples (whichever is more frequent).

12.2.1 A method blank cannot contain target analytes at or above the reporting limit.

12.2.2 The surrogate recoveries must meet the QC criteria.

Corrective Action: If the method blank fails the above requirements the entire extraction batch may need to reextracted.

12.3 Sulfur Clean-up Blank Analysis

The sulfur clean-up blank is an aliquot of the method blank carried through the sulfur clean-up and analysis steps. The purpose of the sulfur clean-up blank is to determine the levels of contamination associated with the separate sulfur clean-up steps. A sulfur clean-up blank is required when any of the samples in the associated extraction batch requires sulfur clean-up. If not all of the samples in the associated extraction batch require sulfur clean-up, then both a sulfur cleaned and a non-sulfur cleaned portion of the method blank must be analyzed.

12.4 Matrix Spike/Matrix Spike Duplicate Analysis

An MS/MSD analysis is required for each analytical batch (up to 20 samples). The MS/MSD analysis consists of spiking two aliquots of the same sample with matrix spike before extraction begins. The LCS and matrix spike consists of all the individual pesticides listed below. Recovery limits are generated from control

charts.

Individual component recoveries are calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between matrix spike and matrix spike duplicate analysis is calculated with 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)

12.4.1 MS/MSD/LCS Recovery Limits* - Control Limits from control charted data. These limits will be updated annually.

Compound	Water MS/MSD Recovery Limit (%)	Tissue/Soil MS/MSD Recovery Limit (%)	Water LCS Recovery Limit (%)	Tissue/Soil LCS Recovery Limit (%)	RPD (%)
alpha-BHC	46-117	35-125	46-117	35-125	30
beta-BHC	60-118	42-137	60-118	42-137	30
delta-BHC	59-113	1-167	59-113	1-167	30

Compound	Water MS/MSD Recovery Limit (%)	Tissue/Soil MS/MSD Recovery Limit (%)	Water LCS Recovery Limit (%)	Tissue/Soil LCS Recovery Limit (%)	RPD (%)
gamma-BHC	58-115	35-130	58-115	35-130	30
Heptachlor	66-113	1-248	66-113	1-248	30
Aldrin	48-107	40-137	48-107	40-137	30
Heptachlor Epoxide	70-115	44-146	70-115	44-146	30
Endosulfan I	70-118	48-137	70-118	48-137	30
Dieldrin	66-113	36-146	66-113	36-146	30
4,4'-DDE	55-128	45-157	55-128	45-157	30
Endrin	56-131	37-152	56-131	37-152	30
Endosulfan II	73-120	42-160	73-120	42-160	30
4,4'-DDD	67-126	47-159	67-126	47-159	30
Endosulfan Sulfate	56-124	25-162	56-124	25-162	30
4,4'-DDT	65-125	43-157	65-125	43-157	30
Methoxychlor	70-140	54-159	70-140	54-159	30
Endrin Aldehyde	50-119	5-145	50-119	5-145	30
alpha-chlordane	70-111	31-150	70-111	31-150	30
gamma-chlordane	71-109	33-149	71-109	33-149	30
Endrin ketone	62-124	31-166	62-124	31-166	30

* - If recovery of any matrix compound is outside of these limits the deviation will be investigated and the sample analysis thoroughly reviewed to determine if corrective actions should be taken.

- Limits listed for tissue are advisory at this time and will be updated when sufficient data points become available.

12.4.2 The retention times of each of the component peaks must fall within the established retention time windows.

12.4.3 Matrix spike results will be reviewed in conjunction with surrogate and LCS recoveries to evaluate method performance. If the LCS recoveries are within QC limits the outages will be assumed sample related.

Quality Control and Corrective Action

Chlorinated Pesticides Method 8081			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
Initial calibration	As Required	Correlation coefficient ≥ 0.99	Recalibrate, mix new standards, reanalyze
Continuing Calibration Standard (CCAL)	Every 10 samples	%D≤ 15% for the quantitation column and confirmation column	Re-shoot, check integrations, mix new std. Reanalyze ICAL
Breakdown (BD) Check Standard	Every 10 samples	DDT BD ≤15%, Endrin BD ≤15%	Perform Injection Port Maintenance and recalibrate
Method Blank	Each extraction batch	Targets < Reporting	Reanalyze, check for contamination, correct as required
Samples	--	Concentrations below highest calibration standard	Dilute and reanalyze samples that are more concentrated than the highest calibration standard
Surrogates	Every sample, blank and QC sample must be spiked with surrogate	See control limits in SOP	Any sample with outages must be reanalyzed to confirm. Present both sets of data.
Matrix Spike/Matrix Spike Duplicate	1 set every 20 samples, Full compound list spike required	Comparable results for spike and duplicate	Evaluate LCS. If compounds failing in MS/MSD are acceptable in the LCS the outages will assume to be matrix related.

Chlorinated Pesticides Method 8081			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
LCS	Each extraction batch (full compound list; independent std)	See control limits in the SOP	Check Std., Check Quantitation, Evaluate MS/MSD. Reanalyze batch if failing compounds are present in the samples.
ICV	INDA and INDB from an independent source after the initial calibration	%D≤ 15%	Check standard preparation/Recalibrate

13.0 Compound List and Reporting Limits

Compound	**Quant. Limit in Extract (ug/L)**	**8081A Water (ug/L)**	**8081A Low Level Water (ug/L)**	**8081A Soil Low Level (ug/Kg)**	**8081A Soil Med Level (ug/Kg)**	**8081A Biota Low Level (ug/Kg)**
alpha-BHC	5.0	0.05	0.005	0.7	25	2
beta-BHC	5.0	0.05	0.005	0.7	25	2
delta-BHC	5.0	0.05	0.005	0.7	25	2
gamma-BHC	5.0	0.05	0.005	0.7	25	2
Heptachlor	5.0	0.05	0.005	0.7	25	2
Aldrin	5.0	0.05	0.005	0.7	25	2
Heptachlor	5.0	0.05	0.005	0.7	25	2
Endosulfan I	5.0	0.05	0.005	0.7	25	2
Dieldrin	10.0	0.10	0.010	1.4	50	4.1
4,4'-DDE	10.0	0.10	0.010	1.4	50	4.1
Endrin	10.0	0.10	0.010	1.4	50	4.1

Compound	Quant. Limit in Extract (ug/L)	8081A Water (ug/L)	8081A Low Level Water (ug/L)	8081A Soil Low Level (ug/Kg)	8081A Soil Med Level (ug/Kg)	8081A Biota Low Level (ug/Kg)
Endosulfan II	10.0	0.10	0.010	1.4	50	4.1
4,4'-DDD	10.0	0.10	0.010	1.4	50	4.1
Endosulfan sulfate	10.0	0.10	0.010	1.4	50	4.1
4,4'-DDT	10.0	0.10	0.010	1.4	50	4.1
Methoxychlor	50.0	0.5	0.050	6.8	250	20
Endrin ketone	10.0	0.10	0.010	1.4	50	4.1
Endrin Aldehyde	10.0	0.10	0.010	1.4	50	4.1
alpha-chlordane	5.0	0.05	0.005	0.7	25	2.0
gamma-chlordane	5.0	0.05	0.005	0.7	25	2.0
Tech. Chlordane	50	0.50	0.050	6.8	250	20
Toxaphene	500	5.0	0.50	68	2500	200

* Optional compound - to be reported if requested.

The quantitation limits assume the following extraction information:

8081A water-	1 liter sample concentrated to a 10 mL extract volume
8081A low level water-	1 liter sample concentrated to a 1.0 mL extract volume
8081A low level soil*-	30 gram sample concentrated to a 4 mL extract volume
8081A medium level soil-	2.0 gram sample concentrated to a 10 mL extract volume
8081A low level biota*-	10 gram sample concentrated to a 4 mL extract volume

*i.e. sample wt +GPC+sample split for 8082 to final volume of 1ml

14.0 Standard Qualifiers

U - Indicates compound was analyzed for but not detected above the reporting limit.

J - Indicates an estimated value. The result reported is below the required reporting limit and calibration range.

B - This flag is used when the analyte is found in the associated method blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action. Only the samples get a "B" flag. The method blank does not.

D - This flag identifies all compounds identified in an analysis at a secondary dilution factor. This flag alerts data users that any discrepancies between the concentrations reported for the dilutions may be due to dilution of the sample or extract. This flag is used in all samples that the name carried the "DL" suffix.

X,Y,Z-Laboratory defined flags. These flags must be fully described, and such description attached to the Sample Data Summary Package and the case Narrative. Begin by using "X" and go on to "Y" and "Z" as necessary. These flags may also be used to combine several flags, as needed.

P - Use when there is greater than 25 % difference for detected concentrations between the two analytical columns.

E - Quantitation exceeds the high point of the calibration curve.

15.0 References

15.1 EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Edition, with Update III, December 1996.

APPENDIX A-24

STANDARD OPERATING PROCEDURE FOR POLYCHLORINATED BIPHENYLS (PCB) ANALYSIS

Polychlorinated Biphenyls (PCB) Analysis
Method: 8082:AN

Approvals and Signatures

QA Manager : Kym B. Watson Date: 1-12-98

Extractables Section Manager: [signature] Date: 1-12-98

1.0 Scope and Application

1.1 This method is used to determine the concentration of PCB compounds in sample extracts from water, soil or biota. Specific congeners can be determined by this method but a more comprehensive and specialized approach to congeners is given in Method OR530:AN. These extracts can be split from 8081A extracts before specialized cleanup. Spikes (Matrix Spikes/Spike Duplicates/LCS) must be prepared specifically for this method (i.e. without added pesticides). A compound list and reporting limits are presented in Section 13.0.

2.0 Summary of Method

2.1 A measured volume or weight of sample (approximately 1 L for liquids, 2 g to 30 g for solids) is extracted using the appropriate matrix-specific sample extraction technique.

2.2 Aqueous samples are extracted at neutral pH with methylene chloride using Method 3510C (separatory funnel), Method 3520C (continuous liquid-liquid extractor), or other appropriate technique.

2.3 Solid samples are extracted with hexane-acetone (1:1) or methylene chloride-acetone (1:1) using Method 3540C (Soxhlet), Method 3541 (automated Soxhlet), or other appropriate technique.

2.4 Extracts for PCB analysis may be subjected to a sulfuric acid/potassium permanganate cleanup (Method 3665A) designed specifically for these analytes. This cleanup technique will remove (destroy) many single component organochlorine pesticides. Therefore, Method 8082 is not applicable to the analysis of those compounds. Instead, use Method 8081A.

2.5 After cleanup, the extract is analyzed by injecting a 2-uL aliquot into a gas chromatograph with a narrow- or wide-bore fused silica capillary column and electron capture detector (GC/ECD).

2.6 The chromatographic data may be used to determine the seven Aroclors listed in Section 13. Hexane extracts are analyzed for PCB's using capillary column gas chromatography. The gas chromatograph is set up with two columns of different polarity: One used for quantitation, the second for confirmation. Electron capture detectors are used for analyte detection.

2.7 The GC is calibrated using a five point calibration curve for Aroclor 1660. This curve is used to establish instrument linearity for all Aroclors and to quantify Aroclor 1016 and Aroclor 1260. Mid-point calibration standards are used to identify and quantify for the following multi-component compounds: Aroclor 1221, Aroclor 1232, Aroclor 1242, Aroclor 1248 and Aroclor 1254. Instrument stability is verified every ten sample injections by an Aroclor 1660 at mid-level. If a specific Aroclor is to be determined, linearity and calibration can be established with that particular Aroclor rather than 1660.

2.8 Interferences

2.8.1 Sources of interference in this method can be grouped into three broad categories: contaminated solvents, reagents or sample processing hardware; contaminated GC carrier gas, parts, column surfaces or detector surfaces; and the presence of coeluting compounds in the sample matrix to which the ECD will respond. Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired degrees of discrimination and quantitation.

2.8.2 Interferences by phthalate esters introduced during sample preparation can pose a major problem in pesticide determinations. Common flexible plastics contain varying amounts of phthalate esters which are easily extracted or leached from such materials during laboratory operations. These contaminants will be removed by 3665A cleanup.

2.8.3 The presence of elemental sulfur will result in broad peaks that interfere with the detection of early-eluting organochlorine pesticides. Sulfur contamination should be expected with sediment samples. Sulfur can be removed with 3660B cleanup.

3.0 Sample Preparation

3.1 Samples are prepared following the extraction procedures of method SW-846.

4.0 Apparatus and Materials

4.1 Gas Chromatograph

An analytical system equipped with a packed or split/splitless injection port, two electron capture detectors, and an auto-sampler.

4.2 Data System

The data system must be capable of handling a minimum of 200 chromatographic peaks per detector. Fison's Vax based Multichrom software version 2.0 or higher will be used for this analysis. Thru-put's Target and Quick Forms software will be used for forms and diskette generation.

4.3 Fused Silica Capillary Columns

A two column system provides simultaneous primary and confirmation analyses. Capillary columns which may be used include the following:

4.3.1 RTX-5, 95% dimethyl - 5% diphenyl polysiloxane (or equivalent).

4.3.2 RTX-1, 100% dimethyl polysiloxane (or equivalent).

4.3.3 RTX-35, 65% dimethyl - 35% diphenyl polysiloxane (or equivalent).

4.3.4 RTX-1701, 14% cyanopropylphenyl - 86% methyl polysiloxane (or equivalent).

4.3.5 DB-17, 50% dimethyl - 50% diphenyl polysiloxane (or equivalent).

5.0 Reagents and Standards

5.1 Solvents

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

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

5.2 Standards. Formulation of standards is located in Standards Formulation Notebook under Method 8082. A copy of this can be found in Appendix A.

5.2.1 Standards for this method are purchased from Restek. The stock standards are:

Pesticide Surrogate Spike Mix - Restek Catalog No. 32000

Compound	Concentration (ug/mL)
Tetrachloro-m-xylene (TCX)	200
Decachlorobiphenyl (DCB)	200

Multicomponent Standards

Compound	Concentration (ug/mL)	Catalog No.
Aroclor 1660	1000	32039
Aroclor 1221	1000	32007
Aroclor 1232	1000	32008
Aroclor 1242	1000	32009
Aroclor 1248	1000	32010
Aroclor 1254	1000	32011

Note: Careful attention should be paid to the expiration date of these stocks. Each stock should have the expiration date clearly labeled on the vial. This expiration date must also be noted on each standard vial and standard notebook entry for all subsequent standards prepared from this stock.

5.2.2 Working Standard Concentrations - Working standards must be prepared every 6 months. Store all standards in refrigerator at 4 ± 2°C.

Multicomponent Analyte Five Point Calibration Curves (ug/L)

Compound	Conc 1	Conc 2	Conc 3	Conc 4	Conc 5
Aroclor 1660	50	100	200	400	800

(Each of the calibration standards contains Tetrachloro-m-xylene and Decachlorobiphenyl- each at a concentration 10 times lower than the concentration of the multicomponent analyte in that standard.)

Instrument Blank (PIBLK)

Compound	Concentration (ug/L)
Tetrachloro-m-xylene (TCX)	20

Compound	Concentration (ug/L)
Decachlorobiphenyl (DCB)	20

5.2.3 All standards should be stored in Teflon-lined screw cap vials. They should be protected from light and stored in a refrigerator at 4 ± 2°C.

5.2.4 Standard solutions must be replaced six months after preparation, or sooner if the stock standard expiration date is exceeded or if comparison with quality control standards indicates a problem.

6.0 Instrument Set-Up

6.1 GC Configuration

A five meter deactivated guard column is installed into the injection port. The guard column is connected to the two analytical columns by means of a glass "Y". The two analytical columns are installed into independent electron capture detectors (ECDs).

6.2 Operating Conditions

The following operating conditions are used as guidelines to starting an analytical method. Conditions may vary in order to meet the resolution and linearity requirements of the method.

Initial Temperature: 130 °C
Time 1: 1 minute
Rate: 6 °/min
Final Temperature: 270 °C
Time 2: 5 minutes
Injection Port Temperature: 225 °C
Detector Temperature: 310 °C
Injection Volume: 2 uL*
Carrier Gas Flow: 10 mL/min Hydrogen

ECD Make-up Gas: 60 mL/min % Nitrogen

* A 2 uL injection is used for the analysis. It is assumed that there is a 50:50 split to both columns. Therefore, a one uL injection volume is used for quantitation.

7.0 Initial Calibration

7.1 Initial Calibration Analytical Run Sequence

Injection #	Lab Description
1	PIBLK
2	Aroclor 1660 50 ppb
3	Aroclor 1660 100 ppb
4	Aroclor 1660 200 ppb
5	Aroclor 1660 400 ppb
6	Aroclor 1660 800 ppb
7	ICV

7.2 Initial Calibration Quality Control Requirements

7.2.1 Instrument Blank (PIBLK)

Target analytes must not be present at or above the reporting limit (i.e. the level of the low standards).
The retention time of each of the surrogates must fall within the established retention time windows.

7.2.2 AR1660 ICV - Mid Point Standard independent from the calibration curve.

$$\% \ Drift = \frac{|\ conc.\ (nominal) - conc.\ (calculated)\ |}{conc.\ (nominal)} * 100$$

The concentrations of the analytes in the ICV standard must be ± 15% Drift on the quantitation and confirmation column.The retention time of each major target analyte peak and surrogate must fall within ± 0.05 minutes of the initial curve except decachlorobiphenyl which must be within ± 0.10 minutes.

7.3 QC Non-compliance

If any of the quality control requirements stated above are not met, GC maintenance must be performed and re-calibration is required.

8.0 Continuing Calibration

8.1 Continuing Calibration Analytical Run Sequence

Lab ID
Initial Calibration
ICV
10 samples
AR1660 (Mid)
10 samples
AR1660 (Mid)

If the GC has been left idle for more than 8 hours, the following standards must be run and pass all QC criteria before sample analysis can begin.

PIBLK
AR1660

When sample analysis is completed, the analytical sequence must end with a passing standard. If % drift is greater than 15% and there are no targets compounds in the samples analyzed. The previous samples will not be re-run.

8.2 Continuing Calibration Quality Control Requirements

8.2.1 Instrument Blanks (PIBLK) (As required after high samples)

8.2.2 AR1660 Check Standards - Mid Point Calibration Standard - For continuing calibration.

The concentrations of the analytes in the continuing calibration check standard must be ± 15% Drift on the quantitation and confirmation column.The retention time of each major target analyte peak and surrogate must fall within ± 0.05 minutes of the initial curve except decachlorobiphenyl which must be within ± 0.10 minutes.

8.3 QC Non-Compliance

If any of the quality control requirements stated above are not met, standards may be injected a second time. If they fail again, GC maintenance must be performed and re-calibration is required. All samples must be bracketed with passing check standards.

9.0 Sample Extract Preservation and Holding Times

9.1 Sample extracts are preserved in a refrigerator at 4 ± 2°C.

9.2 Analysis of sample extracts must be performed within 40 days from the start of sample extraction.

10.0 Retention Time Windows

The procedure recommended in SW-846 for the determination of retention time windows is as follows:

Make three injections of all single component standard mixtures and multiresponse products (i.e. PCBs) throughout the course of a 72 hour period. Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples. The retention time window is defined as ± 3 times the standard deviation of the absolute retention times for each standard. The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed.

It is the laboratories experience that the SW-846 procedure results in retention time windows that are very tight and that favor false negatives. This would result in analytes that are present in the sample to not be reported. SW-846 is a guidance document that encourages modifications based on laboratory expertise. For this reason the laboratory has taken a more conservative approach to the establishment of retention time windows.

Each analytical sequence is thoroughly reviewed and a retention time of ± 0.05 minutes from the initial curve (except decachlorobiphenyl which must be within ± 0.10 minutes) is used identification purposes. In addition, the laboratory will look at the retention time shift of the surrogates in each sample to see if further compensation of the retention time window is necessary. This routine, while more time consuming than the SW-846 approach prevents the laboratory from reporting false negatives.

11.0 Sample Quantitation

11.1 A linear curve is used for quantitation of Aroclors 1016 and 1260 (or any other Aroclor specifically chosen by project requirements for a 5 point calibration)

$$y = a_o + (1/a_1) * x$$

For Aroclors quantified by single point calibration use the following formula:

$$y = \frac{x_{spl}}{x_{std}} * C_{std}$$

Where:

y	=concentration
x	=peak height or area (spl = sample; std = standard)
a_o	=intercept
$(1/a_1)$	=slope
C_{std}	=Concentration of standard

11.2 Quantitate Aroclors by comparing the responses of 3-5 major peaks in each appropriate standard with the peaks obtained from the sample extract. The amount of the Aroclor is calculated using an individual response factor for each of the major peaks. The results of the 3 to 5 determinations are averaged. Major peaks are defined as those peaks in the standards that are at least 25% of the height of the largest peak. Late eluting Aroclor peaks are generally the most stable in the environment.

11.3 From injected sample extract concentration the sample concentrations are calculated as follows:

Water

$$Sample\ conc\ \frac{(ug)}{(L)} = extract\ conc\ \frac{(ug)}{(L)} * \frac{ext\ vol.\ (L)}{spl.\ vol.\ (L)} * D.F.$$

Soil/Tissue

$$Sample\ conc\ \frac{(ug)}{(Kg)} = extract\ conc\ \frac{(ug)}{(L)} * \frac{ext\ vol.\ (L)}{spl.\ wt.\ (Kg)} * \frac{100}{\%Solids} * S.F. * GPC * D.F.$$

S.F. = Splitting Factor, to account for extract split for 8081 and 8082 (Factor should be 2)

GPC= GPC Factor, should be 2
D.F. = Dilution Factor

11.4 Method 8000B requires that if the RPD value between the quantitation column result and the confirmation column result are <40% the higher result is reported, if the RPD is >40% and no anomalies are noted report the higher result. This process would be time consuming and could not be coded electronically on the instruments and in the reporting systems. Therefore, ITS will use the following quantitation rules for reporting. Data users will be alerting to column disparity by the use of the "P" flag which is explained in Section 14.0.

11.4.1 If no peak is present on the quantitation column then report the value as non detect.

11.4.2 If a peak is present on the quantitation column and no peak is present on the confirmation column then report the value as non detect.

11.4.3 If a peak is present on the quantitation column and on the confirmation column, and if the confirmation column meets all quantitation column requirements report the lower value.

11.4.4 If a peak is present on the quantitation column and on the confirmation column, and if the confirmation column does not meet all quantitation column requirements report result from the quantitation column.

11.4.5 If the results between the two columns differ by more than 25% flag the result with a "P".

12.0 Quality Control (QC)

12.1 Surrogate Compounds Spike Analysis

All samples and blanks are fortified with surrogates prior to extraction. They are used to monitor the preparation and analysis of samples.

12.1.1 Surrogate Recovery Limits - Limits from control charted data

Compound	Water Recovery Limit (%)	Tissue/Soil Recovery Limit (%)
Tetrachloro-m-xylene (TCX)	30-140*	36-132
Decachlorobiphenyl (DCB)	30-140*	30-140*

*- Control charted limits came out very wide. Therefore the laboratory has defaulted to limits of 30-140. Limits listed for tissue are advisory at this time and will be updated when sufficient data points become available.

Individual component recoveries are calculated with the following equation:

$$Surrogate\ Recovery\ (\%) = \frac{SR}{SA} * 100$$

where:
SR = Spike Result
SA = Spike Added (concentration)

Note - If recovery of any surrogate compound is outside of these limits, the deviation will be investigated and the sample analysis thoroughly reviewed. Corrective action is reanalysis of the sample extract. If the surrogate is still out of recovery limits re-extraction may be required.

