Roy F. Weston, Inc.
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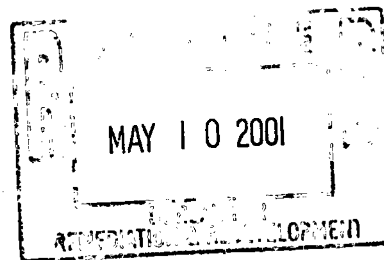

9 May 2001

→ Binyoti Felix - SER/RR

Mr. Russell D. Hart
Remedial Project Manager (HSRW-6J)
U.S. Environmental Protection Agency
Region V
77 West Jackson Boulevard
Chicago, IL 60604

RFW Work Order No. 02687.007.003
KMC Work Order No. 40-50-01-AKW-B

Re: Revised LTTD QAPP Pages
Moss-American Site, Milwaukee, Wisconsin

Dear Mr. Hart:

Attached please find two copies of revised pages to the Project Work Plans prepared by Williams Environmental Services, Inc. (Williams). A cover letter prepared by Williams is also included that documents the responses to individual Agency comments.

The revised QAPP pages should replace existing pages of Appendix B in Section IV (Sampling and Analysis Plan) of the Project Work Plans. The laboratory SOPs should be inserted at the end of Appendix C in Section IV (Sampling and Analysis Plan) of the Project Work Plans.

Should further clarification of this transmittal be required, please contact me at (847) 918-4142 or Keith Watson at (405) 270-3747.

Very truly yours,

ROY F. WESTON, INC.

Thomas P. Graan, Ph.D.
Principal Project Manager

TPG/ld

cc: K. Watson, KMC
G. Edelstein, WDNR

I:\WO\MOSSAMER\30104.WPD

May 3, 2001

Mr. Sam Matheny
Roy F. Weston, Inc.
750 E. Bunker Court, Suite 500
Vernon Hills, IL 60061

Subject: Treatment of Soils Using LTTD System
Moss-American Site
Milwaukee, Wisconsin
Transmittal No.: 048
No. of Pages: 2

Re: Revised QAPP Pages
Williams Project No.: 04302000

Dear Mr. Matheny:

Williams Environmental Services, Inc. (Williams) is in receipt of your e-mail of Wednesday, May 2, 2001, confirming the EPA's approval of Williams' Quality Assurance Project Plan (QAPP) for the Moss-American site. As per Transmittal Nos. 037 and 047, Williams agreed to provide revised pages to the QAPP upon receiving final approval of its responses. Therefore, a finalized QAPP is attached for your use, with revisions as described below:

Transmittal No. 037, Response 1: No revisions to the text are required.

Transmittal No. 037, Response 2: DQOs for environmental data collecting activities have been inserted into the text in Sections 1.3.2 and 1.3.3.

Transmittal No. 037, Response 3: A revised organization chart is provided as Figure 2.1.

Transmittal No. 037, Response 4: Revised SOPs have previously been forwarded via e-mail.

Transmittal No. 037, Response 5: Williams has made the appropriate revision to Section 8.2.2 to again indicate that Williams' QCM will review laboratory data when received to validate compliance with the QA/QC criteria.

Transmittal No. 037, Comments to Appendix C: As noted in Response 4, revised SOPs have previously been forwarded by e-mail. Furthermore, Williams will continue to submit any revisions to the SOPs as they become available.

Transmittal No. 047, Response A: No revisions to the text are required.

A Williams Group International. Inc. Company
2075 West Park Place Stone Mountain. Georgia 30087 770/879-4107 Fax: 770/879-4831

Transmittal No. 047, Response B: A revised organization chart is provided as Figure 2.1.

Transmittal No. 047, Response C: A copy of the SOP for Method 8021B has previously been provided via e-mail.

Transmittal No. 047, Response D: See Response 5 above.

Transmittal No. 047, Response E: No revisions to the text are required.

Transmittal No. 047, Response F: The laboratory's extraction procedure for PAHs in soil is currently undergoing revision and will be forwarded when received. Until that time, as noted in Transmittal No. 047, the preparation method as written in SW-846 Revision III will be followed to ensure consistency throughout the project.

Please review the revised QAPP and distribute copies as appropriate. Should you have any questions, please call Mark Fleri or me at (770) 879-4107.

Sincerely,

WILLIAMS ENVIRONMENTAL SERVICES, INC.

Greg Whetstone
Senior Project Engineer
GTW:pc

Enclosures
cc: Z. Lowell Taylor
Mark A. Fleri
Randy Camp
Brian Yearick
Job File 04302000

APPENDIX B
QUALITY ASSURANCE PROJECT PLAN
MOSS-AMERICAN SITE
MILWAUKEE, WISCONSIN

SUBMITTED TO:

ROY F. WESTON, INC.
750 E. Bunker Court, Suite 500
Vernon Hills, Illinois 60061
Attention: Mr. Tom Graan

KERR-McGEE CHEMICAL, LLC
123 Robert S. Kerr Avenue
Oklahoma City, Oklahoma 73102
Attention: Mr. Keith Watson

SUBMITTED BY:

WILLIAMS ENVIRONMENTAL SERVICES, INC.
2075 West Park Place
Stone Mountain, Georgia 30087
Phone: (800) 247-4030; (770) 879-4107
Fax: (770) 879-4831

Submittal Date: October 27, 2000; Revised February 7, 2001
Approved: May 2, 2001

Williams Project No.: 04302000

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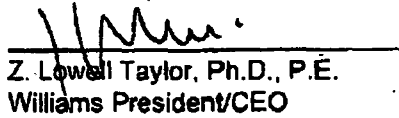
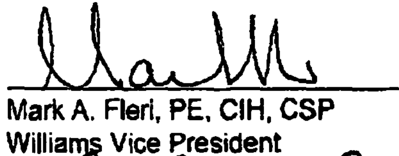
APPROVAL PAGE

By their signatures, the undersigned certify that this Quality Assurance Project Plan (QAPP) is approved and will be utilized at the Moss-American Site.



Z. Lowell Taylor, Ph.D., P.E.
Williams President/CEO

5-3-01
Date



Mark A. Fleri, PE, CIH, CSP
Williams Vice President

5-3-01
Date

Randy Camp
Williams Project Manager

5-3-01
Date

Bryant Burkes
Williams Site Superintendent

5-3-01
Date

Brian Yearick
Williams Quality Control Manager

5-3-01
Date

Sam Matheny
Weston Project Manager

Date

Russell Hart
EPA Project Manager

Date

EPA QA Manager

Date

WDNR Project Manager

Date

Section 1

Introduction

1.1 INTRODUCTION

This Quality Assurance Project Plan (QAPP) is part of the Sampling and Analysis Plan (SAP) for the Moss-American site. The SAP serves as a guide to the sampling activities associated with planning and implementing the Moss-American site remedies specified in the Technical Specifications prepared by Weston. The QAPP presents the analytical methods and procedures to be used during implementation of SAP activities.

This QAPP sets forth the analytical methods and procedures to be used. The Methods for Performance (Appendix A of the SAP) and this QAPP are integrated and cross-referenced where applicable to minimize redundancy.

This QAPP has been prepared in a manner consistent with the following documents:

- Environmental Protection Agency (EPA) reference document, Guidance for Conducting Remedial Investigations and Feasibility Studies under CERCLA – Interim Final (EPA/540/G-89/004);
- Test Methods for Evaluating Solid Waste (SW-846), EPA (1986), Revision 3, 1997;
- EPA Requirements for Preparing Quality Assurance Project Plans, EPA QA/R-5;
- Guidance for Preparation of Combined Work/Quality Assurance Project Plans for Environmental Monitoring, EPA Office of Water Regulations and Standards, May 1984.

Information contained in the QAPP has been organized into the following sections:

Section	Content
1	Project Description
2	Project Organization and Responsibilities
3	Quality Assurance Objectives for Measurement Data
4	Sampling Procedures
5	Sample and Document Custody
6	Calibration Procedures and Frequency
7	Analytical Procedures
8	Data Reduction, Validation, and Reporting
9	Field and Laboratory Quality Control Checks
10	Performance and System Audits
11	Preventive Maintenance
12	Data Assessment Procedures
13	Corrective Action
14	Quality Assurance Reports to Management

Details are provided in subsequent sections. This document contains pertinent information from the SAP, Methods for Performance (Appendix A of the SAP), and the Laboratory Quality Management Plan (LQMP) (Appendix C) related to the measurement and evaluation of remedial action and analytical data.

1.2 SAP OBJECTIVES

The purpose of the QAPP is to present the quality assurance/quality control (QA/QC) procedures to be implemented during the SAP activities. The QAPP has been developed to provide data quality sufficient to meet the SAP objectives. The overall objective for the Moss-American remedial action SAP is to provide analytical data to demonstrate remedial action performance standards have been achieved.

1.3 SAP AND REMEDIAL ACTION DATA QUALITY OBJECTIVES

1.3.1 General

A summary of the analytical requirements and quality objectives for the project is provided in Table 1.2. Quality data for the parameters listed will be achieved if the Relative Percent Deviation and Control Limits identified in Table 1.2 are met. All of these data quality objectives are consistent with EPA SW-846 methodology. The quality criteria identified in Table 1.2 will be used to ensure that the data generated during the remediation will be of adequate quality and sufficient quantity to form a sound, legally defensible database for decision making purposes relative to the above objectives.

To obtain information necessary to meet the objectives stated above and identified in Table 1.2, the following field sampling will be conducted:

- Feed and Treated Soil Sampling for LTTD Performance Monitoring
- Treated Water Sampling to Demonstrate Conformance with Performance Standards.

1.3.2 Feed and Treated Soil Sampling and Analysis

The analysis of feed and treated soil samples collected for monitoring of the LTTD system will take place in an off-site laboratory.

- **Data Uses** – The analysis of soil samples in the off-site laboratory program for LTTD performance monitoring is designed to generate data to verify that the LTTD unit can achieve performance levels for the contaminants of concern during the full-scale implementation.

- **Data Types** – The soil sampling program for LTTD monitoring includes the collection and off-site analysis of samples for the contaminants of concern, as required. Table 1.1 presents the number of each type of analysis including QA/QC samples.

- **Data Quality Objectives** – The 7-step DQO process, as outlined in EPA's *Requirements for Quality Assurance Project Plans (QA/R-5)*, will be implemented for both treated soil and feed soil sampling, as outlined below:

  Treated Soil Sampling

  Step 1: State the Problem – Verify that all treated soil cleanup criteria are achieved for selected VOCs, PAHs, and cPAHs so that treated soil may be backfilled on site.
  Step 2: Identify the Decision – Collect one treated soil sample per 800-ton treated soil batch using the treated soil sampling procedure outlined in Appendix A, Table 2.3 of the SAP.
  Step 3: Identify the Inputs to the Decision – Inputs to the decision to backfill the treated soils will be the results of the treated soil analyses for the contaminants of concern, as identified by the Technical Specifications.
  Step 4: Define the Boundaries – The treated soil cleanup criteria identified for the project will be the initial boundary in determining compliance. It will also be necessary to verify compliance with the QA/QC criteria identified in Table 1.2.
  Step 5: Develop a Decision Rule – If each of the contaminants of concern achieves compliance with the cleanup criteria and is within the

acceptable range for QA/QC compliance, the soils will be backfilled on site. If any of the samples indicates failure to comply with the cleanup criteria, and the QA/QC is acceptable, the soils will be retreated. If any of the samples indicates failure to comply with the cleanup criteria, and the QA/QC is not acceptable, the sample will be reanalyzed.

