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SITEWIDE CERCLA QUALITY ASSURANCE PROJECT PLAN VOLUME III ATTACHMENT I - FEMP LABORATORY ANALYTICAL METHODS MANUAL JULY 15, 1992

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VOLUME III

Fernald Environmental Management Project

SITEWIDE
CERCLA QUALITY ASSURANCE PROJECT PLAN

Attachment I
FEMP Laboratory Analytical Methods Manual

Prepared by

Westinghouse Environmental Management Company of Ohio

for the

United States Department of Energy
Fernald Office

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ATTACHMENT I
FEMP LABORATORY ANALYTICAL METHODS MANUAL

VOLUME III
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Aromatic Volatile Organic Compounds by Gas Chromatography/Photoionization Detection	FM-ORG-0020
Chlorinated Pesticides/PCBs by Gas Chromatography	FM-ORG-0030
Organophosphorus Pesticides by Gas Chromatography	FM-ORG-0040
Volatile Organic Compounds by Gas Chromatography Purge and Trap	FM-ORG-0050
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Toxicity Characteristic Leaching Procedure	FM-MISC-0010
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Reactivity	FM-MISC-0040
Metals by Graphite Furnace Atomic Absorption	FM-INO-0010
Metals by Atomic Absorption Spectrometry, Flame Technique	FM-INO-0020
Metals Analysis by Inductively Coupled Plasma	FM-INO-0030
Mercury Analysis by Cold Vapor (Atomic Absorption Spectrometry)	FM-INO-0040

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Cyanide (Total) Titrimetric	FM-CON-0010
Cyanide (Total) Spectrophotometric, Semiautomatic	FM-CON-0015
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Nitrogen, Nitrate/Nitrite (Colorimetric, Automated, Cadmium Reduction)	FM-CON-0030
Nitrogen, Nitrate/Nitrite (Spectrophotometric, Cadmium Reduction)	FM-CON-0040
Conductivity	FM-CON-0050
Total Kjeldahl Nitrogen	FM-CON-0060
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Alkalinity (Titrimetric)	FM-CON-0090
Alkalinity (Colorimetric Automated)	FM-CON-0100
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Chloride (Colorimetric, Automated Ferricyanide)	FM-CON-0120
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Ammonia (Titrimetric)	FM-CON-0140
Hexavalent Chromium (Cr^{6+})	FM-CON-0150
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Oil and Grease (Gravimetric Only)	FM-CON-0185
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Surfactants (MBAS)	FM-CON-0250
Phenolics, Total Recoverable (colorimetric, Automated 4-AAP with Distillation)	FM-CON-0260
Phenolics, Total Recoverable (Spectrophotometric Manual 4-AAP with Distillation)	FM-CON-0270
Sulfate (Colorimetric, Automated, Methylthymol Blue)	FM-CON-0280
Sulfate (Turbidimetric)	FM-CON-0290
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VOLUME V
Methods for Radiometric and Geotechnical Parameters

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Radium-228 in Water and Air Filters by Beta Counting	FM-RAD-0040
Radium-226 in Water by Emanation/Scintillation Counting	FM-RAD-0050
Radium-226 in Soil/Sediment, Milk, and Air Filters by Emanation/Scintillation Counting	FM-RAD-0060
Lead-210 in Water by Beta Counting	FM-RAD-0070
Isotopic Thorium in Milk, Vegetation, Soil/Sediment, Water and Air Filters by Alpha Spectrometry	FM-RAD-0080
Isotopic Uranium in Vegetation, Milk, Water and by Air Filters by Alpha Spectrometry	FM-RAD-0100
Isotopic Uranium in Soil/Sediment by Alpha Spectrometry	FM-RAD-0110
Uranium in Water, Soil/Sediment, and Air Filters by Pulsed-Laser Phosphorimetry	FM-RAD-0120
Gross Alpha and Gross Beta Radioactivity in Water and Gross Beta Radioactivity in Air Filters by Proportional Counting	FM-RAD-0130
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Wet Preparation of Samples	FM-GTT-0014
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FM-GEN-0010

General Laboratory Requirements

1.0 Purpose

This procedure defines the format to be followed for each method and generally discusses data package deliverables and quality control sample requirements. In an integrated program to generate quality data, some activities can be classified as management related (quality assurance) and others as functional (quality control). The material herein is an overview of the Fernald Environmental Management Program (FEMP) program that laboratories generating analytical data must meet.

2.0 Method Format

The methods will typically contain 15 points. Sections that do not pertain to the specific method will be identified as "not applicable." Other sections may contain generic text common to all analytical methods, as discussed below.

2.1 Scope and Application

This section will consist of introductory comments explaining the method (e.g., specific target analytes) and the applicability of the method to specific sample matrixes. If there is more than one method for determining a specific target compound in the manual, then it will be necessary to define when the specific method should be used instead of another method or technique.

2.2 Method Summary

This section will contain a summary or outline of how the method is performed.

2.3 Interferences

Common interferents must be listed along with a short explanation of techniques to be used to minimize interferences.

2.4 *Safety Precautions*

All methods will include the following statement:

> The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

If acids, bases, organic solvents, or other hazardous chemicals are used, they must be called out specifically and the following statement must be added:

> Because hazardous chemicals are used during the method, procedures for handling [state specific chemicals] must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

The need for the analyst to use a respirator must be stated explicitly.

2.5 *Sample Collection and Handling*

This section will consist of the following sentence: "Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1."

2.6 *Apparatus*

This section will list all apparatus to be used during the procedure, including glassware. Performance specifications, such as Class A glassware or a spectrophotometer capable of measuring absorbance at 450 nm with a 1-cm path length, must be given.

2.7 *Preventive Maintenance*

If no instruments are used, then the statement "No instruments are used in this method" is sufficient. If not, use the following statement: "Perform routine preventive maintenance for [list instruments] according to the manufacturer's [or manufacturers'] directions. All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ." If glassware is used, include the following statement: "Examine glassware before each use for scratches and cracks, and replace as necessary."

2.8 *Reagents and Calibration Standards*

Each reagent will be listed as chemical name, standard chemical symbol, and concentration: e.g., "Hydrochloric Acid, HCl, 1 M." If ASTM Type II water is to be used either in the method or for preparing solutions, then use the following statement: "Water: All references to water assume the use of ASTM Type II water." Directions for preparing solutions will be presented in numbered steps rather than in paragraph form. Directions for preparing calibration standards will refer to use of NIST-traceable standards.

2.9 *Calibration Procedures*

If the method does not involve an instrument or a standardized titrant, state that no calibration procedures are needed. If there is an instrument to calibrate or a titrant to standardize, then calibration directions will be included. If applicable, refer to the manufacturer's directions for specific calibration procedures.

2.10 *Sample Preparation*

If the method does not include a separate sample preparation procedure, then include one of the following statements: "No sample preparation is necessary." Or: "Allow sample to warm to room temperature." If the sample does require preparation, describe the preparation in explicit numbered steps.

2.11 Sample Analysis

All sample analysis steps will be numbered. If another method is referred to in the procedure (e.g., measuring pH or determining percent moisture), refer to the method by its identification number.

2.12 Calculations

All calculations, except those listed in other methods referred to by the method, must be included in Section 12 instead of Section 11. If a calculation is performed in the middle of the analytical process, the calculation will be referenced in Section 11.

Methods that include preparation of a calibration curve will include the following sentence or one similar: "Prepare a calibration curve by plotting absorbance as a function of concentration in mg/L. Determine the concentration of the analyte of interest by comparing the absorbance of the sample with the standard curve and determining the concentration."

2.13 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan. Data package deliverables are discussed below in Section 3.

2.14 Quality Control (QC) Requirements

QC requirements are determined by the method, Analytical Support Levels, and project-specific sampling and analysis plan. Examples of quality control requirements are presented in Section 4. Definitions for each QC sample are included in Section 10 of the SCQ.

2.15 References

All other methods used to prepare the FEMP method will be referenced.

3.0 Data Package Deliverables

As stated in Section 2.13, data package deliverables are determined by the method, Analytical Support Levels, and project-specific sampling and analysis plan. Regardless of the type of method, data package deliverables will include:

- Analytical method
- Detection limit studies
- Chain-of-custody form, including date of sample collection and sample receipt
- Case narrative

Under ASL Level B, there are two categories of data package deliverables: those specified in the analytical method and those determined by the project-specific sampling and analysis plan. They are referred to in the tables as B_{spec} and B_{user}.

3.1 Inorganic Analyses

The following list contains data package deliverables common to inorganic analyses; regardless of the Analytical Support QC level, not all of the information will be required for all analyses. Data package deliverables specific to inorganic analyses may include:

Analytical Support Levels

		B_{spec}	B_{user}	C	D
Sample Results		Yes	Yes	Yes	Yes
Method Blank		Yes	Yes	Yes	Yes
Lab Replicate Sample		Yes	Yes	Yes	Yes
Laboratory Control Sample		Yes	Yes	Yes	Yes
Initial/Continuing Calibration Blanks		No	A/S	Yes	Yes
Initial/Continuing Calibration		No	A/S	Yes	Yes
Matrix Spike		Yes	A/S	Yes	Yes
Interference Check Sample (ICP)	No	A/S	Yes	Yes	
Serial Dilution Samples (ICP)		No	A/S	Yes	Yes
Method of Standard Addition (GFAA)		No	A/S	Yes	Yes
CRDL Standard for AA and ICP	No	A/S	Yes	Yes	
Instrument Detection Limit Study	No	A/S	Yes	Yes	
ICP Interelement Corr. Factor Study		No	A/S	Yes	Yes
ICP Linear Range Study	No	A/S	Yes	Yes	
Preparation Log	No	A/S	Yes	Yes	
Raw Data	No	A/S	No	Yes	

A/S——As specified in the project-specific plan

3.2 *Organic Analyses*

The following list contains data package deliverables common to organic analyses; regardless of the ASL QC level, not all of the information will be required for all analyses. Data package deliverables specific to organic analyses may include:

Analytical Support Levels

		B_{spec}	B_{user}	C	D
Sample Results		Yes	Yes	Yes	Yes
Method Blank		Yes	Yes	Yes	Yes
Laboratory Control Sample		Yes	Yes	Yes	Yes
Matrix Spike/Matrix Spike Duplicates		No	A/S	Yes	Yes
Surrogate Spike Recovery		Yes	Yes	Yes	Yes
GC/MS Tuning and Mass Calibration		No	A/S	Yes	Yes
Initial Calibration Data		No	A/S	Yes	Yes
Continuing Calibration Data		No	A/S	Yes	Yes
Internal Standard Area Summary	No	A/S	Yes	Yes	
Pesticide Evaluation Standards Summary	No	A/S	Yes	Yes	
Pesticide/PCB Standards Summary		No	A/S	Yes	Yes
Pesticide/PCB Identification		No	A/S	Yes	Yes
Second Column Confirmation Results		No	A/S	Yes	Yes
Raw Data	No	A/S	No	Yes	

A/S——As specified in the project-specific plan

3.3 Conventional Analyses

The following list contains data package deliverables common to conventional analyses; regardless of the Analytical Support QC level, not all of the information will be required for all analyses. Data package deliverables specific to conventional analyses may include:

Analytical Support Levels

	B_{spec}	B_{user}
Sample Results	Yes	Yes
Method Blank	Yes	Yes
Lab Replicate Sample	Yes	Yes
Initial and Continuing Calibration	No	A/S
Matrix Spike/Matrix Spike Duplicates	No	A/S
Laboratory Control Samples	Yes	A/S

A/S——As specified in the project-specific plan

4.0 Quality Control Requirements

Quality control requirements are determined by the Analytical Support Levels and the project-specific Sampling and Analysis Plan. A specific discussion of each type of QC sample is presented in the SCQ (Section 10) or the method. These are global acceptance limits and are presented here as an example; specific acceptance ranges are included in each analytical method.

4.1 Inorganic Analyses

Analytical Support Levels B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/20	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Matrix Spike	1/20	75—125%	Qualify data
Lab Replicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10	90—110%	Recalibrate
ICB	Begin	DR*	Qualify data
CCB	1/10	DR*	Qualify data
PB	1/10	DR*	Qualify data
LCS	Begin	90—110%	Recalibrate
Predigestion Spike	1/20	75—125%	Post-dig spike
Postdigestion Spike	as needed	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data
CRA	Begin	DR	Recalibrate
ICS	Begin	DR	Qualify data
Serial Dilution	1/20	DR	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
ICB	initial calibration blank
CCB	continuing calibration blank
PB	preparation blank
LCS	laboratory control sample
CRA	detection limit verification sample
RPD	relative percent difference
DR	Data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ. For DR*, refer to the 1988 CLP SOW for acceptance limit guidance.
ICS	interference check sample

4.2 *Organic Analyses*

Analytical Support Levels B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/20	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80—120%	Qualify data
Surrogate Spikes	every sample	75—125%	Reanalyze then qualify data
Matrix Spike	1/20	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10	90—110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Surrogate Spikes	every sample	75—125%	Reanalyze then qualify data
Matrix Spike	1/20	75—125%	Qualify data
MSD	1/20	75—125%	Qualify data
BFB	Begin	A/S	Recalibrate
Internal Standard	every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
DR	Data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
BFB	bromofluorobenzene
A/S	as specified earlier in this method
RPD	relative percent difference

4.3 Conventional Methods

Analytical Support Levels B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/20	90—110%	Recalibrate
LCS	Begin	80—120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Matrix Spike	1/20	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
RPD	relative percent difference
DR	Data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ

FM-ORG-0010

Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry

Working Linear Range: Analyte- and matrix-dependent
Reporting Limit: Analyte- and matrix-dependent
Reporting Units: Water, μg/L; Soil, μg/kg
Matrix: Water, sediment, soil, and waste

1.0 Scope and Application

1.1 This analytical method is designed to analyze water, sediment, soil, and waste. The method target compound lists and the corresponding practical quantitation limits are summarized in Tables 1 and 2.

2.0 Method Summary

2.1 Water Samples

2.1.1 A sample aliquot is diluted with water (except for low-level samples). An inert gas is bubbled through a 5-mL aliquot of the diluted sample contained in a specifically designed purging chamber at ambient temperature. Purgeables are efficiently transferred from aqueous phase to vapor phase. The vapor is swept through a sorbent column where purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables, which are then detected with a mass spectrometer.

2.2 Soil/Sediment Samples

2.2.1 Low Level: An inert gas is bubbled through a mixture of a 5-gram sample and reagent water contained in a specially designed purging chamber at elevated temperatures. Purgeables are efficiently transferred from aqueous phase to vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables, which are then detected with a mass spectrometer.

Table 1
Target Compound List (TCL) and Practical Quantitation Limits

Soil Parameter	Water (µg/L)	Low Soil (µg/kg)	Medium Soil (µg/kg)
Chloromethane	10	10	1200
Bromomethane	10	10	1200
Vinyl Chloride	10	10	1200
Chloroethane	10	10	1200
Methylene chloride	10	10	1200
Acetone	50	50	6000
Carbon disulfide	50	50	6000
1,1-Dichloroethene	10	10	1200
1,1-Dichloroethane	10	10	1200
1,2-Dichloroethene (total)	10	10	1200
Chloroform	10	10	1200
1,2-Dichloroethane	10	10	1200
1,1,2-Trichloroethane	10	10	1200
Benzene	10	10	1200
cis-1,3-Dichloropropene	10	10	1200
Bromoform	10	10	1200
2-Hexanone	50	50	6000
2-Butanone	50	50	6000
1,1,1-Trichloroethane	10	10	1200
Carbon tetrachloride	10	10	1200
Bromodichloromethane	10	10	1200
1,2-Dichloropropane	10	10	1200
trans-1,3-Dichloropropene	10	10	1200
Trichloroethene	10	10	1200
Dibromochloromethane	10	10	1200
4-Methyl-2-pentanone	50	50	6000
Tetrachloroethene	10	10	1200
Toluene	10	10	1200
Chlorobenzene	10	10	1200
Ethyl benzene	10	10	1200
Styrene	10	10	1200
Total Xylenes	10	10	1200

Table 2
Supplemental Target Compound List (STL) and Practical Quantitation Limits

	Practical Quantitation Limits		
		Low	Medium
	Water	Soil	
Soil Parameter	(μg/L)	(μg/kg)	(μg/kg)
Acetonitrile	200	200	24000
Acrolein	100	100	In review
Acrylonitrile	100	100	In review
Butanol	In review	In review	In review
2-Chloroethyl vinyl ether	10	10	1200
3-Chloropropene	In review	In review	In review
1,2-Dibromoethane	10	10	1200
1,3-Dibromo-3-chloropropane	In review	In review	In review
Dichlorodifluoromethane	20	20	2400
Dioxane	500	500	In review
Ethyl methacrylate	50	50	6000
Methacrylonitrile	50	50	6000
Methyl iodide	In review	In review	In review
Methyl methacrylate	50	50	6000
Methyl bromide	In review	In review	In review
1,1,1,2-Tetrachloroethane	In review	In review	In review
Trichlorofluoromethane	10	10	1200
1,2,3-Trichloropropane	10	10	1200

2.2.2 Medium Level: A measured amount of soil is extracted with methanol, and a portion of the extract is diluted to 5 mL with reagent water. An inert gas is bubbled through the solution in a specifically designed purging chamber at ambient temperature. The purgeables are effectively transferred from aqueous phase to vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb purgeables onto a GC column. The gas chromato-graph is temperature programmed to separate the purgeables, which are then detected with a mass spectrometer.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in the total ion current profiles. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. Matrix interferences may be caused by contaminants coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the site being sampled.

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

3.3 Problems have been associated with the following compounds analyzed by the method:

- Chloromethane, vinyl chloride, bromomethane, and chloroethane can display peak broadening if the compounds are not delivered to the GC column in a tight band.

- Acetone, hexanone, 2-butanone, and 4-methyl-2-pentanone have poor purge efficiencies.

- 1,1,1-Trichloroethane and all the dichloroethanes can dehydrogenate during storage or analysis.

- Tetrachloroethane and 1,1-dichloroethane can be degraded by contaminated transfer lines in purge-and-trap systems or active sites in trapping materials.

- Chloromethane can be lost if purge flow is too fast.

- Bromoform is one of the compounds most likely to be affected adversely by cold spots or active sites in the transfer lines. Response of its quantitation ion (m/z 173) is directly affected by the tuning of the GC/MS to meet the instrument performance criteria for p-

bromofluorobenzene (BFB) at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

3.4 Contamination by carryover can occur whenever high- and low-level samples are analyzed sequentially. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water sample. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high purgeable levels between analyses, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven. The trap and other parts of the system are also subject to contamination, so frequent bakeout and purging of the entire system may be required.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling these compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Microsyringes: 25-μL and larger, 0.006-inch I.D. needle, Hamilton gastight or equivalent.

6.2 Syringe Valve: Two-way, with Luer ends (three each), if applicable to the purging device.

6.3 Syringe: 5-mL, gastight with shutoff valve, Hamilton gastight or equivalent.

6.4 Balance: Analytical, capable of accurately weighing ± 0.0001 gram, and a top-loading balance capable of weighing ± 0.1 gram.

6.5 Glassware

6.5.1 Bottle: 15-mL, screw cap, with Teflon cap liner.

6.5.2 Volumetric Flasks: Class A with ground glass stoppers.

6.5.3 Vials: 2-mL for GC autosampler.

6.6 Purge-and-Trap Device: Consists of a sample purger, a trap, and a desorber. Several complete devices are now commercially available.

6.6.1 The sample purger must be designed to accept 5-mL samples with a water column at least 3 cm deep. Gaseous headspace between water column and trap must have total volume less than 15 mL. Purge gas must pass through water column as finely divided bubbles, each with a diameter of less than 3 mm at the origin. Purge gas must be introduced no more than 5 mm from base of water column.

6.6.2 Trap must be at least 25 cm long and have I.D. of at least 0.105 inch. Trap must be packed to contain at least 8 cm of 2,6-diphenylene oxide polymer (Tenax-GC, 60/80 mesh or equivalent) and 8 cm of silica gel (Davison Chemical, 35/60 mesh, grade 15 or equivalent) and 8 cm of coconut charcoal (prepared from Barneby Cheney, CA-580-26 lot #M-2649 by crushing through a 26 mesh screen, or equivalent). It is recommended that 1 cm of methyl silicone coated packing be inserted at the inlet to extend the life of the trap (3% OV-101, 60/80 mesh Chromosorb W, or equivalent).

6.6.3 Desorber should be capable of rapidly heating trap to 180°C. Polymer section of trap should not be heated higher than 180°C, and remaining sections should not exceed 220°C during bakeout mode.

6.6.4 A heater or heated bath capable of maintaining the purge device at 40° ± 1°C is to be used for low level soils.

6.7 GC/MS System: The GC system must be capable of temperature programming and have a flow controller that maintains a constant column flow rate throughout desorption and temperature program operations. The system must include or be interfaced to a purge-and-trap system as specified above and have all required accessories including syringes, analytical columns, and gases. GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with rubber components are not to be used. If capillary columns are to be used, the column oven must be cooled to 10°C; therefore, a subambient oven controller is required.

6.7.1 GC Capillary Columns: 30 m long × 0.53 mm I.D. VOCOL (Supelco, Inc., or equivalent) fused silica wide-bore capillary column with 3-μm film thickness; or 30 m long × 0.53 mm I.D. DB-624 fused silica wide-bore (J&W Scientific, Inc., or equivalent) column with 3-μm film thickness.

6.7.2 Mass Spectrometer

6.7.2.1 Must be capable of scanning from 35 to 300 amu every 2 seconds or less using 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum that meets all instrument performance acceptance criteria when 50 ng of p-bromofluorobenzene (BFB) is injected through gas chromatograph inlet.

Note: BFB criteria must be met before any sample extracts are analyzed. Any samples analyzed when BFB criteria have not been met will require reanalysis.

6.7.2.2 To ensure sufficient precision of mass spectral data, the MS scan rate should allow acquisition of at least five spectra while a sample compound elutes from the GC. The purge-and-trap GC/MS system must be in a room whose atmosphere is demonstrated to be free of all potential contaminants that could interfere with the analysis. The instrument must be vented to the outside of the facility or to a trapping system that prevents the release of contaminants into the instrument room.

6.7.3 GC/MS Interface: Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points, at 50 ng or less per injection, for each parameter of interest and achieves all acceptance criteria may be used. Interfaces constructed of all-glass or glass-lined materials are recommended. Glass can be chemically deactivated by silanizing with dichlorodimethylsilane.

6.7.4 Data System: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage, on instrument readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Also, for nontarget compounds, software must be available that allows for the comparison of sample spectra against reference library spectra. The most recent release of the NIST/EPA Mass Spectral Library shall be used as the reference library. The data system must be capable of flagging all data files that have been edited manually by laboratory personnel.

6.7.5 Magnetic Tape Storage Device: The magnetic tape storage device must be capable of recording data and suitable for long-term, off-line storage.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the GC/MS according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of water in which target compounds are not detected above the method detection limits.

8.2 Sodium Thiosulfate (ACS): Granular.

8.3 Methanol: Pesticide quality or equivalent.

8.4 Standards

8.4.1 All standards used for calibration must be traceable to NIST standards.

8.4.2 Stock Standard Solutions: Stock standard solutions may be purchased or may be prepared in methanol from neat standard materials.

8.4.2.1 Prepare stock standard solutions by placing about 9.8 mL of methanol into 10-mL ground glass unstoppered volumetric flask. Allow flask to stand, unstoppered for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh flask to nearest 0.1 mg.

8.4.2.2 If compound is a liquid, using a 100-μL syringe immediately add two or more drops of assayed reference material to the flask and reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

8.4.2.3 If compound is a gas at room temperature, fill a valved, gas-tight syringe with the reference standard to 5.0-mL mark. Lower needle to 5 mm above methanol meniscus. Slowly introduce reference standard above surface of liquid. The heavy gas will rapidly dissolve in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (No. 86600). Attach Teflon tubing to side-arm relief valve and direct gentle stream of reference standard into methanol meniscus.

8.4.2.4 Reweigh, dilute to volume, stopper, then mix by inverting flask several times. Calculate concentration in μg/mL from net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. If the compound purity is assayed to be less than 96%, the weight must be corrected when calculating the concentration of the stock solution.

8.4.2.5 Prepare fresh stock standards every 2 months for gases and more often for reactive compounds such as styrene. All other stock standards for nongases and nonreactive purgeable compounds should be replaced after 6 months or sooner if standard has degraded or evaporated.

8.4.3. Secondary Dilution Standards

8.4.3.1 Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. Secondary dilution standard solutions should be prepared at concentrations that can be easily diluted to prepare working standard solutions.

8.4.3.2 Prepare fresh secondary dilution standards for gases and for reactive compounds such as styrene every month or sooner if standard has degraded or evaporated. Secondary dilution standards for the other purgeable compounds should be replaced after 6 months or sooner if standard has degraded or evaporated.

8.4.4 Working Standards

8.4.4.1 Instrument Performance Check Solution [p-Bromofluorobenzene (BFB)]: Prepare 25-ng/μL solution of BFB in methanol. Prepare fresh BFB solution every 6 months or sooner if the solution has degraded or evaporated.

Note: The 25-ng/μL concentration is used with a 2-μL injection volume. The laboratory may prepare a 50-ng/μL solution of BFB if a 1-μL injection volume is used.

8.4.4.2 Calibration Standard: Prepare the working calibration standard solution containing all the purgeable target compounds in methanol. The recommended concentration of the target compounds is 100 μg/mL. Prepare fresh working calibration standard solutions weekly or sooner if solutions have degraded or evaporated.

8.4.4.3 Internal Standard Spiking Solution: Prepare an internal standard spiking solution in methanol at 25.0 μg/mL for each internal standard. The recommended internal standards are chlorobenzene-d_5, 1,4-diclorobenzene-d_4, and 1,4-difluorobenzene. Add 10 μL of spiking solution into 5.0 mL of sample or calibration standard for a concentration of 50 μg/L. Prepare fresh spiking solution weekly or sooner if the solution has degraded or evaporated.

8.4.4.4 Surrogate Spiking Solution: Prepare a system monitoring compound spiking solution containing p-bromofluorobenzene, toluene-d_8, and dibromofluoromethane in methanol at a concentration of 25.0 μg/mL. Other compounds may be used as surrogates, depending upon analysis requirements. Add 10 μL of spiking solution into 5.0 mL of sample for a concentration for 50 μg/L. Prepare fresh spiking solution every 3 months or sooner if solution has degraded or evaporated.

8.4.4.5 Volatile Matrix Standard Spiking Solution: Prepare spiking solution in methanol that contains the following compounds at a concentration of 25.0 μg/mL: 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. Matrix spikes also serve as duplicates, so add an aliquot of this solution to each of two portions from one sample chosen for spiking.

8.4.4.6 Laboratory Control Sample: Prepare just like a medium-level calibration standard (e.g., 50 μg/mL) except that the target compounds must be obtained from a source independent of the calibration standards.

8.4.5 Aqueous Calibration Standard Solutions

8.4.5.1 Prepare five aqueous initial calibration standard solutions containing all the purgeable target compounds and surrogate compounds at the 20-, 50-, 100-, 150- and 200-μg/L levels.

8.4.5.2 Aqueous calibration standards may be prepared in a volumetric flask or the syringe used to inject the standard into the purging device.

8.4.5.2.1 Volumetric Flask: Add appropriate volume of working calibration standard solution to aliquot of reagent water in volumetric flask. Use microsyringe and rapidly inject alcohol standard into expanded area of filled volumetric flack. Remove needle as quickly as possible after injection. Bring to volume. Mix by inverting flask three times only. Discard contents contained in head of flask.

8.4.5.2.2 Syringe: Remove plunger from 5-mL Luerlock syringe. Pour reagent water into syringe barrel to create a positive meniscus. Replace syringe plunger and compress water. Invert syringe, open syringe valve, and vent residual air. Adjust water volume to 5.0 mL minus amount of calibration standard to be added. Withdraw plunger slightly and add appropriate volume of working calibration standard through valve bore of syringe. Close valve and invert three times.

8.4.5.3 The 50-μg/L aqueous calibration standard solution is the mid-level continuing calibration standard.

8.4.5.4 The methanol purged in each of the aqueous calibration standards must not exceed 1% by volume.

8.4.6 Storage of Standards

8.4.6.1 Store stock standards in Teflon-sealed screw-cap bottles with zero headspace at -10° to -20°C. Protect the standards from light.

8.4.6.2 Store secondary dilution standards in Teflon-sealed screw-cap bottles with minimal headspace at -10° to -20°C. Protect the standards from light. Secondary dilution standards must be checked frequently for signs of degradation or evaporation, especially just before preparing the working calibration standards from them.

8.4.6.3 Aqueous standards may be stored for up to 24 hours if held in Teflon-sealed screw-cap vials with zero headspace at 4°C. Protect the standards from light. If not so stored, they should be discarded after 1 hour unless they are set up to be purged by an autosampler. When using an autosampler, the standards may be kept for up to 12 hours in purge tubes connected by the autosampler to the purge-and-trap device.

8.4.6.4 Purgeable standards must be stored separately from other standards.

9.0 Calibration Procedures

9.1 Before the analysis of samples and required blanks and after the instrument performance check solution criteria have been met, each GC/MS system must be calibrated at a minimum of five concentrations to determine instrument sensitivity and linearity of GC/MS response for purgeable target compounds.

9.2 Assemble a purge-and-trap device that meets the specifications summarized in Section 6.6.

9.3 Connect purge-and-trap device to gas chromatograph. Gas chromatograph must be operated using temperature and flow rate parameters equivalent to those listed. Calibrate purge-and-trap GC/MS system using internal standard technique.

9.4 Instrument Operating Conditions

9.4.1 Purge-and-Trap Device: The following are the purge-and-trap analytical conditions:

Purge Conditions

Purge Gas	Helium
Purge Time	11.0 ± 0.1 min
Purge Flow Rate	25 to 40 mL/min
Purge Temperature	Ambient for water, waste and medium-level soil; 40° ± 1°C for low-level soil.

Desorb Conditions

Desorb Temperature	180 ±5 °C
Desorb Flow Rate	15 mL/min
Desorb Time	4.0 ± 0.1 min

Trap Reconditioning Conditions

Reconditioning Temperature	180 ±5 °C
Reconditioning Time	7.0 ± 0.1 min

Before initial use, condition the trap overnight at 180 ±5 °C by backflushing with at least 20 mL/min flow of inert gas. Vent the trap effluent to the room and not the analytical column. Before daily use, condition trap by heating at 180 ±5 °C for 10 minutes while backflushing. Trap may be vented to analytical column during daily conditioning, but the column must be run through the temperature program before analysis of samples.

9.4.2 Gas Chromatograph: The following are the recommended GC analytical conditions:

Capillary Columns

Carrier Gas	Helium
Flow Rate	15 mL/min
Initial Temperature	10 ±1 °C
Initial Hold Time	1.0 to 5.0 min (± 0.1 min precision)
Ramp Rate	6°C/min (±0.2°/min precision)
Final Temperature	160 ±1 °C
Final Hold Time	Until all target compounds have eluted

Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for the analysis of all standards, samples, blanks, matrix spikes, and matrix spike duplicates.

9.4.3 Mass Spectrometer: The following are the required mass spectrometer conditions:

Electron Energy	70 volts (nominal)
Mass Range	35 to 300 amu
Scan Time	To give at least 5 scans per peak, not to exceed 2 seconds per scan

9.4.4 Before analyses of any samples, blanks, or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing BFB. Analysis of instrument performance check solution may be performed:

9.4.4.1 As an injection of up to 50 ng of BFB into the GC/MS

9.4.4.2 By adding 50 ng of BFB to 5.0 mL of reagent water and analyzing resulting solution as if it were an environmental sample.

Note: BFB may not be analyzed simultaneously with a calibration standard.

9.4.5 The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required and must be accomplished using a single scan before elution of BFB.

Note: All instrument conditions must be identical to those used in the sample analysis.

9.4.6 Analysis of instrument performance check solution must meet the ion abundance criteria in Table 3.

Table 3
Ion Abundance Criteria for Bromofluorobenzene (BFB)

Mass (M/2)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of mass 176

9.4.7 The instrument performance check solution must be injected once at the beginning of each 12-hour period, during which samples or standards are to be analyzed. The 12-hour period for GC/MS Instrument Performance Check (BFB), standards calibration (initial or continuing calibration criteria), and method blank analysis begins at the moment of injection of the BFB analysis that the laboratory submits as documentation of a compliant instrument performance check. The time period ends after 12 hours have elapsed according to the system clock.

9.5 Internal Standard Calibration Procedure. The three internal standards are 1,4-dichlorobenzene-d_4, 1,4-difluorobenzene, and chlorobenzene-d_5. The initial calibration is performed at 20, 50, 100, 150, and 200 μg/L levels. Continuing calibrations use 50 μg/L . Extracts of medium-level soil samples may be analyzed using calibrations for water samples. Separate, heated purge is required for low-level soil samples and their calibrations.

9.5.1 Prepare calibration standards at a minimum of five concentration levels for each target compound. Standards may be stored up to 24 hours following the procedures in section 8.4.6. The lowest standard must be above the required detection limit, and the standards must cover the linear response range of the detector.

9.5.2 Prepare a spiking solution containing each internal standard.

9.5.3 Analyze the calibration standard solutions using the method described in Section 11. Characteristic ions for each target, surrogate, and internal standard compound are summarized in Tables 4 and 5.

Table 4
Characteristic Ions for Volatile Target Compounds(M/Z)

Analyte	Primary Ion*	Secondary Ion(s)
Chloromethane	50	52
Bromomethane	94	96
Vinyl Chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 86
Acetone	43	58
Carbon disulfide	76	78
1,1-Dichloroethene	96	61, 63
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethene	96	61, 98
Chloroform	83	85
1,2-Dichloroethane	62	98
2-Butanone	43	57
1,1,1-Trichloroethane	97	99, 61
Carbon tetrachloride	117	119
Bromodichloromethane	83	85, 127
1,1,2,2-Tetrachloroethane	131	113, 119
1,2-Dichloropropane	63	112
trans-1,3-Dichloropropene	75	77
Dibromochloromethane	129	130, 127
Trichloroethene	95	97, 130
1,1,2-Trichloroethane	83	97, 85
Benzene	78	--
cis-1,3-Dichloropropene	75	77
Bromoform	173	175, 254
2-Hexanone	43	58, 57, 100
4-Methyl-2-pentanone	43	58, 100
Tetrachloroethene	166	129, 168
Toluene	92	91
Chlorobenzene	112	77, 114
1,1,2,2-Tetrachloroethane	168	83, 85, 131, 133, 166
Ethyl benzene	91	106
Styrene	104	78
Total Xylenes	106	91

Analyte	Primary Ion*	Secondary Ion(s)
Surrogates		
4-Bromofluorobenzene	95	174, 176
Toluene-d_8	98	70,100
Dibromofluoromethane	113	--
Internal Standards		
1,4-Dichlorobenzene-d_4	152	--
1,4-Difluorobenzene	114	63, 88
Chlorobenzene-d_5	117	82, 119

* The primary ion should be used unless interferences are present; in that case, a secondary ion may be used.

9.5.4 Tabulate area response of characteristic ions in extraction current profile (EICP) against concentration for each compound and internal standard, and calculate relative response factors (RRF) for each compound using equation 1. (1)

$$RRF = \frac{A_x \times C_{IS}}{A_{IS} \times C_x}$$

Where:

A_x = Area of characteristic ion (EICP) for compound to be measured

A_{IS} = Area of characteristic ion (EICP) for specific internal standard

C_{IS} = Concentration of internal standard (μg/L)

C_x = Concentration of compound to be measured (μg/L)

Table 5
Characteristic Ions for Supplemental Volatile Target Compounds

Analyte	Primary Ion*	Secondary Ions*
Acetonitrile	In review	In review
Acrolein	56	55
Acrylonitrile	53	52, 51
2-Butanol	In review	In review
2-Chloroethyl vinyl ether	63	65, 106
3-Chloropropene	In review	In review
1,2-Dibromoethane	In review	In review
1,3-Dibromo-3-chloropropane	In review	In review
Dichlorodifluoromethane	85	87, 50, 101
1,4-Dioxane	In review	In review
Ethyl methacrylate	69	41, 39, 99
Methacrylonitrile	In review	In review
Methyl iodide	142	127, 141
Methyl methacrylate	In review	In review
Methyl bromide	94	96
1,1,1,2-Tetrachloroethane	In review	In review
Trichlorofluoromethane	101	103, 66
1,2,3-Trichloropropane	75	110, 77, 61

* The primary ion should be used unless interferences are present; in that case, a secondary ion may be used.

9.5.5 Then calculate the % Relative Standard Deviation (%RSD) for RRF values over the working range of the curve. (2)

$$\%RSD = \frac{\text{Standard deviation}}{\text{Mean}} \times 100$$

The %RSD for each individual calibration check compound (CCC) must be less than 30%. The CCCs are:

1,1-Dichloroethene, chloroform, 1,2-Dichloropropane, toluene, ethylbenzene, and vinyl chloride.

9.5.6 SPCCs (System Performance Check Compounds) are checked for a minimum response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RRF for these compounds is 0.300 (0.250 for bromoform).

9.5.7 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12-hour) calibration standard, the chromatographic system must be inspected for malfunctions and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

9.6 If time remains in the 12-hour period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard if the initial calibration meets the calibration acceptance criteria above. A method blank is necessary. Quantify all sample results against the initial calibration standard that is the same concentration as the continuing calibration standard (50 μg/L).

9.7 If time does not remain in the 12-hour period beginning with the injection of the instrument performance check solution, a new injection of the instrument performance check solution must be made. If the new injection meets the ion abundance criteria for BFB, then a continuing calibration standard may be injected.

10.0 Sample Preparation

10.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard supernatant liquids. For soils or waste, mix contents of sample container with narrow stainless steel spatula. For medium-level soil or waste that is insoluble in methanol, weigh 4 grams (wet weight) into tared 20-mL vial. Use top loading balance. Record actual weight to nearest 0.1 gram. Determine percent moisture. For waste that is soluble in methanol, weigh 1 gram (wet weight) into a tared 20-mL vial. (The vial must be calibrated prior to use by pipetting 10.0 mL of methanol into the vial and marking the bottom of the meniscus. Discard this solvent.)

10.2 Quickly add 9.0 mL of methanol to the vial. Then add 1.0 mL of surrogate compound spiking solution to vial. Cap and shake for 2 minutes. For MS/MSD samples, add 1.0 mL of matrix spike solution and 8.0 mL of methanol.

Note: The previous two steps must be performed rapidly to avoid loss of volatile organics and in a laboratory free of solvent fumes.

10.3 Shake for two minutes. Using a disposable pipette, transfer about 1 mL of extract into a GC vial for storage. The remainder may be discarded.

10.4 Determine the percent moisture of the sample (Method No. FM-CON-0190) using another aliquot of the sample.

11.0 Sample Analysis

11.1 Water Samples

11.1.1 All water samples must be allowed to equilibrate to ambient temperature prior to analysis.

11.1.2 Before analysis of samples, establish appropriate GC/MS operating conditions, analyze the instrument performance check solution, and calibrate the GC/MS system.

11.1.2.1 If time remains in the 12-hour period samples may be analyzed without analysis of a continuing calibration standard.

11.1.2.2 If time does not remain in the 12-hour period since the injection of the instrument performance check solution, both instrument performance check solution and continuing calibration standard must be analyzed before sample analysis may begin.

11.1.3 Adjust purge gas (helium) flow rate to 25 to 40 mL/minute. Variations from this flow rate may be necessary to achieve better purging and collection efficiencies for some compounds, particularly chloromethane and bromoform.

11.1.4 Remove plunger from 5-mL syringe and attach closed syringe valve. Open sample or standard bottle that has been allowed to come to ambient temperature, and carefully pour sample into syringe barrel to create positive meniscus. Replace syringe plunger and compress sample. Open syringe valve and vent residual air while adjusting sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the sample for future analysis, so if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. The second sample is maintained only until the analyst has determined that the first sample has been analyzed properly. Filling one 5-mL syringe would allow use of only one syringe. If an analysis is needed from the second 5-mL syringe, it must be performed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

11.1.5 The purgeable organics screening procedure, if used, will have shown approximate concentrations of major sample components. If dilution of the sample is indicated, it shall be made just before GC/MS analysis of the sample. All steps in the dilution procedure must be performed without delays until the point at which the diluted sample is in a gas tight syringe. The following procedure will allow for dilutions near the calculated dilution factor from the screening procedure.

11.1.5.1 All dilutions are made in volumetric flasks (10- to 100-mL).

11.1.5.2 Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

11.1.5.3 Calculate approximate volume of reagent water that will be added to volumetric flask and add slightly less than that quantity of reagent water to the flask.

11.1.5.4 Inject proper aliquot from the syringe into volumetric flask. Aliquots of less than 1-mL increments are prohibited. Dilute flask to mark with reagent water. Stopper flask and invert three times.

11.1.5.5 Fill 5-mL syringe with diluted sample.

11.1.5.6 If this is an intermediate dilution, use it and repeat the above procedure to achieve larger dilutions.

11.1.6 Add 10 μL of surrogate spiking solution and 10 μL of internal standard spiking solution through valve bore of syringe; then close the valve. The surrogate compounds and internal standards may be mixed and added as a single spiking solution. Addition of 10 μL of surrogate spiking solution and internal standards to 5 mL of sample is equivalent to a concentration of 50 μg/L of each.

11.1.7 Attach syringe-syringe valve assembly to syringe valve on purging device. Open syringe valves and inject sample into purging chamber.

11.1.8 Close both valves and purge sample for 11.0 $\pm$ 0.1 minutes at ambient temperature.

11.1.9 At conclusion of purge time, attach trap to chromatograph, adjust device to desorb mode, and begin gas chromatographic temperature program. Concurrently, introduce trapped materials to gas chromatographic column by rapidly heating trap to 180°C while backflushing trap with inert gas at 15 mL/minute for 4 minutes.

11.1.10 While trap is being desorbed into gas chromatograph, empty purging chamber. Wash chamber with a minimum of two 5-mL aliquots of reagent water to avoid carryover of target compounds.

11.1.11 After desorbing sample for 4 minutes, recondition trap by returning purge-and-trap device to purge mode. Wait 15 seconds, then close syringe valve on purging device to begin gas flow through trap. Trap temperature should be maintained at 180°C. After about 7 minutes, turn off trap heater and open syringe valve to stop gas flow through trap. When cool, trap is ready for next sample.

11.1.12 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of overall system sensitivity and mass spectral characteristics of that compound. Initial calibration requires that the system should not be saturated for high response compounds at 200 μg/L for VOA target compounds. Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the Sample Delivery Group (SDG) Narrative. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by the analysis of a reagent water blank. If the blank is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank has been analyzed that is free of interferences.

11.1.13 To prepare a matrix spike and matrix spike duplicate for water samples, add 10 μL of the matrix spike solution to each of the 5-mL aliquots of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 μg/L of each matrix spike compound.

11.1.14 A volatile method blank must be analyzed at least once during every 12-hour period on each GC/MS system used for volatile analysis.

11.1.14.1 For water samples, a volatile method blank consists of a 5-mL volume of reagent water spiked with the surrogate compounds and internal standards and carried through the analytical procedure.

11.1.14.2 An acceptable volatile method blank for water samples must contain less than five times the Practical Quantitation Limit (PQL) of methylene chloride, acetone, and 2-butanone and less than or equal to the PQL of any other volatile target compound.

11.1.14.3 All volatile analyses associated with a blank that does not meet the requirements above (i.e., a contaminated blank) must be repurged and reanalyzed.

11.1.14.4 The volatile method blank must be analyzed after the calibration standards to ensure there is no carryover of material from the standards into samples.

11.2 Soil/Sediment Samples: Two approaches may be taken to determine whether the low- or medium-level method must be followed:

- Assume the sample is low level and analyze a 5-gram sample.

- Use the factor calculated from the optional hexadecane screen to determine the appropriate method for analysis.

If peaks are saturated from the analysis of a 5-gram sample, a smaller sample size must be analyzed to prevent saturation. However, the smallest sample size permitted is 1 gram. If smaller than 1-gram sample size is needed to prevent saturation, the medium-level method must be used.

11.2.1 Low-level Soil Method: The low-level soil method is based on purging a heated sediment/soil sample mixed with reagent water containing the system monitoring compounds, the surrogate compounds and internal standards.

11.2.1.1 Analyze all method blanks and standards under the same conditions as the samples.

11.2.1.2 Use 5 grams of sample if expected concentration is < 0.1 mg/kg or 1 gram for expected concentrations between 0.1 and 1.0 mg/kg.

11.2.1.3 The GC/MS system should be set up as described. This will be done before the preparation of the sample to avoid loss of volatile organic compounds from standards and sample. A heated purge calibration curve must be prepared and used for quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions but increase the purge temperature to 40°C.

11.2.1.4 To prepare reagent water containing the surrogate compounds and the internal standards, remove plunger from 5-mL Luerlock type syringe equipped with syringe valve and fill to create a positive meniscus. Replace plunger and compress water to vent trapped air. Adjust volume to 5.0 mL. Add 10 μL of surrogate spiking solution and 10 μL of internal standard solution to syringe through valve.

11.2.1.5 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard supernatant liquids. Mix contents of sample container with narrow stainless steel spatula. Weigh amount into a tared purge device. Use a top loading balance. Note and record actual weight to the nearest 0.1 gram.

11.2.1.6 Add spiked reagent water to purge device and connect device to purge-and-trap system.

Note: Before attaching the purge device, all steps must be performed rapidly to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

11.2.1.7 Heat sample to 40° ± 1°C and purge it for 11.0 ± 0.1 minutes.

11.2.1.8 Proceed with analysis as in sections 11.1.6 through 11.1.12.

11.2.1.9 To prepare a matrix spike and matrix spike duplicate for low-level soils/sediment, add 10 μL for the matrix spike solution to the 5 mL of water added to each of the two additional aliquots of the soil from the sample chosen for spiking. The concentration for a 5-gram sample would be equivalent to 50 μg/kg of each matrix spike compound. The frequency of MS/MSD analysis is given in Section 14.0.

11.2.1.10 A volatile method blank must be analyzed at least once during every 12-hour period, on each GC/MS system used for volatile analysis.

11.2.1.11 For low-level soil/sediment samples, a volatile method blank consists of 5 grams of sodium thiosulfate added to reagent water, spiked with the surrogate compounds and internal standards, and carried through the analytical procedure.

11.2.1.12 An acceptable volatile method blank for low-level soil samples must contain less than five times the Practical Quantitation Limit (PQL) of methylene chloride, acetone, and 2-butanone and less than the PQL of any other volatile target compound.

11.2.1.13 All volatile analyses associated with a blank that do not meet the requirements above (i.e., a contaminated blank), must be repurged, reanalyzed, and reported.

11.2.1.14 The volatile method blank must be analyzed after the calibration standards to ensure there is no carryover of material from the standards into samples.

11.2.2 Medium-level Soil Method

11.2.2.1 The medium-level soil method is based on extracting the soil/sediment sample with methanol. An aliquot of methanol extract is added to reagent water containing the surrogate compounds and the internal standards. Reagent water containing the methanol extract is purged at ambient temperature. All samples with a concentration > 1.0 mg/kg of volatile organics must be analyzed by the medium-level method. If saturated peaks occurred, or would occur when a 1-gram sample was analyzed, the medium-level method must be used.

11.2.2.2 The GC/MS system will be set up before the addition of the methanol extract to reagent water. Because the methanol extract and reagent water mixture is purged at ambient temperature, the instrument performance check, initial calibration, and continuing calibration for water samples may be used for analyses of medium soil sample extracts.

11.2.2.3 The following table can be used to determine the volume of methanol extract to add to the 5 mL for reagent water for analysis.

Note: All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of linear range of the curve.

Estimated Concentration Range[a] (μg/kg)	Take this Volume of Methanol Extract[a] (μL)
500—10,000	100
1,000—20,000	50
5,000—100,000	10
25,000—500,000	100 of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding the table.

[a]Volume of methanol added to the 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a volume of 100 μL added to the syringe.

[b]Dilute an aliquot of the methanol extract and then take 100 μL for analysis.

11.2.2.4 Remove plunger from 5-mL Luerlock type syringe equipped with syringe valve and fill with reagent water to create a positive meniscus. Replace plunger and compress water to vent trapped air. Adjust volume to 4.9 mL. Pull plunger back to 5 mL to allow volume for addition of sample and standards. Add 10 μL each of surrogate spiking solution and of the internal standard solution. Also add the volume for methanol extract determined in step 11.2.2.3 and a volume of clean methanol to total 100 μL (excluding methanol in standards).

11.2.2.5 Attach syringe-syringe valve assembly to syringe valve on purging device. Open syringe valve and inject water/methanol sample into purging chamber.

11.2.2.6 Proceed with analysis. Analyze all method blanks and calibration standards on same instrument as samples.

11.2.2.7 To prepare matrix spike and matrix spike duplicate for medium-level soil/sediment samples, add 8.0 mL of methanol, 1.0 mL of surrogate spiking solution, and 1.0 mL of matrix spike solution to each of two additional aliquots of soil/sediment sample chosen for spiking. This results in a 6,200-μg/kg concentration of each matrix spike compound when added to a 4-gram sample. Add a 100-μL aliquot of this extract to 5 mL of water for purging.

11.2.2.8 A volatile method blank must be analyzed at least once during every 12-hour period on each GC/MS system used for volatile analysis.

11.2.2.9 For medium-level soil/sediment samples, a volatile method blank consists of 100 μL of methanol from vials (prepared in Section 10) injected into 5 mL of reagent water, spiked with 10 μL each of surrogate spiking solution and internal standard solution, and carried through the analytical procedure.

11.2.2.10 An acceptable volatile method blank for medium-level soil/sediment samples must contain less than five times the Practical Quantitation Limit (PQL) of methylene chloride, acetone, and 2-butanone and less than the PQL of any other volatile target compound.

11.2.2.11 All volatile analyses associated with a blank that does not meet the requirements above (i.e., a contaminated blank) must be repurged and reanalyzed.

11.2.2.12 The volatile method blank must be analyzed after the calibration standards to ensure there is no carryover of material from standards into samples.

11.3 Qualitative Analysis

11.3.1 The compounds listed in the Target Compound List (TCL) (i.e., target compounds and supplemental target compounds) shall be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications: (1) elution of the sample component at the same GC relative retention time as the standard component, and (2) correspon-dence of the sample component and standard component mass spectra.

11.3.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run in the same 12-hour time period as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

11.3.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes, only if the contractor's GC/MS meets the daily instrument performance requirements for BFB. These standard spectra may be obtained from the run used to obtain reference RRTs.

11.3.4 Requirements for qualitative verification by comparison of mass spectra are as follows:

11.3.4.1 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) must be present in the sample spectrum.

11.3.4.2 Relative intensities of ions must agree within ± 20% between the standard and sample spectra (e.g., for an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70%).

11.3.4.3 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison.

11.3.5 If a compound cannot be verified by all the criteria in step 11.3.4 but the identification is correct in the technical judgment of the mass spectral interpretation specialist, the contractor shall report that identification and proceed with quantification.

11.3.6 A library search shall be executed for nontarget sample components for the purpose of tentative identification. For that purpose, the 1989 (or more recent) release of the NIST/EPA Mass Spectral Library, containing 50,000 spectra, shall be used. Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

11.3.6.1 Up to 10 organic compounds of greatest apparent concentration not listed in Table 1 for the purgeable organic fraction, excluding the surrogates and internal standards shall be tentatively identified by a forward search of the NIST/EPA library (substances with responses less then 10% of the nearest internal standard are not required to be searched in this fashion). Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

11.3.6.2 Relative intensities of major ions in reference spectrum (ions greater than 10% of the most abundant ion) should be present in sample spectrum.

11.3.6.3 Relative intensities of major ions should agree within ± 20% (e.g., for an ion with an abundance of 50 percent of the standard spectra, the corresponding sample ion abundance must be between 30 and 70%).

11.3.6.4 Molecular ions present in reference spectrum should be present in sample spectrum.

11.3.6.5 Ions present in sample spectrum but not in reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.3.6.6 Ions present in reference spectrum but not in sample spectrum should be reviewed for possible subtraction from sample spectrum because of background contamination or coeluting compounds. Data system library reduction programs can sometimes create these discrepancies.

11.3.7 If in technical judgment of the mass spectral interpretation specialist no valid tentative identification can be made, the compound should be reported as unknown. The mass spectral specialist should give additional classification of the unknown compound if possible (i.e., unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

12.0 Calculations

12.1 Water

$$\text{Concentration } \mu g/L = \frac{(A_x)(I_s)(D_f)}{(A_{IS})(RRF)(V_o)} \quad (3)$$

Where:

A_x	=	Area of characteristic ion (EICP) for compound to be measured
A_{IS}	=	Area of characteristic ion (EICP) for specific internal standard
I_s	=	Amount of internal standard added (ng)
RRF	=	Relative response factor from ambient temperature purge of calibration standard
V_o	=	Volume of water purged (mL)
D_f	=	Dilution factor. The dilution factor for analysis of water samples for volatile organic compounds by this method is defined as the ratio of mL of water purged (i.e., V_o above) to the mL of the original water sample used for purging. For example, if 2.5 mL of sample is diluted to 5.0 mL with reagent water and purged, D_f = 5.0 mL/2.5 mL = 2.0. If no dilution is performed, D_f = 1.0.

12.2 Low Soil (4)

$$\text{Concentration (dry weight basis) } \mu g/kg = \frac{(A_x)(I_s)}{(A_{IS})(RRF)(W_s)}$$

Where:

A_x, I_s, A_{IS} RRFs are as given for water

W_s = Dry weight of sample =

$$\frac{\text{wt. of sample added to purge tube (grams)} \times \text{\% dry wt.}}{100}$$

12.3 Medium Soil (5)

$$\text{Concentration (dry weight basis) } \mu g/kg = \frac{(A_x)(I_s)(V_t)(D_f)}{(A_{IS})(RRF)(V_a)(W_s)}$$

Where:

A_x, A_{IS}, I_s, RRFs are as given for water above

V_t = Total volume of the methanol extract (μL) (e.g., 10,000 μL)

V_a = Volume of the aliquot of the methanol extract in microliters (μL) added to reagent water for purging

W_s = Dry weight of sample as defined for low-level soil (grams)

12.4 Sediment/soil samples are reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The percent dry weight is calculated and reported in either instance.

12.5 An estimated concentration for nontarget components tentatively identified shall be determined by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. An estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

12.6 Xylenes (o-, m- and p-isomers) are to be reported as total xylenes, since o- and p-xylene overlap. The concentration of all three xylene isomers must be added together to give the total xylene quantitation.

12.7 Both trans- and cis- stereo isomers of 1,2-dichloroethene are to be reported as total 1,2-dichloroethene. The concentrations of both isomers must be summed to give the total quantitation.

12.8 If the on-column concentration of any compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample repurged. Guidance in performing dilutions and exceptions to this requirement are given below.

12.8.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

12.8.2 The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

12.8.3 Do not submit data for more than two analyses (i.e., the original sample and one dilution) or, if the volatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

12.8.4 Do not dilute MS/MSD samples to get either spiked or nonspiked analytes within calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the SDG Narrative.

12.8.5 For total xylenes, where three isomers are quantified as two peaks, the calibration of each peak should be considered separately; that is, a diluted analysis is not required for total xylenes unless the concentration of either peak separately exceeds 200 μg/L.

12.9 Calculate the recovery of each surrogate compound in all samples, blanks, matrix spikes, and matrix spike duplicates. Determine if the recovery is within limits (Table 6) and report on appropriate form.

Table 6
Surrogate Spike Target Recovery Limits

Surrogate Compound	%R Water	%R Soil
Toluene-d_8	88-110	81-117
4-Bromofluorobenzene	86-115	74-121
Dibromofluoromethane	86-118	80-120

12.9.1 Calculate concentrations of surrogate compounds using the same equations as used for target compounds. Calculate recovery of each surrogate compound (6) as:

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

12.9.2 If the recovery of any surrogate compound is not within limits, the following steps are required.

12.9.2.1 Check to be sure there are no errors in calculations, formulation of the surrogate compound spiking solutions, and internal standards. Also check instrument performance.

12.9.2.2 Reanalyze sample if none of the above steps reveals a problem.

12.9.2.3 Do not reanalyze diluted samples if surrogate compound recoveries are outside the limits.

12.9.2.4 If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD surrogate compound recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require reanalysis and a reanalysis must not be submitted. Document in the narrative the similarity in recoveries of the surrogate compounds in the sample and associated MS/MSD.

12.9.3 If reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, submit only data from the analysis with surrogate compound recoveries within the limits. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

12.9.4 If reanalysis of the sample does not solve the problem (i.e., the surrogate compound recoveries are outside the limits for both analyses), then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes.

12.9.5 For medium-level soil analyses involving methanol extraction, the treatment of surrogate compound recoveries is similar to that for semivolatile surrogate recoveries. If any surrogate compound recovery is outside the limits, reanalyze the methanol extract first to determine if the problem was with the analysis. If reanalysis of the extract does not solve the problem, reextract the medium soil sample and analyze the second extract.

12.9.6 If the recovery of any one surrogate compound in a method blank is outside the limits, then the method blank and all associated samples must be reanalyzed.

12.10 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, for the following, whichever is most frequent:

- Each case of field samples received
- Each 20 field samples in a case
- Each group of field samples of a similar concentration level (soils/ waste)

- Each 14-day calendar period during which field samples were received beginning with the receipt of the first sample in that Sample Delivery Group

12.10.1 Calculate concentrations of matrix spike compounds using the same equations as used for target compounds. Calculate recovery of each matrix spike compound as follows: (7)

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added

12.10.2 Calculate the relative percent difference (RPD) of the recoveries of each compound in the matrix spike and matrix spike duplicate as follows: (8)

$$RPD = \frac{|MSR - MSDR|}{(1/2)(MSR + MSDR)} \times 100$$

Where:

MSR = Matrix spike recovery
MSDR = Matrix spike duplicate recovery

Note: The vertical bars in the formula above indicate the absolute value of the difference, so RPD is always expressed as a positive value.

12.10.3 The limits for matrix spike compound recovery are given in Table 7. As these limits are only advisory, no further action by the laboratory is required, although this non-conformance must be noted in the data package case narrative.

Table 7
Matrix Spike Recovery Target Acceptance Limits

Compound	%R Water	%R Soil
1,1-Dichloroethane	61-145	59-172
Trichloroethene	71-120	62-137
Benzene	76-127	66-142
Toluene	76-125	59-139
Chlorobenzene	75-130	60-133

12.11 Method Blanks

12.11.1 Determine the concentrations of any target compounds detected in the volatile method blank. The method blank must contain less than or equal to the PQL for the target compounds, except for methylene chloride, acetone, and 2-butanone, which must be less than or equal to 5 times the PQL. For soil/sediment method blanks, PQL value must be adjusted for percent moisture.

12.11.2 If a laboratory method blank exceeds these criteria, the laboratory must consider the analytical system to be out of control. The source of contamination must be investigated and appropriate corrective measures taken and documented before further sample analysis proceeds. All samples processed with a method blank that is out of control (i.e., contaminated) must be reextracted, repurged, and reanalyzed. All problems and corrective actions must be addressed in the case narrative.

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Level, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	Every 12 hours	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	1/20	80—120%	Qualify data
Surrogate Spikes	Every sample	12.9	Reanalyze, then qualify data
Matrix Spike	1/20	12.9	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10	90—110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Surrogate Spikes	Every sample	12.9	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	12.9.3	Qualify data
BFB	Every 12 hours	A/S	Recalibrate
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
BFB	bromofluorobenzene
A/S	as specified earlier in this method
RPD	relative percent difference
LCS	laboratory control sample
12.9	MS/MSD target acceptance limits are summarized in Section 12.9

15.0 References

15.1 *Test Methods for Evaluating Solid Waste,* EPA SW-846, 3rd ed., Method 8260.

15.2 *Contract Laboratory Program Statement of Work.* Rev. February 1988.

FM-ORG-0020

4174

Aromatic Volatile Organic Compounds by Gas Chromatography/Photoionization Detector

Working Linear Range: Matrix and analyte specific
Reporting Limit: Matrix dependent
Reporting Units: Water, μg/L; solids (dry weight), μg/kg
Matrix: Water, soil, sediment, or sludge

1.0 Scope and Application

The method is used to determine the concentration of various aromatic volatile organic compounds. Target compounds and the practical quantitation limits (PQLs) are summarized in Table 1.

Table 1
Practical Quantitation Limits (PQLs)[a] for Aromatic Volatile Organics

Compound	Practical Quantitation Limits Water (μg/L)	Practical Quantitation Limits Soil[b] (μg/kg)
Benzene	1	1
Chlorobenzene	1	1
1,4-Dichlorobenzene	5	5
1,3-Dichlorobenzene	5	5
1,2-Dichlorobenzene	5	5
Ethylbenzene	1	1
Toluene	1	1
Xylenes	5	5

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.
[b]PQLs listed for soil/sediment samples are based on wet weight. Normally, data is reported on a dry weight basis; therefore, PQLs will be higher, based on the percent moisture in each sample.

2.0 Method Summary

1.1 The method describes chromatographic conditions for the detection of aromatic volatile compounds. Samples will be analyzed using a purge-and-trap method, although the method also covers direct injection. The gas chromatograph uses a temperature program to separate the organic compounds. Detection is achieved by a photoionization detector.

1.2 If interferences are encountered, the method specifies an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for confirmation of analytes.

2.0 Interferences

2.1 Contamination by carryover can occur whenever high- and low-level samples are analyzed sequentially. To reduce carryover, the purging device and sampling syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it must be followed by an analysis of reagent water to check for cross-contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high purgeable materials, it may be necessary to wash out the purging device with a detergent solution between analyses, rinse it with distilled water, and then dry it in a 105°C oven. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

2.2 The laboratory where volatile analysis is performed must be completely free of solvents.

3.0 Safety Precautions

3.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

3.2 Because hazardous chemicals are used during the method, procedures for handling organic solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

4.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

5.0 Apparatus

5.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights or peak areas is recommended.

5.2 Columns

5.2.1 Column 1: 30 m × 0.053 mm, I.D. DB-624 (J & W Scientific, Inc. or equivalent) fused silica capillary with 3-μm film thickness.

5.2.2 Column 2: 30 m × 0.32 mm I.D. DB-5 (J & W Scientific, Inc. or equivalent) fused silica capillary with 1-μm film thickness.

5.3 Detector: Photoionization Detector (HNu Systems, Inc. Model PI-51-02 or equivalent).

5.4 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gastight with shutoff valve.

5.5 Volumetric Flasks Class A: 10-, 25-, 50-, 100-, 500-, and 1,000-mL with ground glass stopper.

5.6 Microsyringe: 10- and 25-μL with 0.006-in. I.D. needle (Hamilton 702 N or equivalent), and a 100-μL Hamilton gastight or equivalent.

6.0 Routine Preventive Maintenance

6.1 Perform routine preventive maintenance for the gas chromatograph according to the manufacturer's directions.

6.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

6.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

7.0 Reagents and Calibration Standards

7.1 Water: All references to water assume the use of water in which target compounds are not detected above the method detection limits.

7.2 Stock Standards: Stock solutions may be prepared from commercially available neat standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials must be prepared in a fume hood.

7.2.1 Place about 9.8 mL of methanol in a 10-mL tared ground glass stoppered volumetric flask. Allow the flask to stand unstoppered for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh flask to nearest 0.1 mg.

7.2.2 Using a 100-μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the methanol without contacting the neck of the flask.

7.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting flask several times. Calculate concentration in micrograms per milliliter (μg/mL) from net gain in weight. When compound purity is assayed to be 96% or greater, weight may be used without correction to calculate concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source traceable to NIST.

7.2.4 Transfer stock standard solution into Teflon-sealed screw-cap bottle. Store with minimal headspace at 4°C and protect from light.

7.2.5 All standards should be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.3 Secondary Dilution Standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed. Secondary dilution standards should be prepared at concentrations such that aqueous calibration standards prepared will bracket the working range of the analytical system. Secondary dilution standards should be stored at less than 4°C with minimal headspace for volatiles and checked frequently for signs of degradation or evaporation, especially just before preparing calibration standards from them.

7.4 Calibration Standards: Calibration standards at a minimum of five concentration levels are prepared in water from the secondary dilution of the stock standards. One concentration level should be near but above the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or define the working range of the gas chromatograph. Each standard should contain each analyte for detection by this method (i.e., all compounds listed in Table 1 should be included). To prepare accurate aqueous standard solutions, the following precautions must be observed.

7.4.1 Do not inject more than 20 μL of alcoholic standards into 100 mL of reagent water.

7.4.2 Use only a 25-μL Hamilton 702 N gastight microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

7.4.3 Rapidly inject alcoholic standard into filled volumetric flask, removing needle as fast as possible after injection.