12.1.2 All surrogate retention times should fall within the established retention time windows.

12.2 Method Blank Analysis

Method blanks are required at a frequency of one per extraction batch, Sample Delivery Group (SDG) or for every 20 samples (whichever is more frequent).

12.2.1 A method blank cannot contain target analytes at or above the reporting limit.

12.2.2 The surrogate recoveries must meet the QC criteria.

Corrective Action: If the method blank fails the above requirements the entire extraction batch may need to reextracted.

12.3 Sulfur Clean-up Blank Analysis

The sulfur clean-up blank is an aliquot of the method blank carried through the sulfur clean-up and analysis steps. The purpose of the sulfur clean-up blank is to determine the levels of contamination associated with the separate sulfur clean-up steps. A sulfur clean-up blank is required when any of the samples in the associated extraction batch requires sulfur clean-up. If not all of the samples in the associated extraction batch require sulfur clean-up, then both a sulfur cleaned and a non-sulfur cleaned portion of the method blank must be analyzed.

12.4 Matrix Spike/Matrix Spike Duplicate Analysis

An MS/MSD analysis is required for each analytical batch (up to 20 samples). The MS/MSD analysis consists of spiking two aliquots of the same sample with matrix spike before extraction begins. The LCS and matrix spike consists of all the individual pesticides listed below. Recovery limits are generated from control charts.

Individual component recoveries are calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between matrix spike and matrix spike duplicate analysis is calculated with 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)

12.4.1 MS/MSD/LCS Recovery Limits* - These limits will be updated as sufficient data points are available.

Compound	Water MS/MSD Recovery Limit (%)	Tissue/Soil MS/MSD Recovery Limit (%)	Water LCS Recovery Limit (%)	Tissue/Soil LCS Recovery Limit (%)	RPD (%)
Aroclor 1016	50-150	50-150	50-150	50-150	30
Aroclor 1260	50-150	50-150	50-150	50-150	30

* - If recovery of any matrix compound is outside of these limits the deviation will be investigated and the sample analysis thoroughly reviewed to determine if corrective actions should be taken.

Limits listed for tissue are advisory at this time and will be updated when sufficient data points become available.

12.4.2 The retention times of each of the component peaks must fall within the established retention time windows.

12.4.3 Matrix spike results will be reviewed in conjunction with surrogate and LCS recoveries to evaluate method performance. If the LCS recoveries are within QC limits the outages will be assumed sample related.

Quality Control and Corrective Action

Chlorinated Pesticides Method 8082			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
Initial calibration	As Required	Correlation coefficient ≥ 0.99	Recalibrate, mix new standards, reanalyze
Continuing Calibration Standard (CCAL)	Every 10 samples	% Drift ≤ 15% for the quantitation column and confirmation column	Re-shoot, check integrations, mix new std. Reanalyze ICAL
Method Blank	Each extraction batch	Targets < Reporting	Reanalyze, check for contamination, correct as required
Samples	--	Concentrations below highest calibration standard	Dilute and reanalyze samples that are more concentrated than the highest calibration standard
Surrogates	Every sample, blank and QC sample must be spiked with surrogate	See control limits in SOP	Any sample with outages must be reanalyzed to confirm. Present both sets of data.
Matrix Spike/Matrix Spike Duplicate	1 set every 20 samples, AR 1660 or project specific Aroclor	Comparable results for spike and duplicate	Evaluate LCS. If compounds failing in MS/MSD are acceptable in the LCS the outages will assume to be matrix related.
LCS	Each extraction batch (AR 1660 or project specific Aroclor; independent std)	See control limits in the SOP	Check Std., Check Quantitation, Evaluate MS/MSD. Reanalyze batch if failing compounds are present in the samples.

Chlorinated Pesticides Method 8082			
Quality Control Criteria	**Frequency**	**Acceptance**	**Corrective Action**
ICV	AR 1660 from an independent source; analyze after the initial calibration	%D≤ 15%	Check standard preparation/Recalibrate

13.0 Compound List and Reporting Limits

Compound	Quant. Limit in Extract (ug/L)	8082 Water (ug/L)	8082 Low Level Water (ug/L)	8082 Soil Low Level (ug/Kg)	8082 Soil Med Level (ug/Kg)	Biota (ug/Kg)
Aroclor 1016	50	0.50	0.050	17	250	20
Aroclor 1221	50	0.50	0.050	17	250	20
Aroclor 1232	50	0.50	0.050	17	250	20
Aroclor 1242	50	0.50	0.050	17	250	20
Aroclor 1248	50	0.50	0.050	17	250	20
Aroclor 1254	50	0.50	0.050	17	250	20
Aroclor 1260	50	0.50	0.050	17	250	20

NR = Not reported

The quantitation limits assume the following extraction information:

8082 water- 1 liter sample concentrated to a 10 mL extract volume

8082 low level water- 1 liter sample concentrated to a 1.0 mL extract volume

8082 low level soil*- 30 gram sample concentrated to a 10 mL extract volume

8082 medium level soil- 2.0 gram sample concentrated to a 10 mL extract volume

8082 biota*- 10 gram sample concentrated to a 4 mL extract volume

* i.e. sample wt + GPC + sample split for 8081 to final volume of 1 mL

14.0 Standard Qualifiers

U - Indicates compound was analyzed for but not detected above the reporting limit.

J- Indicates an estimated value. The result reported is below the required reporting limit and calibration range.

B - This flag is used when the analyte is found in the associated method blank as well as in the sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action. Only the samples get a "B" flag. The method blank does not.

D - This flag identifies all compounds identified in an analysis at a secondary dilution factor. This flag alerts data users that any discrepancies between the concentrations reported for the dilutions may be due to dilution of the sample or extract. This flag is used in all samples that the name carried the "DL" suffix.

X,Y,Z -Laboratory defined flags. These flags must be fully described, and such description attached to the Sample Data Summary Package and the case Narrative. Begin by using "X" and go on to "Y" and "Z" as necessary. These flags may also be used to combine several flags, as needed.

P - Use when there is greater than 25 % difference for detected concentrations between the two analytical columns.

E - Quantitation exceeds the high point of the calibration curve.

15.0 References

15.1 EPA SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd Edition, with Update III, December 1996.

APPENDIX A-25

STANDARD OPERATING PROCEDURE FOR ORGANOPHOSPHORUS PESTICIDES BY CAPILLARY GC

Appendix 9
Organophosphorus Pesticides by Capillary Gas Chromatography
Method: 8141_AP9:AN

Approvals and Signatures

QA Officer: Martha E. Boy Date: 6/7/95

GC Manager: Gary B. Stidam Date: 6/7/95

1.0 Scope and Application

1.1 This method is used to determine the concentration of organophosphorus pesticides in sample extracts.

2.0 Summary of Method

2.1 This method provides the gas chromatographic conditions for the detection of ppb levels of organophosphorus pesticides. A compound list and quantitation limits are presented in Section 11.0

2.2 Prior to sample analysis, the instrumentation is calibrated using five point calibration curves for all analytes of interest. Instrument stability is verified every ten sample injections with the mid point standard. The gas chromatograph is set up with two capillary columns of different polarity: one used for the primary analysis and the second used for the confirmation analysis. Quantitation may be performed on either column provided all QC criteria has been met.

3.0 Sample Preparation

3.1 Samples are prepared following extraction procedures of the USEPA SW-846 methodology. In general, 1 liter of a water sample is extracted and concentrated to 1 mL. For soil/sediment samples, 30 grams is extracted and concentrated to 10 mL. The final extract solvent is hexane.

4.0 Apparatus and Materials

4.1 Gas Chromatograph:

An analytical system equipped with a packed or split/splitless injection port, NPD detectors, and an auto-sampler.

4.2 Data System:

Fision's Vax based Multi-Chrom GC software is used for collecting and processing data.

4.3 Fused Silica Capillary Columns:

A two column system provides simultaneous primary and confirmation analyses. Capillary columns which may be used include the following:

4.3.1 RTX-5, 95% dimethyl - 5% diphenyl polysiloxane (or equivalent).

4.3.2 RTX-35, 65% dimethyl - 35% diphenyl polysiloxane (or equivalent).

4.3.3 RTX-1701, 14% cyanopropylphenyl - 86% methyl polysiloxane (or equivalent).

5.0 Reagents and Standards

5.1 Solvents

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

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

5.2 Standards

Organophosphorus calibration standards should be replaced after one or two months, or sooner if comparison with check samples or historical data indicates that there is a problem.

5.2.1 8141_9 Mixture

Five Point Calibration Curve Concentrations (ug/L)

Compound	8141_9A	8141_9B	8141_9C	8141_9D	8141_9E
Sulfotepp	100	200	400	800	1600
Dimethoate	100	200	400	800	1600
Ethyl parathion	100	200	400	800	1600
Phorate	100	200	400	800	1600
Disulfoton	100	200	400	800	1600
Methyl Parathion	100	200	400	800	1600
Thionazin	100	200	400	800	1600
O,O,O-Triethylphosphorothioate	100	200	400	800	1600
Famphur	100	200	400	800	1600
Tributylphosphate (TBP)	100	200	400	800	1600
Triphenylphosphate (TPP)	100	200	400	800	1600

6.0 GC Set-Up

6.1 GC Configuration:

A five meter deactivated guard column is installed into the injection port. The guard column is connected to the two analytical columns by means of a glass "Y". The two analytical columns are installed into independent NPD detectors.

6.2 Operating Conditions

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

Initial Temperature: 100°C
Time 1: 1 minute
Rate: 6°/min
Final Temperature: 250°C
Time 2: 5 minutes
Injection Port Temperature: 225°C
Detector Temperature: 310°C
Injection Volume: 2 uL
Carrier Gas Flow: 10 mL/min He

6.3 Retention Time Windows:

Prior to sample analysis, retention time windows should be established for each of the target analytes and surrogates. These windows are determined statistically. Three injections of a standard containing all compounds of interest are injected over a period of 12-72 hours. The retention time window is ± 3 times the standard deviation of the three retention times for each of the compounds. The center of the window will be the mean retention time for each of the compounds in the 5 point calibration curve (established for each analytical run). Retention time windows are GC and column specific. The laboratory must calculate new retention time windows yearly or any time a new column is installed.

7.0 Initial Calibration

Prior to sample analysis, a five point calibration for each organophosphorus mix is analyzed.

Initial Calibration Analytical Sequence

inj	Lab ID
1	PIBLK
2	8141_9A
3	8141_9B
4	8141_9C
5	8141_9D
6	8141_9E
7	PIBLK

7.1 The initial calibration must meet the following QC criteria:

7.1.1 The correlation coefficient must be≥ 0.995 (using linear regression), or if the average response factor is used the %RSD must be ≤ 15.0%.

7.1.2 All target analyte and surrogate retention times must fall within the established retention time windows (See Section 6.3).

8.0 Continuing Calibration:

Instrument stability is checked at a minimum of once every 10 sample injections.

Analytical Sequence

inj	Lab ID
1-7	Initial Calibration
8-17	Samples
18	PIBLK
19	8141_9C
20-29	Samples
30	PIBLK
31	8141_9C

8.1 An instrument blank (PIBLK) is analyzed at a minimum of one for every 10 samples injected. The instrument blank demonstrates that the system is free of contamination. Additional PIBLKs are recommended when highly contaminated sample extracts are analyzed. An instrument blank (PIBLK) must meet the following criteria:

8.1.1 The PIBLK must not contain target analytes at or above the reporting limit.

8.1.2 The surrogate retention times must fall within the established retention time windows.

8.2 The 8141_9C standard must be analyzed every 10 sample injections. In order to continue the analysis, the check standards must meet the following criteria:

8.2.1 The percent Difference (%D) between the calculated and nominal concentration of all standard components must be ≤ 15.0%.

$$\%D = \left| \frac{\text{Conc. (nominal)} - \text{Conc. (calc)}}{\text{Conc. (nominal)}} \right| * 100$$

8.2.2 The retention times of all chromatographic peaks in the quantitation and confirmation analyses must fall within the established retention time windows.

Note: If the criteria stated above is not met, standards may be reinjected a second time. If they fail, GC maintenance must be performed to correct the problem and re-calibration is required.

8.3 If the GC has been left idle for more than 8 hours an instrument blank (PIBLK) and the 8141_9C standard must be acquired and pass QC criteria before sample analysis can begin.

8.4 When the sample analysis is completed, the analytical sequence must end with the 8141_9C standard.

9.0 Sample Extract Preservation

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

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

10.0 Quality Control (QC)

10.1 Method Blank

One per extraction batch, Sample Delivery Group (SDG), or every 20 samples.

10.1.1 Target analytes must not be present at or above the reporting limit.

10.1.2 The % recovery of surrogates should fall within the QC criteria set forth in Section 10.2.

10.1.3 Surrogate retention times must fall within the established retention time windows.

Note: If a method blank fails the criteria in Section 10.1.1, all samples in the associated extraction batch must be re-extracted.

10.2 Surrogate Standard Compounds

Method blank and samples are fortified with surrogate spike before extraction begins.

% Recovery Limits		
Compound	**Water**	**Soils/Sediments**
Tributylphosphate (TBP)	40-140	40-140
Triphenylphosphate (TPP)	40-140	40-140

The recovery limits are advisory. If recovery of any surrogate compound is outside of these limits, the deviation will be investigated and the sample analysis thoroughly reviewed to determine if corrective actions should be taken.

10.3 Matrix Spike/Matrix Spike Duplicate

An MS/MSD analysis is required every 20 samples, or one per extraction batch. The MS/MSD analysis consists of spiking two aliquots of the same sample with matrix spike before extraction begins. Recovery limits for analytes used as matrix spikes are listed below.

Compound	**Water Limits (%)**	**Soil Limits (%)**	**RPD (%)**
Sulfotepp	40-140	40-140	30
Dimethoate	40-140	40-140	30
Ethyl parathion	40-140	40-140	30
Phorate	40-140	40-140	30

Compound	Water Limits (%)	Soil Limits (%)	RPD (%)
Disulfoton	40-140	40-140	30
Methyl Parathion	40-140	40-140	30
Thionazin	40-140	40-140	30
Famphur	40-140	40-140	30

The recovery limits are advisory. If the recovery of any matrix compound is outside of these limits, the deviation will be investigated and the sample analysis thoroughly reviewed to determine if corrective actions should be taken.

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

11.0 Compound List and Reporting Limits

Compound	Water (ug/L)	Soil (ug/Kg)
Sulfotepp	1.0	34
Dimethoate	1.0	34
Ethyl parathion	1.0	34
Phorate	1.0	34
Disulfoton	1.0	34
Methyl Parathion	1.0	34
Thionazin	1.0	34
O,O,O-Triethylphosphorothioate	1.0	34
Famphur	1.0	34

12.0 Reporting

12.1 Positive identification of an analyte occurs when a peak or both the primary and confirmation analysis falls within the established retention time window for that analyte.

12.2 Results can be reported from the primary or confirmation analysis provided all QC criteria has been met. Compounds will not be reported below the detector response of the low standard.

12.3 Results will be reported to two significant figures.

12.4 Do not round quantitation limits up. The value will be determined by normal rounding.

13.0 Standard Qualifiers

U = Compound not detected at or above reporting limit.

E = Compound concentration exceeds the calibration range.

D = Compound concentration is reported from a secondary dilution of the sample.

APPENDIX A-26

STANDARD OPERATING PROCEDURE FOR CHLORINATED HERBICIDES BY ECD

Chlorinated Herbicides
by Electron Capture Detector (ECD)
Method: 8150_AP9:AN

Approvals and Signatures

QA Officer: Martha E. Roy Date: 6/7/95

GC Section Head: Gary B. Stricker Date: 6/7/95

1.0 Scope and Application

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

2.0 Summary of Method

2.1 This method provides the gas chromatographic conditions for the analysis of chlorinated acid herbicides. A compound list and reporting limits are presented in Section 11.0.

2.2 The gas chromatograph is calibrated using five point calibration curves for all analytes of interest. Instrument stability is verified every ten sample injections with the mid point calibration standard. The gas chromatograph is set up with two capillary columns of different polarity: one used for the primary analysis, the second used for the confirmation analysis. Quantitation may be performed on either column provided all QC criteria has been met.

3.0 Sample Preparation

3.1 Samples are prepared following the extraction procedures of the USEPA SW-846 methodology. In general, 1 liter of a water sample is extracted and concentrated to 10 mL. For soil/sediment samples, 50 grams is extracted and concentrated to 25 mL. The final extract solvent is hexane.

4.0 Apparatus and Materials

4.1 Gas Chromatograph:

An analytical system equipped with a packed or split/splitless injection port, two electron capture detectors, and an auto-sampler.

4.2 Data System:

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

4.3 Fused Silica Capillary Columns:

A two column system provides simultaneous primary and confirmation analyses. Capillary columns which may be used are:

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

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

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

5.0 Reagents and Standards

5.1 Solvents:

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

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

5.2 Standards:

5.2.1 Herbicide standards are purchased and analyzed as methyl esters. The concentrations used for quantitation are for the herbicides in their acid form. Therefore, quantitation will yield final results for herbicides in their acid form. Do not report herbicides as methyl esters.

5.2.2 Stock standard solutions should be stored at 4° C and should be protected from light. Stock standard solutions must be replaced at a minimum of once a year. The solutions should be checked frequently for signs of degradation, evaporation, or contamination, especially prior to preparing calibration standards from them.

5.2.3 Calibration solutions must be replaced after six months, or sooner if comparison with QC samples indicates a problem.

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

Compound	8150-9A	8150-9B	8150-9C	8150-9D	8150-9E
2,4-D	94**	190	380	750	1500
Dalapon	230	460	910	1800	3600
2,4-DB	95	190	380	760	1500
Dicamba	9.4	19	38	75	150
Dichlorprop	94	190	380	760	1500
Dinoseb	47	94	190	380	760
MCPA	9300	19000	37000	75000	150000
MCPP	9400	19000	38000	75000	150000
Silvex	9.5	19	38	76	150
2,4,5-T	9.5	19	38	76	150
2,4-DB/Dinoseb*	142	284	568	1136	2272

*Dinoseb and 2,4-DB may coelute on the RTX-5 analytical column. If they do, identify the peak as both compounds and add standard concentrations together.

** 100 ug/L as methyl ester form

6.0 GC Set-Up

6.1 GC Configuration:

A five meter deactivated guard column is installed into the injection port. The guard column is connected to the two analytical columns by means of a glass "Y". The two analytical columns are installed into independent electron capture detectors (ECDs).

6.2 Operating Conditions:

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

Initial Temperature: 90 °C
Time 1: 2 minute
Rate: 6°/min
Final Temperature: 270°C
Time 2: 5 minutes
Injection Port Temperature: 225°C
Detector Temperature: 310°C
Injection Volume: 2 uL
Carrier Gas Flow: 10 mL/min He
ECD Make-up Gas: 60 mL/min % Argon/methane

6.3 Retention Time Windows:

Prior to sample analysis, retention time windows should be established for each of the target analytes and surrogates. These windows are determined statistically. Three injections of a standard containing all compounds of interest are injected over a period of 12-72 hours. The retention time window is ± 3 times the standard deviation of the three retention times for each of the compounds. The center of the windows will be the mean retention time for each of the compounds in the 5 point calibration curve (established for each analytical run). Retention time windows are GC and column specific. The laboratory must calculate new retention time windows yearly or any time a new column is installed.

7.0 Initial Calibration

Prior to sample analysis, a five point calibration for each chlorinated herbicide mix is analyzed.

Initial Calibration
Analytical Run Sequence

inj	Lab ID
1	PIBLK
2	8150_9A
3	8150_9B
4	8150_9C
5	8150_9D
6	8150_9E
7	PIBLK

7.1 The initial calibration must meet the following QC criteria:

7.1.1 The correlation coefficient (r) must be ≥ 0.995 using a linear regression or if average response factor is used, the %RSD must be $\leq 20.0\%$.

7.1.2 All target analytes and surrogate retention times must fall within the established retention time windows (See Section 6.3).

8.0 Continuing Calibration

Instrument stability is checked at a minimum of once every 10 sample injections.

Continuing Calibration
Analytical Run Sequence

inj	Lab ID
1-7	Initial Calibration
8-17	Samples
18	PIBLK
19	8150_9C
20-29	Samples
30	PIBLK
31	8150_9C

8.1 Instrument Blank (PIBLK):

An instrument blank (PIBLK) is analyzed at a minimum of one for every 10 samples injected. The instrument blank demonstrates that the system is free of contamination. Additional PIBLK's are recommended when highly contaminated sample extracts are analyzed. An instrument blank (PIBLK) must meet the following QC criteria:

8.1.1 The PIBLK must not contain target analytes at or above the reporting limit.

8.1.2 The surrogate retention times must fall within the established retention time windows.

8.2 8150_9C Check Standard:

The 8150_9C standard must be analyzed every 10 sample injections. In order to continue the analysis, the check standards must meet the following criteria:

8.2.1 The percent difference (%D) between the calculated and nominal concentration of all standard components must be $\leq$ 15.0% to be used for quantitation.

$$\%D = \frac{|\text{Conc. (nominal)} - \text{Conc. (calc)}|}{\text{Conc. (nominal)}} * 100$$

8.2.2 The retention times of all chromatographic peaks used for quantitation and confirmation analysis must fall within the established retention time windows.

Note: If the criteria stated above is not met, standards and instrument blanks may be reinjected a second time. If they fail, GC maintenance must be performed to correct the problem and re-calibration is required.

8.3 If the GC has been left idle for more than 8 hours, an instrument blank (PIBLK) and the 8150_9C standard must be acquired and pass QC criteria before sample analysis can begin.

8.4 When the sample analysis is completed, the analytical sequence must end with the 8150_9C standard.

9.0 Sample Extract Preservation

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

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

10.0 Quality Control (QC)

10.1 Method Blank or Laboratory Reagent Blank (LRB):

One per extraction batch, Sample Delivery Group (SDG), or every 20 samples.

10.1.1 Target analytes must not be present at or above the reporting limit.

10.1.2 The percent recovery of surrogates should fall within the QC criteria set forth in Section 10.2.

10.1.3 Surrogate retention times must fall within the established retention time windows.

Note: If a method blank fails to meet the criteria in Section 10.1.1, all samples in the associated extraction batch must be re-extracted.

10.2 Surrogate Standard Compounds:

10.2.1 Method blanks and samples are fortified with surrogate spike (2,4-DA) before extraction begins.

10.2.2 At a minimum, the laboratory should update surrogate recovery limits on a matrix-by matrix basis, annually. See method 8000 (Section 8.10) to determine how to set the QC limits.

10.2.3 Advisory Surrogate Recovery Limits

Compound	Water (%)	Soil (%)
2,4-DA	40-150	40-150

The recovery limits are advisory. If the recovery of any surrogate compound is outside of these limits the deviation will be investigated and the sample analysis thoroughly reviewed to determine if corrective actions should be taken.

10.3 Matrix Spike/Matrix Spike Duplicate:

10.3.1 An MS/MSD analysis is required every 20 samples. The MS/MSD analysis consists of spiking two aliquots of the same sample with matrix spike before extraction beings.

10.3.2 Percent Recovery Limits

% Recovery Limits			
Compound	**Water**	**Soil**	**RPD**
2,4-D	40-150	40-150	30
Silvex	40-150	40-150	30
2,4,5-T	40-150	40-150	30
Dinoseb	0-60	0-60	30

The recovery limits are advisory. If the recovery of any matrix compound is outside of these limits, the deviation will be investigated and the sample analysis thoroughly reviewed to determine if corrective actions should be taken.

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

10.5 Quality Control Sample (QCS):

10.5.1 The QCS should contain each analyte of interest.

10.5.2 The QCS standard must be prepared independently from those used for calibration. (The QCS must be extracted, so the extraction laboratory is responsible for the preparation of this standard.)