Step 6: Specify Limits on Decision Errors – QA/QC criteria for each of the methods are delineated in Table 1.2. If the QA/QC criteria fall within the specified ranges, the analyses are acceptable.

Step 7: Optimize the Design for Obtaining Data – Sample collection procedures are identified in Appendix A, Table 2.3 of the SAP, and sample analysis procedures are identified in the SOPs. No changes to these procedures are anticipated.

Feed Soil Sampling

Step 1: State the Problem – Determine the feed concentrations of selected VOCs, PAHs, and cPAHs, as well as moisture content, to verify data presented in the Technical Specifications and optimize process controls.

Step 2: Identify the Decision – Collect one sample per 800 tons of feed soil using the feed soil sampling procedure outlined in Appendix A, Table 2.2 of the SAP.

Step 3: Identify the Inputs to the Decision – The feed soil sampling frequency will be the same as the treated soil sampling frequency, so that necessary correlations may be drawn between the feed soil results, treated soil results, and the LTTD operating parameters. The collection frequency of samples for the determination of moisture content is as specified by Weston.

Step 4: Define the Boundaries – There are no defined boundaries for the analysis of contaminants in the feed soil. This information has no regulatory significance and will be used by Williams only to verify the data presented in the Technical Specifications.

Step 5: Develop a Decision Rule – Not applicable.

Step 6: Specify Limits on Decision Errors – Not applicable.

Step 7: Optimize the Design for Obtaining Data – Not applicable.

- **Data Quantity** – Table 1.1 provides a summary of the sample quantity estimated for the Moss-American site based on the Technical Specifications and the best estimate of soil quantity (currently 99,000 tons).

Table 1.1
Moss-American Field and QC Sample Quantity Summary

Sample Matrix/ Parameters	Estimated Sample Quantity	Field QC Analysis						Estimated Field QC Total	Laboratory QC Analyses				Estimated Overall Total
		Trip Blank		Field Duplicate		Rinse Blank			MS		MSD		
		Freq.	No.	Freq.	No.	Freq.	No.		Freq.	No.	Freq.	No.	
Feed Soil Samples													
VOCs, cPAHs, PAHs	124	0	0	1/20	7	1/20	7	138	1/20	7	1/20	7	152
Moisture	124	0	0	1/20	7			131	0	0	0	0	131
Treated Soil Samples for Treatment System Performance Monitoring													
VOCs, cPAHs, PAHs	124	0	0	1/20	7	1/20	7	138	1/20	7	1/20	7	152
Wastewater Samples Prior to Discharge													
VOCs, Metals, TSS	3	1/disch.	3	1/20	1	N/A	N/A	7	1/20	1	1/20	1	9

Estimated Quantity of Soil Requiring Treatment 99,000 tons

Notes:

a) Specific VOCs, cPAHs, PAHs and metals to be analyzed are defined in the specifications.

b) Sample quantities are based on the estimated soil quantity and a sampling frequency of 1/800 tons for feed and treated soil. Should the sampling frequency change, Table 1.1 will be modified accordingly.

Table 1.2
Summary of Analytical Requirements and QA/QC Criteria

Matrix	Parameter	Method [a]	Treatment Standard	Units	PQL	MDL	(%) RPD	(%) Control Limits
Soil	Benzene	8021 B	0.0055	mg/kg	0.001	0.0007	20	70-130
Soil	Ethylbenzene	8021 B	2.9	mg/kg	0.001	0.0002	20	70-130
Soil	Toluene	8021 B	1.5	mg/kg	0.001	0.0008	20	70-130
Soil	Xylene (total)	8021 B	4.1	mg/kg	0.001	0.0009	20	70-130
Soil	Fluorene	8270 C	100	mg/kg	0.3	0.040	20	59-121
Soil	Naphthalene	8270 C	0.4	mg/kg	0.3	0.037	20	21-133
Soil	cPAHs [b]	8270 C	1.9	mg/kg	---------- see breakdown below ----------			
	Benzo(a)anthracene			mg/kg	0.3	0.038	20	33-143
	Benzo(b)fluoranthene			mg/kg	0.3	0.029	20	24-159
	Benzo(k)fluoranthene			mg/kg	0.3	0.031	20	11-162
	Benzo(a)pyrene		48	mg/kg	0.3	0.022	20	17-163
	Benzo(g,h,i)perylene			mg/kg	0.3	0.028	20	D-219
	Chrysene			mg/kg	0.3	0.019	20	17-168
	Dibenzo(a,h)anthracene			mg/kg	0.3	0.029	20	D-227
	Indeno(1,2,3-cd)pryrene			mg/kg	0.3	0.026	20	D-171
Water	VOCs [c]	8021 B	5	mg/l	0.001	Note d	20	Note d
Water	Chromium	6010 [e]	8	mg/l	0.002	0.00053	20	85-115
Water	Copper	6010 [e]	6	mg/l	0.002	0.00144	20	85-115
Water	Lead	6010 [e]	2	mg/l	0.005	0.0017	20	85-185
Water	Mercury	7470	0.0026	mg/l	0.0002	0.000025	20	85-115
Water	Nickel	6010 [e]	4	mg/l	0.005	0.00056	20	85-115
Water	Zinc	6010 [e]	8	mg/l	0.005	0.00289	20	85-115
Water	TSS	160.2	100	mg/l	2	0.513	20	126-166

D - a reportable detection

<u>Notes:</u>
a) Methods are from SW-846 unless otherwise noted.
b) cPAHs include benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene.
c) The specific list of VOCs is defined in Table 00800-01 of the Technical Specifications.
d) The MDL and Control limits vary for individual volatiles. Control limits for most volatiles are 70 - 130 %.
e) Use GFAA methods (7000 series) if the ICP method (6010) does not achieve sufficiently low detection limits.

- **Sampling and Analytical Methods** – The laboratory analytical methods to be utilized are listed on Table 1.2. Field sampling procedures are described in Appendix A of the SAP (Methods for Performance).

- **QC Limits** – Project analytical precision and accuracy for soil samples will comply with laboratory reported QC limits stated in Table 1.2. Any excursions outside these limits will be evaluated to determine project impact.

1.3.3 Treated Wastewater Sampling and Analysis

The treated wastewater sampling program will be implemented to demonstrate that any required discharges meet permit requirements for the operation of the system.

- **Data Uses** – The treated wastewater sampling program is designed to demonstrate conformance with performance standards to verify that wastewater discharge performance standards are achieved by the wastewater treatment system during full-scale operation.

- **Data Types** – As described in Section 3 of the SAP, wastewater quality data will consist of sampling the treated wastewater for the contaminants of concern summarized in Tables 1.1 and 1.2.

- **Data Quality Objectives** – The 7-step DQO process, as outlined in EPA's *Requirements for Quality Assurance Project Plans (QA/R-5)*, will be implemented for treated water sampling, as outlined below:

  Step 1: State the Problem – Verify that all treated water cleanup criteria are achieved prior to acceptance by the MMSD and discharge to the on-site sanitary sewer.

  Step 2: Identify the Decision – Collect one treated water sample prior to discharge to the MMSD via the on-site sanitary sewer, as per Appendix A, Table 2.4 of the SAP.

  Step 3: Identify the Inputs to the Decision – Inputs to the decision to discharge the treated water will be the results of the treated water analyses for the parameters identified in Williams' discharge permit, issued by the MMSD.

  Step 4: Define the Boundaries – The treated water discharge criteria identified in the permit will be the initial boundary in determining compliance. It will also be necessary to verify compliance with the QA/QC criteria identified in Table 1.2.

  Step 5: Develop a Decision Rule – If each of the parameters achieves compliance with the discharge limits and is within the acceptable range for QA/QC compliance, the water will be discharged to the on-site sanitary sewer, in accordance with Williams' permit. If any

of the samples indicates failure to comply with the discharge limits, and the QA/QC is acceptable, the water will be retreated. If any of the samples indicates failure to comply with the discharge limits, and the QA/QC is not acceptable, the sample will be reanalyzed.

Step 6: Specify Limits on Decision Errors – QA/QC criteria for each of the methods are delineated in Table 1.2. If the QA/QC criteria fall within the specified ranges, the analyses are acceptable.

Step 7: Optimize the Design for Obtaining Data – Sample collection procedures are identified in Appendix A, Table 2.4 of the SAP, and sample analysis procedures are identified in the SOPs. No changes to these procedures are anticipated.

- **Data Quantity** – The treated wastewater sampling program to demonstrate conformance with performance standards will consist of grab samples prior to discharge of any wastewater. The frequency of QA/QC samples for off-site analytical work is summarized on Table 1.1.

- **Sampling and Analytical Methods** – the laboratory analytical methods for chemical constituents are summarized on Table 1.2. Field sampling procedures are presented in Appendix A of the SAP.

- **QC Limits** – Precision and accuracy QC limits for the analytes of concern are listed on Table 1.2. These limits will be used during data evaluation to assess analytical performance.

1.3.4 Other Data Quality Objectives

Data representativeness is addressed by the sample quantities and locations specified in the Technical Specifications and included in the SAP. Data comparability is intended to be achieved through the use of standard EPA-approved methods. Data completeness will be assessed daily/weekly (whichever is appropriate for sampling schedule) and at the conclusion of SAP activities as discussed in Section 12.

1.4 PROJECT SCHEDULE

The anticipated schedule for completion of remediation activities at the Moss-American site is provided as Figure 1.1.

Section 2

Project Organization and Responsibility

The remedial activities at the Moss-American site are being performed under the oversight of Weston. The sampling and analysis program will be performed by a project team consisting of representatives from Williams. Individual responsibilities are further described below, with an organization chart provided as Figure 2.1. Analytical services will be provided by Philip Analytical Services located in Reading, Pennsylvania.

Williams' Principal-in-Charge is the corporate officer with overall responsibility for the financial, operational, and health and safety aspects of the project. The Principal-in-Charge interacts with the client, regulatory agencies, and Williams' Project Manager as required.

Williams' Project Manager is responsible for coordinating LTTD operations with the sampling team and providing liaison with the Weston Project Manager, WDNR representatives, and other designated representatives. Some of his responsibilities include:

- Management and coordination of all aspects of the project as defined in the SAP and Technical Specifications with an emphasis on adhering to the objectives of the SAP and Technical Specifications;
- Review of documents and deliverables prepared by Williams; and
- Assuring corrective actions are taken for deficiencies cited during audits of SAP activities.