7.4.4 Mix aqueous standards by inverting flask three times only.

7.4.5 Fill sample syringe from standard solution contained in bowl of flask. Do not use any solution contained in neck of flask.

7.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

7.4.7 Aqueous standards are not stable and should be discarded after 1 hour, unless properly sealed and stored. Aqueous standards can be stored below 4°C, up to 24 hours, if held in sealed vials with zero headspace.

7.4.8 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest.

7.4.9 Analyze each calibration standard, adding 10 μL of internal standard spiking solution directly to syringe.

7.5 Internal Standards: The compound 1,4-difluorobenzene will be used as an internal standard. The working standard will be at a concentration of 15 ng/μL.

7.6 Surrogate Standards: The compound bromofluorobenzene will be used as the surrogate spiking compound. The working standard will be at a concentration of 15 ng/μL.

7.7 Methanol: Burdick and Jackson, purge-and-trap grade or equivalent must be demonstrated to be free of volatile target analyte contamination before use by analyzing 100 μL of methanol in 5 mL reagent water. Store away from other solvents.

7.8 Matrix Spike Solution: Use a mid-range calibration standard, e.g., 15 ng/μL.

7.9 Laboratory Control Sample: Identical to the 15-ng/μL standard, but the target compound calibration standards are obtained from an independent source.

8.0 Calibration Procedures

8.1 Calibrate chromatographic system using internal standard technique.

8.2 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent.

8.3 One standard should be at a concentration near but above the method detection limit. The other concentrations should correspond to expected range of concentrations found in real samples or define working range of gas chromatograph detector.

8.4 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g., 2- to 5-μL injection, purge-and-trap, etc.). For soil/sediment samples, a separate calibration is required using heated purge-and-trap techniques. Tabulate the peak height or area responses against concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows.

$$RF = (A_s C_{IS})/(A_{IS} C_s) \quad (1)$$

Where:

A_s = Response for analyte to be measured
C_{IS} = Concentration of internal standard (μg/L)
A_{IS} = Response for internal standard
C_S = Concentration of analyte (μg/L)

8.5 If the RF value over the working range is constant (< 20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculation. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{IS} versus RF.

8.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the predicted response by more than $\pm$ 15%, a new calibration curve must be prepared for the compound.

8.7 Retention-Time Windows: Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms (Table 2).

Table 2
Chromatographic Retention Times

Compound	Retention Time (minutes) Column 1	Column 2
Benzene	5.67	7.41
Chlorobenzene	13.01	14.33
1,4-Dichlorobenzene	18.39	17.63
1,3-Dichlorobenzene	18.14	17.47
1,2-Dichlorobenzene	19.17	17.79
Ethylbenzene	13.39	14.73
Toluene	10.00	11.51
Xylenes	13.69	15.30

8.7.1 When the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

8.7.2 The laboratory must calculate retention time windows for each standard on each gas chromatograph column and whenever a new column is installed.

9.0 Sample Preparation

Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap techniques.

10.0 Sample Analysis

10.1 Gas Chromatography Conditions (Recommended)

10.1.1 Column 1: Set helium gas flow rate at 15 mL/min. The temperature program sequences are as follows: operate at 10°C isothermal for 5 minutes; then program at 6°C/minute to 160°C and hold until all compounds have eluted. Column 1 can separate a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column.

10.1.2 Column 2: Set helium gas flow rate at 4 mL/minute. The temperature program sequence is as follows: 10°C isothermal for 5 minutes, then 6°C/minute to 145°C and hold until all compounds have eluted. Resolution between some of the aromatics is not as efficient as with Column 1; Column 2 should be used as a confirmatory column.

10.1.3 Introduce volatile compounds into the gas chromatograph using either purge-and-trap or the direct injection method. For the internal standard calibration technique, add 10 μL of internal standard to the sample before purging.

10.1.4 In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10-μL syringe may be appropriate. The detection limit is very high (about 10,000 μg/L); therefore, it is only permitted when concentrations exceeding 10,000 μg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

10.1.5 Table 2 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method.

10.1.6 If analytical interferences are suspected or for the purpose of confirmation, analysis use of the second column is recommended.

10.1.7 If the response for a peak is off-scale, prepare a dilution of the sample with reagent water. The dilution must be performed on a second aliquot of the sample that has been properly sealed and stored before use.

10.1.8 A mid-level standard must be injected at the end of the analysis sequence. The calibration factor for each analyte to be quantitated must not exceed a 10% difference when compared to the initial standard of the analysis sequence.

10.2 Water Samples: Remove 5-mL syringe barrel from oven and allow to cool to ambient temperature; then attach closed syringe valve. Open sample, which has been allowed to come to ambient temperature, and carefully pour sample into syringe barrel to create a positive meniscus. Replace syringe plunger and compress sample. Open syringe valve and vent residual air while adjusting sample volume to 5 mL. This process of taking an aliquot destroys the validity of the sample for future analysis, so if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample

integrity. The second sample is maintained only until the analyst has determined that the first sample has been analyzed properly. If a second analysis is needed, it must be analyzed within 24 hours. Care must also be taken to prevent air from leaking into the syringe.

10.2.1 The following procedure will allow for dilutions near the calculated dilution factor from a screening procedure:

10.2.1.1 Make all dilutions in volumetric flasks (10- to 100-mL).

10.2.1.2 Select volumetric flask that will allow for necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

10.2.1.3 Calculate approximate volume of reagent water that will be added to volumetric flask, and add slightly less than this quantity of reagent water to flask.

10.2.1.4 Inject proper aliquot from syringe into volumetric flask. Aliquots in less than 1-mL increments are prohibited. Dilute flask to mark with reagent water. Cap flask and invert three times.

10.2.1.5 If this is an intermediate dilution, use it and repeat above procedure to achieve larger dilutions.

10.2.1.6 Fill 5-mL syringe with diluted sample.

10.2.2 Add 10 μL of the surrogate spiking solution and 10 μL of the internal standard spiking solution through valve bore of syringe; then quickly close valve.

10.2.3 Attach syringe-syringe valve assembly to syringe valve on purging device. Open syringe valves and inject sample into purging chamber.

10.2.4 Close both valves and purge sample onto trap for 12.0 $\pm$ 0.1 minutes at ambient temperature.

10.3 Water-miscible Liquids: Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with reagent water.

10.3.1 Initial and serial dilutions can be prepared by transferring 2 mL of sample to 100-mL volumetric flask and diluting to volume with reagent water. Transfer immediately to 5-mL gastight syringe.

10.3.2 Alternatively, prepare dilutions directly in 5-mL syringe filled with reagent water by adding at least 20 μL but not more than 100 μL of liquid sample. Sample is ready for addition of 10-μL surrogate, 10-μL internal and, if applicable, matrix spiking standards. Attach syringe valve on purging device. Open syringe valves and inject sample into purging chamber. Close both valves and purge sample onto trap for 12.0 $\pm$ 0.1 minutes at ambient temperature.

10.4 Sediment/Soil and Waste Samples: It is highly recommended that all samples of this type be screened before purge-and-trap gas chromatograph analysis. Samples may contain percent quantities of purgeable organics that will contaminate purge-and-trap system, requiring extensive cleanup and instrument downtime.

10.4.1 Low-level Method: The low-level method is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste of a similar consistency (granular and porous). The method is based on purging a heated sediment/soil sample mixed with reagent water containing the surrogate and internal, and if applicable, matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples.

10.4.1.1 Use 5-gram sample if expected concentration is < 0.1 mg/kg or 1-gram sample for expected concentrations between 0.1 and 1 mg/kg.

10.4.1.2 Prepare and use heated purge calibration curve for quantitation of all samples analyzed with low-level method.

10.4.1.3 Remove the plunger from 5-mL Luerlock type syringe equipped with syringe valve and fill to create positive meniscus with reagent water. Replace plunger and compress water to vent trapped air. Adjust volume to 5.0 mL. Add 10 μL each of surrogate spiking solution and internal standard solution to syringe through valve (surrogate spiking solution and internal standard solution may be mixed together). Matrix spiking solutions, if indicated, should be added (10 μL) to sample at this time.

10.4.1.4 Add spiked reagent water to purge device containing weighed amount of sample and connect device to purge-and-trap system.

10.4.1.5 Heat sample to 40° $\pm$ 1°C and purge sample for 12.0 $\pm$ 0.1 minutes at 40-mL/minute flow rate.

10.4.1.6 If saturated peaks occurred or would occur if 1-gram sample were analyzed, the high-level method must be followed.

10.4.2 High-level Method: The high-level method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. An aliquot is added to reagent water containing surrogate, internal standard, and if applicable, matrix spiking standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

10.4.2.1 For sediment/soil and waste that are insoluble, weigh 4 grams of sample into tared 20-mL vial. For waste that is soluble in methanol, weigh 1 gram into tared scintillation vial.

10.4.2.2 Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

10.4.2.3 Use disposable pipet to transfer approximately 1 mL of extract to gas chromatograph vial for storage. Dispose of remaining solution. Transfer about 1 mL of reagent methanol to a separate gas chromatograph vial for use as the method blank for each set of samples. Extracts should be stored at 4°C in the dark before analysis.

10.4.2.4 Remove plunger from 5.0-mL Luerlock type syringe equipped with syringe valve and fill to create positive meniscus with reagent water. Replace the plunger and compress water to vent trapped air. Adjust volume to 4.9 mL. Pull plunger back to 5.0 mL to allow volume for addition of sample extract and of standards. Add 10 μL of internal standard solution. Also add volume of methanol extract to a total of 100 μL (excluding methanol in standards).

10.4.2.5 Attach syringe/syringe valve assembly to the syringe valve on purging device. Open syringe valve and inject the water/methanol sample into purging chamber. Close both valves and purge sample for 12.0 $\pm$ 0.1 minutes at ambient temperature.

10.4.2.6 Analyze all reagent blanks on same instrument as that used for samples. Standards and blanks should also contain 100 μL of methanol to simulate sample conditions.

10.4.2.7 For a matrix spike in the high-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of working surrogate spike solution, and 1.0 mL of working matrix spike solution. Add 100-μL aliquot of extract to 5 mL of water for purging.

11.0 Calculations

12.1 Water Samples: Calculate the concentration of target analytes in the sample using the equation: (3)

$$\text{Concentration } \mu g/L = \frac{(A_x)(I_s)(D_f)}{(A_{IS})(RRF)(V_o)}$$

Where:

A_x = Area of characteristic ion (EICP) for compound to be measured

A_{IS} = Area of characteristic ion (EICP) for specific internal standard

I_s = Amount of internal standard added in (ng)

RRF = Relative response factor from ambient temperature purge of calibration standard

V_o = Volume of water purged (mL)

D_f = Dilution factor. The dilution factor for analysis of water samples for volatile organic compounds by this method is defined as the ratio of mL of water purged (i.e., V_o above) to the mL of the original water sample used for purging. For example, if 2.5 mL of sample is diluted to 5.0 mL with reagent water and purged, D_f = 5.0 mL/2.5 mL = 2.0. If no dilution is performed, D_f = 1.0.

12.2 Low-level Soil/Sediment Samples: Calculate the concentration of target analytes in the sample using the equation: (4)

(3)

$$\text{Concentration (dry weight basis) } \mu g/kg = \frac{(A_x)(I_s)}{(A_{IS})(RRF)(W_s)}$$

Where:

A_x, I_s, A_{IS} RRFs are as given for water

W_s = Dry weight of sample =

$$\frac{\text{wt. of sample added to purge tube (grams)} \times \text{\% dry wt.}}{100}$$

12.3 Medium- and High-level Soil/Sediment Samples: Calculate the concentration of target analytes in the sample using the equation: (5)

(4)

$$\text{Concentration (dry weight basis) } \mu g/kg = \frac{(A_x)(I_s)(V_t)(D_f)}{(A_{IS})(RRF)(V_a)(W_s)}$$

Where:

A_x, A_{IS}, I_s, RRFs are as given for water above

V_t = Total volume of the methanol extract (μL) (e.g., 10,000 μL)

V_a = Volume of the aliquot of the methanol extract in microliters (μL) added to reagent water for purging

W_s = Dry weight of sample as defined for low-level soil (grams)

12.4 Calculate concentrations of surrogate compounds using the same equations as used for target compounds. Calculate recovery of each surrogate compound as:

$$\%R = \frac{\text{Concentration (or amount) found} \times 100}{\text{Concentration (or amount) spiked}}$$ (6)

12.5 Calculate concentrations of matrix spike compounds using the same equations as used for target compounds. Calculate recovery of each matrix spike compound as follows: (7)

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control and reporting requirements are determined by the method, Analytical Support Level, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	Begin and end	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	1/20	80—120%	Qualify data
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike	1/20	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	Begin and end	90—110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	1/20	80—120%	Recalibrate
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike	1/20	75—125%	Qualify data
MSD	1/20	75—125%	Qualify data
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
End	end of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
A/S	as specified earlier in this method
RPD	relative percent difference

15.0 References

Test Methods for Evaluating Solid Waste, 3rd ed., EPA SW-846, Method 8020. 1986.

FERNALD\btex.51

FM-ORG-0030

Chlorinated Pesticides/PCBs by Gas Chromatography

Working Linear Range:	To be determined. Analyte- and matrix-dependent
Reporting Limits:	Required reporting limits are listed in Table 1
Reporting Units:	Liquids, μg/L; solids, μg/kg
Matrix:	Waters, soils, sludges, and wastes

1.0 Scope and Application

1.1 This method describes procedures to analyze water, soil, sludges, and wastes for chlorinated pesticides/PCBs. The extraction procedure to be used must be appropriate for sample matrix.

1.2 Target compounds and the corresponding practical quantitation limits (PQLs) for this method are listed in Table 1.

2.0 Method Summary

A measured amount of sample is extracted with methylene chloride. Appropriate cleanup procedures are employed to remove or minimize interferences from the matrix. The extract is then dried and exchanged to hexane during concentration to a volume of 10 mL or less. The extract is separated by gas chromatography, and the parameters of interest are measured with an electron capture detector (ECD) or Hall electrolytic conductivity detector (HECD). Confirmation of tentatively identified parameters is required. This may be accomplished by using a second confirmation GC column or GC/MS techniques.

Table 1
Target Analytes and Required Reporting Limits

Compound	Water/Matrix (µg/L)	Soil/Sediment (µg/kg)
Aldrin	0.01	8.0
a-BHC	0.01	8.0
6b-BHC	0.02	8.0
d-BHC	0.01	8.0
g-BHC	0.01	8.0
Chlordane	0.1	80
4,4'-DDD	0.02	16
4,4'-DDE	0.02	16
4,4'-DDT	0.02	16
Dieldrin	0.02	16
Endosulfan I	0.02	8.0
Endosulfan II	0.02	16
Endosulfan Sulfate	0.02	16
Endrin	0.02	16
Endrin Aldehyde	0.02	16
Endrin Ketone	0.02	16
Heptachlor	0.01	8.0
Heptachlor Epoxide	0.01	8.0
Methoxychlor	0.5	160
Toxaphene	0.5	160
PCB 1016	0.8	80
PCB 1221	2	80
PCB 1232	2	80
PCB 1242	0.8	80
PCB 1248	0.4	80
PCB 1254	0.2	160
PCB 1260	0.2	160

3.0 Interferences

3.1 It is not unusual for interferences to be present in most extracts. Interferences can cause extraneous peaks, deteriorate peak resolution, degrade column efficiency, lower detector sensitivity, and shorten the life of columns. They may be removed or minimized by one or more cleanup procedures. The choice of procedure to be employed is dictated by the extent and type of interferences present. (Endrin aldehyde can be removed by alumina cleanup, so alumina cleanup is usually not recommended if endrin aldehyde is to be quantitated.)

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. Interference from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

3.3 Interferences may also be caused by contamination in solvents, reagents, glassware, and other sample-processing hardware. All these materials must be demonstrated to be free of interferences under the conditions of the analysis by running laboratory method blanks.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids and bases must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

4.3 The following have been tentatively classified as known or suspected carcinogens: 4,4′-DDT, 4,4′-DDD, BHCs, and PCBs. These materials must be handled under a fume hood.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Separatory Funnel Extraction (for Water Samples)

6.1.1 Separatory Funnel: 2-liter, with Teflon stopcock.

6.1.2 Drying Column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom or equivalent and a Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing the column with adsorbent.

6.1.3 Kuderna-Danish (K-D) Apparatus

6.1.3.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Use ground-glass stopper to prevent evaporation of extracts.

6.1.3.2 Evaporation Flask: 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.1.3.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.1.3.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.1.4 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.1.5 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath must be used in a fume hood.

6.1.6 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

6.1.7 pH Indicator Paper: pH range including the desired extraction pH.

6.1.8 Erlenmeyer Flask: 250-mL, glass.

6.1.9 Syringe: 5-mL, Hamilton gastight or equivalent.

6.1.10 Graduated Cylinder: 1-liter, glass.

6.2 Continuous Liquid-Liquid Extraction (for Water Samples)

6.2.1 Continuous Liquid-Liquid Extractor: Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor—Ace Glass Company, Vineland, New Jersey, P/N 6841-10, or equivalent).

6.2.2 Drying Column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom or equivalent and a Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing the column with adsorbent.

6.2.3 Kuderna-Danish (K-D) Apparatus

6.2.3.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Use ground-glass stopper to prevent evaporation of extracts.

6.2.3.2 Evaporation Flask: 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.2.3.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.2.3.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.2.4 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.2.5 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). Bath must be used in a fume hood.

6.2.6 Vials: Glass, 2-, 10-, and 20-mL capacity, with Teflon-lined screw cap.

6.2.7 pH Indicator Paper: pH range including the desired extraction pH.

6.2.8 Heating Mantle: Rheostat controlled.

6.2.9 Syringe: 5-mL, Hamilton gastight or equivalent.

6.2.10 Graduated Cylinder: 1-liter, glass.

6.3 Sonication Extraction (for Soils, Sludges and Wastes)

6.3.1 Sonication: Use a horn-type sonicator equipped with a titanium tip. The following sonicator, or an equivalent brand and model, is recommended.

> Ultrasonic Cell Disrupter: Heat Systems–Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent. Power wattage must be at least 375 with pulsing capability and No. 200 1/2-inch Tapped Disrupter Horn) plus No. 207 3/4-inch Tapped Disrupter Horn, and No. 419 1/8-inch Standard Tapered microtip probe.

6.3.2 Sonabox: Recommended with above disrupters for decreasing cavitation sound (Heat Systems–Ultrasonics, Inc., Model 432B or equivalent).

6.3.3 Apparatus for Determining Percent Moisture

6.3.3.1 Drying Oven.

6.3.3.2 Desiccator.

6.3.3.3 Porcelain Crucibles.

6.3.4 Pasteur Glass Pipets: Disposable, 1-mL.

6.3.5 Beakers: 400-mL.

6.3.6 Vacuum Filtration Apparatus

6.3.6.1 Buchner Funnel.

6.3.6.2 Filter Paper: Whatman No. 41 or equivalent.

6.3.7 Kuderna-Danish (K-D) Apparatus

6.3.7.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent).

6.3.7.2 Evaporator Flask: 500-mL (Kontes K-570001-0500 or equivalent).

6.3.7.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.3.7.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.3.8 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.3.9 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). Bath must be used in a fume hood.

6.3.10 Balance: Top-loading, capable of accurately weighing 0.01 gram.

6.3.11 Vials and Caps: 2-mL volume, suitable for GC autosampler tray.

6.3.12 Glass Scintillation Vials: At least 20-mL, with screw-cap and Teflon or aluminum foil liner.

6.3.13 Spatula: Stainless steel or Teflon.

6.3.14 Drying Column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use small pad of Pyrex glasswool to retain adsorbent. Prewash glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing column with adsorbent.

6.3.15 Syringe: 5-mL, Hamilton gastight or equivalent.

6.4 Soxhlet Extraction (for Soils, Sludges and Wastes)

6.4.1 Soxhlet Extractor: 40-mm I.D., with 500-mL round-bottom flask.

6.4.2 Drying Column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use small pad of Pyrex glass wool to retain adsorbent. Prewash glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing column with adsorbent.

6.4.3 Kuderna-Danish (K-D) Apparatus

6.4.3.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Use ground-glass stopper to reduce evaporation of extracts.

6.4.3.2 Evaporation Flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

6.4.3.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.4.3.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.4.4 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.4.5 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). Bath must be used in a fume hood.

6.4.6 Vials: Glass, 2-, 10-, and 20-mL capacity, with Teflon-lined screw cap.

6.4.7 Glass or Paper Thimble or Glass Wool: Contaminant free.

6.4.8 Heating Mantle: Rheostat controlled.

6.4.9 Syringe: 5-mL, Hamilton gastight or equivalent.

6.4.10 Apparatus for Determining Percent Moisture

6.4.10.1 Drying Oven.

6.4.10.2 Desiccator

6.4.10.3 Porcelain Crucibles

6.4.11 Apparatus for Grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue No. 8-323, or an equivalent brand and model, is recommended for sample processing. The grinder should handle most solid samples, except gummy, fibrous, or oily materials.

6.5 Florisil Column Cleanup

6.5.1 Beaker: 500-mL, glass.

6.5.2 Chromatographic Column: 300-mm long × 10-mm I.D. or 400-mm-long × 20-mm I.D., with Pyrex glass wool at bottom and a Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use small pad of Pyrex glass wool to retain adsorbent. Prewash glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing column with adsorbent.

6.5.3 Kuderna-Danish (K-D) Apparatus

6.5.3.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Use ground-glass stopper to prevent evaporation of extracts.

6.5.3.2 Evaporation Flask: 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.5.3.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.5.3.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.5.4 Muffle Furnace

6.5.5 Reagent bottle: 500-mL.

6.5.6 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). Bath must be used in a fume hood.

6.5.7 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.5.8 Erlenmeyer Flasks: 50- and 250-mL, glass.

6.6 Sulfur Cleanup

6.6.1 Mechanical Shaker or Mixer: Vortex Genie or similar.

6.6.2 Pipets: Disposable, Pasteur type, glass.

6.6.3 Centrifuge Tubes: Calibrated, 12-mL.

6.6.4 Glass Bottles or Vials: 10-mL and 50-mL, with Teflon-lined screwcaps.

6.7 Gel-Permeation Cleanup

6.7.1 Gel Permeation Chromatography System: Analytical Biochemical Laboratories, Inc., GPC auto prep Model 1002A or equivalent. An automated system of this type is not required, but if one is not used, equivalency of an alternative system must be shown.

6.7.1.1 Chromatographic column: 600- to 700-mm × 25-mm I.D. glass column fitted for upward flow operation.

6.7.1.2 Bio-beads S-X3: 70 grams per column.

6.7.1.3 Pump: Capable of constant flow of 0.1 to 5 mL/min at up to 100 psi.

6.7.1.4 Injector: With 5-mL sample loop.

6.7.1.5 Ultraviolet Detector: Wavelength set at 254 nm (optional).

6.7.1.6 Strip-chart Recorder: Optional.

6.7.1.7 Syringe: 10-mL with Luerlok fitting.

6.7.1.8 Syringe Filter Holder and Filter: Biorad "Prep Disc" sample filter No. 343-0005 and 5-μm size filters or equivalent.

6.7.2 Beakers: 400-mL, glass.

6.8 Gas Chromatograph

6.8.1 The gas chromatograph (GC) system must adequately regulate temperature to give a reproducible temperature program. In addition, it must also have a flow controller that maintains a constant column flow rate throughout the temperature program operations. The system must be suitable for splitless injection and all accessories including syringes, analytical columns, and gases must be available.

6.8.2 Gas chromatographs may have difficulty meeting the pesticides QC requirements because of endrin or DDT degradation in the injector. This problem can be minimized by operating the injector at 200° to 205°C using a Pyrex (not quartz) methyl silicone deactivated injector liner, in addition to deactivating any metal parts in the injector with dichlorodimethyl silane. In some cases, using a 0.25-inch packed column injector converted for use with 0.53-mm capillary columns works better than a Grob-type injector. If a Grob-type injector is used, a 4-mm liner may be required to meet degradation criteria.

6.9 Autosampler

6.10 Data System: Capable of integrating peak signals and producing area counts or heights.

6.11 Chromatographic Columns

6.11.1 J & W DB-5, 30 m × 0.53 mm I.D., 1.0-μm film thickness megabore, or equivalent.

6.11.2 J & W DB-608, 30 m × 0.53 mm I.D., 0.5 to 1.0-μm film thickness megabore, or equivalent.

6.12 Volumetric Flasks, Class A.

6.13 Microsyringe: 10-μL, Hamilton gastight or equivalent.

6.14 Syringe: 5-mL, Hamilton gastight or equivalent.

6.15 Vials: Glass/Teflon with Teflon-lined cap.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the gas chromatograph according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Separatory Funnel Extraction (for Water Samples)

8.1.1 Water: All references to water assume the use of water in which target compounds are not detected above the method detection limits.

8.1.2 Sodium Hydroxide Solution, 10 N NaOH (ACS): Dissolve 40 grams NaOH in water and dilute to 100 mL.

8.1.3 Sodium Sulfate (ACS): Granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

8.1.4 Sulfuric Acid Solution (1:1): Slowly add 50 mL of H_2SO_4 (specific gravity 1.84) to 50 mL of water. Perform in a fume hood. **Caution:** Heat-liberating reaction.

8.1.5 Extraction/Exchange Solvent: Methylene chloride, hexane (pesticide quality or equivalent).

8.2 Continuous Liquid-Liquid Extraction (for Water Samples): Same as 8.1.1 through 8.1.5.

8.3 Sonication Extraction (for Soils, Sludges, and Wastes)

8.3.1 Sodium Sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a pre-labelled glass bottle. (Baker anhydrous powder, catalogue No. 73898, or equivalent.)

8.3.2 Extraction Solvents: Methylene chloride, acetone (pesticide quality or equivalent).

8.3.3 Exchange Solvent: Hexane (pesticide quality or equivalent).

8.4 Soxhlet Extraction (for Soils, Sludges, and Wastes)

8.4.1 Water: All references to water assume the use of water in which target compounds are not detected above the method detection limits.

8.4.2 Sodium Sulfate (ACS): Granular, anhydrous. Purify by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

8.4.3 Extraction Solvents

8.4.3.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems.

- Toluene/Methanol, 10:1 v/v: Pesticide quality or equivalent.
- Acetone/Hexane, 1:1 v/v: Pesticide quality or equivalent.

8.4.3.2 Methylene Chloride: Pesticide quality or equivalent.

8.4.4 Exchange Solvent: Hexane (pesticide quality or equivalent).

8.5 Florisil Column Cleanup

8.5.1 Florisil: Pesticide residue (PR) grade (60/100 mesh); purchase activated at 1,250° F (677°C), stored in glass containers with ground glass stoppers or foil-lined screw caps.

8.5.1.1 Activation of Florisil: Just before use, activate each batch at least 16 hours at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the Florisil in an oven at 130°C. Cool the Florisil before use in a desiccator.

8.5.2 Sodium Sulfate (ACS): Granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray.

8.5.3 Eluting Solvents

8.5.3.1 Diethyl Ether: Pesticide quality or equivalent.

(1) Must be free of peroxides as indicated by EM Quant test strips (available from EM Laboratories Inc., 500 Executive Boulevard, Elmsford, NY 10523).

(2) Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

8.5.3.2 Hexane: Pesticide quality or equivalent.

8.6 Sulfur Cleanup: Triple distilled mercury.

Caution: Elemental mercury is highly toxic; refer to section 10.7.1.

8.7 Gel-Permeation Cleanup

8.7.1 Methylene Chloride: Pesticide quality or equivalent.

8.7.2 GPC Calibration Solutions.

8.7.2.1 Corn Oil: 200 mg/mL in methylene chloride.

8.7.2.2 Bis(2-ethylhexyl)phthalate and Pentachlorophenol Solution: 4.0 mg/mL in methylene chloride.

8.7.2.3 If a UV detector is to be used, prepare 8.7.2.2 as one solution. The individual concentrations should remain the same.

8.8 Surrogate Standard Spiking Solution: 1 μg/mL dibutylchlorendate and 2,4,5,6-tetrachloro-meta-xylene in acetone for waters, soils, and sludges; 10 μg/mL of dibutylchlorendate and 2,4,5,6-tetrachloro-meta-xylene in acetone for wastes.

8.9 Matrix Spiking Solution: Prepare spiking solution of acetone or methanol containing the following pesticides in the following concentrations.

Pesticide	Concentration (μg/mL)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4′-DDT	0.5

8.10 Calibration Standards

8.10.1 Stock Standards: Prepare stock standard solutions at a concentration of 1.00 μg/μL by dissolving 0.010 gram of reference material (traceable, certified material) in the solvent (isooctane, methanol, or toluene) and diluting to volume in a 10-mL volumetric flask. Larger volumes may be prepared. Transfer stock standard solutions into vials with Teflon-lined screw caps or crimp tops. Store at 4°C protected from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just before preparing calibration standards from them. Stock standard solutions should be replaced after 1 year, or sooner if comparison with check standards indicates a problem. When compound purity is 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

8.10.2 Working Calibration Standards: Calibration standards at a minimum of five concentrations for each parameter of interest are prepared through dilution of the stock standards with solvent (methanol or isooctane). One

concentration should be at a concentration near but above the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions should be replaced after 6 months or sooner if comparison with check standards indicates a problem.

8.10.3 For multiresponse pesticides, a single working standard at mid-concentration of the range is prepared.

8.10.4 Internal Standards (if internal standard calibration is used): One or more internal standards that are similar in analytical behavior to the parameters of interest may be used. It must be demonstrated that measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no single internal standard may apply to all samples. 2,4′-DDD is suggested as a possible internal standard for this method. Prepare an internal standard solution containing 20 µg/mL in the solvents. A 10-µL aliquot of this solution is to be spiked into all standards, and extracts of blanks, samples, and control samples.

8.11 Degradation Check Standard: Prepare a midrange-concentration standard solution containing Endrin and 4,4′-DDT in the solvent (isooctane or methanol).

8.12 Laboratory Control Sample: The QC check sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4′-DDD, 10 µg/mL; 4,4′-DDT, 10 µg/mL; endosulfan II, 10 µg/mL; endosulfan sulfate, 10 µg/mL; methoxychlor, 10 µg/mL; and any other single-component pesticide at 2 µg/mL. If the method is to be used only to analyze PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 µg/mL in acetone.

9.0 Calibration Procedures

9.1 Initial Calibration: Calibrate chromatographic system using either external standard technique or internal standard technique (non-CLP).

9.1.1 External Standard Calibration

9.1.1.1 Perform initial calibration by using at least five concentrations of single response standards. One external standard should be at a concentration near but above the required method detection limits. The other concentrations should correspond to the expected range of concentrations found in real samples or define the working range of the detector.

9.1.1.2 Inject 1 μL of each single-response standard. Calculate the calibration factor for each parameter as follows.

$$CF = \frac{A_s}{C_s} \qquad (1)$$

Where:

A_s = Area response for parameter to be measured

C_s = Concentration for parameter to be measured

Calculate relative standard deviation (RSD) of response factors for each parameter as follows:

$$RSD, \% = \frac{\text{Standard deviation } (100)}{\text{Average CF}} \qquad (2)$$

If RSD is less than 20%, average calibration factor may be used to calculate results. Alternatively, prepare a calibration curve of area responses versus the mass injected. If the RSD exceeds 30%, the 5-point calibration must be re-established.

9.1.1.3 A single midrange-concentration standard is used for all multiresponse pesticides.

9.1.2 Internal Standard Calibration

9.1.2.1 Proceed as described for external calibration, except that a 10-μL aliquot of internal standard is added to the standards before injection.

9.1.2.2 Calculate relative response factor (RRF) for each compound in each standard as follows:

$$RRF = \frac{(A_s)\ (C_{IS})}{(A_{IS})\ (C_s)} \qquad (3)$$

Where:

A_s	=	Area response for parameter to be measured
A_{IS}	=	Area response of internal standard
C_s	=	Concentration of parameter to be measured (μg/L)
C_{IS}	=	Concentration of internal standard (μg/L)

If the RSD of the RRFs is less than 20%, the average RF may be used to calculate results. Alternatively, the calibration curve of response ratios A_s/A_{IS} vs. RFs may be used. However, if the RSD exceeds 30%, the 5-point calibration must be re-established.

9.1.2.3 A single midrange concentration to which 10 μL of internal standard solution has been added is used for all multiresponse pesticides.

A set of three to five major peaks is selected for each analyte. Retention times and calibration factors are determined from the initial calibration analysis for each peak.

Quantitation must be accomplished by comparing areas of each of the three to five major peaks of the multiresponse analyte in the sample with the calibration factor for the same peaks established during initial calibration. The concentration of multiresponse analytes is calculated from the area for each major peak of the multiresponse analyte. The concentration of each peak is determined, and then an average concentration for three to five major peaks is determined and reported.

If more than one multiresponse analyte is observed in a sample, the analyst must choose separate peaks to quantitate the different multiresponse analytes. A peak common to both analytes present in the sample must not be used to quantitate either compound.

9.2 Continuing Calibration

9.2.1 Calibration must be verified on each workday and after every 10 determinations using a midrange-concentration standard of each single-response analyte. The standard must also be analyzed at the end of the analytical sequence. The calibration or response factor for each analyte to be quantitated must not exceed a 15% difference when compared to the initial average calibration or response factor. The retention times of all single-response analytes must be within the established retention time windows. No samples may be reported unless they are bracketed by acceptable continuing calibration standards. If the above criteria are not met, determine the cause and perform the maintenance required. Recalibrate the analytical system and reanalyze all samples affected.

9.2.2 Use the retention time of the first continuing calibration standard as the midpoint of the retention time window defined by ± three times the standard deviation. The retention time of all subsequent continuing calibration standards must fall within the window. Otherwise, perform corrective action, recalibrate the system, and reanalyze all affected samples.

9.2.3 Degradation Check Standard: Analyze the degradation check standard to check for endrin and 4,4′-DDT degradation. Calculate the percent breakdown of endrin and 4,4′-DDT as follows:

$$\text{\% Breakdown of 4,4'-DDT} = \frac{\text{Total DDT degrad. peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100 \qquad (4)$$

$$\text{\% Breakdown of endrin} = \frac{\text{(endrin aldehyde + endrin ketone)}}{\text{(endrin + endrin aldehyde + endrin ketone)}} \times 100 \qquad (5)$$

If degradation of either endrin or 4,4′-DDT exceeds 20% or if combined degradation exceeds 30%, perform necessary instrument maintenance and recalibrate analytical system. All samples injected since the last acceptable degradation check must be reanalyzed.

9.3 Acceptance Criteria for Chromatograms of Calibration Standards

9.3.1 Identification of pesticides is based on retention time data and confirmed by both GC columns.

9.3.2 The identification of single-component pesticides by gas chromatographic methods is based primarily on retention time data. The retention time of the apex of a peak can be verified only from an on-scale chromatogram. The identification of multi-response analytes is based primarily on recognition of patterns of retention times displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single-response and multiresponse analytes.

9.3.3 The standard chromatograms of the single-response analytes during the initial calibration sequence must display the analytes present in each standard at greater than 10% of full scale but less than 100% of full scale.

9.3.4 The chromatograms of the standards for the multiresponse analytes analyzed during the initial calibration sequence must display the peaks chosen for identification of each analyte at greater than 25% and less than 100% of full scale.

9.3.5 For any standard containing alpha-BHC, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

9.3.6 If a chromatogram is replotted electronically to meet requirements, the scaling factor used must be displayed on the chromatogram.

9.3.7 If the chromatogram of any standard needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

10.0 Sample Preparation

10.1 Water samples may be extracted using separatory funnel techniques. If emulsions prevent phase separation with separatory funnel extraction, continuous extraction techniques may be used. Separatory funnel extraction is the method of choice for wastewater. Nonaqueous samples are to be extracted using either the Soxhlet or sonication method.

10.2 Separatory Funnel Extraction (for Water Samples)

10.2.1 Measure a 1-liter aliquot of the sample and place into 2-liter separatory funnel. Measure and record native pH of the sample using wide range pH paper. Adjust sample pH to a value between 6 and 8. Pipet 1.0 mL of surrogate spiking solution into separatory funnel and mix well. Add 1.0 mL of surrogate spiking solution and 1.0 mL of matrix spiking solution to matrix spike and matrix spike duplicate samples. Add twice as much surrogate and matrix spiking solutions if using GPC cleanup.

10.2.2 Check sample pH with wide-range pH paper and, if necessary, adjust pH to 5 to 9.

10.2.3 Add 60 mL of methylene chloride to separatory funnel and extract sample by shaking funnel for 2 minutes, with periodic venting to release excess pressure.

Caution: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Allow organic layer to separate from water phase. If an emulsion interface between layers is more than one-third of the total solvent volume, centrifugation must be employed to improve phase separation. If centrifugation fails to separate the layers, then continuous liquid-liquid extraction techniques must be used.

10.2.4 Collect methylene chloride extract in a 250-mL Erlenmeyer flask. Add a second 60-mL volume of methylene chloride to separatory funnel and repeat extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.2.5 Prepare a drying column about 10 cm high using granular anhydrous sodium sulfate. Pre-rinse column with about 20 mL of methylene chloride allowing rinse to be wasted. Attach a 10-mL concentrator tube to a 500-mL K-D evaporative flask and position the apparatus below the drying column as a receiver.

10.2.6 Dry combined pesticide/PCB extract by pouring it through the drying column. Post-rinse column with about 20 mL of methylene chloride to quantitatively transfer extract to K-D receiver. Add a boiling chip to the extract, and connect a three-ball macro Snyder column. Extract is now ready for concentration and solvent exchange.

Caution: If extract is allowed to approach dryness, compounds of interest will be lost. If extract accidentally goes to dryness, discard extract and start over.

10.2.7 Prewet Snyder column with about 1 mL of methylene chloride. Support K-D apparatus on water bath allowing concentrator tube to extend below surface of boiling water while lower regions of K-D flask are bathed with steam. At proper rate of solvent evaporation, the balls of the Snyder column will chatter. When apparent volume of extract reaches 2 mL, remove K-D apparatus from steam bath and allow glassware to cool at least 10 minutes.

10.2.8 After cooling, K-D apparatus may be disassembled beginning with 3-ball Snyder column. A 5-mL syringe filled with methylene chloride should be used to rinse upper joint and interior walls of the K-D. Disconnect K-D from concentrator tube and rinse lower joint surface areas also, allowing rinse solvent to mix with extract, and connect 2-ball Snyder column to concentrator tube.

10.2.9 Prewet Snyder column with about 0.5 mL of methylene chloride. Return to hot water bath and further concentrate extract to about 2 mL. Allow extract to cool.

10.2.10 Momentarily, remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Concentrate the solvent extract as before. When the apparent volume of liquid reaches 3 to 5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Do not allow the evaporator to go dry.

10.2.11 Allow extract to cool before detaching Snyder column. Rinse down joint and interior walls of concentrator tube with small amount of hexane. If alumina column cleanup is not to be performed at this step, then adjust volume of extract to 10 mL for screening and analysis.

10.3 Continuous Liquid-Liquid Extraction (for Water Samples)

10.3.1 Transfer 1-liter aliquot of sample to continuous extractor. Check sample pH with wide-range pH paper and adjust pH, if necessary to 5 to 9. Add 1.0 mL of surrogate spiking solution. For any matrix spike, add both surrogate spiking solution and 1.0 mL of matrix spiking solution. Add twice as much surrogate and matrix spiking solution if GPC cleanup is to

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be done. Ensure that enough methylene chloride solvent is present in distilling flask for proper operation of extractor (300-500 mL). Add 2 or 3 boiling chips and extract sample for 18 to 24 hours.

10.3.2 Collect, dry, and concentrate the extract according to procedures described for separatory funnel extraction (paragraph 10.2).

10.4 Sonification Extraction (for Soils, Sludges, and Wastes)

10.4.1 Decant and discard any water layer on sediment sample. Mix sample thoroughly and discard any foreign objects such as sticks, leaves, and rocks.

10.4.2 Waste samples consisting of multiple phases should be separated into different phases before extraction. The percent weight or volume of each phase should be determined and each phase analyzed individually.

10.4.3 Grind or otherwise subdivide dry waste amenable to grinding so that it either passes through a 1-mm sieve or can extruded through a 1-mm hole.

10.4.4 Weigh 30 grams of the sample to the nearest 0.1 gram into a 400-mL beaker and add 60 grams of anhydrous sodium sulfate. Mix well until a dry sandy texture is obtained. Add more sodium sulfate if necessary to achieve a dry texture. Immediately add 1.0 mL of surrogate spiking solution and 1.0 mL of matrix spiking solution if performing matrix spike analysis. Add twice as much surrogate and matrix spiking solution if GPC cleanup is to be done. Mix thoroughly. Perform mixing step rapidly to prevent loss of volatile compounds. Add 100 mL of 50:50 methylene chloride:acetone.

10.4.5 Weigh 5 to 10 grams of sediment into a tared aluminum weighing boat. Determine percent moisture by drying overnight at 105°C. Allow to cool before weighing. Concentrations of individual analytes will be reported relative to dry weight.

10.4.6 Place bottom surface of tip of disrupter horn about 0.5 inch below surface of solvent but above sediment layer. Sonicate soil for 3 minutes. Sonicator should be adjusted to minimum output power required to suspend matrix using 50% duty cycle. Centrifuge and decant solvent into a 500-mL Erlenmeyer flask.

10.4.7 Repeat the extraction two more times with two additional 100-mL portions of 1:1 methylene chloride:acetone combining extract into Erlenmeyer flask.

10.4.8 Dry and concentrate extracts as described for separatory funnel extraction (paragraph 10.2).

10.5 Soxhlet Extraction (for Soils, Sludges, and Wastes)

10.5.1 Decant and discard any water layer in a sediment sample. Mix sample thoroughly, especially composite samples. Discard foreign objects such as sticks, leaves, and rocks.

10.5.2 Waste samples consisting of multiple phases should be separated into different phases before extraction. The percent weight or volume of each phase should be determined, and each phase analyzed individually.

10.5.3 Grind or otherwise subdivide dry waste amenable to grinding so that it either passes through a 1-mm sieve or can be extracted through a 1-mm hole.

10.5.4 Weigh 10 grams of sample to nearest 0.1 gram. Blend it with 10 grams of anhydrous sodium sulfate and place in extraction thimble. Extraction thimble must drain freely for duration of extraction period. A glass wool plug above and below a sample in the soxhlet extractor is an acceptable alternative to the thimble. Add 1.0 mL of surrogate spiking solution and 1.0 mL of matrix spiking solution if performing matrix spike analysis. If GPC cleanup is to be done, add twice as much surrogate and matrix spiking solution.

10.5.5 Place 300 mL of extraction solvent into 500-mL round-bottom flask containing one or two clean boiling chips. Attach flask to extractor and extract for 16 to 24 hours. Allow extract to cool after extraction is complete.

10.5.6 Collect, dry, and concentrate extract according to procedure described for separatory funnel extraction (10.2).

10.6 Florisil Cleanup

10.6.1 Reduce sample extract volume to 10 mL before cleanup. The extract solvent must be hexane.

10.6.2 Add a weight of Florisil (nominally 20 grams), predetermined by calibration, to a 20-mm I.D. chromatographic column. Settle Florisil by tapping column. Add anhydrous sodium sulfate to top of Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse sodium sulfate and Florisil. Just before exposure of sodium sulfate to air, stop elution of hexane by closing stopcock on chromatographic column. Discard eluate.

10.6.3 Adjust sample extract volume to 10 mL with hexane and transfer it from K-D concentrator tube to Florisil column. Rinse tube twice with 1 to 2 mL of hexane, adding each rinse to column.

10.6.4 Place 500-mL K-D flask and clean concentrator tube under chromatographic column. Drain column into flask until sodium sulfate layer is nearly exposed. Elute column with 200 mL of 6% ethyl ether in hexane (v/v; Fraction 1) using drip rate of about 5 mL/min. All haloethers are in this fraction. Remove K-D flask and set aside for later concentration. Elute column again, using 200 mL of 15% ethyl ether in hexane (v/v; Fraction 2), into a second K-D flask. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v; Fraction 3 will contain fewest target analytes, but many interferences may be observed because of the 50% ether rinses extracting them out) and a final elution with 200 mL of 100% ethyl ether (Fraction 4 is for the analysis of organophosphate pesticides) into separate K-D flasks.

10.6.5 These fractions **cannot** be mixed.

10.6.6 Concentrate eluates by standard K-D techniques using water bath at about 85°C (75°C for Fraction 4). Adjust final volume to whatever volume is required (1 to 10 mL). Analyze by gas chromatography.

10.7 Sulfur Cleanup

10.7.1 Add small bead of elemental mercury to sample extract (10.0 mL).

Caution: Mercury is a highly toxic metal and therefore must be used with great care. Before using mercury, the analyst should become acquainted with proper handling and cleanup techniques associated with this metal. Stopper concentrator tube securely and shake tube for several seconds. Use mechanical shaker if prolonged shaking is necessary. Look for precipitation of black solid (mercury sulfide). Low levels of sulfur in extract may only discolor surface of mercury toward

brown. No change in the shiny mirror-like mercury surface indicates sulfur is not present. Oil in extract may lower surface tension of mercury and cause several very small beads of mercury to form.

10.7.2 If sulfur is present in extract, then tube must be shaken until all sulfur has precipitated. For cases where a large concentration of sulfur is present, additional mercury may need to be added as it is consumed to form the precipitate.

10.7.3 Experience will be the best guide for knowing when to discontinue shaking extract against mercury and to test extract for residual sulfur. To test extract for remaining sulfur, place a drop of extract into a small clean screw cap vial already containing a drop of clean mercury. Extracts still containing sulfur will discolor the mercury surface, and the extract will need more shaking to finish precipitating all sulfur from solution.

10.7.4 Once the sulfur is precipitated and settled, draw off the bulk of the extract and transfer to clean Teflon-lined screw cap vial.

Note: A 10-mL sample volume was established before the sulfur removal began, so it is not necessary to transfer all the extract away from the mercury sulfide precipitate.

10.7.5 The extract is ready for GC/ECD screening.

10.8 Gel-Permeation Cleanup (GPC)

10.8.1 Packing the Column: Place about 70 grams of Bio Beads SX-3 in a 400-mL beaker. Cover beads with methylene chloride. Allow beads to swell overnight (before packing columns). Transfer swelled beads to column and start pumping solvent through column, from bottom to top, at 5.0 mL/minute. After about 1 hour, adjust pressure on column to 7 to 10 psi and pump an additional 4 hours to remove air from column. Adjust column pressure periodically as required to maintain 7 to 10 psi.

10.8.2 Calibration of Column: Column can be calibrated manually by gravimetric/ GC/FID techniques or automatically if a recording UV detector with a flow through cell is available.

10.8.2.1 Manual Calibration: Load 5 mL of corn oil solution into sample loop No. 1 and 5 mL of phthalate-phenol solution into loop No. 2. Inject corn oil and collect 10-mL fractions (i.e., change fractions at 2-minute

intervals) for 36 minutes. Inject phthalate-phenol solution and collect 15-mL fractions for 60 minutes. Determine corn oil elution pattern by evaporation of each fraction to dryness followed by gravimetric determination of residue. Analyze phthalate-phenol fractions by GC/FID using a DB-5 capillary column, a UV spectrophotometer, or a GC/MS system. Plot concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose dump time that allows ≥ 85% removal of corn oil and ≥ 85% recovery of bis(2-ethylhexyl)phthalate. Choose collect time to extend at least 10 minutes after elution of pentachlorophenol. Wash column with methylene chloride at least 15 minutes between samples. Typical parameters selected are dump time, 30 minutes (150 mL); collect time, 36 minutes (180 mL); and wash time, 15 minutes (75 mL).

10.8.2.2 Automated Calibration: Column can also be calibrated by use of a 254-nm detector in place of gravimetric and GC analyses of fractions. Use corn oil-phthalate-phenol mixture when using UV detector. Load 5 mL into sample loop No. 1. Use same criteria for choosing dump time and collect time as for manual calibration.

10.8.2.3 The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. Recalibrate system once weekly.

10.8.3 GPC Extract Cleanup: Extract must be in methylene chloride or primarily methylene chloride. All other solvents must be concentrated to 1 mL and diluted to 10.0 mL with methylene chloride. Prefilter or load all extracts by filter holder to avoid particulates that might cause flow stoppage or damage valve. Load one 5.0-mL aliquot of extract onto GPC column. Do not apply excessive pressure when loading. Purge sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carryover. Process extracts using dump, collect, and wash parameters determined from calibration, and collect cleaned extracts in 400-mL beakers tightly covered with aluminum foil.Note: Half the 10-mL extract is lost during the loading of the GPC, so divide sample size by two when calculating analyte concentration.

10.8.4 Concentrate extract by standard K-D technique described under one of the extraction procedures.

11.0 Sample Analysis

11.1 Add 10 μL of internal standard to extracts of all method blanks, samples, and control samples (if using internal calibration method).

11.2 Auto injection of 1-μL samples. Injection tolerance of ± 0.05 μL.

11.3 If sample chromatograms have interfering peaks, a high baseline, or off-scale peaks, then the samples must be reanalyzed following dilution, further cleanup, or reextraction. Samples that cannot be made to meet given specifications after one reextraction and cleanup are reported and require no further analysis. No limit is placed on the number of reextractions of samples that may be required because of contaminated method blanks.

11.4 The sample must be analyzed at the most concentrated level consistent with achieving satisfactory chromatography. If dilution is employed solely to bring a peak within the calibration range or to get a multiresponse pattern on scale, the results for both more and less concentrated extracts must be reported. Resulting changes in quantitation limits and surrogate recovery must also be reported for diluted samples.

11.5 If the laboratory has reason to believe that diluting the final extracts will be necessary, an undiluted run may not be required. If an acceptable chromatogram is not achieved with undiluted extract, an additional extract 10 times the concentration of the undilute sample must be injected and reported with the sample data.

11.6 No single component target analyte concentrations should exceed the upper limit of the initial calibration.

11.7 Gas Chromatograph Operation Conditions

11.7.1 The following are recommended gas chromatographic analytical conditions, to be used unless otherwise noted.

Carrier Gas	Helium (Hydrogen may be used)
Column Flow	5 mL/minute
Makeup Gas	P-5/P-10 or N_2 (required)
Injector Temperature	≥ 200°C
Injection	On-column
Injection Volume	1–5 μL
Injector	Grob-type, splitless
Initial Temperature	150°C

Initial Hold Time	0.5 minute
Temperature Ramp	5 to 6°C/min
Final Temperature	275°C
Final Hold Time	Until after decachlorobiphenyl has eluted (about 10 minutes)

11.7.2 Optimize GC conditions for analyte separation and sensitivity. Once optimized, the same GC conditions must be used for analysis of all standards, samples, blanks, and MS/MSDs.

11.7.3 Linearity of the ECD may depend greatly on flow rate of makeup gas. Care must be taken to maintain stable and appropriate flow of makeup gas to detector.

11.8 Analytical Sequence

11.8.1 Perform the following analytical sequence after an acceptable initial calibration. Alternate a continuing calibration standard with a degradation check standard every five determinations.

11.8.1.1 Instrument Blank: Consists of solvent with internal standard added.

11.8.1.2 Degradation Check Standard

11.8.1.3 Single-response Standards

11.8.1.4 Chlordane Standard

11.8.1.5 Toxaphene Standard

11.8.1.6 PCB Standards: Individual PCBs except PCB 1016 and PCB 1260 may be in the same standard.

11.8.1.7 Method Blank: For water, 1 liter of reagent water treated as the water sample aliquots; for soil, 30 grams sodium sulfate treated as the soil sample aliquots.

11.8.1.8 Four Samples

11.8.1.9 Instrument Blank

11.8.1.10 Degradation Check Standard

11.8.1.11 Five Samples

11.8.1.12 Instrument Blank

11.8.1.13 Continuing Calibration Standard (mid-level)

11.8.1.14 Five Samples

11.8.1.15 Instrument Blank

11.8.1.16 Degradation Check Standard

11.8.2 End each analytical sequence with an instrument blank and a mid-level continuing calibration standard of all single-response pesticides.

11.8.3 The analytical sequence must also include the required matrix spike/matrix spike duplicate samples and the laboratory control sample. They may be analyzed at any point in the sequence.

11.8.4 A standard of any identified multi-response parameter must be analyzed within 72 hours of its detection in a sample.

11.8.5 After a break in sample analyses, the laboratory may resume analysis of samples using current initial calibration for quantitation only by analyzing an acceptable instrument blank, degradation check standard, and mid-level continuing calibration standard. Otherwise the initial 5-point calibration must be re-established.

11.9 Retention Time Windows

11.9.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multiresponse products (e.g., PCBs) throughout course of 72-hour period. Serial injections over less than 72 hours result in retention time windows that are too tight.

11.9.2 Calculate standard deviation of three absolute retention times for each single response standard. For multiresponse products, choose one major peak and calculate standard deviation of three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

11.9.2.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window. The experience of the analyst, however, should weigh heavily in interpretation of chromatograms. For multiresponse analytes, the analyst should use the retention time window but primarily rely on pattern recognition.

11.9.2.2 In cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a similar closely eluting compound to develop a valid retention window.

11.9.2.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. Data must be retained by the laboratory.

11.10 Acceptance Criteria for Sample Chromatograms

11.10.1 Identification of pesticides is based on retention time data and confirmed by both GC columns.

11.10.2 Identification of single-response pesticides by gas chromatographic methods is based primarily on retention time data. Retention time of the apex of a peak can be verified only from an on-scale chromatogram. Identification of multiresponse analytes is based primarily on recognition of patterns of retention times displayed on a chromatogram. Therefore, the following requirements apply to all data presented for single component and multicomponent analytes.

11.10.2.1 When no analytes are identified in a sample, chromatograms from analyses of sample extract must use the same scaling factor as used for the low point standard of initial calibration associated with those analyses.

11.10.2.2 Chromatograms must display single-response pesticides detected in the sample at less than full scale.

11.10.2.3 Chromatograms must display the largest peak of any multicomponent analyte detected in the sample at less than full scale.

11.10.2.4 If an extract must be diluted, chromatograms must display single component pesticides between 10 and 100% of full scale.

11.10.2.5 If an extract must be diluted, chromatograms must display the peaks chosen for quantitation of multicomponent analytes between 25 and 100% of full scale.

11.10.2.6 For any sample, the baseline of the chromatogram must return to below 50% of full scale before the elution time of alpha-BHC, and return to below 25% of full scale after the elution time of alpha-BHC and before the elution time of decachlorobiphenyl.

11.10.2.7 If a chromatogram is replotted electronically to meet these requirements, the scaling factor used must be displayed on the chromatogram.

11.10.2.8 If the chromatogram of any sample needs to be replotted electronically to meet these requirements, both the initial chromatogram and the replotted chromatogram must be submitted in the data package.

11.10.3 Surrogate spike and MS/MSD target acceptance ranges are summarized in Tables 2 and 3 below.

11.10.3.1 If the surrogate spike recovery for dibutylchlorendate is outside the target acceptance limits, then evaluate the 2,4,5,6-tetra chloro-meta-xylene for acceptance. If both surrogate recoveries are outside limits, then the sample is re-extracted and reanalyzed. If the surrogate spike recovery of the reanalyzed sample is still outside the acceptance range, the sample results of both analyses are reported and noted in the case narrative.

11.10.3.2 If the MS/MSD recoveries are not within the target acceptance limits, the analysis is not repeated. The data are reported as is and noted in the case narrative.

Table 2
Pesticide Surrogate Recovery Target Acceptance Limits

Compound	Water	Soil
Dibutylchlorendate	24-154%	24-150%
2,4,5,6 Tetrachlorometaxylene	60-150%	60-150%

Table 3
Pesticide Matrix Spike/Matrix Spike Duplicate Recovery Target Acceptance Limits

Compound	Water	Soil
gamma-BHC (Lindane)	56-123%	46-127%
Heptachlor	40-131%	35-130%
Aldrin	40-120%	34-132%
Dieldrin	52-126%	31-134%
Endrin	56-121%	42-139%
4,4'-DDT	38-127%	23-134%

11.11 Quantitation Requirements

11.11.1 To be quantitated, the detector response (peak area or height) of all of the single-response analytes must lie between the response of the low and high concentrations in the initial calibration. If the analytes are detected below the required reporting limits, they are reported as estimated and flagged accordingly. If they are detected at a level greater than the high calibration point, the sample must be diluted either to a maximum of 1:100,000 or until the response is within the linear range established during calibration. Guidance in performing dilutions and exceptions to this requirement are given below.

11.11.2 If the response is still above the high calibration point after the dilution of 1:100,000, the laboratory shall report the result as estimated and flag it accordingly.

11.11.3 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

11.11.4 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the initial calibration range of the instrument.

11.11.5 Do not submit data for more than two analyses (i.e., the original sample extract and one dilution) or, if a screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

11.11.6 Do not dilute MS/MSD samples to get either spiked or nonspiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis and note the problem in the case narrative.

11.12 Evaluation of Chromatograms

11.12.1 Consider the sample negative when its peaks, depending on the pesticide's response factor, result in concentrations less than the required quantitation level. The sample is complete at this point. Confirmation is not required.

11.12.2 Tentative identification is made when the unknown's retention time matches the retention time of a corresponding standard that was chromatographed on the same instrument within a 72-hour period.

11.12.3 Determine if any pesticides or PCBs are present. Pattern recognition techniques, based on chromatograms of standards, are recommended for the identification of PCB compounds.

11.12.3.1 If the response for any compound is 100% or less of full scale, the extract is ready for confirmation and quantitation.

11.12.3.2 If the response for any compound is greater than full scale, dilute the extract so that the peak will be between 50 and 100% full scale and reanalyze. Use this dilution also for confirmation and quantitation.

11.12.3.3 For dilution greater than 10-fold, also inject an aliquot of a dilution 10-fold more concentrated to determine if other compounds of interest are present at lower concentrations.

11.12.3.4 Computer reproductions of chromatograms manipulated to ensure all peaks are on scale over a 100-fold range are an accepted substitute. However, this can be no greater than a 100-fold range. This is to prevent retention time shifts by column or detector overload. Linearity must be demonstrated over the 100-fold range using higher concentrations of the evaluation mixture.

11.12.4 Quantitation may be performed on the primary analysis, with the exception of possibly toxaphene and the DDT series. If DDT exceeds the 10% RSD linearity criterion, then quantitations for any DDE, DDD,

and DDT in a sample must be on the confirmation analysis, provided the confirmation calibration meets the 20% RSD criterion. Toxaphene must always be quantitated on the confirmation analysis.

11.12.5 If identification of compounds of interest is prevented by the presence of interferences, further cleanup is required.

11.12.6 When selecting a GC column for confirmation or quantitation, be sure that none of the compounds to be confirmed or quantitated overlap. When samples are very complex, it may be necessary to use more than one column to achieve adequate separation of all compounds being quantitated.

11.13 Confirmation Analysis

11.13.1 All tentatively identified parameters must be confirmed by second GC column or by GC/MS.

11.13.2 If second GC column confirmation is done, the same analytical sequence is to be followed. The only parameters that need to be present in the standards are those to be confirmed.

11.13.3 The RSD criterion for initial calibration does not have to be met for confirmation analysis. The calibration or response factors of continuing calibration standards cannot exceed a 25% difference when compared with average initial calibration or response factor. Retention times of continuing calibration standards must fall within the windows.

11.13.4 Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

11.13.4.1 The GC/MS would normally require a minimum concentration of 10 ng/μL in the final extract, for each single-component compound.

11.13.4.2 The pesticide extract and associated blank should be analyzed in the same analytical batch.

11.13.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractable extracts (sample and blank). If the compounds are not detected in the base/neutral-acid extract even though the concentration is

high enough, the GC/MS analysis of the pesticide extract should be performed.

11.13.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm pesticides or PCBs identified by GC/ECD.

12.0 Calculations

12.1 External Standard Calibration: The concentration of each analyte in the sample may be determined by calculating the amount of standard injected, from the peak response, using the calibration curve or the calibration factor. The concentration of a specific analyte is calculated as follows:

12.1.1 Water Samples

$$\text{Concentration } (\mu g/L) = \frac{[(A_x)(A)(V_t)(D)]}{[(A_s)(V_i)(V_s)]} \qquad (6)$$

Where:

A_x = Response for the analyte in the sample

A = Amount of standard injected (ng)

A_s = Response for the external standard

V_i = Volume of extract injected (μL)

D = Dilution factor, if dilution was made on sample before analysis (if no dilution was made, D = 1, dimensionless)

V_t = Volume of total extract (μL)

V_s = Volume of sample extracted (mL)

12.1.2 Soil/Sludge/Waste

$$\text{Concentration } (\mu g/kg) = \frac{[(A_x)(A)(V_t)(D)]}{[(A_s)(V_i)(W)]} \quad (7)$$

Where:

W = Weight of sample extracted (grams). (Dry weight is generally used, although wet weight may be used depending upon specific applications of the data.)

A_x, A_s, A, V_t, D, and V_i have the same definition as for water samples.

12.2 Internal Standard Calibration: For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

12.2.1 Water Samples

$$\text{Concentration } (\mu g/L) = \frac{[(A_x)(C_{IS})(D)]}{[(A_{IS})(RF)(V_s)]} \quad (8)$$

Where:

A_x = Response of analyte being measured

C_{IS} = Amount of internal standard added to extract (ng)

D = Dilution factor, if dilution was made on sample before analysis. (If no dilution was made, D = 1, dimensionless.)

A_{IS} = Response of the internal standard

RF = Response factor for analyte

V_s = Volume of water extracted (mL)

12.2.2 Soil/Sludge/Waste

$$\text{Concentration } (\mu g/kg) = \frac{[(A_s)(C_{IS})(D)]}{[(A_{IS})(RF)(W_s)]} \quad (9)$$

Where:

W_s = Weight of sample extracted (grams). (Wet weight is generally used, although dry weight may be used, depending upon specific application of the data.)

A_S, C_{IS}, D, A_{IS}, and RF have the same definition as for water samples.

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control and reporting requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	Begin and end	90–110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80–120%	Qualify data
Surrogate Spikes	Every sample	11.10.3	Reanalyze, then qualify data
Matrix Spike	1/20	11.10.3	Qualify data
Duplicate Sample	1/20	0–20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90–110%	Recalibrate
CCVS	Begin and end	90–110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	Begin	80–120%	Recalibrate
Surrogate Spikes	Every sample	11.10.3	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	11.10.3	Qualify data
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0–20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
End	end of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
A/S	as specified earlier in this method
RPD	relative percent difference

15.0 References

15.1 *Test Methods for Evaluating Solid Waste,* 3rd ed., Method 8080. September 1986.

FERNALD/pest-pcb.51

FM-ORG-40

Organophosphorus Pesticides by Gas Chromatography

Working Linear Range: Analyte- and matrix-dependent
Reporting Limit: Analyte-dependent
Reporting Units: Water, μg/L; solids, μg/kg
Matrix: Water, soil, sediment and waste

1.0 Scope and Application

This method is applicable to water, wastewater, sediment, and soil samples. The method target compound list and practical quantitation limits (PQLs) are summarized in Table 1.

Table 1. Organophosphorus Pesticides Target Compound List and Practical Quantitation Limits (PQLs)[a]

Compounds (including alternate names)	PQL Water (μg/L)	PQL Soil/Sediment (μg/kg)[b]
Azinphos methyl (Guthion)	1	50
Bolstar (Sulprofos)	1	50
Chloropyrifos	1	50
Coumaphos (Co-Ral)	1	50
Demeton, O & S	2	100
Diazinon	1	50
Dichlorvos (DDVP)	1	50
Ethoprop	1	50
Fensulfothion (Daasanit)	2	100
Fenthion	1	50
Parathion, methyl	1	50
Phorate (Thimet)	1	50
Ronnel (Trolene)	1	50
Stirophos (Rabon)	10	500
Tokuthn (Prothiofos)	1	50
Trichloronate (Agritox)	1	50

[a] Sample PQLs are matrix-dependent.
[b] PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, PQLs will be higher, based on percent moisture in each sample.

2.0 Method Summary

2.1 A measured aliquot of a water sample at native pH is extracted with methylene chloride using the separatory funnel technique. A measured aliquot of soil/sediment is dried with sodium sulfate and extracted with 50:50 methylene chloride:acetone using sonication. The extract is dried and concentrated, and the solvent is exchanged into hexane.

2.2 Typically, no cleanup efforts of organophosphorus pesticides are made before analysis. If peak detection and identification are prevented because of interferences, cleanup may be considered. Before using any cleanup procedure, the analyst must process a standard through the procedure to validate elution pattern and absence of interference from reagents.

2.3 A gas chromatograph (GC) with a flame photometric detector (FPD) in the phosphorus mode or a thermionic bead detector (TID) or nitrogen phosphorus detector (NPD) is used in the capillary mode for purposes of examining multicomponent, multilevel organic residues extracted from water and soil/sediment matrixes. A digital computer is used to acquire and process the associated data, based on available multi-internal standard techniques. Chemical components are qualitatively identified by relative retention times (RRT) and quantified by relative response factors (RRF), both values being calculated relative to appropriate internal standards.