10.5.3 QC Limits (See Section 10.3)

11.0 Compound List and Limits of Reporting (as acid herbicides)

Compound	Water (ug/L)	Soil (ug/Kg)
2,4-D	0.94	47
Dinoseb	0.47	24
Silvex	0.095	4.8
2,4,5-T	0.095	4.8

11.1 Calculations

Quantitation of Soil Sample:

$$\text{conc in ext } \frac{(\text{ug})}{\text{L}} \times \frac{\text{ext vol (L)}}{\text{spl wt (Kg)}} \times \frac{100}{\%\ \text{Solids}} \times \text{D.F.} = \frac{\text{ug}}{\text{Kg}}\ \text{dry wt.}$$

Quantitation of Water Sample:

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

D.F. = Dilution Factor

12.0 Reporting

12.1 Positive identification of an analyte occurs when a peak on both the primary and confirmation analysis falls within the established retention time windows for that analyte.

12.2 Results can be reported from the primary or confirmation analysis as long as all QC criteria has been met. Compounds will not be reported below the detector response of the low standard.

12.3 Results will be reported to two significant figures.

12.4 Do not round quantitation limits up. The value will be determined by normal rounding.

13.0 Standard Qualifiers

U = Compound not detected at or above reporting limit.

E = Compound concentration exceeds the calibration range.

D = Compound concentration is reported from a secondary dilution of the sample.

APPENDIX A-27

STANDARD OPERATING PROCEDURE FOR PURGE AND TRAP OF AQUEOUS SAMPLES

5030B
STANDARD OPERATING PROCEDURES FOR THE PURGE AND TRAP OF AQUEOUS SAMPLES

Applicable matrix or matrices: Aqueous, Extracts from Method 5035
Standard Compound List and Reporting Limits: Table 1

Approvals and Signatures

Laboratory Director: [signature] Date: 9-21-98

QA Manager: Kim B. Watson Date: 9/21/98

Organics Section Manager: [signature] Date: 9/21/98

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1.0 SCOPE AND APPLICATION

1.1 This SOP is based on Method 5030B (USEPA Test Methods for Evaluating Solid Waste, Dec. 1996). This method describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of high concentration soil and waste sample extracts prepared in Method 5035. The gas chromatography/ mass spectroscopy determinative steps are found in Method 8260B. The compounds amenable to this method are listed in Table 1 along with their respective Chemical Abstract Services Numbers and their reporting limits.

Table 1. Analytes, Chemical Abstract Services Numbers and Reporting Limits

Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
Acetone	67-64-1	5.0	5.0
Acrolein	107-02-8	5.0	5.0

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Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
Acrylonitrile	107-13-1	5.0	1.0
Allyl Chloride	107-05-1	5.0	1.0
Benzene	71-43-2	5.0	1.0
Bromobenzene	108-86-1	5.0	1.0
Bromochloromethane	74-97-5	5.0	1.0
Bromodichloromethane	75-27-4	5.0	1.0
Bromoform (SPCC)	75-25-2	5.0	1.0
Bromomethane	74-83-9	5.0	1.0
2-Butanone	78-93-3	5.0	5.0
n-Butylbenzene	104-51-8	5.0	1.0
sec-Butylbenzene	135-98-8	5.0	1.0
tert-Butylbenzene	98-06-6	5.0	1.0
Carbon Disulfide	75-15-0	5.0	1.0
Carbon Tetrachloride	56-23-5	5.0	1.0
Chlorobenzene (SPCC)	108-90-7	5.0	1.0
Chloroethane	75-00-3	5.0	1.0
2-Chloroethyl Vinyl Ether	110-75-8	5.0	1.0
Chloroform (CCC)	67-66-3	5.0	1.0
Chloromethane (SPCC)	74-87-3	5.0	1.0
Chloroprene	126-99-8	5.0	1.0
2-Chlorotoluene	95-49-8	5.0	1.0
4-Chlorotoluene	106-43-4	5.0	1.0
1,2-Dibromo-3-chloropropane	96-12-8	5.0	1.0

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Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
Dibromochloromethane	124-48-1	5.0	1.0
1,2-Dibromoethane	106-93-4	5.0	1.0
Dibromomethane	74-95-3	5.0	1.0
1,2-Dichlorobenzene	95-50-1	5.0	1.0
1,3-Dichlorobenzene	541-73-1	5.0	1.0
1,4-Dichlorobenzene	106-46-7	5.0	1.0
cis-1,4-Dichloro-2-butene	1476-11-5	5.0	1.0
trans-1,4 Dichloro-2-butene	110-57-6	5.0	1.0
Dichlorodifluoromethane	75-71-8	5.0	1.0
1,1-Dichloroethane (SPCC)	75-34-3	5.0	1.0
1,2-Dichloroethane	107-06-2	5.0	1.0
1,1-Dichloroethene (CCC)	75-35-4	5.0	1.0
cis-1,2-Dichloroethene	156-59-2	10	1.0
trans-1,2-Dichloroethene	156-60-5	10	1.0
1,2-Dichloropropane (CCC)	78-87-5	5.0	1.0
1,3-Dichloropropane	142-28-9	5.0	1.0
2,2-Dichloropropane	594-20-7	5.0	1.0
1,1-Dichloropropene	563-58-6	5.0	1.0
cis-1,3-Dichloropropene	10061-01-5	5.0	1.0
trans-1,3-Dichloropropene	10061-02-6	5.0	1.0
Diethyl Ether	60-29-7	5.0	1.0
1,4-Dioxane	123-91-1	250	50
Ethyl Methacrylate	97-63-2	5.0	1.0

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Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
Ethylbenzene (CCC)	100-41-4	5.0	1.0
Freon TF	76-13-1	5.0	1.0
Hexachlorobutadiene	87-68-3	5.0	1.0
2-Hexanone	591-78-6	5.0	5.0
Isobutyl alcohol	78-83-1	250	50
Isopropylbenzene	98-82-8	5.0	1.0
4-Isopropyltoluene	99-87-6	5.0	1.0
Methacrylonitrile	126-98-7	5.0	1.0
Methyl Iodide	74-88-4	5.0	1.0
Methyl Methacrylate	80-62-6	5.0	1.0
4-Methyl-2-pentanone	108-10-1	5.0	5.0
Methyl-t-Butyl Ether	1634-04-4	5.0	1.0
Methylene Chloride	75-09-2	5.0	1.0
Naphthalene	91-20-3	5.0	1.0
Propionitrile	107-12-0	20	4.0
n-Propylbenzene	103-65-1	5.0	1.0
Styrene	100-42-5	5.0	1.0
1,1,1,2-Tetrachloroethane	630-20-6	5.0	1.0
1,1,2,2-Tetrachloroethane (SPCC)	79-34-5	5.0	1.0
Tetrachloroethene	127-18-4	5.0	1.0
Tetrahydrofuran	109-99-9	70	10
Toluene (CCC)	108-88-3	5.0	1.0
1,2,3-Trichlorobenzene	87-61-6	5.0	1.0

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Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
1,2,4-Trichlorobenzene	120-82-1	5.0	1.0
1,2,4-Trimethylbenzene	95-63-6	5.0	1.0
1,3,5-Trimethylbenzene	108-67-8	5.0	1.0
1,1,1-Trichloroethane	71-55-6	5.0	1.0
1,1,2-Trichloroethane	79-00-5	5.0	1.0
Trichloroethene	79-01-6	5.0	1.0
Trichlorofluoromethane	75-69-4	5.0	1.0
1,2,3-Trichloropropane	96-18-4	5.0	1.0
Vinyl Acetate	108-05-4	5.0	1.0
Vinyl Chloride (CCC)	75-01-4	5.0	1.0
Xylene (m,p)	1330-20-7	5.0	1.0
Xylene (o)	95-47-6	5.0	1.0

(SPCC) System Performance Compounds
(CCC) Calibration Check Compounds

2.0 SUMMARY OF METHOD

2.1 Aqueous Samples

A 5.0 ml aliquot of a liquid sample is purged with helium gas to extract volatile organic compounds. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a highly adsorbent pre-column where the purged compounds are efficiently adsorbed (trapped). The trap is then heated and backflushed with helium to desorb the purgeables onto a gas chromatographic column.

2.2 High Concentration Extracts from Method 5035

An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water. It is then analyzed by purge-and-trap GC/MS following the normal aqueous method.

3.0 DEFINITIONS

3.1 INTERNAL STANDARD (IS)

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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 containing all target analytes, surrogate and internal standard compounds that are prepared from a source external to the laboratory and different from the supplier 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 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 (VBLK, 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 VBLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.9 TRIP BLANK

An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the trip blank is to determine if method analytes or other interferences are present in the field environment.

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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 LFM 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: chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene and 1,1,2,2-tetrachloroethane.

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: 1,-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride.

4.0 INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

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

4.3 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross-contamination.

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4.4 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. Extraction laboratory personnel should not enter the volatile analytical laboratory.

4.5 Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination, and should be assessed before standards are prepared in the methanol.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material Safety Data Sheets (MSDS) are available in the volatile laboratory in a three ring binder.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4 dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

6.0 EQUIPMENT AND SUPPLIES

6.1 Containers:

Sample Storage Containers:	40 mL screw cap vials equipped with a Teflon faced silicone septum, certified clean, known volume of 44 mL
Standard Storage Containers:	1-5 mL Mininert Teflon lined screw caps

6.2 Instrumentation

VOA Autosampler: or equivalent	Tekmar ALS 2050™, ALS 2016, Tekmar AQUATEK 50™, Archon™
Trap:	Tekmar LSC 2000™; VOCARB 3000 trap or equivalent
Purging Chamber:	Tekmar LSC 2000; 5 mL sample volume.

6.3 Syringes

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6.3.1 250 µL-5 mL gas tight hypodermic syringes with Luer-Lok tip

6.3.2 Micro syringe 10-100 µL

7.0 REAGENTS AND STANDARDS

7.1 Trap Packing Materials

VOCARB 3000 or equivalent traps may be used, following the manufacturer's instructions.

7.2 Reagents

7.2.1 Methanol

Purge and Trap Grade, demonstrated to be free of analytes.

7.2.2 Reagent water

Deionized water is filtered using a Milli Q plus ™ filtration system and then boiled for one hour. Finally, the water is purged with helium for a minimum of fifteen minutes. The water is stored in clean, narrow-mouth bottles with Teflon lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1)

Measured volumes of conc. HCl are carefully added to an equal volume of reagent water

7.3 Fortification Solutions for Internal Standard and Surrogates

Two separate fortification solutions are required to prepare laboratory reagent blanks, standards and to fortify each sample. A fortification solution is prepared containing fluorobenzene, chlorobenzene-d_5 and 1,4-Dichlorobenzene-d_4 (internal standards) in methanol. A separate fortification solution is prepared containing 1,2-dichlorobenzene-d_4, BFB, 1,2-Dichloroethane-d_4, Toluene-d_8 (surrogates) in methanol. The internal standards are present in each 5 ml sample, blank or standard at a concentration of 50 µg/L (Low Water Analysis at 5 µg/L). Surrogate compounds are at the same concentration as the analytes in the initial calibration standards. In all other standards, samples and blanks the surrogate compounds are at a concentraiton of 50 µg/L (Low Water Analysis at 5 µg/L).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample collection

Aqueous samples should be poured into the vial without introducing any air bubbles within the vial. The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed, and the vial is inverted, no headspace is visible. A minimum of three vials should be filled per sample location. To monitor possible contamination, a trip blank prepared from organic-free reagent water should be carried throughout the sampling, storage, and shipping process. The collection of solid samples is described in Method 5035.

8.2 Preservation

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8.2.1 The pH of aqueous samples is routinely adjusted to < 2 at the time of the collection, with two drops of 1:1 HCl for each 40 mL of sample. The sample bottles are sealed with the Teflon face down and mixed for one minute. Please note that samples from New York State sites should not be preserved.

8.2.2 A sample that foams vigorously when HCl is added is discarded. A set of triplicate samples that are not acidified are collected. The samples are flagged "not acidified" and shorter holding times are applied to these samples (Section 8.3).

8.2.3 The samples are chilled to 4°±2°C and maintained at that temperature until analysis. Field samples are packed for shipment with sufficient ice to ensure that they will arrive at the laboratory with a substantial amount of ice remaining in the cooler.

8.3 Storage

Samples are analyzed within fourteen days of collection. Other holding times may be selected by the client to conform with local regulatory requirements. Aqueous samples which have not been preserved are analyzed within 7 days of collection. Samples from New York State sites are analyzed within seven days of the validated time of sample receipt (VTSR). Samples are stored at temperatures 4°±2°C in a storage area free of organic solvent vapors and direct or intense light.

9.0 QUALITY CONTROL REQUIREMENTS

9.1 Refer to Method 8260B for specific quality control procedures and requirements. Standard quality assurance practices include the following: mass spectroscopy tuning criteria, a minimum detection limit study, a calibration verification, a method blank, a laboratory control sample, a matrix spike/matrix spike duplicate and the use of surrogate standards.

10.0 CALIBRATION AND STANDARDIZATION

10.1 The calibration and standardization procedures are followed according to the GC/MS determinative Method 8260B.

11.0 PROCEDURE

11.1 All samples are screened prior to purge-and-trap analysis (refer to the Extract Screening SOP). The screening results provide guidance on whether sample dilution is necessary and may prevent contamination of the purge and trap system.

11.2 Prior to the use of this introductory technique, the GC/MS system is properly calibrated. The calibration procedure is discussed in Method 8260B.

11.3 Sample Introduction and Purging

A 44 mL sample vial is spiked with the appropriate amount of internal standard and surrogate directly through the vial septum. The sample is then loaded onto the Tekmar™ 2050 autosampler, which automatically

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transfers 5 mLs to the purge vessel. Alternatively, a manual injection may be used to directly place 5 mLs of sample and/or standard into the purge vessel. In this case, surrogate and internal standards are spiked with the appropriate volumes to achieve the stated final concentrations.
The sample is purged for 11.0 minutes at ambient temperature while the trap is maintained at a temperature of 30°C. After the sample is purged the trap system is preheated to 240°C without a flow of desorption gas. Simultaneously, the temperature of the trap is heated to 250°C, and the flow of the desorption gas, GC temperature program and data acquisition are started. While the trapped components are being introduced into the gas chromatograph, the automated sampling system will drain and rinse the purge vessel twice during the sample desorption step.

11.4 Trap Reconditioning

After desorbing the sample for four minutes, the trap is reconditioned by returning the purge and trap system to the purge mode. The trap temperature is maintained at 260°C for approximately seven minutes. When the trap is cool, the next sample can be analyzed.

11.5 Dilution

If a dilution is necessary a 44 mL sample vial is partially filled with reagent water. The appropriate volume of sample is then added by a syringe or calibrated automatic pipette. Reagent water is then added to fill the entire volume of the sample vial (known volume of 44 mL). The diluted sample is spiked with surrogate and internal standard directly through the septum. Aliquots used for sample dilution preparation should not exceed a minimum volume of 1 mL.

11.6 Analysis of extracts from High Concentration Samples prepared by Method 5035

Extracts from the High Concentration Samples (Method 5035) are analyzed as water samples after first diluting them with organic free water. A 44 ml sample vial is partially filled with reagent water. The appropriate volume of sample is then added by a syringe or calibrated automatic pipette. Reagent water is then added to fill the entire volume of the sample vial (known volume of 44 mL). The diluted sample is spiked with surrogate and internal standards directly through the septum. Analysis is performed as in Section 11.2.

11.7 Analysis of water-miscible liquids

Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with organic-free reagent water. A 44 ml sample vial is partially filled with reagent water. The appropriate volume of sample is then added by a syringe or calibrated automatic pipette. Reagent water is then added to fill the entire volume of the sample vial (known volume of 44 mL). The diluted sample is spiked with surrogate and internal standards directly through the septum. Analysis is performed as in Section 11.2.

11.8 Gas chromatography/ Mass Spectroscopy

See Method 8260

12.0 CALCULATIONS

12.1 See method 8260

13.0 METHOD PERFORMANCE

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13.1 Laboratory accuracy and precision data were obtained for the method analytes using laboratory control spikes. The analytes were at a concentration of 2.5 µg/L (propionitrile at 7.5 µg/L, tetrahydrofuran at 25 µg/L, 1,4-Dioxane and iso-butyl alcohol at 125 µg/L) for the procedural combination of Methods 5030 and 8260. . Results were obtained using the analytical instrumentation described in section 6.

13.2 With this data, method detection limits were calculated using the formula (3):

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

Where:

$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = 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 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials used in preparing standards and sample preservatives.

15.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data assessment, acceptance criteria and corrective action for out of control data is summarized in Table 6 of Method 8260

16.0 WASTE MANAGEMENT

16.1 The samples that are not utilized in the analysis are disposed of as hazardous waste. All methanol waste and expired standards are disposed of as hazardous waste.

17.0 REFERENCES

1. "Test Methods for Evaluating Solid Waste ", USEPA Method 5030B, revision 2, 1996.

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APPENDIX A-28

STANDARD OPERATING PROCEDURE FOR EXTRACTABLE SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS

I. METHOD 8270: AN
DETERMINATION OF EXTRACTABLE SEMIVOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

Approvals and Signatures

QA Officer:_____ Date:_____

GC/MS Section Head:_____ Date:_____

1.0 Scope and Application

1.1 This method is based on the SW846 Method 8270B. The analytical method that follows is designed to analyze water, soil and sediment from hazardous waste sites for the semivolatile organic compounds on the Target Compound List (TCL).

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 is spiked with a surrogate compound mixture and then extracted with methylene chloride. The final extract is concentrated to 1000 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. 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 Interferences

3.1 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.

4.0 Safety

4.1 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.

5.0 Equipment

SVOA Autosampler: HP 7673A

Gas Chromatograph: Hewlett-Packard 5890 GC

Mass Spectrometer: Hewlett-Packard 5971 MSD

Primary Column: Restek RTx-5 30m x 0.25mm x .25 um

5.1 Hewlett Packard Gas Chromatograph - Mass Spectrometer MSD system

5.1.1 Gas chromatograph- Hewlett-Packard model 5890 Series II, equipped with a CTC autosampler and a Lauber injector port for split/splitless analysis and all the required accessories, including syringes, septa, injector port liners, and column. Alternatively, a Hewlett-Packard Model 7673A autosampler may be used, with a standard 5890 series II injection port.

5.1.2 Column - Restek, (Rtx-5 30 meter x 0.25 mm ID with 0.25 um film thickness), or equivalent.

5.1.3 Mass Spectrometer-Hewlett-Packard Mass Selective Detector Model 5971 operated in full scan mode: (35-500 amu).

5.1.4 Data System -The data system is controlled by the HP Chemsystem Unix based computer. Target 3.1 software is used for data processing.

5.2 Gas Chromatograph/Mass Spectrometer

5.2.1 GC Maintenance - Prior to running DFTPP, replace the injection port liner and septa and also clip about 10 cm of column from the injector end.

5.2.2 GC Conditions

Initial column conditions: 35°C for 2 minutes.
Column temperature: 35°C to 320°C at 14°/min.
Final temperature: 320°C for 5.6 min, or until Benzo (g,h,i) perylene has eluted
Injector temperature: 250°C
Transfer line temperature: 300°C
Injector: Grob-like, splitless
Sample volume: 2 uL

5.2.3 MS Conditions

Electron Energy: 70 volts
Mass Range: 35-500 amu
Scantime: Not to exceed 1 second per scan

6.0 Method Criteria

6.1 Instrument Detection Limits

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.

6.2 Reporting Limits

CRQL's = 10 and 25 ug/L or 330 or 800 ug/Kg (See Table 1)
The OLM03.2 method CRQL's are presented in Table 1 below. Diluted sample reporting limits will be raised by the dilution factor. If a medium level extraction is performed, the base CRQL's will be 10000 and 25000 ug/Kg. For all soils, the CRQL's will be raised by the moisture content of the sample.

The analytes and their respective Chemical Abstract Services (CAS) numbers and reporting limits are

given in Table 1 below.

Table 1. Analytes

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
1,3-Dichlorobenzene	541-73-1	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)
1,4-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
3-Nitroaniline	99-09-2	25	800	25000
4-Nitroaniline	100-01-6	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)
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

Appendix A provides the list of the characteristic ions for SVOA compounds; the SVOA internal standards with corresponding target compounds and surrogates assigned for quantitation; and characteristic ions for internal standards for SVOA compounds.

7.0 Sample Requirements

7.1 Matrix

Liquids: This method is applicable to determinations in surface water, ground water, processed water, and waste waters.
Solids: This method is applicable to determinations in soils and sediments.

7.2 Minimum Sample Volume
Liquids: A minimum of 1 liter is required for extraction. Additional sample volume is required for Matrix Spike and Matrix Spike Duplicate.
Solids: A minimum of 50 grams of sample is required. Additional sample volume is required for Matrix Spike and Matrix Spike Duplicate.

7.3 Sample Preparation
Perform preanalysis screening for all extracts. Please refer to the Sample and Extract Screening SOP. Extracts are received from the screening analyst and logged into the analytical laboratory. For analysis, add a 100 uL aliquot of sample to 4 uL of 500 ug/L Internal Standard Stock. To perform a dilution take the appropriate amount of sample and a volume of methylene chloride sufficient to make a 100 uL final volume, and add 4 uL of the Internal Standard Stock. For instance, to perform a 20% analysis (dilution factor =5), 4 uL of 500 ug/L Internal Standard Stock, 20 uL of sample, and 80 uL of methylene chloride

are combined. A 2 uL injection is required.

8.0 Tune and Standards Requirements

Semivolatile organic standards are received in ampules and are to be stored in the GC-MS preparation laboratory freezer. Ampules should only be opened prior to use, and in order of date received (oldest expiration date first). Expired standards must never be used and should be disposed of properly. The expiration date is as provided by the manufacturer, when the manufacturer's expiration date is not provided, the expiration date will be set at 2 years from the preparation date.

All primary and intermediate standards are to be maintained at -10 to -20°C and all working standards are to be maintained at 4± 2°C.

Standards Preparation Procedures

Calibration standards are obtained from Restek, Inc; independent calibration standards are purchased from Supelco. A listing of standard sources can be found in Appendix A. The standards are accompanied by a data package which is to be maintained on file to verify the integrity of the standard solutions. The data packages include:

1. mass spectral identification confirmation of the neat materials
2. purity confirmation of the neat material
3. chromatographic and quantitative documentation that the solution standard was QC checked.

The formulation of calibration standards must be documented in logbooks and should include information to show traceability.

8.1 DFTPP

8.1.1 Standard Prep

25 ppm DFTPP Tuning Standard

Conc.	Vendor	Description	Cat#	Total Volume = 1000 uL Amount Used
2500 ug/mL	Restek	DFTPP	31001	10 uL
		Methylene Chloride		990 uL

Injection Volume = 2 uL

A 2 uL injection of DFTPP is made under isothermal conditions (oven temperature is set at 120° C).
The ion abundances shown in Table 2 must be met before analysis of calibration standards may proceed.

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

Mass	Ion Abundance Criteria
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

8.1.2 Evaluation and Corrective Action

Before data collection establish that the GC/MS system meets the standard mass spectral abundance criteria specified in Table 2 above. The initiation of an analysis window begins at the moment of injection of the performance standard (DFTPP) that meets the criteria. Within this window, all calibration standards, method blank analysis, and sample analysis will be performed. DFTPP criteria must be met before any standards, samples or blanks are analyzed. All instrument conditions for standard and sample analyses, except for the temperature program, must be identical to those used in the acquisition of DFTPP. Whenever corrective action is taken that may affect the tune of the instrument, the tune must be verified with DFTPP regardless of the window status.