The Site Manager will be responsible for management and coordination of on-site activities and management of site personnel.

A Quality Control Manager (QCM) who reports to Williams' Project Manager will also be appointed. The duties of the QCM include overall responsibility of quality control functions to ensure work is performed in accordance with the specifications and submittals. The QCM, or his representative, will also be responsible for sampling activities as outlined below:

- Preparing and shipping soil sampling equipment, soil sample containers, and shipping containers to the test site
- Assigning and recording soil sample numbers

- Reviewing and approving Sample Collection Sheets
- Directing and/or participating in soil sampling activities
- Overseeing preservation of soil samples in the field
- Preparing soil samples and packaging them for shipment to the laboratory
- Preparing chain-of-custody and request for analysis forms for soil samples
- Shipping soil samples to the laboratory.

One Laboratory Project Manager (LPM) will be appointed for each laboratory that provides analytical services for the project. His/her responsibilities will include:

- Receiving, verifying, and documenting that incoming field samples correspond to the chain-of-custody information
- Maintaining records of incoming samples
- Tracking samples through processing, analysis, and disposal
- Preparing QC samples for analysis during the project
- Verifying that personnel are trained and qualified in specified laboratory QC and analytical procedures
- Verifying that laboratory QC and analytical procedures are being followed as specified in the laboratory QA/QC Plan
- Reviewing QC and sample data during analysis and determining if repeat samples or analyses are needed
- Submitting certified QC and sample analysis results and data packages to the designated personnel
- Archiving analytical data.

In addition to Williams' personnel, EPA personnel associated with the project include the USEPA Region 5 Remedial Project Manager (RPM) and the Quality Assurance Reviewer (QAR). Their management responsibilities are identified below:

- USEPA Region 5 RPM: Responsible for directing and/or overseeing and coordinating all project activities.
- USEPA Region 5 QAR: Responsible for QAPP review and approval. The QAR is also responsible for any internal and external performance and system audits.

QUALITY CONTROL PROJECT ORGANIZATION

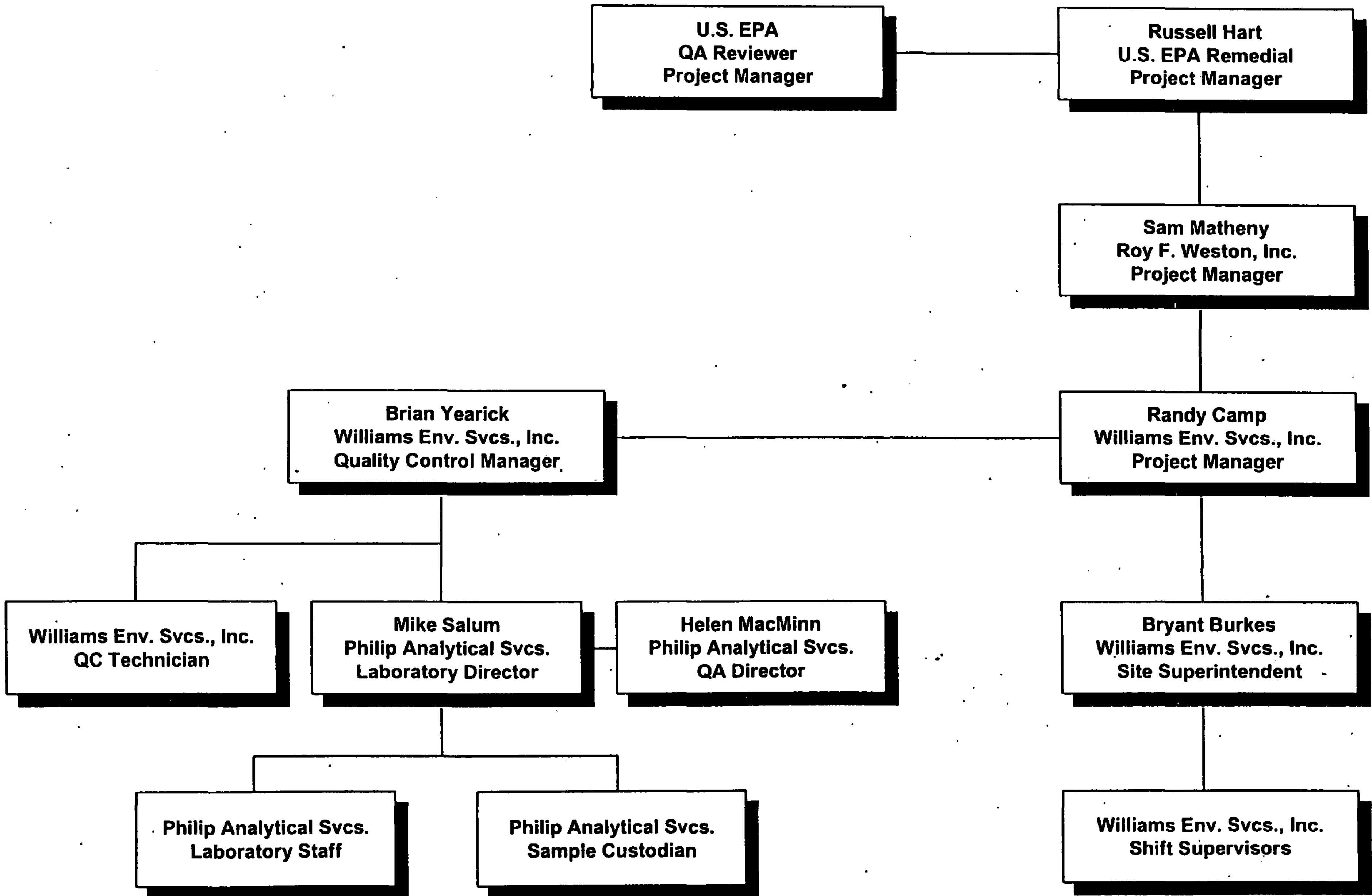


Figure 2.1

Section 3

Quality Assurance Objectives

3.1 QUALITY ASSURANCE OBJECTIVES

The overall quality assurance objective for the SAP is to develop and implement procedures for sampling, chain-of-custody, laboratory analysis, instrument calibration, data reduction, reporting, internal quality control, audits, preventive maintenance, and corrective action such that valid data will be generated for site evaluation purposes. These procedures are presented or referenced in the following sections of the SAP. Specific QC checks are discussed in Section 9 of this QAPP.

Quality assurance objectives are generally defined in terms of five parameters.

1. Precision;
2. Accuracy;
3. Representativeness;
4. Comparability; and
5. Completeness.

Each parameter is defined below. Specific objectives for the SAP are set forth in other sections of this QAPP as referenced below.

3.1.1 Precision

Precision is a measure of the reproducibility of sample results. The goal is to maintain a level of analytical precision consistent with the objectives of the SAP. To maximize precision, sampling and analytical procedures will be strictly followed. All work for this SAP will adhere to established protocols presented in the QAPP and Methods for Performance. Checks for analytical precision will include the analysis of matrix spike/matrix spike duplicate pairs, and laboratory replicates. Further discussion of precision QC checks is provided in Sections 9 and 12 of this QAPP. The precision objectives are summarized in Table 1.2. Generated data will be compared to the specified precision limits (RPD).

3.1.2 Accuracy

Accuracy is a measure of how close a measured result is to the true value. Recovery of reference standards, matrix spikes, blank spikes, and surrogate standards will be used to assess the accuracy of the analytical data. Further discussion of these QC samples is provided in Sections 9 and 12 of this QAPP. Accuracy limits are summarized in Table 1.2. Generated data will be compared to the specified percent recovery (control limits).

3.1.3 Representativeness

Representativeness is the degree to which sample data accurately and precisely represent site conditions, and is dependent on sampling and analytical variability and the variability (or homogeneity) of the site itself. The SAP has been designed to assess the presence and concentrations of the chemical constituents and supplemental parameters at the site for sampling. The SAP and this QAPP present field sampling methodologies and laboratory analytical protocols. The use of the prescribed field and laboratory analytical methods with associated holding times and preservation requirements is intended to provide representative data. Further discussion of QC checks is presented in Section 9 of this QAPP.

3.1.4 Comparability

Comparability is the degree of confidence with which one data set can be compared to another. Comparability between phases of the SAP activities, and to the extent possible, between new and existing data will be maintained through consistent use of the sampling and analytical methodologies set forth in the QAPP and the SAP, through stringent application of established QA/QC procedures, and through utilization of appropriately trained personnel. The comparability of the SAP data with existing data will be limited by uncertainties associated with sampling and analytical procedures used in the previously implemented investigations as compared to these SAP activities.

3.1.5 Completeness

Completeness is defined as a measure of the amount of the valid data obtained from an event compared to the total amount that was obtained. This will be determined upon final assessment of the analytical results, as discussed in Section 12 of this QAPP. The completeness objective for the Moss-American project is 90%.

Section 4

Sampling Procedures

Feed soil, treated soil and treated wastewater samples will be collected as described in Appendix A of the SAP, Methods of Performance. In addition, the Methods of Performance contains the procedures for handling, packing, and shipping SAP samples.

Section 5

Sample Custody

5.1 FIELD PROCEDURES

The objective of field sample custody is to ensure that samples are not tampered with from the time of collection through transport to the analytical laboratory. Personnel will have "custody of samples" when the samples are in their physical possession, in their view after being in their possession, or in their physical possession and secured so they cannot be tampered with. In addition, when samples are secured in a restricted area accessible only to authorized personnel, they will be deemed to be in the custody of such authorized personnel. Both discussion of sample custody and directions for use of chain-of-custody records are provided in the Methods for Performance. An example field chain-of-custody record is also provided in the Methods for Performance.

5.2 LABORATORY PROCEDURES – OFF-SITE LABORATORY

5.2.1 General

Upon sample receipt, laboratory personnel will take responsibility for sample custody by signing each chain-of-custody record in the designated space. The original field chain-of-custody record will accompany all samples requiring laboratory analysis. The laboratory will follow internal chain-of-custody guidelines described in the Laboratory Quality Management Plan (LQMP), as appropriate. Samples will be kept secured in the laboratory until all stages of analysis are complete. All laboratory personnel having samples in their custody will be responsible for documenting and maintaining sample integrity at all stages of sample processing.

5.2.2 Sample Receipt and Storage

Immediately upon sample receipt, the laboratory sample custodian will verify the package seal, open the package, record the internal temperature, and compare the contents against the field chain-of-custody. At this time, the laboratory sample custodian will also be responsible for logging the samples in, assigning a unique laboratory identification number to each sample, and labeling each sample container with the laboratory identification number. The project name, field sample code, date sampled, date received, analysis required, storage location and date, and action for final disposition will be recorded in the laboratory logbook. If a sample container is broken, if the sample is in an

inappropriate container, if the sample has not been preserved by appropriate means, or if any discrepancy between the samples received and the chain-of-custody documentation is found, Williams' QCM will be notified immediately for resolution of the problem(s) prior to analysis.