2.4 Before extracts are analyzed, an initial calibration must be completed that demonstrates lack of instrument contamination and active degradation and adequate resolution and identification of analytes. Continuing calibration standards must be injected and evaluated for criteria compliance after every group of 10 or 20 extract injections (depending on analytical support level [ASL]) and at the end of the analytical sequence. Internal standards are used to determine RRTs and RRFs.

2.5 Target compounds tentatively identified by the primary analysis must be confirmed by at least one qualitative technique, either a second gas chromatograph analysis using a dissimilar analytical column or by GC/MS (if the concentration of the target parameter is above GC/MS detection limits). Confirmation analysis **must** be qualitative and **may** be quantitative.

2.6 A variety of problems may be encountered during the course of sample analysis. If data are acquired using automation without the immediate attendance of an analyst, calibration problems may require partial or complete reanalysis of the affected extracts. If extracts are not screened before primary analysis, targets may exceed the instrument calibration range. These extracts must be diluted and reanalyzed. Matrix interference will sometimes persist even after all optional cleanups are applied. Poor surrogate recovery can seldom be completely rectified by reextraction since the holding time for the raw sample has usually expired before the surrogate recovery is measured (if enough raw sample is available for reextraction).

2.7 The laboratory prepares a case narrative and submits it with the sample data package. The analyst documents all problems and observations as samples are processed. The documentation is then used to qualify noncompliances in the data or analytical problems.

3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. Method blanks are prepared with field samples to demonstrate that reagents and glassware are free of interference.

3.2 Matrix interferences may be caused by contaminants coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

3.3 Analytical difficulties may be encountered with various organophosphorus pesticides because of their chemical instability.

3.4 The use of Florisil cleanup materials for some of the compounds in this method has been demonstrated to yield recoveries less than 85% and is therefore not recommended for all compounds. Use of phosphorus or halogen specific detectors, however, often reduces the necessity for cleanup of relatively clean sample matrices. If particular circumstances demand the use of cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is no less than 85%.

3.5 Use of a FPD in the phosphorus mode will minimize interferences from materials that do not contain phosphorus. Elemental sulfur, however, may interfere with the determination of certain organophosphorus compounds by flame photometric gas chromatography. Sulfur cleanup may alleviate such interference. The analyst should verify that no targets are adversely affected by sulfur removal procedures.

3.6 A halogen-specific detector (i.e., Hall electrolytic conductivity detector (HECD) or microcoulometric) is very selective for halogen-containing compounds and may be used for the determination of chloropyrifos, ronnel, coumaphos, tokuthion, trichloronate, dichlorvos, EPN, naled, and stirophos only.

3.7 Some analytes coelute on certain columns. Therefore, select a second column for confirmation where coelution of the analytes of interest does not occur.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling organic solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservation requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Continuous Liquid——Liquid Extraction

6.1.1 Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor——Ace Glass Company, Vineland, New Jersey, P/N 6841-10, or equivalent).

6.1.2 Drying Column: 20-mm I.D., Pyrex chromatographic column with Pyrex glass wool at bottom and Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

6.1.3 Kuderna-Danish (K-D) Apparatus

6.1.3.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

6.1.3.2 Evaporation Flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

6.1.3.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.1.3.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.1.4 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.1.5 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath must be used in a fume hood.

6.1.6 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap.

6.1.7 pH Indicator Paper: pH range including the desired extraction pH.

6.1.8 Heating Mantle: Rheostat controlled.

6.1.9 Syringe: 5-mL, Hamilton gastight or equivalent.

6.1.10 Graduated Cylinder: 1-liter, glass.

6.2 Sulfur Cleanup

6.2.1 Mechanical Shaker or Mixer: Such as the Vortex Genie.

6.2.2 Pipets: Disposable, Pasteur type, glass.

6.2.3 Centrifuge Tubes: Calibrated, 12-mL.

6.2.4 Glass Bottles or Vials: 10- and 50-mL, with Teflon-lined screwcaps.

6.3 Gel-Permeation Cleanup

6.3.1 Gel Permeation Chromatography System: Analytical Biochemical Laboratories, Inc. GPC autoprep Model 1002A, or equivalent.

6.3.2 Chromatographic Column: 600- to 700-mm × 25-mm I.D. glass column fitted for upward flow operation.

6.3.3 Bio-beads S-X3: 70 grams per column.

6.3.4 Pump: Capable of constant flow of 0.1 to 5 mL/min at up to 100 psi.

6.3.5 Injector: With 5-mL loop.

6.3.6 Ultraviolet detector: 254-nm wavelength (optional).

6.3.7 Stripchart Recorder: (optional).

6.3.8 Syringe: 10-mL with Luerlok fitting, Hamilton gastight or equivalent.

6.3.9 Syringe Filter Holder and Filter: BioRad "Prep Disc" sample filter No. 343-0005 and 5-μm size filters, or equivalent.

6.3.10 Beakers: 400-mL, glass.

6.4 Sonication Extraction (Soils, Sludges, and Wastes)

6.4.1 Sonication: Use horn-type sonicator equipped with titanium tip. The following sonicator, or an equivalent brand and model, is recommended:

Ultrasonic Cell Disrupter: Heat Systems—Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent (wattage must be at least 375 with pulsing capability and No. 200 1/2-inch Tapped Disrupter Horn) plus No. 207 3/4-inch Tapped Disrupter Horn, and No. 419 1/8-inch Standard Tapered microtip probe.

6.4.2 Sonabox: Recommended with above disrupters for decreasing cavitation sound (Heat Systems—Ultrasonics, Inc., Model 432B or equivalent).

6.4.3 If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue No. 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

6.4.4 Apparatus for Determining Percent Moisture

6.4.4.1 Drying Oven.

6.4.4.2 Desiccator.

6.4.4.3 Porcelain Crucibles.

6.4.5 Pasteur Glass Pipets: Disposable, 1-mL, glass.

6.4.6 Beakers: 400-mL, glass.

6.4.7 Vacuum Filtration Apparatus

6.4.7.1 Buchner Funnel.

6.4.7.2 Filter Paper: Whatman No. 41 or equivalent.

6.4.8 Kuderna-Danish (K-D) Apparatus

6.4.8.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent).

6.4.8.2 Evaporator Flask: 500-mL (Kontes K-570001-0500 or equivalent).

6.4.8.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.4.8.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.4.9 Boiling Chips: Solvent extracted, 10/40 mesh (silicon carbide or equivalent).

6.4.10 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). Bath must be used in fume hood.

6.4.11 Balance: Top-loading, capable of accurately weighing 0.01 gram.

6.4.12 Vials and Caps: 2-mL crimp top for gas chromatograph autosampler.

6.4.13 Glass Scintillation Vials: At least 20-mL, with screw-cap and Teflon or foil liner.

6.4.14 Spatula: Stainless steel or Teflon.

6.4.15 Drying Column: 20-mm I.D., Pyrex chromatographic column with Pyrex glass wool at bottom and Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use small pad of Pyrex glass wool to retain adsorbent. Prewash glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing column with adsorbent.

6.4.16 Syringe: 5-mL, Hamilton gastight or equivalent.

6.5 Gas Chromatograph

6.5.1 The gas chromatograph system must adequately regulate temperature to give a reproducible temperature program. It must also have a flow controller that maintains a constant column flow rate throughout temperature program operations. The system must be suitable for splitless injection, and all necessary accessories including syringes, analytical columns, and gases must be available.

6.5.2 Certain gas chromatographs may have difficulty in meeting pesticide QC requirements because of target decomposition in the injector. This problem can be minimized by operating the injector at 200° to 205°C or lower using a Pyrex (not quartz) methyl silicone deactivated injector liner, and by deactivating any metal parts in the injector with dichlorodimethyl silane. In some cases, using a 0.25-inch packed column injector converted for use with 0.53-mm capillary columns works better than a Grob-type injector. If a Grob-type injector is used, a 4-mm liner may be required to meet degradation criteria.

6.6 Autosampler

6.7 Data System

6.8 Chromatographic Columns

6.8.1 Preferred Columns

6.8.1.1 Primary Analysis: Analytical column, designated HYBRID2, is prepared by adding following together with presstight zero volume connectors:

J & W DB-210, 15-m × 0.53-mm I.D., 1.0-μm film thickness, wide-bore, capillary, or equivalent, Supelco SPB-608, 15-m × 0.53-mm I.D., 1.5-μm film thickness, wide-bore, capillary, or equivalent J & W DB-5, 15-m × 0.53-mm I.D., 1.0-μm film thickness, wide-bore, capillary, or equivalent

6.8.1.2 Confirmation Analysis: J & W DB-1, 25-m × 0.32-mm I.D., 0.50-μm film thickness, capillary, or equivalent.

6.8.2 J & W DB-1701, 30-m × 0.53-mm I.D., 1.0-μm film thickness, megabore or equivalent. This column stationary phase will potentially bleed and causes interferences, high baselines, etc. in some systems.

6.8.3 J & W DB-608, 30-m × 0.53-mm I.D., 0.5- to 1.0-μm film thickness, megabore or equivalent. May be less sensitive than other capillary column.

6.9 Volumetric Flasks, Class A.

6.10 Microsyringe: 10-μL, Hamilton gastight or equivalent.

6.11 Syringe: 5-mL, Hamilton gastight or equivalent.

6.12 Vials: Glass/Teflon with Teflon-lined cap.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the gas chromatograph according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Continuous Liquid——Liquid Extraction

8.1.1 Water: All references to water assume the use of water in which target compounds are not detected above method detection limits.

8.1.2 Sodium Hydroxide Solution (10 N NaOH, ACS): Dissolve 40 grams NaOH in water and dilute to 100 mL.

8.1.3 Sodium Sulfate (Na_2SO_4, ACS): Granular, anhydrous (purified by heating at 400°C for 4 hours in a shallow tray).

8.1.4 Sulfuric Acid Solution (H_2SO_4), 1:1: Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water. **Caution:** Heat-liberating reaction.

8.1.5 Extraction/Exchange Solvent: Methylene chloride, hexane (pesticide quality or equivalent).

8.2 Gel-Permeation Cleanup

8.2.1 Methlyene Chloride: Pesticide quality or equivalent.

8.2.2 GPC Calibration Solutions

8.2.2.1 Corn Oil: 200 mg/mL in methylene chloride.

8.2.2.2 Bis(2-ethylhexyl)phthalate and Pentachlorophenol Solution: 4.0 mg/mL in methylene chloride.

8.2.2.3 Mix corn oil with phthalate/phenol solution if UV detector is used. Concentrations should remain the same.

8.3 Separatory Funnel Extraction (for Water Samples)

8.3.1 Water: All references to water assume the use of water in which target compounds are not detected above the method detection limits.

8.3.2 Sodium Hydroxide Solution (10 N NaOH, ACS): Dissolve 40 grams NaOH in water and dilute to 100 mL.

8.3.3 Sodium Sulfate (Na_2SO_4, ACS): Granular, anhydrous (purified by heating at 400°C for 4 hours in a shallow tray).

8.3.4 Sulfuric Acid Solution, 1:1, v:v: Slowly add 50 mL of H_2SO_4 (specific gravity of 1.84) to 50 mL of water in a fume hood. **Caution:** Heat-liberating reaction.

8.3.5 Extraction/Exchange Solvent: Methylene chloride and hexane (pesticide quality or equivalent).

8.4 Sulfur Cleanup

8.4.1 Mercury, triple distilled. **Caution:** Elemental mercury is highly toxic.

8.5 Sonication Extraction (for Soils, Sludges, and Wastes)

8.5.1 Sodium Sulfate (Na_2SO_4): Anhydrous, granular, and reagent grade (purified by heating at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle). Baker anhydrous powder, catalogue No. 73898, or equivalent.

8.5.2 Extraction Solvents: Methylene chloride:acetone (1:1, v:v) (pesticide quality or equivalent).

8.6 Stock Standard Solutions

8.6.1 Stock standard solutions are prepared by accurately weighing about 0.0100 gram of neat (pure) material and dissolving the material in 10 mL methanol or other suitable solvent to achieve a final concentration of 1 mg/mL. The stock standard solutions are stored in Teflon-sealed, screw cap vials.

Note: Store at 4° ± 2°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used if they are certified by the manufacturer or by an independent source.

8.6.2 Stock standards are diluted to obtain working standards.

8.7 Working Calibration Standard Solution

8.7.1 Working calibration standards are prepared at the appropriate compound concentration for immediate use. The working solutions are prepared by combining the appropriate stock standards, diluting with isooctane to achieve the desired concentration of each compound. Working solutions are verified by comparison with a standard from a secondary source when such a standard is available.

8.7.2 Calibration standards at a minimum of 5 concentration levels for each parameter of interest should be prepared by dilution of stock standards with isooctane. One concentration level should be near, but above the method detection limit. The remaining concentration levels should correspond to the range of concentrations found in real samples or should define the working range of the GC. Calibration standards must be replaced after 6 months or sooner if comparison with check standards indicates a problem.

8.8 Surrogate Solution: The surrogate spiking solution is added to all field samples and quality control samples. Prepare a methanolic solution of Aspon at a concentration of 10 μg/mL.

8.9 Matrix Spike Solution

8.9.1 Prepare a methanolic solution containing the pesticides at concentrations listed in Table 2.

Table 2. Matrix Spike Solution Concentrations

Compound	µg/mL
Phorate	10
Methyl parathion	10
Rabon	10
Diazinon	10
Dichlorvos	10
Ronnel	10

8.10 Internal Standard Working Solution

8.10.1 The analyst should choose internal standards similar in analytical behavior to the compounds of interest. The analyst should also demonstrate that measurement of the internal standard is not affected by method or matrix interference.

8.10.2 Prepare an internal standard working solution with the compounds listed in Table 3 at 200 µg/mL.

8.10.3 A 100-µL aliquot of this internal standard (IS) solution is added to 1.0-mL aliquots of standards, blanks and sample extracts providing internal standard concentrations of 20 µg/mL (see note on Table 3). The levels suggested offer large detector response that will minimize the effects of compound coelution. Depending on response of chromatographic system, the levels may be adjusted.

Table 3. Recommended Internal Standards

Compounds	Amount* (µg)
4-Nitrotoluene	20
Azobenzene	20
EPN	20
Ethyl Guthion	20

* Amount of each internal standard that must be mixed to 1 mL of solution before injection.

8.11 Laboratory Control Sample: The components of this standard are identical to those in a mid-range calibration standard except that the target compound standards are obtained from an independent source.

9.0 Calibration Procedures

9.1 Various forms of calibration can be performed throughout the sample analysis procedure. Five common forms of calibration are described in the method. For each form of calibration, the minimum recommendations are described. The analyst may chose to expand the extent of calibration. Extra calibration might include additional standards, additional concentrations, or analysis of standards at a higher frequency.

9.2 Primary Calibration

9.2.1 The algorithms to be used by the digital computer to process the data will be set and saved as an acquisition method. The following items will be part of the acquisition method.

9.2.1.1 Parameters that cannot be changed after data are acquired:

- Acquisition Time
- Sampling Rate
- A/D Range

9.2.1.2 Parameters that can be changed/optimized after data are acquired:

- Integration parameters (peak area or peak height tabulation, peak rejection minimum, area/height threshold, peak search windows, etc.)

- Algorithms used by the computer to make calculations (standard and time references, retention times, type of curve fit, etc.)

Note: Peak area is independent of broadening effects.

9.2.1.3 The acquisition method used for processing **final** data are documented in the instrument injection log book.

9.2.2 Primary Initial Calibration: Library retention times are primarily established during initial calibration. The library retention times may be the actual retention times of one level of the five calibration levels (usually the midpoint) or the average of two or more of the five calibration levels (depending on capabilities of data system). Before establishing library retention times by actual or average retention times, the analyst should review the retention times for stability and mass shifts. If retention times are erratic, the analyst should not proceed until an investigation of abnormal behavior has been completed. If the retention times seem to shift relative to mass injected, the analyst may choose to average retention times. Search windows (can be absolute or relative depending on capabilities of data system) should be optimized considering the most difficult windows, such as nearly coeluting peaks, but continuing to bias favoring false positives.

Note: Documentation is not recommended for the initial injections after instrument standby or maintenance. Standards and samples should be analyzed when the instrument is consistent and stabilized.

9.2.2.1 Primary Initial Calibration Sequence

Instrument blank
Instrument sensitivity check (reporting limit level standard)
Minimum of five levels of calibration standards
Laboratory control sample

9.2.2.2 Primary Initial Calibration Criteria

Instrument blank——minimal background contamination.
Sensitivity——algorithms can detect and integrate low mass.
Linearity of five calibration levels.
Accuracy of low point of curve (as unknown).
Resolution of peaks.
Laboratory control sample.
Historical——validity of response factors.

9.2.2.3 Instrument Blank: Establishes absence of instrument contamination. Target compounds should not be present at levels exceeding the reporting limit. Instrument contamination levels should be considered when deciding to report a target near or below the normal reporting limit.

9.2.2.4 Instrument Sensitivity Check: This standard is not required to evaluate instrument linearity, but the analyst may choose to use this level as part of the calibration curve. However, this standard is used to ensure instrument reporting limit sensitivity. The machine algorithms (which are also applied to the field samples) must identify every compound present at a level above the area rejection set for integration.

Example: Reporting limit of pesticides in water = 1 μg/L. If 0.5 liter of sample is extracted and concentrated to 2.5 mL, the sensitivity level of the instrument would have to be at least 0.2 μg/mL injected. (1)

$$1\ \mu g/L \times \frac{0.5\ L}{2.5\ mL} = 0.2\ \mu g/mL$$

9.2.2.5 Minimum of Five Levels of Calibration Standards: Establish linearity of the system. Low level should be at or near the reporting level. All initial calibration criteria must be met before any samples are analyzed. Results can be used to prepare a calibration curve for each compound. Alternatively, results can be used to tabulate the peak area (or height) responses against the concentration of each compound and internal standard (RRF). Peak area is independent of broadening effects. (2)

$$RRF = \frac{A_S \times C_{IS}}{A_{IS} \times C_S}$$

Where:

A_S	=	Area of compound to be measured
C_{IS}	=	Concentration of internal standard (μg/L)
A_{IS}	=	Area of internal standard
CS	=	Concentration of compound to be measured (μg/L)

If the RRF value over the working range of every compound of interest is constant ($\leq$ 20% RSD), the RRF can be assumed to be invariant, and the midlevel or mean RRF or closest point can be used for calculation. The RRF and percent relative standard deviation (RSD) may be calculated manually or with computer assistance. (3)

9.2.2.6 Resolution: Resolution between peaks should be adequate so that machine algorithms separate and identify all peaks at all concentrations.

$$\% \text{ RSD} = \frac{\text{standard deviation}}{\text{mean}} \times 100$$

9.2.2.6 Resolution: Resolution between peaks should be adequate so that machine algorithms separate and identify all peaks at all concentrations. Recommended resolution is 25%. Poor chromatographic resolution diminishes the evidence for proper peak identification and quantitation. The resolution recommendations are not for target peaks only. Extra peaks should be adequately resolved from target peaks. Percent resolution is calculated by dividing the height of the valley by the height of the smaller peak being resolved, multiplied by 100. (4)

$$\% \text{ Resolution} = \frac{HT^{valley}}{HT^{smaller\ pk}} \times 100$$

9.2.2.7 Accuracy of Low Point of Curve: To gain confidence in quantitation of targets at or near the reporting limits, the lowest point of the curve is reprocessed as an unknown standard (not part of calibration). The acceptance criteria of this calibration check is:

Concentration of lowest standard ± concentration of reporting limit standard = acceptance range

For example, if the reporting limit level standard (sensitivity check) is the lowest point of the curve, for this analyte:

Concentration of lowest standard = 0.2 μg/mL
Concentration of reporting limit standard (sensitivity level) = 0.2 μg/mL
0.2 μg/mL ± 0.2 μg/mL = 0 to 0.4 μg/mL

When the low point is reprocessed as a noncalibration standard, the calculated concentration of the pesticide must be between 0 and 0.4 μg/mL. Using reporting limit level standard as part of the curve theoretically permits nondetection of the peak as acceptable. Obviously the peak must be detected and integrated for initial calibration to be valid.

Note: When deciding on calibration levels, the analyst should consider that the closer the lowest point of the curve is to the RL level, the wider the acceptance range. This will help define how well low masses of the compounds will be calculated accurately.

9.2.2.8 Matrix Spike Mixture: The components of this standard are identical to those in the recommended spiking solution (see Table 2). The compounds are either the most common to the various method lists or peaks that nearly coelute with other targets. This standard checks the algorithm's ability to identify one compound where library retention times are very close. It also checks the machine algorithm's ability to accurately calculate one compound where response factors were developed from nearly coeluting compounds. (5) The calculation for this standard is:

$$\% \text{ D (difference)} = \frac{\text{Conc}_{expected} - \text{Conc}_{calculated}}{\text{Conc}_{expected}} \times 100$$

The acceptance criteria for % D shall be ± 15%.

9.2.2.9 Laboratory Control Sample: The standards used to prepare the calibration curve must be verified against standards from another source. Prepare and analyze a standard (from an independent source) at a concentration near the midpoint calibration level. All target compounds calculated from the initial calibration curve or initial RRF must be within ± 25%D.

The initial calibration should remain valid for extended periods of time. However, the conditions listed below require fresh calibration:

1. Resolution criteria cannot be achieved.
2. Use of standard materials that produce unacceptable comparison to the laboratory control sample (> 25%D).
3. Major detector maintenance.
4. Use of a different electrometer range.
5. Any major change of instrument configuration.
6. Repeated failure to pass response factor or resolution continuing calibration criteria.
7. Implementation of one or more new internal standards.

9.2.3 Primary Continuing Calibration

9.2.3.1 The continuing calibration standards offer a mechanism to monitor small fluctuations in instrument response and ensure that the initial calibration is still valid for sample analysis. Concentrations are determined using routine internal standard calculations (the same used for field sample calculations).

9.2.3.2 After prolonged instrument standby or minor maintenance, standard retention times may shift. If this shift is stable and all other criteria are satisfied, the new retention times may be used to update the library retention times (either absolute or average, depending on capabilities of the data system).

9.2.3.3 Continuing calibration consists of:

1. Analysis of a midlevel calibration standard after injection of every 10 samples and at the end of the analytical sequence. The last midlevel continuing calibration check analyzed in an analytical sequence is referred to as the closure.

2. During a continuous analytical sequence (one not interrupted by prolonged instrument standby), an instrument blank and a sensitivity check must be analyzed about every 24 hours of sample analysis. These continuing calibration checks must pass the same criteria as during initial calibration.

3. To restart (new analytical sequence) after a prolonged instrument standby or minor instrument maintenance, the following continuing calibration standards must be analyzed and required criteria met before the analysis of samples may begin: Instrument Blank, Sensitivity Check, and Midlevel Calibration Standard. This will verify that the initial calibration is still valid for sample analysis.

9.2.3.4 Continuing Calibration Criteria

Midlevel calibration standard must be within ± 10% difference of the expected concentration. (6)

$$\% \text{ Difference} = \frac{\text{Conc}_{\text{expected}} - \text{Conc}_{\text{calculated}}}{\text{Conc}_{\text{expected}}} \times 100$$

Daily instrument blank and sensitivity check must meet same criteria as during initial calibration.

For valid analysis, samples must be bracketed by acceptable continuing calibration checks. If during the sequence continuing calibration criteria can no longer be met, all samples analyzed after the last valid continuing calibration check must be reanalyzed.

9.3 Confirmation Calibration/Analysis: Target compounds tentatively identified by the primary analysis must be confirmed by at least one additional qualitative technique. In deciding which type of confirmation to perform, the analyst should consider the level of QC deliverables required. Another consideration is that reporting a compound not present is a form of quantitation. If a target is tentatively identified during primary GC analysis and its presence is not confirmed, it is reported as a nondetect and the quantitation (report limit) is based on the confirmation data.

9.3.1 GC Confirmation Analysis (for Qualitative Data Only): When performing qualitative confirmation only, the analyst may compare the quantitations from both columns for consistency. No quantitative data may be reported from this confirmation analysis. The following injections are to be included for qualitative confirmation only:

9.3.1.1 Instrument Blank: Target compounds should not be present at levels exceeding the reporting limit when treating the instrument blank as a method blank.

9.3.1.2 Instrument Sensitivity Check (of compounds being confirmed): Confirmation calibration standard at the reporting limit level. This standard is used to ensure instrument reporting limit sensitivity. The machine algorithms (which are also applied to the field samples) must identify every compound present at a level above the area rejection set for integration.

9.3.1.3 Calibration Standard mixes of compounds being confirmed at levels similar to expected concentrations in samples.

9.3.1.4 Method Blanks associated with samples to be confirmed.

9.3.1.5 Samples to be Confirmed: Samples should be analyzed at the same dilutions as in primary analysis.

9.3.1.6 Calibration Standard mix to be injected after every 10 extracts to compare RT and peak shapes. Should be ± 15% difference from the single-point initial calibration standard.

9.3.2 GC Confirmation Analysis (for Qualitative and Quantitative Data): This is similar to the Primary Initial and Continuing Calibration, except the confirmation calibration standard is a mixture composed of only those compounds being confirmed. The same criteria must be met before samples are analyzed and reported.

9.3.2.1 Instrument Blank: Background/contamination below reporting limit.

9.3.2.2 Sensitivity Check: Algorithms identify and integrate all peaks.

9.3.2.3 Linearity Check: Minimum of five levels (correlation coefficient or % RSD).

9.3.2.4 Methods Blanks associated with samples to be confirmed.

9.3.2.5 Samples to be confirmed.

9.3.2.6 Midlevel Standard to be injected after every 10 extracts and at the end of the analytical sequence. Calculated concentration must be within ± 10% difference of expected concentration.

9.3.3 GC/MS Confirmation

9.3.3.1 GC/MS analysis normally requires a minimum concentration of 10 ng/μL in the field sample extract for each compound. To convert the sample concentration to the extract concentration: (7)

$$C^{extract} = (C^{sample}) \times \frac{T^{sample}}{FV^{extract}}$$

Where:

$C^{extract}$	=	Concentration in the extract (μg/L)
C^{sample}	=	Concentration in the sample (μg/L)
T^{sample}	=	Total sample producing total extract
$FV^{extract}$	=	Final volume of extract to be analyzed by GC/MS (mL)

For example, the primary GC analysis tentatively identifies diazinon present at 50 μg/L. A 0.5-L aliquot of raw sample was extracted and concentrated to a 2.5-mL final volume. Before primary GC analysis, 1 mL was removed and combined with IS in a 2-mL autosampler vial.

Assume:

1. If the sample concentration is 50 μg/L, 0.5 L contains 25 μg of diazinon. 0.5 L $\times$ 50 μg/L = 25 μg total mass.

2. The 25 μg of diazinon in the raw sample was extracted and concentrated to a final volume of 2.5 mL. Although 1 mL was removed, the effective final volume is still 2.5 mL (no dilution or concentration was performed).

Then:

$$C^{extract} = (50\ \mu g/L) \times \frac{0.5\ L}{2.5\ mL} = 10\ \mu g/mL \text{ or } 10\ ng/\mu L \tag{8}$$

The entire mass (25 μg) of diazinon is in the 2.5-mL extract solution. The concentration of the extract is 10 μg/mL. The concentration of the final extract is sufficient for GC/MS analysis.

9.3.3.2 To increase the concentration in the final extract, the volume of the final extract could be decreased. Nitrogen blowdown can be used to further concentrate the extract. A known portion of the extract should be removed and concentrated to a known final volume. Using the example above, the concentration of the final extract is at the minimum level. To increase the concentration and improve possibilities for successful GC/MS confirmation the analyst could remove 1 mL from the remaining 1.5 mL of extract. Using nitrogen blowdown, the final volume could be adjusted to 0.5 mL. In that case, the final volume of the extract has been adjusted by a dilution factor of 0.5.

9.3.3.3 A reference standard for the compound must also be analyzed by GC/MS. The reference standard concentration must be at a level that would demonstrate the ability to confirm the organophosphorus pesticide identified by GC analysis. Use of the sample concentration of the reference standard should be no greater than the sample *extract* concentration predicted from the GC sample concentration.

To confirm an identification of a compound, the background corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions.

9.3.3.4 The requirements for qualitative verification by comparison of mass spectra are as follows:

1. All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100%) should be present in the sample spectrum. However, the GC/MS analyst should use experience and discretion when deciding qualitatively to identify a target.

2. The relative intensities of ions specified must agree within ± 20% between the standard and the sample spectra.

3. Ions greater than 10% in the **sample** but not present in the **standard** spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives.

4. The RRT of the compound in the sample must be within ± 0.06 RRT units of the RRT of the same compound in the standard solution.

5. Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

9.3.3.5 GC/MS techniques should be judiciously employed to support qualitative identifications made with the method. Should GC/MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate capillary GC column and extract cleanup.

10.0 Sample Preparation

10.1 Water samples may be extracted using separatory funnel techniques. If emulsions prevent phase separation with separatory funnel extraction, continuous extraction techniques will be used. Separatory funnel extraction is the method of choice for wastewater. Nonaqueous samples are to be extracted using the sonication method.

10.2 Continuous Liquid——Liquid Extraction (for Water Samples)

10.2.1 Using a graduated cylinder, measure out 1 liter (nominal) of sample and transfer it to the continuous extractor. Measure the pH of the sample with wide-range pH paper and adjust the pH to 6 to 8. Pipet 1.0 mL of the surrogate standard spiking solution into each sample into the extractor and mix well. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. If gel-permeation cleanup is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

10.2.2 Add 300 to 500 mL of methylene chloride to the distilling flask. Add several boiling chips to the flask.

10.2.3 Add sufficient reagent water to the extractor to ensure proper operation and extract for 18 to 24 hours.

10.2.4 Allow to cool; then detach the boiling flask.

10.2.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

10.2.6 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20 to 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

10.2.7 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80° to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 to 2 mL of extraction solvent.

Warning: If extract is allowed to approach dryness, compounds of interest will be lost. If extracts accidentally go to dryness, discard extract and start over.

10.2.8 After cooling, K-D apparatus may be disassembled beginning with three-ball Snyder column. A 5-mL syringe filled with methylene chloride should be used to rinse upper joint and interior walls of the K-D. Disconnect the K-D from concentrator tube and rinse lower joint surface areas also allowing rinse solvent to mix with extract, and connect two-ball Snyder column to concentrator tube.

10.2.9 Prewet Snyder column with about 0.5 mL of methylene chloride. Return to hot water bath and further concentrate extract to about 2 mL. Allow extract to cool.

10.2.10 Allow extract to cool before detaching Snyder column. Rinse down joint and interior walls of concentrator tube with small amount of methylene chloride. Adjust volume of extract to 10 mL for screening and analysis.

10.3 Separatory Funnel Extraction (for Water Samples)

10.3.1 Measure a 1-liter aliquot of the sample and place into a 2-liter separatory funnel. Pipet 1.0 mL of the surrogate spiking solution into the separatory funnel mix well. Add 1.0 mL of matrix spiking solution to the matrix spike and the matrix spike duplicate samples. Add twice as much surrogate and matrix spiking solutions if using GPC cleanup.

10.3.2 Check the pH of the sample with wide-range pH paper. Adjust the pH to a value between 6 and 8.

10.3.3 Add 60 mL of methylene chloride to separatory funnel and extract sample by shaking funnel for 2 minutes, with periodic venting to release excess pressure. Allow organic layer to separate from water phase. If an emulsion interface between layers is more than one-third the total solvent volume, centrifugation must be employed to improve phase separation. If centrifugation fails to separate the layers, then continuous liquid-liquid extraction techniques must be used.

10.3.4 Collect methylene chloride extract in 250-mL Erlenmeyer flask. Add second 60-mL volume of methylene chloride to separatory funnel and repeat extraction procedure a second time, combining extracts in Erlenmeyer flask. Perform a third extraction in the same manner.

10.3.5 Dry and concentrate as in 10.2.

10.4 Sonification Extraction (for Soils, Sludges, and Wastes)

10.4.1 Decant and discard any water layer on sediment sample. Mix sample thoroughly and discard any foreign objects such as sticks, leaves, and rocks.

10.4.2 Waste samples consisting of multiple phases must be separated into different phases before extraction. The percent weight or volume of each phase should be determined and each phase analyzed individually.

10.4.3 Grind or otherwise subdivide dry waste amenable to grinding so that it either passes through a 1-mm sieve or can extruded through a 1-mm hole.

10.4.4 Weigh 30 grams of sample to nearest 0.1 gram into 400-mL beaker and add 60 grams of anhydrous sodium sulfate. Mix well until dry sandy texture is obtained. Add more sodium sulfate if necessary to achieve dry texture. Immediately add 1.0 mL of surrogate spiking solution and 1.0 mL of matrix spiking solution if performing matrix spike analysis. Add twice as much surrogate and matrix spiking solution if GPC cleanup is to be done. Mix well. Perform mixing step rapidly to prevent loss of volatile compounds. Add 100 mL of 50:50 methylene chloride:acetone.

10.4.5 Place bottom surface of tip of disrupter horn about 0.5 inch below surface of solvent but above sediment layer. Sonicate soil for 3 minutes. Sonicator should be adjusted to minimum output power required to suspend matrix using 50% duty cycle. Centrifuge and decant solvent into 500-mL Erlenmeyer flask.

10.4.6 Repeat extraction two more times with two additional 100-mL portions of 1:1 methylene chloride:acetone, combining extract into Erlenmeyer flask.

10.4.7 Dry and concentrate extracts as previously described for separatory funnel extraction.

10.5 All solid sample results are reported on a dry weight basis. Determine the percent moisture of the sample using Method No. FM-CON-0190.

10.6 Procede with Gel Permeation Cleanup (GPC) as in FM-ORG-0030 sections 10.8 through 10.8.4

11.0 Sample Analysis

11.1 Sample extracts should be refrigerated until analysis.

11.2 Sample extracts should be prepared for screening or analysis by placing internal standard solution into a labelled autosampler vial, then placing solvent (if dilution is being prepared) into the vial, and finally placing a known portion of the sample extract into the vial before capping and mixing. Instrument standards are prepared in the same manner.

Note: All working solutions should be prepared for injection in such a way that a constant amount (mass) of each internal standard is injected for all acquisitions.

The recommended internal standards are listed in Table 3. The suggested levels offer large detector response that will serve to minimize the effects of compound coelution.

11.3 The minimal total volume requirements for the autosampler vial are dependent on the model and configuration of the autosampler.

11.4 Inject 1 to 5 μL ($\pm$ 0.05 μL) of standards and samples (do not change injection volume after beginning initial calibration). Small volumes (1 μL) can be injected only if an automated system that consistently injects a constant volume is used.

11.4.1 If screening or analysis indicates that targets are present in the sample, the analyst must ensure that the calibration range is not exceeded. It is recommended that the analyst check acquired data periodically during the analytical sequence and reanalyze samples that need dilutions, reanalysis, etc., within the same sequence when possible.

11.5 The results of all samples that follow a high sample that has the potential for crossover must by examined carefully for the possibility of crossover. If there is uncertainty or questionable data, affected samples should be reanalyzed. Wash vials can be used to rinse the autodelivery system. Instrument blanks can be run between suspect samples to show lack of instrument contamination.

11.6 Summarized in Table 4 are the chromatographic conditions for primary column analysis.

11.7 Summarized in Table 5 are the chromatographic conditions for confirmation column analysis. It is not **required** to achieve primary initial calibration criteria to simply confirm the qualitative identity of a suspected target analyte. It is required that the confirmation criteria listed in GC Confirmation Analysis (for qualitative data only) section be achieved. However, it is **recommended** that primary initial calibration criteria (see GC Confirmation Analysis, qualitative and quantitative data) be achieved so that the quantitative data from both columns may be compared and either can be reported. The analyst must use his or her experience and discretion in deciding which value to report (considering such factors as peak shape, distance from the internal standard, surrounding chemical noise, etc.).

11.8 Qualitative Analysis

11.8.1 It is recommended that the nearest internal standard (for each compound) not suffering from coelution be used for calculation and comparison.

Table 4
Chromatographic Conditions——Primary Analysis

Detector Nitrogen Phosphorus Detector
Column The analytical column, designated HYBRID2, was prepared by adding the following together with presstight connector:

- J & W DB-210, 15-m × 0.53-mm I.D., 1.0-μm film thickness, wide-bore, capillary, or equivalent
- Supelco SPB-608, 15-m ×-0.53-mm I.D., 1.5-μm film thickness, wide-bore, capillary, or equivalent
- J & W DB-5, 15-m × 0.53-mm I.D., 1.0-μm film thickness, wide-bore, capillary, or equivalent

Carrier GasHelium, 10.5-psig inlet pressure
Detector Makeup GasNitrogen, 30 mL/minute
Injections 1.0 μL, splitless (split on at 0.5 minute)
Injector Temperature200°C.
Detector Temperature290°C.
Column Temperature Program80°C for 2 minutes, then 20°C/minute to 120°C (hold 0 minute), then 7°C/minute to 260°C (hold 0 minute), then 5°C/minute to 280°C (hold 5 minutes)

Table 5
Chromatographic Conditions——Confirmation Analysis

Detector	Nitrogen Phosphorus Detector
Column	J & W DB-1, 30-m × 0.32-mm I.D., 0.50-μm film thickness, capillary
Carrier Gas	Helium, 10.5-psig inlet pressure
Detector Makeup Gas	Nitrogen, 30 mL/minute
Injections	1.0 μL, splitless (split on at 0.5 minute)
Injector Temperature	200°C.
Detector Temperature	290°C.
Column Temperature Program	80°C for 2 minutes, then 20°C/minute to 120°C (hold 0 minute), then 7°C/minute to 260°C (hold 0 minute), then 5°C/minute to 280°C (hold 5 minutes)

11.8.2 Peak identification is based upon relative retention time comparison to calibration data. Library retention times are usually established during initial calibration (or in some cases from continuing calibration standards). Internal standards serve as time references for all chromatographic acquisitions. A target compound should be identified in a sample if the chromatographic peak matches the predicted retention time within 0.05 minute.

11.8.2.1 Other chromatographic features such as peak shape, resolution, and distance from the internal standard must be considered. The experienced analyst can also graphically overlay sample and standard chromatograms, thus comparing reference peaks and tentatively identified compounds. Peaks tentatively identified in a sample require confirmation analysis. Compound concentrations too low for GC/MS analysis must be scheduled for GC confirmation using a dissimilar capillary column.

11.8.3 When graphically comparing sample and standard chromatograms, standards with responses similar to those in the samples should be used for retention time and peak shape evaluation. As the mass injected fluctuates, the column may begin to experience overload, which can result in retention time shifts, distorted peak shapes, and other anomalies.

11.8.4 The width of a retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of the day. Three times the standard deviation of a retention time can be used to calculate a suggested retention time window size for a compound.

Note: The performance check mix and the five levels of calibration standards check the machine algorithms ability to identify peaks at various concentrations.

11.8.5 The acquisition method peak search criteria should be optimized to identify targets but not to identify peaks of significantly different retention times. The system should bias favoring false positives to alert the analyst to potential targets and necessitate further analytical investigation.

Note: The analyst should not rely exclusively on either quantitation reports or chromatograms for qualitative decisions.

11.8.6 When deciding qualitatively to identify a peak, the analyst should also consider peak shape (i.e., is the retention time distorted due to coelution?).

11.8.7 Standard addition is another qualitative technique that can be employed to gain confidence in the qualitative identification of a component. When a target has been tentatively identified, a known amount of the tentative target can be added to the sample extract (which cannot be used for primary or confirmation analysis after standard addition). If the peak increases in size and quantitation by the expected amount and no abnormal peak shapes are observed, the target is additionally confirmed. If a new peak or misshapen target peak (poorly resolved) is observed, the evidence is not strong that the identification is correct.

11.9 Surrogate spikes are added to each sample. Target acceptance ranges for surrogate spikes are 75 to 125% recovery. If one or more of the surrogate spike recoveries is outside the acceptance limits, then the sample is reanalyzed. If the surrogate spike recoveries of the reanalyzed samples are still outside the target acceptance range, then the sample results of both analyses are reported and noted in the case narrative.

11.10 One MS/MSD sample is analyzed for every 20 samples of the same matrix, or one per sample batch, whichever is more frequent. Target acceptance ranges are 75 to 125%. If the MS/MSD recoveries are not within the target acceptance limits, the analysis is not repeated. The data is reported as is and noted in the case narrative.

12.0 Calculations

12.1 Internal Standard Calibration: For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

12.1.1 Water Samples (9)

$$\text{Concentration } (\mu g/L) = \frac{[(A_x)(C_{IS})(D)]}{[(A_{IS})(RF)(V_s)]}$$

Where:

A_x = Response of analyte being measured

C_{IS} = Amount of internal standard added to extract (ng)

D = Dilution factor, if dilution was made on sample before analysis. (If no dilution was made, D = 1, dimensionless.)

A_{IS} = Response of the internal standard

RF = Response factor for analyte

V_s = Volume of water extracted (mL)

(10)

12.1.2 Soil/Sludge/Waste

$$\text{Concentration } (\mu g/kg) = \frac{[(A_s)(C_{IS})(D)]}{[(A_{IS})(RF)(W_s)]}$$

Where:

W_s = Weight of sample extracted (grams). (Wet weight is generally used, although dry weight may be used, depending upon specific application of the data.)

A_S, C_{IS}, D, A_{IS}, and RF have the same definition as for water samples.

12.2 Data Reduction

12.2.1 When reviewing chromatographic data before reduction, the analyst should evaluate the baseline and ensure that targets could be detected at the reporting limit level (above any chemical interference).

12.2.2 The results of all samples that follow a high sample that has the potential for crossover in the autosampler must be examined carefully for the possibility of crossover. The data must be reviewed against instrument run logs.

12.2.3 Sample results (confirmed compounds and reporting limits) should be reported to one or two significant figures. The analyst may decide to report surrogate recovery to either two or three significant figures.

12.2.4 The expected reporting limit should be calculated before data reduction begins. The expected reporting limit is the lowest reporting limit that can be issued for a sample. The total sample producing the total extract and any dilution factors are used to correct the nominal reporting limit. If interference prevents the detection of a target (at the expected reporting limit), the analyst may chose to raise the reporting limit to reflect level of interference. Raised reporting limits should be addressed in the case narrative.

12.2.5 The reporting limits must be issued with correction for any extract dilution and percent solids.

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control and reporting requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	Begin and end	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80—120%	Qualify data
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike	1/20	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10 and end	90—110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	75—125%	Qualify data
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
End	end of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
A/S	as specified earlier in this method
RPD	relative percent difference
LCS	laboratory control sample

15.0 References

Test Methods for Evaluating Solid Waste, 3rd ed., Method 8140. September 1986.

FERNALD/org-pest.51

FM-ORG-0050

Volatile Organic Compounds by Gas Chromatography, Purge and Trap

Working Linear Range:	1 to 200 μg/L
Reporting Limit:	Matrix dependent
Reporting Units:	μg/L or μg/kg dry weight
Matrix:	Water, soil, sediment or sludge

1.0 Scope and Application

This method describes procedures to analyze water, soil, and sediment samples for selected volatile organic compounds by using purge-trap-desorb gas chromatographic techniques. The target compound list and method detection limits are summarized in Table 1.

2.0 Method Summary

2.1 Water samples are analyzed directly by bubbling an inert gas through a sample contained in a specially designed purging chamber at ambient temperature.

2.2 Soil, sediment, and sludge samples are analyzed by one of two methods depending on the concentration of volatile components in the matrix. For low-level solid samples, the matrix is suspended in water and the suspension purged in a heated sparging chamber. Medium- to high-level solid samples are extracted with methanol. An aliquot of the methanol extract is spiked into reagent water and analyzed according to procedures described for water samples.

2.3 The volatile components from the different matrixes are thus transferred efficiently from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column (analytical trap) where the volatile components are stripped from the purge gas. After purging is completed, the sorbent column is heated and backflushed with an inert gas directed into a gas chromato-graph. The volatile components are transferred to a gas chromatographic column that is temperature programmed to separate the compounds. The gas chromatograph is equipped with a photoionization detector (PID) connected in series with a Hall electrolytic conductivity detector (HECD). The PID can detect aromatic compounds, and the HECD can detect the halogenated compounds.

Table 1
Target Compound List and Method Detection Limits

Compound	MDL (µg/L) 5-mL Sample	MDL (µg/L) 25-mL Sample
Chloromethane	1.0	0.5
Bromomethane	1.0	0.5
Dichlorodifluoromethane	1.0	0.5
Vinyl chloride	1.0	0.5
Chloroethane	1.0	0.5
Methylene chloride	1.0	0.5
Trichlorofluoromethane	1.0	0.5
1,1-Dichloroethene	1.0	0.5
1,1-Dichloroethane	1.0	0.5
trans-1,2-Dichloroethene	1.0	0.5
Chloroform	1.0	0.5
1,2-Dichloroethane	1.0	0.5
1,1,1-Trichloroethane	1.0	0.5
Carbon tetrachloride	1.0	0.5
Bromodichloromethane	1.0	0.5
1,2-Dichloropropane	1.0	0.5
cis-1,3-Dichloropropene	1.0	0.5
Trichloroethene	1.0	0.5
Dibromochloromethane	1.0	0.5
1,1,2-Tetrachloroethane	1.0	0.5
trans-1,3-Dichloropropene	1.0	0.5
Bromoform	1.0	0.5
1,1,2,2-Tetrachloroethane	1.0	0.5
Tetrachloroethene	1.0	0.5
2-Chloroethyl vinyl ether	1.0	0.5
1,2-Dibromo-3-chloropropane (DBCP)	1.0	0.5
1,1,2-Tetrachloropropane	1.0	0.5
Methylene bromide	1.0	0.5
1,2-Dibromoethane (Ethylene dibromide)	1.0	0.5
Benzene	1.0	0.5
Chlorobenzene	1.0	0.5
Toluene	1.0	0.5
Ethylbenzene	1.0	0.5
1,3-Dichlorobenzene	1.0	0.5
1,2-Dichlorobenzene	1.0	0.5
1,4-Dichlorobenzene	1.0	0.5
Xylenes (total)	1.0	0.5
Styrene	1.0	0.5

3.0 Interferences

3.1 Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap account for most contamination problems. The analytical system must be demonstrated to be free of contamination under the conditions of the analysis by running laboratory method blanks.

3.2 The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge-and-trap system should be avoided.

3.3 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and common laboratory solvents such as acetone, toluene, and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol (trip blank) can serve as a check on such contamination. Diffusion of contaminants may be minimized by storing sample containers inverted.

3.4 Contamination by carryover can occur whenever high- and low-level samples are sequentially analyzed. To reduce carryover, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling organic solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Sample Containers: 40-mL VOA vials with screw cap and Teflon-faced, silicone-coated septum placed inside screw cap so that Teflon-coated side comes into contact with sample. Vials and septa are routinely purchased precleaned (with certificate of analysis) from suppliers and are not reused. Certificates of analysis for precleaned VOA vials will be archived in the laboratory files.

6.2 Teflon Squirt Bottle, labeled "Methanol."

6.3 Conical Glass Vials with stop-go caps: 1-, 2-, and 5-mL.

6.4 Syringes: Hamilton gastight syringes, or equivalent. Syringes used for standard solutions will be designated by color coding. Syringes used for sample preparation will not be used for standard preparation.

6.4.1 Microliter Syringes: 10-, 25-, 50-, 100-, 500-, and 1,000-μL.

6.4.2 Milliliter Syringes: 5-, 10-, and 25-mL with syringe valve.

6.5 Volumetric Flasks Class A: 2-, 10-, 25-, 50-, 100-, and 1,000-mL.

6.6 Purge-trap-desorb System: Tekmar LSC-2, or equivalent.

6.7 Gas Chromatograph: Analytical system suitable for temperature programming and all required accessories for proper operation. It should also be equipped with variable-constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

6.8 Data System: Minimally capable of measurement of chromatographic peak areas or heights.

6.9 Detectors

6.9.1 HNu Model PI-51-02 with a 10.2-eV lamp or equivalent.

6.9.2 Tracor Model 700A Hall Electrolytic Conductivity Detector or equivalent.

6.10 Gas Chromatographic Columns: Any capillary column that meets or exceeds the QC criteria of the method and produces acceptable resolution of all target analytes. Acceptable resolution is achieved if the baseline to valley height between two closely eluting peaks is less than 25% of the sum of the two peak heights. Three useful columns have been identified.

6.10.1 Column 1: 60 m × 0.75 mm I.D. VOCOL (Supelco, Inc.) with 1.5-μm film thickness.

6.10.2 Column 2: 30 m × 0.53 mm I.D. DB-624 (J&W Scientific, Inc.) with 3-μm film thickness.

6.10.3 Column 3: 105 m × 0.53 mm I.D. RT_x-1 (Restek, Inc.) with 3-μm film thickness.

6.11 Analytical Trap: Tekmar 14-0124-003 or equivalent. Trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. Trap must be packed with one-third each of Tenax, silica gel, and coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap.

6.12 Heater or Heated Water Bath: Capable of maintaining the sparging vessel at 40°C for soil, sediment, and sludge analysis.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the gas chromatograph according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Methanol: Purge-and-trap methanol, Burdick and Jackson or equivalent. Each separate lot of methanol (as designated by the vendor) must be demonstrated to be free of volatile target analyte contamination before use by analyzing 100-μL of methanol in 5-mL of reagent water. Methanol can be temporarily stored for convenience in a labeled Teflon squirt bottle.

8.2 Reagent Water: This is organic-free water in which any target compound or an interferant are not observed above the method detection limits. Prepare by passing deionized water through a carbon filter, followed by bubbling with contaminant-free inert gas for 1 hour.

8.3 *Stock Standard Solutions:* Stock solutions may either be prepared from neat standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed EPA-certified liquids or gases, as appropriate. Because of the toxicity of some of the organohalides and aromatic hydrocarbons, primary dilutions of these materials must be prepared in a fume hood.

8.3.1 Place about 9.8 mL of methanol in 10-mL tared, ground glass stoppered volumetric flask. Allow flask to stand unstoppered for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh flask to nearest 0.1 mg.

8.3.2 Add assayed reference material, as described below.

8.3.2.1 Liquids: Using 100-μL syringe, immediately add two or more drops of assayed reference material to flask; then reweigh. Liquid must fall directly into alcohol without contacting neck of flask.

8.3.2.2 Light Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill 5-mL valved gastight syringe with reference standard to 5-mL mark. Lower needle to 5 mm above methanol meniscus. Slowly introduce reference standard above surface of liquid. The gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (No. 86600). Attach Teflon tubing to side-arm relief valve and direct gentle stream of gas into methanol meniscus.

8.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting flask several times. Calculate concentration in milligrams per liter (mg/L) from net gain in weight. When compound purity is assayed to be 96% or greater, weight may be used without correction to calculate concentration of stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by manufacturer or by an independent source.

8.3.4 Transfer stock standard solution into bottle with Teflon-lined screw-cap or crimp top. Store with minimal headspace at -10° to -20°C and protect from light.

8.3.5 Prepare fresh stock standards every 2 months for gases. Reactive compounds such as 2-chloroethylvinyl ether and styrene may need to be prepared more frequently. All other standards should be replaced after 6 months. Both gas and liquid standards must not show more than 25% difference from independently prepared LCS standards. If such is the case, solutions containing compounds not meeting this criterion must be replaced.

8.4 Prepare secondary dilution standards as needed using stock standard solutions, in methanol, containing compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that aqueous calibration standards will bracket working range of analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just before preparing calibration standards from them.

8.5 Calibration standards, at a minimum of five concentrations are prepared in organic-free reagent water from secondary dilution of stock standards as summarized in Table 2. One concentration should be near but above the method detection limit. Other concentrations should correspond to the expected range of concentrations found in real samples or should define working range of GC. Standards (one or more) should contain each analyte for detection by this method (e.g., some or all of target analytes may be included). To prepare accurate aqueous standard solutions, the following precautions must be observed.

8.5.1 Do not inject more than 20 μL of alcoholic standards into 100 mL of water.

8.5.2 Use a 25-μL Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

8.5.3 Rapidly inject alcoholic standard into filled volumetric flask. Remove needle as fast as possible after injection.

8.5.4 Mix aqueous standards by inverting flask three times.

8.5.5 Fill sample syringe from standard solution contained in expanded area of flask (do not use any solution contained in neck of flask).

Table 2
Standard Solution Preparation

Description	Final Concentration (µg/mL)	Volume to Use (µL)	Concentration (µg/L)
Calibration Standards	25	1	5
		2	10
		8	40
		16	80
		40	200
Surrogate Standards	15	10	30
Internal Standards	15	10	30

Applies only to 5-mL water samples

$$\text{Vol. to use } (\mu L) = \frac{(\text{Final concen., } \mu g/L) \times (\text{purge vol., mL})}{(\text{Stock standard conc., } \mu g/mL)}$$

8.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

8.5.7 Aqueous standards are not stable and should be discarded after 1 hour, unless properly sealed and stored. Aqueous standards can be stored up to 12 hours if held in sealed vials with zero headspace.

8.6 Internal Standards (IS): Prepare spiking solution in methanol using procedures described in Sections 8.3 and 8.4. It is recommended that secondary dilution standard be prepared at a concentration of 15 µg/mL of each internal standard compound. Addition of 10 µL of such standard to 5 mL of sample or calibration standard would be equivalent to 30 µg/mL.

8.7 Surrogate Standards (SS): The analyst should monitor both performance of analytical system and effectiveness of method in dealing with each sample matrix by spiking each sample, standard, and method blank with two or more surrogate compounds. A combination of bromochloromethane, 2-bromo-1-chloropropane and 1,4-dichlorobutane is recommended to encompass the range of the

temperature program used in the method. An alternative surrogate for the PID would be α,α,α-trifluorotoluene. From stock standard solutions, add a volume to give 750 μg of each surrogate to 45 mL water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/μL. Add 10 μL of surrogate spiking solution directly into 5-mL syringe with every sample and reference standard analyzed. If internal standard calibration procedure is used, surrogate compounds may be added directly to internal standard spiking solution.

8.8 Laboratory Control Sample (LCS) Standards: Independently prepared LCS standards should be obtained from a separate source. The LCS should be prepared at a concentration of 10 μg/mL. A 10-μL spike of LCS standard into 5 mL reagent water will yield a concentration of 20 μg/L.

8.9 Matrix Spike Solution: Prepare like a medium-level calibration standard, e.g., 40 μg/L.

9.0 Calibration Procedures

9.1 General Considerations

9.1.1 The linear calibration range of the instrument must be determined before analysis of any samples. The low point in the range should be close to the method detection limit and should be regarded as the lower limit for reporting. For general purposes, a range of 1 to 200 μg/L has been found to be a useful range.

9.1.2 The instrument must be calibrated using the same instrument conditions that are used to analyze the samples.

9.1.3 For aqueous samples in which 5 mL will be analyzed, the initial calibration curve and all continuing calibrations and quality control checks must be prepared by spiking of purge water with the appropriate volume of the initial calibration stock standard.

9.1.4 For soils/sediments/sludges that will be analyzed using the heated purge technique, the initial calibration curve and all continuing calibrations and quality control checks must be performed using the heated purge technique.

9.1.5 For medium-level soils treated by solvent (methanol) extraction, the calibration curve and continuing calibration checks must incorporate a 100-μL spike of the solvent into each calibration point.

9.2 Initial Calibration: The response of the analytical instrument across the established range of analytical concentrations must be verified to be linear over this range. This is done by analyzing at least five calibration points, the lowest of which should be at a concentration equal to the stated reporting limit or less.

9.2.1 Rinse a 5-mL gastight syringe three times with deionized water, once with methanol (use Teflon squirt bottle for convenience), and again with water.

9.2.2 Cap tip of syringe with a stop-go syringe valve or using any other suitable means, and add water to create a positive meniscus. Slowly insert plunger, invert syringe, and press plunger to remove excess water and air bubbles. Final volume in syringe should be 5 mL.

9.2.3 Add the amounts of calibration standards, surrogate standards, and internal standards as summarized in Table 2 to the open end of the syringe. Use syringes specifically designated for each solution.

9.2.4 Analyze each calibration standard and calculate relative response factor (RRF) for each compound at each of five calibration levels according to the equation: (1)

$$\text{RRF} = \frac{(\text{Area of target analyte}) \times (\text{concentration of IS})}{(\text{Area of IS}) \times (\text{concentration of target analyte})}$$

9.2.5 Calculate standard deviation(s) for RRF of each compound using n-1 degrees of freedom. Calculate corresponding relative standard deviation (% RSD) using the equation: (2)

$$\%\ \text{RSD} = \frac{\text{Standard deviation}}{\text{Mean RRF}} \times 100$$

9.2.6 The RSD of each compound must be less than 20%. This minimum criterion must be achieved for calibration to be valid. If it is not consistently met, the expected calibration range may be too extended.

9.2.7 A calibration curve generated with the calibration data may be prepared and used to calculate sample concentrations. The calibration curve should plot the response ratio (area of target analyte/area of IS) against the RRF for each calibration point. Interpolated RRFs will be used to calculate sample concentrations. The use of calibration curves is more complex but may be used for certain compounds.

9.3 Continuing Calibration: The average RRF for each target analyte obtained during initial calibration must be verified daily by analysis of a mid-range continuing calibration standard. The daily continuing calibration results must be compared to the initial calibration curve to verify that the system is in compliance with method requirements. The continuing calibration check must be performed at least after every 10 or 20 injections (depending on analytical support level [ASL]; see 14.0).

9.3.1 Analyze continuing calibration standard and calculate relative response factor (RRF) for each of target compounds.

9.3.2 For each analyte, calculate percent difference (%D) between continuing calibration RRF and average RRF from initial calibration curve using the equation: (3)

$$\% D = \frac{RRF_{CC} - RRF_{IC}}{RRF_{IC}} \times 100$$

9.3.3 The criterion for acceptable continuing calibration is 10%D. Failing to meet this criterion may be indicative of degenerating standards or instrumental problems. The problem must be identified and corrected, then the instrument recalibrated. All the samples analyzed since the last successful continuing calibration check must be reanalyzed before sample analysis continues.

10.0 Sample Preparation

10.1 Water samples require only equilibration to ambient temperatures.

10.2 Sediment or soil samples are analyzed in one of two ways, depending on the relative concentration of the target analytes in the sample.

10.3 Low-level Method: The low-level method involves the analysis of a 1- to 5-gram aliquot of the sample suspended in water using the heated purge technique. The smallest sample size permitted for analysis is 1 gram. If the level of analytes is high enough that a 1-gram aliquot is outside the linear calibration range, the sample must be analyzed by the high-level protocol.

10.3.1 Weigh out a purging device and record the initial weight. Measurements should be made to an accuracy of ± 0.01 gram to allow reporting to two significant figures.

10.3.2 Mix sample using stainless steel or Teflon spatula and transfer 1 to 5 grams of sample to preweighed purging device. Record final weight. The weight of the actual sample is the difference between the final weight (purging vessel plus sample) and the initial weight (purging vessel).

10.3.3 Place sample vessel in purging device. All operations with sample should be expedited to minimize loss of target analytes. It is recommended that cold samples be used.

10.4 High-level Method: The high-level method involves extracting the soil sample with methanol, spiking an aliquot of the extract into reagent water, and analyzing the spiked water in the same manner as a water sample. The methanol extracts should be analyzed within the same 24-hour period as the extraction.

10.4.1 Weigh an amber VOA vial and record the tare weight. Measurements should be made to an accuracy of ± 0.01 gram to allow reporting to two significant figures.

10.4.2 Mix sample using stainless steel or Teflon spatula and transfer 4 grams of sample to preweighed VOA vial. Record final weight. The weight of the actual sample is the difference between the final weight (VOA vial plus sample) and the initial weight (VOA vial).

10.4.3 Add appropriate volume of surrogate standards solution to sample and quickly add 9 mL of methanol to vial. Cap vial and shake for 2 minutes. If possible transfer two 1.5-mL portions of extract to two 2-mL GC autosampler vials. If an emulsion occurs, centrifuge vials until adequate phase separation is attained, then transfer the aliquots. If the sample is not going to be analyzed immediately, store at 4° ± 2°C in the dark. It is recommended that samples be analyzed on the same day as extraction.

11.0 Sample Analysis

11.1 Analysis of Water Samples: The following guidelines apply to samples of which 5 mL will be analyzed. Certain samples require analysis of 25 mL to attain increased sensitivity, thereby lowering detection limits. In such situations, the entire procedure described below should be proportionally scaled to the larger volume.

11.1.1 Allow all samples and standard solutions to equilibrate with ambient temperature before analysis.

11.1.2 Rinse 5-mL gastight syringe three times with deionized water, once with methanol (use Teflon squirt bottle for convenience), and once with reagent water.

11.1.3 Cap tip of syringe with stop-go syringe valve or using any other suitable means, and add sample to create positive meniscus. Invert syringe and slowly press plunger to remove excess water and air bubbles. Final volume in syringe should be 5 mL. Close syringe valve and set aside.

11.1.4 Transfer balance of sample to a 20-mL (or smaller) VOA vial. Fill vial slowly, avoiding turbulence, to create positive meniscus and cap. Label the vial, invert, and tap lightly making certain there are no air bubbles. Store at 4°C protected from the light. By removing a portion of the original sample, significant headspace is introduced into the sample, thereby invalidating the balance of the sample. Saving an aliquot of the sample allows reanalysis or dilution of a valid sample.

11.1.5 Add 10 μL of surrogate standards solution and 10 μL of internal standards solution and 10 μL of matrix spike/matrix spike duplicate, if applicable, to the open end of sample-filled syringe. Use spiking syringe specifically designated for each solution.

11.1.6 Inject sample into purging device, and begin purge-trap-desorb-bake cycle. GC analysis should start automatically at the end of the desorb cycle as the sample is backflushed onto the column.

11.1.7 Calculate sample concentrations of target analytes using the equations in Section 12.1. All target analytes detected must be within the linear calibration range established for the instrument. If a target analyte exceeds the calibration range, the sample must be diluted in such a manner that response of the major constituents are in the upper half of the calibration range.

11.1.8 If sample must be diluted, dilutions should be made using Class A volumetric flasks, gastight syringes, and reagent water. Select volumetric flasks so that at least 1 mL of sample is used for dilutions. Operations that cause sample turbulence or introduce headspace should be avoided.

11.2 Low-level Soil Analysis

11.2.1 Rinse 5-mL gastight syringe three times with deionized water, once with methanol (use Teflon squirt bottle for convenience), and once with reagent water.

11.2.2 Cap tip of syringe with stop-go syringe valve or using other suitable means, and add reagent water to create positive meniscus. Invert syringe and slowly press plunger to remove excess water and air bubbles. Final volume in syringe should be 5 mL.

11.2.3 Add appropriate volumes of surrogate standards solution, internal standards solution, and matrix spike/matrix spike duplicate if applicable to open end of sample-filled syringe. Use syringes specifically designated for each solution.

11.2.4 Inject spiked water into purging device containing the soil/sediment sample, heat sample to 40°C, and start purge-trap-desorb-bake cycle. GC analysis should start automatically at the end of the desorb cycle as the sample is backflushed onto the column.

11.2.5 Calculate sample concentrations of the target analytes using the equations in Section 12.2. All target analytes detected must be within the linear calibration range established for the instrument. If a target analyte (in a 1-gram sample) exceeds the calibration range, the sample must be reanalyzed using the high-level method described below.

11.2.6 For each batch of samples prepared by this method, a method blank must also be analyzed. The method blank is prepared by subjecting 1 to 5 grams of the method blank material and treating it as a regular sample.

11.3 High-level Soil Analysis

11.3.1 Cap tip of 5-mL gastight syringe with stop-go syringe valve or using other suitable means and add reagent water to create positive meniscus. Invert syringe and slowly press plunger to remove excess water and air bubbles. Final volume in syringe should be 5 mL.

11.3.2 Add 100 μL of sample extract (or other volume as determined by optional sample screening process) and appropriate volume of internal standards solution to open end of sample-filled syringe. Use spiking syringes specifically designated for each solution.

11.3.3 Inject sample into purging device, and begin purge-trap-desorb-bake cycle. GC analysis should start automatically at the end of the desorb cycle as the sample is backflushed onto the column.

11.3.4 Calculate sample concentrations of target analytes using the equations in Section 12.3. All target analytes detected must be within the linear calibration range established for the instrument. If a target analyte exceeds the calibration range, adjust volume of sample to be added to reagent water accordingly. The response of the major constituents should be in the upper half of the calibration range.

11.3.5 For each batch of samples prepared by this method, a method blank must also be prepared. The method blank consists of a 1-mL aliquot of the same methanol as used to extract the samples, transferred into a GC vial at the same time as the sample extracts. A 100-μL portion of the method blank is analyzed after spiking with surrogate and internal standards.