Background subtraction is required when tuning the GC/MS system. The background subtraction must be straightforward and eliminate only column bleed or instrument background ions. Background subtraction resulting in spectral distortions for the sole purpose of meeting contract specifications is unacceptable. In such a case, the window would be invalid and all samples analyzed within the window would require reanalysis. The OLM03.2 SOW requires summing spectral information over a range from one scan before to one scan after the total RIC maxima and subtracting spectral information for a single scan no more than 20 scans prior to the elution of the performance evaluation compound that is representative of background noise. This is employed for method 8270 as well.

8.2 Internal Standards

8.2.1 Standard Prep

500 ppm Internal Standard

Conc.	Vendor	Description	Cat #	Total Volume=4000 uL Amount used (uL)
4000 ug/mL	Restek	SV Internal Std. Mix	31006	500
		Methylene Chloride		3500

Volume Added

Add internal standard mixture containing 1,4-Dichlorobenzene-d4, Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12 to all calibration standards, blanks, and samples to give a final concentration of 20 ug/mL. A 4 uL aliquot of the 500 ppm stock is added to 100 uL of standards or extracts prior to analysis.

ISTD +/- 2x from last CCAL

Internal standard quantitation ion area must not vary by more than a factor of two (-50% to +100%) from the latest calibration standard. Retention times of internal standards must not vary by more than 0.5 minutes (30 seconds) from the latest calibration standard. If sample analysis fails any single instance of these criteria, the sample must be reanalyzed to determine whether the failure was due to analytical error or matrix effect. If the sample meets the criteria upon reanalysis, only the passing analysis is submitted. If reanalysis confirms the original failure, both analyses are submitted.

8.2.2 Evaluation and Corrective Action

Internal standard responses and retention times in all samples and blanks must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be checked for malfunctions, and corrections made. If the area of the internal standard compound changes by more than a factor of two from the latest daily calibration standard, then the mass spectrometric system must be checked for malfunction and corrective action taken. Poor spiking technique, evaporation or degradation of the standard stock mixture, or autosampler malfunction can result in erratic internal standard areas. Affected blanks and samples must be reanalyzed; no samples associated with a non-compliant blank are valid.

If a sample has unacceptable internal standard area results, reanalysis of the sample is necessary. If the sample continues to show unacceptable internal standard areas, and intervening samples have been acceptable, then the problem is outside of the laboratory's control, and both analyses are submitted.

8.3 Initial Calibration

Concentrations of organic compounds will be determined by GC/MS using an internal standard and fixed response model. Prior to the analysis of samples and blanks, DFTPP tuning requirements must be satisfied according to the method. Once the tune has been established, the GC/MS system will be calibrated to determine the linearity of instrument response. 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:

$$RRF = \frac{A_x * C_{is}}{A_{is} * C_x}$$

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)

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 compound 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)

8.3.1 Standard Prep

8270 Calibration

160 ppm A Mix

Conc.	Vendor	Description	Cat #	Total Volume=3750 uL Amount used (uL)
1500 ug/mL	Restek	Acid Surr Mix	31003	400
1000 ug/mL	Restek	BN Surr Mix	31002	600
2000 ug/mL	Restek	SV_Cal Mix 1	31007	300
2000 ug/mL	Restek	SV_Cal Mix 2	31008	300
2000 ug/mL	Restek	SV_Cal Mix 3	31009	300
2000 ug/mL	Restek	SV_Cal Mix 4	31010	300
2000 ug/mL	Restek	SV_Cal Mix 5	31011	300
2000 ug/mL	Restek	3,3'-Dichlorobenzidine	31026	300
2000 ug/mL	Restek	SV_Cal Mix 7	31013	300
	Baker	Methylene Chloride		650

Volume Added

The 5 concentrations for the initial calibration must give 20, 50, 80, 120, and 160 ng on-column with a 2.0 uL injection. All target analytes and surrogates are included in the calibration. The aliquot volumes are given below.

Curve

Std. Conc.	160 ppm Restek "A" Mix	500 ppm Internal Standard	$MeCl_2$
20	6.25 uL	4 uL	93.8 uL
50	15.6 uL	4 uL	84.4 uL
80	25.0 uL	4 uL	75.0 uL
120	37.5 uL	4 uL	62.5 uL
160	50.0 uL	4 uL	50.0 uL

Calibration Criteria

The RSD should be less than 15% for each compound. However, the RSD for each compound check compound (CCC) must be less than 30%. If the minimum RRF's and maximum %RSD's given in Table 3 below are met, and time remains in the 12 hour window, analysis of samples may proceed.

Chromatography

The analytical run must begin at least 30 seconds before the elution of the first target analyte and must last until at least 3 minutes after the last target analyte. Use the following temperature program to acquire semivolatile analytical data:

Table 3

Analyte	Minimum RRF	Maximum %RSD	Maximum %Diff
Acenaphthene	0.900	20.5	± 25
Acenaphthylene	0.900	20.5	± 25
Anthracene	0.700	20.5	± 25
Benzo(a)anthracene	0.800	20.5	± 25
Benzo(b)fluoranthene	0.700	20.5	± 25
Benzo(k)fluoranthene	0.700	20.5	± 25
Benzo(g,h,i)perylene	0.500	20.5	± 25
Benzo(a)pyrene	0.700	20.5	± 25
4-Bromophenyl-phenylether	0.100	20.5	± 25
Butylbenzylphthalate	0.010	40	± 40
Carbazole	0.010	40	± 40
4-Chloroaniline	0.010	40	± 40
bis(2-Chloroethoxy)methane	0.300	20.5	± 25
bis(2-Chloroethyl)ether	0.700	20.5	± 25
4-Chloro-3-methylphenol	0.200	20.5	± 25
2-Chloronaphthalene	0.800	20.5	± 25
2-Chlorophenol	0.800	20.5	± 25
2-Chlorophenol-d4	0.800	20.5	± 25
4-Chlorophenyl-phenylether	0.400	20.5	± 25
2,2'-oxybis(1-Chloropropane)	0.010	40	± 40
Chrysene	0.700	20.5	± 25
Dibenzofuran	0.800	20.5	± 25
Dibenz(a,h)anthracene	0.400	20.5	± 25
Di-n-butylphthalate	0.010	40	± 40
1,2-Dichlorobenzene	0.400	20.5	± 25
1,2-Dichlorobenzene-d4	0.400	20.5	± 25
1,3-Dichlorobenzene	0.600	20.5	± 25

Analyte	Minimum RRF	Maximum %RSD	Maximum %Diff
1,4-Dichlorobenzene	0.500	20.5	± 25
3,3'-Dichlorobenzidine	0.010	40	± 40
2,4-Dichlorophenol	0.200	20.5	± 25
Diethylphthalate	0.010	40	± 40
2,4-Dimethylphenol	0.200	20.5	± 25
Dimethylphthalate	0.010	40	± 40
2,4-Dinitrophenol	0.010	40	± 40
2,4-Dinitrotoluene	0.200	20.5	± 25
2,6-Dinitrotoluene	0.200	20.5	± 25
4,6-Dinitro-2-methylphenol	0.010	40	± 40
Di-n-octylphthalate	0.010	40	± 40
bis(2-Ethylhexyl)phthalate	0.010	40	± 40
Fluoranthene	0.600	20.5	± 25
Fluorene	0.900	20.5	± 25
2-Fluorobiphenyl	0.700	20.5	± 25
2-Fluorophenol	0.600	20.5	± 25
Hexachlorobenzene	0.100	20.5	± 25
Hexachlorobutadiene	0.010	40	± 40
Hexachlorocyclopentadiene	0.010	40	± 40
Hexachloroethane	0.300	20.5	± 25
Indeno(1,2,3-cd)pyrene	0.500	20.5	± 25
Isophorone	0.400	20.5	± 25
2-Methylnaphthalene	0.400	20.5	± 25
2-Methylphenol	0.700	20.5	± 25
4-Methylphenol	0.600	20.5	± 25
Naphthalene	0.700	20.5	± 25
2-Nitroaniline	0.010	40	± 40
3-Nitroaniline	0.010	40	± 40

Analyte	Minimum RRF	Maximum %RSD	Maximum %Diff
4-Nitroaniline	0.010	40	± 40
Nitrobenzene	0.200	20.5	± 25
Nitrobenzene-d5	0.200	20.5	± 25
2-Nitrophenol	0.100	20.5	± 25
4-Nitrophenol	0.010	40	± 40
N-Nitrosodiphenylamine	0.010	40	± 40
N-Nitroso-di-n-propylamine	0.500	20.5	± 25
Pentachlorophenol	0.050	20.5	± 25
Phenanthrene	0.700	20.5	± 25
Phenol	0.800	20.5	± 25
Phenol-d5	0.800	20.5	± 25
Pyrene	0.600	20.5	± 25
Terphenyl-d14	0.500	20.5	± 25
2,4,6-Tribromophenol	0.010	40	± 40
1,2,4-Trichlorobenzene	0.200	20.5	± 25
2,4,5-Trichlorophenol	0.200	20.5	± 25
2,4,6-Trichlorophenol	0.200	20.5	± 25

8.4 Continuing Calibration

A continuing calibration standard of specified concentration containing all TCL compounds including surrogates must be analyzed every 12 hours or as specified by the method. The relative response factors from the continuing calibration standard are calculated and compared to the average relative response factor from the initial calibration. The percent difference (%D) is calculated with the following equation:

$$\%\ Difference = \frac{RRF_i - RRF_c}{RRF_i} * 100$$

where:
RRF_i = average relative response factor from initial calibration
RRF_c = relative response factor from current calibration check std.

8.4.1 Standard Prep

The continuing calibration is prepared from the 160 ppm "A" Mix as described above.

Volume Added
The final concentration for these standards is at the mid-level concentration of the five point calibration curve (50 ng on-column).

Std. Conc.	160 ppm Restek "A" Mix	500 ppm Internal Standard	$MeCl_2$
50	15.6 uL	4 uL	84.4 uL

Criteria
A check of the calibration curve must be performed once every 12 hours before sample analysis. Following a successful DFTPP analysis, a 50 ng calibration standard is acquired. If the minimum RRF's and maximum %D's shown in Table 3 are met, and time remains in the 12 hour window, analysis of samples may proceed. Up to four target analytes with a maximum %D of 25% may fail to meet the criteria in Table 3, if the minimum RRF is not less than 0.01 and the maximum %D is not greater than 40%.

9.0 Method QC

9.1 Blanks

1 blank every extraction set
A method blank must be extracted with every extraction set, and must meet the most frequent of the following criteria. There must be at least one blank for:

- Each extraction batch

The method blank must be analyzed on each instrument which has been used to analyze associated samples, and must not contain any target analytes at concentrations greater than or equal to their CRQL's, with the exception of the phthalate esters, which may be present at less than five (5) times their CRQL.

9.2 Surrogates

All surrogates in method blanks and samples must meet the required recovery criteria (shown in Table 4). Note that limits for two surrogates are only advisory. One acid and one base neutral surrogate may fail to meet the required criteria, as long as recovery is at least 10%. For sample analysis, if required surrogate criteria are not met, the sample must be reanalyzed. If the sample meets the criteria upon reanalysis, only the passing analysis is submitted. If reanalysis confirms the original failure, the sample must be reextracted. If a method blank fails recovery criteria, the blank and all associated samples must be reextracted. Samples which have been diluted at or more than three to one (i.e., a 25% or lower concentration analysis) may exhibit recovery failures due to the dilution. These do not require reanalysis or reextraction. Each surrogate retention time in a sample must agree within ± 0.06 relative retention time (RRT) units with the continuing calibration standard. Reanalyze to confirm failures of retention time stability. Submit a single passing analysis or both failing analyses.

Individual component recoveries are calculated with the following equation:

$$Surrogate\ Recovery\ (\%) = \frac{SR}{SA} * 100$$

where:
SR = Spike Result
SA = Spike Added (concentration)

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.

9.3 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

MS and MSD per SDG per matrix

A MS and MSD are required for each group of samples of a similar matrix at the most frequent occurrence of the following:

- Each field group or "Case" of field samples received, OR
- Each 20 field samples in a group, OR
- Each 7 day calendar period during which field samples in a group were received, OR
- Each group of field samples of a similar concentration level (soils only)

Extraction and analysis of MS and MSD samples will be performed according to themethod. The MS and MSD should be analyzed at the same or a higher concentration than the associated sample. Individual component recoveries are calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between matrix spike and matrix spike duplicate analysis is calculated with 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)

Recovery limits (shown in Table 5) for these spikes 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

10.0 Data Acquisition

10.1 Autosamplers

Autosamplers should be utilized as much as possible to perform sample analysis when operators are not available. The following procedures are used to set up an autosampler run.

The 7673A autosampler is used to position vials for injection, either as single injections or as a sequence. The autosampler needle and rinse vials should be checked daily for cleanliness and proper function. For operation in a sequence, the vial positions in the autosampler tray must correspond to the vial positions in the software sequence. After typing in a sequence (Appendix D, Section 5), print the sequence and check it against the vials loaded in the autosampler tray.

11.0 Calculations

11.1 Concentrations of Unknowns: Chromatographic peaks not identified by the automated search routines as TCL 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:

Water

$$C_{(x)} = \frac{Amt_{(IS)} * H_{(x)} * V_{(t)}}{H_{(IS)} * V_{(o)} * V_{(i)}} * DF$$

$C_{(x)}$= 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)
$V_{(o)}$ = Sample volume (mL)
$V_{(i)}$ = Volume injected (uL)

Soil

$$C_{(x)} = \frac{Amt_{(IS)} * H_{(x)} * V_{(t)} * GPC * DF * 10^3 g/Kg}{H_{(IS)} * W_{(s)} * \frac{100 - M}{100} * V_{(i)} * 10^3 ng/ug}$$

$C_{(x)}$ = 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

11.2 Identified TCL 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:

Water

$$C_{(x)} = \frac{A_{(x)} * Amt_{(IS)} * V_{(t)}}{A_{(IS)} * RRF * V_{(o)} * V_{(i)}} * DF$$

$C_{(x)}$ = 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)

Soil

$$C_{(x)} = \frac{A_{(x)} * Amt_{(IS)} * V_{(t)} * GPC * 10^3 g/Kg}{A_{(IS)} * RRF * W_{(s)} * \frac{100-M}{100} * V_{(i)} * 10^3 ng/ug} * DF$$

$C_{(x)}$ = 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

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.

12.0 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).

12.1 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.

13.0 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 A:

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(1-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
2,4,6-Trichlorophenol	196	198, 200

Parameter	Primary Quantitation Ion	Secondary Ion (s)
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
Fluoranthene	202	101, 100
Pyrene	202	101, 100
Butylbenzylphthalate	149	91, 206

Parameter	Primary Quantitation Ion	Secondary Ion (s)
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. 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

1,4-Dichlorobenzene-d(4)	**Naphthalene-d(8)**	**Acenaphthene-d(10)**
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
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 8: 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

Appendix B: Sources

Compounds	Sources		Compounds	Sources	
	Calibration	IDL		Calibration	IDL
	Restek	Supelco		Restek	Supelco
Acenaphthene	SV Cal Mix #5	TCL PAH Mix	4,6-Dinitro-2-methylphenol	SV Cal Mix #2	TCL Phenols
Acenaphthylene	SV Cal Mix #5	TCL PAH Mix	Di-n-octylphthalate	SV Cal Mix #3	TCL B/N Mix #1
Anthracene	SV Cal Mix #5	TCL PAH Mix	bis(2-Ethylhexyl)phthalate	SV Cal Mix #3	TCL B/N Mix #1
Benzo(a)anthracene	SV Cal Mix #5	TCL PAH Mix	Fluoranthene	SV Cal Mix #5	TCL PAH Mix
Benzo(b)fluoranthene	SV Cal Mix #5	TCL PAH Mix	Fluorene	SV Cal Mix #5	TCL PAH Mix
Benzo(k)fluoranthene	SV Cal Mix #5	TCL PAH Mix	2-Fluorobiphenyl	B/N Surr Mix	B/N Surr Mix
Benzo(g,h,i)perylene	SV Cal Mix #5	TCL PAH Mix	2-Fluorophenol	Acid Surr Mix	Acid Surr Mix
Benzo(a)pyrene	SV Cal Mix #5	TCL PAH Mix	Hexachlorobenzene	SV Cal Mix #4	TCL B/N Mix #2
4-Bromophenyl-phenylether	SV Cal Mix #3	TCL B/N Mix#1	Hexachlorobutadiene	SV Cal Mix #4	TCL B/N Mix #2
Butylbenzylphthalate	SV Cal Mix #3	TCL B/N Mix#1	Hexachlorocyclopentadiene	SV Cal Mix #4	TCL B/N Mix #2
Carbazole	SV Cal Mix #4	TCL B/N Mix#2	Hexachloroethane	SV Cal Mix #4	TCL B/N Mix #2
4-Chloroaniline	SV Cal Mix #1	TCL HAZ Sub Mix #2	Indeno(1,2,3-cd)pyrene	SV Cal Mix #5	TCL PAH Mix
bis(2-Chloroethoxy)methane	SV Cal Mix #3	TCL B/N Mix#1	Isophorone	SV Cal Mix #4	TCL B/N Mix #2
bis(2-Chloroethyl)ether	SV Cal Mix #3	TCL B/N Mix#1	2-Methylnaphthalene	SV Cal Mix #4	TCL Haz Sub Mix #2
4-Chloro-3-methylphenol	SV Cal Mix #2	Total Phenols	2-Methylphenol	SV Cal Mix #2	TCL Haz Sub Mix #1
2-Chloronaphthalene	SV Cal Mix #3	TCL B/N Mix#2	4-Methylphenol	SV Cal Mix #2	TCL Haz Sub Mix #1
2-Chlorophenol	SV Cal Mix #2	TCL Phenols	Naphthalene	SV Cal Mix #5	TCLPAH Mix
2-Chlorophenol-d4	Acid Surr Mix	Acid Surr Mix	2-Nitroaniline	SV Cal Mix #1	TCL Haz Sub Mix #2
4-Chlorophenyl-phenylether	SV Cal Mix #3	TCL B/N Mix#1	3-Nitroaniline	SV Cal Mix #1	TCL Haz Sub Mix #2
2,2'-oxybis(1-Chloropropane)	SV Cal Mix #3	TCL B/N Mix#1	4-Nitroaniline	SV Cal Mix #1	TCL Haz Mix #2
Chrysene	SV Cal Mix #5	TCL PAH Mix	Nitrobenzene	SV Cal Mix #4	TCL B/N Mix #2
Dibenzofuran	SV Cal Mix #4	TCL Haz Sub Mix #2	Nitrobenzene-d5	B/N Surr Mix	B/N Surr Mix
Dibenz(a,h)anthracene	SV Cal Mix #5	TCL PAH Mix	2-Nitrophenol	SV Cal Mix #2	TCL Phenols
Di-n-butylphthalate	SV Cal Mix #3	TCL B/N Mix#1	4-Nitrophenol	SV Cal Mix #2	TCL Phenols
1,2-Dichlorobenzene	SV Cal Mix #7	TCL B/N Mix#2	N-Nitrosodiphenylamine	SV Cal Mix #3	TCL B/N Mix #1
1,2-Dichlorobenzene-d4	B/N Surr Mix	B/N Surr Mix	N-Nitroso-di-n-propylamine	SV Cal Mix #3	TCL B/N Mix #1

	Sources			Sources	
	Calibration	IDL		Calibration	IDL
Compounds	Restek	Supelco	Compounds	Restek	Supelco
1,3-Dichlorobenzene	SV Cal Mix #7	TCL B/N Mix#2	Pentachlorophenol	SV Cal Mix #2	TCL Phenols
1,4-Dichlorobenzene	SV Cal Mix #7	TCL B/N Mix#2	Phenanthrene	SV Cal Mix #5	TCL PAH Mix
3,3'-Dichlorobenzidine			Phenol	SV Cal Mix #2	TCL Phenols
2,4-Dichlorophenol	SV Cal Mix #2	TCL Phenols	Phenol-d5	Acid Surr Mix	Acid Surr Mix
Diethylphthalate	SV Cal Mix #4	TCL B/N Mix#1	Pyrene	SV Cal Mix #5	TCL PAH Mix
2,4-Dimethylphenol	SV Cal Mix #2	TCL Phenols	Terphenyl-d14	B/N Surr Mix	B/N Surr Mix
Dimethylphthalate	SV Cal Mix #3	TCL B/N Mix#1	2,4,6-Tribromophenol	Acid Surr Mix	Acid Surr Mix
2,4-Dinitrophenol	SV Cal Mix #2	TCL Phenols	1,2,4-Trichlorobenzene	SV Cal Mix #4	TCL B/N Mix #2
2,4-Dinitrotoluene	SV Cal Mix #4	TCL B/N Mix#1	2,4,5-Trichlorophenol	SV Cal Mix #2	TCL Haz Sub Mix #1
2,6-Dinitrotoluene	SV Cal Mix #4	TCL B/N Mix#2	2,4,6-Trichlorophenol	SV Cal Mix #2	TCL Phenols

Appendix C: 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 D: 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 Run Control and click on the appropriate box.

APPENDIX A-29

STANDARD OPERATING PROCEDURE FOR EXTRACTABLE PAHs BY GC/MS SELECTIVE ION MONITORING

I. METHOD — SIMPAH: AN DETERMINATION OF EXTRACTABLE PAH's BY GC/MS SELECTIVE ION MONITORING (SIM)

Approvals and Signatures

QA Officer: Martha Ray Date: 3-13-96

Assistant Lab Director: Jon J. Arsi Date: 3-13-96

This method applies to samples received for analysis under the NOAA Status and Trends Methods for low level polynuclear aromatic hydrocarbons.

II. SUMMARY

A. *Basic Principles*

A one liter aliquot of a liquid sample or a 40 g aliquot of a soil or tissue sample is spiked with a surrogate compound mixture and then extracted with methylene chloride. The final extract is concentrated to either 1000 uL (waters) or 1000 uL (soils/tissue). 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. Target compound concentrations are corrected for the recovery of the surrogate compounds.

B. *General Method*

The mass spectrometer is calibrated to recognize m/z values in the range of 35-500 amu. Instrument performance is verified by the injection of Decafluorotriphenylphosphine (DFTPP). The ion abundances must meet the criteria shown in Table 3 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 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.

C. *Instrumentation*

SVOA Autosampler: CTC A200S

Gas Chromatograph: Hewlett-Packard 5890 GC

Mass Spectrometer: Hewlett-Packard 5971 MSD

Primary Column: Restek RTx-5 30m x 0.25mm x .25 um or equivalent
OLM03.1 (D-10/SVOA Section 6.19.2.1) states a capillary column is equivalent if :

- The column does not introduce contaminants which interfere with the identification and quantitation of the target compounds.
- The analytical results generated using the column meet the initial and continuing calibration technical acceptance criteria listed in the SOW, and the CRQL's for the target compounds.
- The column can accept up to 160 ng of each target compound.
- The column provides equal or better resolution of the target compounds.

D. *Analytes*

The analytes and their respective Chemical Abstract Services (CAS) numbers are given in Table 1 below.

Table 1. Analytes

Analyte	CAS No.
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Benzo(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(g,h,i)perylene	191-24-2
Benzo (a) pyrene	50-32-8
Benzo(e)pyrene	192-97-2
Biphenyl	92-52-4
Chrysene	218-01-9
Dibenz(a,h)anthracene	53-70-3
2,6 Dimethylnaphthalene	581-42-0
Dibenzothiophene	132-65-0
Fluoranthene	206-44-0
Fluorene	86-73-7
Indeno(1,2,3-cd)pyrene	193-39-5
1-Methylnaphthalene	1321-94-4

Analyte	CAS No.
2-Methylnaphthalene	91-57-6
1 Methylphenanthrene	832-69-9
Naphthalene	91-20-3
Phenanthrene	85-01-8
Perylene	198-55-0
Pyrene	129-00-0
2,3,5 Trimethylnaphthalene	2245-38-7

III. SAMPLE REQUIREMENTS

A. *Matrix*

Liquids

This method is applicable to determinations in surface water, ground water, processed water, and waste waters.