5.2.3 Sample Analysis

Analysis of an acceptable sample will be initiated by a worksheet which will contain all pertinent information for analysis. The routing sheet will be forwarded to the analyst, and the sample will be moved into an appropriate storage location to await analysis. The analyst will sign and date the laboratory chain-of-custody record when removing the samples from storage. The document control officer will file all chain-of-custody records in the project file.

Samples will be organized into sample delivery groups (SDGs) by the laboratory according to both matrix and analysis parameter. A SDG may contain up to 20 field samples (field duplicates and trip blanks are considered field samples for the purposes of SDG assignment). All field samples assigned to a single SDG must be received by the laboratory over a maximum of seven calendar days (less when seven-day holding times for extraction must be met) and must be processed through the laboratory (preparation, analysis, and reporting) as a group.

A minimum of one matrix spike/matrix spike duplicate (MS/MSD) will be analyzed for each SDG containing greater than 10 and fewer than 20 samples. If fewer than 10 samples are received by the laboratory per day, a MS/MSD will be conducted upon receipt of 10 or more samples. All samples within a SDG will be extracted and analyzed together in the laboratory. At no time will the laboratory be allowed to run any sample (including QC samples) at an earlier or later time than the rest of the SDG. These rules for analysis will ensure that the quality control samples for an SDG are applicable to the field samples of the same SDG and that the best possible comparisons may be made.

Information regarding the sample, analytical procedures performed, and the results of the testing will be recorded in a laboratory notebook by the analyst. These notes will be dated, and also identify the analyst, the instrument used, and the instrument conditions.

5.2.4 Laboratory Project Files

During SAP activities, the analytical laboratory will establish a file for all pertinent data. These files will include the chain-of-custody records, raw data, chromatograms (required for all constituents analyzed by chromatography), and sample preparation information. The laboratory will retain project records until

the conclusion of the SAP activities, at which time they will be transferred to Williams (as appropriate) for continued storage.

5.2.5 Laboratory Documentation

- **Documentation** – Details regarding PAS documentation procedures are presented in the PAS Laboratory Quality Management Plan (LQMP) which is Appendix C of the SAP.
- **Sample Storage Following Analysis** – Once an analysis is complete, the unused portion of sample and all identifying tags and laboratory records will be maintained by PAS. Samples will be retained at PAS for a period of three months, after which Williams and Weston personnel will determine the need for continued storage.

5.3 PROJECT FILE

During project operations, the SAP file will be kept on site. At the conclusion of the project, SAP documentation will be placed in a single project file at Williams' office in Stone Mountain, Georgia. This file will consist of the following components:

- Agreements (filed chronologically);
- Correspondence (filed chronologically);
- Memos (filed chronologically); and
- Notes and Data (filed by topic and chronologically).

Reports (including QA reports) will be filed with correspondence. Analytical laboratory documentation (when received) and field data will be filed with notes and data. Filed materials may be removed and signed out by personnel on a temporary basis only. All files will be maintained at Williams' Stone Mountain office for a period of no less than 3 years, or as required by the contract.

Section 6

Calibration Procedures and Frequency

The laboratory instruments will be calibrated as specified by the appropriate method before analyzing the samples. The calibration procedures are based on instructions in the referenced analytical methods. Copies of the Laboratory Quality Management Plan and the appropriate analytical methods are provided as Appendix C of the SAP. The calibrations performed and the results obtained will be reported as appropriate to ensure the quality of data in the sample analysis report.

Section 7

Analytical Procedures

The analytical procedures will be implemented by PAS, which has demonstrated experience in analyzing samples for the parameters of concern at the Moss-American site. Standard methods will be employed for the analyses of all collected samples, whenever possible, as per the Table 1.2 in Section 1.

PAS standard operating procedures for the methods to be used at this site are included as part of the LQMP in Appendix C of the SAP. PAS has also provided copies of the appropriate Standard Operating Procedures for the required analytical methods.

Section 8

Data Reduction, Validation, and Reporting

After field and laboratory data are obtained, these data will be subject to:

1. Validation;
2. Reduction or manipulation mathematically or otherwise into meaningful and useful forms; and
3. Organization, interpretation, and reporting.

Initially, data is reviewed and validated internally by the laboratory. Then, upon receipt of the analytical data, Williams' QCM will review and verify the results by comparing the data to the QA/QC criteria in Table 1.2. Any apparent discrepancies will be discussed with the laboratory until defensible data is received.

8.1 FIELD DATA REDUCTION, VALIDATION, AND REPORTING

8.1.1 Field Data Reduction

Information which is collected in the field through visual observation, manual measurement and/or field instrumentation will be recorded in field notebooks, data sheets, and/or forms. Such data will be reviewed by the QCM for adherence to the Methods for Performance and for consistency. Any concerns identified as a result of this review will be discussed with the field personnel, corrected if possible, and incorporated as necessary into the data evaluation process.

8.1.2 Field Data Validation

Field data calculation, transfers, and interpretations will be performed, as necessary, by the field personnel and reviewed for accuracy by the QCM. All logs and documents will be checked for:

- General completeness;
- Readability;
- Usage of appropriate procedures;

- Appropriate instrument calibration and maintenance;
- Reasonableness in comparison to present and past data collected;
- Correct sample location; and
- Correct calculations and interpretations.

8.1.3 Field Data Reporting

Where appropriate, field data forms and calculations will be processed and included in appendices to the SAP deliverables. The original field logs, documents, and data reductions will be kept in the project file at Williams' office in Stone Mountain, Georgia.

8.2 LABORATORY DATA REDUCTION, VALIDATION, AND REPORTING

8.2.1 Laboratory Data Reduction

Laboratory analytical data will be transferred from the instrument to the computer or the data rerouting form (as applicable) by the analyst. Calculation of sample concentrations is performed using the calculation procedures specified by the analytical method used including (as applicable) use of regression analysis, response factors, and dilution factors.

8.2.2 Laboratory Data Validation

Laboratory data validation procedures will be consistent with the analytical methods used and accepted regulatory standards. The laboratory LQMP provides a description of the laboratories data validation procedures. The LQMP is Appendix C of the SAP. Upon receipt of the analytical data, Williams' QCM will then review and verify the results by comparing the data to the QA/QC criteria in Table 1.2. Any apparent discrepancies will be discussed with the laboratory until defensible data is received.

8.2.3 Laboratory Data Reporting

PAS is responsible for reporting sample data in tabular form and in electronic data packages, as requested. Tabulated data will be organized by method and sample with reference to the sample by both field and laboratory identifications. The data tables will also provide a cross-reference between each sample and the appropriate SDG. Data reporting requirements will be consistent with the analytical requirements and QA/QC criteria delineated in Table 1.2, as well as the SOPs for each method.

Section 9

Internal Quality Control Checks

Field and laboratory quality control checks are proposed for the Moss-American site. In the event that there are any deviations from these checks, Williams' QCM will be notified. The proposed field and laboratory control checks for each analytical program are indicated on Tables 1.2 and discussed generally below.

9.1 FIELD QUALITY CONTROL CHECKS

9.1.1 Sample Containers

Certified-clean sample containers will be supplied by PAS.

9.1.2 Field Duplicates/Sample Splits

Field duplicates will be collected for water and soil samples to check within batch measurement variability of the sampling methods. In general, soil and water sample field duplicates will be analyzed at a five percent frequency (every 20 samples) for the chemical constituents. Table 1.1 provides an estimated number of field duplicates to be prepared for each applicable parameter and matrix. At the request of Weston, sample splits or co-located samples will be provided. The protocol for splits/co-located samples is included in Appendix A of the SAP.

9.1.3 Trip Blanks

Trip blanks will be used to assess whether cross-contamination has occurred during liquid sample storage and transport. Trip blanks will be analyzed at a frequency of one per day per shipment of treated wastewater samples to be analyzed for volatile organic constituents. A trip blank will consist of a container filled with analyte-free water (supplied by the laboratory) which remains unopened with field samples throughout the sampling event. Trip blanks will only be analyzed for volatile organic constituents. Table 1.1 provides an estimated number of trip blanks to be collected for each matrix and parameter during the SAP.

9.2 ANALYTICAL LABORATORY QUALITY CONTROL CHECKS

Internal laboratory quality control checks will be used to monitor data integrity. These checks will include method blanks, matrix spikes (and matrix spike duplicates), blank spikes, internal standards, surrogate standards, calibration standards, and reference standards. Project QC limits for spike recovery and

duplicate precision will be in accordance with stated EPA Analytical Methodologies (Table 1.2). Further discussion of PAS's internal QA/QC procedures is provided in Appendix C of the SAP.

Section 10

Performance and System Audits

Field sampling performance audits will be accomplished through observation of the sampling operations by the oversight representatives and the QCM. If deemed necessary, USEPA Region 5 may also conduct its own field and laboratory audits

Analytical performance audits will consist primarily of replicate analyses of field samples and the scheduled analysis of blanks, spikes, and standards. If deemed necessary by the QCM, standard reference materials or performance evaluation samples will be submitted for analysis as unknowns.

A system audit will be performed before any new laboratory experimental procedures are implemented that are not described in standard analytical protocols. This audit may be performed by the Laboratory Project Manager, QCM, or another designee of the Williams Project Manager. The audit may include an on-site inspection and review of the analytical operations and the associated QA activities being employed, review of results of method detection limit studies, review of analytical results from audit samples, or other QA procedures. Additionally, the LPM(s) and QCM will frequently review data to ensure that all required QC checks are being made and that evaluation criteria are being followed.

Section 11

Preventive Maintenance

Preventive maintenance of sampling and analytical equipment used during the project will be performed according to the procedures and schedules set forth in manufacturers' maintenance manuals and as described in appropriate parts of standard methods (copies of PAS' LQMP and SOPs are provided as Appendix C to the SAP).

All preventive maintenance performed will be recorded in a service record log for each instrument. The log shall include a signature and date. If the performance of the instrument could have been affected by the maintenance procedure, calibration check samples (where appropriate) will be analyzed and the results recorded in the record notebook before any samples are analyzed. Whenever parts are replaced, the serial number of the new part (if available) or an assigned serial number will be logged into the maintenance record notebook.

Section 12

Procedures for Assessing Data Accuracy and Precision

The QA activities implemented in this study will provide a basis for assessing the accuracy and precision of the analytical measurements. Section 3 discusses the QA activities that will generate the accuracy and precision data for each sample type. The generalized forms of the equations that will be used to calculate accuracy and precision are presented below.