11.4 Surrogate spikes are added to each sample. Target acceptance ranges for surrogate spikes are 75 to 125% recovery. If one or more of the surrogate spike recoveries is outside the acceptance limits, then the sample is reanalyzed. If the surrogate spike recoveries of the reanalyzed samples are still outside the target acceptance range, then the sample results of both analyses are reported and noted in the case narrative.

11.5 One MS/MSD sample is analyzed for every 20 samples of the same matrix, or one per sample batch, whichever is more frequent. Target acceptance ranges are summarized in Tables 3 and 4. If the MS/MSD recoveries are not within the target acceptance limits, the analysis is not repeated. The data is reported as is and noted in the case narrative.

12.0 Calculations

12.1 Water Samples: Calculate the concentration of target analytes in the sample using the equation: (4)

$$\text{Conc. } (\mu g/L) = \frac{\text{Area of target} \times \text{conc. of IS} \times \text{dilution factor}}{\text{Area of IS} \times \text{RRF} \times \text{vol. of sample purged}}$$

Where:

Concentration of IS (μg)	=	Concentration of IS solution (μg/mL) × volume spiked (μL)
RRF	=	Average RRF from initial calibration curve
Volume of sample purged	=	mL

Table 3
Purgeable Halocarbon Matrix Spike Target Acceptance Ranges

Compound	Acceptable Recovery Range
Chloromethane	D—193
Bromomethane	D—144
Dichlorodifluoromethane	*
Vinyl Chloride	28—163
Chloroethane	46—137
Methylene chloride	25—162
Trichlorofluoromethane	21—156
1,1-Dichloroethene	28—167
1,1-Dichloroethane	47—132
trans-1,2-Dichloroethane	38—155
Chloroform	49—133
1,2-Dichloroethane	51—147
1,1,1-Trichloroethane	41—138
Carbon tetrachloride	43—143
Bromodichloromethane	42—172
1,2-Dichloropropane	44—156
cis-1,3-Dichloropropene	22—178
Trichloroethene	35—146
Dibromochloromethane	24—191
1,1,2-Trichloroethane	39—136
trans-1,3-Dichloropropene	22—178
Bromoform	13—159
1,1,2,2-Tetrachloroethane	8—184
Tetrachlorothene	26—162

*Criteria not listed.

Table 4
Purgeable Aromatic Matrix Spike Target Acceptance Ranges

Compound	Acceptable Recovery Range
Benzene	39—150
Chlorobenzene	55—135
Toluene	46—148
Ethylbenzene	32—160
1,3-Dichlorobenzene	50—141
1,2-Dichlorobenzene	37—154
1,4-Dichlorobenzene	42—143

12.2 Low-level Soil/Sediment Samples: Calculate the concentration of target analytes in the sample using the equation:

$$\text{Conc. } (\mu g/kg) = \frac{\text{Area of target} \times \text{conc. of IS } (\mu g) \times \text{dilution factor}}{\text{Area of IS} \times \text{RRF} \times \text{D} \times \text{weight of sample analyzed}} \quad (5)$$

Where:

Concentration of IS (μg)	=	Concentration of IS solution (μg/mL) × volume spiked (μL)
RRF	=	Average RRF from initial calibration curve
D	=	(100 - % moisture)/100
Weight of sample anal.	=	grams

12.3 Medium- and High-level Soil/Sediment Samples: Calculate the concentration of target analytes in the sample using the equation:

$$\text{Conc. } (\mu g/kg) = \frac{\text{Area of target} \times \text{conc. of IS} \times \text{extract vol.} \times \text{dilution factor}}{\text{Area of IS} \times \text{RRF} \times \text{vol. extract anal.} \times \text{D} \times \text{wt. of sam. anal.}} \times 1{,}000 \quad (6)$$

Where:

Concentration of IS (μg)	=	Concentration of IS solution (μg/mL) × volume spiked (μL)
RRF	=	Average RRF from initial calibration curve
D	=	(100 - % moisture)/100
Weight of sample anal.	=	grams
Extract volume	=	Total volume of extract (μL)
Volume extract anal.	=	Volume of total extract analyzed (μL)

12.4 Spiking Concentration: Recovery calculations (matrix spike, surrogates) require that the spike level be calculated.

12.4.1 Water and Low-level Soil/Sediment

$$SC = \frac{SSC \times SV}{Amount} \qquad (7)$$

Where:

SC	=	Spike concentration (μg/L or μg/kg)
SSC	=	Spike solution concentration (μg/mL)
SV	=	Spike volume (μL)
Amount	=	Amount of sample analyzed (mL or gram)

(8)

12.4.2 Medium-level Soil/Sediment

$$SC = \frac{SSC \times SV \times extract}{Amount \times VEA} \times 1{,}000$$

Where:

SC	=	Spike concentration (μg/kg)
SSC	=	Spike solution concentration (μg/mL)
SV	=	Spike volume (μL)
Amount	=	Amount of sample analyzed (mL or gram)
VEA	=	Volume extract analyzed (μL)
Extract	=	Total volume of extract (mL)

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/20	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	1/20	80—120%	Qualify data
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike	1/20	11.5	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10	90—110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	1/20	80—120%	Recalibrate
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	11.5	Qualify data
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
A/S	as specified earlier in this method
RPD	relative percent difference
11.5	target acceptance range (see Section 11.5)

15.0 References

U.S. EPA. *Test Methods for Evaluating Solid Waste*, 3rd ed., SW846, Methods 8010 and 8020.

FERNALD/voc-gcpt.51

FM-ORG-0060

Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry

Working Linear Range:	Detection limit to 200 ppb
Reporting Limit:	Analyte- and matrix-dependent
Reporting Units:	μg/L or μg/kg
Matrix:	Water, soils, sediments and wastes

1.0 Scope and Application

1.1 The method is based on the use of gas chromatography (GC) in combination with mass spectrometry (MS) to identify and quantitate organic compounds in a sample. The components are separated in a GC column and identified and quantified by an MS detector.

1.2 Identification is based on the ionization of a compound into charged fragments using an electron beam. The fragmentation (called mass spectrum) pattern is unique to each compound. Since the MS cannot usually distinguish between isomers with the same mass spectra, the GC retention times provide a means for determining the identity of isomers.

1.3 Quantification is accomplished by comparing the area integration of a particular mass ion (called characteristic ion) in a compound's mass spectrum to that of a standard of known concentration.

1.4 Summarized in Table 1 are the target compounds and the corresponding practical quantitation limits.

2.0 Method Summary

2.1 The method is used for the determination of semivolatile organic compounds in waters, soils, sediments, and wastes.

2.2 The method covers the determination of organic compounds that may be partitioned into methylene chloride and are amenable to GC/MS. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols including nitrophenols.

Table 1
Practical Quantitation Limits
for Semivolatile Compounds[a]

Compound	Water (µg/L)	Soil/Sediment (µg/kg)
Acenaphthene	10	330
Acenaphthylene	10	330
Acetophenone	10	330
Aniline	20	660
Anthracene	10	330
4-Aminobiphenyl	50	2,400
Benzidine	50	2,400
Benzoic acid	50	2,400
Benzo(a)anthracene	10	330
Benzo(b)fluoranthene	10	330
Benzo(k)fluoranthene	10	330
Benzo(g,h,i)perylene	10	330
Benzo(a)pyrene	10	330
Benzyl alcohol	20	660
Bis (2-chloroethoxy)methane	10	330
Bis (2-chloroethyl)ether	10	330
Bis (2-chloroisopropyl)ether	10	330
Bis (2-ethylhexyl)phthalate	10	330
4-Bromophenyl phenyl ether	10	330
Benzyl butyl phthalate	10	330

(Continued)

Table 1
Practical Quantitation Limits
for Semivolatile Compounds[a]

Compound	Water (µg/L)	Soil/Sediment (µg/kg)
4-Chloroaniline	20	660
1-Chloronaphthalene	10	330
2-Chloronaphthalene	10	330
4-Chloro-3-methylphenol	20	660
2-Chlorophenol	10	330
4-Chlorophenyl phenyl ether	10	330
Chrysene	10	330
Dibenzo(a,h)anthracene	10	330
Dibenzofuran	10	330
Di-n-butylphthalate	10	330
1,3-Dichlorobenzene	10	330
1,4-Dichlorobenzene	10	330
1,2-Dichlorobenzene	10	330
3,3′-Dichlorobenzidine	10	330
2,4-Dichlorophenol	10	330
2,6-Dichlorophenol	10	330
Diethylphthalate	10	330
p-Dimethylaminoazobenzene	50	2,400
7,12-Dimethylbenz(a)anthracene	10	330

(Continued)

Table 1
Practical Quantitation Limits
for Semivolatile Compounds[a]

Compound	Water (µg/L)	Soil/Sediment (µg/kg)
2,4-Dimethylphenol	10	330
Dimethylphthalate	10	330
4,6-Dinitro-2-methylphenol	50	330
2,4-Dinitrophenol	50	330
2,4-Dinitrotoluene	10	330
2,6-Dinitrotoluene	10	330
Diphenylamine	20	660
Di-n-octylphthalate	10	330
Ethyl methanesulfonate	10	330
Fluoranthene	10	330
Fluorene	10	330
Hexachlorobenzene	10	330
Hexachlorobutadiene	10	330
Hexachlorocyclopentadiene	10	330
Hexachloroethane	10	330
Indeno(1,2,3-cd)pyrene	10	330
Isophorone	10	330
3-Methylcholanthrene	10	330
Methyl methanesulfonate	10	330

(Continued)

Table 1
Practical Quantitation Limits
for Semivolatile Compounds[a]

Compound	Water (µg/L)	Soil/Sediment (µg/kg)
2-Methylnaphthalene	10	330
2-Methylphenol (o-cresol)	10	330
4-Methylphenol (p-cresol)	10	330
Naphthalene	10	330
1-Naphthylamine	50	2,400
2-Naphthylamine	50	2,400
2-Nitroaniline	50	2,400
3-Nitroaniline	50	2,400
4-Nitroaniline	50	2,400
Nitrobenzene	10	330
2-Nitrophenol	10	330
4-Nitrophenol	50	2,400
N-Nitroso-di-n-butylamine	10	330
N-Nitrosodimethylamine	10	330
N-Nitrosodiphenylamine	10	330
N-Nitrosodi-n-propylamine	10	330
N-Nitrosopiperidine	10	330
Pentachlorobenzene	10	330
Pentachloronitrobenzene	50	2,400

(Continued)

Table 1
Practical Quantitation Limits
for Semivolatile Compounds[a]

Compound	Water (µg/L)	Soil/Sediment (µg/kg)
Pentachlorophenol	10	2,400
Phenacetin	10	330
Phenanthrene	10	330
Phenol	10	330
2-Picoline	50	2,400
Pyrene	10	330
1,2,4,5-Tetrachlorobenzene	10	330
2,3,4,6-Tetrachlorophenol	50	2,400
1,2,4-Trichlorobenzene	10	330
2,4,5-Trichlorophenol	50	2,400
2,4,6-Trichlorophenol	50	2,400

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance.

[b]PQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, PQLs will be higher, based on the percent of moisture in each sample.

2.3 Problems have been associated with some compounds covered by the method. Dichlorobenzidine and 4-chloroaniline are subject to oxidative losses during solvent concentration, and chromatography is poor. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the GC inlet forming diphenylamine and consequently cannot be separated from diphenylamine native to the sample. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

2.4 Pesticides and PCBs should be analyzed by GC procedures provided for the specific pesticide class.

2.5 The method may be used for confirmation of chlorinated pesticides and PCBs identified by gas chromatography using electron capture detection (ECD) if concentrations permit.

3.0 Interferences

3.1 Contaminants in solvents, reagents, glassware, and other sample processing hardware may cause method interferences such as discrete artifacts or elevated baselines in the total ion current profiles (TICPs). All these materials must routinely be demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks.

3.2 Matrix interferences may be caused by contaminants coextracted from the sample. The extent of matrix interferences will vary considerably from source to source.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling hazardous materials must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

4.3 The following parameters have been tentatively classified as known or suspected carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, and N-nitrosodimethylamine. These materials must be handled under a fume hood, and a NOISH/MESA-approved toxic gas respirator must be worn when handling high concentrations.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 GC/MS System

6.1.1 Gas Chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

6.1.2 Column: 30-m × 0.25-mm ID (or 0.32-mm ID) 1-μm film thickness methyl-silicone-coated fused-silica capillary column (J & W Scientific DB-5 or equivalent). A film thickness of 0.25 or 0.5 μm may be used.

6.1.3 Mass Spectrometer: Capable of scanning from 35 to 450 amu every 1 second or less, using 70 volts (nominal) electron energy in the electron impact ionization mode.

6.1.4 GC/MS Interface: Any GC/MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

6.1.5 Data System: A computer system must be interfaced to the mass spectrometer. The system must allow continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

6.2 Syringe: 10-μL, Hamilton gastight or equivalent.

6.3 Volumetric Flasks: Class A, 10- to 1,000-mL.

6.4 Balance: Analytical, capable of weighing accurately to 0.0001 gram.

6.5 Bottles: Glass, Teflon-lined screw caps or crimp tops.

6.6 Separatory Funnel: 2-liter, Teflon stopcock.

6.7 Continuous Liquid Extractor, with Teflon joints and stopcocks.

6.8 Drying Column: 19-mm I.D. chromatographic column.

6.9 Concentrator Tube: 10-mL, graduated.

6.10 Evaporative Flask: 500-mL.

6.11 Snyder Columns: Three-ball and two-ball.

6.12 Silicon Carbide Boiling Chips: 10/40 mesh, heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride. Store chips in airtight jar.

6.13 Soxhlet Extractor: 40-mm I.D., with 500-mL round bottom flask.

6.14 Drying Column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use small pad of Pyrex glass wool to retain absorbent. Prewash glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing column with absorbent.

6.15 Water Bath: Heated, with concentric ring cover, capable of temperature control (high, medium, low). Bath must be used in a fume hood.

6.16 Vials: Glass, 2-mL capacity, with Teflon-lined screw or crimp top.

6.17 Glass or paper Thimble or glass wool: Contaminant-free.

6.18 Heating Mantle: Rheostat controlled.

6.19 Sonication Extraction

6.19.1 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

6.19.2 Sonication: A horn-type sonicator equipped with a titanium tip should be used. The following sonicator, or an equivalent brand and model, is recommended:

> Ultrasonic cell disrupter: Heat Systems—Ultrasonics, Inc., Model W-385 (475-watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 $^{1}/_{2}$-inch Tapped Disrupter Horn) plus No. 207 $^{3}/_{4}$-inch Tapped Disrupter Horn, and No. 419 $^{1}/_{8}$-inch Standard Taper microtip probe.

6.19.3 Sonabox: Recommended with above disrupters for decreasing cavitation sound (Heat Systems—Ultrasonics, Inc., Model 432B or equivalent).

6.19.4 Pasteur Glass Pipets: Disposable, 1-mL.

6.19.5 Beakers: 400-mL, glass.

6.19.6 Vacuum Filtration Apparatus

6.19.6.1 Buchner Funnel.

6.19.6.2 Filter Paper: Whatman No. 41 or equivalent.

6.19.7 Kuderna-Danish (K-D) apparatus:

6.19.7.1 Concentrator Tube: 10-mL graduated (Kontes K-570050-1025 or equivalent).

6.19.7.2 Evaporator Flask: 500-mL (Kontes K-570001-0500 or equivalent).

6.19.7.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.19.7.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.19.8 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.19.9 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath must be used in a fume hood.

6.19.10 Balance: Top-loading, capable of accurately weighing 0.01 gram.

6.19.11 Vials and Caps: 2-mL for GC autosampler.

6.19.12 Glass Scintillation Vials: At least 20-mL, with screw-cap and Teflon or aluminum foil liner.

6.19.13 Spatula: Stainless steel or Teflon.

6.19.14 Drying Column: 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

6.19.15 Syringe: 5-mL, Hamilton gas tight or equivalent.

6.20 Apparatus for Determining Percent Dry Weight

6.20.1 Drying Oven.

6.20.2 Desiccator.

6.20.3 Crucibles: Porcelain or disposable aluminum.

6.20.4 Filter Paper: Whatman No. 41, or equivalent.

6.21 Gel Permeation Chromatography (GPC) Cleanup Device: GPC Autoprep Model 1002 A or B (Analytical Biochemical Laboratories, Inc. or equivalent). Systems that perform very satisfactorily also have been assembled from an HPLC pump, an autosampler or valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet all calibration requirements.

Note: GPC is required for all soil/sediment extracts.

6.21.1 Chromatographic Column: 700-mm × 25-mm I.D. glass column. Flow is upward. To simplify switching from UV detector during calibration to GPC collection device during extract cleanup, an optional double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve No. 10-262 or equivalent) may be attached so that the column exit flow can be shunted either to the UV flow-through cell or the GPC collection device.

6.21.2 Guard Column (Optional): 5-cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

6.21.3 Bio Beads (S-X3): 200-400 mesh, 70 grams (Bio-Rad Laboratories, Richmond, CA, Catalog No. 152-2750 or equivalent). An additional 5 grams of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. Besides having a detrimental effect on chromatography, fines also can pass through the column screens and damage the valve.

6.21.4 Ultraviolet Detector: Fixed wavelength (254 nm) with a semiprep flow-through cell.

6.22 Strip Chart Recorder, Recording Integrator, or Laboratory Data System.

6.23 Syringe: 10-mL with Luerlok fitting, Hamilton gas tight or equivalent.

6.24 Syringe Filter Assembly, disposable: Bio-Rad "Prep Disc" sample filter assembly No. 343-0005, 25 mm, and 5 micro filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (before use) with methylene chloride if necessary.

6.25 Waste Dilution

6.25.1 Glass Scintillation Vials: At least 20-mL, with Teflon or aluminum-foil-lined screw-cap.

6.25.2 Spatula: Stainless steel and Teflon.

6.25.3 Balance: Capable of weighing 100 gram to the nearest 0.01 gram.

6.25.4 Vials and Caps: 2-mL for GC autosampler.

6.25.5 Disposable Pipets: Pasteur, glass.

6.25.6 Test Tube Rack.

6.25.7 Pyrex Glass Wool.

6.25.8 Volumetric Flasks Class A: 10-mL (optional).

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the GC/MS system according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 Water: All references to water assume the use of water which does not contain target analytes at or above the method detection limits.

8.3 Stock Standard Solutions (1,000 mg/L): Standard solutions can be prepared from neat standard materials or purchased as certified solutions.

8.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 gram of neat material. Dissolve material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

8.3.2 Transfer stock standard solutions into bottles with Teflon-lined screw caps. Store at 4° ± 2°C and protect from light. Check stock standard solutions frequently for signs of degradation or evaporation, especially just before preparing calibration standards from them.

8.3.3 Replace stock standard solutions after 1 year or sooner if comparison with quality control check samples indicates a problem.

8.4 Calibration Standards: At least five calibration standards should be prepared. One standard should be at a concentration near but above the method detection limit; the others should correspond to the range of concentration found in real samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte of interest. Each 1-mL aliquot of calibration standard should be spiked with 10 μL of the 4,000 ng/μL internal standard solution before analysis. All standards should be stored at -10° to -20°C and should be freshly prepared once a year or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4° $\pm$ 2°C.

8.5 Internal Standard Solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Dissolve 0.200 gram of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is about 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/μL. Each 1-mL sample extract undergoing analysis should be spiked with 10 μL of the internal standard solution, resulting in a concentration of 40 ng/μL of each internal standard. Store at 4° $\pm$ 2°C protected from light when not being used.

8.6 GC/MS Tuning Standard: A methylene chloride solution containing 50 ng/μL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/μl each of pentachlorophenol and benzidine to verify injection port inertness and GC column performance. Store at 4° $\pm$ 2°C, protected from light.

8.7 Surrogate Spiking Solution: The surrogate spiking solution is added to all field samples and quality control samples. Prepare a methanolic solution containing the following surrogates at the given concentrations:

Compounds	Water (µg/mL)	Soil (µg/mg)
Nitrobenzene-d_5	100	500
2-Fluorobiphenyl	100	500
p-Terphenyl-D_{14}	100	500
Phenol-d5	200	1,000
2-Fluorophenol	200	1,000
2,4,6-Tribromophenol	200	1,000

8.8 Matrix Spike Standard Solution: Prepare a methanolic solution containing the following designated matrix/base neutral spike compounds at 100 µg/mL and the acid compounds at 200 µg/mL.

Base/Neutral	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methlyphenol
1,4-Dichlorobenzene	4-Nitrophenol
N-nitroso-di-n-propylamine	

8.9 Sodium Sulfate: Granular, anhydrous, reagent grade. Heat at 400°C for at least 4 hours, cool in a desiccator, and store in a glass bottle with Teflon seal.

8.10 Sodium Hydroxide Solution, 10 N: Dissolve 40 grams of NaOH in reagent water and dilute to 100 mL.

8.11 Prepare a 1:1 sulfuric acid (H_2SO_4) solution by carefully mixing equal volumes of water and concentrated sulfuric acid. **Caution:** Heat-liberating reaction.

8.12 pH Paper: Wide range.

8.13 Methylene Chloride, Hexane, Methanol, and Acetone: Pesticide grade or equivalent.

8.14 Sonication

8.14.1 Sodium Sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hours, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog No. 73898, or equivalent.

8.14.2 Extraction Solvents: Methylene chloride: acetone (1:1, v:v), methylene chloride, hexane (pesticide quality or equivalent).

8.14.3 Exchange Solvents: Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

8.15 Waste Dilution

8.15.1 Sodium Sulfate (ACS): Granular, anhydrous (purified by heating at 400°C for 4 hours in a shallow tray).

8.15.2 Solvents: Methylene chloride and hexane (pesticide quality or equivalent).

8.16 Laboratory Control Sample: Prepare like a medium-level calibration standard (100 μg/mL). Target compound standards must be obtained from a source independent of the calibration standards.

9.0 Calibration Procedures

9.1 Operating Conditions: The following operating conditions are recommended.

9.1.1 Gas Chromatograph: Capillary column

9.1.1.1 Injector: Grobe splitless injection, split delay of 1.0 minute.

9.1.1.2 Oven Temperature Program: Begin at 40°C for 4 minutes. Then increase the temperature at a rate of 8°C per minute until 310°C is reached and remain at 310°C for 25 minutes before recycling.

9.1.1.3 Injector Temperature: 250° to 300°C.

9.1.1.4 Column: 30-m × 0.32-mm I.D. bonded phase capillary column (J & W DB-5 or equivalent), 0.25- or 0.50-micron film thickness.

Note: A 1.0-micron film thickness capillary column can be used.

9.1.1.5 Injection Volume: 1 to 2 μL.

9.1.1.6 Carrier Gas: Helium at 30 cm^3/s or hydrogen at 50 cm^3/s.

9.1.1.7 Transfer line temperature: 250 to 300°C.

9.1.2 Mass Spectrometer

9.1.2.1 Electron Energy: 70 volts.

9.1.2.2 Mass Range: 35 to 500.

9.1.2.3 Scan Time: Scan time must be set to give at least 5 scans per chromatographic peak. Scan time of 1.0 s/scan for capillary column is recommended.

9.2 Tuning

9.2.1 Each GC/MS system must have the hardware tuned to meet the criteria listed below for a 50-ng injection of decafluorotriphenylphosphine (DFTPP). No sample analyses can begin until all the criteria are met. Tuning must be done every 12 hours. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to "snip" 6 to 12 inches of the capillary column at the injector end.

Table 2
Ion Abundance Criteria for DFTPP

Mass	Ion Abundance Criteria
51	30—60% of mass 198
68	< 2.0% of mass 69
70	< 2.0% of mass 69
127	40—60% of mass 198
197	< 1% of mass 198
198	base peak, 100% relative abundance
199	5—9% of mass 198
275	10—30% of mass 198
365	> 1% of mass 198
441	present but < mass 443
442	> 40% of mass 198
443	17—23% of mass 442

9.2.2 Documentation of achieving the abundance criteria must be archived and maintained in the form of both a bar graph spectrum and a mass listing of the spectrum.

9.3 Initial Calibration

9.3.1 Before analysis of samples and after tuning criteria have been met, the linear calibration range of the instrument must be determined before samples are analyzed. The instrument must be calibrated using the same instrument conditions and relative amounts of reagents used to analyze samples. Once the system has been initially calibrated, calibration must be verified for each 12 hours of data acquisition.

9.3.2 Prepare calibration standards at a minimum of five concentration levels for each parameter analyzed. Concentrations of calibration standards for initial calibration are 20, 50, 80, 120, and 160 μg/mL. Summarized in Table 3 are the characteristic ions for the internal standards, surrogate, and target compound list compounds. (1)

9.3.3 Analyze each calibration standard and calculate the relative response factor (RRF) for each of compounds as:

$$RRF = \frac{(A_s) \times (C_{IS})}{(A_{IS}) \times (C_s)}$$

Where:

A_s = Area of analyte
A_{IS} = Area of internal standard
C_{IS} = Concentration of internal standard (μg/L)
C_s = Concentration of analyte (μg/L)

Use the base peak ion from the specified internal standard (Table 4) as the primary ion for quantitation. If interferences are noted, use the next most intense ion as the secondary ion.

Table 3
Characteristic Ions for Internal Standards and for Target Compounds and Surrogates for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion
Acenaphthene	154	153, 152
Acenaphthene-d_{10} (IS)	164	162, 160
Acenaphthylene	152	151, 153
Acetophenone	105	77, 51
Aniline	93	66, 65
Anthracene	178	176, 179
4-Aminobiphenyl	169	168, 170

(Continued)

Table 3
Characteristic Ions for Internal Standards and for Target Compounds and Surrogates for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion
Benzidine	184	92, 185
Benzoic acid	122	105, 77
Benzo(a)anthracene	228	229, 226
Benzo(b)fluoranthene	252	253, 125
Benzo(k)fluoranthene	252	253, 125
Benzo(g,h,i)perylene	276	138, 277
Benzo(a)pyrene	252	253, 125
Benzyl alcohol	108	79, 77
Bis (2-chloroethoxy)methane	93	95, 123
Bis (2-chloroethyl)ether	93	63, 95
Bis (2-chloroisopropyl)ether	45	77, 121
Bis (2-ethylhexyl)phthalate	149	167, 279
4-Bromophenyl phenyl ether	248	250, 141
Butyl benzyl phthalate	149	91, 206
4-Chloroaniline	127	129
1-Chloronaphthalene	162	127, 164
2-Chloronaphthalene	162	127, 164
4-Chloro-3-methylphenol	107	144, 142
2-Chlorophenol	128	64, 130

(Continued)

Table 3
Characteristic Ions for Internal Standards and for Target Compounds and Surrogates for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion
4-Chlorophenyl phenyl ether	204	206, 141
Chrysene	228	226, 229
Chrysene-d_{12} (IS)	240	120, 236
Dibenz(a,j)acridine	279	280, 277
Dibenz(a,h)anthracene	278	139, 279
Dibenzofuran	168	139
Di-n-butylphthalate	149	150, 104
1,3-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene	146	148, 111
1,4-Dichlorobenzene-d_4 (IS)	152	150, 115
1,2-Dichlorobenzene	146	148, 111
3,3′-Dichlorobenzidine	252	254, 126
2,4-Dichlorophenol	162	164, 98
2,6-Dichlorophenol	162	164, 98
Diethylphthalate	149	177, 150
p-Dimethylaminoazobenzene	120	225, 77
7,12-Dimethylben(a)anthracene	256	241, 257
2,4-Dimethylphenol	122	107, 121
Dimethylphthalate	163	194, 164

(Continued)

Table 3
Characteristic Ions for Internal Standards and for Target Compounds and Surrogates for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion
4,6-Dinitro-2-methylphenol	198	51, 105
2,4-Dinitrophenol	184	63, 154
2,4-Dinitrotoluene	165	63, 89
2,6-Dinitrotoluene	165	63, 89
Diphenylamine	169	168, 167
Di-n-octylphthalate	149	167, 43
Fluoranthene	202	101, 203
Fluorene	166	165, 167
2-Fluorobiphenyl (surr.)	172	171
2-Fluorophenol (surr.)	112	64
Hexachlorobenzene	284	142, 249
Hexachlorobutadiene	225	223, 227
Hexachlorocyclopentadiene	237	235, 272
Hexachloroethane	117	201, 199
Indeno(1,2,3-cd)pyrene	276	138, 227
Isophorone	82	95, 138
3-Methylcholanthrene	268	253, 267
Methyl methanesulfonate	80	79, 65
2-Methylnaphthalene	142	141

(Continued)

Table 3
Characteristic Ions for Internal Standards and for Target Compounds and Surrogates for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion
2-Methylphenol (o-cresol)	108	107, 79
4-Methylphenol (p-cresol)	108	107, 79
Naphthalene	128	129, 127
Naphthalene-d_8 (IS)	136	68
1-Naphthylamine	143	115, 116
2-Naphthylamine	143	115, 116
2-Nitroaniline	65	92, 138
3-Nitroaniline	138	108, 92
4-Nitroaniline	138	108, 92
Nitrobenzene	77	123, 65
Nitrobenzene-d_5 (surr.)	82	128, 54
2-Nitrophenol	139	109, 65
4-Nitrophenol	139	109, 65
N-Nitroso-di-n-butylamine	84	57, 41
N-Nitrosodimethylamine	42	74, 44
N-Nitrosodiphenylamine	169	168, 167
N-Nitrosodi-n-propylamine	70	42, 101, 130
N-Nitrosopiperidine	42	114, 55
Pentachlorobenzene	250	252, 248

(Continued)

Table 3
Characteristic Ions for Internal Standards and for Target Compounds and Surrogates for Semivolatile Compounds

Compound	Primary Ion	Secondary Ion
Pentachloronitrobenzene	295	237, 142
Pentachlorophenol	266	264, 268
Perylene-d_{12} (IS)	264	260, 265
Phenacetin	108	109, 179
Phenanthrene	178	179, 176
Phenanthrene-d_{10} (IS)	188	94, 80
Phenol	94	65, 66
Phenol-d_6 (surr.)	99	42, 71
2-Picoline	93	66, 92
Pyrene	202	200, 203
Terphenyl-d_{14} (surr.)	244	122, 212
1,2,4,5-Tetrachlorobenzene	216	214, 218
2,3,4,6-Tetrachlorophenol	232	230, 131
2,4,6-Tribromophenol (surr.)	330	332, 141
1,2,4-Trichlorobenzene	180	182, 145
2,4,5-Trichlorophenol	196	198, 200
2,4,6-Trichlorophenol	196	198, 200

IS = internal standard
surr. = surrogate

Table 4
Semivolatile Internal Standards with Corresponding Target Compounds and Surrogates Assigned for Quantitation

1,4-dichlorobenzene-d_4	naphthalene-d_8
phenol	nitrobenzene
bis(2-chloroethyl) ether	isophorone
2-chlorophenol	2-nitrophenol
1,3-dichlorobenzene	2,4-dimethylphenol
1,2-dichlorobenzene	2,4-dichlorophenol
2-methylphenol	1,2,4-trichlorobenzene
bis(2-chloroisopropyl ether)	naphthalene
4-methylphenol	4-chloroaniline
N-nitroso-di-n-propylamine	hexachlorobutadiene
hexachloroethane	4-chloro-3-methylphenol
2-fluorophenol (surr.)	2-methylnaphthalene
phenol-d_6 (surr.)	nitrobenzene-d_8 (surr.)
aniline	acetophenone
benzyl alcohol	benzoic acid
ethyl methanesulfonate	2,6-dichlorophenol
methyl methanesulfonate	N-nitroso-di-n-butylamine
N-nitrosodimethylamine	N-nitrosopiperidine
2-picoline	1-chlorohaphthalene

bis(2-chloroethoxy) methane

acenaphthene-d_{10}

2,4,5-trichlorophenol	2-naphthylamine
2-chloronaphthalene	Pentachlorobenzene
2-nitroaniline	1,2,4,5-tetrachlorobenzene
dimethyl phthalate	2,3,4,6-tetrachlorophenol
acenaphthylene	3-nitroaniline
acenaphthene	diethyl phthalate
2,4-dinitrophenol	4-chlorophenyl phenyl ether
4-nitrophenol	fluorene
dibenzofuran	4-nitroaniline
2,4-dinitrotoluene	2-fluorofiphenyl (surr.)
2,6-dinitrotoluene	2,4,6-tribromophenol (surr.)
hexachlorocyclopentadiene	2,4,6-trichlorophenol
1-napthylamine	1-chloronapthalene

phenanthrene-d_{10}

4,6-dinitro-2-methylphenol	di-n-butyl-phthalate
n-nitrododiphenylamine	4-aminobiphenyl
4-bromophenyl phenyl ether	diphenylamine
hexachlorobenzene	1,2-diphenylhydrazine
pentachlorophenol	pentachloronitrobenzene
phenanthrene	phenacetin
fluoranthene	anthracene

chrysene-d_{12}	perylene-d_{12}
pyrene	di-n-octyl-phthalate
butylbenzylphthalate	benzo(b)fluoranthene
3,3′-dichlorobenzidine	benzo(f)fluoranthene
benzo(a)anthracene	benzo(a)pyrene
bis(2-ethylhexyl) phthalate	indeno(1,2,3-cd)pyrene
chrysene	dibenz(a,h)anthracene
terphenyl-d_{14} (surr)	benzo(g,h,i)perylene
benzidine	dibenz(a,j)acridine
p-dimethylaminoazobenzene	7,12-dimethylbenz(a)anthracene
	3-methylchoranthrene

9.3.4 Calculate standard deviations and percent relative standard deviation (%RSD) of RRFs for compounds as:

$$S = \sqrt{\frac{\sum (RRF_i - RRF_m)^2}{N - 1}} \quad (2)$$

Where:

RRF_i = Individual RRF
RRF_m = Mean RRF
N = Number of RRFs

$$\% \ RSD = \frac{S \times 100}{RRF_m} \quad (3)$$

9.3.5 The following criteria must be met before the initial calibration curve can be used for analysis.

9.3.5.1 Certain compounds in the calibration standards are designated System Performance Check Compounds (SPCC). These compounds tend to decrease in response as the chromatographic system or calibration standard begins to deteriorate and are usually the first compounds to show poor performance. They are n-nitroso-di-n-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol. The mean RRF for each compound must be at least 0.05.

9.3.5.2 Compounds in the calibration standards designated as Calibration Check Compounds (CCC) must have a %RSD of RRFs of not more than 30.0%. They are:

Base/Neutral	Acid
Acenaphthene	4-Chloro-3-methylphenol
1, 4-Dichlorobenzene	2, 4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

9.3.6 Initial calibration should be performed at the start of a project and whenever corrective action is taken that may change or affect the initial calibration criteria (e.g., ion source cleaning or repair, column replacement) or if continuing calibration acceptance criteria have not been met.

9.4 Continuing Calibration: The working calibration curve or relative response factor for each analyte must be verified for each 12 hours of instrument operation by analysis of a continuing calibration standard. The ongoing 12-hour continuing calibration must be compared to the initial calibration curve to verify that the measurement system is in control.

9.4.1 Analyze the 50-μg/mL continuing calibration standard and calculate the relative response factor (RRF) of each target analyte. All SPCC compounds must have a minimum relative response factor of 0.05. For each analyte,

calculate the percent difference between the continuing calibration RRF and (4) the mean RRF from the initial calibration curve using the equation:

$$\%D = \frac{[\ RRF_m - RRF\ ] \times 100}{RRF_m}$$

Where:

RRF_m = Mean relative response factor from initial calibration curve

RRF = Daily continuing calibration relative response factor

9.4.1.1 The percent difference for the CCC compounds must not exceed 25.0%.

9.4.2 Both SPCC and CCC criteria must be met every 12 hours for sample analysis to continue. If the CCC or SPCC criteria are not met, the system must be evaluated and corrective actions taken before further sample analysis can continue.

9.4.2.1 If the calibration criteria cannot be met, then fresh calibration standards must be prepared and a new initial calibration curve must be established.

9.4.3 Internal standard responses and retention times in all standards must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12-hour) calibration standard, the chromatographic system must be inspected for malfunctions and corrections made as required. The extracted ion current profile (EICP) of the internal standards must be monitored and evaluated for each standard. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made. When corrections are made, samples analyzed while the system was malfunctioning must be reanalyzed.

9.4.4 No samples may be analyzed after a continuing calibration standard that has failed acceptance criteria.

10.0 Sample Preparation

10.1 Sample Preparation for Extractable Semivolatiles (BNA) in Water

10.1.1 Liquid-Liquid Extraction: Continuous liquid-liquid extraction will be used for water samples. A 1-liter aliquot of sample is acidified to pH of 2 and extracted with methylene chloride using a continuous liquid-liquid extractor.

10.1.1.1 Add methylene chloride to the bottom of the extractor and fill it to a depth of at least 1 inch above the bottom side arm (300 to 500 mL).

10.1.1.2 Using 1-liter graduated cylinder, measure out 1-liter sample aliquot and transfer to continuous extractor. Pipet 1.0 mL of surrogate standard spiking solution into the sample and mix well. Check sample pH with pH paper and adjust pH >11 with 10 N NaOH. If gel permeation cleanup is to be used, add twice the volume of surrogates and matrix spiking compounds. For waste samples, adjust volume of surrogates to 5 mL.

10.1.1.3 Following the procedures in paragraphs 10.1.1.1 and 10.1.1.2 above, prepare two additional 1-liter aliquots of the sample chosen for spiking. Add 1.0 mL of the BNA matrix spiking solution to each additional aliquot. The frequency of MS/MSD analysis is one per 20 samples of the same type of matrix.

10.1.1.4 Extract sample for 18 hours. Allow to cool; then detach the distilling flask and label it. Add several boiling chips and distilling flask. Extract for 18 to 24 hours. Allow to cool; then detach the boiling flask and label it. Carefully, while stirring, adjust the pH of the aqueous phase to <2 with 1:1 sulfuric acid. Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extraction. Extract for 18 to 24 hours, allow to cool, and detach and label the distilling flask.

10.1.1.5 Prepare a method blank with each group of water samples extracted. For semivolatile analyses, a method blank for water samples consists of a 1-liter volume of reagent water, spiked with the surrogates and carried through the entire analytical procedure. The frequency of method blank analysis is one per 20 samples or every analytical batch of the same type of matrix.

10.2 Extraction Method for Soil Samples Expected to Contain Low Concentrations of Organics and Pesticides (≤ 20 mg/kg)

10.2.1 Sonication Extraction: Determination of Percent Moisture: Immediately after weighing the sample for extraction, weight 5 to 10 grams of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\frac{\text{Grams of sample} - \text{grams of dry sample}}{\text{Grams of dry sample}} \times 100 = \%\ \text{Moisture} \qquad (5)$$

10.2.2 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 grams of sample into a 400-mL beaker. Record the weight to the nearest 0.1 gram. Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 grams of anhydrous sodium sulfate using a spatula. The sample should be free-flowing at this point. Add 1 mL of surrogate standards to all samples, spikes, and blanks. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. If gel-permeation cleanup (GPC) is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

10.2.3 Place the bottom surface of the tip of the No. 207 3/4-inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

10.2.4 Sonicate for 3 minutes, with output control knob set at 10 and with mode switch on Pulse and percent-duty cycle knob set at 50%. Do not use microtip probe.

10.2.5 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

10.2.6 Repeat the extraction two or more times with two additional 100-mL portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

10.3 Extraction method for soil samples expected to contain medium concentrations of target compounds (>20 mg/kg).

10.3.1 Follow procedure as in 10.2 except use a 2 gram sample.

10.4 Sample Concentration

10.4.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D, if equivalency is demonstrated for all semivolatile target compounds.

10.4.2 Transfer extract by pouring it through a drying column containing about 10 cm of anhydrous sodium sulfate or drying funnel with 80 grams Na_2SO_4, and collect extract in K-D concentrator. Rinse Erlenmeyer flask containing solvent extract with 20 to 30 mL of methylene chloride and add it to the column to complete quantitative transfer.

10.4.3 Add one or two muffled boiling chips and attach a three-ball Snyder column to evaporative flask. Pre-wet Snyder column by adding about 1 mL methylene chloride to top of column. Place K-D apparatus in hot water bath (80° to 90°C) so that concentrator tube is partially immersed in hot water and entire lower rounded surface of flask is bathed with hot vapor. Adjust vertical position of apparatus and water temperature as required to complete concentration in 10 to 20 minutes. At proper rate of distillation, column balls will chatter actively, but chambers will not flood with condensed solvent. When apparent volume of liquid reaches 1 mL, remove K-D apparatus from water bath and allow it to drain and cool for at least 10 minutes. Remove Snyder column and rinse flask and its lower joint into concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Adjust volume to 10 mL.

10.5 Gel-Permeation Cleanup (GPC)

10.5.1 Packing the Column: Place about 70 grams of Bio Beads SX-3 in a 400-mL beaker. Cover beads with methylene chloride. Allow beads to swell overnight (before packing columns). Transfer swelled beads to column and start pumping solvent through column, from bottom to top, at 5.0 mL/minute. After about 1 hour, adjust pressure on column to 7 to 10 psi and pump an additional 4 hours to remove air from column. Adjust column pressure periodically as required to maintain 7 to 10 psi.

10.5.2 Calibration of Column: Column can be calibrated manually by gravimetric/GC/FID techniques or automatically if a recording UV detector with a flow-through cell is available.

10.5.2.1 Manual Calibration: Load 5 mL of corn oil solution into sample loop No. 1 and 5 mL of phthalate-phenol solution into loop No. 2. Inject corn oil and collect 10-mL fractions (i.e., change fractions at 2-minute intervals) for 36 minutes. Inject phthalate-phenol solution and collect 15-mL fractions for 60 minutes. Determine corn oil elution pattern by evaporation of each fraction to dryness followed by gravimetric determination of residue. Analyze phthalate-phenol fractions by GC/FID using a DB-5 capillary column, a UV spectrophotometer, or a GC/MS system. Plot concentration of each component in each fraction versus total eluent volume (or time) from the injection points. Choose dump time that allows ≥ 85% removal of corn oil and ≥ 85% recovery of bis(2-ethylhexyl)phthalate. Choose collect time to extend at least 10 minutes after elution of pentachlorophenol. Wash column with methylene chloride at least 15 minutes between samples. Typical parameters selected are dump time, 30 minutes (150 mL); collect time, 36 minutes (180 mL); and wash time, 15 minutes (75 mL).

10.5.2.2 Automated Calibration: Column can also be calibrated by use of a 254-nm detector in place of gravimetric and GC analyses of fractions. Use corn oil-phthalate-phenol mixture when using UV detector. Load 5 mL into sample loop No. 1. Use same criteria for choosing dump time and collect time as for manual calibration.

10.5.2.3 The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. Recalibrate system once weekly.

10.5.3 GPC Extract Cleanup: Extract must be in methylene chloride or primarily methylene chloride. All other solvents must be concentrated to 1 mL and diluted to 10.0 mL with methylene chloride. Prefilter or load all extracts by filter holder to avoid particulates that might cause flow stoppage or damage the valve. Load one 5.0-mL aliquot of extract onto GPC column. Do not apply excessive pressure when loading. Purge sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carryover. Process extracts using dump, collect, and wash parameters determined from calibration, and collect cleaned extracts in 400-mL beakers tightly covered with aluminum foil.

Note: Half the 10-mL extract is lost during the loading of the GPC, so divide sample size by two when calculating analyte concentration.

10.5.4 Concentrate extract by standard K-D technique described under one of the extraction procedures.Two concentration techniques are permitted to obtain the final 1.0-mL volume: micro Snyder column and nitrogen blowdown.

10.5.4.1 Micro Snyder Column Technique: Add another one or two clean boiling chips to concentrator tube and attach two-ball micro Snyder column. Pre-wet Snyder column by adding about 0.5 mL of methylene chloride to top of column. Place K-D apparatus in hot water bath so that concentrator tube is partially immersed in hot water. Adjust vertical position of apparatus and water temperature as required to complete concentration in 5 to 10 minutes. At proper rate of distillation, column balls will chatter actively, but chambers will not flood with condensed solvent. When apparent volume of liquid reaches about 0.5 mL, remove K-D apparatus from water bath and allow it to drain for at least 10 minutes while cooling. Remove Snyder column and rinse its flask and lower joint into concentrator tube with 0.2 mL of methylene chloride. Adjust final volume to 1.0 mL with methylene chloride. Transfer extract to Teflon-sealed screw cap bottle, label bottle, and store at 4° ± 2°C, protected from light.

10.5.4.2 Nitrogen Blowdown Technique: Place concentrator tube with open micro Snyder attached in warm water bath (30° to 35°C) and evaporate solvent volume to just below 1 mL by blowing gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) above extract.

Caution: Gas lines from gas source to blowdown apparatus must be stainless steel, copper, or Teflon tubing. Internal wall of concentrator tube must be rinsed down several times with methylene chloride during operation and final volume brought to 1.0 mL with methylene chloride. During evaporation, tube solvent level must be kept below water level of bath. Extract must never be allowed to become dry. Transfer extract to Teflon-sealed screw cap bottle, label bottle, and store at 4° ± 2°C, protected from light.

10.5.5 Sample extracts are ready for GC/MS analysis. If high concentrations are suspected (e.g., highly colored extracts), the optional GC/FID screen is recommended.

10.6 Waste Dilution

10.6.1 The sample dilution may be performed in a 10-mL volumetric flask. If disposable glassware is preferred, the 20-mL scintillation vial may be calibrated for use. Simply pipet 10 mL of extraction solvent into the scintillation vial and mark the bottom of the meniscus. Discard this solvent.

10.6.2 Transfer approximately 1 gram of each phase (record weight to the nearest 0.1 gram) of the sample to separate 20-mL vials or 10-mL volumetric flasks. Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

10.6.3 Add 2.0 mL surrogate spiking solution to all samples and blanks. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 200 ng/μL of each base/neutral analyte and 400 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1-μL injection). If gel-permeation cleanup (GPC) is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

10.6.4 Immediately dilute to 10 mL with methylene chloride solvent.

10.6.5 Add 2.0 grams of anhydrous sodium sulfate to the sample.

10.6.6 Cap and shake the sample for 2 minutes.

10.6.7 Loosely pack disposal Pasteur pipets with 2 to 3 cm glass wool plugs. Filter the extract through the glass wool and collect 5 mL of the extract in a tube or vial.

10.6.8 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

10.7 Sample Preparation for Extractable Semivolatiles (BNA) in Soil/Sediment

10.7.1 It is mandatory that all soil/sediment samples be characterized as to concentration level so that the appropriate analytical protocol is chosen to ensure proper quantitation limits for the sample. Note that the terms "low-level" and "medium-level" are not used as a judgment of degree of contamination but rather as a description of concentration ranges encompassed by the low- and medium-level procedures.

10.7.2 The laboratory may screen samples using either of the methods below.

10.7.2.1 Screen an aliquot from the low-level 30-gram extract or an aliquot from the medium-level 2-gram extract.

10.7.2.2 Screen using either GC/FID or GC/MS as the screening instrument.

10.7.3 The concentration ranges covered by these two procedures may be considered to be $\leq$ 20 mg/kg for the low-level analysis and > 20 mg/kg for medium-level analysis for semivolatile extractables.

10.7.4 Screen from Medium-level Method: A 2-gram sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. The sample is extracted three times using sonication. Take 5.0 mL from 10-mL total extract, concentrate to 1.0 mL, and screen. If sample concentration is > 20 mg/kg for individual organic components, proceed with GC/MS analysis of organics. If sample concentration is < 20 mg/kg for individual organic components, discard medium-level extract and follow low-level method.

10.7.5 Screen from Low-level Method: A 30-gram sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This sample is extracted three times using sonication. The extract is separated form the sample by vacuum filtration or centrifugation and concentrated. Take 5.0 mL from 300-mL (approximate) total extract from 30-gram sample, concentrate to 1.0 mL, and screen. If original sample concentration is > 20 mg/kg for individual organic components, discard 30-gram extract and follow medium-level methods for organics using medium-level surrogates. If sample concentration is < 20 mg/kg, proceed with concentration and remainder of low-level method.

10.7.6 Mandatory GPC: Some soil/sediment sample extracts must be subjected to cleanup by gel permeation chromatography (GPC). Because the effectiveness of GPC can be adversely affected by the amount of material loaded onto the GPC column, it may be advisable to screen the sample extracts described here before employing GPC.

11.0 Sample Analysis

11.1 Analysis may begin only after tuning and calibration criteria have been met. The same instrument conditions used for calibration must be used for sample analysis.

11.2 Surrogate spikes should have been added to all samples, blanks, and matrix spike/matrix spike duplicate samples before extraction.

11.2.1 Summarized in Table 5 are the target acceptance limits for surrogate spikes. If more than one surrogate spike per fraction (acid or base/neutral) exceeds the target acceptance limits, then the sample must be re-extracted and reanalyzed. If the surrogate spike recoveries still exceed the acceptance limits, then the results of both analyses are reported and noted in the case narrative.

Table 5
Semivolatile Surrogate Recovery Target Acceptance Limits

Compound	Water	Soil/Sediment
Nitrobenzene-d_5	35—114	23—120
2-Fluorobiphenyl	43—116	30—115
Terphenyl-d_{14}	33—141	18—137
Phenol-d_6	10—94	24—113
2-Fluorophenol	21—100	25—121
2,4,6-Tribromophenol	10—123	19—122

11.3 At least one method blank must be analyzed with each analytical batch for each matrix. The method blank must undergo the same preparation steps as the associated samples.

11.4 A matrix spike and matrix spike duplicate must be analyzed per 20 samples of the same matrix processed through the same sample preparation steps, or every 14 calendar days, whichever is more frequent.

11.4.1 Summarized in Table 6 are the target acceptance limits for MS/MSDs. If the MS/MSD recoveries are not within the target acceptance limits, the analysis is not repeated. The data is reported as is and noted in the case narrative.

Table 6
Semivolatile Matrix Spike/Matrix Spike Duplicate Recovery
Target Acceptance Limits

Compound	Water	Soil/Sediment
Phenol	12—110	26—90
2-Chlorophenol	27—123	25—102
1,4-Dichlorobenzene	35—97	28—104
N-Nitroso-di-n-propylamine	41—116	41—126
1,2,4-Trichlorobenzene	39—98	38—107
4-Chloro-3-methylphenol	23—97	26—103
Acenaphthene	46—118	31—137
4-Nitrophenol	10—80	11—114
2,4-Dinitrotoluene	24—96	28—89
Pentachlorophenol	9—103	17—109
Pyrene	26—127	35—142

11.5 Internal standard solution must be added to each extract before analysis. Add 10 μL of internal standard solution to each accurately measured 1.0 mL of sample extract.

11.5.1 Make any extract dilution indicated by characterization before the addition of internal standards. If any further dilutions of water or soil/sediment extracts are made, additional internal standards must be added to maintain the required 40 ng/μL of each internal standard in the extract volume.

11.6 Inject 1 to 2 μL of sample extract into the GC/MS.

11.7 A laboratory control sample must be analyzed per 20 samples. Target acceptance criteria are summarized in Table 7.

Table 7
LCS Target Acceptance Ranges

Parameter	Target Acceptance Range (% rel)
Acenaphthene	47-145
Acenaphthylene	33-145
Anthracene	27-133
Benzo(a)anthracene	33-143
Benzo(b)fluoranthene	24-159
Benzo(k)fluoranthene	11-162
Benzo(a)pyrene	17-163
Benzo(ghi)perylene	D-219
Benzy butyl phthalate	D-152
Bis (2-chloroethyl) ether	12-158
Bis (2-chloroethoxy) methane	33-184
Bis (2-chloroisopropyl) ether	36-166
Bis (2-ethylhexyl) phthalate	8-158
4-Bromophenyl phenyl ether	53-127
2-Chloronaphthalene	60-118
4-Chlorophenyl phenyl ether	25-158
Chrysene	17-168
Dibenzo(a,h)anthracene	D-227
Di-n-butyl phthalate	1-118
1,2-Dichlorobenzene	32-129
1,3-Dichlorobenzene	D-172
1,4-Dichlorobenzene	20-124
3,3'-Dichlorobenzidine	D-262
Diethyl phthalate	D-114
Dimethyl phthalate	D-112
2,4-Dinitrotoluene	39-139
2,6-Dinitrotoluene	50-158
Di-n-octylphthalate	4-146
Fluoranthene	26-137
Fluorene	59-121
Hexachlorobenzene	D-152
Hexachlorobutadiene	24-116
Hexachloroethane	40-113
Indeno(1,2,3-cd)pyrene	D-171
Isophorone	21-196
Naphthalene	21-133
Nitrobenzene	35-180
N-Nitroso-di-n-propylamine	D-230
Phenanthrene	54-120
Pyrene	52-115
1,2,4-Trichlorobenzene	44-142
4-Chloro-3-methylphenol	22-147
2-Chlorophenol	23-134
2,4-Chlorophenol	39-135
2,4-Dimethylphenol	32-119
2,4-Dinitrophenol	D-191
2-Methyl-4,6-dinitrophenol	D-181
2-Nitrophenol	29-182
4-Nitrophenol	D-132
Pentachlorophenol	14-176
Phenol	5-112
2,4,6-Trichlorophenol	37-144

11.8 Qualitative Analysis of Target Compounds

11.8.1 The target compounds must be identified by an analyst competent in the interpretation of mass spectra by comparison of the sample mass spectrum to the mass spectrum of a standard of the suspected compound. Two criteria must be satisfied to verify the identifications:

11.8.1.1 Elution of the sample component at the same GC relative retention time as the standard component.

11.8.1.2 Correspondence of the sample component and standard component mass spectra.

11.8.2 For establishing correspondence of the GC relative retention time (RRT), the sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run on the same shift as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

11.8.3 For comparison of standard and sample component mass spectra, mass spectra obtained on the laboratory's GC/MS are required. Once obtained, these standard spectra may be used for identification purposes **only** if the laboratory's GC/MS meets the DFTPP daily instrument performance requirements. Standard spectra may be obtained from the run used to obtain reference RRTs.

11.8.3.1 For qualitative verification by comparison of 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%) must be present in the sample spectrum.

11.8.3.2 The relative intensities of ions must agree within ± 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30% and 70%.)

11.8.4 Ions greater than 10% in the sample spectrum but not present in the standard spectrum must be considered and accounted for by the analyst making the comparison. The verification process should favor false positives. All compounds meeting the identification criteria must be reported with their spectra.

11.8.5 If a compound cannot be verified by all the above criteria but in the technical judgment of the mass spectral interpretation specialist the identification is correct, then the laboratory shall report that identification and proceed with quantification. This must be discussed in the case narrative.

11.9 Qualitative Analysis of Nontarget Compounds: A library search will be made for nontarget sample components for the purpose of tentative identification. The most recent release of the NIST/EPA mass spectral library, containing approximately 50,000 spectra, will be used.

11.9.1 Up to 20 nonsurrogate organic compounds of greatest apparent concentration not listed for the semivolatile fraction will be identified tentatively by a forward search of the NIST/EPA mass spectral library. Substances with responses less than 10% of the nearest internal standard are not required to be searched in this fashion. Only after visual comparison of sample spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

Note: Computer-generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

11.9.2 Guidelines for Making Tentative Identification

11.9.2.1 Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

11.9.2.2 Relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample ion abundance must be between 30% and 70%.)

11.9.2.3 Molecular ions present in reference spectrum should be present in sample spectrum.

11.9.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

11.9.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting compounds.

Note: Data system library reduction programs sometimes can create these discrepancies.

11.9.3 If in the technical judgment of the mass interpretation spectral specialist no valid tentative identification can be made, the compound should be reported as unknown. The specialist should give additional classification of the unknown compound if possible (e.g., unknown phthalate, unknown hydrocarbon, unknown acid type, unknown chlorinated compound). If probable molecular weights can be distinguished, include them.

12.0 Calculations

12.1 Target components identified shall be quantified by the internal standard method. The internal standard used shall be the one nearest the retention time to that of a given analyte (see Table 1). The extracted ion current profile (EICP) area of characteristic ions of analytes listed in Table 3 are used for quantitation.

12.1.1 Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the latest daily (12-hour) calibration standard, the chromatographic system must be inspected for malfunctions, and corrections made as required. The EICP of the internal standards must be monitored and evaluated for each sample, blank, matrix spike, and matrix spike duplicate. If the EICP area for any internal standard changes by more than a factor of two (-50% to +100%), the mass spectrometric system must be inspected for malfunction and corrections made as required. Samples or standards with EICP areas outside the limits must be reanalyzed and treated according to paragraphs 12.1.2 and 12.1.3 below. If corrections are made, then the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by analysis of a standard or sample that does meet the EICP criteria. After corrections are made, the samples analyzed while the system was malfunctioning must be reanalyzed.

12.1.2 If after reanalysis the EICP areas for all internal standards are inside the contract limits (-50% to +100%), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, submit only data from the analysis with EICPs within the contract limits. This is considered the initial analysis and must be reported as such on all data deliverables.

12.1.3 If reanalysis of the sample does not solve the problem (i.e., the EICP areas are outside the acceptance limits for both analyses), then submit the EICP data and sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using appropriate sample designations. Document in the case narrative all inspection and corrective actions taken.

12.1.4 Do not reanalyze MS/MSD samples that do not meet the EICP area limits.

12.2 The RRF from the daily standard analysis is used to calculate the concentration in the sample. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the case narrative. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion.

12.2.1 Calculate the concentration in the sample using the RRF as determined in the following equations:

(6)

12.2.1.1 Water

$$\text{Concentration } \mu g/L = \frac{(A_x)\ (I_{IS})\ (V_t)\ (Df)}{(A_{IS})\ (RRF)\ (V_o)\ (V_i)}$$

Where:

A_x = Area of characteristic ion for compound to be measured

A_{IS} = Area of characteristic ion for internal standard

I_{IS} = Amount of internal standard injected (ng)

V_o = Volume of water extracted (mL)

V_i = Volume of extract injected (μL)

V_t = Volume of the concentrated extract (μL). If half the base/neutral extract and half the acid extract are combined, V_t = 2000.

Df = Dilution factor. The dilution factor for analysis of water samples for semivolatiles by this method is:

$$\frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

If no dilution is performed, Df = 1. (7)

12.2.1.2 Soil/Sediment

$$\text{Concentration } \mu g/kg = \frac{(A_x)(I_{IS})(V_t)(Df)}{(A_{IS})(RRF)(V_i)(W_s)(D)}$$

Where:

A_X, I_{IS}, A_{IS} are as given above for water (8)
V_t = Volume of concentrated extract (μL)
V_i = Volume of extract injected (μL)

$$D = \frac{100 - \%\text{ moisture}}{100}$$

Where:

W_s = Weight of sample extracted in (grams)

Df = Dilution factor. The dilution factor for analysis of soil samples for semivolatiles by this method is:

$$\frac{\mu L \text{ most conc. extract used to make dilution} + \mu L \text{ clean solvent}}{\mu L \text{ most conc. extract used to make dilution}}$$

If no dilution is performed, DF = 1.

12.2.1.3 If GPC is performed, multiply results by 2.0 to account for the amount of extract not recovered from GPC. Concentrating the 5 mL of extract collected after GPC to 0.5 mL rather than 1.0 mL for water samples not subjected to GPC maintains the sensitivity of the soil method comparable to that of the water method, but correction of the numerical result is still required.

12.3 An estimated concentration for nontarget components tentatively identified will be quantified by the internal standard method. For quantification, the nearest internal standard free of interferences shall be used. The formula for calculating concentrations is the same as in paragraph 12.2. Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one is to be assumed. An estimated concentration should be calculated for all tentatively identified compounds as well as those identified as unknowns.

12.4 If the on-column concentration of any target compound in any sample exceeds the initial calibration range, the sample must be diluted, the internal standard concentration readjusted, and the sample extract reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

12.4.1 Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

12.4.2 The dilution factor chosen should keep the response of the largest peak for a target compound in the upper half of the initial calibration range of the instrument.

12.4.3 Do not submit data for more than two analyses (e.g., the original sample extract and one dilution) or, if the semivolatile screening procedure was employed, from the most concentrated dilution analyzed and one further dilution.

12.4.4 Do not dilute MS/MSD samples to get either spiked or nonspiked analytes within the calibration range. If the sample from which the MS/MSD aliquots were taken contains high levels of the spiked analytes, calculate the concentration and recovery of the analytes from the undiluted analysis, and note the problem in the SDG Narrative.

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control and reporting requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	Every 12 hours	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	1/20	80—120%	Qualify data
Surrogate Spikes	Every sample	11.2.1	Reanalyze, then Qualify data
Matrix Spike	1/20	11.4.1	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10	90—110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	1/20	80—120%	Recalibrate
Surrogate Spikes	Every sample	11.2.1	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	11.4.1	Qualify data
BFB	Every 12 hours	A/S	Recalibrate
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
BFB	bromofluorobenzene
A/S	as specified earlier in this method
RPD	relative percent difference

15.0 References

15.1 *Test Methods for Evaluating Solid Waste*, 3rd ed. Method 8270. September 1986.

15.2 *CLP Statement of Work for Organic Analysis.* Multi-Media, Multi-Concentration. February 1988.

FM-ORG-0070

Herbicides

Working Linear Range: Matrix- and analyte-specific
Reporting Limit: To be determined
Reporting Units: Water, μg/L; soil (dry weight), μg/kg
Matrix: Water, soil, waste, sediment, or sludge

1.0 Scope and Application

1.1 This is a gas chromatographic method applicable to the determination of the chlorinated acid herbicides listed in Table 1 in water, soil waste, sediment, and sludge.

1.2 The method detection limits for each target compound are summarized in Table 1. Because the method is matrix-dependent, practical quantitation limits are summarized in Table 2.

Table 1. Chromatographic Detection Limits for Chlorinated Herbicides

Compound	Method Detection Limit (μg/L)
2,4-D	1.2
2,4-DB	0.91
2,4,5-T	0.20
2,4,5-TP (Silvex)	0.17
Dalapon	5.8
Dicamba	0.27
Dichloroprop	0.65
Dinoseb	0.07
MCPA	249.0
MCPP	192.0

Table 2. Determination of Practical Quantitation Limits (PQL) for Various Matrices[a]

Matrix	Factor[b]
Ground Water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a] Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b] PQL = [Method detection limit (Table 1)] × [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet weight basis.

2.0 Method Summary

2.1 The method includes extraction, esterification, and gas chromatographic conditions for analysis of chlorinated acid herbicides. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. The extract is cleaned by passing it through a micro-absorption column. After excess reagent is removed, the esters are analyzed by gas chromatography employing an electron capture detector. The results are reported as acid equivalents.

2.2 The sensitivity of the method usually depends on the level of interferences rather than on instrumental limitations.

3.0 Interferences

3.1 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with the method.

3.2 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.3 Herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid before use to avoid this possibility.

3.4 Contamination by carryover can occur whenever high- and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed between samples with water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or water to check for cross contamination. For volatile samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash the syringe with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling organic solvents must be practiced. Personal protective equipment must includes goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

4.3 **Caution:** Diazomethane is very toxic. It can explode under certain conditions. The following precautions must be observed.

- Avoid breathing vapors.
- Use only in well-ventilated fume hood.
- Use safety screen.
- Do not pipette any solution, especially diazomethane, by mouth.
- Pour solutions of diazomethane using gloves.
- Do not heat solutions to 100°C (explosion hazard).

4.3.1 Store solutions of gas at low temperatures (i.e., in the freezer compartment of an explosion-proof refrigerator).

4.3.2 Avoid ground glass apparatus, glass stirrers, and sleeve bearings where grinding and friction may occur (explosion hazard).

4.3.3 Keep solutions away from alkali metals (explosion hazard).

4.3.4 Solutions of diazomethane decompose rapidly in the presence of solid material such as copper powder, calcium chloride, and boiling stones. These solid materials produce solid polyethylene and nitrogen gas.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Gas Chromatograph: Analytical system complete with gas chromatograph (GC) suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas or peak heights is recommended.

6.1.1 Columns

6.1.1.1 Column 1: Rt_x-5; 20 m × 0.32 mm I.D., 0.25-μm film thickness capillary column or equivalent (Restek, Co.).

6.1.1.2 Column 2: Rt_x-35; 30 m × 0.32 mm I.D., 0.25-μm film thickness, capillary column or equivalent (Restek, Co.).

6.1.2 Electron Capture Detector.

6.2 Erlenmeyer Flasks: 250- and 500-mL Pyrex, with 24/40 ground glass joint.

6.3 Beaker: 500-mL.

6.4 Diazomethane Generator: Refer to Section 10.3 to determine which method of diazomethane generation should be used for a particular application.

6.4.1 Diazald Kit: Recommended for generation of diazomethane using the procedure given in Section 10.3.2 (Aldrich Chemical Co., Cat. No. 210.025-2 or equivalent).

6.4.2 Assemble from two 20- × 150-mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. Exit tube must be drawn to a point to bubble diazomethane through the sample extract. The procedure for use of this type of generator is given in Section 10.3.3.

6.5 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw cap.