Solids

This method is applicable to determinations in soils, sediments and tissues.

B. *Sample Preparation*

For analysis, add a 100 uL aliquot of sample to 1 uL of 10 ug/L Internal Standard Stock. To perform a dilutions take the appropriate amount of sample and a volume of hexane sufficient to make a 100 uL final volume, and add 1 uL of the Internal Standard Stock. For instance, to perform a 20% analysis (dilution factor =5), 4 uL of 500 ug/L Internal Standard Stock, 20 uL of sample, and 80 uL of hexane are combined. A 2 uL injection is required.

IV. METHOD CRITERIA

Semivolatile organic standards are received in ampules or as neats and are to be stored in the GC-MS preparation laboratory freezer. Ampules should only be opened prior to use, and in order of date received (oldest expiration date first). Expired standards must never be used and should be disposed of properly.

All primary and intermediate standards are to be maintained at -10 to -20°C and all working standards are to be maintained at 4± 2°C.

Standards Preparation Procedures

Calibration standards are obtained from Restek, Inc; independent calibration standards are purchased from Supelco. A listing of standard sources can be found in Appendix A. The standards are accompanied by a data package which is to be maintained on file to verify the integrity of the standard solutions. The data packages include:

1. mass spectral identification confirmation of the neat materials
2. purity confirmation of the neat material
3. chromatographic and quantitative documentation that the solution standard was QC checked.

The formulation of calibration standards must be documented in logbooks and should include information to show traceability.

A. *Instrument Detection Limits*
Determine Instrument detection limits (IDLs) annually in accordance with the method described in 40 CFR, Part 136, Appendix B.

B. *Reporting Limits*
CRQL's = 5 ug/Kg (See Table 2)
The method CRQL's are presented in Table 2 below. Diluted sample reporting limits will be raised by the dilution factor.

Table 2. CRQL's

Analyte	Aqueous Reporting Limits (ug/L)	Soil/Tissue Reporting Limits (ug/Kg)*
Acenaphthene	0.02	5
Acenaphthylene	0.02	5
Anthracene	0.02	5
C_1- Phenanthrenes/anthracenes	0.02	TBD
C_2- Phenanthrenes/anthracenes	0.02	TBD
C_3- Phenanthrenes/anthracenes	0.02	TBD
C_4- Phenanthrenes/anthracenes	0.02	TBD
Benzo(a)anthracene	0.02	5
Benzo(b)fluoranthene	0.02	5
Benzo(k)fluoranthene	0.02	5
Benzo(g,h,i)perylene	0.02	5
Benzo (a) pyrene	0.02	5
Benzo(e)pyrene	0.02	5
Biphenyl	0.02	5
Chrysene	0.02	5
C_1- Chrysenes	0.02	TBD
C_2- Chrysenes	0.02	TBD
C_3- Chrysenes	0.02	TBD

Analyte	Aqueous Reporting Limits (ug/L)	Soil/Tissue Reporting Limits (ug/Kg)*
C_4- Chrysenes	0.02	TBD
Dibenz(a,h)anthracene	0.02	5
2,6 Dimethylnaphthalene	0.02	5
Dibenzothiophene	0.02	5
C_1- Dibenzothiophenes	0.02	TBD
C_2- Dibenzothiophenes	0.02	TBD
C_3- Dibenzothiophenes	0.02	TBD
Fluoranthene	0.02	5
C_1-Fluoranthenes/pyrene	0.02	TBD
Fluorene	0.02	5
C_1- Fluorenes	0.02	TBD
C_2- Fluorenes	0.02	TBD
C_3- Fluorenes	0.02	TBD
Indeno(1,2,3-cd)pyrene	0.02	5
1-Methylnaphthalene	0.02	5
2-Methylnaphthalene	0.02	5
1 Methylphenanthrene	0.02	5
Naphthalene	0.02	5
C_1- Naphthalenes	0.02	TBD
C_2- Naphthalenes	0.02	TBD
C_3- Naphthalenes	0.02	TBD
C_4- Naphthalenes	0.02	TBD
Phenanthrene	0.02	5
Perylene	0.02	5
Pyrene	0.02	5
2,3,5 Trimethylnaphthalene	0.02	5

* Reporting Limits based on 40 grams of sample extracted
TBD= To Be Determined

C. *Tune and Standards Criteria*

1. DFTPP

Standard Prep

2.5 ppm DFTPP Tuning Standard

Conc.	Vendor	Description	Cat#	Total Volume = 1000 uL Amount Used
2500 ug/mL	Restek	DFTPP Methylene Chloride	31001	1 uL 999 uL

Injection Volume = 2 uL

A 2 uL injection of DFTPP is made under isothermal conditions (oven temperature is set at 120° C). The ion abundances shown in Table 3 must be met before analysis of calibration standards may proceed.

Table 3. DFTPP Criteria

DFTPP Key Ions and Ion Abundance 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	40.0-110.0 percent of mass 198
443	17.0-23.0 percent of mass 442

Evaluation and Corrective Action

Before data collection establish that the GC/MS system meets the standard mass spectral abundance criteria specified in Table 3 above. The initiation of an analysis window begins at the moment of injection of the performance standard (DFTPP) that meets the criteria. Within this window, all calibration standards, method blank analysis, and sample analysis will be performed. DFTPP criteria must be met before any standards, samples or blanks are analyzed. All instrument conditions for standard and sample analyses, except for the temperature program, must be identical to those used in the acquisition of DFTPP. Whenever corrective action is taken that may affect the tune of the instrument, the tune must be verified with DFTPP regardless of the window status.

Background subtraction is required when tuning the GC/MS system. The background subtraction must be straightforward and eliminate only column bleed or instrument background ions. Background subtraction resulting in spectral distortions for the sole purpose of meeting contract specifications is unacceptable. In such a case, the window would be invalid and all samples analyzed within the window would require reanalysis.

2. Internal Standards

Standard Prep

10 ppm Internal Standard Mix

Conc.	Description	Total Volume = 4000 uL Amount Used
20000 ug/mL	Fluorene-d_{10}	2 uL
20000 ug/mL	Benzo (a)pyrene- d_{12}	2 uL
	Hexane	3996 uL

Volume Added

Add internal standard mixture containing Fluorene-d_{10} and Benzo (a)pyrene- d_{12} to all calibration standards, blanks, and samples to give a final concentration of 0.1 ug/mL. A 1 uL aliquot of the 10 ppm stock is added to 100 uL of standards or extracts prior to analysis.

ISTD +/- 2x from last CCAL

Internal standard quantitation ion area must not vary by more than a factor of two (-50% to +100%) from the latest calibration standard. Retention times of internal standards must not vary by more than 0.5 minutes (30 seconds) from the latest calibration standard. If sample analysis fails any single instance of these criteria, the sample must be reanalyzed to determine whether the failure was due to analytical error or matrix effect. If the sample meets the criteria upon reanalysis, only the passing analysis is submitted. If reanalysis confirms the original failure, both analyses are submitted.

Evaluation and Corrective Action

Internal standard responses and retention times in all samples and blanks must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds, the chromatographic system must be checked for malfunctions, and corrections made. If the area of the internal standard compound changes by more than a factor of two from the latest daily calibration standard, then the mass spectrometric system must be checked for malfunction and corrective action taken. Poor spiking technique, evaporation or degradation of the standard stock mixture, or autosampler malfunction can result in erratic internal standard areas. Affected blanks and samples must be reanalyzed; no samples associated with a non-compliant blank are valid.

If a sample has unacceptable internal standard area results, reanalysis of the sample is necessary. If the sample continues to show unacceptable internal standard areas, and intervening samples have been acceptable, then the problem is outside of the laboratory's control, and both analyses are submitted.

3. Surrogate Mix

Standard Prep

1.5 ug/mL Surrogate Mix

Conc.	Vendor	Description	Total Volume= 10000 uL Amount used (uL)
4000 ug/mL	Restek	SV ISTD Mix	3.75
		Hexane	9996.25

4. Initial Calibration

Standard Prep

2000 pg/uL PAH Calibration Standard Mix

Conc.	Vendor	Description	Total Volume= 4000 uL Amount used (uL)
2000 ug/mL	Supelco	PAH Mix	4
200 ug/mL		Added PAH Mix	40
		Hexane	3956

Volume Added

The 5 concentrations for the initial calibration must give 0.04, 0.2, 0.5, 1.0, and 2.0 ng on-column with a 2.0 uL injection. All target analytes and surrogates are included in the calibration. The aliquot volumes are given below.

PAH SIM Curve

Calibration Standard Concentration (pg/uL)	uL of 2000 pg/uL PAH Calibration Standard Mix	uL of 1.5 ppm Surrogate Mix	uL of 10 ppm Internal Standard Mix	uL of Hexane
1000	50	10	1	40
500	25	10	1	65
250	12.5	10	1	77.5
100	5	10	1	85
20	1	10	1	89

Calibration Criteria

If the minimum RRF's and maximum %RSD's given in Table 4 below are met, and time remains in the 12 hour window, analysis of samples may proceed. Maximum %RSD of 25 may fail the criteria in Table 4, if the minimum RRF is not less than 0.200 and the maximum % RSD is not greater than 25.0%. Up to three quantitation ions may saturate the detector in the high standard.

Oven Temperature Program:

Initial Temperature: 45°C for 1.2 minutes
Ramp: 10°C/minute to 300°C
Final Temperature: 300°C Hold for 8 minutes
This program should only be changed when improvements to the chromatography can be made (approval from the GC/MS

Supervisor or designee is required).

Table 4

Analyte	Minimum RRF	Maximum%RSD	Maximum %Diff
Acenaphthene	0.200	25	25
Acenaphthylene	0.200	25	25
Anthracene	0.200	25	25
Benzo(a)anthracene	0.200	25	25
Benzo(b)fluoranthene	0.200	25	25
Benzo(k)fluoranthene	0.200	25	25
Benzo(g,h,i)perylene	0.200	25	25
Benzo (a) pyrene	0.200	25	25
Benzo(e)pyrene	0.200	25	25
Biphenyl	0.200	25	25
Chrysene	0.200	25	25
Dibenz(a,h)anthracene	0.200	25	25
2,6 Dimethylnaphthalene	0.200	25	25
Dibenzothiophene	0.200	25	25
Fluoranthene	0.200	25	25
Fluorene	0.200	25	25
Indeno(1,2,3-cd)pyrene	0.200	25	25
1-Methylnaphthalene	0.200	25	25
2-Methylnaphthalene	0.200	25	25
1 Methylphenanthrene	0.200	25	25
Naphthalene	0.200	25	25
Phenanthrene	0.200	25	25
Perylene	0.200	25	25
Pyrene	0.200	25	25
2,3,5 Trimethylnaphthalene	0.200	25	25

5. Continuing Calibration

Standard Prep

The 250 pg/uL curve standard level is used for the continuing calibration standard.

Criteria

A check of the calibration curve must be performed once every 12 hours before sample analysis. Following a successful DFTPP analysis, a continuing calibration standard is acquired. If the minimum RRF's and maximum %D's shown in Table 4 are met, and time remains in the 12 hour window, analysis of samples may proceed.

V. HOLDING TIMES

Analyze all samples within 40 days of extraction.

VI. METHOD QC

A. *Blanks*

1 blank every extraction set

A method blank must be extracted with every extraction set, and must meet the most frequent of the following criteria. There must be at least one blank for:

- Each field group or "Case" of field samples received, OR
- Each 20 samples (including matrix spikes) in a group that are of similar matrix or concentration (soil only)

The method blank must be analyzed on each instrument which has been used to analyze associated samples, and must not contain any target analytes at concentrations greater than or equal to their CRQL's.

B. *Surrogates*

All surrogates in method blanks and samples must meet the required recovery criteria (shown in Table 5). For sample analysis, if required surrogate criteria are not met, the sample must be reanalyzed. If the sample meets the criteria upon reanalysis, only the passing analysis is submitted. If reanalysis confirms the original failure, the sample must be reextracted. If a method blank fails recovery criteria, the blank and all associated samples must be reextracted. Samples which have been diluted at or more than three to one (i.e., a 25% or lower concentration analysis) may exhibit recovery failures due to the dilution. These do not require reanalysis or reextraction. Each surrogate retention time in a sample must agree within ± 0.06 relative retention time (RRT) units with the continuing calibration standard. Reanalyze to confirm failures of retention time stability. Submit a single passing analysis or both failing analyses. Target compound concentrations are corrected for the recovery of the surrogate compounds.

Table 5. Surrogate Recoveries

Compound	Water (% Recovery)	Soil (% Recovery)
Naphthalene - d_8	20-130	20-130
Acenaphthene - d_{10}	20-130	20-130
Phenanthrene-d_{10}	20-130	20-130
Chrysene-d_{12}	20-130	20-130
Perylene- d_{12}	20-130	20-130

C. *Matrix Spike (MS) and Matrix Spike Duplicate (MSD)*

MS and MSD per SDG per matrix

A MS and MSD are required for each group of samples of a similar matrix at the most frequent occurrence of the following:

- Each field group or "Case" of field samples received, OR
- Each 20 field samples in a group, OR
- Each group of field samples of a similar concentration level (soils only)

The MS and MSD should be analyzed at the same or a higher concentration than the associated sample. Recovery limits (shown in Table 6) for these spikes are advisory only.

Table 6. Matrix Spike Recoveries

Compound	% Recovery Water	% Recovery Soil
Acenaphthene	70-120	70-120
Acenaphthylene	70-120	70-120
Anthracene	70-120	70-120
Benzo(a)anthracene	70-120	70-120
Benzo(b)fluoranthene	70-120	70-120
Benzo(k)fluoranthene	70-120	70-120
Benzo(g,h,i)perylene	70-120	70-120
Benzo (a) pyrene	70-120	70-120
Benzo(e)pyrene	70-120	70-120
Biphenyl	70-120	70-120
Chrysene	70-120	70-120
Dibenz(a,h)anthracene	70-120	70-120
2,6 Dimethylnaphthalene	70-120	70-120
Dibenzothiophene	70-120	70-120
Fluoranthene	70-120	70-120
Fluorene	70-120	70-120
Indeno(1,2,3-cd)pyrene	70-120	70-120
1-Methylnaphthalene	70-120	70-120
2-Methylnaphthalene	70-120	70-120
1 Methylphenanthrene	70-120	70-120
Naphthalene	70-120	70-120
Phenanthrene	70-120	70-120

Compound	% Recovery Water	% Recovery Soil
Perylene	70-120	70-120
Pyrene	70-120	70-120
2,3,5 Trimethylnaphthalene	70-120	70-120

VII. DATA ACQUISITION

A. 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.

B. Autosamplers

Autosamplers should be utilized as much as possible to perform sample analysis when operators are not available. The following procedures are used to set up an autosampler run.

C. 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 Inchcape 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(Aquatec Lab No. 112097 analyzed for BNA on 5971Q).
R121191DS (Aquatec Lab No. 121191 analyzed at a dilution for BNAs on 5971R).

E. Matrix Spikes and Duplicates

- The six digit Aquatec 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 (Aquatec Lab No. 112934MS analyzed for BNA matrix spike on 5971Q).
Q112934MSDS (Aquatec Lab No. 112934MS analyzed for BNA matrix spike on 5971Q analyzed at a dilution, as indicated by screening results).
R120954MDS (Aquatec 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 Aquatec Sample No. 120986 analyzed for BNA on 5971Q)
Q120986E2I2S (2nd injection of re-extract of Aquatec Sample No. 120986 analyzed for BNA on 5971Q)

D. 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.

E. 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 BITLAB 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.

2. 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.

3. 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 Run Control and click on the appropriate box.

VIII. CALCULATIONS

See Table 7 for the target compound quantitations associations.

A. *Concentrations of Calibrated Compounds*:

Water

$$C_{(x)} = \frac{A_{(x)} * Amt_{(SS)} * V_{(t)}}{A_{(SS)} * RRF * V_{(o)} * V_{(i)}} * DF$$

$C_{(x)}$ = Concentration of compound (ug/L)
$Amt_{(SS)}$ = Amount of associated surrogate standard (ng)
DF = Dilution Factor.
$A_{(SS)}$ = Area of quantitation ion for associated surrogate 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)

Soil

$$C_{(x)} = \frac{A_{(x)} * Amt_{(SS)} * V_{(t)} * GPC * 10^3 g/Kg}{A_{(SS)} * RRF * W_{(s)} * \frac{100-M}{100} * V_{(i)} * 10^3 ng/ug} * DF$$

$C_{(x)}$ = Concentration of compound (ug/Kg)
$Amt_{(SS)}$ = Amount of associated surrogate standard (ng)
DF = Dilution Factor.
$A_{(SS)}$ = Area of quantitation ion for associated surrogate 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

C. *Spike Recoveries*

Surrogates must be calculated for acceptance of recovery. Matrix spike compounds are used to demonstrate matrix effect on recoveries of selected compounds.

$$\%Recovery = \frac{\text{Actual Concentration}}{\text{Theoretical Concentration}} \times 100$$

IX. REPORTING QUALIFIERS

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

Table 7: Quantitation Associations

Analyte	Quantitation Ion	Confirmation Ions	Associations
Internal Standards:			
Fluorene - d_{10} (GC ISA)	176	174	NA
Benzo (a)pyrene - d_{12} (GC ISB)	264	260	NA
Surrogate Standards:			
Naphthalene - d_8 (IS1)	136	134	GC ISA
Acenaphthene - d_{10} (IS2)	164	162	GC ISA
Phenanthrene-d_{10} (IS3)	188	184	GC ISA
Chrysene-d_{12} (IS4)	240	236	GC ISB
Perylene- d_{12} (IS5)	264	260	GC ISB
Target Compounds:			
Acenaphthene	154	153	IS2
Acenaphthylene	152	153	IS2
Anthracene	178	176	IS3
C_1- Phenanthrenes/anthracenes	192	191	IS3
C_2- Phenanthrenes/anthracenes	206	191	IS3
C_3- Phenanthrenes/anthracenes	220	205	IS3
C_4- Phenanthrenes/anthracenes	234	219	IS3
Benzo(a)anthracene	228	226	IS4
Benzo(b)fluoranthene	252	253	IS4
Benzo(k)fluoranthene	252	253	IS4
Benzo(g,h,i)perylene	276	277	IS4
Benzo (a) pyrene	252	253	IS4
Benzo(e)pyrene	252	253	IS4
Biphenyl	154	152	IS2
Chrysene	228	226	IS4
C_1- Chrysenes	242	241	IS4
C_2- Chrysenes	256	241	IS4

Table 7: Quantitation Associations

Analyte	Quantitation Ion	Confirmation Ions	Associations
C_3- Chrysenes	270	255	IS4
C_4- Chrysenes	284	269	IS4
Dibenz(a,h)anthracene	278	279	IS4
2,6 Dimethylnaphthalene	156	141	IS2
Dibenzothiophene	184	152	IS3
C_1- Dibenzothiophenes	198	184	IS3
C_2- Dibenzothiophenes	212	197	IS3
C_3- Dibenzothiophenes	226	211	IS3
Fluoranthene	202	101	IS3
C_1-Fluoranthenes/pyrene	216	215	IS3
Fluorene	166	165	IS2
C_1- Fluorenes	180	165	IS2
C_2- Fluorenes	194	179	IS2
C_3- Fluorenes	208	193	IS2
Indeno(1,2,3-cd)pyrene	276	277	IS4
1-Methylnaphthalene	142	141	IS1
2-Methylnaphthalene	142	141	IS1
1 Methylphenanthrene	192	191	IS3
Naphthalene	128	127	IS1
C_1- Naphthalenes	142	141	IS1
C_2- Naphthalenes	156	141	IS2
C_3- Naphthalenes	170	155	IS2
C_4- Naphthalenes	184	169	IS2
Phenanthrene	178	176	IS3
Perylene	252	253	IS4
Pyrene	202	101	IS3
2,3,5 Trimethylnaphthalene	170	155	IS2

APPENDIX A-30

STANDARD OPERATING PROCEDURE FOR PETROLEUM HYDROCARBONS (BY INFRARED SPECTROPHOTOMETRY)

Petroleum Hydrocarbons (By Infrared Spectrophotometry)
Method 418.1, IN670:IRS

Approvals and Signatures

QA Officer: Martha Roy Date: 1/22/97

Wet Chemistry Section Head: David E. Meeden Date: 01/22/97

1.0 Scope and Application

1.1 This method is for the measurement of fluorocarbon- 113 extractable petroleum hydrocarbons from surface and saline waters, industrial and domestic wastes.

1.2 The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.

1.3 The reporting limit is 0.4 mg/L for waters and 41 mg/Kg as received for soils.

2.0 Summary of Method

2.1 The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences are removed with silica gel adsorbent. Infrared analysis of the extract is performed by direct comparison with standards.

3.0 Definitions

3.1 As in the case of Oil and Grease, the parameter of Petroleum Hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly.

3.2 Oil and Grease is a measure of biodegradable animal greases and vegetable oils along with the relative non-biodegradable mineral oils. Petroleum hydrocarbons

is the measure of only the mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease of all sources.

4.0 Sampling and Storage

4.1 For water samples collect a minimum of 1 liter of sample in an amber glass bottle. The sample should be preserved with 5 mL 1:1 HCl:DIH_2O.

4.2 For soil samples a minimum sample amount of 100 grams should be collected in a glass 250 mL amber wide mouth bottle.

4.3 All samples are stored at 4 ± 2°C. The holding time is 28 days from collection.

5.0 Apparatus

5.1 Separatory funnel, 2000 mL, with Teflon stopcock.

5.2 Filter paper, Whatman No. 40, 11 cm.

5.3 Infrared spectrophotometer, scanning or fixed wavelength, for measurement around 2950 cm-1.

5.4 Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.

5.5 Magnetic stirrer, with Teflon coated stirring bars.

6.0 Standards and Reagents

All prepared standards and reagents are assigned an expiration date of six (6) months from the date of preparation; unless the expiration date of the parent solution expires sooner than that expiration date is used. All standards and reagents are stored at room temperature unless otherwise noted. The preparation of all standards is recorded in the wet chemistry standard preparation notebook.

6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc HCl and distilled water.

6.2 Fluorocarbon-113,(1,1,2-trichloro-1,2,2-trifluoroethane) (Freon), boiling point

48°C.

6.3 Sodium sulfate, anhydrous crystal.

6.4 Silica gel, 60-200 mesh, Davidson Grade 950 or equivalent. Should contain 1-2% water as defined by residue test at 130°C. Adjust by overnight equilibration if needed.

6.5 Calibration mixtures

6.5.1 Reference oil: Pipet 15.0 mL n-hexadecane, 15.0 mL isooctane, and 10.0 mL chlorobenzene into a 50 mL glass stoppered bottle. Maintain the integrity of the mixture by keeping stoppered except when withdrawing aliquots. Store in refrigerator. Expires one year from preparation date.

6.5.2 Stock standard: Using a Hamilton syringe, transfer 25 uL Reference Oil (6.5.1) to a 50 mL volumetric flask and bring to volume with Freon (6.2). True value = 410 mg/L.