12.1 ACCURACY

When a reference standard material is used in the analysis, Percent Accuracy (A) will be calculated as follows:

$$A = \frac{\text{Found concentration}}{\text{True concentration}} \times 100 \qquad \text{Equation 12-1}$$

Percent analyte Recovery (R) will be calculated as follows:

$$R = \frac{(X-N)}{S} \times 100 \qquad \text{Equation 12-2}$$

where X is the experimentally determined value, N is the amount of native material in the sample, and S is the amount of spiked material of the species being measured. Recoveries are used to determine accuracy when standards are not available.

12.2 PRECISION

When less than four analyses of the same parameter are available, precision will be calculated as a Range Percent (RP) from the average of replicate measurements according to:

$$RP = \frac{(X1 - X2)}{\text{Average } X} \times 100 \qquad \text{Equation 12-3}$$

where X1 and X2 are the highest and lowest results of replicate measurements.

Where four or more analyses of the same parameter are available, the precision will be determined as the Relative Standard Deviation (RSD) according to:

$$RSD = \frac{\text{Standard deviation}}{\text{Average X}} \times 100 \qquad \text{Equation 12-4}$$

12.3 COMPLETENESS

Percent Completeness (C) is calculated as:

$$C = \frac{\text{Number of Valid Results}}{\text{Total Number of Samples}} \times 100 \qquad \text{Equation 12-5}$$

Section 13

Corrective Action

The need for corrective action occurs when a circumstance arises that threatens the quality of the data output. For corrective action to be initiated, awareness of a problem must exist. In most instances, the personnel conducting the field work and the laboratory analyses are in the best position to recognize a problem or nonconformance that will affect data quality. Keen awareness on their part can frequently detect minor instrument changes, drifts, or malfunctions which can be corrected. If major problems arise, sampling and laboratory personnel are in the best position to decide upon the proper corrective action and initiate it immediately, thus minimizing data loss. Therefore, the field sampling and laboratory analysis personnel will have prime responsibility for recognizing a nonconformance. Each nonconformance shall be documented by the personnel identifying it or originating the corrective action. For this purpose, a variance log, testing procedure record, notice of equipment calibration failure, results of laboratory analysis QC tests, audit report, internal memorandum, or letter shall be used as appropriate. Documentation shall include:

- Identification of the individual(s) identifying or originating the nonconformance
- Description of the nonconformance
- Any required approval signatures
- Method(s) for correcting the nonconformance (corrective action) or description of the variance granted
- Schedule for completing corrective action.

Documentation in the form of a nonconformance report shall be made available to project and laboratory management and the QCM. It is the responsibility of the LPM(s) and/or QCM to notify appropriate personnel of the nonconformance. Samples affected will be listed on the nonconformance report.

Decisions on whether to take corrective action and what action(s) to take will be made by the LPM(s) and/or QCM. When a corrective action is taken by any of the operations or analytical laboratory personnel, they will be responsible for notifying the QCM so that, if deemed necessary, QA surveillance of the affected sampling or analysis system can be intensified. Nonconformance and corrective action reports will become part of the Daily Report.

A second recognition level of the need for corrective action will be determined by the QCM. The QCM is responsible for determining the need for corrective action based on the results of the audits described in Section 10 and from review of the QA data generated during the study. The QCM will be responsible for initiating corrective action as required. The appropriate manager will then be responsible for instituting corrective action and ensuring that the corrective actions produce the desired results.

Ultimately, the personnel performing and checking the sampling and analysis procedures and results must participate in decisions to take correct actions. To reach the proper decision, each individual must understand the program objectives and data quality required to meet these objectives. Data quality objectives for this program are presented in Section 3. All personnel involved in the analytical components of this project will receive an approved copy of this QA Plan and will be informed of these objectives. Each individual will have a responsibility to notify the QCM or LPM whenever a measurement system is not yielding data within these objectives.

If a situation arises requiring corrective action, the following closed-loop corrective action system will be used:

- Define the problem
- Assign responsibility for investigating the problem
- Investigate and determine the cause of the problem
- Determine corrective action course to eliminate the problem, including resampling and reanalysis, as necessary
- Assign responsibility for implementing the corrective action
- Determine the effectiveness of the corrective action and implement the correction
- Verify that the corrective action has eliminated the problem
- If not completely successful, loop back to first step.

Section 14

Quality Assurance Reports to Management

The key staff responsible for sampling, analysis, and data management will review the QAPP periodically while data are being generated. The QCM will immediately notify the Williams Project Manager of any event or occurrence that could have a significant effect on the validity of the sample results. Notification will be verbal followed by a written memorandum which includes the proposed corrective action. The results of the periodic QA review will be summarized in a memorandum which will specifically identify any areas that may require corrective action and present the proposed corrective action. In addition, the memorandum will present the results of previous corrective actions.

14.1 DAILY QA/QC REPORT

The Quality Control Manager will also complete a daily QA/QC report that summarizes the activities at the site. Information presented in the daily reports will include the following:

- Date;
- List of all sampling personnel and responsibilities/duties;
- Time of arrival at site;
- General weather conditions (i.e. rain, snow);
- Total number of samples and sample identification numbers for all samples collected;
- Any significant problems or unusual situations encountered while sampling; and
- Time of departure from site.

14.2 DISTRIBUTION LIST

The following list of individuals will receive copies of the daily QA/QC reports, as prepared by the QCM:

- Williams' Vice President of Operations
- Williams' Project Manager

- Williams' Site Manager
- Weston's Site Manager

Additional personnel can be added to the distribution list as required.

METHOD 3500B

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 Method 3500 provides general guidance on the selection of methods used in the quantitative extraction (or dilution) of samples for analysis by one of the semivolatile or nonvolatile determinative methods. Cleanup and/or analysis of the resultant extracts are described in Chapter Two as well as in Method 3600 (Cleanup) and Method 8000 (Analysis).

1.2 The following table lists the extraction methods, the matrix and the analyte category.

SAMPLE EXTRACTION METHODS FOR SEMIVOLATILES AND NONVOLATILES

Method #	Matrix	Extraction Type	Analytes
3510	Aqueous	Separatory Funnel Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3520	Aqueous	Continuous Liquid-Liquid Extraction	Semivolatile & Nonvolatile Organics
3535	Aqueous	Solid-Phase Extraction (SPE)	Semivolatile & Nonvolatile Organics
3540	Solids	Soxhlet Extraction	Semivolatile & Nonvolatile Organics
3541	Solids	Automated Soxhlet Extraction	Semivolatiles & Nonvolatile Organics
3542	Air Sampling Train	Separatory Funnel & Soxhlet Extraction	Semivolatile Organics
3545	Solids	Pressurized Fluid Extraction (ASE) (Heat & Pressure)	Semivolatile & Nonvolatile Organics
3550	Solids	Ultrasonic Extraction	Semivolatile & Nonvolatile Organics
3560/ 3561	Solids	Supercritical Fluid Extraction (SFE)	Semivolatile Petroleum Hydrocarbons & Polynuclear Aromatic Hydrocarbons
3580	Non-aqueous Solvent Soluble Waste	Solvent Dilution	Semivolatile & Nonvolatile Organics

1.3 Method 3580 may be used for the solvent dilution of non-aqueous semivolatile and nonvolatile organic samples prior to cleanup and/or analysis.

1.4 Methods 3545, 3560, and 3561 are techniques that utilize pressurized solvent extraction to reduce the amount of solvent needed to extract target analytes and reduce the extraction time when compared to more traditional techniques such as Soxhlet extraction.

1.5 Prior to employing this method, analysts are advised to consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the allowed flexibility in the choice of apparatus, reagents, and supplies. In addition, unless specified in a regulation, the use of SW-846 methods is not mandatory in response to Federal testing requirements. The information contained in this procedure is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to meet the data quality objectives or needs for the intended use of the data.

2.0 SUMMARY OF METHOD

2.1 A sample of a known volume or weight is extracted with solvent or diluted with solvent. Method choices for aqueous samples include liquid-liquid extraction by separatory funnel or by continuous extractor and solid-phase extraction (SPE). Method choices for soil/sediment and solid waste samples include standard solvent extraction methods utilizing either Soxhlet, automated Soxhlet, or ultrasonic extraction. Solids may also be extracted using pressurized extraction techniques such as supercritical fluid extraction or heated pressurized fluid extraction.

2.2 The resultant extract is dried and concentrated in a Kuderna-Danish (K-D) apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Sec. 8.0).

NOTE: Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish evaporative concentrators. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program.

2.3 See Sec. 7.0 for additional guidance to assist in selection of the appropriate method.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

3.2 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.4 Soap residue (e.g. sodium dodecyl sulfate), which results in a basic pH on glassware surfaces, may cause degradation of certain analytes. Specifically, Aldrin, Heptachlor, and most organophosphorus pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

4.2 Solvent recovery apparatus is recommended for use in methods that require the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Stock standards for spiking solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. The stock solutions used for the calibration standards are acceptable (dilutions must be made in a water miscible solvent) except for the quality control check sample stock concentrate which must be prepared independently to serve as a check on the accuracy of the calibration solution.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure compound. Dissolve the compound in a water miscible solvent (i.e., methanol, acetone, 2-propanol, etc.) and dilute to volume in a 10-mL volumetric flask. If compound purity is 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard solution. Commercially-prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.2 Stock standard solutions should be stored in polytetrafluoroethylene (PTFE)-sealed containers at 4°C or below. The solutions should be checked frequently for stability. Refer to the determinative method for holding times of the stock solutions.

5.4 Surrogate standards - A surrogate (i.e., a compound that is chemically similar to the analyte group but is not expected to occur in an environmental sample) should be added to each sample, blank, laboratory control sample (LCS), and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits.

5.4.1 Recommended surrogates for certain analyte groups are listed in Table 1. For methods where no recommended surrogates are listed, the lab is free to select compounds that fall within the definition provided above. Even compounds that are on the method target analyte list may be used as a surrogate as long as historical data are available to ensure their absence at a given site. Normally one or more standards are added for each analyte group.

5.4.2 Prepare a surrogate spiking concentrate by mixing stock standards prepared above and diluting with a water miscible solvent. Commercially prepared spiking solutions are acceptable. The concentration for semivolatile/nonvolatile organic and pesticide analyses should be such that a 1-mL aliquot into 1000 mL of a sample provides a concentration of 10 times the quantitation limit or near the mid-point of the calibration curve. Where volumes of less than 1000 mL are extracted, adjust the volume of surrogate standard proportionately. For matrices other than water, 1 mL of surrogate standard is still the normal spiking volume. However, if gel permeation chromatography will be used for sample cleanup, 2 mL should be added to the sample. See Table 1 for recommended surrogates. The spiking volumes are normally listed in each extraction method. Where concentrations are not listed in a method, a concentration of 10 times the quantitation limit is recommended. If the surrogate quantitation limit is unknown, the average quantitation limit of method target analytes may be utilized to estimate a surrogate quantitation limit. As necessary or appropriate to meet project objectives, the surrogates listed in Table 1 may be modified by the laboratory. The concentration of the surrogate in the sample (or sample extract) should either be near the middle of the calibration range or approximately ten times the quantitation limit.