6.6 Separatory Funnels: 2-L, 125-mL, and 60-mL.

6.7 Drying Column: 400- × 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

Note: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use small pad of Pyrex glass wool to retain adsorbent. Prewash glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent before packing column with adsorbent.

6.8 Kuderna-Danish (K-D) Apparatus

6.8.1 Concentrator Tube: 10-mL, graduated (Kontes K-570050-1025 or equivalent) with ground glass stoppers to prevent evaporation of extracts.

6.8.2 Evaporation Flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

6.8.3 Snyder Column: Three-ball macro (Kontes K-503000-0121 or equivalent).

6.8.4 Snyder Column: Two-ball micro (Kontes K-569001-0219 or equivalent).

6.9 Boiling Chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

6.10 Water Bath: Heated, with concentric ring cover, capable of temperature control (± 5°C). Bath should be used in a fume hood.

6.11 Microsyringe: 10-μL, Hamilton gastight or equivalent.

6.12 Wrist Shaker: Burrell Model 75 or equivalent.

6.13 Glass Wool: Pyrex, acid washed.

6.14 Analytical Balance: Capable of accurately weighing to the nearest 0.0001 gram.

6.15 Syringe: 5-mL, Hamilton gastight or equivalent.

6.16 Glass Rod.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the gas chromatograph according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of water in which target compounds are not detected above the method detection limits.

8.2 Sulfuric Acid Solution

8.2.1 1:1 v/v: Slowly add 50 mL H_2SO_4 (specific gravity = 1.84) to 50 mL of water. **Caution:** Heat-liberating reaction.

8.2.2 1:3 v/v: Slowly add 25 mL H_2SO_4 (specific gravity = 1.84) to 75 mL of water. **Caution:** Heat-liberating reaction.

8.3 Hydrochloric Acid (ACS), 1:9 v/v: Add one volume of concentrated HCl to nine volumes of water. **Caution:** Heat-liberating reaction.

8.4 Potassium Hydroxide Solution, 37% aqueous solution w/v: Dissolve 37 grams ACS grade potassium hydroxide pellets in water and dilute to 100 mL.

8.5 Carbitol (Diethylene Glycol Monoethyl Ether, ACS): Available from Aldrich Chemical Company.

8.6 Solvents

8.6.1 Acetone, Methanol, Ethanol, Methylene Chloride, and Hexane: Pesticide quality or equivalent.

8.6.2 Diethyl Ether: Pesticide quality or equivalent. Must be free of peroxides, as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethanol preservative must be added to each liter of ether.

8.7 Sodium Sulfate (ACS): Granular, acidified, anhydrous. Heat treat in shallow tray at 400°C for at least 4 hours to remove phthalates and other interfering organic substances. Alternatively, heat 16 hours at 400° to 500°C in shallow tray, or Soxhlet extract with methylene chloride for 48 hours. Acidify by slurrying 100 grams sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove ether under a vacuum. Mix 1 gram of the resulting solid with 5 mL of reagent water and measure pH of mixture. It must be below a pH of 4. Store at 130°C.

8.8 N-Methyl-n-nitroso-p-toluenesulfonamide (Diazald; ACS): Available from Aldrich Chemical Company.

8.9 Silicic Acid: Chromatographic grade, nominal 100 mesh. Store at 130°C.

8.10 Stock Standard Solutions: Stock standard solutions can be prepared from neat standard materials or purchased as certified solutions.

8.10.1 Prepare stock standard solutions by accurately weighing about 0.0100 gram of neat acids. Dissolve material in pesticide quality diethyl ether and dilute to volume in 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if certified by the manufacturer or an independent source.

8.10.2 Transfer stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° ± 2°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just before preparing calibration standards from them.

8.10.3 Stock standard solutions should be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

8.11 Calibration Standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of stock standards with diethyl ether. One concentration level should be near but above the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions should be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

8.12 Internal Standards (if internal standard calibration is used): To use this approach, the analyst should select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

8.12.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest.

8.12.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with diethyl ether.

8.12.3 Analyze each calibration standard according to Section 10.0.

8.13 Surrogate Standards: The analyst should monitor performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two herbicide surrogates (i.e., herbicides not expected to be present in the sample) recommended to encompass the range of the temperature program used in the method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis because of coelution problems.

9.0 Calibration Procedures

9.1 Gas Chromatography Conditions (Recommended)

9.1.1 Injection Port: 210°C; Initial Temperature: 60°C (2 minutes); Ramp: 11°C/minute; Final Temperature 270°C (3 minutes).

9.1.2 Helium Flow: 15.4 psig.

9.1.3 Detector: 320°C

9.1.4 Injection Volume: 1 μL.

9.2 Retention Time Windows

9.2.1 Before establishing windows, make sure GC system is within optimum operating conditions. Make three injections of standard mixtures throughout course of a 72-hour period. Serial injections over less than 72 hours may result in retention time windows that are too restrictive.

9.2.2 Calculate the standard deviation of the three absolute retention times for each single response standard. For multiresponse products, choose one major peak 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.

9.2.3 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window.

9.2.4 In cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close-eluting, similar compound to develop a valid retention window.

9.2.5 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data will be retained by the laboratory.

9.2.6 The windows should serve as a recommended treatment for peak identification. The experienced analyst must consider other chromatographic features such as peak shape, resolution, and distance from the internal standard.

9.3 Calibration

9.3.1 Initial Calibration

9.3.1.1 Perform initial calibration by using at least five concentrations of single response standards. One standard should be at a concentration near but above the required detection limits. The other concentrations should correspond to the expexted range found in field samples, or they should define the working range of the

detector. An aliquot of the internal standard is added to the standard before injection.

9.3.1.2 Calculate the response factor (RF) for each compound in each standard as follows:

$$RF = \frac{(A_s)\ (C_{IS})}{(A_{IS})\ (C_s)} \qquad (1)$$

Where:

A_s	=	Area response for parameter to be measured
C_{IS}	=	Concentration of internal standard (μg/L)
A_{IS}	=	Area response of internal standard
C_s	=	Concentration of parameter to be measured (μg/L)

If the RSD of the response factors is less than 15%, the average RF may be used to calculate results. Any time the RSD exceeds 30%, the five-point calibration must be reestablished.

9.3.2 Continuing Calibration

9.3.2.1 Calibration must be verified on each work day and after every 10 determinations with a mid-concentration standard of each analyte. This standard must also be analyzed at the end of the analytical sequence. The calibration or response factor for each analyte to be quantitated must not exceed a 10.0% difference when compared to the initial average calibration or response factor. The retention times of all analytes should be within the established retention time windows. No samples may be reported unless they are bracketed by acceptable continuing calibration standards. If the above criteria are not met, determine the reason and perform the required maintenance. Recalibrate the analytical system and reanalyze all samples affected.

9.3.2.2 To establish daily retention time windows use the retention time of the first continuing calibration standard as the midpoint of the retention time window defined by $\pm$ three times the standard deviation. The retention time of all subsequent continuing calibration standards should fall within the window. Otherwise, perform corrective action, recalibrate the system, and reanalyze all affected samples.

9.4 Use Tables 1 and 2 as guidance on selecting the lowest point on the calibration curve.

10.0 Sample Preparation

10.1 Preparation of Solid Samples

10.1.1 Extraction

10.1.1.1 To a 500-mL, wide-mouth Erlenmeyer flask add 50 grams (wet weight) of the well-mixed, moist solid sample. Adjust pH to 2 with concentrated HCl, and monitor pH for 15 minutes with occasional stirring. If necessary, add HCl until pH remains at 2.

10.1.1.2 Add 20 mL acetone to flask and mix contents with wrist shaker for 20 minutes. Add 80 mL diethyl ether to the same flask and shake again for 20 minutes. Decant extract, and measure volume of solvent recovered.

10.1.1.3 Extract sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken for 10 minutes with the wrist shaker and the acetone-ether extract decanted.

10.1.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine extracts in 2-liter separatory funnel containing 250 mL of 5% acidified sodium sulfate (anhydrous). If an emulsion forms, slowly add 5 grams of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added if necessary.

10.1.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at desired pH. Gently mix contents of separatory funnel for 1 minute and allow the layers to separate. Collect aqueous phase in a clean beaker and extract phase (top layer) in a 500-mL ground glass Erlenmeyer flask. Place aqueous phase back into separatory funnel and reextract using 25 mL of diethyl ether. Allow layers to separate and discard aqueous layer. Combine ether extracts in 500-mL Erlenmeyer flask.

10.1.2 Hydrolysis

10.1.2.1 Add 30 mL of reagent water, 5 mL of 37% KOH, and one or two clean boiling chips to the flask. Place three-ball Snyder column on flask, evaporate diethyl ether on water bath, and continue to heat for a total of 90 minutes.

10.1.2.2 Remove flask from water bath and allow to cool. Transfer water solution to 125-mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for layers to separate and discard ether layer each time. The phenol acid herbicides remain soluble in the aqueous phase as potassium salts.

10.1.3 Solvent Cleanup

10.1.3.1 Adjust pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to separatory funnel. Be sure to check pH at this point. Extract herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard aqueous phase.

10.1.3.2 Combine ether extracts in 125-mL Erlenmeyer flask containing 1.0 gram of acidified anhydrous sodium sulfate. Stopper and allow extract to remain in contact with acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store sample overnight in refrigerator.

10.1.3.3 Transfer ether extract through funnel plugged with acid-washed glass wool into 500-mL K-D flask equipped with 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse Erlenmeyer flask and column with 20 to 30 mL of diethyl ether to complete the quantitative transfer.

10.1.3.4 Add one or two clean boiling chips to flask, and attach three-ball Snyder column. Prewet Snyder column by adding approximately 1 mL of diethyl ether to the top. Place apparatus on hot water bath (60° to 65°C) so that the concentrator tube is partially immersed in hot water and entire lower rounded surface of flask is bathed in vapor. Adjust vertical position of apparatus and water temperature, as required, to complete concentration in

15 to 20 minutes. At proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove K-D apparatus from water bath and allow it to drain and cool for at least 10 minutes.

10.1.3.5 Remove Snyder column and rinse flask and its lower joints into concentrator tube with 1 to 2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach micro-Snyder column to concentrator tube, and prewet column by adding 0.5 mL of ethyl ether to top. Place micro-K-D apparatus on water bath so that concentrator tube is partially immersed in hot water. Adjust vertical position of apparatus and water temperature as required to complete concentration in 5 to 10 minutes. When apparent volume of liquid reaches 0.5 mL, remove micro-K-D from bath and allow it to drain and cool. Remove Snyder column and add 0.1 mL of methanol. Rinse walls of concentrator tube while adjusting extract volume to 1.0 mL with diethyl ether. Proceed to Section 10.3 for esterification.

10.1.4 Determine the percent moisture of another aliquot of the solid sample with Method No. FM-CON-0190.

10.2 Preparation of Liquid Samples

10.2.1 Extraction

10.2.1.1 Mark water meniscus on side of sample container for later determination of sample volume. Pour entire sample into a 2-liter separatory funnel and check pH with wide-range pH paper. Adjust pH to less than 2 with sulfuric acid (1:1).

10.2.1.2 Add 150 mL of diethyl ether to sample bottle, seal, and shake for 30 seconds to rinse walls. Transfer solvent wash to separatory funnel and extract sample by shaking funnel for 2 minutes with periodic venting to release excess pressure. Allow organic layer to separate from water layer for at least 10 minutes. If emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of emulsion through glass wool, centrifugation, or other physical methods. Drain aqueous phase into 1-liter Erlenmeyer flask. Collect solvent extract in 250-mL ground glass Erlenmeyer flask containing 2 mL of 37% KOH. Approximately 80 mL of the diethyl ether will remain dissolved in the aqueous phase.

10.2.1.3 Repeat extraction two more times using 50 mL of diethyl ether each time. Combine extracts in Erlenmeyer flask. (Rinse 1-liter flask with each additional aliquot of extracting solvent.)

10.2.2 Hydrolysis

10.2.2.1 Add one or two clean boiling chips and 15 mL of reagent water to 250-mL flask and attach three-ball Snyder column. Prewet Snyder column by adding 1 mL of diethyl ether to top of column. Place apparatus on hot water bath (60° to 65°C) so that bottom of flask is bathed with hot water vapor. Although diethyl ether will evaporate in about 15 minutes, continue heating for a total of 60 minutes, beginning from time flask is placed in water bath. Remove apparatus and let stand at room temperature for at least 10 minutes.

10.2.2.2 Transfer solution to 60-mL separatory funnel using 5 to 10 mL of reagent water. Wash basic solution twice by shaking for 1 minute with 20-mL portions of diethyl ether. Discard organic phase. Herbicides remain in aqueous phase.

10.2.3 Solvent Cleanup

10.2.3.1 Acidify contents of separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 minutes. Drain aqueous layer into 250-mL Erlenmeyer flask, and pour organic layer into 125-mL Erlenmeyer flask containing about 0.5 gram of acidified sodium sulfate. Repeat extraction twice more with 10-mL aliquots of diethyl ether, combining all solvent in 125-mL flask. Allow extract to remain in contact with sodium sulfate about 2 hours.

10.2.3.2 Transfer ether extract through funnel plugged with acid-washed glass wool into 500-mL K-D flask equipped with 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse Erlenmeyer flask and column with 20 to 30 mL of diethyl ether to complete quantitative transfer.

10.2.3.3 Add one or two clean boiling chips to flask and attach three-ball Snyder column. Prewet Snyder column by adding about 1 mL of diethyl ether to the top. Place apparatus on hot water bath (60° to 65°C) so that concentrator tube is partially immersed in hot water and entire lower rounded surface of flask is bathed in vapor. Adjust vertical position of apparatus and water temperature, as required, to complete concentration in 15 to 20 minutes. At proper rate of distillation, column balls will actively chatter but the chambers will not flood. When apparent volume of liquid reaches 1 mL, remove K-D apparatus from water bath and allow it to drain and cool for at least 10 minutes.

10.2.3.4 Remove Snyder column and rinse flask and its lower joints into concentrator tube with 1 to 2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add fresh boiling chip, attach micro-Snyder column to concentrator tube, and prewet column by adding 0.5 mL of ethyl ether to top. Place micro-K-D apparatus on water bath so that concentrator tube is partially immersed in hot water. Adjust vertical position of apparatus and water temperature as required to complete concentration in 5 to 10 minutes. When apparent volume of liquid reaches 0.5 mL, remove micro-K-D from bath and allow it to drain and cool. Remove Snyder column and add 0.1 mL of methanol. Rinse walls of concentrator tube while adjusting extract volume to 1.0 mL with diethyl ether.

10.2.3.5 Determine original sample volume by refilling sample bottle to mark with water and transferring to 1-liter graduated cylinder. Record sample volume to nearest 5 mL.

10.3 Esterification

10.3.1 Two methods may be used to generate diazomethane: The bubbler method and the Diazald kit method. The bubbler method is suggested when small batches (10 to 15) of samples require esterification. The method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. It is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization procedures (U.S. EPA 1971), described below, will react efficiently with all the chlorinated herbicides described in this method and should be used only by experienced analysts because of the potential hazards associated with its use. The following precautions should be taken:

Caution: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use mechanical pipetting aids.
- Do not heat above 90°C (explosion hazard).

- Avoid grinding surfaces, ground glass joints, sleeve bearings, glass stirrers (explosion hazard).
- Store away from alkali metals (explosion hazard).
- Diazomethane solutions decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

10.3.2 Diazald Kit Method

10.3.2.1 Instructions for preparing diazomethane are provided with the generator kit.

10.3.2.2 Add 2 mL of diazomethane solution and let sample stand for 10 minutes with occasional swirling.

10.3.2.3 Rinse inside wall of ampule with several hundred μL of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

10.3.2.4 Dissolve residue in 5 mL of hexane. Analyze by gas chromatography.

10.3.3 Bubbler Method

10.3.3.1 Assemble diazomethane bubbler (Figure 1).

10.3.3.2 Add 5 mL of diethyl ether to first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1 to 0.2 gram Diazald to second test tube. Immediately place exit tube into concentrator tube containing sample extract.

10.3.3.3 Apply nitrogen flow (10 mL/min) to bubble diazomethane through extract for 10 minutes or until yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of three sample extracts. An additional 0.1 to 0.2 gram of Diazald may be added (after initial Diazald is consumed) to extend generation of diazomethane. There is sufficient KOH in the original solution to perform about 20 minutes of total esterification.

10.3.3.4 Remove concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in fume hood for 20 minutes.

Figure 1. Diazomethane generator.

10.3.3.5 Destroy any unreacted diazomethane by adding 0.1 to 0.2 gram silicic acid to concentrator tube. Allow to stand until evolution of nitrogen gas has stopped. Adjust sample volume to 10.0 mL with hexane. Stopper concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize transesterification and other potential reactions that may occur. Analyze by gas chromatography.

11.0 Sample Analysis

11.1 Extracts should be refrigerated until analysis.

11.2 A 10-μL aliquot of internal standard solution is added to 1.0-mL aliquots of standards, blanks, and sample extracts providing concentrations of 20 μg/mL of the internal standards. Sample extracts should be prepared for screening or analysis by placing the internal standard solution into a labelled autosampler vial, then placing solvent (if dilution is being prepared) into the vial, and finally placing a known portion of the sample extract into the vial before capping and mixing. Instrument standards are prepared in the same manner.

Note: All working solutions should be prepared for injection in such a way that a constant amount (mass) of each internal standard is injected for all acquisitions.

11.3 The suggested levels of internal standards offer large detector response that will serve to minimize the effects of compound coelution. The minimum total volume requirements for the autosampler vial depend on the model and configuration of the autosampler.

11.4 Inject 2 to 5 μL of standards and samples (do not change injection volume after beginning initial calibration). Small volumes (1 μL) can be injected only if an automated system that consistently injects a constant volume is used.

11.5 If screening or analysis indicates that targets are present in the sample, the analyst must ensure that the calibration range is not exceeded. The analyst should check acquired data periodically during the analytical sequence and reanalyze samples that need dilutions, reanalysis, etc., within the same sequence when possible.

11.6 The results of all samples that follow a high sample with potential for crossover must by examined carefully for the possibility of crossover. If there is uncertainty or questionable data, affected samples should be reanalyzed. Wash

vials can be used to rinse the autodelivery system. Instrument blanks should be analyzed between suspect samples to show lack of instrument contamination.

11.7 It is not required to achieve primary initial calibration criteria to simply confirm the qualitative identity of a suspected target analyte. It is recommended that primary initial calibration criteria be achieved so that the quantitative data from both columns may be compared and either can be reported.

11.8 Qualitative Analysis

11.8.1 It is recommended that the nearest internal standard (for each compound) not suffering from coelution be used for calculation and comparison, but discretion of the analyst should prevail.

11.8.2 Peak identification is based upon relative retention time comparison to (recent) calibration data. Library retention times are usually established during initial calibration (or in some cases from continuing calibration standards). Internal standards serve as time references for all chromatographic acquisitions. A target compound should be identified in a sample if the chromatographic peak matches the predicted retention time within 0.05 minute.

11.8.3 The experienced analyst must consider other chromatographic features such as peak shape, resolution, and distance from internal standard. The experienced analyst can also graphically overlay sample and standard chromatograms, thus comparing reference peaks and tentatively identified compounds. Peaks tentatively identified in a sample require confirmation analysis. Compound concentrations too low for GC/MS analysis must be confirmed using a dissimilar GC capillary column.

11.8.4 When graphically comparing sample and standard chromatograms, standards with responses similar to those in the samples should be used for retention time and peak shape evaluation. As the mass injected fluctuates, the column may begin to experience overloading that can result in retention time shifts, distorted peak shapes, and other anomalies.

11.8.5 The width of a retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of the day. Three times the standard deviation of a retention time will be used to calculate a suggested retention time window size for a compound.

Note: The five levels of calibration standards check the instrument algorithm's ability to identify peaks at various concentrations.

11.8.6 The acquisition method peak search criteria should be optimized to identify targets but should not identify peaks of significantly different retention times. The system should bias favoring false positives to alert the analyst to potential targets and necessitate further analytical investigation.

11.8.7 The optimized machine algorithm retention time search should alert the analyst to possible target hits. The analyst will then use experience and discretion in deciding if a possible hit is an acceptable retention time "hit" and requires confirmation.

Note: The analyst should not rely exclusively on either quantitation reports or chromatograms for qualitative decisions.

11.9 Quantitative Analysis

11.9.1 When a compound has been identified, quantitation is based on the curve equation or the RF established during the initial calibration.

11.9.2 It is recommended that the nearest internal standard (for each compound) not suffering from coelution be used for calculation, but the analyst's discretion should prevail.

11.9.3 Before calculating a target, the analyst should ensure that the peak is integrated well and is not inflated by coeluting peaks, etc.

11.9.4 The identified target analytes are quantified by the internal standard method. Target parameters are assigned relative response factors as a result of initial calibration. Refer to section 9.3.1.2 for the response factor calculation.

11.10 Data Reduction

11.10.1 When reviewing chromatographic data before reduction, the analyst should evaluate the baseline and ensure that targets could be detected at the reporting limit level (above any chemical interference).

11.10.2 The results of all samples that follow a high sample that has the potential for crossover in the autosampler must be examined carefully for crossover. The data must be reviewed against instrument run logs.

11.10.3 Sample results and surrogate recovery (confirmed compounds and reporting limits) should be reported to two significant figures.

11.10.4 All surrogate recoveries should be within the three standard deviation acceptance range. If more than 50% of the surrogates within the period of an analytical sequence are outside the 2 standard deviation acceptance range, the analyst should investigate possible problems and reanalyze the samples.

11.10.5 The expected reporting limit should be calculated before data reduction begins. The expected reporting limit is the lowest reporting limit that can be issued for a sample. The total sample producing the total extract and any dilution factors are used to correct the nominal reporting limit. If interference prevents detection of a target (at the expected reporting limit), the analyst may choose to raise the reporting limit to reflect level of interference. Raised reporting limits should be addressed in the comment field in the case narrative.

12.0 Calculations

12.1 Water Samples: Calculate the concentration as in method FM-ORG-0040, section 12.1.1.

12.2 Sludge, Soil, and Waste: Calculate the concentration as in method FM-ORG-0040, section 12.1.2.

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control and reporting requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/20+End	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80—120%	Qualify data
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike	1/20	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10+End	90—110%	Recalibrate
Blank	1/10	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Surrogate Spikes	Every sample	75—125%	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	75—125%	Qualify data
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
A/S	as specified earlier in this method
RPD	relative percent difference
End	end of analytical period

15.0 References

Test Methods for Evaluating Solid Waste, 3rd ed., Method 8150, September 1986.

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FM-ORG-0100

Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry——Drinking Water

Working Linear Range: Analyte- and matrix-dependent
Reporting Limit: Analyte- and matrix-dependent
Reporting Units: Liquids, μg/L

1.0 Scope and Application

1.1 This is a general-purpose method for identification and simultaneous measurement of purgeable volatile organic compounds in finished drinking water. The method is applicable to a wide range of organic compounds, including the four trihalomethane disinfection byproducts, that have sufficiently high volatility and low water solubility to be removed efficiently from water samples with purge-and-trap procedures. The following compounds (Table 1) can be determined by the method:

Table 1
Practical Quantitation Limits for Volatile Organics[a]

Compound	PQL (μg/L)
Benzene	5.0
Bromobenzene	25.0
Bromochloromethane	5.0
Bromodichloromethane	5.0
Bromoform	5.0
Bromomethane	5.0
n-Butylbenzene	25.0
sec-Butylbenzene	25.0
tert-Butylbenzene	25.0
Carbon tetrachloride	5.0
Chlorobenzene	5.0
Chloroethane	5.0
Chloroform	5.0
Chloromethane	5.0
2-Chlorotoluene	5.0
4-Chlorotoluene	5.0
1,2-Dibromo-3-chloropropane	5.0
1,2-Dibromoethane	5.0

Table 1
Practical Quantitation Limits for Volatile Organics[a]
(Continued)

Compound	PQL (μg/L)
Dibromomethane	5.0
1,2-Dichlorobenzene	5.0
1,3-Dichlorobenzene	5.0
1,4-Dichlorobenzene	5.0
Dichlorofluoromethane	5.0
1,1-Dichloroethane	5.0
1,2-dichloroethane	5.0
1,1-Dichloroethene	5.0
cis-1,2-dichloroethene	5.0
trans-1,2-dichloroethene	5.0
1,2-Dichloropropane	5.0
cis-1,3-Dichloropropane	5.0
trans-1,3-Dichloropropane	5.0
2,2-Dichloropropane	5.0
1,1-Dichloropropene	5.0
Ethylbenzene	5.0
Hexachlorobutadiene	5.0
Isopropylbenzene	25.0
4-Isopropyltoluene	25.0
Methylene chloride	25.0
Naphthalene	5.0
n-Propylbenzene	5.0
Styrene	5.0
1,1,1,2-Tetrachloroethane	5.0
1,1,2,2-Tetrachloroethane	25.0
Tetrachloroethene	5.0
Toluene	5.0
1,2,3-Trichlorobenzene	5.0
1,2,4-Trichlorobenzene	5.0
1,1,1-Trichloroethane	5.0
1,1,2-Trichloroethane	5.0
Trichloroethene	5.0
Trichlorofluoromethane	5.0
1,2,3-Trichloropropane	5.0
1,2,4-Trimethylbenzene	5.0

Table 1
Practical Quantitation Limits for Volatile Organics[a]
(Continued)

Compound	PQL (μg/L)
1,3,5-Trimethylbenzene	5.0
Vinyl chloride	5.0
o-Xylene	5.0
m-Xylene	5.0
p-Xylene	5.0

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

1.2 Method Detection Limits (MDLs) are chemical- and instrument-dependent and can range from 0.02 to 0.20 μg/L. The applicable concentration range of the method is primarily column-dependent and ranges from 0.02 to 200 μg/L for the wide-bore, thick-film columns. Narrow-bore, thin-film columns may have a loading capacity limit that will lower the range from 0.02 to 20 μg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present at higher concentrations. Practical quantitation limits are included in Table 1.

1.3 Analytes not separated chromatographically but having different mass spectra and noninterfering quantitation ions can be identified and measured in the same calibration mixture or water sample. Analytes that have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water sample unless they have different chromatographic retention times. Co-eluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column and, if not, must be reported as isomeric pairs.

2.0 Method Summary

Volatile organic compounds and surrogates with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas such as helium through the

aqueous sample. Purged sample components are then trapped in a stainless steel tube containing suitable sorbent materials such as coconut charcoal, Tenax, or silica gel. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample components onto a capillary gas chromatography (GC) column interfaced to a mass spectrometer (MS). The GC is temperature programmed to produce separation between the method analytes by their differing boiling points and sorption capacity, which are then detected with the MS. Compounds eluting from the GC column into the MS are identified by comparing their measured mass spectra and chromatographic retention times to standard reference spectra and retention times in the system's database. Reference spectra and retention times for method analytes are obtained by the initial measurement of calibration standards under the same system conditions used for analyzing the samples. The concentration of each component identified 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 used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure to monitor purging efficiency or possible matrix interference.

3.0 Interferences

3.1 Major contaminant sources of the method are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. Cross-contamination could occur through improperly cleaned purging vessels.

3.2 Use of non-polytetrafluoroethylene (PTFE) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided because such materials out-gas organic compounds that will be concentrated in the trap during the purge operation.

3.3 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 multiple portions of reagent water. After analysis of a sample containing high concentrations of volatile organic compounds, one or more laboratory reagent water blanks should be analyzed to check for cross-contamination.

3.4 Special precautions must be taken to determine proper quantitation of methylene chloride. The analytical and sample storage area should be isolated

from atmospheric sources of methylene chloride or random background levels may result.

3.4.1 Because methylene chloride will permeate PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling such compounds must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

4.3 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Neat, primary standard materials and stock standard solutions of these compounds must be handled in a fume hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Purge-and-Trap System: The purge-and-trap system consists of three separate pieces of equipment: purging device, trap, and desorber. Systems are

commercially available from several sources that meet all the following specifications.

6.1.1 Purging Device: The all glass purging device should be designed to accept 25-mL samples with a water column at least 5 cm deep. A smaller (5-mL) device is recommended if the GC/MS system has adequate sensitivity to obtain the method detection limits required. Gaseous volumes above the sample must be kept to a minimum (< 15 mL) to eliminate dead volume effects. A glass frit should be installed at the base of the sample chamber so the purge gas passes through the water column as finely divided bubbles with a diameter of < 3 mm at the origin. Needle spargers may be used, but the purge gas must be introduced at a point about 5 mm from the base of the water column.

6.1.2 Trap: The trap must be at least 25 cm long and have an inside diameter of at least 0.105 inch. Starting from the inlet, the trap should contain 1.0 cm of methyl silicone coated packing and the following amounts of adsorbents: 1/3 Tenax polymer, 1/3 silica gel, and 1/3 coconut charcoal. If it is not necessary to determine dichloro-difluoromethane, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/minute. Vent the trap effluent to the room, not to the analytical column. Before daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning, but the column must be run through the temperature program before analysis of samples.

6.1.3 Packing: The use of the methyl silicone coated packing is recommended but not mandatory. The packing protects the Tenax adsorbent from aerosols and ensures that the Tenax is fully enclosed within the heated zone of the trap, thus eliminating potential cold spots. Alternatively, silanized glass wool may be used as a spacer at the trap inlet.

6.1.4 Desorber: The desorber must be capable of rapidly heating the trap to 180°C either before or at the beginning of the flow of desorption gas. The polymer section of the trap should not be heated higher than 200°C or the life expectancy of the trap will decrease. Trap failure is characterized by a pressure drop greater than 3 pounds per square inch across the trap during purging or by poor bromoform sensitivities.

6.2 Gas Chromatography/Mass Spectrometer/Data System (GC/MS/DS). The GC must be capable of temperature programming and should be equipped with variable-constant differential flow controllers so that the column flow rate will

remain constant throughout desorption and temperature program operation. With certain columns, the oven must be cooled to 10°C; therefore, a subambient oven controller may be required. If syringe injections of 4-bromofluorobenzene will be used, a split/splitless injection port is required.

6.2.1 Capillary Gas Chromatography Columns: Any gas chromatography column that meets the performance specifications of the method may be used. Separations of the calibration mixture must be equivalent or better than those described in the method. Three useful columns have been identified.

6.2.1.1 Column 1: 60-m × 0.75-mm I.D. VOCOL (Supelco, Inc.) glass wide-bore capillary with 1.5-μm film thickness.

6.2.1.2 Column 2: 30-m × 0.53-mm I.D. DB-624 (J & W Scientific, Inc.) fused silica capillary with 3-μm film thickness.

6.2.1.3 Column 3: 30-m × 0.32-mm I.D. DB-5 (J & W Scientific, Inc.) fused silica capillary with 1-μm film thickness.

6.2.2 Interfaces between the GC and MS: The interface used depends on the column selected and the gas flow rate. Wide-bore columns 1 and 2 have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface, or an all-glass jet separator are acceptable interfaces. Any interface can be used if the performance specifications described in the method can be achieved. The end of the transfer line after the interface, or the end of the analytical column if no interface is used, should be placed within a few millimeters of the MS ion source.

6.2.2.1 The narrow bore column 3 cannot accept the thermal desorption gas flow, and a cryogenic interface is required. This interface (Tekmar Model 1000 or equivalent) condenses the desorbed sample components at liquid nitrogen temperature, and allows the helium gas to pass through to an exit. The condensed components are frozen in a narrow band on an uncoated fused silica precolumn. When all components have been desorbed from the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. A potential problem with this interface is blockage

of the interface by frozen water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution.

6.2.3 Electron Ionization: The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV. The spectrometer must be capable of scanning from 35 to 300 amu with a complete scan cycle time (including scan overhead) of 2 seconds or less. (Scan cycle time = total MS data acquisition time in seconds divided by number of scans in the chromatogram.) The spectrometer must produce a mass spectrum that meets all criteria when 25 ng or less of 4-bromofluorobenzene is introduced into the GC. An average spectrum across the GC peak may be used to test instrument performance.

6.2.4 Data System: An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software should be capable of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectra from the GC peak with spectral data in a user-created database, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must allow integration of the ion abundance of any specific ion between specified times or scan numbers, calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Section 12.0.

6.3 Syringe and Syringe Valves

6.3.1 Two 5- or 25-mL glass, gas-tight syringes with Luer-Lok tip.

6.3.2 Two 2-way Syringe Valves with Luer ends (three each).

6.3.3 Microsyringes: 10- to 100.0-μL.

6.4 Miscellaneous: Standard solution Storage Bottles with PTFE-lined screw caps.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the GC/MS system according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Trap Packing Materials

8.1.1 2,6-Diphenylene Oxide Polymer: 60/80 mesh, chromatographic grade (Tenax GC grade or equivalent).

8.1.2 Methyl Silicone Packing (optional): OV-1 (3%) on Chromosorb W, 60/80 mesh, or equivalent.

8.1.3 Silica Gel: 35/60 mesh, Davison, grade 15 or equivalent.

8.1.4 Coconut Charcoal: Prepare from Barnebey Cheney, CA-580-26 lot No. M-2649 by crushing through 26 mesh screen.

8.2 Reagents

8.2.1 Methanol: Demonstrated to be free of analytes, pesticide quality or equivalent.

8.2.2 Reagent Water: Free of target compounds. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon, by using a water purification system, or by boiling distilled water for 15 minutes followed by a 1-hour purge with inert gas while the water temperature is held at 90°C. Store in clean, narrow-mouth bottles with PTFE-lined septa and screw caps.

8.2.3 Hydrochloric Acid (1:1): Slowly add measured volumes of concentrated HCl to an equal volume of reagent water. **(Caution:** This is an exothermic process. Heat will be liberated.)

8.2.4 Vinyl Chloride: Certified mixtures of vinyl chloride in nitrogen and pure vinyl chloride are commercially made and available (Matheson, Ideal Gas Products, and Scott Specialty Gases).

8.2.5 Ascorbic Acid: ACS reagent grade, granular.

8.3 Stock Standard Solutions: These solutions may be purchased as certified solutions or prepared from neat standard materials using the following procedures. One solution is required for every analyte of concern, every surrogate, and the internal standard. A useful working concentration is about 1 to 5 mg/mL.

8.3.1 Place about 9.8 mL of methanol into a 10-mL ground-glass, stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried and weigh to the nearest 0.1 mg.

8.3.2 If the analyte is a liquid at room temperature, use a 100-μL syringe and immediately add two or more drops of reference standard to the flask. Be sure that the reference standard falls directly into the alcohol without contacting the neck of the flask. If the analyte is a gas at room temperature, fill a 5-mL valved gastight syringe with the standard to the 5.0-mL mark, lower the needle to 5 mm above the methanol meniscus, and slowly inject the standard into the neck area of the flask. The heavy gas will rapidly dissolve in the methanol.

8.3.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μg/μL from the net gain in weight. When compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard.

8.3.4 Store stock standard solutions in bottles equipped with PTFE-lined screw caps. Methanol solutions prepared from liquid analytes are stable for at least 4 weeks when stored at -10°C to -20°C. Methanol solutions prepared from gaseous analytes are not stable for more than 1 week when stored at -10°C to -20°C; at room temperature, they should be discarded after 1 day. Stock standards should be protected from light.

8.4 Secondary Dilution Standards: Use stock standard solutions to prepare primary dilution standard solutions that contain all the analytes of concern (but not the internal standard!) in methanol. The primary dilution standards should be prepared at concentrations that can be easily diluted to prepare aqueous calibration solutions that will bracket the working concentration range. Store the primary dilution standard solutions with minimal headspace, and check frequently for signs of deterioration or evaporation, especially just before preparing calibration solutions. Storage times described for stock standard solutions also apply to dilution standard solutions.

8.5 Fortification Solutions for Internal Standard and Surrogates: A solution containing the internal standard and the surrogates is required to prepare laboratory reagent blanks and to fortify each sample. Prepare a fortification solution containing fluorobenzene (internal standard), 1,2-dichlorobenzene-d4 (surrogate), and BFB (surrogate) in methanol at concentrations of 5 μg/mL of each. A 5-μL aliquot of this solution added to a 25-mL water sample volume results in a concentration of 1 μg/L of each analyte. A 5-μL aliquot of this solution added to a 5-mL water sample volume delivers a concentration of 5 μg/L of each. Additional internal standards and surrogate analytes are optional.

8.6 Preparation of Laboratory Reagent Blank (LRB): Fill a 25-mL (or 5-mL) syringe with reagent water and adjust to the mark (no air bubbles). Inject 10 μL of the fortification solution containing the internal standard and surrogates through the Luer-Lok valve into the reagent water. Transfer the LRB to the purging device.

8.7 Preparation of Laboratory Control Sample: Prepare this exactly like a calibration standard except use standards obtained from an independent source. This is a calibration standard that is treated as a sample.

8.8 Preparation of Calibration Standards

8.8.1 The number of calibration solutions (CALs) needed depends on the calibration range desired. At least three CAL solutions are required to calibrate a range of a factor of 20 in concentration. For a factor of 50, use at least four standards; for a factor of 100, use at least five standards. One calibration standard should contain each analyte of concern and each surrogate at a concentration of 2 to 10 times the method detection limit for that compound. The other CAL standards should contain each analyte of concern at concentrations that define the range of the method. Every CAL solution contains the internal standard at the same concentration (5 μg/L suggested for a 5-mL sample; 1 μg/L for a 25-mL sample).

8.8.2 To prepare a calibration standard, add an appropriate volume of a primary dilution standard to an aliquot of reagent water in a volumetric flask. Use a microsyringe and rapidly inject the methanol solutions into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable in a volumetric flask and should be discarded after 1 hour unless transferred to a sample bottle and sealed immediately.

8.9 Volatile Matrix Spiking Solution: Prepare a spiking solution in Methanol that contains the following compounds at a concentration of 25.0 μg/mL: 1,1-dichloroethene, chlorobenzene, trichloroethene, toluene, and benzene. Matrix spikes also act as duplicates, so add an aliquot of this solution to each of two portions from one sample chosen for spiking.

9.0 Calibration Procedures

9.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required at the beginning of each 8-hour period during which analyses are performed.

9.2 Initial Calibration

9.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements.

Table 2
Ion Abundance Criteria for Bromofluorobenzene (BFB)

Mass (M/Z)	Relative Abundance Criteria
50	15 to 40% of mass 95
75	30 to 80% of mass 95
95	Base peak, 100% relative abundance
96	5 to 9% of mass 95
173	<2% of mass 174
174	>50% of mass 95
175	5 to 9% of mass 174
176	>95% but <101% of mass 174
177	5 to 9% of mass 176

9.2.2 Introduce into the GC (either by purging or making a syringe injection) 25 ng of BFB and acquire mass spectra for m/z 35 to 300 at 70 eV (nominal). If the spectrum does not meet all criteria summarized in the table above, the MS must be retuned and adjusted to meet all criteria before proceeding with

calibration. An average spectrum across the GC peak may be used to evaluate the performance of the system.

9.2.3 Purge a medium CAL solution (e.g., 10 to 20 μg/L) using the procedure.

9.2.4 Performance criteria for the medium calibration. Examine the stored GC/MS data with the data system software.

9.2.4.1 MS Sensitivity. The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each compound in calibration solution and make correct tentative identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. Summarized in Tables 3 and 4 are the retention times and primary and secondary ions for each target analyte.

9.2.4.2 GC Performance. Good column performance will produce symmetrical peaks with minimum tailing. If peaks are broad or sensitivity poor, remedial actions are required which may include but are not limited to adjusting the GC and/or MS conditions, cleaning or replacing the injection liner, or breaking off a short portion of the GC column.

Table 3
Chromatographic Retention Times for Method Analytes on Three Columns with Four Sets of Conditions

Compound	Retention Time (min:sec) Column 1[a]	Column 2[a]	Column 3[b]	Column 4[c]
Internal standard				
Fluorobenzene	8:49	6:27	14:06	8:03
Surrogates				
4-Bromofluorobenzene	18:38	15:43	23:38	
1,2-Dichlorobenzene-d_4	22:16	19:08	27:25	
Target Analytes				
Benzene	8:14	5:40	13:30	7:25
Bromobenzene	18:57	15:52	24:00	16:25
Bromochloromethane	6:44	4:23	12:22	5:38
Bromodichloromethane	10:35	8:29	15:48	9:20
Bromoform	17:56	14:53	22:46	15:42
Bromomethane	2:01	0:58	4:48	1:17
n-Butylbenzene	22:13	19:29	27:32	17:57
sec-Butylbenzene	20:47	18:05	26:08	17:28
tert-Butylbenzene	20:17	17:34	25:36	17:19
Carbon tetrachloride	7:37	5:16	13:10	7:25
Chlorobenzene	15:46	13:01	20:40	14:20
Chloroethane	2:05	1:01		1:27
Chloroform	6:24	4:48	12:36	5:33
Chloromethane	1:38	0:44	3:24	0:58
2-Chlorotoluene	19:20	16:25	24:32	16:44
4-Chlorotoluene	19:30	16:43	24:46	16:49
1,2-Dibromo-3-chloropropane	24:32	21:05		18:02
1,2-Dibromoethane	14:44	11:50	19:24	13:36
Dibromochloromethane	14:23	11:51	19:12	12:48
Dibromomethane	10:39	7:56	15:26	9:05
1,2-Dichlorobenzene	22:31	19:10	27:26	17:47
1,3-Dichlorobenzene	21:13	18:08	26:22	17:28
1,4-Dichlorobenzene	21:33	18:23	26:36	17:38
Dichlorofluoromethane	1:33	0:42	3:08	0:53
1,1-Dichloroethane	4:51	2:56	10:48	4:02
1,2-Dichloroethane	8:24	5:50	13:38	7:00
1,1-Dichloroethene	2:53	1:34	7:50	2:20
cis-1,2-Dichloroethene	6:11	3:54	11:56	5:04
trans-1,2-Dichloroethene	3:59	2:22	9:54	3:32
1,2-Dichloropropane	10:05	7:40	15:12	8:56
1,3-Dichloropropane	14:02	11:19	18:42	12:29
2,2-Dichloropropane	6:01	3:48	11:52	5:19
1,1-Dichloropropene	7:49	5:17	13:06	7:10
Ethylbenzene	15:59	13:23	21:00	14:44
Hexachlorobutadiene	26:59	23:41	32:04	19:14
Isopropylbenzene	18:04	15:28	23:18	16:25

Table 3
Chromatographic Retention Times for Method Analytes on Three Columns with Four Sets of Conditions (Continued)

Compound	Retention Time (min:sec) Column 1	Column 2	Column 3	Column 4
4-Isopropyltoluene	21:12	18:31	26:30	17:38
Methylene chloride	3:36	2:04	9:16	2:40
Naphthalene	27:10	23:31	32:12	19:04
n-Propylbenzene	19:04	16:25	24:20	16:49
Styrene	17:19	14:36	22:24	15:47
1,1,1,2-Tetrachloroethane	15:56	13:20	20:52	14:44
1,1,2,2-Tetrachloroethane	18:43	16:21	24:04	15:47
Tetrachloroethene	13:44	11:09	18:36	13:12
Toluene	12:26	10:00	17:24	11:31
1,2,3-Trichlorobenzene	27:47	24:11	32:58	19:14
1,2,4-Trichlorobenzene	26:33	23:05	31:30	18:50
1,1,1-Trichloroethane	7:16	4:50	12:50	6:46
1,1,2-Trichloroethane	13:25	11:03	18:18	11:59
Trichloroethene	9:35	7:16	14:48	9:01
Trichlorofluoromethane	2:16	1:11	6:12	1:46
1,2,3-Trichloropropane	19:01	16:14	24:08	16:16
1,2,4-Trimethylbenzene	20:20	17:42	31:30	17:19
1,3,5-Trimethylbenzene	19:28	16:54	24:50	16:59
Vinyl chloride	1:43	0:47	3:56	1:02
o-Xylene	17:07	14:31	22:16	15:47
m-Xylene	16:10	13:41	21:22	15:18
p-Xylene	16:07	13:41	21:18	15:18

[a] GC conditions given in section 11.3.1
[b] GC conditions given in section 11.3.2
[c] GC conditions given in section 11.3.3

Table 4
Quantitation Ions for Method Analytes

Compound	Primary Quantitation Ion	Secondary Quantitation Ions
Internal Standard		
Fluorobenzene	96	77
Surrogates		
4-Bromofluorobenzene	95	174, 176
1,2-Dichlorobenzene-d_4	152	115, 150
Target Analytes		
Benzene	78	77
Bromobenzene	156	77, 158

Table 4
Quantitation Ions for Method Analytes
(Continued)

Compound	Primary Quantitation Ion	Secondary Quantitation Ions
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 252
Bromomethane	94	96
n-Butylbenzene	91	134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91
Carbon tetrachloride	117	119
Chlorobenzene	112	77, 114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
1,2-Dibromoethane	107	109, 188
Dibromochloromethane	129	127
Dibromomethane	93	95, 174
1,2-Dichlorobenzene	146	111, 148
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111,148
Dichlorofluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110, 77
Ethylbenzene	91	106
Hexachlorobutadiene	225	260
Isopropylbenzene	105	120
4-Isopropyltoluene	119	134, 91
Methylene chloride	84	86, 49
Naphthalene	128	
n-Propylbenzene	91	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	166	168, 129
Toluene	92	91
1,2,3-Trichlorobenzene	180	182
1,2,4-Trichlorobenzene	180	182

Table 4
Quantitation Ions for Method Analytes
(Continued)

Compound	Primary Quantitation Ion	Secondary Quantitation Ions
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	130, 132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91

9.2.5 If all performance criteria are met, purge an aliquot of each of the other CAL solutions using the same GC/MS conditions.

9.2.6 Calculate a response factor (RF) for each analyte, surrogate, and isomer pair for each CAL solution using the internal standard fluorobenzene. This calculation is supported in acceptable GC/MS data system software and many other software programs. RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent. (1)

$$RF = \frac{(A_x)\ (Q_{IS})}{(A_{IS})\ (Q_x)}$$

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 ng or concentration units

Q_{IS} = Quantity of internal standard purged in ng or concentration units

9.2.7 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for all compounds. The percent RSD is calculated as follows: (2)

$$\% \text{ RSD} = \frac{SD}{\bar{x}} \times 100$$

Where:

RSD	=	Relative standard deviation
$\bar{x}$	=	Mean of 5 initial RFs for a compound.
SD	=	Standard deviation of average RFs for a compound

(3)

$$SD = \sqrt{\sum_{v=1}^{n} \frac{(x_i - \bar{x})^2}{N-1}}$$

If the RSD of any analyte or surrogate mean RF exceeds 20%, either analyze additional aliquots of the appropriate CAL solution to obtain accepable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance.

9.3 Continuing Calibration Check

9.3.1 Verify the MS tune and initial calibration at the beginning of each 8-hour work shift during which analyses are performed using the following procedure.

9.3.2 Introduce into the GC (either by purging an LRB or making a syringe injection) 25 ng of BFB and acquire a mass spectrum that includes data for m/z 35 to 300. If the spectrum does not meet all criteria, the MS must be retuned and adjusted to meet all criteria before proceeding with the continuing calibration check.

9.3.3 Purge a medium concentration CAL solution and analyze with the same conditions used during the initial calibration.

9.3.4 Demonstrate acceptable performance for the criteria in 9.2.4.

9.3.5 Determine that the absolute areas of the quantitation ions of the internal standard have not changed by a factor of two (-50% to +100%) from the areas measured in the most recent continuing calibration check. If these areas have changed by more than these amounts, adjustments must be made to restore system sensitivity. Then the instrument must be recalibrated before sample analysis begins.

9.3.6 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. If these conditions do not exist, the problem must be identified and resolved and the instrument must be recalibrated before samples are analyzed.

10.0 Sample Preparation

Remove plungers from two 5- or 25-mL syringes and attach a closed syringe valve to each. Warm sample to room temperature slowly as not to accelerate volatilization of components. Open sample bottle and carefully pour sample into one of the syringe barrels to just short of overflowing. Replace syringe plunger, invert syringe, and compress sample. Open syringe valve and vent residual air while adjusting sample volume to 5 or 25 mL. For samples and blanks, add the same concentrations of internal standard and surrogate contained in the CAL standards. Close valve. Fill second syringe in identical manner from same sample bottle. Reserve second syringe for reanalysis if necessary.

11.0 Sample Analysis

11.1 Sample Introduction and Purging: The method is designed for a 5- or 25-mL sample volume.

11.1.1 Adjust purge gas (nitrogen or helium) flow rate to 40 mL/minute (Do not change the purge flow rate between CAL standards and sample analysis). Attach trap inlet to purging device and open syringe valve on purging device.

11.1.2 Attach sample syringe valve to syringe valve on purging device. Be sure that trap is cooler than 25°C; then open sample syringe valve and inject sample into purging chamber. Close both valves and initiate purging. Purge sample for 11 minutes at ambient temperature.

11.2 Sample Desorption

11.2.1 Noncryogenic Interface: After 11-minute purge, place purge-and-trap system in desorb mode and preheat trap to 180°C without flow of desorption gas. Then simultaneously start flow of desorption gas at 15-mL/minute for about 4 minutes. Begin temperature program of gas chromatograph and start data acquisition.

11.2.2 Cryogenic Interface: After 11-minute purge, place purge-and-trap system in desorb mode, make sure cryogenic interface is at -150°C or lower, and rapidly heat trap to 180°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes. At end of 5-minute desorption cycle, rapidly heat cryogenic trap to 250°C , simultaneously begin temperature program of gas chromatograph, and start data acquisition.

11.2.3 While trapped components are being introduced into gas chromatograph (or cryogenic interface), empty purging device using sample syringe and wash chamber with two 25-mL flushes of reagent water. After purging device has been emptied, leave syringe valve open to allow purge gas to vent through sample introduction needle.

11.3 Gas Chromatography/Mass Spectrometry: Acquire and store data over mass range 35 to 300 with a total cycle time (including scan overhead time) of 2 seconds or less. Cycle time must be adjusted to measure five or more spectra during elution of each GC peak. Several alternative temperature programs can be used.

11.3.1 Single Ramp Linear Temperature Program for Wide-Bore Columns 1 and 2 with a Jet Separator: Adjust helium carrier gas flow rate to about 15 mL/minute. Column temperature is reduced to 10°C and held for 5 minutes from beginning of desorption, then programmed to 160°C at 6°C/minute and held until all components have eluted.

11.3.2 Multi-Ramp Linear Temperature Program for Wide-Bore Column 2 with the Open Split Interface: Adjust helium carrier gas flow rate to about 4.6 mL/minute. Column temperature is reduced to 10°C and held for 6 minutes from beginning of desorption, then heated to 70°C at 10°C/minute, heated to 120°C at 5°C/minute, heated to 180°C at 8°C/minute, and held at 180°C until all compounds have eluted.

11.3.3 Single Ramp Linear Temperature Program for Narrow-Bore Column 3 with a Cryogenic Interface: Adjust helium carrier gas flow rate to about 4 mL/minute. Column temperature is reduced to 10°C and held for 5 minutes from beginning of vaporization from cryogenic trap, programmed at 6°C/minute for 10 minutes, then 15°C/minute for 5 minutes to 145°C, and held until all components have eluted.

11.4 Trap Reconditioning: After desorbing sample for 4 minutes, recondition trap by returning purge-and-trap system to purge mode. Wait 15 seconds, then close syringe valve on purging device to begin gas flow through trap. Maintain trap temperature at 180°C. After about 7 minutes, turn off trap heater and open syringe valve to stop gas flow through trap. When trap is cool, the next sample can be analyzed.

11.5 Termination of Data Acquisition: When all sample components have eluted from the GC, terminate MS data acquisition. Use appropriate data output software to display full range mass spectra and appropriate plots of ion abundance as function of time. If any ion abundance exceeds the system working range, dilute sample aliquot in second syringe with reagent water and analyze diluted aliquot.

11.6 Identification of Analytes: Identify sample component by comparing its mass spectrum (after background subtraction) to a reference spectrum in the user-created database. GC retention time of sample component should be within 3 standard deviations of the mean retention time of compound in calibration mixture.

11.6.1 In general, all ions 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 to 50%. Some ions, particularly the molecular ions, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.6.2 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 shoulders 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.

11.6.3 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 and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary columns. If unresolved, these groups of isomers must be reported as isomeric pairs.

11.6.4 Methylene chloride 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 acceptable because the concentration of the background in the blank is highly variable.

11.6.5 Surrogate spike and matrix spike/matrix spike duplicate target acceptance ranges are summarized in Table 5 and Table 6.

11.6.5.1 If one or more of the surrogate spike recoveries is outside the acceptance limits, then the sample is reanalyzed. If the surrogate spike recovery of the reanalyzed sample is still outside the acceptance range, then the sample results of both analyses are reported and noted in the case narrative.

Table 5
Volatile Surrogate Recovery Target Acceptance Limits, %

Compound	Water 254
Bromofluorobenzene	86-115
1,2-Dichlorobenzene-d4	75-125

Table 6
Volatile Matrix Spike/Matrix Spike Duplicate Recovery Target Acceptance Limits, %

Compound	Water
1,1-Dichloroethene	61-145
Trichloroethene	71-120
Benzene	76-127
Toluene	76-125
Chlorobenzene	75-130

11.6.5.2 If the MS/MSD recoveries are not within the target acceptance limits as shown in Table 6, the analysis is not repeated. The data is reported as is and noted in the case narrative.

12.0 Calculations

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation.

12.1.1 Calculate analyte and surrogate concentrations. (4)

$$C_x = \frac{(A_x)\ (Q_{IS})\ 1000}{(A_{IS})\ (RF)\ (V)}$$

Where:

C_x = Concentration of analyte or surrogate (μg/L) in the water sample

A_x = Integrated abundance of the quantitation ion of the analyte in the sample

A_{IS} = Integrated abundance of the quantitation ion of the internal standard in the sample

Q_{IS} = Total quantity of internal standard added to the water sample (μg)

V = Original water sample volume (mL)

RF = Mean response factor of analyte from the initial calibration

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute concentrations of analytes and surrogates from the second- or third-order regression curves.

12.1.3 Calculations should use all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Three significant figures may be used for concentrations above 99 μg/L, two significant figures for concentrations between 1 and 99 μg/L, and one significant figure for lower concentrations.

12.1.4 Calculate the total trihalomethane concentration by summing the four individual trihalomethane concentrations in μg/L.

12.2 A matrix spike and matrix spike duplicate must be performed for each group of samples of a similar matrix, for the following, whichever is most frequent:

- Each case of field samples received
- Each 20 field samples in a case
- Each group of field samples of a similar concentration level (soils/waste)
- Each 14-day calendar period during which field samples were received beginning with the receipt of the first sample in that Sample Delivery Group

12.2.1 Calculate the matrix spike recovery as in FM-ORG-0010, section 12.10.1.

12.2.2 Calculate the relative percent differences of recoveries as in FM-ORG-0010, section 12.10.2.

12.3 Calculate the recovery of each surrogate compound in all samples, blanks, matrix spikes, and matrix spike duplicates. Determine if the recovery is within limits (Table 6) and report on appropriate form.

12.3.1 Calculate concentrations of surrogate compounds using the same equations as used for target compounds. Calculate recovery of each surrogate compound as:

$$\%R = \frac{\text{Concentration (or amount) found} \times 100}{\text{Concentration (or amount) spiked}} \quad (6)$$

12.3.2 If the recovery of any surrogate compound is not within limits, the following steps are required.

12.3.2.1 Check to be sure there are no errors in calculations, formulation of the surrogate compound spiking solutions, and internal standards. Also check instrument performance.

12.3.2.2 Reanalyze sample if none of the above steps reveals a problem.

12.3.2.3 Do not reanalyze diluted samples if surrogate compound recoveries are outside the limits.

12.3.2.4 If the sample associated with the matrix spike and matrix spike duplicate does not meet specifications, it should be reanalyzed only if the MS/MSD surrogate compound recoveries are within the limits. If the sample and associated MS/MSD show the same pattern (i.e., outside the limits), then the sample does not require reanalysis and a reanalysis must not be submitted. Document in the narrative the similarity in recoveries of the surrogate compounds in the sample and associated MS/MSD.

12.3.3 If reanalysis of the sample solves the problem, then the problem was within the laboratory's control. Therefore, submit only data from the analysis with surrogate compound recoveries within the limits. This shall be considered the initial analysis and shall be reported as such on all data deliverables.

12.3.4 If reanalysis of the sample does not solve the problem (i.e., the surrogate compound recoveries are outside the limits for both analyses), then submit the data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes.

12.3.5 If the recovery of any one surrogate compound in a method blank is outside the limits, then the method blank and all associated samples must be reanalyzed.

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control and reporting requirements are determined by the method, Analytical Support Level, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	Every 8 hours	90—110%	Recalibrate
Method Blank	Every 8 hours	DR	Qualify data
LCS	Every 8 hours	80—120%	Qualify data
Surrogate Spikes	Every sample	11.6.5	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	11.6.5	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	Every 8 hours	90—110%	Recalibrate
Blank	Every 8 hours	DR	Qualify data
LCS	Every 8 hours	80—120%	Recalibrate
Surrogate Spikes	Every sample	11.6.5	Reanalyze, then qualify data
Matrix Spike/MSD	1/20	11.6.5	Qualify data
BFB	Every 8 hours	9.2.1	Recalibrate
Internal Standard	Every sample	A/S	Qualify data
Duplicate Sample	1/10	0—20% RPD	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
LCS	laboratory control sample
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
MSD	matrix spike duplicate
BFB	bromofluorobenzene
A/S	as specified earlier in this method
RPD	relative percent difference

15.0 References

15.1 *Test Methods for Evaluating Solid Waste*, 3rd ed. Method 8240.

15.2 *Safe Drinking Water Methods*, Method 524.2, Revision 3.0, 1989.

FERNALD/voc-ms-1.51

FM-MISC-0010

Toxicity Characteristic Leaching Procedure

Working Linear Range: Method- and analyte-specific
Reporting Limit: See list in Section 1.2
Reporting Units: mg/L
Matrix: Liquid or solid

1.0 Scope and Application

1.1 The TCLP is an analytical method designed to simulate the climatic leaching action expected to occur in landfills. Ideally, it determines the mobility of both organic and inorganic target analytes present in liquid, solid, and multiphasic wastes. The target analyte list includes 25 organic compounds (volatiles, semivolatiles, pesticides, and herbicides) and 8 metals.

1.2 Rather than defining a method detection limit and working range, the TCLP rule invokes a regulatory limit, when exceeded causes the waste to be deemed hazardous. For the target analytes of this operating procedure, the regulatory levels at which the waste is deemed hazardous are:

Target Analyte	Limit (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon Tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethene	0.7

Target Analyte	Limit (mg/L)
2,4-Dinitrotoluene	0.13 **
Endrin	0.02
Heptachlor (and its epoxide)	0.008
Hexachlorobenzene	0.13 **
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0 **
Selenium	1
Silver	5
Tetrachloroethene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl Chloride	0.2

*If o-, m-, and p-cresol concentrations cannot be differentiated, then total cresol concentration is used. The regulatory level for total cresol is 200 mg/L.

**Quantitation limit is greater than the regulatory level. The quantitation limit therefore becomes the regulatory level.

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

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile contaminant exceeds the regulatory threshold for that compound, then the waste is hazardous and extraction using zero headspace extraction (ZHE) is not necessary. However, the extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory threshold.

1.5 The analytical methods must have a method detection limit less than the regulatory limit.

1.6 If a total analysis of the waste demonstrates that individual contaminants are not present in the waste, or that they are present at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

2.0 Method Summary

Two extraction methods are detailed in this procedure: one for volatiles compounds only, the other for the remaining target compounds. The overall process is broken down into four major steps:

- Determining percent solids
- Identifying the appropriate extraction solution
- Extracting the sample
- Analyzing the sample for target compounds

3.0 Interferences

Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 Safety Precautions

4.1 The analyst must practice laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids must be practiced. The procedure should be performed in a fume hood or other vented area. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

Note: Only EPA-approved TCLP equipment will be used.

6.1 Agitation Apparatus: Capable of rotating extraction vessel end-over-end at 30 ± 2 rpm.

6.2 Bottle Extraction Vessel: Borosilicate or Teflon bottle with sufficient capacity to hold sample and extraction fluid.

6.3 Zero Headspace Extraction Unit (ZHE): 500- to 600-mL (minimum 300 mL), equipped to accommodate a 90- to 110-mm filter (minimum 47 mm). For mobility of volatile organic compounds only. The ZHE is an extraction vessel that allows for liquid/solid separation within the device and effectively precludes headspace. The piston within the ZHE must be able to be moved with approximately 15 psi or less and must withstand 50 psi. The ZHE must be checked after every extraction.

6.4 ZHE Collection Devices.

6.5 ZHE Extraction/Fluid Transfer Devices.

6.6 Filter and Filter Holder: Glass filter of borosilicate glass fiber with an effective pore size of 0.6 to 0.8 μm. Any filter holder capable of supporting the glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. Choice of filter holder is dependent upon the physical characteristics of the filtered material.

6.7 pH Meter: Accurate to ± 0.05 unit.

6.8 Laboratory Balance: Accurate to ± 0.01 gram.

6.9 Borosilicate Beakers.

6.10 Hot Plate/Magnetic Stirrer Unit.

6.11 Watchglasses.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for extraction units and pH meter according to the manufacturers' directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Hydrochloric Acid (HCl), 1 N: Slowly, and while stirring, add 82 mL concentrated HCl to about 500 mL water. Dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.3 Nitric Acid (HNO_3), 1 N: Slowly, and while stirring, add 63 mL concentrated HNO_3 (16 M) to about 500 mL water. Dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.4 Sodium Hydroxide (NaOH), 1 N: Dissolve 40 grams of NaOH in about 500 mL water. Dilute to 1 liter and mix well.

8.5 Glacial Acetic Acid (CH_3COOH): Reagent grade or better.

8.6 Extraction Fluid No. 1: Add 5.7 mL glacial acetic acid to 500 mL of water. Then add 64.3 mL of 1 N NaOH and dilute to 1 liter. When correctly prepared, the pH of solution must be 4.93 ± 0.05. If it is not, prepare the solution again

8.7 Extraction Fluid No. 2: Dilute 5.7 mL glacial acetic acid with water to a final volume of 1 liter. When correctly prepared, the pH of this solution should be 2.88 ± 0.05; if not, prepare the solution again.

9.0 Calibration Procedure

No instruments are used for the extraction procedure, but a pH meter is used. Calibration of the pH meter is discussed in Method No. FM-CON-0110.

10.0 Sample Preparation

10.1 If the sample consists of more than one phase, each phase must be analyzed separately and the results combined arithmetically. Therefore, if the analysis of any phase indicates that a target analyte is present at a concentration greater than the regulatory limit, the waste is deemed hazardous and it is not necessary to analyze the other liquid extracts.

10.2 Determination of Percent Solids

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

10.2.2 If a sample is essentially solid and under applied pressure will not yield any liquid, then proceed directly to Section 10.3.

10.2.3 Preweigh filter and container that will receive filtrate and record weights.

10.2.4 Assemble filter holder and filter following manufacturer's directions. Place filter on support screen and secure.

10.2.5 Weigh out approximately 100 grams of waste sample, and record weight.

10.2.6 Quantitatively transfer waste sample to filter holder. If necessary, spread sample evenly over filter.

10.2.7 Gradually apply vacuum or gentle pressure of 1 to 10 psi until air or pressurizing gas moves through filter. If this point is not reached under 10 psi and if no additional liquid has passed through the filter for 2 minutes, slowly increase pressure to a maximum of 50 psi in 10-psi increments. Wait at least 2 minutes at each increment for pressurizing gas to move through filter.

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

10.2.8 When pressurizing gas begins to move through filter or when liquid flow has ceased at 50 psi, stop filtration.

10.2.9 The material left in the filter holder is defined as the solid phase of the waste. The filtrate is defined as the liquid phase.

10.2.10 Weigh container holding filtrate. The weight of the filtrate solution is the difference in weight between the container before and after filtration. Record weight of filtrate.

10.2.11 Calculate percent solids using the equation: (1)

$$\% \text{ Solids} = \frac{\text{Weight of waste (10.2.5)} - \text{Weight of liquid (step 10.2.10)}}{\text{Weight of waste (step 10.2.5)}} \times 100$$

If the percent solids calculated above is $< 0.5\%$, proceed directly to Section 11. If calculated percent solids is $\geq 0.5\%$, continue to 11.4.4.

10.2.12 Remove solid phase and filter from filtration apparatus.

10.2.13 Dry the filter and solid phase in a 100° ± 20°C oven until two successive weighings yield the same value within ± 1%. Record all weights.

10.2.14 Calculate percent dry solids using the equation: (2)

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

If the percent dry solids calculated above is < 0.5%, proceed directly to Section 11. If the percent dry solids is ≥ 0.5%, continue.

10.3 Evaluating Particle Size

10.3.1 Weigh out approximately 100 grams of fresh waste sample and record weight on bench sheet.

10.3.2 Sieve the sample through a 0.375-inch Teflon-coated screen (9.5 mm). If all the sample passes through the screen, then proceed to Section 10.2.3.