6.5.3 Standard Curve: prepare 10 point calibration curve as follows:

mLs of 410 mg/L Stock (6.5.2) standard used	mLs of Freon used	Final curve concentration (ppm)
6.0	4.0	246
4.0	6.0	164
3.0	7.0	123
2.0	8.0	82.0
5.0	5.0	41.0

mLs of 41.0 mg/L Standard standard used	mLs of Freon used	Final curve concentration (ppm)
7.0	3.0	28.7
5.0	5.0	20.5
3.0	7.0	12.3

mLs of 41.0 mg/L Standard standard used	mLs of Freon used	Final curve concentration (ppm)
2.0	8.0	8.2
1.0	9.0	4.1

6.5.4 Calibration Verification Standard:

A second Reference Oil is prepared exactly as in 6.5.1 using components from a separate source. To prepare a working standard, use a Hamilton syringe to transfer 2.5 uL of this Reference Oil to a 50 mL volumetric flask and bring to volume with Freon. True value = 41.0 mg/L.

7.0 Procedure

7.1 Mark the sample bottle at the water meniscus for later determination of sample volume. If the sample was not acidified at time of collection, add 5 mL hydrochloric acid (6.1) to the sample bottle. After mixing the sample, check the pH by touching pH-sensitive paper to the cap to insure that the pH is 2 or lower. Add more acid if necessary.

7.2 Pour the sample into a separatory funnel.

7.3 Add 30 mL fluorocarbon-113 (6.2) to the sample bottle and rotate the bottle to rinse the sides. Transfer the solvent into the separatory funnel. Extract by shaking vigorously for 2 minutes. Allow the layers to separate.

7.4 Filter the solvent layer through a funnel containing solvent moistened filter paper into a 125 mL amber glass bottle, pre-weighed to 0.01 gram.

NOTE 1: An emulsion that fails to dissipate can be broken by pouring about 1 g sodium sulfate (6.3) into the filter paper cone and slowly draining the emulsion through the salt. Additional 1 g portions can be added to the cone as required.

7.5 Repeat (7.3 and 7.4) twice more with 30 mL portions of fresh solvent, combining all solvent into the volumetric flask.

7.6 Rinse the tip of the separatory funnel, filter paper, and the funnel with a total of

5-10 mL solvent and collect the rinsate in the bottle. Weigh bottle/extracts/rinses to the nearest 0.01 gram. This weight minus the weight of the empty bottle, divided by the density of freon (1.5635 g/mL) gives the final volume of freon extract.

7.7 Add 3 g silica gel (6.4) and a stirring bar; stopper the volumetric flask, and stir the solution for a minimum of 5 min on a magnetic stirrer.

7.8 Calibrate the instrument using a series of working standards (6.5.3). It is not necessary to add silica gel to the standards. Determine absorbance directly for each solution at the absorbance maximum at about 2930 cm-1. Prepare a calibration plot of absorbance vs. mg/L TPH. The correlation of the curve must be $\geq$ 0.995 for the analysis to proceed.

7.9 After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract. If the absorbance exceeds the highest standard, a dilution must be prepared using extract from the method blank (not straight freon).

NOTE 2: The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

7.10 Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot.

8.0 Modifications for Soil Analysis

8.1 Ten grams of well mixed sample are transferred to a clean, tared beaker and weighed to the nearest 0.01 gram.

8.2 The sample is made acidic with 7 drops of conc. H_2SO_4 followed with 15 grams of $MgSO_4$. The mixture is stirred and allowed to stand for 15 minutes.

8.3 The contents of the beaker are transferred to a Soxhlet thimble and the thimble is inserted into the Tecator Soxtec System HT 1043 Extraction Unit.

8.4 The extraction unit is preprogrammed to boil for 15 minutes, rinse for 45 minutes

and cool down for 12 minutes. The collected freon is then transferred to a clean, preweighed amber glass bottle, along with two 10 mL freon rinses.

8.5 The weight of the bottle/extract/rinses is recorded to the nearest 0.01 gram. This weight minus the weight of the empty bottle, divided by the density of freon (1.5635 g/mL) gives the final volume of the freon extract.

8.6 Analysis continues as described from section 7.7 on.

9.0 Calculations

9.1 Calculate the petroleum hydrocarbons in the sample.

Waters

$$mg/L = \frac{Amt.\ off\ curve\ (ppm) * Ext.\ volume\ (mL) * DF}{Amt.\ sample\ (mL)}$$

Soils

$$mg/Kg\ (as\ rec'd) = \frac{Amt.\ off\ curve\ (ppm) * Ext.\ volume\ (mL) * DF}{Amt.\ sample\ (g)}$$

10.0 Quality Control

Control charts provide a means for long term trend analysis as well as a tool for real time data assessment. Statistical control charts are prepared for this method. The % recovery of laboratory control samples, matrix spikes and surrogates are monitored and charted. The relative % difference (RPD) of laboratory duplicates is also monitored and charted.

Control limits derived from laboratory data are calculated in terms of multiple standard deviation from a mean or other reference point. Warning limits are set at ± 2 standard deviations and control limits are set at ± 3 standard deviations. Initial limits are established after a minimum of twenty data points are available. Once established, the control limits are updated whenever at least annually. If method specified limits are available the calculated control limits are compared to them. The laboratory adopts method specified limits whenever available rather than use laboratory generated limits for actual evaluation of data. This is to provide consistency over time, particularly for projects which may be ongoing. It also clarifies the data review process and SOP revision process to have limits which are not frequently changing. In the case where acceptance limits are not specified in methodology laboratory generated control limits will be used for data evaluation.

In addition to control limits, the control charts are used to determine if trends are occurring. Data points consistently above or below the mean or points becoming steadily high or low over time indicate the occurrences of trending or bias in the procedure. Investigation and corrective action is taken if these situations are observed.

10.1 A method blank is analyzed with each batch of samples. The method blank must be less than the reporting limit.

10.2 A Laboratory Control Standard made up of paraffin oil is extracted and analyzed with each batch. The control limits for this standard are 80-120%.

10.3 A replicate and matrix spike analysis are analyzed with each batch. The spike recovery should be between 75-125%. The replicate analysis should have an RPD <20%.

The matrix spike recovery is calculated with the following equation:

$$MS\ Recovery\ (\%) = \frac{SSR - SR}{SA} * 100$$

where:
SSR = Spike Sample Results
SR = Sample Results
SA = Spike Added (concentration)

The Relative Percent Difference (%RPD) between the sample and replicate analysis is calculated with 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)

Freon Distillation SOP

1. All freon waste from Oil & Grease and TPH analysis is collected and redistilled. This waste is separated into high and low levels of contamination, and is redistilled and stored separately. High level contamination is defined as 500 mg/L or greater for either Oil & Grease or TPH.

2. Filter waste freon through Whatman 541 filter paper prior to distillation.

3. Bring water bath to 32°C, and make sure condenser cooling water has been turned on.

4. Pour 1 liter filtered freon into boiling flask (make sure there are several boiling chips in the flask) and connect to distilling apparatus.

5. Submerge the boiling flask in the water bath and distill.

6. Pour the redistilled freon into one of the storage cans reserved for this purpose. (Remember: high level or low level). To remove any water, pour through a funnel containing Whatman 541 filter paper with approximately 100 grams sodium sulfate.

7. When a storage container is full, collect an aliquot in a 40 mL vial. Read the absorbance of this distillate using the Buck Scientific Hydrocarbon analyzer. Record this result on the storage container.

8. Now add 2 gram silica gel to the vial and shake. Allow the gel to settle, then re-read the distillate on the Buck. This result should be the same as the first. If the second reading is lower, it suggests that Oil and Grease may still be present, and the entire contents of that container must be redistilled.

APPENDIX A-31

STANDARD OPERATING PROCEDURE FOR IGNITABILITY

Ignitability Method 1010
Pensky-Martens Closed-Cup Method For Determining Ignitability

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Approvals and Signatures

QA Officer: Martha E. Roy Date: 9/14/94

Wet Chemistry Manager: [signature] Date: 15 Sept 94

1.0 Scope and Application

1.1 Method 1010 uses the Pensky-Martens closed-cup tester to determine the flash point of liquids. The method may be modified to include soils (See section 5.3).

2.0 Summary of Method

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

3.0 Sample Handling and Preservation

3.1 Collect a minimum of 100 mls of sample in glass or plastic bottles. No preservation is required. Sample must be analyzed within 14 days of collection.

4.0 Reagents

a. p-xylene.

5.0 Procedures

5.1 The p-xylene serves as the standard.

5.2 For liquid samples: mix sample by repeated inversions, then fill to the line in the sample cup. Place the cup in the heating head and attach the top. Be sure to press

the top down firmly and check that it is level. It is important to ensure a closed system - no leaks.

Attach and activate the stirring mechanism. Insert the thermometer and wait for temperature to stabilize.

Light the flame and dip it to check for ignition. Assuming the sample did not flash, turn the heating unit to approximately 40. Dip the flame every two degrees to check for ignition. At least 15 seconds must pass between checks, otherwise not enough volatile components will accumulate to allow for combustion. If the temperature begins to rise too quickly, immediately turn the heater down to approximately 30.

Continue checking for ignitability up to 150 °F, recording the first temperature at which a flash occurs. The flash may be quite subtle, so allow only enough light to read the thermometer, and pay close attention when dipping the flame.

5.3 For soil samples: remove the stirring blade from the top of the sample cup. Loosely fill the sample cup to the line. Proceed as with liquids. Once the temperature has passed 100 °F, turn the heating unit up to approximately 80 and continue up to 150 °F.

Be aware that at approximately 130 °F, many soil samples will produce a "greenish glow" when the flame is dipped. Should this occur, make a brief note of temperature and observations. Remember that you are looking for ignition; a flash should appear inside the sample cup. Again, record the first temperature that produces a flash.

5.4 Between samples, remove the heating unit and cool under running water. Rinse and dry the sample cup after each sample.

5.5 Record the barometric pressure in the laboratory at the time of analysis.

6.0 Calculations

6.1 Record the temperature in degees F. that the sample flashed at. Also record the barometric pressure. If the barometric pressure falls between 744 and 776 mm Hg, the correction is <1 ° F and may be ignored. Should the barometric pressure fall outside this range, the following equation applies:

Corrected Flashpoint = F + 0.06 (760-P)

Where: F= observed flashpoints, °F.
P= ambient barometric pressure, mm Hg

6.2 If no flash occured during the sample analysis report the result as >150° F.

7.0 Quality Control

7.1 p-xylene is the laboratory control sample. The "true flashpoint" for this standard is 81 °F, although the acceptable range is 80-83 °F. This standard must be analyzed prior to sample analysis and at a frequency of 10%.

7.2 Replicate analysis are performed at a frequency of 5%.

APPENDIX A-32

STANDARD OPERATING PROCEDURE FOR REACTIVITY (CYANIDE/SULFIDE)

Reactivity (Cyanide/Sulfide)
Method: IN703:RCN; IN703:RS

Approvals and Signatures

QA Officer: Martha E. Roy Date: 12/14/95

Wet Chemistry Section Head: [signature] Date: 14 Dec 95

1.0 Scope and Application

1.1 This method is intended to identify wastes that, because of their extreme instability and tendency to react violently or explode, pose a problem at all stages of the waste management process.

1.2 This method determines samples that are explosive when percussed, and samples which are cyanide and/or sulfide bearing wastes.

1.3 This method is applicable to all wastes (aqueous or solid).

1.4 The detection limit for soil samples is 29 mg/kg for cyanide and 20 mg/kg for sulfide. For waters: 2.9 mg/l for cyanide and 2.0 mg/l for sulfide.

2.0 Summary of Method

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified.

3.0 Sample Handling and Preservation

3.1 Samples should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all headspace.

3.2 Samples must be analyzed 7 days after collection.

3.3 At least 100 mLs of sample must be collected for waters and 10 grams for soils. Samples should be stored in the dark and at 4° C.

4.0 Reagents

4.1 NaOH (0.25N):

10.0 gram NaOH plus DIH_2O to 1 liter.

4.2 H_2SO_4 (1 N):

Slowly add 51 gram concentrated H_2SO_4 to approximately 900 mL DIH_2O. Bring to 1 liter with DIH_2O.

4.3 H_2SO_4 (0.01 N):

10 mL H_2SO_4 plus DIH_2O to 1 liter.

4.4 DABR Indicator:

Dissolve 20 mg p-Dimethylaminobenzalrhodanine (DABR) in 100 mL acetone.

4.5 Silver Nitrate Titrant (0.0141 N):

2.395 gram $AgNO_3$ DIH_2O to 1 liter. Standardize against 1000 mg/l Cl standard stock (1000 mg/l Cl equals 0.0282 N).

4.6 Cyanide Standard: 1000 mg/L:

2.51 grams and 2.00 grams KOH plus DIH_2O to 1 liter. Concentration checked weekly by titration with $AgNO_3$.

4.7 Iodine Solution (0.025 N):

Dissolve 25 gram KI in 700 mL DIH_2O. Add 3.2 gram I_2 and allow to dissolve. Bring to 1 liter with DIH_2O.

4.7.1 Standardize as follows: Dissolve approximately 2 gram KI in 150 mL DIH_2O. Add exactly 20 mL Iodine solution and mix. Bring to 200 mL

with DIH_2O.

4.7.2 Titrate with 0.025 N Thiosulfate (using starch indicator, endpoint = blue to clear)

$$Normality = \frac{mL\ Titrant * N\ Titrant}{mLs\ iodine\ solution}$$

4.8 Sulfide Standard:

Preparation of Sulfide Stock:

- small crystal (approximately 0.5 g) $Na_2S.9H_2O$ in tri-corner beaker. Rinse 3 times with DIH_2O. Dry crystal thoroughly with kimwipes.
- weigh crystal to 0.1 mg and dissolve in 500 mL DIH_2O.

$$Concentration\ stock\ \frac{mg}{L} = \frac{(crystal\ wgt)\ (0.1335^*)\ (1000\frac{mg}{g})}{0.51}$$

(*0.1335→ $Na_2S.9H_2O$ = 13.35 % S)
The stock should be approximately 100-150 mg/l.

4.9 Sodium thiosulfate titrant:

Refer to D.O. SOP for preparation.

5.0 Procedures

5.1 Put 10 grams of soil sample into a round bottom flask containing a stir bar. Be sure to rinse the sides of the flask down with about 20 mLs of DI water. For liquid samples use 100 mLs and rinse likewise.

5.1.1 Sulfide LCS: Pipet 20-25 mL Sulfide Stock plus DIH_2O to 100 mL in round bottom flask.

5.1.2 Cyanide LCS: 5 mL 1000 mg/L Cyanide Stock plus DIH_2O to 100 mL in round bottom flask.

5.2 Pipette 25 mLs of 0.25 N NaOH (sodium hydroxide) solution into each of the two scrubbers used per apparatus.

5.3 Pour 250 mLs of 0.005 M H_2SO_4 (sulfuric acid) into the upper funnel unit with the stopcock in closed position.

5.4 Close the system and adjust the nitrogen flow rate with a rotometer to 60 mLs/minute. Watch for possible leaks in the system and be sure the nitrogen flow remains constant. Allow nitrogen to purge system for at least 10 minutes before continuing.

5.5 Slowly open the funnel stopcock to allow the 0.005 M H_2SO_4 to mix with the sample. Watch for possible reaction that may occur either by noticing a rapid burst of bubbles in the scrubbers or heat reaction in the round bottom flask which could be felt as a temperature increase. Be prepared to slow or stop the flow of H_2SO_4 to the sample until it has stabilized. If reaction is minimal it should take about two minutes to complete H_2SO_4 transfer.

5.6 Set a timer for 30 minutes. By use of stir bar, maintain a good vortex of the sample in flask and be sure the nitrogen flow remains constant.

5.7 Following the 30 minute reaction time, turn off the nitrogen gas and disassemble the apparatus.

Transfer the NaOH scrubber solution into a 100 mL volumetric flask. Using a pipette bulb, blow out any solution contained within the scrubber and follow up with three DI water rinses of all internal parts in contact with solution. Bring to mark and cap.

5.8 Repeat transfer of each scrubber to its corresponding volumetric flask and label each. Be sure to invert all flasks 10 times to ensure they are mixed well.

Continue with Cyanide and Sulfide Test

Cyanide Test

5.9 Pipette 50 mLs of the 100 mL solution into a 250 mL flat bottom flask. Add 10 drops of Rhodanine indictor (DABR) and follow up with a DI water rinse around sides and swirl.

5.10 Titrate with standardized 0.0141 N silver nitrate to the first change of color from yellow to brownish-pink and record.

Hydrogen Sulfide Test

5.11 Pipette 50 mLs of the 100 mL solution into a 250 mL Erlenmeyer flask. Add 1 mL of 50% HCl and 5 mLs of 0.025 N Iodine solution followed by a DI water rinse around sides and swirl.

5.12 Titrate with 0.025 N Thiosulfate to a change in color from dark yellow to straw yellow. Add a squirt of starch solution and continue same titration to an end point of blue to clear and record.

6.0 Calculations

6.1 See below:

Aqueous Sulfide Calculation:

$$Sulfide\ (mg/L) = \frac{[(mL\ I * N\ I) - (mL\ Thio\ *\ N\ Thio)]\ *\ 16000}{mL\ sample\ *\ \frac{vol\ Titrated}{total\ volume}}$$

Soil Sulfide Calculation:

$$Sulfide\ (mg/Kg) = \frac{[(mL\ I * N\ I) - (mL\ Thio\ *\ N\ Thio)]\ *\ 16000}{g\ sample\ *\ \frac{vol\ Titrated}{total\ volume}}$$

Aqueous Cyanide Calculation:

$$Cyanide\ (mg/L) = \frac{[(A * N\ AgNO3) - (B * N\ AgNO3)] * 52000}{mL\ sample * \frac{vol\ Titrated}{total\ volume}}$$

Soil Cyanide Calculation:

$$Cyanide\ (mg/Kg) = \frac{[(A * N\ AgNO3) - (B * N\ AgNO3)] * 52000}{g\ sample * \frac{vol\ Titrated}{total\ volume}}$$

7.0 Quality Control

7.1 A method blank is brought through the procedure and must be less than the reporting limits.

7.2 Sulfide and cyanide LCS are prepared and analyzed with the samples. The recovery limits will be determined by control charts.

7.3 A replicate analysis is also recommended if sufficient sample volume is available.

APPENDIX A-33

STANDARD OPERATING PROCEDURE FOR pH

pH
Method 150.1/9040/9045

Approvals and Signatures

QA Officer: Martha E. Roy Date: 9/15/94

Wet Chemistry Manager: [signature] Date: 15 Sept 94

1.0 Scope and Application

1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes and acid rain (atmospheric deposition).

2.0 Summary of Method

2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.

3.0 Sample Handling and Preservation

3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.

3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.

4.0 Interferences

4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.

4.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1 + 9) may be necessary to remove any remaining film.

5.0 Apparatus

5.1 All pH measurement is done on the Beckman ϕ 45 pH meter.

5.2 Magnetic stirrer and Teflon-coated stirring bar.

5.3 Thermometer or temperature sensor for automatic compensation.

6.0 Reagents

6.1 Standard buffer solutions available from commercial vendors. pH 4, 6, 7 and 10 buffer solutions are necessary.

6.2 Occasionally, it is necessary to prepare pH standards to bracket a sample with a pH of less than 4 or greater than 10. These are prepared as follows:

pH 1.0 standard: 67 ml 0.2M HCl + 25 ml 0.2 M KCl plus DIH_2O to 100 ml.

pH 2.0 standard: 6.5 ml 0.2M HCl + 25 ml 0.2 M KCl plus DIH_2O to 100 ml.

pH 13.0 standard: 66.0 ml 0.2M NaOH + 25 ml 0.2 M KCl plus DIH_2O to 100 ml.

6.3 1.1098 gram $CaCl_2$ plus DIH_2O to 1 liter. Standardize by titrating an aliquot with 0.1 N $AgNO_3$, using 1 ml 5% K_2CrO_4 as an indicator. The final pH of this solution should be between 5 and 6.5 (adjust with $Ca(OH)_2$ or HCL as needed) and should have a specific conductance of between 2240-2400 umhos/cm.

7.0 Calibration

7.1 The electrode is stored immersed in pH 7 buffer. Be sure to remove the rubber plug attached to the electrode prior to use. Also, check that the level of saturated KCl is not more than 1 inch below the vent hole.

7.2 Now immerse the electrode in fresh pH 7 Standard Buffer and press the Calibrate Button. This pH meter is programmed to "recognize" several different Standard Buffers, and should quickly begin flashing "7.00" for "Standard 1". when the measurement has stabilized, the instrument will beep, the "eye" symbol will appear, and the readout will freeze. Immediately press thecalibrate button a second time and wait for the beep.

7.3 Immerse electrode in pH 4 Standard Buffer for 15-30 seconds. Replace with fresh pH 4 Buffer and after 15-30 seconds, press the calibrate button. Again, repeat immediately.

7.4 Once the pH meter has been calibrated, verify calibration with pH 6 Standard Buffer. Do not press the calibrate button; instead, use the "ph" button directly below it. The accepted range for this buffer is 5.93-6.03. If the result falls outside this range, repeat the calibration procedure until the pH 6 Check Standard passes.

8.0 Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 Analyze samples as follows:

8.2.1 Any aqueous sample, or multiphasic sample where the aqueous phase constitutes at least 20% of the total volume, may be measured directly. Samples must be analyzed as soon as possible, but should be allowed to reach room temperature first.

8.2.2 Solid samples may be analyzed by accurately weighing 15-20 g of sample into a clean, dry beaker, then adding an equal gram weight of DIH_2O. Sample and water should be mixed and allowed to stand for 30 minutes. When measuring pH, do not use a stir bar (for these samples) and do not bury the electrode in the solid component. An ash or extremely powdery sample may require the addition of more DIH_2O to produce a mixture of measurable consistency. If required, note the volume of water actually added.

8.2.3 Occasionally, a soil sample will require mixing with 0.01 M $CaCl_2$ (See Reagent Section). Preparation and measurement of sample is the same as when mixing with DIH_2O. Report results as "soil pH measured in 0.01M

$CaCl_2$.

8.3 Now analyze all samples. Remember to include the pH 6 Check Standard every ten samples. Should any sample fall below pH 4 or above 8.3, additional check standards must be run. Samples greater than 8.3, but less than 10, require analyzing the prepared pH 10 Standard Buffer. Samples less than 4 or greater than 10 require the preparation of an appropriate standard using 0.2 M KCl and either 0.2 M HCl or 0.2 M NaOH. The formulas for these standards are provided in the reagent section.

NOTE: Do not recalibrate the meter, simply analyze the check standard and report the result. However, the result must be + 0.1 of the true value or the meter must be recalibrated.

9.0 Calculation

9.1 Report all pH results to 0.01 units.

APPENDIX A-34

STANDARD OPERATING PROCEDURE FOR VOLATILE ORGANIC COMPOUNDS BY GC/MS

8260B

STANDARD OPERATING PROCEDURES FOR THE DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROSCOPY

Applicable matrix or matrices: ground and surface water, waste solvents, oily wastes, soils and sediments
Standard Compound List and Reporting Limits: see Table 1

Approvals and Signatures

Laboratory Director: _____ Date: 9-21-98

QAManager: Kim B. Watson Date: 9/21/98

Organics Section Manager: _____ Date: 9/21/98

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1.0 SCOPE AND APPLICATION

1.1 This SOP is based on Method 8260B (USEPA Test Methods for Evaluating Solid Waste, Dec. 1996). Method 8260B describes the GC/MS procedure for the analysis of volatile organic compounds. The techniques by which compounds may be introduced into the GC/MS system are described in Method 5030 (purge-and-trap of aqueous samples) and Method 5035 (purge-and-trap of solid and waste oil samples). This method is applicable to nearly all types of samples regardless of water content, including ground and surface water, waste solvents, oily wastes, soils and sediments. The compounds amenable to this method are shown in Table 1. A chromatographic column utilizing a temperature program is used to separate the desorbed purgeables followed by mass spectral detection.