5.5 Matrix spike standards - The following are recommended matrix spike standard mixtures for a few analyte groups. Prepare a matrix spike concentrate by mixing stock standards prepared above and diluting with a water miscible solvent. Commercially-prepared spiking solutions are acceptable. The matrix spike standards should be independent of the calibration standard. A few methods provide guidance on concentrations and the selection of compounds for matrix spikes (see Table 2).

5.5.1 Base/neutral and acid matrix spiking solution - Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 mg/L and the acid compounds at 200 mg/L for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.5.2 Organochlorine pesticide matrix spiking solution - Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations listed for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (mg/L)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.5.3 For methods with no guidance, select five or more analytes (select all analytes for methods with five or less) from each analyte group for use in a spiking solution. Where matrix spike concentrations in the sample are not listed it should be at or below the regulatory concentration or action level, or 1 to 5 times higher than the background concentration, whichever, concentration would be larger.

5.5.4 Sec. 8.3.3 provides guidance on determining the concentration of the matrix spike compounds in the sample. As necessary or appropriate to meet project objectives, the matrix spiking compounds listed in Secs. 5.5.1, 5.5.2, and/or the concentrations listed in the spiking solutions may be modified by the laboratory. When the concentration of an analyte is <u>not</u> being checked against a regulatory limit or action level (see Sec. 8.3.3.3) the concentration of the matrix spike compound in the sample (or sample extract) should be near the middle of the calibration range or approximately ten times the quantitation limit.

5.6 Laboratory control spike standard - Use the matrix spike standard prepared in Sec. 5.5 as the spike standard for the laboratory control sample (LCS). The LCS should be spiked at the same concentration as the matrix spike.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See Chapters Two and Four for guidance on sample collection.

7.0 PROCEDURE

7.1 Water, soil/sediment, sludge, and waste samples requiring analysis for semivolatile and nonvolatile organic compounds (within this broad category are special subsets of analytes, i.e., the different groups of pesticides, explosives, PCBs etc.), must undergo solvent extraction prior to analysis. This manual contains method choices that are dependent on the matrix, the physical properties of the analytes, the sophistication and cost of equipment available to a given laboratory, and the turn-around time required for sample preparation.

7.1.1 The laboratory should be responsible for ensuring that the method chosen for sample extraction will provide acceptable extraction efficiency for the target analytes in a given matrix. There are several approaches that may be employed to ensure the appropriateness of the extraction method.

7.1.1.1 Prior to employing any extraction procedure on samples submitted for regulatory compliance monitoring purposes, the laboratory should complete the initial demonstration of proficiency described in Sec. 8.2. This demonstration applies to all SW-846 extraction methods, including those for which specific performance data are provided in a determinative method.

7.1.1.2 In addition, when a new or different extraction technique is to be applied to samples, the laboratory should also demonstrate that their application of the technique provides acceptable performance in the matrix of interest for the analytes of interest. One approach to demonstrating extraction method performance is to make a direct comparison between the chosen method and either Method 3520 (continuous liquid-liquid extraction of aqueous samples) or Method 3540 (Soxhlet extraction of solid samples), as these methods have the broadest applicability to environmental matrices.

When direct comparisons are performed, they should be conducted using either standard reference materials derived from real-world matrices or samples from a given site that can be reasonably expected to contain the analytes of interest. Because of concerns with the incorporation of spiking materials into samples, the use of samples spiked by the laboratory is generally a less useful comparison relative to either real-world contaminated samples or standard reference materials, and thus should generally only be employed when neither of these latter materials are available. Analyze at least four portions of a well homogenized sample by the extraction method of interest and either Method 3520 or Method 3540, depending on the matrix.

7.1.1.3 When direct comparisons between methods are conducted, the laboratory may use statistical tests such as an F-test to determine if the results are comparable between the methods. The laboratory may employ the method of interest provided that the demonstrated performance can be shown to be either as good or better than that of the "reference" method, or adequate for project needs, that is, meeting the requirements of the QA Project Plan for a specific project.

7.1.1.4 Whatever approaches are taken to ensure the adequacy of the extraction procedure for the matrix of interest, it is the responsibility of the laboratory to document the results and maintain records of such demonstrations.

7.1.2 Each method has QC requirements that normally include the addition of surrogates to each analytical sample and QC sample as well as the inclusion of a matrix spike/matrix spike duplicate (or matrix spike and duplicate sample), a laboratory control sample, and a method blank in each sample extraction batch. As defined in Chapter One, a "batch" consists of up to 20 environmental samples processed as a unit. In the case of samples that must undergo extraction prior to analysis, each group of 20 samples extracted together by the same method constitutes an extraction batch.

The decision of whether to prepare and analyze a matrix spike/matrix spike duplicate pair or a matrix spike and a duplicate sample should be based on knowledge of the samples in the extraction batch. If the samples are expected to contain the analytes of interest, then the analysis of a duplicate sample may yield data on the precision of the analytical process and the analysis of the matrix spike will yield data on the accuracy of the process. In contrast, when the samples are not known or expected to contain the analytes of interest, then the batch should include a matrix spike/matrix spike duplicate pair to ensure that both accuracy and precision data will be generated within the extraction batch.

7.2 Method 3510 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Separatory funnel extraction utilizes relatively inexpensive glassware and is fairly rapid (three, 2-minute extractions followed by filtration) but is labor intensive, uses fairly large volumes of solvent and is subject to emulsion problems. Method

3520 should be used if an emulsion forms between the solvent-sample phases, which cannot be broken by mechanical techniques.

7.3 Method 3520 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Continuous extractors are excellent for samples with particulates (of up to 1% solids) that cause emulsions, provide more efficient extraction of analytes that are more difficult to extract and once loaded, require no hands-on manipulation. However, they require more expensive glassware, use fairly large volumes of solvent and extraction time is rather lengthy (6 to 24 hours).

7.4 Method 3535 - Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of water is pumped through an appropriate medium (e.g., disk or cartridge) containing a solid phase that effects the extraction of organics from water. A small volume of extraction solvent is passed through the medium to elute the compounds of interest. The eluant is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Appropriate solid-phase extraction media allow extraction of water containing particulates, are relatively fast and use small volumes of solvent. However, they do require some specialized pieces of equipment.

7.5 Method 3540 - This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Soxhlet extraction uses relatively inexpensive glassware, once loaded requires no hands-on manipulation, provides efficient extraction, but is rather lengthy (16 to 24 hours) and uses fairly large volumes of solvent. It is considered a rugged extraction method because there are very few variables that can adversely affect extraction efficiency.

7.6 Method 3541 - This method utilizes a modified Soxhlet extractor and is applicable to the extraction of semivolatile/nonvolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in an automated Soxhlet extractor. This device allows the extraction thimble to be lowered into the boiling liquid for the first hour and then extracted in the normal thimble position for one additional hour. The automated Soxhlet allows equivalent extraction efficiency in 2 hours, combines the concentration step within the same device but requires a rather expensive device.

7.7 Method 3542 - This method is applicable to the extraction of semivolatile organic compounds from the Method 0010 air sampling train. The solid trapping material (i.e., glass or quartz fiber filter and porous polymeric adsorbent resin) are extracted using Soxhlet extraction and the condensate and impinger fluid are extracted using separatory funnel extraction.

7.8 Method 3545 - This method is applicable to the extraction of nonvolatile/semivolatile organic compounds from solids such as soils, relatively dry sludges, and solid wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction cell and extracted under pressure with small volumes of solvent. The extract is concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The method is rapid and efficient, in that it uses small volumes of solvent, but does require the use of an expensive extraction device.

7.9 Method 3550 - This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of ultrasonic extraction. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using ultrasonic extraction. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Ultrasonic extraction is fairly rapid (three, 3-minute extractions followed by filtration) but uses relatively large volumes of solvent, requires a somewhat expensive device and requires following the details of the method very closely to achieve acceptable extraction efficiency (proper tuning of the ultrasonic device is very critical). This technique is much less efficient than the other extraction techniques described in this section. This is most evident with very non-polar organic compounds (e.g., PCBs, etc.) that are normally strongly adsorbed to the soil matrix. EPA has not validated Method 3550 for the extraction of organophosphorus compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorus compounds (see Reference 1). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

7.10 Methods 3560 and 3561 - These methods are applicable to the extraction of total recoverable petroleum hydrocarbons and PAHs from solids such as soils, sludges, and wastes using the technique of supercritical fluid extraction (SFE). SFE normally uses CO_2 (which may contain very small volumes of solvent modifiers). Therefore, there is no solvent waste for disposal, may be automated, provides relatively rapid extraction, but, is currently limited to total recoverable petroleum hydrocarbons and PAHs. It also requires a rather expensive device and sample size is more limited. Research on SFE is currently focusing on optimizing supercritical fluid conditions to allow efficient extraction of a broader range of RCRA analytes in a broad range of environmental matrices.

7.11 Method 3580 - This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent. When using this method, the analyst must use caution in the addition of surrogate compounds, so as not to dilute out the surrogate response when diluting the sample.

7.12 Sample analysis - Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. Samples prepared for semivolatile/nonvolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures. Each laboratory using SW-846 methods should maintain a formal quality assurance program. Each extraction batch of 20 or less samples should contain: a method blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate samples; and a laboratory control sample, unless the determinative method provides other guidance.

8.2 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean reference matrix. This will include a combination of the sample extraction method (usually a 3500 series method for extractable

organics) and the determinative method (an 8000 series method). The laboratory should also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

8.2.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials, or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate should be made using stock standards prepared independently from those used for calibration.

8.2.2 The procedure for preparation of the reference sample concentrate is dependent upon the method being evaluated. Guidance for reference sample concentrations for certain methods are listed below. In other cases, the determinative methods contain guidance on preparing the reference sample concentrate and the reference sample. If no guidance is provided, prepare a reference sample concentrate in methanol (or other water miscible solvent). Spike the reference sample at the concentration on which the method performance data are based. The spiking volume added to water should not exceed 1 mL/L so that the spiking solvent will not decrease extraction efficiency. If the method lacks performance data, prepare a reference standard concentrate at such a concentration that the spike will provide a concentration in the clean matrix that is 10 - 50 times the MDL for each analyte in that matrix.

The concentration of target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.3.1 for information on selecting an appropriate spiking level.

8.2.3 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Therefore, 1 mL (unless the method specifies a different volume) of the reference sample concentrate is spiked into each of four (minimum number of replicates) 1-L aliquots of organic-free reagent water (now called the reference sample), extracted as per the method. For matrices other than water or for determinative methods that specify a different volume of water, add 1.0 mL of the reference sample concentrate to at least four replicates of the volume or weight of sample specified in the method. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds) e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix.