10.3.3 If all the sample is not able to pass through the screen, reduce particle size by crushing, cutting, or grinding the waste until it pass through the screen. A minimum sample size of 100 grams is recommended. Return to section 10.2.3.

11.0 Sample Analysis

11.1 Choosing Extraction Fluid for Nonvolatiles

11.1.1 Weigh a 250-mL borosilicate beaker and note the weight.

11.1.2 Weigh out approximately 5 grams of sample left on filter after pressure filtration in tared beaker and note weight. If necessary, reduce particle size of sample by crushing, cutting, or grinding. Ideally, the particles should be less than 1 mm in diameter. The weight of the sample is the difference in the beaker weight.

11.1.3 Add 96.5 mL of water to beaker and cover with watch glass. Stir vigorously for 5 minutes using magnetic stirrer.

11.1.4 Measure pH using the procedure outlined in the pH operating procedure. If pH is < 5, proceed to step 11.2.6.

11.1.5 If pH is > 5, add 3.5 mL 1 N HCl, slurry briefly, and cover with watch glass. Place on hot plate and heat to 50°C. After 10 minutes, remove beaker from hot plate and cool to room temperature. Measure the pH.

11.1.6 If pH is < 5, use extraction fluid No. 1. If pH is ≥ 5, then use extraction fluid No. 2.

11.2 Preparing Sample for Extraction

11.2.1 If the waste contained less than 0.5% dry solids as determined in Section 10.2, proceed to 11.4.4.

11.2.2 If sample is multiphasic, liquid and solid must be separated using the filtration device. Be sure to use a large enough waste sample so that after filtration there are at least 100 grams of solid material for extraction.

11.2.3 If waste sample is sludge, allow it to sit overnight to allow solids to settle and liquid to separate. Decant liquid and analyze phases separately.

11.2.4 If waste will not yield any liquid when subjected to pressure filtration, weigh out 100 grams of solid and liquid phases of sample and proceed to 11.3, 11.3.2, or 11.4.

11.2.5 Weigh filter and container that will receive filtrate and note the weight.

11.2.6 Assemble filter holder and filter following manufacturer's directions. Place filter on support screen and secure.

11.2.7 Weigh out approximately 100 grams of waste sample and record the weight.

11.2.8 Quantitatively transfer waste sample to filter holder. If necessary, spread sample evenly over filter.

11.2.9 Gradually apply vacuum or gentle pressure of 1 to 10 psi, until air or pressurizing gas moves through filter. If this point is not reached under 10 psi and if no additional liquid has passed through filter for 2 minutes, slowly increase pressure to a maximum of 50 psi in 10-psi increments. Wait at least 2 minutes at each increment for pressurizing gas to move through filter.

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

11.2.10 When pressurizing gas begins to move through filter or when liquid flow has ceased at 50 psi, stop filtration.

11.2.11 The material left in the filter holder is defined as the solid phase of the waste. The filtrate is defined as the liquid phase.

11.2.12 Weigh filtrate container. The weight of the filtrate solution is the difference in weight between the filtrate container before and after filtration. Record weight of filtrate container on bench sheet. Filtrate may now be either analyzed or stored at 4° ± 2°C until time of analysis.

11.2.13 Sieve the sample through a 0.375-inch Teflon-coated screen (9.5 mm). If all the sample passes through the screen, proceed to Section 11.3, 11.3.2, or 11.4.

11.2.14 If all the sample is not able to pass through the screen, reduce particle size by crushing, cutting, or grinding the waste until it is able to pass through the screen.

11.3 Extracting the Sample

11.3.1 Zero Headspace Extraction for Volatile Compounds Only

Note: Only extraction fluid No. 1 is used for ZHE.

11.3.1.1 The ZHE device is used to obtain extracts for volatile analysis only. Extracts obtain using the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides). The ZHE has an internal capacity of about 500 mL. It is charged with sample only once and is not opened until the final extract has been collected. Although the following procedure allows for particle size reduction during the procedure, this could result in the loss of volatile compounds. If possible, particle size should be reduced as the sample is being taken but it may be performed during the procedure. In carrying out the following steps, do not allow the soil to be exposed to the atmosphere for any more time than is absolutely necessary. The materials should be handled when cold (4°C) to minimize loss of volatiles. Weigh the evacuated container that will receive the filtrate, and set aside. If using a Tedlar® bag, all air must be expressed from the device.

11.3.1.2 Place ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the position within the ZHE body to a height that will minimize the distance the piston will have to move once it is charged with sample. Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

11.3.1.3 Quantitatively transfer waste to the ZHE. Weight is determined using the following equation for wastes > 5% dry solids:

$$\text{Weight of waste} = \frac{25}{\%\ \text{Solids}} \times 100 \qquad (3)$$

Secure filter and support screens into top flange of the device, and secure flange to ZHE body in accordance with the manufacturer's directions. Tighten all ZHE fittings and place device in vertical position (gas inlet/outlet flange on the bottom). Do not attach the extraction collection device to the top plate. Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1 to 10 psi to a maximum of 50 psi to force all of the headspace out of the device.

11.3.1.4 With ZHE in vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open liquid inlet/outlet valve, and begin transferring extraction fluid into ZHE until the appropriate amount of fluid has been introduced into the device.

11.3.1.5 After extraction fluid has been added, close inlet/outlet valve immediately and disconnect extraction fluid line. Check ZHE to ensure that all valves are in closed positions. Physically rotate device end-over-end two or three times. Reposition ZHE in vertical position with liquid inlet/outlet valve on top. Put 5 to 10 psi behind piston (if necessary) and slowly open liquid inlet/outlet valve to bleed into a fume hood any headspace that may have been introduced by the addition of extraction fluid. Bleeding must be done quickly and stopped at the first appearance of liquid from the valve. Repressurize ZHE with 5 to 10 psi and check all ZHE fittings to ensure that they are closed.

11.3.1.6 Place ZHE in rotary extractor apparatus and rotate ZHE at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature will be maintained at 22° ± 3°C during agitation.

11.3.1.7 Following the 18-hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check ZHE for leaking and redo extraction with a new sample. If pressure within device has been maintained, material in the extractor vessel is separated into its component liquid and solid phases.

11.3.1.8 Attach evacuated, weighed filtrate collection container to liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1 to 10 psi to force liquid phase into filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When liquid flow has ceased and continued pressure filtration at 50 psi does not result in any additional filtrate within any 2-minute period, filtration is stopped. Close inlet/outlet valve, discontinue pressure to piston, and disconnect filtration collection container.

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

11.3.1.9 Following collection of the extract, aliquots for analysis should be prepared immediately and stored with minimal headspace at 4°C until analyzed. The extract will be prepared and analyzed according to the appropriate analytical methods.

11.3.2 Extraction for Nonvolatile Compounds

11.3.2.1 Calculate amount of extraction fluid to add to extractor vessel as follows: (4)

$$\text{Weight of extraction fluid} = \frac{20\ (\%\ \text{solids})(\text{wt. of filtered waste})}{100}$$

11.3.2.2 Slowly add appropriate extraction fluid to extractor vessel. Note volume of extraction fluid.

11.3.2.3 Close extractor bottle tightly using Teflon tape to ensure a tight seal. Place extractor bottle in rotary agitation device and secure.

11.3.2.4 Rotate bottle at 30 ± 2 rpm for 18 ± 2 hours. Note start and finish time. Ambient temperature in the room must be maintained at 20° ± 3°C during extraction period.

Note: During agitation, pressure may build within extractor bottle. To relieve excess pressure, extractor bottle may be opened periodically (e.g., after 15 minutes, 30 minutes, 1 hour) and vented into a fume hood. Note on the bench sheet any time the extractor bottle is opened.

11.3.2.5 At the end of the 18-hour extraction period, the extractor bottle contents are filtered to separate the solid and liquid phases.

11.3.2.6 Weigh filter and container that will receive filtrate. Note the weights.

11.3.2.7 Assemble filter holder and filter following the manufacturer's directions. Place filter on support screen and secure.

11.3.2.8 Transfer contents of extractor bottle to filter holder. If necessary, spread sample evenly over the filter.

11.3.2.9 Gradually apply vacuum or gentle pressure of 1 to 10 psi, until air or pressurizing gas moves through filter. If this point is not reached under 10 psi and if no additional liquid has passed through filter for 2 minutes, slowly increase pressure to a maximum of 50 psi in 10-psi increments. Wait at least 2 minutes at each increment for pressurizing gas to move through filter.

Note: Instantaneous application of high pressure can degrade glass fiber filter and may cause premature plugging.

11.3.2.10 When pressurizing gas begins to move through filter or when liquid flow has ceased at 50 psi, stop filtration.

11.4 Preparation of TCLP Extraction

11.4.1 If the waste contained no initial liquid phase, then the filtered liquid obtained from extraction is the TCLP extract.

11.4.2 If the waste sample originally was two phases, solid and liquid, combine the original liquid with the TCLP extraction liquid. Do not combine liquid phases if there is any chance of incompatibility.

11.4.3 If there are two liquid phases due to incompatibility, treat each liquid as a separate extraction liquid.

11.4.4 Measure the pH of the liquids according to the pH operating procedure and record the pH.

11.4.5 Transfer an aliquot of the extraction liquid to a clean sample container and preserve with several drops of concentrated nitric acid to pH < 2. This sample is for metals analysis.

11.4.6 Transfer the remaining extraction liquids to a clean sample container and store in refrigerator until it can be analyzed.

12.0 Calculations

12.1 If individual phases liquid/liquid or liquid/solid were analyzed separately, the results can be combined to yield a total TCLP result using the calculation: (5)

$$\text{Final analyte conc.} = \frac{(V_1)(C_1) + (V_2)(C_2)}{V_1 + V_2}$$

Where:

V_1 = volume of first phase (L)
C_2 = concentration of analyte in second phase (mg/L)
V_2 = volume of second phase (L)
C_1 = concentration of analyte in first phase (mg/L)

12.2 Measured values for samples must be corrected for analytical bias using the equation: (6)

$$X_c = \frac{X_u}{\%R} \times 100$$

Where:

X_c = corrected sample value
X_u = measured value of unspiked sample

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan. A specific discussion of each type of quality control sample is presented in the SCQ (Section 2) or the analytical method. Except for blanks and matrix spikes, there are no QC samples or acceptance limits for this procedure.

15.0 References

15.1 40 CFR Part 261, Appendix II, 7/1/1991.

FERNALD/tclp.51

FM-MISC-0020

Corrosivity

Working Linear Range: None
Reporting Limit: None
Reporting Units: None
Matrix: Liquid

1.0 Scope and Application

1.1 The corrosivity characteristic, as defined in 40 CFR Part 261.22, is designed to identify wastes that might pose a hazard to human health or the environment because of their ability to:

- Mobilize toxic metals if discharged into a landfill environment
- Corrode handling, storage, transportation, and management equipment
- Destroy human or animal tissue in the event of inadvertent contact

1.2 A solid waste is corrosive if a representative sample of the waste has either of the following properties:

- It is aqueous and has a pH of < 2 or ≥ 12.5 as determined by a pH meter using FM-CON-0110.
- It is a liquid and corrodes steel (SAE 1020) at a rate greater than 6.35 mm (0.250 inch) per year at a test temperature of 55°C (130°F) as determined by this method.

1.3 Rather than defining a method detection limit and working range, corrosivity is defined as a regulatory limit that, when exceeded, causes a liquid waste to be deemed hazardous. To designate a waste as corrosive towards steel (SAE 1020), it must corrode steel at a rate greater than 6.35 mm (0.250 inch) per year at a test temperature of 55°C (130°F).

2.0 Method Summary

Corrosivity can be evaluated in two ways for a waste of interest. If the waste is an aqueous liquid, then the pH of the solution can be measured using Method No. FM-CON-0110. If it is not aqueous, then a preweighed steel coupon is immersed in the waste in a closed vessel at 55° ± 1°C for 24 hours and the loss of steel to corrosion is measured. If the rate of corrosion is greater than 6.35 mm per year, the waste is deemed corrosive.

3.0 Interferences

Because the test is designed to evaluate a physical property rather than determine the concentration of a target analyte, little interferes with the test. The test is always conducted in duplicate, and duplicate results are typically within ± 10%. Large differences in corrosion rates may occur, however, when the waste causes passivation of the metals surface. Passivation can be either a chemical or physical process in which the metal surface is no longer able to corrode.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids and bases must be practiced. This procedure should be performed in a fume hood or other vented area. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Coupon Corrosivity Apparatus: Available commercially. Apparatus consists of a flask of appropriate size (usually 500 to 5,000 mL), a reflux condenser, a thermowell and temperature regulating device, a heating mantle, and a coupon support system.

6.1.1 The supporting device and container shall be constructed of materials that are not affected by, or cause contamination of, the waste under test.

6.1.2 The method of supporting the coupons will vary with the apparatus used for conducting the test, but it should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon, or coated metal.

6.1.3 The shape and form of the coupon support should ensure free contact with the waste.

6.1.4 Steel Coupons: Available commercially. Coupons are made of SAE 1020 steel and are usually circular in shape. Coupons are usually 3.75 cm (1.5 inches) in diameter and 0.32 cm (0.125 inch) thick with a 0.80-cm (0.4-inch) hole for mounting the coupon in the flask.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the coupon corrosivity unit and the analytical balance according to the manufacturers' directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

8.0 Reagents and Calibration Standards

8.1 Water: All references to water assume the use of ASTM Type II water.

8.2 Sodium Hydroxide (NaOH), 20%: Dissolve 200 grams NaOH in 800 mL water and dilute to 1 liter.

8.3 Zinc Dust.

8.4 Hydrochloric Acid (HCl): Concentrated.

8.5 Stannous Chloride ($SnCl_2$).

8.6 Antimony Chloride ($SbCl_3$).

9.0 Calibration Procedure

The balance calibration is checked before each weighing session with Class S weights. The thermometer must be accurate to within ± 0.1°C as traceable to an NIST thermometer.

10.0 Sample Preparation

Sample preparation is not required.

11.0 Sample Analysis

Note: If the sample has failed the pH test as mentioned in section 1.2, report the sample as having the corrosivity characteristic and stop.

Note: The minimum ratio of volume of waste to area of the metal coupon to be used is 40 mL/cm^2.

11.1 Assemble test apparatus as described by manufacturer's instructions.

11.2 Fill container with appropriate amount of waste as determined by size of flask.

11.3 Weigh two clean steel coupons and record weight (to within ± 0.01 gram). Insert coupons into sample holder as described by manufacturer's directions and close apparatus.

11.4 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

11.5 Turn on heating mantle and adjust so that temperature of waste is kept at an even 55° ± 1°C (130°F). Note the start date and time (to the nearest minute).

11.6 After 24 hours, turn off heating mantle and note completion date and time (to nearest minute) on bench sheet.

11.7 To determine accurately the amount of material lost to corrosion, coupons must be cleaned before they are weighed. Coupons can be cleaned using either (or both) mechanical or chemical cleaning. It may be necessary to combine both methods; for example soaking coupon in hot basic solution, rinsing copiously with water, and scraping off residual corrosion material.

11.7.1 Mechanical Cleaning: Includes scrubbing, scraping, brushing, and ultrasonic procedures. The easiest method for removing corrosion is scrubbing vigorously with a stiff bristle brush and then rinsing carefully. For all mechanical cleaning methods, care should be taken so that no sound metal is removed.

11.7.2 Chemical Cleaning: Consists of dissolving corrosion materials from surface of coupon with an appropriate solvent. Two suitable solutions are:

11.7.2.1 20% NaOH and 200 g/L Zinc Dust: Bring solution to boiling and soak coupon in solution for 5 minutes.

11.7.2.2 Concentrated HCl + 50 g/L $SnCL_2$ + 20 g/L $SbCl_3$: Soak coupons in solution at room temperature until clean, or for 24 hours, whichever occurs first.

11.7.2.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed uses:

Solution:	50 g/L H_2SO_4
Anode:	Carbon or lead
Cathode:	Steel coupon
Cathode current density:	20 amp/cm^2 (129 amp/in^2)
Inhibitor:	2 cc organic inhibitor/L
Temperature:	74°C (165°F)
Exposure period:	3 minutes

Note: Precautions must be taken to ensure good electrical contact with the coupon to avoid contamination of the cleaning solution with easily reducible metal ions and to ensure that inhibitor decomposition has not occurred. Instead of a proprietary inhibitor, 0.5 g/L of either diorthotolyl thiourea or quinoline ethiodide can be used.

11.8 It is possible to remove sound metal during the cleaning process. Therefore, clean a blank coupon with the corroded coupons to monitor the effect of cleaning on the sample result. A clean, preweighed coupon is subjected to the same cleaning process as the corresponding samples. After rinsing and drying, the blank coupon is weighed and its weight loss subtracted from the final result for the corroded coupons.

11.9 Once corroded coupons have been thoroughly cleaned and dried, weigh each one and record weight (± 0.01 gram).

12.0 Calculations

Weight loss is employed as principal measure of corrosion. Use of weight loss as a measure of corrosion assumes that all weight loss has been the result of general corrosion and not local pitting. The corrosion rate (in mm/yr) is calculated using the equation: (1)

$$\text{Corrosion rate (mm/yr)} = \frac{(\text{Coupon wt. loss} - \text{blank wt loss})\ (11.145)}{(\text{area})\ (\text{time})}$$

Where:

Wt. loss	=	mg
Area	=	cm^2
Time	=	hr

(2)

Area is calculated as:

$$\text{Area} = \frac{3.14(D^2 - d^2)}{4} + (t)(3.14)(D)+(t)(3.14)(d)$$

Where:

t	=	thickness (cm)
D	=	diameter of coupon (cm)
d	=	diameter of mounting hole (cm)

Note: These calculations work only for round coupons.

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Levels, and the project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	1/20	80-120%	Qualify data
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0-20% RPD	Qualify data

Where:

LCS laboratory control sample
DR data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
RPD relative percent difference

15.0 References

Test Methods for Evaluating Solid Waste, 3rd ed., SW-846. Methods 9040 and 1110.

FERNALD/corros.51

FM-MISC-0030

Ignitability

Working Linear Range: None
Reporting Limit: None
Reporting Units: °C (or °F)
Matrix: Liquid

1.0 Scope and Application

1.1 The ignitability characteristic is used to identify wastes that either present fire hazards under routine storage, disposal, and transportation or are capable of severely exacerbating a fire once started. A waste is ignitable if a representative sample has any of the following properties:

- It is a liquid, other than an aqueous solution, and has a flash point less than 60°C (140°F) and also contains less than 24% alcohol by volume, as determined by this method.
- It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption of moisture, or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.
- It is an ignitable compressed gas.
- It is an oxidizer.

1.2 Flash point measures the tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively nonvolatile or inflammable material.

1.3 This method is the Pensky-Martens closed-cup test for determining the flash point of liquids. Rather than defining a method detection limit and working range, ignitability is defined as a regulatory limit that, when exceeded, causes the waste to be deemed hazardous. To designate a waste as ignitable it must have a flash point less than 60°C (140°F).

2.0 Method Summary

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

3.0 Interferences

3.1 Because the method is designed to evaluate a physical property rather than determine the concentration of a target analyte, little interferes with the test. Occasionally, particularly near the actual flash point, application of the test flame will cause a blue halo or an enlarged flame that may be confused with a flash.

3.2 Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Sample containers should not be opened unnecessarily. Ideally, sample material should only be transferred from the sample container to the cup at temperatures at least 18°F (or 8°C) below the expected flash point of the sample.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 The analyst must take appropriate safety precautions during the initial application of the test flame, since samples containing low-flash material may give an abnormally strong flash when the test flame is first applied. The procedure should be performed in a fume hood or other vented area. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Pensky-Martens Closed Flash Tester: Available commercially.

6.2 Thermometer: Three standard thermometers will be used with the ASTM Pensky-Martens tester as follows:

6.2.1 Use an ASTM 9F Pensky-Martens Low-range Thermometer for tests in which the indicated reading falls within 50° to 140°F (10° to 60°C). Thermometer range is 20° to 230°F (-5° to 110°C).

6.2.2 Use an ASTM 88F Vegetable Oil Flash Thermometer for tests in which the indicated reading falls within 140° to 284°F (60° to 140°C). Thermometer range is 50° to 392°F (10° to 200°C).

6.2.3 Use an ASTM 10F High-range Thermometer for tests in which the indicated reading falls within 265° to 700°F (130° to 370°C). Thermometer range is 200° to 700°F (90° to 370°C).

6.3 Barometer.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the Pensky-Martens flash point unit according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

8.0 Reagents and Calibration Standards

No reagents are used for this procedure.

9.0 Calibration Procedures

9.1 The thermometer reading should be compared periodically to the certified thermometer as described in Method No. FM-CON-0160. If the working thermometer differs from the certified thermometer, temperature measurement for the flash point can be adjusted appropriately.

9.2 The flash point tester unit is tested each day of use with p-xylene, which yields a flash point of 27.2° ± 1.1°C (81° ± 2°F).

10.0 Sample Preparation

Sample preparation is not required.

11.0 Sample Analysis

Note: Each sample should be analyzed twice——once to find the approximate flash point range and again to measure the flash point more precisely.

11.1 Thoroughly clean and dry all parts of the cup and its accessories before starting the test, being sure to remove any solvent that has been used to the clean the apparatus.

11.2 Fill cup to fill line.

11.3 Replace lid on cup and set it in stove. Be sure that locking device is properly engaged.

11.4 Insert thermometer and bring material to either 60° ± 10°F (15° ± 5°C) or 20°F (11°C) lower than estimated flash point, whichever is lower.

11.5 Light test flame and adjust it to 5/32 inch (4 mm) in diameter. Supply heat at such a rate that temperature as indicated by thermometer increases 9° to 11°F (5° to 6°C) per minute. Adjust stirrer to 90 to 120 rpm, stirring in a downward direction.

Note: Application of test flame is controlled by a shutter between flame and cup. The shutter is manipulated by a turn-knob on top of the cup. Turning the knob opens the shutter so that the flame is lowered into the vapor space of the cup for 0.5 second, left in place for 1 second, and quickly returned to its ready position. The sample should not be stirred when the flame is applied.

11.6 If sample is known to have a flash point of 230°F (110°C) or lower, apply test flame when temperature of sample is about 30°F (17°C) below expected flash point, and thereafter at 2°F increments.

11.7 If sample is known to have a flash point above 230°F (110°C), the test flame is applied in 5°F increments starting about 30°F (17°C) below the expected flash point.

11.8 The observed flash point is the temperature at which test flame application causes a distinct flash in the interior of the cup. Record that temperature.

11.9 Record time and barometric pressure.

12.0 Calculations

12.1 When ambient barometric pressure at the time the flash point differs from 760 mm Hg, flash point must be corrected using the formula:

$$\text{Corrected flash point} = F + 0.06(760 - P)$$

or

$$\text{Corrected flash point} = C + 0.033(760 - P)$$

Where:

F = flash point in °F
C = flash point in °C
P = ambient barometric pressure in mm Hg

12.2 Record corrected flash point to the nearest °F (or °C).

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80—120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Where:

LCS	laboratory control sample
Begin	beginning of the analytical period
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
RPD	relative percent difference

15.0 Reference

15.1 *Test Methods for Evaluating Solid Waste,* 3rd ed., SW-846, Method 1010.

15.2 *Standard Test Method for Flash Point by Penskey——Marten Closed Cap Tester,* ASTM Method D 93-80.

FERNALD/ignit.51

Reactivity

Working Linear Range: None
Reporting Limit: None
Reporting Units: mg/kg
Matrix: Liquid or solid
Holding Time: None

Introduction

A solid waste is considered to be reactive if it exhibits any of the following characteristics:

- It is normally unstable and readily undergoes violent change without detonation.
- It reacts violently with water.
- It forms potentially explosive mixtures with water.
- When mixed with water, it generates toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.
- It is a cyanide- or sulfide-bearing waste that, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment.
- Is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.
- It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.
- It is a forbidden explosive, as defined in 49 CFR 173.51, .53, or .88.
- A solid waste that exhibits the characteristic of reactivity, but is not listed as a hazardous waste in Subpart D, and has the EPA Hazardous Waste Number of D003.

Of the nine characteristics listed above, only one (level of releasable cyanide or sulfide) can be quantified. Currently the EPA regulatory limit that, when exceeded, causes the waste to be deemed hazardous is:

- Total releasable cyanide: 250 mg HCN/kg waste
- Total releasable sulfide: 500 mg H_2S/kg waste

This operating procedure discusses separately the determination of releasable cyanide and sulfide.

1.0 *Determination of* Releasable Hydrogen Cyanide

1.1 Scope and Application

The method is applicable to all wastes, with the condition that the waste is not explosive when combined with acids. The method provides a way to estimate the specific rate of release of hydrogen cyanide upon contact with an aqueous acid. The procedure measures only the hydrogen cyanide evolved under the test conditions, and it is not intended to measure other forms of cyanide. Rather than defining a method detection limit and working range, reactivity is defined as a regulatory limit that, when exceeded, causes the waste to be deemed hazardous. To designate a waste as reactive, it must have a total releasable cyanide concentration greater than 250 mg CN/kg waste.

1.2 Method Summary

An aliquot of the waste is acidified to pH 2 in a closed system. Any gas generated by the waste is swept into a scrubber, and the releasable cyanide is measured titrametrically using method FM-CON-0010 with the following exceptions.

1.3 Interferences

No exceptions to FM-CON-0010.

1.4 Safety Precautions

No exceptions to FM-CON-0010.

1.5 Sample Collection and Handling

No exceptions to FM-CON-0010

1.6 Additional Apparatus

Add: 6.5 Stirring Apparatus.

1.7 Routine Preventive Maintenance

No exceptions to FM-CON-0010.

1.8 Additional Reagents and Calibration Standards

1.8.1 Sulfuric Acid (H_2SO_4), 0.005 M: Add 2.8 mL concentrated H_2SO_4 to 500 mL of water. Dilute to 1 liter. Pipette 100 mL of solution to 1-liter volumetric flask and dilute to 1 liter. This is used instead of reagent 8.2.3 in FM-CON-0010.

1.8.2 Sodium Hydroxide Solution (NaOH), .25 N: Dissolve 10g of NaOH in water and dilute to 1 liter.

1.8.3 Other reagents as in FM-CON-0010.

1.9 Calibration Procedures

No exceptions to FM-CON-0010.

1.10 Sample Preparation

1.10.1 Allow sample to equilibrate to room temperature before beginning procedure.

1.10.2 Add 50 mL of 0.25 N NaOH solution (1.8.2) to absorber tube (i.e., the scrubber). Dilute with water to obtain adequate depth of liquid.

1.10.3 Close system and adjust nitrogen flow rate to 60 mL/min.

1.10.4 Weigh out approximately 10 grams of waste, and record weight.

1.10.5 Open system and add 10 grams of waste to reaction flask.

1.10.6 Begin stirring and slowly add enough 0.005 M H_2SO_4 solution (1.8.1) to fill reaction flask approximately half-full. Close system and record start time (to *nearest second*). Elapsed time may also be monitored using a stop watch.

1.10.7 After 30 minutes, close off nitrogen and disconnect scrubber. Note time that nitrogen was turned off. Determine amount of cyanide.

1.10.8 Drain solution from absorber into 250-mL volumetric flask and bring volume to mark with water.

1.11 Sample Analysis

1.11.1 Transfer solution to 500-mL Erlenmeyer flask. Add 10 to 12 drops of rhodanine indicator.

1.11.2 Titrate with standard silver nitrate to first change in color from yellow to brownish-pink. A 5- to 10-mL microburette may be conveniently used to obtain precise titration.

1.11.3 Repeat titration with a reagent blank.

1.12 Calculations

1.12.1 The concentration of cyanide released is calculated using the formula: (1)

$$\text{CN mg/L} = \frac{(A - B)\ (1{,}000)}{(\text{mL original sample})} \times \frac{250}{\text{mL of aliquot titrated}}$$

Where:

A	=	volume of $AgNO_3$ for titration of sample (mL)
B	=	volume of $AgNO_3$ for titration of blank (mL)
original sample	=	50 mL in absorber tube
aliquot titrated	=	250 mL

1.12.2 To calculate the specific rate of release for hydrogen cyanide: (2)

$$R = \frac{(C)\ (L)}{(W)\ (S)}$$

Where:

R	=	specific rate of release
C	=	concentration of HCN in absorber tube
L	=	volume of solution in absorber tube (L)
W	=	weight of waste used (kg)
S	=	Time N_2 stopped - time N_2 started (s)

1.12.3 To calculate total releasable cyanide:

Total releasable HCN (mg/kg) = 1800 x R (from 1.12.2)

1.13 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific sampling and analysis plan and are discussed in the General Laboratory Requirements.

1.14 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80—120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Where:

LCS	laboratory control sample
Begin	beginning of the analytical period
DR	data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
RPD	relative percent difference

1.15 Reference

Test Methods for Evaluating Solid Waste. SW-846, 3rd ed., Chapter 7.3.3.2 and Method 9010A. November 1990.

2.0 Determination of Releasable Hydrogen Sulfide

2.1 Scope and Application

The method is applicable to all wastes, with the condition that the waste is not explosive when combined with acids. The method provides a way to estimate the specific rate of release of hydrogen sulfide upon contact with an aqueous acid. The procedure measures only the hydrogen sulfide evolved under the test conditions, and it is not intended to measure other forms of sulfide. Rather than defining a method detection limit and working range, reactivity is defined as a regulatory limit that, when exceeded, causes the waste to be deemed hazardous. To designate a waste as reactive, it must have a total releasable sulfide concentration greater than 500 mg H_2S/kg waste.

2.2 Method Summary

An aliquot of waste is acidified to pH 2 in a closed system. Any gas generated by the waste is swept into a scrubber, and the releasable sulfide is quantified titrimetrically as in method FM-CON-0130.

2.3 Interferences

No exceptions to FM-CON-0130.

2.4 Safety Precautions

No exceptions to FM-CON-0130.

2.5 Sample Collection and Handling

No exceptions to FM-CON-0130.

2.6 Apparatus

Use apparatus as in section 1.6, except do not use the sulfide scrubber apparatus as in FM-CON-0010.

2.7 Routine Preventive Maintenance

No exceptions to FM-CON-0130.

2.8 Reagents and Calibration Standards

2.8.1 Water: All references to water assume the use of ASTM Type II water.

2.8.2 Sulfuric Acid (H_2SO_4), 0.005 M: Add 2.8 mL concentrated H_2SO_4 to approximately 500 mL of water. Dilute to 1 liter. Pipette 100 mL of solution to 1-liter volumetric flash and dilute to 1 liter. **Caution:** Heat liberating reaction.

2.8.3 Hydrochloric Acid (HCl), 6 N: Dilute 492 mL of concentrated HCl to 1 liter with water. **Caution:** Heat-liberating reaction.

2.8.4 Sulfide Reference Solution, 1 mg S/L: Dissolve 4.02 grams of $Na_2S \cdot 9H_2O$ in 500 mL of water. Dilute to 1 liter. Stock solution can be diluted to prepare standard solutions within working analytical range (100 to 680 ppm). **Note:** Sulfide standard solutions are very unstable and must be prepared just before use.

2.8.5 Sodium Hydroxide Solution (NaOH), 1.25 N: Dissolve 50 grams of NaOH in 500 mL of water. Dilute to 1 liter.

2.8.6 NaOH Solution, 0.25 N: Pipette 200 mL of the 1.25 N solution into a 1-liter volumetric flask. Dilute to 1 liter.

2.8.7 Other reagents as in FM-CON-0130.

2.9 Calibration Procedures

There is no instrument to calibrate for this procedure. Operation of the system can, however, be checked using sulfide reference solution. The iodine solution must be standardized before the samples can be analyzed.

2.10 Sample Preparation

Allow sample to equilibrate to room temperature before beginning procedure.

2.11 Sample Analysis

2.11.1 Add 50 mL of 0.25 N NaOH solution to absorber tube (i.e., the scrubber). Dilute with water to obtain an adequate depth of liquid.

2.11.2 Close system and adjust nitrogen flow rate to 60 mL/min.

2.11.3 Weigh 10 grams of waste and record weight.

2.11.4 Open system and add 10 grams of waste to reaction flask.

2.11.5 Begin stirring and slowly add enough 0.005 M H_2SO_4 solution to fill reaction flask approximately half full. Close system and record start time to nearest second. Elapsed time may also be monitored using a stop watch.

2.11.6 After 30 minutes, close off nitrogen and disconnect scrubber. Record time that nitrogen was turned off.

2.11.7 Drain solution from absorber tube into 200-mL volumetric flask and bring volume to mark with water.

2.11.7.1 Add enough standard iodine solution estimated to be over amount of sulfide present to 500-mL Erlenmeyer flask. Record starting volume of standard iodine solution on bench sheet.

2.11.7.2 Add 2 mL of 6 N HCl to Erlenmeyer flask.

2.11.7.3 Pipette 200 mL of sample to Erlenmeyer flask with tip of pipette beneath surface of iodine solution. If iodine color disappears, add more iodine so that color remains. Record final volume of iodine.

2.11.7.4 Back titrate with PAO, adding a few drops of starch solution as end point is approached, and continue until blue color disappears. Record start and completion volumes for PAO.

2.12 Calculations

2.12.1 1 mL of 0.025 N iodine solution reacts with 0.4 mg of sulfide. Therefore, the concentration of sulfide can be calculated as: (4)

$$\text{mg sulfide/L} = \frac{[(A \times B) - (C \times D)] \times 16{,}000}{\text{mL sample}}$$

Where:

A	=	standard iodine solution (mL)
B	=	normality of iodine solution
C	=	PAO solution (mL)
D	=	normality of PAO solution (0.025 N)

2.12.2 To calculate the specific rate of release for hydrogen sulfide: (5)

$$R = \frac{(A)\ (L)}{(W)\ (S)}$$

Where:

R	=	specific rate of release
A	=	concentration of H_2S in absorber tube (mg/L)
L	=	volume of solution in absorber tube (L)
W	=	weight of waste used (kg)
S	=	Time N_2 stopped - time N_2 started (s)

2.12.3 To calculate total releasable sulfide:

Total releasable Sulfide (mg/kg) = 1800 x R (from 2.12.2)

2.13 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Level, and project-specific Sampling and Analysis Plan and are discussed in the General Laboratory Requirements.

2.14 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Level, and project-specific Sampling and Analysis Plan.

Requirement	Frequency	Acceptance Range	Corrective Action
LCS	Begin	80—120%	Recalibrate
Method Blank	1/20	DR	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data

Where:

LCS laboratory control sample
Begin beginning of the analytical period
DR data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ
RPD relative percent difference

2.15 References

Test Methods for Evaluating Solid Waste, 3rd ed., SW-846. Chapter 7.3.4.2 and Method 9030.

FERNALD/react.51

FM-INO-0010

Metals by Graphite Furnace Atomic Absorption

Working Linear Range:	Metal-dependent; see specific metal
Reporting Limits:	Metal-dependent; see specific metal
Reporting Units:	μg/L for water; mg/kg for solids
Matrix:	Water, soil, sediment, and waste

1.0 Scope and Application

1.1 Metals in solution may be readily determined by several techniques, including atomic absorption spectroscopy. The graphite furnace technique often offers the advantage of lower detection limits than the conventional flame and the inductively coupled plasma techniques. Another advantage of the technique is that it requires only a small volume for analysis. It is, however, subject to more interferences than the flame technique and requires longer analysis time.

1.2 The graphite furnace technique is applicable to the analysis of metals in aqueous and nonaqueous samples following digestion. It is recommended for determinations that require detection limits that cannot be achieved by other methods. Estimated detection limits are listed in Table 1. Detection limits are dependent on the spectrometer and the sample matrix.

2.0 Method Summary

The sample is subjected to an acid digestion procedure to ensure that the metals are in solution (the digestion procedure may be done using microwave energy). The digestate is then analyzed by graphite furnace atomic absorption spectroscopy and the concentration determined using a calibration curve. Most metals may require the addition of matrix modifiers to sample during the sample injection process.

3.0 Interferences

3.1 The graphite furnace technique is vulnerable to various interferences. When using the technique, each sample matrix will be examined for interference effects. If detected, matrix effects will be treated accordingly to ensure valid data.

Table 1
Recommended Wavelengths and Estimated Detection Limits for Graphite Furnace Analysis

Element	Wavelength (nm)	Estimated Detection Limit—Waters (μg/L IDL)	Required Reporting Limit—Waters (μg/L CRDL)	Required Reporting Limit—Soils (mg/kg)
Antimony	217.6	3	60	12
Arsenic	193.7	1	10	2
Beryllium	234.9	0.2	5	1
Cadmium	228.8	0.1	5	1
Chromium	357.9	1	10	2
Cobalt	240.7	1	50	50
Lead	283.3	1	3	0.6
Selenium	196.0	2	5	1
Silver	328.1	0.2	10	2
Thallium	276.8	1	10	2
Vanadium	318.4	4	50	50

3.2 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects that will be determined and taken into consideration in the analysis of each different matrix encountered. To verify the absence of matrix or chemical interference, post-spiked samples are analyzed. Samples that indicate the presence of interference will be treated in the following ways.

3.2.1 Successively dilute and reanalyze samples to eliminate interferences.

3.2.2 Modify sample matrix either to remove interferences or to stabilize the analyte. Manufacturers list recommended matrix modifiers for each element.

3.2.3 Analyze sample by method of standard additions, keeping in mind the precautions and limitations of its use.

3.3 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. Background correction will be used at all times and should assist in overcoming many interferents. Alternative wavelengths may also be used. Background correction may compensate for nonspecific broad-band absorption interference.

3.4 Continuum background correction cannot correct for many types of background interference. When background interference cannot be compensated for, chemically remove the analyte or use an alternative.

3.5 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or using an ashing cycle in the presence of air. Care must be taken to prevent loss of the analyte.

3.6 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption should be minimized.

3.7 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to nitric is required, a minimum amount should be used. This applies particularly to hydrochloric acid (exception: antimony) and, to a lesser extent, sulfuric and phosphoric acids (which are often used as matrix modifiers.)

3.8 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will be erroneously high because of the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp or from a metal

impurity in the lamp cathode falls within the bandpass of the slit setting when the other metal is present in the sample. This type of interference may be reduced by narrowing the slit width.

3.9 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. Therefore, special attention will be given to reagent blanks in both analysis and in correction of analytical results.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 250-mL Beaker or other appropriate vessel.

6.2 Watch Glasses.

6.3 Thermometer covering range of 0° to 200°C.

6.4 Whatman No. 42 Filter Paper, or equivalent.

6.5 Microwave oven with programmable power settings up to at least 600 watts. Commercial kitchen or home-use microwave ovens will not be used for sample digestion. Oven cavity will be corrosion resistant and well ventilated. All electronics will be protected against corrosion for safe operation.

6.6 PFA Teflon Digestion Vessels: 120-mL capacity capable of withstanding pressures up to 110 ± 10 psi (7.5 ± 0.7 atm). Vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

6.7 Turntable: To ensure homogeneous distribution of microwave radiation within the oven. Turntable speed will be at least 3 rpm.

6.8 Polymeric Volumetric Ware: In plastic (Teflon or polyethylene) 50- or 100-mL capacity.

6.9 Whatman No. 41 Filter Paper, or equivalent.

6.10 Disposable polypropylene Filter Funnel.

6.11 Analytical Balance: 300-gram capacity, and minimum ± 0.01 gram.

6.12 Polyethylene Bottles: 125-mL, with caps.

6.13 Atomic Absorption Spectrophotometer: Single or dual-channel, single- or double-beam instrument having grating monochromator, 800 nm, and provisions for interfacing with a graphical display or data handling system, with background correction capability.

6.14 Appropriate Data Handling System.

6.15 Hollow Cathode Lamps: Single-element lamps are preferred, but multielement lamps may be used. Electrodeless discharge lamps may be used when available.

6.16 Graphite Furnace: Any furnace device capable of reaching the specified temperatures is satisfactory.

6.17 Graphical Display and Recorder: A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, and peak shape can be easily recognized.

6.18 Pipets: Microliter, with disposable tips. Sizes can range from 5 to 100 μL as required. Pipet tips will be checked as a possible source of contamination before use.

6.19 Pressure-reducing Valves: Fuel and oxidant supplies will be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

6.20 Glassware: All glassware, polypropylene, or Teflon containers, including sample bottles, will be washed in the following sequence: Detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and Type II water. Chromic acid must not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme. If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

6.21 Hot plate or steam bath capable of maintaining temperature at 100°C.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the graphite furnace atomic absorption spectrophotometer according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Digestion

8.1.1 Water: All references to water assume the use of ASTM Type II water.

8.1.2 Concentrated Nitric Acid (HNO_3), sp. gr. 1.41: Spectrograde or equivalent.

8.1.3 Concentrated Hydrochloric Acid (HCl), sp. gr. 1.19: Spectrograde or equivalent.

8.1.4 Hydrogen Peroxide (H_2O_2), 30%.

8.1.5 Hydrochloric Acid 1:1: Add 500 mL concentrated HCl (sp. gr. 1.19) to 400 mL water and dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.1.6 Nitric Acid, 1:1: Add 500 mL concentrated HNO_3 (sp. gr. 1.41) to 400 mL water and dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.1.6.1 Acids used in the preparation of standards and for sample processing must be spectrograde or equivalent. Redistilled acids are acceptable.

8.2 Analysis

8.2.1 Water: All references to water assume the use of ASTM Type II water.

8.2.2 Concentrated Nitric Acid (HNO_3): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by slowly adding concentrated acid to equal volume of water. **Caution:** Heat-liberating reaction.

8.2.3 Hydrochloric Acid (HCl, 1:1): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by slowly adding concentrated acid to equal volume of water. **Caution:** Heat-liberating reaction.

8.2.4 Gas: Standard, commercially available argon, welding grade or better.

8.2.5 Gas: Standard, commercially available nitrogen, welding grade or better.

8.2.6 Stock Standard Metal Solutions

8.2.6.1 Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic reagent-grade salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. Stock solutions are prepared at concentrations of 1,000 mg of metal per liter. Commercially available standard solutions may also be used.

8.2.7 Calibration Standards: Refer to individual metal procedures for specific standard preparation. Calibration standards are prepared by diluting stock

standards at time of analysis. Calibration standards will be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing.

9.0 Calibration Procedures

9.1 Calibration standards are prepared by diluting stock standards at the time of analysis. They are prepared fresh each time an analysis is performed and discarded after each use. If a matrix modifier is added to the samples, it will also be added to the standards.

9.2 Prepare an instrument blank and at least three calibration standards in graduated amounts in the range expected for the samples to be analyzed. One standard will be at the required reporting limit.

9.3 Instrument calibration will be performed at least once every 24 hours and each time the instrument is set up.

9.4 Beginning with the blank and working toward the highest standard, make at least two analyses of the blank and each standard.

9.5 Construct a standard curve by plotting the average peak absorbances or peak areas of standards versus their concentrations. Alternatively use electronic calibration if available.

10.0 Sample Preparation

10.1 Acid Digestion for Metals Other Than Antimony in Water Samples: Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 1 mL of 1:1 HNO_3 and 2 mL 30% of H_2O_2 to sample. Cover with watch glass or similar cover, and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 15 and 20 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material.

Note: In place of filtering, the sample may, after dilution and mixing, be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.1.1 Adjust sample volume to 100 mL with water. The sample is ready for analysis.

10.2 Acid Digestion for Antimony in Water Samples: Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 2 mL of 1:1 HNO_3 and 10 mL of 1:1 HCl to sample. Cover with watch glass or similar cover, and heat on steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material.

Note: In place of filtering, the sample may, after dilution and mixing, be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.2.1 Adjust sample volume to 100 mL with water. The sample is ready for analysis.

10.3 Acid Digestion of Soil Samples

10.3.1 Mix sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to nearest 0.01 gram) a 1.0- to 1.5-gram portion of sample and transfer to beaker.

10.3.2 Add 10 mL of 1:1 nitric acid (HNO_3), mix slurry, and cover with watch glass. Heat sample to 95°C and reflux for 10 minutes without boiling. Allow sample to cool, add 5 mL of concentrated HNO_3, replace watch glass, and reflux for 30 minutes. Do not allow volume to be reduced to less than 5 mL while maintaining a covering of solution over bottom of beaker.

10.3.3 After second reflux step has been completed and sample has cooled, add 2 mL of water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return beaker to hot plate for warming to start the peroxide reaction. Take care to ensure that losses do not occur because of excessively vigorous effervescence. Heat until effervescence subsides and cool beaker.

10.3.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until effervescence is minimal or until general sample appearance is unchanged.

Note: Do not add more than a total of 10 mL 30% H_2O_2.

10.3.5 If sample is being prepared for furnace AA analysis of Sb, add 5 mL of 1:1 HCl and 10 mL of water, return covered beaker to hot plate, and heat for 10

more minutes. After cooling, filter through Whatman No. 42 filter paper, and dilute to 100 mL with water.

Note: In place of filtering, the sample may, after dilution and mixing, be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.3.5.1 The diluted sample has an approximate acid concentration of 2.5% v/v HCl and 5% v/v HNO_3. Dilute digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is ready for analysis.

10.3.6 If the sample is being prepared for furnace analysis of As, Be, Cd, Cr, Co, Pb, Se, Ag, and Tl, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 mL, add 10 mL of water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper and dilute sample to 100 mL with Type II water.

Note: In place of filtering, the sample may, after dilution and mixing, be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.3.6.1 The diluted digestate solution contains about 2% v/v HNO_3. Dilute digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength.

10.4 Percent Solids Determination for Soil Samples: If results for soil samples are to be reported on a dry weight basis, perform percent solids determination as follows:

10.4.1 Immediately after weighing the sample to be processed for analysis, add 5 to 10 grams of sample to tared weighing dish. Weigh and record weight to nearest 0.01 gram.

10.4.2 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying over maintained at 103° to 105°C. Sample handling and drying will be conducted in a well-ventilated area.

10.4.3 Dry sample overnight (12 to 24 hours) but no longer than 24 hours. If dried less than 12 hours, document that constant weight was attained. Remove sample from oven and cool in desiccator with weighing dish cover in place

before weighing. Weigh and record weight to nearest 0.01 gram. Do not analyze dried sample.

10.4.4 Calculate percent solids as:

$$\% \text{ Solids} = \frac{\text{Sample dry weight}}{\text{Sample wet weight}} \times 100 \qquad (1)$$

This value shall be used for calculating analytical concentration on a dry weight basis.

10.4.5 Concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S} \qquad (2)$$

Where:

C = Concentration (mg/L)
V = Final volume after sample preparation (L)
W = Weight of wet sample (kg)
S = % Solids/100

10.5 Microwave Sample Preparation

10.5.1 Microwave Calibration Procedure: Calibration is a critical step before the use of any microwave unit. The microwave unit should be calibrated every 6 months. Calibration data for each calibration will be available for review during onsite audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power will be determined.

10.5.1.1 Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between output power and the scale used in controlling the microwave unit, the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple point calibration, then the point where linearity begins will be identified. For example: Calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% power settings can be applied and the

data plotted. The nonlinear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to 5.5 to 6 watts and becomes the smallest unit of power that can be controlled. If 20 to 40 watts are contained from 99 to 100%, that portion of the microwave calibration is not controllable by 3 to 7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

10.5.1.2 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The water is placed in a Teflon beaker (or a beaker made of material that does not absorb microwave energy) and stirred before measuring the temperature. Glass beakers absorb microwave energy and may not be used. The initial water temperature shall be between 19° and 25°C. The beaker is circulated continuously through the field for at least 2 minutes at full power. The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements shall be accurate to ± 0.1°C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

10.5.1.3 The absorbed power is determined as:

$$P = \frac{(K)\,(Cp)\,(m)\,(DT)}{t} \qquad (3)$$

Where:

P = Apparent power absorbed by sample in watts (joules per second)

K = Conversion factor for thermochemical calories per second to watts (= 4.184)

Cp = Heat capacity, thermal capacity, or specific heat (cal. $g^{-1} \cdot {}^{\circ}C^{-1}$) of water (=1.0)

m = Mass of sample (grams)

DT = Final temperature minus initial temperature (°C)

t = Time (seconds)

Using 2 minutes and 1 kg of distilled water, the equation simplifies to:

$$P = (DT)(34.87) \quad (4)$$

The microwave user can now relate power in watts to the percent power setting of the microwave.

10.5.2 Cleaning Procedure

10.5.2.1 Initial Cleaning of PFA Vessels

10.5.2.1.1 New vessels shall be annealed before first use. A pretreatment/cleaning procedure shall be followed. Heat vessels for 96 hours at 200°C. The vessels shall be disassembled during annealing, and sealing surfaces (the top of the vessel or its rim) shall not be used to support the vessel during annealing.

10.5.2.1.2 Rinse in water.

10.5.2.1.3 Immerse in 1:1 HCl for at least 3 hours after cleaning bath has reached a temperature just below boiling.

10.5.2.1.4 Rinse in water.

10.5.2.1.5 Immerse in 1:1 HNO_3 for at least 3 hours after cleaning bath has reached a temperature just below boiling.

10.5.2.1.6 Vessels are then rinsed with copious amounts of water before use for any analyses.

10.5.2.2 Cleaning Procedure between Sample Digestions

10.5.2.2.1 Wash entire vessel in hot water using laboratory-grade nonphosphate detergent.

10.5.2.2.2 Rinse with 1:1 nitric acid (HNO_3).

10.5.2.2.3 Rinse three times with water. If contaminants are found in preparation blank, steps for initial cleaning must be reported and strictly adhered to.

10.5.3 Microwave Digestion Procedure

Note: The microwave digestion procedure is not appropriate for samples to be analyzed for Antimony.

10.5.3.1 Water Sample Microwave Digestion Procedure

10.5.3.1.1 Measure a 45-mL aliquot of sample into a Teflon digestion vessel using volumetric glassware.

10.5.3.1.2 Add 5 mL of high purity concentrated HNO_3 to digestion vessels.

10.5.3.1.3 Record weight of each vessel to 0.01 gram.

10.5.3.1.4 Place caps with pressure release valves on vessels hand tight, and then tighten using constant torque to 12 ft/lb. Place five sample vessels evenly spaced around the periphery of the carousel in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of overpressurization. Vessels may be assembled into the carousel inside or outside the microwave.

10.5.3.1.5 This procedure is energy balanced for five 45-mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than five samples are digested, the remaining vessels shall be filled with 45 mL of tap, or Type II water, and 5 mL of concentrated nitric acid. Newer microwave ovens may be capable of higher power settings that may allow a larger number of samples. If the analyst wishes to digest more than five samples at a time, the analyst may use different power settings as long as they result in the same time-temperature conditions defined in the power programming for the method.

10.5.3.1.6 The initial temperature of the samples will be 24° ± 1°C. The preparation blank will have 45 mL of water and the same amount (5 mL) of acid added to the samples.

10.5.3.1.7 The microwave unit first-stage program will be set to give 545 watts for 10 minutes, and the second-stage program to give 344 watts for 10 minutes.

This sequence brings the samples to 160° ± 4°C in 10 minutes and permits a slow rise to 165° to 170°C during the second 10 minutes.

10.5.3.1.8 Following the 20-minute program, leave samples to cool in microwave unit for 5 minutes with exhaust fan ON. Samples or carousel may then be removed from microwave unit. Before opening vessels, let cool until they are no longer hot to the touch.

10.5.3.1.9 After the sample vessel has cooled, weigh vessel and compare to initial weight as reported in the preparation log. Any sample vessel exhibiting a ≤ 0.5-gram loss shall have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with sample preparation. Any sample vessel exhibiting a > 0.5-gram loss shall be identified in the preparation log and the sample redigested.

10.5.3.2 Sample Filtration: Digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. The digestates are then filtered into 50-mL glass volumetric flasks through ultraclean filter paper and diluted to 50 mL (if necessary). The samples are ready for analysis. Sample results shall be corrected by a factor of 1.11 to report final concentration values based on an initial volume of 45 mL.

10.5.3.3 Soil Sample Microwave Digestion Procedure

10.5.3.3.1 Add a representative 0.5 ± 0.050 gram of sample to the Teflon PFA tubing.

10.5.3.3.2 Add 10 ± 0.1 mL of concentrated nitric acid. If vigorous reaction occurs, allow reaction to stop before capping vessel.

10.5.3.3.3 Cap vessel, then tighten using constant torque to 12 ft/lb according to manufacturer's direction.

10.5.3.3.4 Connect sample vessel to overflow vessel using Teflon PFA tubing.

10.5.3.3.5 Weigh the vessel assembly to the nearest 0.01 gram.

10.5.3.3.6 Place sample vessels in microwave unit in groups of two or six vessels in carousel, evenly spaced around its periphery. If fewer samples are to be digested (e.g., three samples plus one blank), then remaining vessels shall be filled with 10 mL of water to achieve to full complement of vessels.

10.5.3.3.7 Attach each sample vessel to a clean, double-ported vessel to collect any sample expelled from vessel in the event of overpressurization. Vessels may be assembled into carousel inside or outside the microwave. Connect overflow vessel to center well of oven.

10.5.3.3.8 The preparation blank shall have 0.5 mL of water and the same amount (10 mL) of acid that is added to the samples. The preparation blank shall later be diluted to 50 mL in the same manner as the samples.

10.5.3.3.9 Irradiate the two-sample vessel group at 344 watts for 10 minutes, or the six-vessel group at 574 watts for 10 minutes.

10.5.3.3.10 This program brings the sample to 175°C in 5.5 minutes and remains between 170° and 180°C for the balance of the 10-minute irradiation period. The pressure shall peak at less than 6 atmospheres for most samples. Pressure may exceed these limits in the case of high concentrations of carbonate or organic compounds. In those cases, pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atmospheres.

10.5.3.3.11 Allow vessels to cool for at least 5 minutes with exhaust fan ON before removing them from microwave unit. Allow vessels to cool to room temperature before opening. Vessels shall be carefully uncapped and vented in a fume hood.

10.5.3.3.12 Weigh each vessel assembly. If weight of acid plus sample has decreased by more than 10% from original weight, discard digests and determine reason for loss. Losses typically are attributed to use of digestion time longer than 10 minutes, using too large of a sample, or having improper heating conditions. Once source of losses has been corrected, prepare new set of samples for digestion.

10.5.3.4 Sample Filtration: Shake sample well to mix in any condensate within digestion vessel before being opened. Filter digestion vessel into a 50-mL glass volumetric flask through ultraclean filter paper. Rinse sample digestion vessel, cap, connecting tube, and (if venting occurred) overflow vessel into the 50-mL glass flask. Dilute to 50 mL. Samples are ready for analysis.

10.5.3.5 Calculations: The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample:

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{}$$

$$W \times S \qquad (5)$$

Where:

C	=	Concentration (mg/L)
V	=	Final volume after sample preparation (L)
W	=	Weight of wet sample (kg)
S	=	% Solids/100

11.0 Sample Analysis

11.1 Operating Conditions

11.1.1 Because of differences between various makes and models of instruments, no detailed operating instructions can be given for each instrument. The manufacturers' instructions should be followed in developing a program (time and temperature) that should yield optimum response for each metal. In developing each program, inclusion of as many different matrices as possible will be considered. Program development will also address using the specific matrix modifier intended for each method.

11.1.2 Operating conditions are listed in each metal method included, but they should be used as guidelines only. A char and atomization study must always be conducted. Attention shall be paid to the characteristic mass of the element.

11.2 Sample Analysis: Samples may be determined directly if they are demonstrated to be free of matrix interferences. When matrix interferences prevent accurate direct determination, the MSA may be used. The need for MSA is determined by the results of analytical spike analysis discussed in the section on Quality Control. Samples shall be analyzed by direct determination first, and MSA performed only if indicated by analytical spike results.

11.2.1 Direct Determination

11.2.1.1 Make at least two replicate injections of the sample (digested and treated with required matrix modifier). Use the same volume as that used for the standards.

11.2.1.2 Determine concentration of metal of interest by comparing average absorbance or peak area of sample with standard curve. Alternatively, read results directly if instrument is equipped with this capability.

11.2.1.3 Sample responses must fall within calibration range. Sample dilution will be made, if necessary, to bring response within calibration range.

11.2.1.4 If resulting sample concentrations are greater than required reporting limit, replicate injection results must agree within 20% RSD (relative standard deviation) or CV (coefficient of variation). If this criterion is not met, the sample will be rerun (i.e., two additional burns). If readings are still out, flag the results with an "M."

11.2.2 Method of Standard Addition

11.2.2.1 Only single injections are required for MSA analyses.

11.2.2.2 The sample and three spikes will be analyzed consecutively for MSA quantitation.

Note: Do not include matrix spike sample, intended as a quality control sample, as one of the three spikes for MSA analysis.

11.2.2.3 Each full MSA counts as two analytical samples towards determining 10% QC frequency (i.e., five full MSAs can be performed between calibration verifications).

11.2.2.4 For analytical runs containing only MSAs, single injections can be used for QC samples during that run. For instruments that operate in an MSA mode only, MSA can be used to determine QC samples during that run.

11.2.2.5 Spikes will be prepared such that:

11.2.2.5.1 Spike 1 is 50% of the sample concentration.

11.2.2.5.2 Spike 2 is 100% of the sample concentration.

11.2.2.5.3 Spike 3 is 150% of the sample concentration.

11.2.2.6 The data for each MSA analysis will be clearly identified in the raw data documentation (using added concentration as the z-variable and absorbance as the y-variable) along with the slope, x-intercept, y-intercept and correlation

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coefficient (r) for the least squares fit of the data. The results will be reported on the designated form. Reported values obtained by MSA will be flagged on the analysis report sheet with the letter "S" if the correlation coefficient is ≥ 0.995.

11.2.2.7 If the correlation coefficient (r^2) for a particular analysis is < 0.995, the MSA analysis must be repeated once. If the correlation coefficient is still < 0.995, report the results from the run with the letter "R" and flag the result with a "+" on the analysis report sheet and on the MSA report sheet.

11.2.2.8 Data from MSA calculations will be within the linear range as determined by the calibration curve generated at the beginning of the analytical run.

11.3 Analytical Sequence

11.3.1 At least two replicate injections are required for each determination. Different injection volumes may not be used for samples and standards.

11.3.2 The following sequence will be followed:

11.3.2.1 Initial Calibration Verification (ICV) Standard.

11.3.2.2 Initial Calibration Blank (ICB).

11.3.2.3 Detection Limit (CRA) Standard.

11.3.2.4 First four samples. An analytical spike sample will be analyzed immediately after each sample.

11.3.2.5 Continuing Calibration Verification (CCV) Standard.

11.3.2.6 Continuing Calibration Blank (CCB).

11.3.2.7 Next five samples. An analytical spike will be analyzed immediately after each sample.

11.3.2.8 Continuing Calibration Verification (CCV) Standard and Continuing Calibration Blank (CCB) bracketing every 10 or 20 samples.

11.3.2.9 Last five samples. An analytical spike will be analyzed immediately after each sample.

11.3.2.10 Continuing Calibration Verification (CCV) Standard.

11.3.2.11 Continuing Calibration Blank (CCB).

11.3.3 The ICV Standard will be analyzed immediately after instrument calibration.

11.3.4 The ICB will follow the ICV Standard.

11.3.5 The CRA standard will be analyzed at the beginning of each analytical run.

11.3.6 The CCV Standard will be analyzed every 10 samples or every 2 hours during an analysis, whichever is more frequent. It will also be analyzed after the last sample.

11.3.7 The CCB will be analyzed after each CCV Standard.

11.3.8 Each field sample to be analyzed will require an analytical spike to determine if the MSA will be required for quantitation. An analytical spike is a post-digestion spike to be prepared before analysis by adding a known quantity of analyte to an aliquot of the digested sample. The unspiked sample aliquot will be compensated for any volume change in the analytical spike sample by addition of water to the unspiked sample aliquot. The volume of the spiking solution added will not exceed 10% of the analytical spike sample volume. The amount of analytical spike to be added will be such that its resulting concentration in the sample will be 2 times the required reporting limit (for lead the resulting concentration will be 20 μg/L).

11.3.9 The analytical spike requirement also applies to the preparation blank, the duplicate, and the laboratory control sample (LCS).

11.3.10 The term "sample" (when not qualified) as used in this procedure includes not only field samples but also the CRA and the QCS (Preparation Blank, Matrix Spike, Duplicate, Laboratory Control Sample, and the analytical spike). The quality control samples may be analyzed at any time during the analytical run.

11.4 Spiked Sample Analysis: The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion (i.e., before addition of other reagents). At least one spiked sample analysis must be performed per 20 samples or per analytical batch of a similar matrix type, whichever is more frequent.

11.4.1 If the spiked sample analysis is performed on the same sample chosen for the duplicate sample analysis, spiked sample calculations will be performed using the results of the sample designated as the "original sample." The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. Specific samples may be designated to be used for the spiked sample analysis.

11.4.2 The analyte spike shall be added in the amount given in the following table for each element analyzed:

Element	Water (μg/L)	Soil* (mg/kg)
Antimony	100	20
Arsenic	40	8
Cadmium	5	1
Lead	20	4
Selenium	10	2
Thallium	50	10

* The levels shown indicate concentrations in the final digestate of the spiked sample when the wet weight of 1 gram of sample is taken for analysis. Adjustment will be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. Appropriate adjustment will be made for microwave digestion procedure where 0.5 gram of sample or 50.0 mL (45 mL of sample plus 5.0 mL of acid) of aqueous sample are required for analysis.

11.4.3 If spike recovery is not at or within the limits of 75 to 125%, the data of all samples received associated with that spike sample and determined by the same analytical method will be flagged with the letter "N." An exception is granted in situations where sample concentration exceeds spike concentration by a factor of four or more. In such an event, the data will be reported unflagged even if the percent recovery does not meet the 75 to 125% recovery criteria.

11.4.4 When predigestion spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion spike will be performed for elements that do not meet the specified criteria. Spike the unspiked aliquot of the sample at two times, the indigenous level or two times the required reporting limit, whichever is greater.

11.4.5 In the instance where there is more than one spike sample per matrix, if one spike sample recovery is not within acceptance criteria, flag all samples of the same matrix. Individual component percent recoveries (%R) are calculated as:

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} \times 100 \qquad (6)$$

Where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added

11.5 Duplicate Sample Analysis. At least one duplicate sample will be analyzed every 20 samples or per analytical batch of a similar matrix type, whichever is more frequent. Duplicates cannot be averaged for reporting purposes.

11.5.1 Samples identified as field blanks cannot be used for duplicate sample analysis. Specific samples may be designated to be used for duplicate sample analysis.

11.5.2 The relative percent difference (RPD) for each component are calculated as:

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100 \qquad (7)$$

Where:

RPD = Relative percent difference
S = First sample value (original)
D = Second sample value (duplicate)

11.5.3 A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to five times the required reporting limit. A control limit of ± the required reporting limit will be used for sample values less than five times the required reporting limit, and the absolute value of the control limit will be entered in the "Control Limit" column on the duplicate analysis report.

11.5.4 If one result is above the fives times required reporting level and the other is below, use the ± required reporting limit criteria. If both sample values are less than the IDL, the RPD is not calculated on the report form. For solid sample or duplicate results less than five times the required reporting limit, enter the absolute value of the required reporting limit, corrected for sample weight and percent solids, as the control limit.

11.5.5 If duplicate sample results are outside control limits, flag all data for samples received associated with that duplicate sample with an asterisk (*). In the instance where there is more than one duplicate sample per batch, if one duplicate result is not within contract criteria, flag all samples of the same matrix.

11.6 Analytical Spike Sample Analysis

11.6.1 All furnace analyses for each field sample, including those requiring an "M" flag, will require at least an analytical spike to determine if the MSA will be required for quantitation. The analytical spike shall be required to be at a concentration (in the sample) two times the required reporting limit (except for lead, which will be at 20 μg/L). This requirement for an analytical spike will include the LCS and the preparation blank. The LCS will be quantitated from the calibration curve and corrective action, if needed, taken accordingly. MSA is not to be performed on the LCS or preparation blank, regardless of spike recovery results. If the preparation blank analytical spike recovery is out of control (85 to 115%), the spiking solution will be verified by respiking and rerunning the preparation blank once. If the preparation blank analytical spike recovery is still out of control, correct the problem and reanalyze all analytical samples associated with that blank. An analytical spike is not required on the predigestion spike sample.

11.6.2 The analytical spike of a sample will be run immediately after that sample. The percent recovery (%R) of the spike, calculated by the same formula as Spike Sample Analyses, will then determine how the sample shall be quantitated, as follows:

11.6.2.1 If spike recovery is less than 40%, the sample will be diluted and rerun with another spike. Dilute the sample by a factor of 5 to 10 and rerun. This step should only be performed once. If after the dilution the spike recovery is still < 40%, report data and flag with an "E" to indicate an interference problem.

11.6.2.2 If spike recovery is ≥ 40% and sample absorbance or concentration is < 50% of the "spike," report the sample results to the IDL. If the spike recovery is < 85% or > 115%, flag the result with a "W."