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Table 1. Analytes, Chemical Abstract Services Numbers and Reporting Limits (RL)

Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
Acetone	67-64-1	5.0	5.0
Acrolein	107-02-8	5.0	5.0
Acrylonitrile	107-13-1	5.0	1.0
Allyl Chloride	107-05-1	5.0	1.0
Benzene	71-43-2	5.0	1.0
Bromobenzene	108-86-1	5.0	1.0
Bromochloromethane	74-97-5	5.0	1.0
Bromodichloromethane	75-27-4	5.0	1.0
Bromoform (SPCC)	75-25-2	5.0	1.0
Bromomethane	74-83-9	5.0	1.0
2-Butanone	78-93-3	5.0	5.0
n-Butylbenzene	104-51-8	5.0	1.0
sec-Butylbenzene	135-98-8	5.0	1.0
tert-Butylbenzene	98-06-6	5.0	1.0
Carbon Disulfide	75-15-0	5.0	1.0
Carbon Tetrachloride	56-23-5	5.0	1.0
Chlorobenzene (SPCC)	108-90-7	5.0	1.0
Chloroethane	75-00-3	5.0	1.0
2-Chloroethyl Vinyl Ether	110-75-8	5.0	1.0
Chloroform (CCC)	67-66-3	5.0	1.0
Chloromethane (SPCC)	74-87-3	5.0	1.0
Chloroprene	126-99-8	5.0	1.0

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Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
2-Chlorotoluene	95-49-8	5.0	1.0
4-Chlorotoluene	106-43-4	5.0	1.0
1,2-Dibromo-3-chloropropane	96-12-8	5.0	1.0
Dibromochloromethane	124-48-1	5.0	1.0
1,2-Dibromoethane	106-93-4	5.0	1.0
Dibromomethane	74-95-3	5.0	1.0
1,2-Dichlorobenzene	95-50-1	5.0	1.0
1,3-Dichlorobenzene	541-73-1	5.0	1.0
1,4-Dichlorobenzene	106-46-7	5.0	1.0
cis-1,4-Dichloro-2-butene	1476-11-5	5.0	1.0
trans-1,4 Dichloro-2-butene	110-57-6	5.0	1.0
Dichlorodifluoromethane	75-71-8	5.0	1.0
1,1-Dichloroethane (SPCC)	75-34-3	5.0	1.0
1,2-Dichloroethane	107-06-2	5.0	1.0
1,1-Dichloroethene (CCC)	75-35-4	5.0	1.0
cis-1,2-Dichloroethene	156-59-2	5.0	1.0
trans-1,2-Dichloroethene	156-60-5	5.0	1.0
1,2-Dichloropropane (CCC)	78-87-5	5.0	1.0
1,3-Dichloropropane	142-28-9	5.0	1.0
2,2-Dichloropropane	594-20-7	5.0	1.0
1,1-Dichloropropene	563-58-6	5.0	1.0
cis-1,3-Dichloropropene	10061-01-5	5.0	1.0
trans-1,3-Dichloropropene	10061-02-6	5.0	1.0

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Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
Diethyl Ether	60-29-7	5.0	1.0
1,4-Dioxane	123-91-1	250	50
Ethyl Methacrylate	97-63-2	5.0	1.0
Ethylbenzene (CCC)	100-41-4	5.0	1.0
Freon TF	76-13-1	5.0	1.0
Hexachlorobutadiene	87-68-3	5.0	1.0
2-Hexanone	591-78-6	5.0	5.0
Isobutyl alcohol	78-83-1	250	50
Isopropylbenzene	98-82-8	5.0	1.0
4-Isopropyltoluene	99-87-6	5.0	1.0
Methacrylonitrile	126-98-7	5.0	1.0
Methyl Iodide	74-88-4	5.0	1.0
Methyl Methacrylate	80-62-6	5.0	1.0
4-Methyl-2-pentanone	108-10-1	5.0	5.0
Methyl-t-Butyl Ether	1634-04-4	5.0	1.0
Methylene Chloride	75-09-2	5.0	1.0
Naphthalene	91-20-3	5.0	1.0
Propionitrile	107-12-0	20	4.0
n-Propylbenzene	103-65-1	5.0	1.0
Styrene	100-42-5	5.0	1.0
1,1,1,2-Tetrachloroethane	630-20-6	5.0	1.0
1,1,2,2-Tetrachloroethane (SPCC)	79-34-5	5.0	1.0
Tetrachloroethene	127-18-4	5.0	1.0

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Analyte	CAS No.	RL (µg/L or µg/Kg)	Low Water RL (µg/L)
Tetrahydrofuran	109-99-9	70	10
Toluene (CCC)	108-88-3	5.0	1.0
1,2,3-Trichlorobenzene	87-61-6	5.0	1.0
1,2,4-Trichlorobenzene	120-82-1	5.0	1.0
1,2,4-Trimethylbenzene	95-63-6	5.0	1.0
1,3,5-Trimethylbenzene	108-67-8	5.0	1.0
1,1,1-Trichloroethane	71-55-6	5.0	1.0
1,1,2-Trichloroethane	79-00-5	5.0	1.0
Trichloroethene	79-01-6	5.0	1.0
Trichlorofluoromethane	75-69-4	5.0	1.0
1,2,3-Trichloropropane	96-18-4	5.0	1.0
Vinyl Acetate	108-05-4	5.0	1.0
Vinyl Chloride (CCC)	75-01-4	5.0	1.0
Xylene (m,p)	1330-20-7	5.0	1.0
Xylene (o)	95-47-6	5.0	1.0

(SPCC) System Performance Check Compounds
(CCC) Calibration Check Compounds

2.0 SUMMARY OF METHOD

2.1 Basic Principles

The analytes are introduced into the GC/MS by purge-and-trap techniques (Method 5030 or Method 5035). Upon desorption from the trap, the volatile compounds are introduced directly to a wide-bore capillary column. A temperature program is used to separate the purgeables. The eluted analytes pass through a jet separator and they are carried on the gas stream into the ion source of a mass spectrometer. The ionized molecules are focused and separated according to their mass/charge (m/z) ratio 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.

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2.2 General Method

The mass spectrometer is calibrated to recognize m/z values in the range of 35-300 amu. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. Analytes are quantitated using procedural standard calibration. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. The performance of the mass spectrometer is verified by the injection of 4-Bromofluorobenzene (BFB). Next, the instrument must demonstrate acceptable chemical calibration and linearity by the analysis of five concentrations of a standard mix containing the analytes of interest, as well as the surrogates and internal standards. Before any samples are analyzed, a method blank must be analyzed to demonstrate that the instrument is free from contamination, and that surrogate recovery criteria are met. All analyses must occur within 12 hours of the injection of the passing BFB. Another analytical sequence may be started by the analysis of a passing BFB MS tune followed by a continuing calibration standard.

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.

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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 (VBLK, 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 VBLK is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.9 TRIP BLANK

An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the trip blank is to determine if method analytes or other interferences are present in the field environment (originating from the proximity of sample containers to one another during shipment and storage).

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: chloromethane, 1,1-dichloroethane, bromoform, chlorobenzene and 1,1,2,2-tetrachloroethane.

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: 1,1- dichloroethene, chloroform, 1,2- dichloropropane, toluene, ethylbenzene and vinyl chloride.

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4.0 INTERFERENCES

4.1 During analysis, major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of Teflon tubing, Teflon thread sealants, or flow controllers with rubber components in the purging device should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of laboratory reagent blanks provide information about the presence of contaminants. Subtracting blank values from sample results is not permitted.

4.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing relatively high concentrations of volatile organic compounds. A preventive technique is between-sample rinsing of the purging apparatus and sample syringes with two to three portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent blanks should be analyzed to check for cross-contamination.

4.3 Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate Teflon tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory worker's clothing should be cleaned frequently since clothing previously exposed to methylene chloride fumes during common extraction procedures can contribute to sample contamination. Extraction laboratory personnel should not enter the volatile analytical laboratory.

4.4 Traces of ketones, methylene chloride, and some other organic solvents can be present even in the highest purity methanol. This is another potential source of contamination, and should be assessed before standards are prepared in the methanol.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Material Safety Data Sheets (MSDS) are available in the volatile preparation laboratory in a three ring binder.

5.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4 dichlorobenzene, 1,2-dichlorethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood.

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6.0 EQUIPMENT AND SUPPLIES

6.1 Containers:

Sample Storage Containers:	40 mL screw cap vials equipped with a Teflon faced silicone septum, certified clean, known volume of 44 mL (see also Method 5035)
Standard Storage Containers:	1 - 5 mL Mininert vials with Teflon lined screw caps

6.2 Instrumentation

VOA Autosampler:	Tekmar ALS 2050 or ALS 2016, Tekmar AQUATEK 50 or equivalent Varian Chromatography Systems Archon Purge-and-Trap
Purge & Trap:	Tekmar LSC 2000; VOCARB 3000 trap or equivalent
Gas Chromatograph:	Hewlett-Packard 5890 Series II
Mass Spectrometer:	Hewlett-Packard 5971 MSD, Hewlett-Packard 5972 MSD
Primary Column: or	Fused silica capillary column, J&W DB624 75 m x 0.53 mm x 3.0 um equivalent

6.3 Syringes

6.3.1	250 µL - 10 mL gas tight hypodermic syringes with Luer-Lok tip
6.3.2	Micro syringe 10 - 100 µL
6.4 Data System:	Hewlett-Packard Chem Server, Target 3.1 software is used for data processing

7.0 REAGENTS AND STANDARDS

7.1 Trap Packing Materials

VOCARB 3000 or equivalent traps may be used, following the manufacturer's instructions.

7.2 Reagents

7.2.1 Methanol

Purge and Trap Grade, demonstrated to be free of analytes.

7.2.2 Reagent water

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Deionized water is filtered using a Milli Q plus ™ filtration system and then boiled for one hour. Finally, the water is purged with helium for a minimum of fifteen minutes. The water is stored in clean, narrow-mouth bottles with Teflon lined septa and screw caps.

7.2.3 Hydrochloric acid (1+1)

Measured volumes of conc. HCl are carefully added to an equal volume of reagent water

7.3 Stock Standard Solutions

These solutions are purchased as certified solutions or prepared from pure standard materials. Commercial standards arrive ampulized in concentrations ranging from 1-5 mg/mL.

7.4 Primary Dilution Standards

Stock standard solutions are used to prepare primary dilution standard solutions that contain all the analytes of interest in methanol. The primary dilution standards are prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. The primary dilution standard is prepared at a concentration of 100 µg/mL (Low water analysis 25 µg/mL). Exceptions include the following: propionitrile at 400 µg/mL, tetrahydrofuran at 1000 µg/mL, 1,4-dioxane at 5000 µg/mL and isobutyl alcohol at 5000 µg/mL (Low water analysis exceptions: propionitrile at 100 µg/mL, acrolein and ketones at 125 µg/mL , tetrahydrofuran at 350 µg/mL, 1,4-dioxane and isobutyl alcohol at 1250 µg/mL). The primary dilution standard solutions are stored with minimal headspace and checked frequently for signs of deterioration or evaporation. Methanol solutions of gaseous standards are not stable for more than one week at <0°C.

7.5 Preparation of Calibration Standards

The five concentrations for the initial calibration are 5, 20, 50, 100, and 200 µg/L (propionitrile at 20, 80, 200, 400 and 800 µg/L, tetrahydrofuran at 50, 200, 500, 1000 and 2000 µg/L, 1,4-dioxane and isobutyl alcohol at 250, 1000, 2500, 5000 and 10000 µg/L). The calibration standards are prepared by adding 2.2 µL, 8.8µL ,22 µL , 44 µL, 88 µL of the primary dilution standard to 44 mLs of reagent water. Internal standards are added by spiking 44 µL of the 50µg/mL fortification solution. The primary dilution standard used to prepare the calibration standard contain the surrogate compounds at the same concentration as the analytes.

For the low water analysis, the five concentrations for the initial calibration are 1, 5, 10, 25 and 50 µg/L (propionitrile at 4, 20, 40, 100 and 200 µg/L,acrolein and ketones at 5, 25, 50, 125 and 250 µg/L, tetrahydrofuran at 14, 70, 140, 350 and 700 µg/L, 1,4-dioxane and isobutyl alcohol at 50, 250, 500, 1250 and 2500 µg/L). The calibration standards are prepared by adding 1.8 µL, 8.8 µL, 17.6 µL , 44 µL, 88 µL of the primary dilution standard to 44 mLs of reagent water. Internal standards are added by spiking 8.8 µL of the 25µg/mL fortification solution. The primary dilution standard used to prepare the calibration standard contain the surrogate compounds at the same concentration as the analytes.

Additionally, for manual injections these standards may be prepared in a 5 mL gas tight syringe and spiked with the appropriate volumes to achieve the analyte concentrations specified above.

7.6 Preparation of Initial Calibration Verification (ICV)

Standards are obtained from a source external to the laboratory and independent from the source of the inital calibration standards. An ICV is prepared by spiking reagent water, in a 44 mL sample vial, with 44 µL of a fortification solution containing internal standards at a concentration of 50 µg/mL and 44 µL of a fortification

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solution containing surrogate compounds at a concentration of 50 µg/mL. The ICV is spiked by injecting 22 µL of the primary dilution standard at a concentration of 100µg/mL (propionitrile at 400 µg/mL, tetrahydrofuran at 1,000µg/mL, 1,4-dioxane and isobutyl alcohol at 5,000 µg/mL). All standards are spiked directly through the septum of the 44 mL vial.

For the low water analysis, the ICV is prepared by spiking reagent water, in a 44 mL sample vial, with 8.8 µL of a fortification solution containing internal standards at 25 µg/mL and 8.8 µL of the fortification solution containing surrogate standards at 25 µg/mL. The ICV is spiked by injecting 8.8 µL of the primary dilution standard at a concentration of 25 µg/mL (propionitrile at 100 µg/mL, acrolein and ketones at 125 µg/mL, tetrahydrofuran at 350 µg/mL, 1,4-dioxane and isobutyl alcohol at 1250 µg/mL). All standards are spiked directly through the septum of the 44 mL vial. Additionally, for manual injections these standards may be prepared in a 5 mL gas tight syringe and spiked with the appropriate volumes to achieve the analyte concentrations specified above.

7.7 Preparation of Continuing Calibration Verification (CCV)

Prepare this exactly like a calibration standard (Section 7.5). The compounds have a concentration of 50 µg/L (propionitrile at 200 µg/L, tetrahydrofuran at 500 µg/L, 1,4-dioxane and isobutyl alcohol at 2500 µg/L). For the low water analysis, the compounds have a concentration of 10 µg/L (propionitrile at 40 µg/L, acrolein and ketones at 50 µg/L, tetrahydrofuran at 140 µg/L, 1,4-dioxane and isobutyl alcohol at 500 µg/L). Additionally, for manual injections these standards may be prepared in a 5 mL gas tight syringe and spiked with the appropriate volumes to achieve the analyte concentrations specified above.

7.8 Preparation of Laboratory Method Blank (VBLK)

A 44 mL sample vial is filled with reagent water (no air bubbles). Internal and surrogate standards are added separately by the injection of two 44 µL aliquots of the fortification solutions (containing internal standards and surrogate standards at 50 µg/mL) through the septum of the 44 mL sample vial. For the low water analysis, the internal and surrogate standards are added separately by the injection of two 8.8 µL aliquots of the fortification solutions (containing internal and surrogate standards at 25 µg/mL) through the septum of the 44 mL sample vial. For solid matrices, 5 grams of clean sand is added to a 44 mL sample vial. The preservative technique utilized in the preparation of samples is performed on the method blank. 5 mLs of reagent water containing 50 µg/L of internal and surrogate standards is spiked either manually or automatically through the septum of the vial. Additionally, for manual injections the blank may be prepared in a 5 mL gas tight syringe and spiked with the appropriate volumes of internal standards and surrogates to achieve the concentrations specified above.

7.9 Preparation of Laboratory Control Sample (LCS)

A 44 mL sample vial is filled with reagent water (no air bubbles). Internal and surrogate standards are added separately by the injection of two 44 µL aliquots of the fortification solutions (containing internal standards and surrogate standards at 50 µg/mL) through the septum of the 44 mL sample vial. The LCS is spiked by injecting 22 µL of the primary dilution standard at 100 µg/mL (propionitrile at 400 µg/mL, tetrahydrofuran at 1000 µg/mL, 1,4-dioxane and isobutyl alcohol at 5000 µg/mL) through the septum of the 44 mL sample vial. For solid samples, 5 grams of clean sand is placed in a 44 mL sample vial. The LCS is prepared by initially spiking a 5 mL syringe with two 5 µL aliquots of both fortification standards at a concentration of 50 µg/mL. 2.5 µL of the primary dilution standard at a concentration of 100 µg/mL (propionitrile at 400 µg/mL, tetrahydrofuran at 1000 µg/mL, 1,4-dioxane and isobutyl alcohol at 5000 µg/mL) is spiked into the same syringe. The full 5 mLs of the syringe is then spiked onto the soil sample.

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For the low water analysis, a 44 mL sample vial is filled with reagent water (no air bubbles). Internal and surrogate standards are added separately by the injection of two 8.8 µL aliquots of the fortification solutions (containing internal standards and surrogate standards at 25 µg/mL) through the septum of the 44 mL sample vial. The LCS is spiked by injecting 17.6 µL of the primary dilution standard at a concentration of 25 µg/mL (propionitrile at 100 µg/mL, acrolein and ketones at 125 µg/mL, tetrahydrofuran at 350 µg/mL, 1,4-dioxane and isobutyl alcohol at 1250 µg/mL) through the septum of the 44 mL sample vial.

Additionally, for manual injections the LCS may be prepared in a 5 mL gas tight syringe and spiked with the appropriate volumes to achieve the analyte concentrations specified above.

7.10 Preparation of Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Matrix spikes and matrix spike duplicates are prepared and analyzed with each batch of 20 client specific samples of the same matrix. Internal and surrogate standards are added separately by the injection of two 44 µL aliquots of the fortification solutions (containing internal standards and surrogate standards at 50 µg/mL) through the septum of the 44 mL sample vial through the septum of the 44 mL sample vial. The MS/MSD is spiked by injecting 22 µL of the primary dilution standard at a concentration of 100 µg/mL (propionitrile at 400 µg/mL, tetrahydrofuran at 1000 µg/mL, 1,4-dioxane and isobutyl alcohol at 5,000 µg/mL) through the septum of the 44 mL sample vial. For solid samples, the MS/MSD is prepared by initially spiking a 5 mL syringe with two 5 µL aliquots of both fortification standards at a concentration of 50 µg/mL. 2.5 µL of the primary dilution standard at a concentration of 100 µg/mL (propionitrile at 400 µg/mL, tetrahydrofuran at 1000 µg/mL, 1,4-dioxane and isobutyl alcohol at 5,000 µg/mL) is spiked into the same syringe. The full 5 mLs of the syringe is then spiked onto the soil sample contained in the sample vial.

For the low water analysis, internal and surrogate standards are added separately by the injection of two 8.8 µL aliquots of the fortification solutions (containing internal standards and surrogate standards at 25 µg/mL) through the septum of the 44 mL sample vial. The MS/MSD is spiked by injecting 17.6 µL of the primary dilution standard at a concentration of 25 µg/mL (propionitrile at 100 µg/mL, acrolein and ketones at 125 µg/mL, tetrahydrofuran at 350 µg/mL, 1,4-dioxane and isobutyl alcohol at 1250 µg/mL) through the septum of the 44 mL sample vial. Additionally, for manual injections these standards may be prepared in a 5 mL gas tight syringe and spiked with the appropriate volumes to achieve the analyte concentrations specified above.

7.11 Fortification Solutions for Internal Standard and Surrogates

Two separate fortification solutions are required to prepare laboratory reagent blanks, standards and to fortify each sample. A fortification solution is prepared containing fluorobenzene, chlorobenzene-d_5 and 1,4-Dichlorobenzene-d_4 (internal standards) in methanol. A separate fortification solution is prepared containing 1,2-dichlorobenzene-d_4, BFB, 1,2-Dichloroethane-d_4, Toluene-d_8 (surrogates) in methanol. The internal standards are present in each 5 ml sample, blank or standard at a concentration of 50 µg/L (Low Water Analysis at 5 µg/L). Surrogate compounds are at the same concentration as the analytes in the initial calibration standards. In all other standards, samples and blanks the surrogate compounds are at a concentration of 50 µg/L (Low Water Analysis at 5 µg/L).

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8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample collection

Sample collection for aqueous samples is described in method 5030. Sample collection for solid samples is described in method 5035.

8.2 Preservation

Sample preservation for aqueous samples is described in method 5030. Sample preservation for solid samples is described in method 5035.

8.3 Storage

Samples are analyzed within fourteen days of collection. Other holding times may be selected by the client to conform with local regulatory requirements (i.e., NYS samples must be analyzed within 7 days of receipt). Aqueous samples which have not been preserved are analyzed within 7 days of collection. Samples are stored at 4°±2°C in a storage area free of organic solvent vapors and direct or intense light. Upon receipt all samples are screened by the laboratory and the pH of the liquid sample documented on the screening request worksheet.

9.0 QUALITY CONTROL REQUIREMENTS

9.1 4-Bromofluorbenzene

Prior to the acquisition of a calibration curve or the analysis of samples, a 2 µL aliquot of BFB (25 µg/mL) is manually introduced into the GC. If the spectrum does not meet all criteria in Table 2, another BFB tune is injected into the instrument. If the second BFB tune fails the criteria in Table 2, the MS should be retuned and adjusted to meet all criteria before proceeding with the calibration or the analysis.

9.2 Method Detection Limits

Method detection limits (MDLs) are determined annually in accordance with the method described in 40 CFR, Part 136, Appendix B. The results of these studies are kept on file by the QA Manager. Typical values for most analytes are in the range of 0.5 to 1.0 µg/L for aqueous samples (Method 5030 and Method 8260). For soil samples, typical values for most analytes are in the range of 1.5 to 3.5 µg/L (Method 5035 and Method 8260). The mean accuracy should be 80 - 120% and the precision (%RSD) for each analyte should be ≤20% for all compounds. For the low water analysis, the analytes are in the range of 0.1 to 0.5 µg/L for most compounds (Method 5030 and Method 8260)

9.3 Initial Calibration Verification

An ICV must be run following the acquisition of the five-point initial calibration. The ICV is prepared from a source external to the laboratory and independent from the source of the initial calibration standards. The compounds should be at a concentration of 50 µg/L (propionitrile at 200 µg/L, tetrahydrofuran at 500 µg/L, 1,4-dioxane and isobutyl alcohol at 2500 µg/L). The ICV recovery limits are shown in Table 6. For the low water analysis, the compounds should be at a concentration of 10 µg/L (propionitrile at 40 µg/L, acrolein and ketones at 50 µg/L, tetrahydrofuran at 140 µg/L, 1,4-dioxane and isobutyl alcohol at 500 µg/L).

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9.4 Method Blank

One blank must be run with every batch of samples after the calibration standard. A 5.0 mL aliquot of laboratory blank reagent water must be analyzed prior to any aqueous samples. 5.0 grams of clean sand must be analyzed prior to any solid samples. An acceptable blank must not contain any volatile target analytes at concentrations greater than their reporting limits with the following exceptions: Methylene Chloride, acetone and 2-butanone, which must be less than or equal to five times (5X) their reporting limits. If the method blank exceeds these criteria, the analytical system may be out of control. The source of the contamination must be investigated and appropriate corrective measures must be taken and documented before further sample analysis proceeds.