8.2.4 Preparation of reference samples

The following sections provide guidance on the QC reference sample concentrates for many SW-846 determinative methods. The concentration of the target analytes in the QC reference sample for the methods listed below may need to be adjusted to more accurately reflect the concentrations of interest in different samples or projects. If the concentration of an analyte is being evaluated relative to a regulatory limit or action level, see Sec. 8.3.3 for information on selecting an appropriate spiking level. In addition, the analyst may vary the concentration of the spiking solution and the volume of solution spiked into the sample. However, because of concerns about the effects of the spiking solution solvent on the sample, the total volume spiked into a sample should generally be held to no more than 1 mL.

8.2.4.1 Method 8041 - Phenols: The QC reference sample concentrate should contain each analyte at 100 mg/L in 2-propanol.

8.2.4.2 Method 8061 - Phthalate esters: The QC reference sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 mg/L; bis(2-ethylhexyl)phthalate, 50 mg/L; di-n-octyl phthalate, 50 mg/L; and any other phthalate at 25 mg/L.

8.2.4.3 Method 8070 - Nitrosamines: The QC reference sample concentrate should contain each analyte at 20 mg/L in isooctane.

8.2.4.4 Method 8081 - Organochlorine pesticides: The QC reference sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; and any other single-component pesticide at 2 mg/L. If the method is only to be used to analyze chlordane or toxaphene, the QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.2.4.5 Method 8082 - PCBs: The QC reference sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 mg/L in acetone.

8.2.4.6 Method 8091 - Nitroaromatics and cyclic ketones: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 mg/L; and isophorone and nitrobenzene at 100 mg/L.

8.2.4.7 Method 8100 - Polynuclear aromatic hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene 5 mg/L; and any other PAH at 10 mg/L.

8.2.4.8 Method 8111 - Haloethers: The QC reference sample concentrate should contain each analyte at a concentration of 20 mg/L in isooctane.

8.2.4.9 Method 8121 - Chlorinated hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 mg/L; and any other chlorinated hydrocarbon, 100 mg/L.

8.2.4.10 Method 8131 - Aniline and selected derivatives: The QC reference sample concentrate should contain each analyte at the following concentrations in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.11 Method 8141 - Organophosphorus compounds: The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.12 Method 8151 - Chlorinated herbicides: The QC reference sample concentrate should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.4.13 Method 8260 - Volatile organics: The QC reference sample concentrate should contain each analyte in methanol at a concentration of 10 mg/L. This concentrate is spiked into 100 mL of organic-free reagent water, producing enough reference sample for four aliquots of up to 25 mL each.

8.2.4.14 Method 8270 - Semivolatile organics: The QC reference sample concentrate should contain each analyte in acetone at a concentration of 100 mg/L.

8.2.4.15 Method 8310 - Polynuclear aromatic hydrocarbons: The QC reference sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 mg/L; acenaphthylene, 100 mg/L; acenaphthene, 100 mg/L; fluorene, 100 mg/L; phenanthrene, 100 mg/L; anthracene, 100 mg/L; benzo(k)fluoranthene, 5 mg/L; and any other PAH at 10 mg/L.

8.2.5 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples (Sec. 7.0 of each of the methods). This will include a combination of the sample preparation method (usually a 3500 series method for extractable organics) and the determinative method (an 8000 series method). Follow the guidance on data calculation and interpretation presented in Method 8000, Sec. 8.0.

8.2.6 The following methods contain specific extraction and sample preparation requirements applicable only to that method. Refer to these individual methods for extraction and preparation procedures required prior to instrumental analysis, and for information on the preparation of QC reference samples.

8.2.6.1 Method 8275 - Thermal Extraction/Gas Chromatography/Mass Spectrometry (TE/GC/MS) for Semivolatile Organic Compounds.

8.2.6.2 Method 8280 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.3 Method 8290 - Polychlorinated Dibenzo-*p*-dioxins and Polychlorinated Dibenzofurans.

8.2.6.4 Method 8318 - N-Methylcarbamates by High Performance Liquid Chromatography (HPLC).

8.2.6.5 Method 8321 - Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection.

8.2.6.6 Method 8325 - Solvent Extractable Nonvolatiles by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS).

8.2.6.7 Method 8330 - Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC).

8.2.6.8 Method 8331 - Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC).

8.2.6.9 Method 8332 - Nitroglycerine by High Performance Liquid Chromatography (HPLC) or Thin-Layer Chromatography (TLC).

8.2.6.10 Method 8410 - Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics.

8.2.6.11 Method 8430 - Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR.

8.2.6.12 Method 8440 - Total Recoverable Petroleum Hydrocarbons (TRPH) by Infrared (IR) Spectrophotometry.

8.3 Sample Quality Control for Preparation and Analysis

8.3.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair per analytical batch. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the laboratories should use a matrix spike and matrix spike duplicate pair. See Sec. 5.5 for additional guidance on matrix spike preparation. Sec. 8.3.3 provides guidance on establishing the concentration of the matrix spike compounds in the sample chosen for spiking. The choice of analytes to be spiked should reflect the analytes of interest for the specific project. Thus, if only a subset of the list of target analytes provided in a determinative method are of interest (e.g., Method 8270 is used for the analysis of only PAHs), then these would be the analytes of interest for the project. In the absence of project-specific analytes of interest, it is suggested that the laboratory periodically change the analytes that are spiked with the goal of obtaining matrix spike data for most, if not all, of the analytes in a given determinative method.

8.3.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume: e.g., organic-free reagent water for the water matrix or sand or soil (free of organic interferences) for the solid matrix. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.3.3 The concentration of the matrix spike sample and/or the LCS should be determined as described in the following sections.

8.3.3.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory limit or action level, the spike should be at or below the regulatory limit or action level, or 1 - 5 times the background concentration (if historical data are available), whichever concentration is higher.

8.3.3.2 If historical data are not available, it is suggested that an uncontaminated sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculation of recoveries.

8.3.3.3 If the concentration of a specific analyte in a sample is not being checked against a limit specific to that analyte, then the spike should be at the same concentration as the reference sample (Sec. 8.2.4) or 20 times the quantitation limit in

the matrix of interest. It is again suggested that a background sample of the same matrix from the site be submitted as a sample for matrix spiking purposes.

8.3.4 Analyze these QC samples (the LCS and the matrix spikes or the optional matrix duplicates) following the procedure (Sec. 7.0) of the selected determinative method. Calculate and evaluate the QC data as outlined in Sec. 8.0 of Method 8000.

8.3.5 Blanks - Use of method blanks and other blanks are necessary to track contamination of samples during the sampling and analysis processes. Refer to Chapter One for specific quality control procedures.

8.3.6 Surrogates - A surrogate is a compound that is chemically similar to the analyte group but not expected to occur in an environmental sample. Surrogate should be added to all samples when specified in the appropriate determinative method (See Table 1). See Sec. 5.4 for additional guidance on surrogates.

8.4 The laboratory must have procedures in place for documenting and charting the effect of the matrix on method performance. Refer to Chapter One and Method 8000 for specific guidance on developing method performance data.

9.0 METHOD PERFORMANCE

9.1 The recovery of surrogates is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds, when compared to laboratory control sample (LCS) recoveries, indicates the presence or absence of unusual matrix effects.

9.2 The performance of each 3500 method will be dictated by the overall performance of the sample preparation in combination with the cleanup method and/or the analytical determinative method.

10.0 REFERENCES

None required.

TABLE 1

SURROGATES FOR SW-846 CHROMATOGRAPHIC METHODS
FOR SEMIVOLATILE AND NONVOLATILE COMPOUNDS

Method Number	Technique	Suggested Surrogates*
8041	Phenols by GC	2-Fluorophenol, and 2,4,6-Tribromophenol
8061	Phthalate Esters by GC	Diphenyl phthalate, Diphenyl isophthalate, and Dibenzyl phthalate
8070	Nitrosamines by GC	None listed**
8081	Organochlorine Pesticides by GC	2,4,5,6-Tetrachloro-m-xylene, and Decachlorobiphenyl
8082	Polychlorinated Biphenyls by GC	Decachlorobiphenyl
8091	Nitroaromatics by GC	2-Fluorobiphenyl
8100	PAHs by GC	2-Fluorobiphenyl, and 1-Fluoronaphthalene
8111	Haloethers by GC	None listed**
8121	Chlorinated Hydrocarbons by GC	α,2,6-Trichlorotoluene, 2,3,4,5,6-Pentachlorotoluene, and 1,4-Dichloronaphthalene
8131	Anilines by GC	None listed**
8141	Organophosphorus Pesticides by GC	None listed**
8151	Acid Herbicides by GC	2,4-Dichlorophenylacetic acid
8270	Semivolatiles by GC/MS	Phenol-d_6, 2-Fluorophenol, 2,4,6-Tribromophenol, Nitro-benzene-d_5, 2-Fluorobiphenyl, and p-Terphenyl-d_{14}
8275	Semivolatiles by TE/GC/MS	Not listed**
8280	PCDDs and PCDFs by HRGC/LRMS	Internal standards added at time of extraction. No surrogates.
8290	PCDDs and PCDFs by HRGC/HRMS	Internal standards added at time of extraction. No surrogates.
8310	PAHs by HPLC	Decafluorobiphenyl
8318	Carbamates by HPLC	None listed**
8321	Nonvolatiles by HPLC/TS/MS or UV Detection	None listed**

Table 1 (continued)

Method Number	Technique	Suggested Surrogates*
8325	Nonvolatiles by HPLC/PB/MS or UV/Vis	Benzidine-d_8, Caffeine-$^{15}N_2$, 3,3'-Dichlorobenzidine-d_6, Bis-(perfluorophenyl)-phenylphosphine oxide
8330	Explosives by HPLC	None listed**
8331	Tetrazene by HPLC	None listed**
8332	Nitroglycerine by HPLC or TLC	None listed**
8410	GC/FT-IR for Semivolatiles	None listed**
8430	Bis(2-chloroethyl) ether and Hydrolysis Products by GC/FT-IR	None listed**
8440	Total Recoverable Petroleum Hydrocarbons by IR	None listed**

* Suggested water concentration = 10 times the quantitation limit or near the mid-point of the calibration curve. See Sec. 5.4.2.

** Surrogate compounds selected should be similar in analytical behavior to the analytes of interest, but which are not expected to be present in the sample matrix or extract.

GC = Gas Chromatography
HR = High Resolution
LR = Low Resolution
IR = Infrared
TS = Thermospray
PB = Particle Beam
MS = Mass Spectrometry
HPLC = High Performance Liquid Chromatography
PCDD = Polychlorinated Dibenzo-*p*-dioxins
PCDF = Polychlorinated Dibenzofurans
FT-IR = Fourier Transform Infrared Detector
UV = Ultraviolet
TLC = Thin-Layer Chromatography
TE = Thermal Extraction

METHOD 3550B

ULTRASONIC EXTRACTION

See Disclaimer. See manufacturer's specifications for operational settings.