11.6.2.3 If sample absorbance or concentration is ≥ 50% of the spike and the spike recovery is at or between 85% and 115%, the sample will be quantitated directly from the calibration curve and reported down to the IDL.

11.6.2.4 If the sample absorbance or concentration is ≥ 50% of the spike and the spike recovery is < 85% or > 115%, the sample will be quantitated by MSA.

11.6.3 Analytical Spikes are post-digestion spikes to be prepared before analysis by adding a known quantity of analyte to an aliquot of the digested sample. The unspiked sample aliquot will be compensated for any volume change in the spike samples by addition of water to the unspiked sample aliquot. The volume of spiking solution added will not exceed 10% of the analytical sample volume; this requirement also applies to MSA spikes.

12.0 Calculations

12.1 For determination of metal concentration, read the metal value in μg/L from the calibration curve or directly from readout system of instrument.

12.2 If dilution of sample is required:

$$\mu g/L \text{ Metal in sample} = A \frac{(C + B)}{C} \qquad (8)$$

Where:

A = Metal in diluted aliquot from calibration curve (μg/L)

B = Acid blank matrix used for dilution (mL)

C = Sample aliquot (mL)

12.3 For solid samples, calculate concentrations as mg/kg as follows:

$$\mu g \text{ Metal/kg sample} = \frac{A \times V}{W} \quad (9)$$

Where:

A = Metal in processed sample from calibration curve (mg/L)

V = Final volume of the processed sample (mL)

W = Weight of sample (grams)

If results are to be reported on a dry-weight basis, adjustment will be made for solids content.

12.4 Different volumes will not be used for samples and standards. Instead, the sample will be diluted and the same size volume be used for both samples and standards. If dilution of the sample was required:

$$\mu g/L \text{ Metal in sample} = Z \frac{(C + B)}{C} \quad (10)$$

Where:

Z = Metal read from calibration curve or readout system (μg/L)

B = Acid blank matrix used for dilution (mL)

C = Sample aliquot (mL)

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific sampling and analysis plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Level, and project-specific sampling and analysis plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/20	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Matrix Spike	1/20	75—125%	Qualify data
Lab Replicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10	90—110%	Recalibrate
ICB	Begin	DR*	Qualify data
CCB	1/10	DR*	Qualify data
PB	1/10	DR*	Qualify data
LCS	Begin	90—110%	Recalibrate
Predigestion Spike	1/20	75—125%	Post-dig. spike
Postdigestion Spike	As needed	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data
CRA	Begin	DR	Recalibrate
ICS	Begin	DR	Qualify data
Serial Dilution	1/20	DR	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
ICB	initial calibration blank
CCB	continuing calibration blank
PB	preparation blank
LCS	laboratory control sample
CRA	detection limit verification sample
RPD	*relative percent difference*

DR	Data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ. For DR*, refer to the 1988 CLP SOW for acceptance limit guidance.
ICS	interference check sample

15.0 References

15.1 *CLP Statement of Work for Inorganic Analysis.* Multi-Media, Multi-Concentration. July 1988.

15.2 *Test Methods for Evaluating Solid Waste,* SW-846, 3rd ed., Method 7000.

Appendix

General Comments to Individual Methods

1. Alternate matrix modifiers as recommended by the manufacturer may be used if proper studies are performed to verify applicability (e.g., palladium).

2. An atomization and char study must be performed to optimize the temperature program for each element. Temperatures listed should be considered only as guides, since differences in instrumentation, background correction, tubes, and platforms affect the GFAA process.

1.0 Antimony

Optimum Concentration Range: 20 to 300 μg/L.
Approximate Detection Limit: 3 μg/L.

1.1 Preparation of Standard Solution

1.1.1 Water: All references to water assume the use of ASTM Type II water.

1.1.2 Stock Solution: Carefully weigh 2.7426 grams of antimony potassium tartrate (analytical reagent grade) and dissolve in water. Dilute to 1 liter with water. 1 mL = 1 mg Sb (1000 mg/L).

1.1.3 Prepare dilutions of stock solution to be used as calibration standards at the time of analysis and for "standard additions."

1.1.4 Calibration standards will be prepared using the same type of acid and at the same concentration as shall result in the sample to be analyzed after sample preparation.

1.2 Instrument Parameters (General)

1.2.1 Drying Time and Temperature: 30 seconds at 125°C.

1.2.2 Ashing Time and Temperature: 30 seconds at 800°C.

1.2.3 Atomizing Time and Temperature: 10 seconds at 2,700°C.

1.2.4 Purge Gas Atmosphere: Argon.

1.2.5 Wavelength: 217.6 nm.

1.2.6 Other operating parameters shall be set as specified by particular settings.

1.3 Notes

1.3.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be

operated using lower atomization temperatures for shorter time periods than the settings recommended above.

1.3.2 Background correction is required.

1.3.3 Nitrogen may be used as the purge gas.

1.3.4 If chloride concentration presents a matrix problem or causes loss before atomization, add an excess 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until recommended ashing temperature is reached.

1.3.5 Verification is necessary for every sample analyzed to determine that MSA is not required.

1.3.6 If MSA is required, follow the procedure given in the SOP.

2.0 Arsenic

Optimum Concentration Range: 5 to 100 μg/L
Approximate Detection Limit: 1 μg/L

2.1 Preparation of Standard Solution

2.1.1 Water: All references to water assume the use of ASTM Type II water.

2.1.2 Stock Solution: Dissolve 1.320 grams of arsenic trioxide (As_2O_3, analytical reagent grade) in 100 mL of water containing 4 grams NaOH. Acidify solution with 20-mL concentration HNO_3 and dilute to 1 liter. 1 mL = 1 mg As (1,000 mg/L).

2.1.3 Nickel Nitrate Solution, 5%: Dissolve 24.780 grams of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in water and make up to 100 mL.

2.1.4 Nickel Nitrate Solution, 1%: Dilute 20-mL of the 5% nickel nitrate to 100 mL with water.

2.1.5 Working Arsenic Solution: Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Withdraw appropriate aliquots of stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of 5% nickel nitrate solution. Dilute to 100 mL with water.

2.2 Sample Preparation: Add 100 μL of the 5% nickel nitrate solution to 5 mL of the digested sample. Sample is now ready for injection into furnace.

2.3 Instrument Parameters (General)

2.3.1 Drying Time and Temperature: 30 seconds at 125°C.

2.3.2 Ashing Time and Temperature: 30 seconds at 1,100°C.

2.3.3 Atomizing Time and Temperature: 10 seconds at 2,700°C.

2.3.4 Purge Gas Atmosphere: Argon.

2.3.5 Wavelength: 193.7 nm.

2.3.6 Other operating parameters will be set as specified by the instrument manufacturer.

2.4 Notes

2.4.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, purge gas interrupt, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the setting recommended above.

2.4.2 Background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (e.g., Al, Fe). If conditions occur where significant interference is suspected, the laboratory will switch to an alternate wavelength or take other appropriate actions to compensate for interference effects.

2.4.3 Verification is necessary for every sample analyzed to determine that MSA is not required.

2.4.4 If MSA is required, follow the procedure given in the SOP.

2.4.5 Use of an electrodeless discharge lamp (EDL) for the light source is recommended.

3.0 Beryllium

Optimum Concentration Range: 1 to 30 μg/L
Appropriate Detection Limit: 0.2 μg/L

3.1 Preparation of Standard Solution

3.1.1 Water: All references to water assume the use of ASTM Type II water.

3.1.2 Stock solution: Dissolve 11.6586 grams of beryllium sulfate ($BeSO_4$) in water containing 2 mL concentrated nitric acid and dilute to 1 liter. 1 mL = 1 mg Be (1,000 mg/L).

3.1.3 Prepare dilutions of stock solution to be used as calibration standards at time of analysis and for "standard additions."

3.1.4 Calibration standards will be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

3.2 Instrument Parameters (General)

3.2.1 Drying Time and Temperature: 30 seconds at 125°C.

3.2.2 Ashing Time and Temperature: 30 seconds at 1,000°C.

3.2.3 Atomizing Time and Temperature: 10 seconds at 2,800°C.

3.2.4 Purge Gas Atmosphere: Argon.

3.2.5 Wavelength: 234.9 nm.

3.2.6 Operating parameters will be set as specified by the instrument manufacturer.

3.3 Notes

3.3.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the settings recommended above.

3.3.2 Background correction is required.

3.3.3 Because of possible chemical interaction, nitrogen must not be used as a purge gas.

3.3.4 Verification is necessary for every sample analyzed to determine that MSA is not required.

3.3.5 If MSA is required, follow the procedure given in the SOP.

4.0 Cadmium

Optimum Concentration Range: 0.5 to 10 μg/L
Approximate Detection Limit: 0.1 μg/L

4.1 Preparation of Standard Solution

4.1.1 Water: All references to water assume the use of ASTM Type II water.

4.1.2 Stock solution: Carefully weigh 2.282 grams of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in water. Make up to 1 liter with water. 1 mL = 1 mg Cd (1000 mg/L).

4.1.3 Ammonium Phosphate Solution (40%): Dissolve 40 grams of ammonium phosphate ($NH_4 \cdot 2HPO_4$, analytical reagent grade) in water and dilute to 100 mL.

4.1.4 Prepare dilutions of stock cadmium solution to be used as calibration standards at time of analysis. To each 100 mL of standard and sample alike, add 2.0 mL of ammonium phosphate solution.

4.1.5 Calibration standards will be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

4.2 Instrument Parameters (General)

4.2.1 Drying Time and Temperature: 30 seconds at 125°C.

4.2.2 Ashing Time and Temperature: 30 seconds at 500°C.

4.2.3 Atomizing Time and Temperature: 10 seconds at 1,900°C.

4.2.4 Purge Gas Atmosphere: Argon.

4.2.5 Wavelength: 228.8 nm.

4.2.6 Operating parameters will be set as specified by the instrument manufacturer.

4.3 Notes

4.3.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

4.3.2 Background correction is required.

4.3.3 Contamination from the work area is critical in cadmium analysis. Use pipette tips that are free of cadmium.

4.3.4 Verification is necessary for every sample analyzed to determine that MSA is not required.

4.3.5 If MSA is required, follow the procedure given in the SOP.

5.0 Chromium

Optimum Concentration Range: 5 to 100 μg/L
Approximate Detection Range: 1 μg/L

5.1 Preparation of Standard Solution

5.1.1 Water: All references to water assume the use of ASTM Type II water.

5.1.2 Stock Solution: Dissolve 1.923 grams of chromium trioxide (Cr_2O_3) in water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with water. 1 mL = 1 mg Cr (1,000 mg/L).

5.1.3 Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate ($Ca(NO_3)_2 \cdot 4H_2O$, analytical reagent grade) in water and dilute to 100 mL. 1 mL = 20 mg calcium.

5.1.4 Prepare dilutions of stock chromium solution to be used as calibration standards at the time of analysis.

5.1.5 The calibration standards will be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike, add 1 mL of 30% H_2O_2 and 1 mL of the calcium nitrate solution.

5.2 Instrument Parameters (General)

5.2.1 Drying Time and Temperature: 30 seconds at 125°C.

5.2.2 Ashing Time and Temperature: 30 seconds at 1,000°C.

5.2.3 Atomizing Time and Temperature: 10 seconds at 2,700°C.

5.2.4 Purge Gas Atmosphere: Argon

5.2.5 Wavelength: 357.9 nm

5.2.6 Other operating parameters will be set as specified by the instrument manufacturer.

5.3 Notes

5.3.1 The concentration values and instrument conditions are for a Perkin Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite and are to be used as guidelines only.

5.3.2 Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/L where its suppressive effect becomes constant up to 1,000 mg/L.

5.3.3 Background correction is required.

5.3.4 Nitrogen must not be used as a purge gas because of possible CN band interference.

5.3.5 Pipette tips have been reported to be a possible source of contamination.

5.3.6 For every sample analyzed, verification is necessary to determine that MSA is not required.

5.3.7 If MSA is required, follow the procedure given in the SOP.

6.0 Cobalt

Optimum Concentration Range: 5 to 100 μg/L
Approximate Detection Range: 1 μg/L

6.1 Preparation of Standard Solution

6.1.1 Water: All references to water assume the use of ASTM Type II water.

6.1.2 Stock Solution: Carefully weigh 1 gram of cobalt metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with water. Chloride or nitrate salts of cobalt (II) may be used. Although numerous hydrated forms exist, they are not recommended unless the exact composition of the compound is known. 1 mL = 1 mg Co (1,000 mg/L).

6.1.3 Working Cobalt Solution: Prepare dilutions of stock cobalt solution to be used as calibration standards at time of analysis.

6.2 Instrument Parameters (General)

6.2.1 Drying Time and Temperature: 30 seconds at 125°C.

6.2.2 Ashing Time and Temperature: 30 seconds at 900°C.

6.2.3 Atomizing Time and Temperature: 10 seconds at 2,700°C.

6.2.4 Purge Gas Atmosphere: Argon.

6.2.5 Wavelength: 240.7 nm.

6.2.6 Other operating parameters will be set as specified by the instrument manufacturer.

6.3 Notes

6.3.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the settings recommended above.

6.3.2 Background correction is required.

6.3.3 Verification necessary for every sample analyzed to determine that MSA is not required.

6.3.4 If MSA is required, follow the procedure given in the SOP.

7.0 Lead

Optimum Concentration Range: 5 to 100 μg/L
Approximate Detection Range: 1 μg/L

7.1 Preparation of Standard Solution

7.1.1 Water: All references to water assume the use of ASTM Type II water.

7.1.2 Stock Solution: Carefully weigh 1.599 grams of lead nitrate ($Pb(NO_3)_2$, analytical reagent grade) and dissolve in water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 liter with water. 1 mL = 1 mg Pb (1,000 mg/L).

7.1.3 Lanthanum Nitrate Solution: Dissolve 58.64 grams of ACS reagent grade La_2O_3 in 100 mL concentrated HNO_3, and dilute to 1,000 mL with water. 1 mL = 50 mg lanthanum.

7.1.4 Working Lead Solution: Prepare dilutions of stock lead solution to be used as calibration standards at time of analysis.

7.1.5 Calibration standards will be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of diluted standard add 10 mL of the lanthanum nitrate solution.

7.2 Sample Preparation: To each 100 mL of prepared sample solution add 10 mL of the lanthanum nitrate solution.

7.3 Instrument Parameters (General)

7.3.1 Drying Time and Temperature: 30 seconds at 125°C.

7.3.2 Ashing Time and Temperature: 30 seconds at 500°C.

7.3.3 Atomizing Time and Temperature: 10 seconds at 2,700°C.

7.3.4 Purge Gas Atmosphere: Argon.

7.3.5 Wavelength: 283.3 nm.

7.3.6 Other operating parameters will be set as specified by the instrument manufacturer.

7.4 Notes

7.4.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the settings recommended above.

7.4.2 Background correction is required.

7.4.3 Greater sensitivity can be achieved using the 217.0-nm line, but the optimum concentration range is reduced. Use of a lead electrodeless discharge lamp at the lower wavelength has been found to be advantageous. Also a lower atomization temperature (2,400°C) may be preferred.

7.4.4 To suppress sulfate interference (up to 1,500 ppm), lanthanum is added as the nitrate to both samples and calibration standards. [*Atomic Absorption Newsletter* 15(3): 71, May—June 1976.]

7.4.5 Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately before use and, once cleaned, not be open to the atmosphere except when necessary.

7.4.6 Verification is necessary for every sample analyzed to determine that MSA is not required.

7.4.7 If MSA is required, follow the procedure given in the SOP.

8.0 Selenium

Optimum Concentration Range: 5 to 100 μg/L
Approximate Detection Limit: 2 μg/L

8.1 Preparation of Standard Solution

8.1.1 Water: All references to water assume the use of ASTM Type II water.

8.1.2 Stock Selenium Solution: Dissolve 0.3453 gram of selenous acid (actual assay 94.6% H_2SeO_3) in water and make up to 200 mL. 1 mL = 1 mg selenium (1,000 mg/L).

8.1.3 Nickel Nitrate Solution, 5%: Dissolve 24.780 grams of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in water and make up to 100 mL.

8.1.4 Nickel Nitrate Solution, 1%: Dilute 20 mL of 5% nickel nitrate to 100 mL with water.

8.1.5 Working Selenium Solution: Prepare dilutions of stock solution to be used as calibration standards at the time of analysis.

8.1.6 Calibration standards will be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of 5% nickel nitrate solution. Dilute to 100 mL with water.

8.2 Sample Preparation: Add 100 μL of the 5% nickel nitrate solution to 5 mL of digested sample. The sample is ready for injection into the furnace.

8.3 Instrument Parameters

8.3.1 Drying Time and Temperature: 30 seconds at 125°C.

8.3.2 Charring Time and Temperature: 30 seconds at 1,200°C.

8.3.3 Atomizing Time and Temperature: 10 seconds at 2,700°C.

8.3.4 Purge Gas Atmosphere: Argon.

8.3.5 Wavelength: 196.0 nm.

8.3.6 Other operating parameters will be set as specified by the instrument manufacturer.

8.4 Notes

8.4.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, purge gas interrupt, and nonpyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

8.4.2 Background correction is required. Background correction made by the deuterium arc method does not adequately compensate for high levels of certain interferents (e.g., Al, Fe). If conditions occur where significant interference is suspected, the laboratory will switch to an alternative wavelength or take other appropriate actions to compensate for interference effects.

8.4.3 Selenium analysis suffers interference from chlorides (> 800 mg/L) and sulfate (> 200 mg/L). For analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2,000 mg/L, both samples and standards shall be prepared to contain 1% nickel.

8.4.4 Verification is necessary for every sample analyzed to determine that MSA is not required.

8.4.5 If MSA is required, follow the procedure given in the SOP.

8.4.6 The use of the electrodeless discharge lamp (EDL) for the light source is recommended.

9.0 Silver

Optimum Concentration Range: 1 to 25 μg/L
Approximate Detection Limit: 0.2 μg/L

9.1 Preparation of Standard Solution

9.1.1 Water: All references to water assume the use of ASTM Type II water.

9.1.2 Stock solution: Dissolve 1.575 grams of silver nitrate ($AgNO_3$) analytical reagent grade) in water. Add 10 mL of concentrated HNO_3 and make up to 1 liter. 1 mL = 1 mg Ag (1,000 mg/L).

9.1.3 Prepare dilutions of stock solution to be used as calibration standards at time of analysis and for "standard additions."

9.1.4 Calibration standards will be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

9.1.5 Iodine Solution, IN: Dissolve 20 grams potassium iodide (KI), analytical reagent grace in 50 mL water. Add 12.7 grams iodine (I_2), analytical reagent grade, and dilute to 100 mL. Keep in a brown bottle.

9.1.6 Cyanogen Iodine Solution: To 50 mL of water add 4.0 mL concentrated ammonium hydroxide (NH_4OH), 6.5 grams potassium cyanide (KCN), and 5.0 ml iodine solution. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

Caution: This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

9.2 Instrument Parameters (General)

9.2.1 Drying Time and Temperature: 30 seconds at 125°C.

9.2.2 Ashing Time and Temperature: 30 seconds at 400°C.

9.2.3 Atomizing Time and Temperature: 10 seconds at 2,700°C.

9.2.4 Purge Gas Atmosphere: Argon.

9.2.5 Wavelength: 328.1 nm.

9.2.6 Other operating parameters will be set as specified by the instrument manufacturer.

9.3 Notes

9.3.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas, and nonpyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

9.3.2 Background correction is required.

9.3.3 Use of halide acids shall be avoided.

9.3.4 If absorption to container walls or formation of AgCl is suspected, make simple basic using concentrated NH_4OH and add 1 mL of CNI solution per 100 mL of sample. Mix sample and allow to stand for 1 hour before proceeding with analysis.

9.3.5 Verification is necessary for every sample analyzed to determine that MSA is not required.

9.3.6 If MSA is required, follow the procedure given in the SOP.

10.0 Thallium

Optimum Concentration Range: 5 to 100 μg/L
Approximate Detection Limit: 1 μg/L

10.1 Preparation of Standard Solution

10.1.1 Water: All references to water assume the use of ASTM Type II water.

10.1.2 Stock Solution: Dissolve 1.303 grams of thallium nitrate ($TlNO_3$, analytical reagent grade) in water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with water. 1 mL = 1 mg Tl (1,000 mg/L).

10.1.3 Prepare dilutions of stock solution to be used as calibration standards at time of analysis and for "standard additions."

10.1.4 Calibration standards will be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

10.2 Instrument Parameters (General)

10.2.1 Drying Time and Temperature: 30 seconds at 125°C.

10.2.2 Ashing Time and Temperature: 30 seconds at 400°C.

10.2.3 Atomizing Time and Temperature: 10 seconds at 2,400°C.

10.2.4 Purge Gas Atmosphere: Argon.

10.2.5 Wavelength: 276.8 nm.

10.2.6 Other operating parameters will be set as specified by the instrument manufacturer.

10.3 Notes

10.3.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas and nonpyrolytic graphite and are to used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be

operated using lower atomization temperatures for shorter time periods than the above recommended settings.

10.3.2 Background correction is required.

10.3.3 Nitrogen may be used as the purge gas.

10.3.4 Verification is necessary for every sample analyzed to determine that MSA is not required.

10.3.5 If MSA is required, follow the procedure given in the SOP.

11.0 Vanadium

Optimum Concentration Range: 10 to 200 μg/L
Approximate Detection Limit: 4 μg/L

11.1 Preparation of Standard Solutions

11.1.1 Water: All references to water assumes the use of ASTM Type II water.

11.1.2 Stock Solution: Dissolve 1.7854 grams of vanadium pentoxide, V_2O_5 (analytical reagent grade), in 10 mL of concentrated nitric acid and dilute to 1 liter with water.

11.1.3 Prepare dilutions of stock solution to be used as calibration standards at time of analysis (0.5% v/v HNO_3).

11.2 Instrument Parameters

11.2.1 Drying Time and Temperature: 30 seconds at 125°C.

11.2.2 Ashing Time and Temperature: 30 seconds at 1,400°C.

11.2.3 Atomizing Time and Temperature: 10 seconds at 2,800°C.

11.2.4 Purge Gas Atmosphere: Argon.

11.2.5 Wavelength: 318.4 nm.

11.2.6 Other operating parameters will be set as specified by the instrument manufacturer.

11.3 Notes

11.3.1 The concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-μL injection, continuous flow purge gas and nonpyrolytic graphite and are to used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

11.3.2 Background correction is required.

11.3.3 Verification is necessary for every sample analyzed to determine that MSA is not required.

11.3.4 If MSA is required, follow the procedure given in the SOP.

FERNALD/gfaa.51

FM-INO-0020

Metals by Atomic Absorption Spectrometry, Flame Technique

Working Linear Range: Metal-dependent; see specific metal
Reporting Limit: Metal-dependent; see specific metal
Reporting Units: Water, μg/L; solids, mg/kg
Matrix: Water, soil, sediment, and waste

1.0 Scope and Application

1.1 Scope and Application: The method is applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. Drinking water free of particulate matter may be analyzed directly, but groundwater, other aqueous samples, TCLP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion before analysis.

1.2 Detection limits, sensitivity, and optimum ranges for analysis will vary with sample matrix and the model of atomic absorption system used (and method of background correction). Table 1 lists typical detection limits for clean samples. Detection limits may be improved by sample concentration or by solvent extraction techniques.

1.3 Table 1 lists metals that may be analyzed using the flame technique. Where the flame technique does not offer detection low enough to meet the required reporting limits, other techniques must be used.

2.0 Method Summary

An aliquot of sample is acid-digested on a steam bath or hot plate, or using microwave energy. The volume of the digestate is adjusted. The digestate is then aspirated into the flame and the absorbance measured at a characteristic wavelength. The concentration of the sample is determined using a calibration curve.

3.0 Interferences

3.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This

Table 1
Detection and Reporting Limits
Flame Atomic Absorption

Metal	Wavelength (nm)	Detection Limits (Water)(μg/L)	Required Reporting Limits (Water)(μg/L)	Required Reporting Limits (Soil)(mg/kg)
Aluminum	309.3	100	200	40
Antimony	217.6	200	60	12
Barium	553.6	100	200	40
Beryllium	234.9	5	5	1
Cadmium	228.8	5	5	1
Calcium	422.7	10	5,000	1,000
Chromium	357.9	50	10	2
Cobalt	240.7	50	50	10
Copper	324.7	20	25	5
Iron	248.3	30	100	20
Lead	283.3	100	3	0.6
Magnesium	285.2	1	5,000	1,000
Manganese	279.5	10	15	3
Nickel	232.0	40	40	8
Potassium	766.5	10	5,000	1,000
Silver	328.1	10	10	2
Sodium	589.6	2	5,000	1,000
Thallium	276.8	100	10	2
Vanadium	318.4	200	50	10
Zinc	213.9	5	20	4

phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.3 The presence of high dissolved solids in the sample may result in interference from nonatomic absorbance such as light scattering; therefore, background correction will be used.

3.4 Ionization interferences occur when the flame temperature is sufficiently high to remove an electron from a neutral atom, giving a positively charged ion. Such interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li, or Cs.

3.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high because of the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multi-element lamp or from a metal impurity in the lamp cathode falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate. Method of Standard Addition (MSA) may be employed.

3.7 All metals are not equally stable in the digestate, especially if it contains only HNO_3, not HNO_3 and HCl. The digestate should be analyzed as soon as possible. However, flame digestates are all HCl and HNO_3.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 250-mL Beaker or other appropriate vessel.

6.2 Watch Glasses.

6.3 Thermometer covering range of 0° to 200°C.

6.4 Whatman No. 42 Filter Paper, or equivalent.

6.5 Microwave Oven with programmable power settings up to at least 600 W or a hot plate.

6.5.1 Commercial kitchen or home-use microwave ovens will not be used for digestion of samples under this contract. The oven cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.

6.5.2 The system must use PFA Teflon Digestion Vessels (120-mL capacity) capable of withstanding pressures of up to 110 ± 10 psi (7.5 ± 0.7 atm). The vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

6.5.3 A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be at least 3 rpm.

6.5.4 Polymeric Volumetric Ware in plastic (Teflon or polyethylene) 50- or 100-mL capacity.

6.6 Whatman No. 41 Filter Paper, or equivalent.

6.7 Disposable polypropylene Filter Funnel.

6.8 Analytical Balance: 300-gram capacity, minimum sensitivity of $\pm$ 0.01 gram.

6.9 Polyethylene Bottles: 125-mL, with caps.

6.10 Atomic Absorption Spectrophotometer: Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a graphical display and data handling system (optional).

6.11 Burner: The burner recommended by the instrument manufacturer should be used. For certain elements, the nitrous oxide burner is required. (Spoiler is mainly used for high dissolved solids.)

6.12 Hollow Cathode Lamps: Single-element lamps are preferred, but multielement lamps may be used. Electrodeless discharge lamps (EDL) may also be used when available.

6.13 Appropriate Graphical Display (optional).

6.14 Appropriate Data Handling System (optional).

6.15 Pipets: Microliter, with disposable tips. Sizes can range from 5 to 100 μL as required. Pipet tips should be checked as a possible source of contamination before their use.

6.16 Pressure-reducing Valves: The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

6.17 Glassware: All glassware, polypropylene, or Teflon containers, including sample bottles, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and Type II water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) *If it can* be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the atomic absorption spectrophotometer according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Digestion

8.1.1 Water: All references to water assume the use of ASTM Type II water.

8.1.2 Concentrated Nitric Acid (HNO_3), sp. gr. 1.41: Spectrograde or equivalent.

8.1.3 Concentrated Hydrochloric Acid (HCl), sp. gr. 1.19: Spectrograde or equivalent.

8.1.4 Hydrogen Peroxide (H_2O_2), 30%.

8.1.5 Hydrochloric Acid, 1:1: Add 500 mL concentrated HCl (sp. gr 1.19) to 400 mL water and dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.1.6 Nitric Acid, 1:1: Add 500 mL concentrated HNO_3 (sp gr 1.41) to 400 mL water and dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.1.6.1 Acids used in the preparation of standards and for sample processing must be spectrograde or equivalent. Redistilled acids are acceptable.

8.2 Analysis

8.2.1 Water: All references to water assume the use of ASTM Type II water.

8.2.2 Concentrated Nitric Acid, 1:1: Use spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding concentrated acid to an equal volume of water. **Caution:** Heat-liberating reaction.

8.2.3 Hydrochloric Acid, 1:1: Use spectrograde acid certified for AA use. Prepare 1:1 dilution with water by adding concentrated acid to equal volume of water. **Caution:** Heat-liberating reaction.

8.2.4 Fuel and Oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from compressed air line, laboratory compressor, or cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

8.2.5 Stock Standard Metal Solutions: Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic reagent-grade salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions in attached Appendix.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 500 to 1,000 mg of the metal per liter. Commercially available standard solutions may also be used.

8.2.6 Calibration Standards: Refer to individual methods for specific standard preparation. Calibration standards are prepared by diluting stock standards at time of analysis. Calibration standards should be prepared using the same type of acid or combination of acids at the same concentration as will result in the samples following sample preparation.

9.0 Calibration Procedures

9.1 Prepare calibration standards by diluting stock standards at time of analysis. Use of the same type or combination of acids, at the same concentration, and at the same time of sample preparation will provide the analyst with the best results. If a specific element or compound is added to samples to remove or minimize matrix effects (matrix modifier), it must also be added to the standards.

9.2 Prepare instrument blank and at least three calibration standards in graduated amounts in range expected for samples to be analyzed. One standard will be at the required reporting limit.

9.3 Beginning with blank and working toward highest standard, aspirate blank and standards.

9.4 Construct standard curve by plotting peak absorbances or peak areas of standards versus their concentrations. Alternatively use electronic calibration if available. (Do not use peak heights.)

9.5 If AA instrument configuration prevents the required four-point calibration, use as many of the four standards (blank and three standards) as possible to construct the curve. Immediately run remaining standards not used for the curve. Determine concentrations of standards from curve. Resulting concentrations must be within ± 10% of true value. Calculations to show that the ± 10% criterion has been met must be included in the raw data. If the ± 10% criterion is not met, recalibrate instrument. The ± 10% criterion does not apply to the standard at the reporting limit.

10.0 Sample Preparation

10.1 Acid Digestion of Water Samples

10.1.1 Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker. Add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl to the sample. Cover with watch glass or similar cover and heat on steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 15 and 20 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material.

Note: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.1.1.1 Adjust sample volume to 100 mL with water. The sample is ready for analysis.

10.2 Acid Digestion of Soil Samples

10.2.1 Mix sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 gram) a 1.0- to 1.5-gram portion of sample and transfer to a beaker.

10.2.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat sample to 95°C and reflux for 10 minutes without boiling. Allow sample to cool, add 5 mL of concentrated HNO_3, replace watch glass, and reflux for 30 minutes. Do not allow volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the beaker.

10.2.3 After second reflux step has been completed and sample has cooled, add 2 mL of water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return beaker to hot plate for warming to start peroxide reaction. Care must be taken to ensure that losses do not occur because of excessively vigorous effervescence. Heat until effervescence subsides, and cool beaker.

10.2.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

Note: Do not add more than a total of 10 mL 30% H_2O_2.

10.2.5 Add 5 mL of 1:1 HCl and 10 mL of water, return covered beaker to hot plate, and heat for another 10 minutes. After cooling, filter through Whatman No. 42 filter paper and dilute to 100 mL with water.

Note: In place of filtering, sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.2.5.1 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5% (v/v) HNO_3. Dilute digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. The sample is ready for analysis.

10.3 Percent Solids Determination for Soil Samples: If results for soil samples are to be reported on a dry weight basis, perform percent solids determination as follows:

10.3.1 Immediately following weighing of sample to be processed for analysis add 5 to 10 grams of sample to tared weighing dish. Weigh and record weight to the nearest 0.01 gram.

10.3.2 Place weighing dish plus sample in a drying oven maintained at 103° to 105°C with cover tipped to allow for moisture escape. Sample handling and drying should be conducted in a well-ventilated area.

10.3.3 Dry sample overnight (12 to 24 hours) but no longer than 24 hours. Remove sample from oven and cool in desiccator with weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 gram. **Do not analyze the dried sample.**

10.3.4 Calculate percent solids as follows: (1)

$$\% \text{ Solids} = \frac{\text{Sample dry weight}}{\text{Sample wet weight}} \times 100$$

This value will be used for calculating analytical concentration on a dry weight basis.

10.3.5 Concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample. (2)

$$\text{Concentration (dry weight) (mg/kg)} = \frac{C \times V}{W \times S}$$

Where:

C	=	Concentration (mg/L)
V	=	Final volume after sample preparation (L)
W	=	Weight of wet sample (kg)
S	=	% Solids/100

10.4 Microwave Sample Preparation

10.4.1 Microwave Calibration Procedure: The calibration procedure is a critical step prior to use of any microwave unit. The unit must be calibrated every 6 months. Data for each calibration will be available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power will be determined.

10.4.1.1 Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between output power and the scale used in controlling the unit, the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs multiple-point calibration, then the point where linearity begins must be identified. For example: a calibration at power settings of 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% can be applied and the data plotted. The nonlinear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to 5.5 to 6 watts and becomes the smallest unit of power that can be controlled. If 20 to 40 watts are contained from 99 to 100%, that portion of the microwave calibration is not controllable by 3 to 7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

10.4.1.2 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring temperature rise in 1 kilogram of water exposed to microwave radiation for a fixed period of time. The water is placed in a Teflon beaker (or a beaker made of some other material that does not absorb microwave energy) and stirred before measuring the temperature. Glass beakers absorb microwave energy and may not be used. The initial temperature of the water must be between 19° and 25°C. The beaker is circulated continuously through the field for at least 2 minutes at full power.

The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements must be accurate to ± 0.1°C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled to room temperature. Otherwise, use a fresh water sample. (3)

10.4.1.3 Absorbed power is determined by the formula:

$$P = \frac{(K)\ (Cp)\ (m)\ (DT)}{t}$$

Where:

P	=	Apparent power absorbed by the sample in watts (joules per second)
K	=	Conversion factor for thermochemical calories per second to watts (= 4.184)
Cp	=	Heat capacity, thermal capacity, or specific heat (cal. $gram^{-1} \times °C^{-1}$) of water (= 1.0)
m	=	Mass of sample (grams)
DT	=	Final temperature minus initial temperature (°C)
t	=	Time (seconds)

10.4.1.4 Using 2 minutes and 1 kg of water, the calibration equation simplifies to:

$$P = (DT)\ (34.87) \qquad (4)$$

10.4.1.5 The microwave user can now relate power in watts to the percent power setting of the microwave.

10.4.2 Initial Cleaning of PFA Vessels

10.4.2.1 Before first use, new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating vessels for 96 hours at 200°C. Vessels must be disassembled during annealing, and sealing surfaces (top of vessel or its rim) must not be used to support vessel during annealing.

10.4.2.2 Rinse in water.

10.4.2.3 Immerse in 1:1 HCl for at least 3 hours after cleaning bath has reached temperature just below boiling.

10.4.2.4 Rinse in water.

10.4.2.5 Immerse in 1:1 HNO_3 for at least 3 hours after cleaning bath has reached temperature just below boiling.

10.4.2.6 Vessels are then rinsed with copious amounts of water before use for any analyses under this contract.

10.4.3 Cleaning between Sample Digestions

10.4.3.1 Wash entire vessel in hot water using laboratory-grade nonphosphate detergent.

10.4.3.2 Rinse with 1:1 HNO_3.

10.4.3.3 Rinse three times with water. If contaminants are found in preparation blank, steps for initial cleaning must be strictly adhered to.

10.4.4 Water Sample Microwave Digestion Procedure

10.4.4.1 A 45-mL aliquot of sample is measured into a Teflon digestion vessel using volumetric glassware.

10.4.4.2 Add 5 mL of high purity concentrated HNO_3 to digestion vessels.

10.4.4.3 Record weight of each vessel to 0.01 gram.

10.4.4.4 Place caps with pressure release valves on vessels hand-tight, and then tighten using constant torque to 12 ft/lb. Place five sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported vessel to collect sample expelled from sample vessel in the event of overpressurization. Assembly of vessels into the carousel may be done inside or outside the microwave unit.

10.4.4.5 This procedure is energy balanced for five 45-mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than five samples are digested, the remaining vessels must be filled with 45 mL of water and 5 mL of concentrated nitric acid.

Newer microwave ovens may be capable of higher power settings that may allow a larger number of samples. If the analyst wishes to digest more than five samples at a time, the analyst may use different power settings as long as they result in the same time-temperature conditions defined in the power programming for the method.

Initial sample temperature should be 24 ± 1°C. The preparation blank must have 45 mL of water and the same amount (5 mL) of acid that is added to the samples.

The microwave unit first-stage program must be set to give 545 watts for 10 minutes and the second-stage program to give 344 watts for 10 minutes. This sequence brings the samples to 160° ± 4°C in 10 minutes and permits a slow rise to 165° to 170°C during the second 10 minutes.

10.4.4.6 Following the 20-minute program, the samples are left to cool in the microwave unit for 5 minutes with the exhaust fan ON. The samples or carousel may then be removed from the microwave unit. Before opening the vessels, let them cool until they are no longer hot to the touch.

10.4.4.7 After sample vessel has cooled, weigh sample vessel and compare to initial weight as reported in preparation log. Any sample vessel exhibiting a ≤0.5-gram loss must have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with sample preparation. Any sample vessel exhibiting a > 0.5-gram loss must be identified in the preparation log and the sample redigested.

10.4.5 Sample Filtration

10.4.5.1 Shake digested samples well to mix condensate within digestion vessel before being opened. Filter digestates into 50-mL glass volumetric flasks through ultraclean filter paper and dilute to 50 mL (if necessary). The samples are ready for analysis. Sample results must be corrected by a factor of 1.11 to report final concentration values based on an initial volume of 45 mL. Concentrations are reported as "total."

10.4.6 Soil Sample Microwave Digestion Procedure

10.4.6.1 Add representative 0.5 ± 0.050 gram of sample to the Teflon PFA vessel.

10.4.6.2 Add 10 ± 0.1 mL of concentrated nitric acid. If vigorous reaction occurs, allow reaction to stop before capping vessel.

10.4.6.3 Cap vessel; then tighten using constant torque to 12 ft/lb according to manufacturer's direction.

10.4.6.4 Connect sample vessel to overflow vessel using Teflon PFA tubing.

10.4.6.5 Weigh vessel assembly to the nearest 0.01 gram.

10.4.6.6 Place sample vessels in groups of two sample vessels or six sample vessels in carousel, evenly spaced around its periphery in microwave unit. If fewer than recommended number of samples are to be digested (i.e., three samples plus one blank), then remaining unused vessels must be filled with 10 mL of nitric acid to achieve the full complement of vessels for the carousel.

10.4.6.7 Attach each sample vessel to a clean, double-ported vessel to collect sample expelled from sample vessel in the event of overpressurization. Assembly of vessels into carousel may be done inside or outside the microwave unit. Connect overflow vessel to center well of oven.

10.4.6.8 Preparation blank must have 0.5 mL of water and the same amount (10 mL) of acid that is added to the samples. Blank must later be diluted to 50 mL in the same manner as the samples.

10.4.6.9 Irradiate the two-sample vessel group at 344 watts for 10 minutes, or the six-vessel group at 574 watts for 10 minutes.

10.4.6.10 This program brings the sample to 175°C in 5.5 minutes and remains between 170° and 180°C for the balance of the 10-minute irradiation period. Pressure should peak at less than 6 atmospheres for most samples. Pressure may exceed the limits in the case of high concentrations of carbonate or organic compounds. In such cases, pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atmospheres.

10.4.6.11 Allow vessels to cool for at least 5 minutes before removing them from microwave unit, with exhaust fan ON. Allow vessels to cool to room temperature before opening. Vessels must be carefully uncapped and vented in a fume hood.

10.4.6.12 Weigh each vessel assembly. If weight of acid plus sample has decreased by more than 10% from original weight, discard digests. Determine reason for loss. Losses typically are attributed to use of digestion time longer than 10 minutes, using too large of a sample, or having improper heating conditions. Once source of losses has been corrected, prepare new set of samples for digestion.

10.4.6.13 Shake sample well to mix in condensate within digestion vessel before being opened. Filter digestion vessel into a 50-mL glass volumetric flask through ultraclean filter paper. Rinse sample digestion vessel, cap, connecting tube, and (if venting occurred) overflow vessel into 50-mL glass flask. Dilute to 50 mL. Samples are ready for analysis. Concentrations are reported at "total."

11.0 Sample Analysis

11.1 Operating Conditions: Because of differences between various makes and models of instruments, no detailed operating instructions can be given for each instrument. Manufacturer's instructions should be followed in establishing conditions that will yield optimum response for each metal. Operating conditions are listed in each metal procedure in the Appendix, but they should be used as guidelines only.

11.2 Sample Analysis: Add matrix modifier, if required, to sample. Use the same volume as that used for the standards. Aspirate the sample.

11.2.1 Determine concentration of metal of interest by comparing absorbance or peak area of sample with standard curve. Alternatively, read results directly if instrument is equipped with this capability.

11.2.2 Sample responses must fall within the calibration range. Sample dilution must be made, if necessary, to bring the response within the calibration range.

11.3 Analytical Sequence

11.3.1 The following sequence must be followed:

11.3.1.1 Initial Calibration Verification (ICV) Standard.

11.3.1.2 Initial Calibration Blank (ICB).

11.3.1.3 Detection Limit (CRA).

11.3.1.4 First 8 samples.

11.3.1.5 Continuing Calibration Verification (CCV) Standard.

11.3.1.6 Continuing Calibration Blank (CCB).

11.3.1.7 Next 10 samples.

11.3.1.8 Continuing Calibration Verification (CCV) Standard and Continuing Calibration Blank (CCB) bracketing every 10 or 20 samples.

11.3.1.9 Last 10 samples.

11.3.1.10 CCV Standard.

11.3.1.11 CCB.

11.3.2 The ICV standard must be analyzed immediately after instrument calibration.

11.3.3 The ICB must follow the ICV standard.

11.3.4 The CRA standard must be analyzed at the beginning.

11.3.5 The CCV Standard must be analyzed every 10 or 20 samples or every 2 hours during an analysis, whichever is more frequent. It must also be analyzed after the last sample.

11.3.6 The CCB must be analyzed after each CCV standard.

11.3.7 The term "sample" (when not qualified) as used in the method includes not only field samples but also the CRA and the Quality Control Samples (Preparation Blank, Matrix Spike, Duplicate, and the Serial Dilution). Quality control samples may be analyzed at any time during the analytical run.

11.4 Spike Sample Analysis

11.4.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before digestion (i.e., before addition of other reagents). At least one spike sample analysis must be performed per 20 samples or per analytical batch of a similar matrix type, whichever is more frequent. Spike concentration levels are summarized in Table 2.

Table 2
Spiking Levels for Flame AA Spike Analysis

Element	Water (µg/L)	Soil (mg/kg)
Aluminum	2,000	*
Antimony	500	100
Barium	2,000	400
Beryllium	50	10
Cadmium	50	10
Calcium	*	*
Chromium	200	40
Cobalt	500	100
Copper	250	50
Iron	1,000	*
Lead	500	100
Magnesium	*	*
Manganese	500	100
Nickel	500	100
Potassium	*	*
Selenium	2,000	400
Silver	50	10
Sodium	*	*
Thallium	2,000	400
Vanadium	500	100
Zinc	500	100

*No spike required.

11.4.2 If the spike analysis is performed on the same sample chosen for the duplicate sample analysis, spike calculations must be performed using the results of the sample designated as the "original sample." The average of the duplicate results cannot be used for determining percent recovery. Samples identified as field blanks cannot be used for spiked sample analysis. Specific samples may be designated to be used for the spike sample analysis.

11.4.3 The analyte spike must be added in the amount given in the Table 2 for each element analyzed.

11.4.3.1 The levels shown indicate concentrations in the final digestate of the spiked sample when the wet weight of 1 gram of sample is taken for analysis. Adjustment must be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. Appropriate adjustment must be made for microwave digestion procedure where 0.5 gram of sample or 50.0 mL (45 mL of sample plus 5.0 mL of acid) of aqueous sample are required for analysis.

11.4.3.2 If spike recovery is not at or within the limits of 75 to 125%, the data of all samples received associated with that spike sample and determined by the same analytical method must be flagged with an "N." An exception to this rule is granted when the sample concentration exceeds the spike concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75 to 125% recovery criteria.

11.4.3.3 When the predigestion spike recovery falls outside the control limits and the sample result does not exceed 4 times the spike added, a postdigestion/postdistillation spike must be performed for elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at 2 times the indigenous level or 2 times the required reporting limit, whichever is greater.

11.4.3.4 Individual component percent recoveries (%R) are calculated as: (5)

$$\% \text{ Recovery} = \frac{(SSR - SR)}{SA} \times 100$$

Where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added

11.5 Duplicate Sample Analysis (D)

11.5.1 At least one duplicate sample must be analyzed every 20 samples or per analytical batch of a similar matrix type, whichever is more frequent. Duplicates cannot be averaged for reporting purposes.

11.5.2 Samples identified as field blanks cannot be used for duplicate sample analysis. Specific samples may be designated to be used for duplicate sample analysis.

11.5.3 The relative percent difference (RPD) for each component calculated as: (6)

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where:

RPD = Relative percent difference
S = First sample value (original)
D = Second sample value (duplicate)

11.5.4 A control limit of 20% for RPD shall be used for original and duplicate sample values ≥ 5 times the required reporting limit. A control limit of ± the required reporting limit must be used for sample values < 5 times the required reporting limit, and the absolute value of the control limit must be entered in the "Control Limit" column on the duplicate analysis report.

11.5.5 If one result is above the 5 times required reporting level and the other is below, use the ± required reporting limit criteria. If both sample values are < the IDL, the RPD is not calculated on the report form. For solid sample or duplicate results < 5 times the required reporting limit, enter the absolute value of the required reporting limit, corrected for sample weight and percent solids, as the control limit.

11.5.6 If duplicate sample results are outside control limits, flag all the data for samples received associated with that duplicate sample with an asterisk (*.) When there is more than one duplicate sample per batch, if one duplicate result is not within contract criteria flag all samples of the same matrix.

12.0 Calculations

12.1 Calculations for liquid samples: For determination of metal concentration, read metal value in μg/L from calibration curve or directly from readout system of instrument.

12.1.1 If dilution of sample is required: (7)

$$\mu g/L \text{ Metal in sample} = \frac{A\ (C + B)}{C}$$

Where:

A = Metal in diluted aliquot from calibration curve (μg/L)
B = Acid blank matrix used for dilution (mL)
C = Sample aliquot (mL)

12.2 For solid samples, calculate concentrations as: (8)

$$\text{mg Metal/kg sample} = \frac{A \times V}{W}$$

Where:

A = Metal in processed sample from calibration curve (mg/L)
V = Final volume of processed sample (mL)
W = Weight of sample (grams)

12.2.1 If results are to be reported on a dry-weight basis, adjustment must be made for solids content.

The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample as:

$$\text{Concentration (dry weight) (mg/kg)} = \frac{C \times V}{W \times S} \quad (9)$$

Where:

C	=	Concentration (mg/L)
V	=	Final volume after sample preparation (L)
W	=	Weight of wet sample (kg)
S	=	% Solids/100

12.3 Different injection volumes must not be used for samples and standards. Instead, sample should be diluted and same size injection volume used for both samples and standards. If dilution of sample is required: (10)

$$\mu g/L \text{ Metal in sample} = \frac{Z\,(C + B)}{C}$$

Where:

Z	=	Metal read from calibration curve or readout system (μg/L)
B	=	Acid blank matrix used for dilution (mL)
C	=	Sample aliquot (mL)

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific sampling and analysis plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Levels, and project-specific sampling and analysis plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/20	90—110%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Matrix Spike	1/20	75—125%	Qualify data
Lab Replicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	90—110%	Recalibrate
CCVS	1/10	90—110%	Recalibrate
ICB	Begin	DR*	Qualify data
CCB	1/10	DR*	Qualify data
PB	1/10	DR*	Qualify data
LCS	Begin	90—110%	Recalibrate
Predigestion Spike	1/20	75—125%	Post-dig. spike
Postdigestion Spike	as needed	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data
CRA	Begin	DR	Recalibrate
ICS	Begin	DR	Qualify data
Serial Dilution	1/20	DR	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
ICB	initial calibration blank
CCB	continuing calibration blank
PB	preparation blank
LCS	laboratory control sample
CRA	detection limit verification sample
RPD	relative percent difference
DR	Data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ. For DR*, refer to the 1988 CLP SOW for acceptance limit guidance.
ICS	interference check sample

15.0 References

15.1 *CLP Statement of Work for Inorganic Analysis, Multi-Media, Multi-Concentration.* July 1988.

15.2 *Test Methods for Evaluating Solid Waste,* 3rd ed., Method 7000.

6.0 Calcium-Specific Procedure

Optimum Concentration Range: 0.2 to 7 mg/L using a wavelength of 422.7 nm
Sensitivity: 0.08 mg/L
Approximate Detection Limit: 0.01 mg/L

6.1 Preparation of Standard Solution

6.1.1 Stock Solution: Suspend 1.250 grams of calcium carbonate ($CaCO_3$, analytical reagent grade), dried at 180°C for 1 hour before weighing, in water and dissolve cautiously with a minimum of dilute HCl. Dilute to 1,000 mL with water. 1 mL = 0.5 mg Ca (500 mg/L).

6.1.2 Lanthanum Chloride Solution: Dissolve 29 grams of La_2O_3, slowly and in small portions, in 250 mL concentrated HCl and dilute to 500 mL with water.

Caution: Reaction is violent.

6.1.3 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. To each 10 mL of calibration standard and sample alike, add 1.0 mL of lanthanum chloride solution (i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL).

6.2 Instrumental Parameters (General)

6.2.1 Calcium Hollow Cathode Lamp.

6.2.2 Wavelength: 422.7 nm.

6.2.3 Fuel: Acetylene.

6.2.4 Oxidant: Air.

6.2.5 Type of Flame: Reducing.

Note: Phosphate, sulfate and aluminum interfere but are masked by addition of lanthanum. Because low calcium values result if sample pH is above 7, both standards and samples are prepared in dilute HCl solution. Concentrations of magnesium greater than 1,000 mg/L also cause low calcium values. Concentrations of up to 500 mg/L each of sodium, potassium and nitrate cause no interference.

6.2.5.1 Anionic chemical interferences can be expected if lanthanum is not used in samples and standards.

6.2.5.2 The nitrous oxide-acetylene flame will provide two to five times greater sensitivity and freedom from chemical interferences. Ionization interferences should be controlled by adding a large amount of alkali to sample and standards. The analysis appears to be free from chemical suppressions in the nitrous oxide-acetylene flame. [*Atomic Absorption Newsletter,* 14(1975): 29.]

6.2.5.3 The 239.9-nm line may also be used (relative sensitivity of 120).

7.0 Chromium-Specific Procedure

Optimum Concentration Range: 0.5 to 10 mg/L using a wavelength of 357.9 nm
Sensitivity: 0.25 mg/L
Approximate Detection Limit: 0.05 mg/L

7.1 Preparation of Standard Solution

7.1.1 Stock Solution: Dissolve 1.923 grams of chromium trioxide (Cr_2O_3, reagent grade) in water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with water. 1 mL = 1 mg Cr (1,000 mg/L).

7.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

7.2 Instrumental Parameters (General)

7.2.1 Chromium Hollow Cathode Lamp.

7.2.2 Wavelength: 357.9 nm.

7.2.3 Fuel: Acetylene.

7.2.4 Oxidant: Nitrous oxide.

7.2.5 Type of Flame: Fuel rich.

Note: The following wavelengths may also be used:

359.3 nm, relative sensitivity 1.4
425.4 nm, relative sensitivity 2
427.5 nm, relative sensitivity 3
428.9 nm, relative sensitivity 4

7.2.5.1 The fuel rich air-acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame, interference can be lessened but sensitivity will also be reduced.

7.2.5.2 Suppression of both Cr^{3+} and Cr^{6+} absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [*Talanta* 20(1973): 631]. A 1% oxine solution is also reported to be useful.

7.2.5.3 For chromium concentrations between 50 and 200 μg/L where the air-acetylene flame cannot be used or for concentrations below 50 μg/L, use of furnace technique is recommended.

8.0 Cobalt-Specific Procedure

Optimum Concentration Range: 0.5 to 5 mg/L using a wavelength of 240.7 nm
Sensitivity: 0.2 mg/L
Approximate Detection Limit: 0.05 mg/L

8.1 Preparation of Standard Solution

8.1.1 Stock Solution: Dissolve 4.307 grams of cobaltous chloride ($CoCl_2 \cdot 6H_2O$ analytical reagent grade) in water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with water. 1 mL = 1 mg Co (1,000 mg/L).

8.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

8.2 Instrumental Parameters (General)

8.2.1 Cobalt Hollow Cathode Lamp.

8.2.2 Wavelength: 240.7 nm.

8.2.3 Fuel: Acetylene.

8.2.4 Oxidant: Air.

8.2.5 Type of Flame: Oxidizing.

Note: For cobalt concentrations below 100 μg/L, use of furnace technique is recommended.

9.0 Copper-Specific Procedure

Optimum Concentration Range:	0.2 to 5 mg/L using a wavelength of 324.7 nm
Sensitivity:	0.1 mg/L
Approximate Detection Limit:	0.02 mg/L

9.1 Preparation of Standard Solution

9.1.1 Stock Solution: Carefully weigh 1 gram of electrolyte copper (analytical reagent grade). Dissolve in 5 mL redistilled HNO_3 and make up to 1 liter with water. Final concentration is 1 mg Cu per mL (1,000 mg/L).

9.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

9.2 Instrumental Parameters (General)

9.2.1 Copper Hollow Cathode Lamp.

9.2.2 Wavelength: 324.7 nm.

9.2.3 Fuel: Acetylene.

9.2.4 Oxidant: Air.

9.2.5 Type of Flame: Oxidizing.

Note: For copper concentrations below 50 μg/L, use of furnace technique is recommended.

9.2.5.1 Numerous absorption lines are available for determination of copper. By selecting a suitable absorption wavelength, copper samples may be analyzed over a very wide range of concentrations. The following lines may be used:

327.4 nm, relative sensitivity 2
216.5 nm, relative sensitivity 7
222.5 nm, relative sensitivity 20

10.0 Iron-Specific Procedure

Optimum Concentration Range: 0.3 to 5 mg/L using a wavelength of 248.3 nm
Sensitivity: 0.12 mg/L
Approximate Detection Limit: 0.03 mg/L

10.1 Preparation of Standard Solution

10.1.1 Stock Solution: Carefully weigh 1 gram of pure iron wire (analytical reagent grade) and dissolve in 5 mL redistilled HNO_3, warming if necessary. When solution is complete, make up to 1 liter with water. 1 mL = 1 mg Fe (1,000 mg/L).

10.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

10.2 Instrumental Parameters (General)

10.2.1 Iron Hollow Cathode Lamp.

10.2.2 Wavelength: 248.3 nm.

10.2.3 Fuel: Acetylene.

10.2.4 Oxidant: Air.

10.2.5 Type of Flame: Oxidizing.

Note: The following wavelengths may also be used:

248.8 nm, relative sensitivity 2
272.9 nm, relative sensitivity 4
302.1 nm, relative sensitivity 5
252.7 nm, relative sensitivity 6
372.0 nm, relative sensitivity 10

10.2.5.1 For iron concentrations below 0.05 mg/L, use of furnace technique is recommended.

11.0 Lead-Specific Procedure

Optimum Concentration Range: 1 to 20 mg/L using a wavelength of 283.3 nm
Sensitivity: 0.5 mg/L
Approximate Detection Limit: 0.1 mg/L

11.1 Preparation of Standard Solution

11.1.1 Stock Solution: Carefully weigh 1.599 grams of pure lead nitrate ($Pb(NO_3)_2$, analytical reagent grade), and dissolve in water. When solution is complete, acidify with 10 mL redistilled HNO_3 and dilute to 1 liter with water. 1 mL = 1 mg Pb (1,000 mg/L).

11.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

11.2 Instrumental Parameters (General)

11.2.1 Lead Hollow Cathode Lamp.

11.2.2 Wavelength: 283.3 nm.

11.2.3 Fuel: Acetylene.

11.2.4 Oxidant: Air.

11.2.5 Type of Flame: Oxidizing.

Note: Analysis of lead is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust burner to maximize absorbance reading with a lead standard. Then aspirate water blank and make minute adjustments in burner alignment to minimize the signal.

11.2.5.1 For lead concentrations below 200 μg/L, use of furnace technique is recommended.

12.0 Magnesium-Specific Procedure

Optimum Concentration Range: 0.02-0.5 mg/L using a wavelength of 285.2 nm
Sensitivity: 0.007 mg/L
Approximate Detection Limit: 0.001 mg/L

12.1 Preparation of Standard Solution

12.1.1 Stock Solution: Dissolve 0.829 gram of magnesium oxide (MgO, analytical reagent grade) in 10 mL of redistilled HNO_3 and dilute to 1 liter with water. 1 mL = 0.50 mg (500 mg/L).

12.1.2 Lanthanum Chloride Solution: Dissolve 29 grams of La_2O_3, slowly and in small portions in 250 mL of concentrated HCl and dilute to 500 mL with water.

Caution: Reaction is violent.

12.1.3 Prepare dilutions of stock magnesium solution to be used as calibration standards at time of analysis. To each 10-mL volume of calibration standard and sample alike, add 1.0 mL of lanthanum chloride solution (i.e., 20 mL of standard or sample + 2 mL $LaCl_3$ = 22 mL).

12.2 Instrumental Parameters (General)

12.2.1 Magnesium Hollow Cathode Lamp.

12.2.2 Wavelength: 285.2 nm.

12.2.3 Fuel: Acetylene.

12.2.4 Oxidant: Air.

12.2.5 Type of Flame: Oxidizing.

Note: The interference caused by aluminum at concentrations greater than 2 mg/L is masked by addition of lanthanum. Sodium, potassium, and calcium cause no interference at concentrations less than 400 mg/L.

12.2.5.1 The 202.5-nm line may also be used (relative sensitivity of 25).

12.2.5.2 To cover the range of magnesium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that either the 202.5-nm line be used or the burner head be rotated. A 90° rotation of the burner head will produce about one-eighth the normal sensitivity.

13.0 Manganese-Specific Procedure

Optimum Concentration Range: 0.1 to 3 mg/L using a wavelength of 279.5 nm
Sensitivity: 0.05 mg/L
Approximate Detection Limit: 0.01 mg/L

13.1 Preparation of Standard Solution

13.1.1 Stock Solution: Carefully weigh 1 gram of manganese metal (analytical reagent grade), and dissolve in 10 mL redistilled HNO_3. When solution is complete, dilute to 1 liter with 1% (v/v) HCl. 1 mL = 1 mg Mn (1,000 mg/L).

13.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

13.2 Instrumental Parameters (General)

13.2.1 Manganese Hollow Cathode Lamp.

13.2.2 Wavelength: 279.5 nm.

13.2.3 Fuel: Acetylene.

13.2.4 Oxidant: Air.

13.2.5 Type of Flame: Oxidizing.

Note: For manganese concentrations below 25 μg/L, use of furnace technique is recommended.

13.2.5.1 The 403.1-nm line may also be used (relative sensitivity of 10).

14.0 Nickel-Specific Procedure

Optimum Concentration Range: 0.3 to 5 mg/L using a wavelength of 232.0 nm
Sensitivity: 0.15 mg/L
Approximate Detection Limit: 0.04 mg/L

14.1 Preparation of Standard Solution

14.1.1 Stock Solution: Dissolve 4.953 grams of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, analytical reagent grade) in water. Add 10 mL of concentrated nitric acid and dilute to 1 liter water. 1 mL = 1 mg Ni (1,000 mg/L).

14.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

14.2 Instrumental Parameters (General)

14.2.1 Nickel Hollow Cathode Lamp.

14.2.2 Wavelength: 232.0 nm.

14.2.3 Fuel: Acetylene.

14.2.4 Oxidant: Air.

14.2.5 Type of Flame: Oxidizing.

14.3 Interferences: The 352.4-nm wavelength is less susceptible to spectral interference and may be used. The calibration curve is more linear at this wavelength, but there is some loss of sensitivity.

Note: For nickel concentrations below 100 μg/L, use of furnace technique is recommended.

15.0 Potassium-Specific Procedure

Optimum Concentration Range: 0.1 to 2 mg/L using a wavelength of 766.5 nm
Sensitivity: 0.04 mg/L
Approximate Detection Limit: 0.01 mg/L

15.1 Preparation of Standard Solution

15.1.1 Stock Solution: Dissolve 0.1907 grams of potassium chloride (KCl, analytical reagent grade, dried at 110°C) in water and make up to 1 liter. 1 mL = 0.10 mg K (100 mg/L).

15.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

15.2 Instrumental Parameters (General).

15.2.1 Potassium Hollow Cathode Lamp.

15.2.2 Wavelength: 766.5 nm.

15.2.3 Fuel: Acetylene.

15.2.4 Oxidant: Air.

15.2.5 Type of Flame: Slightly oxidizing.

Note: In air-acetylene or other high temperature flames (> 2,800°C), potassium can experience partial ionization, which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce ionization and thereby enhance analytical results. The ionization suppressive effect of sodium is small if the ration of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1,000 μg/L) to both sample and standard solutions. If more stringent control of ionization is required, addition of cesium should be considered. Reagent blanks must be analyzed to correct for potassium impurities in buffer zone.

15.2.5.1 The 404.4-nm line may also be used (relative sensitivity of 500).

15.2.5.2 To cover the range of potassium values normally observed in surface waters (0.1 to 20 mg/L), it is suggested that the burner head be rotated. A 90° rotation of the burner head provides about one-eighth the normal sensitivity.

16.0 Silver-Specific Procedure

Optimum Concentration Range: 0.1 to 4 mg/L using a wavelength of 328.1 nm
Sensitivity: 0.06 mg/L
Approximate Detection Limit: 0.01 mg/L

16.1 Preparation of Standard Solution

16.1.1 Stock Solution: Dissolve 1.575 grams of silver nitrate ($AgNO_3$, analytical reagent grade) in water, add 10 mL concentrated HNO_3, and make up to 1 liter. 1 mL = 1 mg Ag (1,000 mg/L).

16.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

16.1.3 Iodine Solution, 1 N: Dissolve 20 grams of potassium iodide (KI, analytical reagent grade) in 50 mL of water, add 12.7 grams of iodine (I_2, analytical reagent grade), and dilute to 100 mL. Store in an amber-glass bottle.

16.1.4 Cyanogen iodide solution: To 50 mL of water add 4.0 mL concentrated ammonium hydroxide, 6.5 grams potassium cyanide, KCN, and 5.0 mL iodine solution. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

Caution: This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

16.2 Instrumental Parameters (General)

16.2.1 Silver Hollow Cathode Lamp.

16.2.2 Wavelength: 328.1 nm.

16.2.3 Fuel: Acetylene.

16.2.4 Oxidant: Air.

16.2.5 Type of Flame: Oxidizing.

Note: For silver concentrations below 30 μg/L, use of furnace technique is recommended.

16.2.5.1 Silver nitrate standards are light sensitive. Stock dilutions should be discarded after use as concentrations below 10 mg/L are not stable over long periods of time.

16.2.5.2 If absorption to container walls or formation of AgCl is suspected, make sample basic using concentrated NH_4OH and add 1 mL of (CNI) solution per 100 mL of sample. Mix sample and allow to stand for 1 hour before proceeding with analysis.

16.2.5.3 The 338.2-nm wavelength may also be used (relative sensitivity of 2).

17.0 Sodium-Specific Procedure

Optimum Concentration Range: 0.03 to 1 mg/L using a wavelength of 589.6 nm
Sensitivity: 0.015 mg/L
Approximate Detection Limit: 0.002 mg/L

17.1 Preparation of Standard Solution

17.1.1 Stock Solution: Dissolve 2.542 grams of sodium chloride (NaCl, analytical reagent grade), dried at 140°C, in water and make up to 1 liter. 1 mL = 1 mg Na (1,000 mg/L).

17.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

17.2 Instrumental Parameters (General)

17.2.1 Sodium Hollow Cathode Lamp.

17.2.2 Wavelength: 589.6 nm.

17.2.3 Fuel: Acetylene.

17.2.4 Oxidant: Air.

17.2.5 Type of Flame: Oxidizing.

Note: The 330.2-nm resonance line of sodium (relative sensitivity of 185) provides a convenient way to avoid the need to dilute more concentrated solutions of sodium.

17.2.5.1 Low-temperature flames increase sensitivity by reducing the extent of ionization of this easily ionized metal. Ionization may also be controlled by adding potassium (1,000 mg/L) to both standards and samples.