9.5 Laboratory Control Sample

A laboratory control sample should be included with each analytical batch. The compounds should be at a concentration of 50 µg/L (propionitrile at 200 µg/L, tetrahydrofuran at 500 µg/L, 1,4-dioxane and isobutyl alcohol at 2500 µg/L). The LCS recovery limits are shown in Table 6. For the low water analysis, the compounds should be at a concentration of 10 µg/L (propionitrile at 40 µg/L, acrolein and ketones at 50 µg/L, tetrahydrofuran at 140 µg/L, 1,4-dioxane and isobutyl alcohol at 500 µg/L).

9.6 Laboratory Fortified Matrix Spike and Laboratory Fortified Matrix Spike Duplicate (MS/MSD)

The laboratory will analyze one MS/MSD for each client sample delivery group (20 samples). The MS/MSD will be selected by the laboratory if a client has not specified the sample to be analyzed as the MS/MSD. The MS/MSD will be prepared so as to contain the analytes at a concentration of 50 µg/L (propionitrile at 200 µg/L, tetrahydrofuran at 500 µg/L, 1,4-dioxane and isobutyl alcohol at 2500 µg/L). For the low water analysis, the MS/MSD will be prepared so as to contain the analytes at a concentration of 10 µg/L (propionitrile at 40 µg/L, acrolein and ketones at 50 µg/L, tetrahydrofuran at 140 µg/L, 1,4-dioxane and isobutyl alcohol at 500 µg/L). The MS/MSD recovery limits are shown in Table 6. The requirement of analyzing a duplicate sample is satisfied by analyzing both the MS and MSD.

9.7 Surrogates/ Internal Standards

Four compounds are used as surrogates; 1,2-Dichlorethane-d_4, 1,2-Dichlorobenzene-d_4, 4-Bromofluorobenzene, and Toluene-d_8. Three compounds are used as internal standards fluorobenzene, chlorobenzene-d_5 and 1,4-Dichlorobenzene-d_4. Surrogate and internal standard concentrations in the purge vessel are 50 µg/L (Low water analysis at 5 µg/L. Table 4 shows the recommended surrogate recoveries for water samples. Table 5 shows the recommended surrogate recoveries for soil samples.

10.0 CALIBRATION AND STANDARDIZATION

10.1 BFB

The ion abundances shown in Table 2 must be met before analysis of calibration standards may proceed.

10.2 Initial Calibration

The five concentrations for the initial calibration are 5, 20, 50, 100, and 200 µg/L (propionitrile at 20, 80, 200, 400 and 800 µg/L, tetrahydrofuran at 50, 200, 500, 1000 and 2000 µg/L, 1,4-dioxane and isobutyl alcohol at 250, 1000, 2500, 5000 and 10,000 µg/L). For the low water analysis, the five concentrations for the initial calibration are 1, 5, 10, 25 and 50 µg/L (propionitrile at 4, 20, 40, 100 and 200 µg/L, acrolein and ketones at 5, 25,

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50, 125 and 250 µg/L, tetrahydrofuran at 14, 70, 140, 350 and 700 µg/L, 1,4-dioxane and isobutyl alcohol at 50, 250, 500, 1250 and 2500 µg/L). A response factor (RF) is calculated for each analyte and/or isomer pair for each calibration solution using the appropriate internal standard. The calculation is performed as follows:

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where:

A_x = integrated abundance of the quantitation ion of the analyte
A_{is} = integrated abundance of the quantitation ion of the internal standard
Q_x = quantity of analyte purged in nanograms or concentration units
Q_{is} = quantity of internal standard purged in ng or concentration units

10.2.1

For each analyte and surrogate, calculate the mean response factor from analyses of the calibration solutions. Calculate the standard deviation (SD) and relative standard deviation (RSD) from each mean.

$$RSD = 100\frac{SD}{M}$$

System performance check compounds (SPCCs) must meet the required minimum average response factor shown in Table 3. The %RSD average of all analytes must be ≤ 15%. In addition, individual calibration check compounds (CCCs) must have an RSD ≤ 30%. If this criteria is not met maintenance is performed on the instrument and/or a new calibration curve is acquired. Alternatively, if the CCC criteria has been met, however, the %RSD for one or more analytes exceeds the 15%, the initial calibration may still be acceptable if the following conditions are met as specified in method 8000B: the mean of the RSD values for all analytes in the calibration is less than or equal to 15%. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes. The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. The data user must be provided with either a summary of the IC data or a specific list of those compounds for which the RSD exceeded 15% and the results of the mean RSD calculation. Caution: the analyst and the data user must be aware that the use of the this approach will lead to greater uncertainty for those analytes for which the RSD is greater than 15%. Review quality controls carefully, with particular attention to the LCS to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular project objective, then the analyst may employ one of the other calibration approaches (Linear calibration using a least squares regression to non-linear calibration) or adjust the instrument operating conditions.

10.3 Continuing Calibration Verification

Verify the BFB MS tune and perform a continuing calibration verification at the beginning of each 12-hr work shift. The concentration of the CCV is 50 µg/L (propionitrile at 200 µg/L, tetrahydrofuran at 500 µg/L, 1,4-dioxane at 2500 µg/L and isobutyl alcohol at 2500 µg/L). For the low water analysis, the concentration of the CCV is 10 µg/L (propionitrile 40 µg/L, acrolein and ketones 50 µg/L, tetrahydrofuran at 140 µg/L, and 1,4-dioxane and isobutyl alcohol at 500 µg/L). The RF is calculated for each analyte and surrogate compound from the data

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measured in the continuing calibration check. System performance check compounds must meet the required minimum average response factor shown in Table 3. The percent difference is calculated using the following equation:

$$\%\,Difference = \frac{RF_v - RF}{RF}\ (100)$$

RF_v = Response Factor from the analyses of the verification standard
RF = mean Response Factor from the initial calibration

The percent difference for each CCC should be ≤ 20%. In addition, the internal standard retention time should not change by more than 30 seconds from the mid-point standard level of the most recent initial curve sequence. The integrated areas of the internal standards in the calibration verification standard should not change by more than a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence. If the above criteria is not met maintenance is performed on the instrument and/or a new calibration curve is acquired. Alternatively, in keeping with the approach described for the IC, if the CCC and SPCC criteria has been met and if the average of the responses for all analytes is within 15%, then the calibration has been verified. If the calibration still does not meet the 15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions, and if necessary inject another aliquot of the calibration verification standard. If the response for the analyte is still not within +/-15%, then a new IC must be prepared.

11.0 PROCEDURE

11.1 Sample Introduction and Purging

See preparation and introduction Methods 5030 and 5035.

11.2 Gas Chromatography/Mass Spectrometry

Data is acquired and stored over the nominal mass range 35-300 with a total cycle time (including scan overhead time) of two seconds or less. The cycle time is adjusted to measure five or more spectra during the elution of each GC peak. A multi-stage temperature ramp is used to separate the components of interest for this analysis. A typical GC temperature program is described below.

Initial temperature 40° C, initial time 4 min.
Ramp1: 7° C/min. to 100° C, hold for 1 min.
Ramp2: 4.2° C/min. to 120° C, hold for 0 min.
Ramp3 : 28° C/min. to 220° C, hold for 2.1 min.

11.4 Identification of Analytes

A sample is identified by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time for each analyte should be within +/- 0.5 minutes of the midpoint standard's retention time in the initial calibration curve.

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11.4.1 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 within absolute 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.

11.4.2 Identification requires expert judgment when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound. Because purgeable organic compounds are relatively small molecules and produce comparatively simple mass spectra, this is not a significant problem for most method analytes.

11.4.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. Acceptable resolution is achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks. Otherwise, structural isomers are identified as isomeric pairs. Two of the three isomeric xylenes are examples of structural isomers that are not resolved on the capillary column. These groups of isomers will be reported as isomeric pairs.

11.4.4 Methylene chloride, acetone, carbon disulfide, and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured. Subtraction of the concentration in the blank from the concentration in the sample is not performed because the concentration of the background in the blank is highly variable.

12.0 CALCULATIONS

12.1 Concentrations of Unknowns:

Method 8260B does not include reporting of tentatively identified compounds (TIC). However, reporting of up to 10 TIC's whose peak heights are ≥ 10% of the nearest internal standard may be requested or ≥ 40% of the nearest internal standard may be requested for low concentration analyses. Concentrations are calculated using the following formula:

$$C_{(x)} = \frac{C_{(IS)} * A_{(x)}}{A_{(IS)}} * DF$$

$C_{(x)}$= Concentration of Unknown (µg/L).
$C_{(IS)}$= Concentration of internal standard (µg/L).
DF = Dilution Factor
$A_{(x)}$ = Area of Unknown
$A_{(IS)}$= Area of associated internal standard.

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12.2 Concentrations of Calibrated Compounds:

$$C_{(x)} = \frac{A_{(x)} * C_{(IS)}}{A_{(IS)} * \overline{RRF}} * DF$$

$C_{(x)}$ = Concentration of compound (µg/L)
$C_{(IS)}$ = Concentration of associated internal standard (µg/L).
DF = Dilution Factor.
$A_{(IS)}$ = Area of quantitation ion for associated internal standard.
$A_{(x)}$ = Area of quantitation ion for compound.

$\overline{RRF}$ = Average Relative Response Factor from five-point initial calibration.

12.3 Calculation of Recovery

Calculate the recovery of each spiked analyte in the MS/MSD, LCS and ICV by the following equation:

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n} X\,100$$

Cs = Measured concentration of the spiked sample aliquot
Cu = Measured concentration of the unspiked sample aliquot (use 0 for LCS and ICV)
Cn = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spike aliquot (for LCS and ICV)

12.4 Calculation of Precision

Precision is estimated from the relative percent difference (RPD) of the concentrations (not the recoveries) measured for matrix spike/ matrix spike duplicate pairs, or for duplicate analyses of unspiked samples. The RPD is calculated according to the following equation below.

$$RPD = \frac{[C_1 - C_2]}{\left(\frac{C_1 + C_2}{2}\right)} X\,100$$

C1 = Measured concentration of the first sample aliquot
C2 = Measured concentration of the second sample aliquot

12.5 Data Reporting

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Based on the mass spectra, it is appropriate to report values between the MDL and the RL. In this region, an analyte can be qualitatively detected, but not accurately quantified. Any data point reported in this region is flagged with a "J" . STL reports sample specific RL's. Sample specific RL's are derived by taking into account various sample specific data, which can include the amount of the sample subject to testing, % moisture, dilution factor, interferences and the base RL's for the analysis.

12.5.1 Reporting Qualifiers

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

12.5.2 Data Package Definitions

Three levels of reporting are available. The difference between these levels has nothing to do with the quality of the work being performed, only how it is presented.

Level 2

A level 2 data package consists of sample results only, and may be available as either an Analytical Report or in a format similar to the OLM Form 1A's.

Level 3

A level 3 data package consists of sample, CLP-like forms with Quality Control results.

Level 4

A level 4 data package consists of a full set of RAS forms, and all supporting documentation.

Electronic-Diskette available upon request

13.0 METHOD PERFORMANCE

13.1 Laboratory accuracy and precision data were obtained for the method analytes using laboratory control spikes. The analytes were at a concentration of 5 µg/L (propionitrile at 20 µg/L, tetrahydrofuran at 50 µg/L, 1,4-Dioxane and isobutyl alcohol at 250 µg/L) for the procedural combination of Methods 5035 and 8260. The analytes were at a concentration of 2.5 µg/L (propionitrile at 7.5 µg/L, tetrahydrofuran at 25 µg/L, 1,4-Dioxane and isobutyl alcohol at 125 µg/L) for the procedural combination of Methods 5030 and 8260. For the low water analysis, the analytes were at a concentration of 0.5µg/L (propionitrile 2.0 µg/L, acrolein and ketones 2.5 µg/L, tetrahydrofuran at 7.0 µg/L, and 1,4-dioxane and isobutyl alcohol at 25 µg/L Results were obtained using the analytical instrumentation described in section 6.

13.2 With this data, method detection limits were calculated using the formula (3):

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

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Where:

$t_{(n-1,\ 1\text{-alpha} = 0.99)}$ = 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 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials used in preparing standards and sample preservatives.

15.0 DATA ASSESSMENT AND ACCEPTANCE CRITERIA AND CORRECTIVE ACTIONS FOR OUT-OF-CONTROL DATA

15.1 Data assessment, acceptance criteria and corrective action for out of control data is summarized in Table 7.

16.0 WASTE MANAGEMENT

The samples that are not utilized in the analysis are disposed of as hazardous waste. All methanol waste and expired standards are disposed of as hazardous waste.

17.0 REFERENCES

1 "Test Methods for Evaluating Solid Waste", USEPA Method 8260B revision 3, 1996.

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18.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

Table 2. BFB Criteria

BFB Key Ions and Ion Abundance Criteria	
Mass	Ion Abundance Criteria
50	15.0-40.0 percent of mass 95
75	30.0-60.0 percent of mass 95
95	base peak, 100 percent relative abundance
96	5.0-9.0 percent of mass 95
173	less than 2.0 percent of mass 174
174	>50.0 percent of mass 95
175	5.0-9.0 percent of mass 174
176	95.0-101.0 percent of mass 174
177	5.0-9.0 percent of mass 176

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Table 3. Calibration Criteria

Compound	Minimum RRF	Maximum %RSD	Maximum %D
Acetone	0.05	15	20
Acrolein	0.05	15	20
Acrylonitrile	0.05	15	20
Allyl Chloride	0.05	15	20
Benzene	0.05	15	20
Bromochloromethane	0.05	15	20
Bromodichloromethane	0.05	15	20
Bromoform (SPCC)	0.1	15	20
Bromomethane	0.05	15	20
2-Butanone	0.05	15	20
Carbon Disulfide	0.05	15	20
Carbon Tetrachloride	0.05	15	20
Chlorobenzene (SPCC)	0.30	15	20
Chloroethane	0.05	15	20
2-Chloroethyl Vinyl Ether	0.05	15	20
Chloroform (CCC)	0.05	30	20
Chloromethane (SPCC)	0.10	15	20
Chloroprene	0.05	15	20
1,2-Dibromo-3-chloropropane	0.05	15	20
Dibromochloromethane	0.05	15	20
1,2-Dibromoethane	0.05	15	20
Dibromomethane	0.05	15	20

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Compound	Minimum RRF	Maximum %RSD	Maximum %D
1,2-Dichlorobenzene	0.05	15	20
1,3-Dichlorobenzene	0.05	15	20
1,4-Dichlorobenzene	0.05	15	20
cis-1,4-Dichloro-2-butene	0.05	15	20
trans-1,4 Dichloro-2-butene	0.05	15	20
Dichlorodifluoromethane	0.05	15	20
1,1-Dichloroethane (SPCC)	0.1	15	20
1,2-Dichloroethane	0.05	15	20
1,1-Dichloroethene (CCC)	0.05	30	20
cis-1,2-Dichloroethene	0.05	15	20
trans-1,2-Dichloroethene	0.05	15	20
1,2-Dichloropropane (CCC)	0.05	30	20
2,2-Dichloropropane	0.05	30	20
cis-1,3-Dichloropropene	0.05	15	20
trans-1,3-Dichloropropene	0.05	15	20
Diethyl Ether	0.05	15	20
1,4-Dioxane	0.05	15	20
Ethyl Methacrylate	0.05	15	20
Ethylbenzene (CCC)	0.05	15	20
Freon TF	0.05	15	20
Hexachlorobutadiene	0.05	15	25
2-Hexanone	0.05	15	20
Isobutyl alcohol	0.05	15	20

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Compound	Minimum RRF	Maximum %RSD	Maximum %D
Isopropylbenzene	0.05	15	20
Methacrylonitrile	0.05	15	20
Methyl Iodide	0.05	15	20
Methyl Methacrylate	0.05	15	20
4-Methyl-2-pentanone	0.05	15	20
Methyl-t-Butyl Ether	0.05	15	20
Methylene Chloride	0.05	15	20
Naphthalene	0.05	15	20
Propionitrile	0.05	15	20
Styrene	0.05	15	20
1,1,1,2-Tetrachloroethane	0.05	15	20
1,1,2,2-Tetrachloroethane (SPCC)	0.3	15	20
Tetrachloroethene	0.05	15	20
Tetrahydrofuran	0.05	15	20
Toluene (CCC)	0.05	30	20
1,2,4-Trichlorobenzene	0.05	15	20
1,1,1-Trichloroethane	0.05	15	20
1,1,2-Trichloroethane	0.05	15	20
Trichloroethene	0.05	15	20
Trichlorofluoromethane	0.05	15	20
1,2,3-Trichloropropane	0.05	15	20
Vinyl Acetate	0.05	15	20
Vinyl Chloride (CCC)	0.05	30	20

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Compound	Minimum RRF	Maximum %RSD	Maximum %D
Xylene (m,p)	0.05	15	20
Xylene (o)	0.05	15	20

(SPCC) System Performance Check Compounds
(CCC) Calibration Check Compounds

Table 4. Surrogate Recoveries Water - Recoveries based on charted control limits which are updated annually.

Surrogate Recovery Requirements (%Recovery)	
4-Bromofluorobenzene	72-122
1,2-Dichlorobenzene-d4	69-124
1,2-Dichloroethane-d4	72-141
Toluene-d8	88-110

Table 5. Surrogate Recoveries Soil - Recoveries based on charted control limits

Surrogate Recovery Requirements (%Recovery)	
4-Bromofluorobenzene	74-121
1,2-Dichlorobenzene-d4	80-120
1,2-Dichloroethane-d4	80-120
Toluene-d8	81-117

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Table 6. Control Limits- Recoveries based on single laboratory control chart data from Method 8260B. These limits will be updated annually.

Compound	MS Recovery Limit (%)	% RPD	LCS/ICV Recovery Limit (%)
Acetone	60-140	40	60-140
Acrolein	60-140	40	60-140
Acrylonitrile	60-140	40	60-140
Allyl Chloride	60-140	40	60-140
Benzene	78-116	40	78-116
Bromobenzene	84-116	40	84-116
Bromochloromethane	73-107	40	73-107
Bromodichloromethane	78-112	40	78-112
Bromoform	82-120	40	82-120
Bromomethane	72-118	40	72-118
2-Butanone	60-140	40	60-140
n-Butylbenzene	77-123	40	77-123
sec-Butylbenzene	77-123	40	77-123
tert-Butylbenzene	80-124	40	80-124
Carbon Disulfide	60-140	40	60-140
Carbon Tetrachloride	62-106	40	62-106
Chlorobenzene	81-115	40	81-115
Chloroethane	65-113	40	65-113
2-Chloroethyl Vinyl Ether	60-140	40	60-140

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Compound	MS Recovery Limit (%)	% RPD	LCS/ICV Recovery Limit (%)
Chloroform	74-106	40	74-106
Chloromethane	68-118	40	68-118
Chloroprene	60-140	40	60-140
2-Chlorotoluene	73-107	40	73-107
4-Chlorotoluene	74-124	40	74-124
1,2-Dibromo-3-chloropropane	33-133	40	33-133
Dibromochloromethane	72-112	40	72-112
1,2-Dibromoethane	90-114	40	90-114
Dibromomethane	83-117	40	83-117
1,2-Dichlorobenzene	76-110	40	76-110
1,3-Dichlorobenzene	79-119	40	79-119
1,4-Dichlorobenzene	83-123	40	83-123
cis-1,4-Dichloro-2-butene	60-140	40	60-140
trans-1,4 Dichloro-2-butene	60-140	40	60-140
Dichlorodifluoromethane	78-116	40	78-116
1,1-Dichloroethane	81-111	40	81-111
1,2-Dichloroethane	80-110	40	80-110
1,1-Dichloroethene	75-113	40	75-113
cis-1,2-Dichloroethene	81-121	40	81-121
trans-1,2-Dichloroethene	60-140	40	60-140
1,2-Dichloropropane	79-115	40	79-115
2,2-Dichloropropane	42-130	40	42-130

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Compound	MS Recovery Limit (%)	% RPD	LCS/ICV Recovery Limit (%)
1,3-Dichloropropane	79-113	40	79-113
1,1-Dichloropropene	72-124	40	72-124
cis-1,3-Dichloropropene	60-140	40	60-140
trans-1,3-Dichloropropene	60-140	40	60-140
Diethyl Ether	60-140	40	60-140
1,4-Dioxane	60-140	40	60-140
Ethyl Methacrylate	60-140	40	60-140
Ethyl Benzene	74-124	40	74-124
Freon TF	60-140	40	60-140
Hexachlorobutadiene	80-120	40	80-120
2-Hexanone	60-140	40	60-140
Isobutyl alcohol	60-140	40	60-140
Isopropylbenzene	78-124	40	78-124
4-Isopropyltoluene	79-119	40	79-119
Methacrylonitrile	60-140	40	60-140
Methyl Iodide	60-140	40	60-140
Methyl Methacrylate	60-140	40	60-140
4-Methyl-2-pentanone	60-140	40	60-140
Methyl-t-Butyl Ether	60-140	40	60-140
Methylene Chloride	80-110	40	80-110
Naphthalene	78-130	40	78-130
Propionitrile	60-140	40	60-140

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Compound	MS Recovery Limit (%)	% RPD	LCS/ICV Recovery Limit (%)
n-Propylbenzene	83-117	40	83-117
Styrene	80-124	40	80-124
1,1,1,2-Tetrachloroethane	72-108	40	72-108
1,1,2,2-Tetrachloroethane	74-108	40	74-108
Tetrachloroethene	71-107	40	71-107
Tetrahydrofuran	60-140	40	60-140
Toluene	78-126	40	78-126
1,2,3-Trichlorobenzene	81-137	40	81-137
1,2,4-Trichlorobenzene	81-135	40	81-135
1,1,1-Trichloroethane	74-122	40	74-122
1,1,2-Trichloroethane	81-127	40	81-127
Trichloroethene	70-109	40	70-109
Trichlorofluoromethane	67-111	40	67-111
1,2,3-Trichloropropane	81-137	40	81-137
1,2,4-Trimethylbenzene	75-123	40	75-123
1,3,5-Trimethylbenzene	72-112	40	72-112
Vinyl Acetate	60-140	40	60-140
Vinyl Chloride	78-118	40	78-118
Xylene (m,p)	78-116	40	78-116
Xylene (o)	81-125	40	81-125

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Table 7. 8260 Volatile Organic Analytical Run Sequence and Corrective Action

Quality Control Criteria	Frequency	Acceptance	Corrective Action
BFB	12 hour	Per Method	Reshoot, Retune
ICAL: 5, 20, 50, 100, 200 µg/L (Low water 1, 5, 10, 25, 50 µg/L)	As Required	minimum RF for SPCCs maximum %RSD for CCCs and average %RSD of all analytes must be ≤ 15%	System check, Mix new standards, Recalibrate, Reanalyze
ICV/LCS (alternative source)	after every ICAL	minimum RF for SPCCs %Difference each CCC ≤20% Evaluate as an LCS	System Check, Recalibrate
BFB	12 hour	Per Method	Reshoot, Retune
CCV	beginning of each 12 hour window	minimum RF for SPCCs %Difference each CCC ≤20%	System Check, Recalibrate
Method Blank	every analytical batch	Targets < Reporting Limits	Check for contamination, Reanalyze, correct as required
Matrix Spike/Matrix Spike Duplicate	every analytical batch	Control Limits Table 6	Reanalyze if analytical problem. Evaluate LCS
LCS	every analytical batch	Control Limits Table 6	Check Std, Check Quantitation, Evaluate MS/MSD, reanalyze analytical batch.

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