18.0 Thallium-Specific Procedure

Optimum Concentration Range: 1 to 20 mg/L using a wavelength of 276.8 nm
Sensitivity: 0.5 mg/L
Approximate Detection Limit: 0.1 mg/L

18.1 Preparation of Standard Solution

18.1.1 Stock Solution: Dissolve 1.303 grams of thallium nitrate, $TlNO_3$ (analytical reagent grade) in water. Add 10 mL of concentrated nitric acid and dilute to 1 liter with water. 1 mL = mg Tl (1,000 mg/L).

18.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

18.2 Instrumental Parameters (General)

18.2.1 Thallium Hollow Cathode Lamp.

18.2.2 Wavelength: 276.8 nm.

18.2.3 Fuel: Acetylene.

18.2.4 Oxidant: Air.

18.2.5 Type of Flame: Oxidizing.

Note: For thallium concentrations below 0.2 mg/L, use of furnace technique is recommended.

19.0 Vanadium-Specific Procedure

Optimum Concentration Range: 2 to 100 mg/L using a wavelength of 318.4 nm
Sensitivity: 0.8 mg/L
Approximate Detection Limit: 0.2 mg/L

19.1 Preparation of Standard Solution

19.1.1 Stock Solution: Dissolve 1.7854 grams of vanadium pentoxide (V_2O_5, analytical reagent grade) in 10 mL of concentrated nitric acid and dilute to 1 liter with water. 1 mL = 1 mg V (1,000 mg/L).

19.1.2 Aluminum nitrate solution: Dissolve 139 grams aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), in 150 mL of water; heat to effect solution. Allow to cool and dilute up to 200 mL.

19.1.3 Prepare dilutions of stock vanadium solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. Add 2 mL of the aluminum nitrate solution to each 100 mL sample and standard alike.

19.2 Instrumental Parameters (General)

19.2.1 Vanadium Hollow Cathode Lamp.

19.2.2 Wavelength: 318.4 nm.

19.2.3 Fuel: Acetylene.

19.2.4 Oxidant: Nitrous oxide.

19.2.5 Type of Flame: Fuel rich.

19.3 Interferences: It has been reported that high concentrations of aluminum and titanium increase the sensitivity of vanadium. Interference can be controlled by adding excess aluminum (1,000 ppm) to both samples and standards [*Talanta* 15(1968): 871].

Note: For vanadium concentrations below 0.5 mg/L, use of furnace technique is recommended.

20.0 Zinc-Specific Procedure

Optimum Concentration Range: 0.05-1 mg/L using a wavelength of 213.9 nm
Sensitivity: 0.02 mg/L
Approximate Detection Limit: 0.005 mg/L

20.1 Preparation of Standard Solution

20.1.1 Stock Solution: Carefully weigh 1 gram of zinc metal (analytical reagent grade) and dissolve cautiously in 10 mL HNO_3. When solution is complete make up to 1 liter with water. 1 mL = 1 mg Zn (1,000 mg/L).

20.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

20.2 Instrumental Parameters (General)

20.2.1 Zinc Hollow Cathode Lamp.

20.2.2 Wavelength: 213.9 nm.

20.2.3 Fuel: Acetylene.

20.2.4 Oxidant: Air.

20.2.5 Type of Flame: Oxidizing.

Note: High levels of silicon may interfere. The air-acetylene flame absorbs about 25% of the energy at the 213.9-nm line. Sensitivity may be increased by use of low-temperature flames. Some container cap liners can be a source of zinc contamination. To circumvent or avoid this problem, the use of the polypropylene caps is recommended.

Appendix

1.0 Aluminum-Specific Procedure

Optimum Concentration Range: 5 to 50 mg/L using a wavelength of 309.3 nm
Sensitivity: 1 mg/L
Approximate Detection Limit: 0.1 mg/L

1.1 Preparation of Standard Solution

1.1.1 Stock Solution: Carefully weigh 1 gram of aluminum metal (analytical reagent grade). Add 15 mL of concentrated HCl and 5 mL concentrated HNO_3 to the metal, cover beaker, and warm gently. When solution is complete, transfer quantitatively to a 1-liter volumetric flask and make up to volume with water. 1 mL = 1 mg Al (1,000 mg/L).

1.1.2 Potassium Chloride Solution. Dissolve 95 grams potassium chloride (KCl) in water and make up to 1 liter.

1.1.3 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation. To each 100 mL of standard and sample alike add 2.0 mL potassium chloride.

1.2 Instrument Parameters (General)

1.2.1 Aluminum Hollow Cathode Lamp.

1.2.2 Wavelength: 309.3 nm.

1.2.3 Fuel: Acetylene.

1.2.4 Oxidant: Nitrous oxide.

1.2.5 Type of Flame: Fuel rich.

1.3 Interferences: Aluminum is partially ionized in nitrous oxide-acetylene flame. This problem may be controlled by addition of an alkali metal (potassium, 1,000 mg/L) to both sample and standard solutions.

Note: The following may also be used:

308.2 nm, relative sensitivity 1
396.2 nm, relative sensitivity 2
394.4 nm, relative sensitivity 2.5
324.7 nm

1.3.1 For aluminum concentrations below 0.3 mg/L, furnace technique is recommended.

2.0 Antimony-Specific Procedure

Optimum Concentration Range: 1 to 40 mg/L using a wavelength of 217.6 nm
Sensitivity: 0.5 mg/L
Approximate Detection Limit: 0.2 mg/L

2.1 Preparation of Standard Solution

2.1.1 Stock Solution: Carefully weigh 2.7426 grams of antimony potassium tartrate (analytical reagent grade) and dissolve in water. Dilute to 1 liter with water. 1 mL = 1 mg Sb (1,000 mg/L).

2.1.2 Prepare dilutions of the stock solution to be used as calibration standards at time of analysis. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

2.2 Instrument Parameters (General)

2.2.1 Antimony Hollow Cathode Lamp.

2.2.2 Wavelength: 217.6 nm.

2.2.3 Fuel: Acetylene.

2.2.4 Oxidant: Air.

2.2.5 Type of Flame: Fuel lean.

2.3 Interferences

2.3.1 In presence of lead (1,000 mg/L), a special interference may occur at 217.6-nm resonance line. In this case, the 231.1-nm antimony line should be used.

2.3.2 Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards must be matched.

Note: For concentrations of antimony below 0.35 mg/L, furnace technique is recommended.

3.0 Barium-Specific Procedure

Optimum Concentration Range: 1 to 20 mg/L using a wavelength of 553.6 nm
Sensitivity: 0.4 mg/L
Approximate Detection Limit: 0.1 mg/L

3.1 Preparation of Standard Solution

3.1.1 Stock Solution: Dissolve 1.7787 grams of barium chloride ($BaCl_2 \bullet 2H_2O$ analytical reagent grade) in water and dilute to liter. 1 mL = 1 mg Ba (1,000 mg/L).

3.1.2 Potassium Chloride Solution: Dissolve 95 grams potassium chloride (KCl) in water and make up to 1 liter.

3.1.3 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. To each 100 mL of standard and sample alike add 2.0 mL potassium chloride solution. Calibration standards must be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

3.2 Instrumental Parameters (General)

3.2.1 Barium Hollow Cathode Lamp.

3.2.2 Wavelength: 553.6 nm.

3.2.3 Fuel: Acetylene.

3.2.4 Oxidant: Nitrous oxide.

3.2.5 Type of Flame: Fuel rich.

3.3 Interferences

3.3.1 Use of a nitrous oxide-acetylene flame virtually eliminates chemical interference, but barium is easily ionized in this flame and potassium must be added (1,000 mg/L) to standards and samples alike to control this effect.

3.3.2 If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2,000 mg/L lanthanum.

Note: For barium concentrations below 0.2 mg/L, use of furnace technique is recommended.

4.0 Beryllium-Specific Procedure

Optimum Concentration Range: 0.05-2 mg/L using a wavelength of 234.9 nm
Sensitivity: 0.025 mg/L
Approximate Detection Limit: 0.005 mg/L

4.1 Preparation of Standard Solution

4.1.1 Stock Solution: Dissolve 11.6586 grams of beryllium sulfate ($BeSO_4$) in water containing 2 mL of concentrated nitric acid and dilute to 1 liter. 1 mL = 1 mg Be (1,000 mg/L).

4.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

4.2 Instrumental Parameters (General)

4.2.1 Beryllium Hollow Cathode Lamp.

4.2.2 Wavelength: 234.9 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Nitrous oxide.

4.2.5 Type of Flame: Fuel rich.

4.3 Interferences

4.3.1 Sodium and silicon at concentrations greater than 1,000 mg/L have been found to severely depress beryllium absorbance.

4.3.2 Bicarbonate ion is reported to interfere, but its effect is eliminated when samples are acidified to a pH of 1.5.

4.3.3 Aluminum at concentrations of 500 μg/L is reported to depress the sensitivity of beryllium [*Spectrochim Acta*, 22(1966): 1,325].

Note: For beryllium concentrations below 0.02 mg/L, use of furnace technique is recommended.

5.0 Cadmium-Specific Procedure

Optimum Concentration Range: 0.05-2 mg/L using a wavelength of 228.8 nm
Sensitivity: 0.025 mg/L
Approximate Detection Limit: 0.005 mg/L

5.1 Preparation of Standard Solution

5.1.1 Stock Solution: Carefully weigh 2.282 grams of cadmium sulfate (3 $CdSO_4 \cdot 8 H_2O$, analytical reagent grade) and dissolve in water. Make up to 1 liter with water. 1 mL = 1 mg Cd (1,000 mg/L).

5.1.2 Prepare dilutions of stock solution to be used as calibration standards at time of analysis. Calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after sample preparation.

5.2 Instrumental Parameters (General)

5.2.1 Cadmium Hollow Cathode Lamp.

5.2.2 Wavelength: 228.8 nm.

5.2.3 Fuel: Acetylene.

5.2.4 Oxidant: Air.

5.2.5 Type of Flame: Oxidizing.

Note: For cadmium concentrations below 20 μg/L, use of furnace technique is recommended.

Metals by Inductively Coupled Plasma

Working Linear Range:	Matrix- and analyte-dependent
Reporting Limits:	Metal-dependent; see specific metal
Reporting Units:	Water, μg/L; solids, mg/kg
Matrix:	Water, soil, sediment, and waste

1.0 Scope and Application

Dissolved elements are determined in filtered and acidified samples. Total elements are determined after appropriate digestion procedures are performed. Table 1 lists elements with recommended wavelengths and typical estimated instrument detection limits using conventional pneumatic nebulization. Actual method detection limits are instrument dependent and may vary with sample matrix. The required reporting limits are listed in Table 1. The list includes all metals that may be analyzed by ICP. Certain metals, however, have regulatory limits that are often lower than the levels that may be detected by ICP. They normally include arsenic, lead, selenium, and thallium. When low detection limits are required, more sensitive techniques, such as graphite furnace, may have to be considered as the method of choice.

2.0 Method Summary

2.1 Water samples are prepared by digesting an aliquot of the sample with nitric acid and hydrochloric acid to put the metals in solution. After volume adjustment, the digestate is analyzed by ICP. Filtration of the digestate may be necessary.

2.2 A representative aliquot of soil samples is digested in nitric acid and hydrogen peroxide, and the digestate is refluxed with hydrochloric acid. After volume adjustment, the digestate is analyzed by ICP. The digestate must be filtered. A separate aliquot is used for moisture determination if results are to be reported on a dry weight basis.

2.3 Both water and soil samples may be digested with nitric acid using microwave energy. The volume of digestate is adjusted, and analysis by ICP is performed.

Table 1
Recommended Wavelengths and Detection Limits*

Analyte	Wavelength (nm)	Estimated Detection Limit Waters (µg/L)	Required Reporting Limit for Waters (µg/L)	Required Reporting Limit for Soils (mg/kg)
Aluminum	308.215	45	200	40
Antimony	206.833	32	60	12
Arsenic	193.696	53	10	2
Barium	455.403	2	200	40
Beryllium	313.042	0.3	5	1
Boron	249.773	0.3	1,000	200
Cadmium	226.502	4	5	1
Calcium	317.933	10	5,000	1,000
Chromium	267.716	7	10	2
Cobalt	228.616	7	50	10
Copper	324.754	6	25	5
Iron	259.940	7	100	20
Lead	220.353	42	3	0.6
Lithium	670.70	5	5,000	1,000
Magnesium	279.079	30	5,000	1,000
Manganese	257.610	2	15	3
Molybdenum	202.030	8	10	2
Nickel	231.604	15	40	8
Potassium	766.491	263	5,000	1,000
Selenium	196.026	75	5	1
Silver	328.068	7	10	2
Sodium	588.995	29	5,000	1,000
Thallium	190.864	40	10	2
Vanadium	292.402	8	50	10
Zinc	213.856	2	20	4

*The wavelengths listed are recommended because of their sensitivity and overall acceptance. Others may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. The use of alternative wavelengths should be reported (in nm) with the sample data. The actual method detection limits are instrument dependent and may change as the sample matrix varies.

3.1.3 Information on the listed silver and potassium wavelengths is not currently available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

Table 3
Interferent and Analyte Elemental Concentrations Used for Interference Measurements in Table 2

Analytes	mg/L	Interferents	mg/L
Al	10	Al	1,000
As	10	Ca	1,000
B	10	Cr	200
Ba	1	Cu	200
Be	1	Fe	1,000
Ca	1	Mg	1,000
Cd	10	Mn	200
Co	1	Ni	200
Cr	1	Ti	200
Cu	1	V	200
Fe	1		
Mg	1		
Mn	1		
Mo	10		
Na	10		
Ni	10		
Pb	10		
Sb	10		
Se	10		
Si	1		
Tl	10		
V	1		
Zn	10		

3.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies, especially in samples that may contain high dissolved solids or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample or internal standardization. Another problem that can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing nonlinearity. Wetting the argon before nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

3.3 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, but if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 250-mL Beaker or other appropriate vessel.

6.2 Watch Glasses.

6.3 Thermometer: Covering range of 0° to 200°C.

6.4 Whatman No. 42 Filter Paper, or equivalent.

6.5 Microwave Oven with programmable power settings up to at least 600 W (or hot plate at 95°C).

6.5.1 Commercial kitchen or home-use microwave ovens must not be used for digestion of samples under this contract. Oven cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.

6.5.2 The system should use PFA Teflon Digestion Vessels (120-mL capacity) capable of withstanding pressures of up to 110 ± 10 psi (7.5 ± 0.7 atm). Vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

6.5.3 A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. Turntable speed must be at least 3 rpm.

6.6 Polymeric Volumetric Ware in plastic (Teflon or polyethylene) 50- or 100-mL capacity.

6.7 Whatman No. 41 Filter Paper or equivalent.

6.8 Disposable polypropylene Filter Funnel.

6.9 Analytical Balance: 300-gram capacity, minimum sensitivity of ± 0.01 gram.

6.10 Polyethylene Bottles: 125-mL, with caps.

6.11 Inductively Coupled Plasma-Atomic Emission Spectrometer

6.11.1 Computer-controlled atomic emission spectrometer with background correction.

6.11.2 Radio frequency generator.

6.11.3 Argon gas supply, welding grade or better.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the ICP according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Digestion

8.1.1 Water: All references to water assume the use of ASTM Type II water.

8.1.2 Nitric Acid (HNO_3): Concentrated (specific gravity 1.41), ultrahigh purity grade or equivalent.

8.1.3 Hydrochloric Acid (HCl): Concentrated (specific gravity 1.19), ultrahigh purity grade or equivalent.

8.1.4 Hydrogen Peroxide (H_2O_2), 30%.

8.2 ICP Analysis

8.2.1 Acetic Acid (CH_3COOH): Concentrated (specific gravity 1.06), ultrahigh purity grade, TCLP or EPTOX grade, or equivalent.

8.2.2 Hydrochloric Acid (HCl): Concentrated (specific gravity 1.19), ultrahigh purity grade or equivalent.

8.2.3 Hydrochloric Acid, 1:1: Add 500 mL concentrated HCl (specific gravity 1.19) to 400 mL water and dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.2.4 Nitric Acid (HNO_3): Concentrated (specific gravity 1.41), ultrahigh purity grade or equivalent.

8.2.5 Nitric Acid, 1:1: Add 500 mL concentrated HNO_3 (specific gravity 1.41) to 400 mL water and dilute to 1 liter. **Caution:** Heat-liberating reaction.

8.2.6 Standard stock solutions may be purchased or prepared from ultrahigh purity grade chemicals or metals. All salts should be dried for 1 hour at 105°C unless otherwise specified.

8.2.6.1 Stock Aluminum Solution, 1 mL = 100 μg Al: Dissolve 0.100 gram of aluminum metal in an acid mixture of 4 mL of 1:1 HCl and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of 1:1 HCl, and dilute to 1,000 mL with water.

8.2.6.2 Stock Antimony Solution, 1 mL = 100 μg Sb: Dissolve 0.2669 gram $K(SbO)C_4H_4O_6$ in water, add 10 mL 1:1 HCl, and dilute to 1 liter with water.

8.2.6.3 Stock Arsenic Solution, 1 mL = 100 μg As: Dissolve 0.1320 gram of As_2O_3 in 100 mL of water containing 0.4 gram NaOH. Acidify solution with 2 mL concentrated HNO_3 and dilute to 1,000 mL with water.

8.2.6.4 Stock Barium Solution, 1 mL = 100 μg Ba: Dissolve 0.1516 gram $BaCl_2$ (dried at 250°C for 2 hours) in 10 mL water with 1 mL 1:1 HCl. Add 10.0 mL 1:1 HCl and dilute to 1 liter with water.

8.2.6.5 Stock Beryllium Solution, 1 mL = 100 μg Be: Do not dry. Dissolve 1.966 grams $BeSO_4 \cdot 4H_2O$ in water. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.6 Stock Boron Solution, 1 mL = 100 μg B: Do not dry. Dissolve 0.5716 gram anhydrous H_3BO_3 in water and dilute to 1 liter. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered, and store in desiccator to prevent entrance of atmospheric moisture.

8.2.6.7 Stock Cadmium Solution, 1 mL = 100 μg Cd: Dissolve 0.1142 gram CdO in a minimum amount of 1:1 HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.8 Stock Calcium Solution, 1 mL = 100 μg Ca: Suspend 0.2498 gram $CaCO_3$ (dried at 180°C for 1 hour before weighing) in water, and dissolve cautiously with a minimum amount of 1:1 HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.9 Stock Chromium (Hexavalent) Solution, 1 mL = 100 μg Cr: Dissolve 0.1923 gram of CrO_3 in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.10 Stock Cobalt Solution 1 mL = 100 μg Co: Dissolve 0.1000 gram of cobalt metal in a minimum amount of 1:1 HNO_3. Add 10.0 mL 1:1 HCl and dilute to 1 liter with water.

8.2.6.11 Stock Copper Solution, 1 mL = 100 μg Cu: Dissolve 0.1252 gram CuO in a minimum amount of 1:1 HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.12 Stock Iron Solution, 1 mL = 100 μg Fe: Dissolve 0.1430 gram Fe_2O_3 in a warm mixture of 20 mL 1:1 HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5 mL of concentrated HNO_3, and dilute to 1 liter with water.

8.2.6.13 Stock Lead Solution, 1 mL = 100 μg Pb: Dissolve 0.1599 gram $Pb(NO_3)_2$ in a minimum amount of 1:1 HNO_3. Add 10.0 mL of concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.14 Stock Magnesium Solution, 1 mL = 100 μg mg: Dissolve 0.1658 gram MgO in a minimum amount of 1:1 HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.15 Stock Manganese Solution, 1 mL = 100 μg Mn: Dissolve 0.1000 gram of manganese metal in acid mixture of 10 mL concentrated HCl and 1 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.16 Stock Molybdenum Solution, 1 mL = 100 μg Mo: Dissolve 0.2043 gram $(NH_4)_2MoO_4$ in water and dilute to 1 liter.

8.2.6.17 Stock Nickel Solution, 1 mL = 100 μg Ni: Dissolve 0.1000 gram of nickel metal in 10 mL hot concentrated HNO_3 cool, and dilute to 1 liter with water.

8.2.6.18 Stock Potassium Solution, 1 mL = 100 μg K: Dissolve 0.1907 gram KCl, dried at 110°C, in water. Dilute to 1 liter.

8.2.6.19 Stock Selenium Solution, 1 mL = 100 μg Se: Do not dry. Dissolve 0.1727 gram H_2SeO_3 (actual assay 94.6%) in water and dilute to 1 liter.

8.2.6.20 Stock Silver Solution, 1 mL = 100 μg Ag: Dissolve 0.1575 gram $AgNO_3$ in 100 mL of deionized, distilled water and 10 mL concentrated HNO_3. Dilute to 1 liter with water.

8.2.6.21 Stock Sodium Solution, 1 mL = 100 μg Na: Dissolve 0.2542 gram NaCl in water. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.22 Stock Thallium Solution, 1 mL = 100 μg Tl: Dissolve 0.1303 gram $TlNO_3$ in water. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.23 Stock Vanadium Solution, 1 mL = 100 μg V: Dissolve 0.2297 gram NH_4VO_3 in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1 liter with water.

8.2.6.24 Stock Zinc Solution, 1 mL = 100 μg Zn: Dissolve 0.1245 gram ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL HNO_3 and dilute to 1 liter with water.

8.2.7 Mixed Calibration Standard Solutions: Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. Add 2 mL of 1:1 HNO_3 and 10 mL of 1:1 HCl and dilute to 100 mL with deionized, distilled water. Before preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer mixed standard solutions to an FEP fluorocarbon or

unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change with aging. Calibration standards should initially be verified using a quality control sample and monitored weekly for stability. Although not specifically required, some typical calibration standard combinations follow when using the specific wavelengths listed in Table 1.

8.2.7.1 Mixed Standard Solution I: Manganese, beryllium, cadmium, lead, and zinc.

8.2.7.2 Mixed Standard Solution II: Barium, copper, iron, vanadium, and cobalt.

8.2.7.3 Mixed Standard Solution III: Molybdenum, silica, arsenic, and selenium.

8.2.7.4 Mixed Standard Solution IV: Aluminum, calcium, chromium, nickel, potassium, and sodium.

8.2.7.5 Mixed Standard Solution V: Antimony, boron, magnesium, silver, and thallium.

Note: If addition of silver to recommended acid combination results in an initial precipitation, add 15 mL of deionized, distilled water and warm flask until solution clears. Cool and dilute to 100 mL with water. For this acid combination, silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

8.2.8 Two types of blanks are required for analysis. The calibration blank is used in establishing the analytical curve, whereas the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

8.2.8.1 The calibration blank is prepared by diluting 2 mL of 1:1 HNO_3 and 10 mL of 1:1 HCl to 100 mL with water. Prepare sufficient quantity to be used to flush system between standards and samples.

8.2.8.2 The reagent blank (or preparation blank) shall contain all reagents in the same volumes as used in processing samples. The reagent blank should be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

8.2.9 In addition to the calibration standards, a continuing calibration standard, an interference check sample, and a quality control sample are also required for the analysis.

8.2.9.1 The analyst prepares the continuing calibration standard for continuing calibration verification by combining compatible elements at a concentration equivalent to the mid-point of the concentration range expected in the samples. This must be purchased from a different vendor than that from which the calibration standards were obtained.

8.2.9.2 The interference check sample is prepared by the analyst, obtained from the U.S. EPA if available, or purchased as EPA-certified solution.

8.2.9.3 The quality control sample for the initial calibration verification should be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. The EPA will either supply a quality control sample or information on where one of equal quality can be procured. The laboratory control sample (LCS) is digested; it must not be from the calibration stock, although it may be the same as the continuing calibration verification standard (CCVS) or initial calibration verification standard (ICVS).

9.0 Calibration Procedures

9.1 Instrument Calibration

9.1.1 Set up instrument with proper operating parameters for make and model of instrument being used. The instrument should be allowed to become thermally stable before beginning.

9.1.2 Initiate appropriate operating configuration of computer.

9.1.3 Profile and calibrate instrument according to manufacturer's recommended procedures. Begin calibration by aspirating calibration blank. Aspirate mixed calibration standard solutions, flushing system with calibration blank between standards. At least two replicate exposures are required for standardization.

9.1.4 Perform instrument calibration once every 24 hours and each time an analytical run is set up.

10.0 Sample Preparation

10.1 Acid Digestion of Water Samples

10.1.1 Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker.

10.1.2 Add 2 mL of 1:1 HNO_3 and 10 mL of 1:1 HCl to sample.

10.1.3 Cover with watch glass or similar cover and heat on steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil.

10.1.4 Cool sample and filter to remove insoluble material.

Note: In place of filtering, the sample may, after dilution and mixing, be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

10.1.5 Adjust sample volume to 100 mL with water. Sample is now ready for analysis.

10.2 Acid Digestion of Soil Samples

10.2.1 Mix sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 gram) a 1.00- to 1.50-gram portion of sample, recording the weight in a digestion log notebook, and transfer to beaker.

10.2.2 Add 10 mL of 1:1 HNO_3, mix slurry, and cover with watch glass.

10.2.3 Heat sample to 95°C, and reflux for 10 minutes without boiling. Allow sample to cool, add 5 mL of concentrated HNO_3, replace watch glass, and reflux for 30 minutes. Do not allow volume to be reduced to less than 5 mL while maintaining a covering of solution over bottom of beaker.

10.2.4 After second reflux step has been completed and sample has cooled, add 2 mL of water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return beaker to hot plate for warming to start peroxide reaction. Care should be taken to ensure that losses do not occur because of excessively vigorous effervescence. Heat until effervescence subsides, and cool beaker.

10.2.5 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until effervescence is minimal or until general sample appearance is unchanged.

Note: Do not add more than a total of 10 mL 30% H_2O_2.

10.2.6 If sample is being prepared for furnace AA analysis of Sb, the flame AA, or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 mL of 1:1 HCl and 10 mL of water, return covered beaker to hot plate, and heat for 10 minutes more. After cooling, filter through Whatman No. 42 filter paper and dilute to 100 mL with water.

Note: In place of filtering, sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. Diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Dilute digestate 1:1 (200 mL final volume) with acidified water to maintain constant acid strength. Sample is ready for analysis.

10.3 Percent Solids Determination for Soil Samples: If results for soil samples are to be reported on a dry weight basis, determine percent solids as follows.

10.3.1 Immediately after weighing of sample to be processed for analysis, add 5 to 10 grams of sample to tared weighing dish. Weigh and record weight to nearest 0.01 gram.

10.3.2 Place weighing dish plus sample, with cover tipped to allow for moisture escape, in drying oven maintained at 103° to 105°C. Sample handling and drying should be conducted in well ventilated areas.

10.3.3 Dry sample overnight (12 to 24 hours) but no longer than 24 hours. If dried less than 12 hours, should be documented that constant weight was attained.

10.3.4 Remove sample from oven and cool in desiccator with weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 gram. Do not analyze dried sample.

10.3.5 Calculate percent solids as: (1)

$$\% \text{ Solids} = \frac{\text{Dry weight of sample}}{\text{Wet weight of sample}} \times 100$$

This value will be used for calculating analytical concentration on a dry weight basis.

10.3.6 Concentrations determined in the digestate are to be reported on the basis of the dry weight sample using the equation: (2)

$$\text{mg/kg, Dry weight} = \frac{C \times V}{W \times S}$$

Where:

C	=	Concentration (mg/L)
V	=	Final volume (L) after sample preparation
W	=	Weight of wet sample (kg)
S	=	% Solids/100

10.4 Microwave Sample Preparation

10.4.1 Calibration of Microwave Unit

10.4.1.1 Calibration is a critical step that must be performed before use of any microwave unit. The microwave unit should be calibrated every 6 months. Calibration data for each calibration should be available for review during onsite audits. In order that absolute power settings may be interchanged from one microwave to another, actual delivered power should be determined.

10.4.1.2 Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple point calibration, then the point where linearity begins should be identified. For example: calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% power settings can be

applied and the data plotted. The nonlinear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to 5.5 to 6 watts and becomes the smallest unit of power that can be controlled. If 20 to 40 watts are contained from 99 to 100%, that portion of the microwave calibration is not controllable by 3 to 7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in the portion of the power scale.

10.4.1.3 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave unit to another. This is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. Place water in Teflon beaker (or beaker made of material that does not absorb microwave energy) and stir before measuring the temperature. Glass beakers absorb microwave energy and may not be used. The initial temperature of the water should be between 19° and 25°C. The beaker is circulated continuously through the field for at least 2 minutes at full power. Remove beaker from microwave, stir water vigorously, and record final temperature. The final reading is the maximum temperature reading after each energy exposure. The measurements must be accurate to ± 0.1°C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled to room temperature. Otherwise, use a fresh water sample.

10.4.1.4 Absorbed power is determined as: (3)

$$P = \frac{(K)\ (Cp)\ (m)\ (DT)}{t}$$

Where:

P	=	Apparent power absorbed by sample in W (joules per second)
K	=	Conversion factor for thermochemical cal/s to W (= 4.184)
Cp	=	Heat capacity, thermal capacity, or specific heat (calories $gram^{-1} \times °C^{-1}$) of water (=1.0)
m	=	Mass of sample (grams)

DT = Final temperature minus initial temperature (°C)

t = Time (seconds)

Using 2 minutes and 1 kg of distilled water, the equation simplifies to:

$$P = (DT)(34.87) \quad (4)$$

The microwave user can now relate power in watts to the percent power setting of the microwave.

10.4.2 Cleaning Procedure

10.4.2.1 Initial Cleaning of PFA Vessels: Before first use, new vessels should be annealed. A pretreatment/cleaning procedure should be followed. The procedure calls for heating the vessels for 96 hours at 200°C. Vessels should be disassembled during annealing, and sealing surfaces (the top of the vessel or its rim) should not be used to support the vessel during annealing.

10.4.2.1.1 Rinse in water.

10.4.2.1.2 Immerse in 1:1 HCl for at least 3 hours after cleaning bath has reached a temperature just below boiling.

10.4.2.1.3 Rinse in water.

10.4.2.1.4 Immerse in 1:1 HNO_3 for at 3 hours after cleaning bath has reached temperature just below boiling.

10.4.2.1.5 Rinse vessels with copious amounts of water before use for any analyses.

10.4.2.2 Cleaning Procedure between Sample Digestions

10.4.2.2.1 Wash entire vessel in hot water using laboratory-grade nonphosphate detergent.

10.4.2.2.2 Rinse with 1:1 nitric acid (HNO_3).

10.4.2.2.3 Rinse three times with water. If contaminants are found in preparation blank, it is mandatory that steps 9.4.2.1.2 through 9.4.2.1.5 be strictly adhered to.

10.4.3 Water Sample Microwave Digestion Procedure

10.4.3.1 Measure a 45-mL aliquot of sample into Teflon digestion vessels using volumetric glassware.

10.4.3.2 Add 5 mL of high purity concentrated HNO_3 to digestion vessels.

10.4.3.3 Record weight of each vessel to 0.02 gram.

10.4.3.4 Place caps with pressure release valves on vessels hand tight, then tighten using constant torque to 12 foot-pounds. Place five sample vessels in carousel, evenly spaced around its periphery in microwave unit. Connect each sample vessel with a collection vessel using venting tubes. Attach each sample vessel to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of overpressurization. Assembly of vessels into carousel may be done inside or outside the microwave.

10.4.3.5 The procedure is energy balanced for five 45-mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than five samples are digested, fill remaining vessels with 45 mL of tap or Type II water and 5 mL of concentrated HNO_3.

10.4.3.6 Newer microwave ovens may be capable of higher power settings that may allow more samples. If the analyst wishes to digest more than five samples at a time, the analyst may use different power settings as long as they result in the same time temperature conditions defined in the power programming for this method.

10.4.3.7 Initial sample temperature should be 24° ± 1°C. The preparation blank should have 45 mL of water and the same amount (5 mL) of acid added to the samples.

10.4.3.8 The microwave unit first-stage program should be set to give 545 watts for 10 minutes, and the second-stage program to give 344 watts for 10 minutes. This sequence brings the samples to 160° ± 4°C in 10 minutes and permits a slow rise to 165° to 170°C during the second 10 minutes.

10.4.3.9 Following the 20-minute program, the samples are left to cool in the microwave unit for 5 minutes with the exhaust fan ON. The samples or carousel may then be removed from the microwave unit. Before opening any vessel let it cool until no longer hot to the touch.

10.4.3.10 After sample vessel has cooled, weigh sample vessel and compare to initial weight reported in preparation log. Any sample vessel exhibiting a loss $\leq$ 0.5 gram should have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with sample preparation. Any sample vessel exhibiting a > 0.5-gram loss shall be identified in the preparation log and the sample redigested.

10.4.3.11 Sample Filtration: Shake digested samples well to mix in any condensate within digestion vessel before opening. Filter digestates into 50-mL glass volumetric flasks through ultraclean filter paper and dilute to 50 mL (if necessary). Samples are now ready for analysis. Sample results should be corrected by a factor of 1.11 to report final concentration values based on an initial volume of 45 mL.

10.4.4 Soil Sample Microwave Digestion Procedure

10.4.4.1 Add a representative 0.5 $\pm$ 0.050 gram of sample to Teflon PFA vessel.

10.4.4.2 Add 10 $\pm$ 0.1 mL of concentrated nitric acid. If vigorous reaction occurs, allow reaction to stop before capping vessel.

10.4.4.3 Cap vessel, then tighten using constant torque to 12 foot-pounds, according to manufacturer's direction.

10.4.4.4 Connect sample vessel to overflow vessel using Teflon PFA tubing.

10.4.4.5 Weigh vessel assembly to nearest 0.01 gram.

10.4.4.6 Place sample vessels in groups of two sample vessels or six sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. If fewer samples are to be digested (e.g., three samples plus one blank), then remaining vessels should be filled with 10 mL of water to achieve the full complement of vessels.

10.4.4.7 Attach each sample vessel to clean, double-ported vessel to collect any sample expelled from sample vessel in the event of overpressurization. Vessels may be assembled into carousel either inside or outside the microwave. Connect overflow vessel to center well of oven.

10.4.4.8 Preparation blank shall have 0.5 mL of water and the same amount (10 mL) of acid added to samples. It will later be diluted to 50 mL in the same manner as the samples.

10.4.4.9 Irradiate the two-sample vessel group at 344 watts for 10 minutes, or the six-vessel group at 574 watts for 10 minutes. This program brings the samples to 175°C in 5.5 minutes and remains between 170° to 180°C for the balance of the 10-minute irradiation period. Pressure should peak at less than 6 atmospheres for most samples. Pressure may exceed these limits in the case of high concentrations of carbonate or organic compounds. In those cases, pressure will be limited by relief pressure of vessel to 7.5 ± 0.7 atmospheres.

10.4.4.10 Allow vessels to cool for at least 5 minutes with exhaust fan ON before removing them from microwave unit. Allow vessels to cool to room temperature before opening. Uncap vessels carefully and vent in a fume hood.

10.4.4.11 Weigh each vessel assembly. If weight of acid plus sample has decreased by more than 10% from the original weight, discard digestates. Determine reason for loss. Losses typically are attributed to digestion time longer than 10 minutes, using too large of a sample, or having improper heating conditions. Once source of losses has been corrected, prepare a new set of samples for digestion.

10.4.4.12 Sample Filtration: Shake sample well to mix in any condensate within digestion vessel before being opened. Filter digestion vessel into a 50-mL glass volumetric flask through ultraclean filter paper. Rinse sample digestion vessel, cap, connecting tube, and (if venting occurred) overflow vessel into 50-mL glass flask. Dilute to 50 mL. Samples are now ready for analysis.

10.4.4.13 Calculations: Concentrations determined in digestate are to be reported on the basis of dry weight of sample using the equation:(5)

$$\text{mg/kg, Dry weight} = \frac{C \times V}{W \times S}$$

Where:

C	=	Concentration (mg/L)
V	=	Final volume after sample preparation (L)
W	=	Weight of wet sample (kg)
S	=	% Solids/100

11.0 Sample Analysis

11.1 Operating Conditions: Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects should be investigated and established for each individual analyte line on the particular instrument. All measurements should be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

11.2 Analytical Sequence

11.2.1 At least two replicate exposures are required for each determination.

11.2.2 The following sequence will be followed:

11.2.2.1 Initial Calibration Verification (ICV) Standard.

11.2.2.2 Initial Calibration Blank (ICB).

11.2.2.3 Detection Limit Standard (CRI).

11.2.2.4 Interference Check Samples (ICSA and ICAB).

11.2.2.5 First 7 samples.

11.2.2.6 Continuing Calibration Verification (CCV) Standard.

11.2.2.7 Continuing Calibration Blank (CCB).

11.2.2.8 Next 10 samples.

11.2.2.9 CCV Standard and CCB bracketing every 10 or 20 samples.

11.2.2.10 CRI.

11.2.2.11 Interference Check Standards (ICSA and ICSAB).

11.2.2.12 CCV Standard.

11.2.2.13 CCB.

11.2.3 The ICV Standard should be run immediately after instrument calibration.

11.2.4 The ICB should follow the ICV Standard.

11.2.5 The Detection Limit (CRI or two times the CRDL for ICP) Standard and the ICSA and ICSAB should be analyzed at the beginning and end of each analytical run or at least twice per 8-hour work shift, whichever is more frequent.

11.2.6 The CCV Standard should be analyzed every 10 or 20 samples or every 2 hours during an analysis, whichever is more frequent. It should also be analyzed after the last sample.

11.2.7 The CCB should be analyzed after each CCV Standard.

11.2.8 The term "sample" as used in this procedure includes not only field samples but also the CRI, ICSA, and ICSAB, and the Quality Control Samples (Preparation Blank, Matrix Spike, Duplicate, Laboratory Control Sample, and the Serial Dilution). The quality control samples may be analyzed at any time during the analytical run.

11.3 Calculations

11.3.1 If dilutions were performed, the appropriate factor should be applied to the calculated values.

11.3.2 If results are to be reported on a dry weight basis, adjustment should be made for the solids content.

11.3.3 Units should be clearly specified.

11.4 Spiked Sample Analysis

11.4.1 The spiked sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before digestion (i.e., before addition of other reagents). At least one spiked sample analysis should be performed per analytical batch (20 samples or fewer) of a similar matrix type.

11.4.2 If the spiked sample analysis is performed on the same sample chosen for the duplicate sample analysis, spike recovery calculations should be performed using the results of the sample designated as the "original sample." The averages of the duplicate results cannot be used for determining percent recovery.

11.4.3 Samples identified as field blanks cannot be used for spiked sample analysis.

11.4.4 Specific samples may be designated to be used for the spike sample analysis.

11.4.5 The analyte spike should be added in the amount given in Table 4 for each element analyzed.

11.4.6 The levels shown indicate concentrations in the final digestate of the spiked sample when the wet weight of 1 gram of sample is taken for analysis. Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. Appropriate adjustment shall be made for microwave digestion procedure where 0.5 gram of sample or 50.0 mL (45.0 mL of samples plus 5.0 mL of acid) of aqueous sample are required for analysis.

Table 4
Spiking Levels for ICP Spike Sample Analysis

Element	Water (μg/L)	Soil (1) (mg/kg)
Aluminum	2,000	*
Antimony	500	100
Arsenic	2,000	400
Barium	2,000	400
Beryllium	50	10
Cadmium	50	10
Calcium	*	*
Chromium	200	40
Cobalt	500	100
Copper	250	50
Iron	1,000	*
Lead	500	100
Magnesium	*	*
Manganese	500	100
Mercury	N/A	N/A
Nickel	500	100
Potassium	*	*
Selenium	2,000	400
Silver	50	10
Sodium	*	*
Thallium	2,000	400
Vanadium	500	100
Zinc	500	100

*No spike required.

Note: Elements without spike levels and not designated with an asterisk, shall be spiked at appropriate levels.

11.4.7 If spike recovery is not at or within the limits of 75 to 125%, the data of all samples received associated with that spike sample and determined by the same analytical method will be flagged with the letter "N." An exception to this rule is granted when the sample concentration exceeds the spike concentration by a factor of four or more. Then the data should be reported unflagged even if the percent recovery does not meet the 75 to 125% recovery criteria.

11.4.8 When the predigestion spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion will be performed for elements that do not meet the specified criteria (exception: Ag). Spike the unspiked aliquot of the sample at two times the indigenous level or two times the required reporting limit. No acceptance criteria or data validation flag is required.

11.4.9 When there is more than one spiked sample per matrix, if one spiked sample recovery is not within acceptance criteria, flag all the samples of the same matrix. Individual component percent recoveries (%R) are calculated as: (6)

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

Where:

SSR = Spiked sample result
SR = Sample result
SA = Spike added

11.5 Duplicate Sample Analysis

11.5.1 At least one duplicate sample should be analyzed per analytical batch (20 samples or fewer) of a similar matrix type. Duplicates cannot be averaged for reporting purposes.

11.5.2 Samples identified as field blanks cannot be used for duplicate sample analysis. Specific samples may be designated to be used for duplicate sample analysis.

11.5.3 The relative percent difference (RPD) for each component is calculated as: (7)

$$RFD = \frac{S - D}{S + D} \times 200$$

Where:

RPD	=	Relative percent difference
S	=	First sample value (original)
D	=	Second sample value (duplicate)

11.5.4 A control limit of 20% for RPD should be used for original and duplicate sample values greater than or equal to five times the required reporting limit. A control limit of plus or minus the required reporting limit should be used for sample values less than five times required reporting limit, and the value of the control limit should be entered in the "Control Limit" column on the duplicate analysis report.

11.5.5 If one result is above the five times required reporting level and the other is below, use plus or minus required reporting limit as the control limit. If both sample values are less than the IDL, the RPD is not calculated on the report form. For solid sample or duplicate results less than five times the required reporting limit, report the value of the required reporting limit, corrected for sample weight and percent solids, as the control limit.

11.5.6 If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an asterisk (*). When there is more than one duplicate sample per batch, if one duplicate result is not within contract criteria, flag all samples of the same matrix.

11.6 ICP Serial Dilution Analysis

11.6.1 Before reporting concentration data for the analyte elements, the laboratory should analyze and report the results of the ICP Serial Dilution Analysis. The Serial Dilution Analysis should be performed on at least one sample per analytical batch per matrix. Samples identified as field blanks cannot be used for Serial Dilution Analysis.

11.6.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the instrumental detection limit in the original sample), the serial dilution (a fivefold dilution) should then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analyte is not at or within 10%, a chemical or physical interference effect should be suspected, and the data for all affected analytes in the samples received associated with that serial dilution should be flagged with an "E."

11.6.3 The percent difference for each component is calculated as: (8)

$$\% \text{ Difference} = \frac{I - S}{I} \times 100$$

Where:

I = Initial sample result
S = Serial dilution result (instrument reading × 5)

11.6.4 When there is more than one serial dilution per batch, if one serial dilution result is not within acceptance criteria, flag all samples of the same matrix.

11.7 Interelement Corrections for ICP

11.7.1 ICP interelement correction factors should be determined before the start of contract analyses and at least annually thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg should be determined for all ICP instruments at all wavelengths used for each analyte reported by ICP. Correction factors for spectral interference due to analytes other than Al, Ca, Fe, and Mg should be reported if they were applied. The effect of other suspected interferences must be evaluated as specified in the project-specific SAP.

11.7.2 If the instrument was adjusted in a way that may affect the ICP interelement correction factors, the factors should be redetermined and the results submitted for use. Results from interelement correction factors determination should be reported on the designated forms for all parameters.

FM-INO-0040

Mercury Analysis by Cold Vapor (Atomic Absorption Spectrometry)

Working Linear Range:	Matrix specific
Reporting Limit:	0.2 μg/L; 0.04 mg/kg
Reporting Units:	Water, μg/L; Solids, mg/kg
Matrix:	Water, soil, sediment, and waste

1.0 Scope and Application

1.1 The method is based on the absorption of radiation at 253.7 nm by mercury vapor. 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. Absorption is measured as a function of the mercury concentration.

1.2 The method is applicable to the determination of organic and inorganic mercury in water samples, aqueous wastes, mobility-procedure extracts, soils, and solid wastes.

1.3 An automated procedure has been included for the analysis of water samples. The procedure suffers from interference effects from high chloride in the sample. Heavy precipitate formation in some wastewaters and effluents upon the addition of concentrated sulfuric acid has also been reported. When these problems are encountered, the manual method should be used.

2.0 Method Summary

Organic and inorganic forms of mercury in the sample are oxidized to the mercuric state by potassium permanganate and potassium persulfate. Excess oxidizers are reduced using a sodium-chloride-hydroxylamine hydrochloride solution. The mercuric ions are then reduced to the elemental state by adding stannous chloride. The mercury vapor is aerated and swept into an absorption cell. The absorbance reading is measured and compared with those of standard solutions.

3.0 Interferences

3.1 Water Samples——Manual Method

3.1.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

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

3.1.3 Sea waters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL). During the oxidation step, chlorides are converted to free chlorine that will also absorb radiation of 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

3.2 Water Samples——Automated Method

3.2.1 Some seawaters and wastewaters high in chlorides have shown a positive interference, probably because of the formation of free chlorine.

3.2.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the sample cannot be analyzed by the automated method.

3.3 Soil Samples——Manual Method

3.3.1 The same types of interferences that may occur in water samples are also possible with sediments (e.g., sulfides, high copper, high chlorides, etc.).

3.3.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling acids and mercury must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and a lab coat or apron for clothing protection.

4.3 Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into a fume hood or passing the vapor through some absorbing media such as (1) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4 or (2) 0.25% iodine in a 3% KI solution is recommended. A specially treated charcoal that will absorb mercury vapor is also available.

5.0 Sample Collection and Handling

Minimum sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Water Samples——Manual Method

6.1.1 Atomic Absorption Spectrophotometer: Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

Note: Instruments designed specifically for measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.1.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

6.1.3 Recorder: Any multirange variable speed recorder compatible with the UV detection system is suitable.

6.1.4 Absorption Cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1″ O.D. × 4½″. The ends are ground perpendicular to the longitudinal axis, and the quartz windows (1″ diameter × 1/16″ thick) are cemented in place.

6.1.4.1 The cell is strapped to a burner for support and aligned in the light beam by use of two 2″ × 2″ cards. One-inch diameter holes are cut in the middle of each card; the cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to find the maximum transmittance.

6.1.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

6.1.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

6.1.7 Aeration Tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

6.1.8 Drying Tube: 6″- × 3/4″-diameter tube containing 20 grams of magnesium perchlorate.

Note: In place of the magnesium perchlorate drying tube, a small reading lamp with 60 W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6.2 Water Samples——Automated Method

6.2.1 Technicon Auto Analyzer or equivalent instrumentation consisting of:

6.2.1.1 Sampler II with provision for sample mixing.

6.2.1.2 Manifold.

6.2.1.3 Proportioning Pump II or III.

6.2.1.4 High-temperature heating bath with two distillation coils (Technicon Part No. 116-0163 or equivalent) in series.

6.2.2 Vapor-Liquid Separator.

6.2.3 Absorption Cell, 100 mm long, 10-mm diameter with quartz windows.

6.2.4 Atomic Absorption Spectrophotometer: Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

Note: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

6.2.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

6.2.6 Recorder: Any multirange variable speed recorder compatible with the UV detection system is suitable.

6.3 Soil Samples——Manual Method: See Apparatus listed for Water Samples——Manual Method.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the mercury analyzer according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine glassware before each use for scratches and cracks, and replace as necessary.

8.0 Reagents and Calibration Standards

8.1 Water Samples——Manual Method

8.1.1 Water: All references to water assume the use of ASTM Type II water.

8.1.2 Sulfuric Acid (H_2SO_4), Concentrated: Reagent grade.

8.1.3 Sulfuric Acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter with water. **Caution:** Heat-liberating reaction.

8.1.4 Nitric Acid (NHO_3), Concentrated: Reagent grade.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

8.1.5 Stannous Sulfate: Add 25 grams of stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

8.1.6 Sodium Chloride-Hyroxylamine Sulfate Solution: Dissolve 12 grams of sodium chloride and 12 grams of hydroxylamine sulfate in water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

8.1.7 Potassium Permanganate, 5% Solution w/v: Dissolve 5 grams of potassium permanganate, mercury free in 100 mL of water.

8.1.8 Potassium Persulfate, 5% Solution w/v: Dissolve 5 grams of potassium persulfate in 100 mL of water.

8.1.9 Stock Mercury Solution: Dissolve 0.1354 gram of mercuric chloride in 75 mL of water. Add 10 mL of concentrated nitric acid and adjust volume to 100 mL. 1 mL = 1 mg Hg.

8.1.10 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 μg/mL. Working standards and dilutions of stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. The acid should be added to the flask as needed before addition of the aliquot.

8.2 Water Samples——Automated Method

8.2.1 Water: All references to water assume the use of ASTM Type II water.

8.2.2 Sulfuric Acid (H_2SO_4), Concentrated: Reagent grade.

8.2.3 Sulfuric Acid, 2 N: Dilute 56 mL of concentrated sulfuric acid to 1 liter with water. **Caution:** Heat-liberating reaction.

8.2.4 Sulfuric Acid, 10%: Dilute 100 mL of concentrated sulfuric acid to 1 liter with water. **Caution:** Heat-liberating reaction.

8.2.5 Nitric Acid (HNO_3), Concentrated: Reagent grade. If high reagent blank is obtained, it may be necessary to distill the nitric acid.

8.2.6 Nitric Acid, 0.5% Wash Solution: Dilute 5 mL of concentrated nitric acid to 1 liter with water. **Caution:** Heat-liberating reaction.

8.2.7 Stannous Sulfate: Add 50 grams stannous sulfate to 500 mL of 2 N sulfuric acid. The mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

8.2.8 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 grams of sodium chloride and 30 grams of hydroxylamine sulfate in water to 1 liter. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

8.2.9 Potassium Permanganate, 0.5% Solution w/v: Dissolve 5 grams of mercury-free potassium permanganate in 1 liter of water.

8.2.10 Potassium Permanganate, 0.1 N: Dissolve 3.16 grams of potassium permanganate in water and dilute to 1 liter.

8.2.11 Potassium Persulfate: 0.5% Solution, w/v. Dissolve 5 grams potassium persulfate in 1 liter of water.

8.2.12 Stock Mercury Solution: Dissolve 0.1354 gram of mercuric chloride in 75 mL of water. Add 10 mL of concentrated nitric acid and adjust volume to 100 mL. 1.0 mL = 1.0 mg Hg.

8.2.13 Working Mercury Solution: Make successive dilutions of stock mercury solution to obtain working standard containing 0.1 μg/mL. Working standard and dilutions of stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. The acid should be added to the flask as needed before addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 μg Hg/L.

8.2.14 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate and 10% sulfuric acid.

8.3 Soil Samples——Manual Method

8.3.1 Water: All references to water assume the use of ASTM Type II water.

8.3.2 Sulfuric Acid (H_2SO_4), Concentrated: Reagent grade.

8.3.3 Sulfuric Acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter water. **Caution:** Heat-liberating reaction.

8.3.4 Nitric Acid (NHO_3) Concentrated: Reagent grade.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

8.3.5 Stannous Sulfate: Add 25 grams stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

8.3.6 Sodium Chloride-Hyroxylamine Sulfate Solution: Dissolve 12 grams of sodium chloride and 12 grams of hydroxylamine sulfate in water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

8.3.7 Potassium Permanganate, 5% Solution w/v: Dissolve 5 grams of potassium permanganate, mercury free in 100 mL of water.

8.3.8 Potassium Persulfate, 5% Solution w/v: Dissolve 5 grams of potassium persulfate in 100 mL of water.

8.3.9 Stock Mercury Solution: Dissolve 0.1354 gram of mercuric chloride in 75 mL of water. Add 10 mL of concentrated nitric acid and adjust volume to 100 mL. 1 mL = 1 mg Hg.

8.3.10 Working Mercury Solution: Make successive dilutions of stock mercury solution to obtain working standard containing 0.1 μg/mL. Working standard and dilutions of stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. Acid should be added to the flask as needed before addition of the aliquot.

9.0 Calibration Procedures

9.1 Initial Calibration Verification (ICV)

9.1.1 Immediately after the AA system has been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of U.S. EPA ICV Standards (ICVS) at each wavelength used for analysis. When measurements exceed the control limits of 80 to 120% of the true values, the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified.

9.1.2 If the ICVSs are not available from the EPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration but within the calibration range. An independent standard is defined as a standard composed of analytes from a different source than those used for instrument calibration.

9.2 Continuing Calibration Verification (CCV)

9.2.1 To ensure calibration accuracy during each analysis, a standard is to be used for continuing calibration verification (CCVS) and must be analyzed and reported for every wavelength used for analysis of each analyte, at a frequency of one in 10 or every 2 hours during an analysis, whichever is more frequent. The standard must also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the continuing calibration standard must be at or near the mid-range levels of the calibration curve.

9.2.2 The same continuing calibration standard must be used throughout the analysis.

9.2.3 Each CCVS analyzed must reflect the conditions of analysis of all associated analytical samples (the preceding 10 or 20 analytical samples or the preceding analytical samples up to the previous CCVS). The duration of analysis, rinses, and other related operations that may affect the CCVS measured result may not be applied to the CCVS to an extent greater than that applied to the associated analytical samples. For instance, the difference in time between a CCVS analysis and the blank immediately following it, as well as the difference in time between the CCVS and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCVS.

9.2.4 If recovery of the CCVS exceeds the control limits of 80 to 120% of the true value, the analysis must be stopped, the problem corrected, the instrument recalibrated, and calibration verified. The preceding 10 or 20 analytical samples or all analytical samples analyzed since the last compliant calibration verification must be reanalyzed for the analytes affected.

9.3 Detection Limit Standard (CRA): To verify linearity near required reporting limits, the laboratory must analyze an AA Standard (CRA) at the required reporting limit of 0.2 μg/L or the instrument detection limit (IDL), whichever is greater, at the beginning of each analytical run but not before the ICV.

9.4 ICB and CCB Analyses: A calibration blank must be analyzed at each wavelength used for analysis immediately after every initial and continuing calibration verification at a frequency of 10% or every 2 hours during the run, whichever is more frequent for ASL C and D. The blank must be analyzed at the beginning of the run and after the last analytical sample.

Note: A CCB must be run after the last CCV that was run after the last analytical sample of the run. If the absolute value blank result exceeds required reporting limits, terminate analysis, correct the problem, recalibrate, verify the calibration, and reanalyze the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank.

10.0 Sample Preparation

10.1 Water samples containing solids must be blended and then mixed while being sampled if total mercury is to be reported.

10.2 Percent Solids Determination for Soil Samples: Soil samples must be analyzed wet. However, if results of soil samples are to be reported on a dry weight basis, perform percent solids determination as follows on a separate portion of the sample:

10.2.1 Immediately following weighing of the sample to be processed for analysis, add 5 to 10 grams of sample to tared weighing dish. Weigh and record weight to nearest 0.01 gram.

10.2.2 Place weighing dish plus sample, with cover tipped to allow for moisture escape, in drying oven maintained at 103° to 105°C. Sample handling and drying should be conducted in well-ventilated area.

10.2.3 Dry sample overnight (12 to 24 hours) but no longer than 24 hours. If dried less than 12 hours, the analyst must document that constant weight was attained. Remove sample from oven and cool in desiccator with weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 gram. Do not analyze the dried sample.

10.2.4 Calculate percent solids with the following formula: (1)

$$\% \text{ Solids} = \frac{\text{Sample dry weight}}{\text{Sample wet weight}} \times 100$$

The value will be used for calculating analytical concentration on a dry weight basis.

10.2.5 The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample: (2)

$$\text{Concentration, dry weight (mg/kg)} = \frac{C \times V}{W \times S}$$

Where:

C	=	Concentration (mg/L)
V	=	Final volume after sample preparation (L)
W	=	Weight of wet sample (kg)
S	=	% Solids/100

11.0 Sample Analysis

11.1 Operating Conditions: Because of differences between various makes and models of instruments, no detailed operating instructions can be given for each instrument. Instrument settings recommended by the manufacturer should be followed.

11.2 Water Samples——Manual Method

11.2.1 Calibration Standard Reaction: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of working mercury solution containing 0 to 1.0 μg of mercury to a series of 300-mL BOD bottles. Add enough water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated sulfuric acid and 2.5 mL of concentrated nitric acid to each bottle. Add 15 mL of $KMnO_4$ (5%) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (5%) to each bottle and heat for 2 hours in a water bath maintained at 95°C. Alternatively, cover the BOD bottles with foil and heat in an autoclave for 15 minutes at 120°C and 15 pounds. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate. When solution has been decolorized wait 30 seconds, add 5 mL of the stannous sulfate solution, and immediately attach bottle to aeration apparatus to form a closed system. At this point, the sample is allowed to stand without manual agitation.

11.2.2 Sample Reaction

11.2.2.1 Transfer 100 mL, or an aliquot diluted to 100 mL, containing not more than 1.0 μg of mercury, to a 300-mL BOD bottle. Add 5 mL of sulfuric acid and 2.5 mL of concentrated nitric acid mixing after each addition. Add 15 mL of potassium permanganate solution (5%) to each sample bottle.

Note: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

11.2.2.2 For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate (5%) to each bottle and heat for 2 hours in a water bath at 95°C.

11.2.2.3 Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. Purge headspace in BOD bottle for at least 1 minute, add 5 mL of stannous sulfate, and immediately attach bottle to aeration apparatus.

Note: Add reductant in 6-mL increments until $KMnO_4$ is completely reduced.

11.2.3 Analyze Standards and Samples

11.2.3.1 Allow circulating pump, previously adjusted to a rate of 1 liter per minute, to run continuously. The absorbance will increase and reach maximum within 30 seconds.

Note: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

11.2.3.2 As soon as the recorder pen levels off (about 1 minute), open bypass valve and continue aeration until absorbance returns to its minimum value. Close bypass valve, remove stopper and frit from BOD bottle, and continue aeration.

Note: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media such as (1) equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or (2) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is available.

11.3 Water Samples——Automated Method

11.3.1 Standard and Sample Reaction and Analysis: In this method the standards and samples are reacted and analyzed sequentially on the autoanalyzer system.

11.3.1.1 Set up manifold.

11.3.1.2 Feeding all reagents through system with nitric acid (0.5%) wash solution through sample line, adjust heating bath to 105°C.

11.3.1.3 Turn on atomic absorption spectrophotometer and adjust instrument settings as recommended by manufacturer. Align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

11.3.1.4 Arrange working mercury standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0, and 20.0 μg Hg/L in sampler and start sampling.

11.3.1.5 Complete loading of sample tray with samples to be analyzed.

11.3.1.6 After the analysis is complete, put all lines except H_2SO_4 line in water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush coils in high temperature heating bath by pumping stannous sulfate through sample lines followed by water. This will prevent manganese oxide buildup.

11.3.2 Calculations: Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

11.4 Soil Samples——Manual Method

11.4.1 Calibration Standard Reaction: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of working mercury solutions containing 0 to 1.0 μg of mercury to a series of 300-mL BOD bottles. Add enough water to each bottle to make a total volume of 10 mL. Add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 and heat 2 minutes in water bath at 95°C. Allow sample to cool. Add 50 mL distilled water, 15 mL of $KMnO_4$ solution, and 8 mL of potassium persulfate solution to each bottle, and return to water bath for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate. Add 50 mL of water. Treating each bottle individually, add 5 mL of stannous sulfate solution and immediately attach bottle to aeration apparatus. At this point the sample is allowed to stand without manual agitation.

11.4.2 Sample Reaction

11.4.2.1 Weigh a representative 0.2 $\pm$ 0.01-gram portion of wet sample and place in bottom of BOD bottle. Add 5 mL of sulfuric acid and 2.5 mL of concentrated nitric acid, mixing after each addition. Heat 2 minutes in water bath at 95°C. Cool, add 50 mL water, 15 mL potassium permanganate solution (5%), and 8 mL potassium persulfate solution (5%) to each sample bottle. Mix thoroughly and place in water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hyrdoxylamine sulfate to reduce excess permanganate. Add 55 mL of water. Treating each bottle individually, purge headspace of sample bottle for at least 1 minute, add 5 mL of stannous sulfate, and immediately attach bottle to aeration apparatus.

11.4.2.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 gram of sample. Add 5 mL saturated $KMnO_4$ solution and 8 mL potassium persulfate solution to the bottle and cover with a piece of aluminum foil. The sample is autoclaved at 121°C and 15 pounds for 15 minutes. Cool, dilute to 100 mL with water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate. Purge headspace of sample bottle for at least 1 minute.

11.4.3 Analyze Standards and Samples: Allow circulating pump, previously adjusted to a rate of 1 liter per minute, to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as recorder pen levels off (about 1 minute), open bypass valve and continue aeration until absorbance returns to its minimum value. Close bypass valve, remove fritted tubing from the BOD bottle, and continue aeration.

Note: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media such as (a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4, or (b) 0.25% iodine in a 3% KI solution. A specially treated charcoal that will absorb mercury vapor is also available.

11.5 Analytical Sequence

11.5.1 The following sequence must be followed:

- Initial Calibration Verification (ICV) Standard
- Initial Calibration Blank (ICB)
- Detection Limit (CRA)
- First 8 samples
- Continuing Calibration Verification (CCV) Standard
- Continuing Calibration Blank (CCB)
- Next 10 samples
- CCV Standard and CCB bracketing every 10 samples
- Last 10 samples
- CCV Standard
- CCB

11.5.2 The ICV Standard must be analyzed immediately after instrument calibration.

11.5.3 The ICB must follow the ICV Standard.

11.5.4 The CRA standard must be analyzed at the beginning and end of each analytical run or at least twice per 8-hour working shift, whichever is more frequent.

11.5.5 The CCV Standard must be analyzed every 10 samples or every 2 hours during an analysis, whichever is more frequent. It must also be analyzed after the last sample.

11.5.6 The CCB must be analyzed after each CCV Standard.

11.5.7 The term "sample" (when not qualified) as used in this method includes not only field samples but also the CRA and the Quality Control Samples (Preparation Blank, Matrix Spike, and Duplicate). Quality Control Samples may be analyzed at any time during the analytical run.

12.0 Calculations

12.1 For liquid samples:

12.1.1 Construct a standard curve by plotting standard peak heights versus micrograms of mercury.

12.1.2 Determine peak height of sample from chart and read micrograms of mercury from standard curve.

12.1.3 Calculate mercury concentration in the sample as follows: (3)

$$\text{Conc. } (\mu g/L) = \frac{\mu g \text{ Hg (curve)} \times 1{,}000}{\text{Sample volume (mL)}}$$

12.2 For solid samples:

12.2.1 Construct standard curve by plotting standard peak heights versus micrograms of mercury.

12.2.2 Determine peak height of sample from chart and read micrograms of mercury from standard curve.

12.2.3 Calculate mercury concentration in sample as follows: (4)

$$\text{Conc. } (\mu g/kg) \text{ (Dry weight)} = \frac{\mu g \text{ Hg (curve)}}{\text{Sample weight (kg)}}$$

13.0 Data Package Deliverables

Data package deliverables are determined by the method, Analytical Support Levels, and project-specific sampling and analysis plan and are discussed in the General Laboratory Requirements.

14.0 Quality Control Requirements

Quality control requirements are determined by the method, Analytical Support Levels, and project-specific Sampling and Analysis Plan.

Analytical Support Level B

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	80—120%	Recalibrate
CCVS	1/20	80—120%	Recalibrate
Method Blank	1/20	DR	Qualify data
LCS	Begin	80—120%	Recalibrate
Matrix Spike	1/20	75—125%	Qualify data
Lab Replicate Sample	1/20	0—20% RPD	Qualify data

Analytical Support Levels C and D

Requirement	Frequency	Acceptance Range	Corrective Action
ICVS	Begin	80—120%	Recalibrate
CCVS	1/10	80—120%	Recalibrate
ICB	Begin	DR*	Qualify data
CCB	1/10	DR*	Qualify data
PB	1/10	DR*	Qualify data
LCS	Begin	80—120%	Recalibrate
Predigestion Spike	1/20	75—125%	Post-dig. spike
Postdigestion Spike	as needed	75—125%	Qualify data
Duplicate Sample	1/20	0—20% RPD	Qualify data
CRA	Begin	DR	Recalibrate

ICS	Begin	DR	Qualify data
Serial Dilution	1/20	DR	Qualify data

Where:

Begin	beginning of the analytical period
ICVS	initial calibration verification sample
CCVS	continuing calibration verification sample
ICB	initial calibration blank
CCB	continuing calibration blank
PB	preparation blank
LCS	laboratory control sample
CRA	detection limit verification sample
RPD	relative percent difference
DR	Data are qualified based on results using the data review and validation guidance, Section 11 of the SCQ. For DR*, refer to the 1988 CLP SOW for acceptance limit guidance.
ICS	interference check sample

15.0 References

15.1 *CLP Statement of Work for Inorganic Analysis,MultiMedia,Multi-Concentration.* July 1988.

15.2 *Test Methods for Evaluating Solid Waste,*SW-846, Methods 7470 and 7471, 3rd ed. September 1986.

15:3 *Standard Methods for the Examination of Water and Wastewater.* 16th ed. 1985.

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