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of less than or equal to 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of greater than 20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Sec. 4.2.2, for applicable methods.

1.4 Ultrasonic extraction is not as rigorous as other extraction methods for soils/solids. Therefore, it is critical that the method (including the manufacturer's instructions) be followed explicitly in order to achieve the maximum extraction efficiency. See Sec. 7.0 for the critical aspects of the extraction procedure.

1.5 EPA has not validated Method 3550 for the extraction of organophosphorous compounds from solid matrices. In addition, there are concerns that the ultrasonic energy may lead to breakdown of some organophosphorous compounds (see Reference 3). As a result, this extraction technique should not be used for organophosphorous compounds without extensive validation on real-world samples. Such studies should assess the precision, accuracy, ruggedness, and sensitivity of the technique relative to the appropriate regulatory limits or project-specific concentrations of interest.

1.6 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.7 This method is not appropriate for applications where high extraction efficiencies of analytes at very low concentrations is necessary (e.g., demonstration of effectiveness of corrective action).

2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 Medium/high concentration method - A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn-type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.2.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

4.2.2 Use a 3/4" horn for the low concentration method and a 1/8" tapered microtip attached to a 1/2" horn for the medium/high concentration method.

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

4.4 Apparatus for determining percent dry weight.

4.4.1 Drying oven - capable of maintaining 105°C.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1-mL, disposable.

4.6 Beakers - 400-mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.8.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.9 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.10 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.11 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The batch should be used in a hood.

4.12 Balance - Top-loading, capable of accurately weighing to the nearest 0.01 g.

4.13 Vials - 2-mL, for GC autosampler, with polytetrafluoroethylene (PTFE)-lined screw caps or crimp tops.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw caps.

4.15 Spatula - Stainless steel or PTFE.

4.16 Drying column - 20-mm ID 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 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.

4.17 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic reagents shall 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.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

Samples should be extracted using a solvent system that gives optimum, reproducible recovery of the analytes of interest from the sample matrix. Table 1 provides recovery data for selected semivolatile organic compounds extracted from an NIST SRM. The following sections provide guidance on the choice of solvents for various classes of analytes. All solvents must be pesticide quality or equivalent.

5.4.1 Semivolatile organics may be extracted with acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}.

5.4.2 Organochlorine pesticides may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14} or acetone/methylene chloride (1:1,v/v), CH_3COCH_3/CH_2Cl_2.

5.4.3 PCBs may be extracted with acetone/hexane (1:1, v/v), CH_3COCH_3/C_6H_{14}, acetone/methylene chloride (1:1, v/v), CH_3COCH_3/CH_2Cl_2 or hexane, C_6H_{14}.

5.4.4 Other solvent systems may be employed, provided that the analyst can demonstrate adequate performance for the analytes of interest in the sample matrix (see Method 3500, Sec. 8.0).

5.5 Exchange solvents - All solvents must be pesticide quality or equivalent.

5.5.1 Hexane, C_6H_{14}.

5.5.2 2-Propanol, $(CH_3)_2CHOH$.

5.5.3 Cyclohexane, C_6H_{12}.

5.5.4 Acetonitrile, CH_3CN.

5.5.5 Methanol, CH_3OH.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

As noted in Sec. 1.4, ultrasonic extraction is not as rigorous a method as other extraction methods for soils/solids. Therefore, it is critical that the method be followed explicitly (including the manufacturer's instructions) to achieve the maximum extraction efficiency. At a minimum, successful use of this technique requires that:

- The extraction device must have a minimum of 300 watts of power and be equipped with appropriate size disrupter horns (see Sec. 4.2).
- The horn must be properly maintained, including tuning according to the manufacturer's instructions prior to use, and inspection of the horn tip for excessive wear.
- The samples must be properly prepared by thorough mixing with sodium sulfate so that it forms a free-flowing powder prior to the addition of the solvent.
- The extraction horns used for the low concentration and high concentration protocols (Sec. 7.3 and Sec. 7.4, respectively) are not interchangeable. Results indicate that the use of the 3/4" horn is inappropriate for the high concentration method, particularly for extraction of very non-polar organic compounds such as PCBs, which are strongly adsorbed to the soil matrix.
- Three extractions are performed with the appropriate solvent, the extraction is performed in the specified pulse mode, and the horn tip is positioned just below the surface of the solvent yet above the sample.
- Very active mixing of the sample and the solvent must occur when the ultrasonic pulse is activated. The analyst must observe such mixing at some point during the extraction process.

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This extraction procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise reduced in size to allow mixing and maximum exposure of the sample surfaces for the extraction. The addition of anhydrous sodium sulfate to the sample (1:1) may make the mixture amenable to grinding.

7.2 Determination of percent dry weight - When sample results are to be calculated on a dry weight basis, a second portion of sample should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated sample.

Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides (less than or equal to 20 mg/kg):

7.3.1 The following steps should be performed rapidly to avoid loss of the more volatile extractables.

7.3.1.1 Weigh approximately 30 g of sample into a 400-mL beaker. Record the weight to the nearest 0.1 g.

7.3.1.2 Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing.

7.3.1.3 Add 1.0 mL of the surrogate standard solution to all samples, spiked samples, QC samples, and blanks. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of surrogate compounds and concentrations.

7.3.1.4 For the sample in each batch selected for spiking, add 1.0 mL of the matrix spiking solution. Consult Method 3500, Secs. 5.0 and 8.0 for guidance on the appropriate choice of matrix spiking compounds and concentrations.

7.3.1.5 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.3.1.6 Immediately add 100 mL of the appropriate/recommended extraction solvent or solvent mixture (see Sec. 5.4 and Table 1).

7.3.2 Place the bottom surface of the tip of the #207 (or equivalent) 3/4 inch disrupter horn about 1/2 inch below the surface of the solvent, but above the sediment layer.

NOTE: Be sure the horn is properly tuned according to the manufacturer's instructions.

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

7.3.4 Decant the extract and filter it through Whatman No. 41 filter paper (or equivalent) in a Buchner funnel that is attached to a clean 500-mL filtration flask. Alternatively, decant the extract into a centrifuge bottle and centrifuge at low speed to remove particles.

7.3.5 Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent. Apply a vacuum to the filtration flask, and collect the solvent extract. Continue filtration until all visible solvent is removed from the funnel, but do not attempt to completely dry the sample, as the continued application of a vacuum may result in the loss of some analytes. Alternatively, if centrifugation is used in Sec. 7.3.4, transfer the entire sample to the centrifuge bottle. Centrifuge at low speed, and then decant the solvent from the bottle.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10-mL concentrator tube to a 500-mL evaporator flask. Attach the solvent vapor recovery glassware (condenser and collection device) to the Snyder column of the Kuderna-Danish apparatus following manufacturer's instructions. Transfer filtered extract to a 500-mL evaporator flask and proceed to the next section.

7.3.7 Add one to two clean boiling chips to the evaporation flask, and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath (80 - 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 - 15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.8 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Sec. 7.3.10, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1 - 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.3.10 or adjusted to 10.0 mL with the solvent last used.

7.3.10 If further concentration is indicated in Table 1, either micro Snyder column technique (Sec. 7.3.10.1) or nitrogen blowdown technique (Sec. 7.3.10.2) may be used to adjust the extract to the final volume required.

7.3.10.1 Micro Snyder column technique

7.3.10.1.1 Add a clean boiling chip and attach a two-ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the

water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.3.10.2 Nitrogen blowdown technique

7.3.10.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample, since it may introduce contaminants.

7.3.10.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 Extraction method for samples expected to contain high concentrations of organics (greater than 20 mg/kg):

7.4.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20-mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.4.2 Add 2 g of anhydrous sodium sulfate to sample in the 20-mL vial and mix well.

7.4.3 Surrogates are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate spiking solution and on the matrix spike solution).

7.4.3.1 Add 1.0 mL of surrogate spiking solution to sample mixture.

7.4.3.2 For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard.

7.4.3.3 If gel permeation cleanup (Method 3640) is to be employed, the analyst should either add twice the volume of the surrogate spiking solution (and matrix spiking solution, where applicable), or concentrate the final extract to half the normal volume, to compensate for the half of the extract that is lost due to loading of the GPC column.

7.4.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

7.4.4.1 For nonpolar compounds (i.e., organochlorine pesticides and PCBs), use hexane or appropriate solvent.

7.4.4.2 For other semivolatile organics, use methylene chloride.

7.4.5 Loosely pack a disposable Pasteur pipette with 2 to 3 cm of glass wool. Filter the sample extract through the glass wool and collect the extract in a suitable container. The entire 10 mL of extraction solvent cannot be recovered from the sample. Therefore, the analyst should collect a volume appropriate for the sensitivity of the determinative method. For instance, for methods that do not require that the extract be concentrated further (e.g., Method 8081 typically employs a final extract volume of 10 mL), the extract may be collected in a scintillation vial or other sealable container. For extracts that will require further concentration, it is advisable to collect a standard volume for all such samples in order to simplify the calculation of the final sample results. For instance, collect 5.0 mL of extract in a clean concentrator tube. This volume represents exactly half of the total volume of the original sample extract. As necessary, account for the "loss" of half of the extract in the final sample calculations, or concentrate the final extract to one-half the nominal final volume (e.g., 0.5 mL vs. 1.0 mL) to compensate for the loss.

7.4.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

7.5 If analysis of the extract will not be performed immediately, stopper the concentrator tube and refrigerate. If the extract will be stored longer than 2 days, it should be transferred to a vial with a PTFE-lined cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, and replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

2. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes from Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

3. Kotronarou, A., et al., "Decomposition of Parathion in Aqueous Solution by Ultrasonic Irradiation," *ES&T*, 1992, Vol. 26, 1460-1462.

TABLE 1
EFFICIENCIES OF VARIOUS EXTRACTION SOLVENT SYSTEMS[a]

Compound	CAS No.[b]	ABN[c]	Solvent System[d] A %R	A SD	B %R	B SD	C %R	C SD	D %R	D SD	E %R	E SD
4-Bromophenyl phenyl ether	101-55-3	N	64.2	6.5	56.4	0.5	86.7	1.9	84.5	0.4	73.4	1.0
4-Chloro-3-methylphenol	59-50-7	A	66.7	6.4	74.3	2.8	97.4	3.4	89.4	3.8	84.1	1.6
Bis(2-chloroethoxy)methane	111-91-1	N	71.2	4.5	58.3	5.4	69.3	2.4	74.8	4.3	37.5	5.8
Bis(2-chloroethyl) ether	111-44-4	N	42.0	4.8	17.2	3.1	41.2	8.4	61.3	11.7	4.8	1.0
2-Chloronaphthalene	91-58-7	N	86.4	8.8	78.9	3.2	100.8	3.2	83.0	4.6	57.0	2.2
4-Chlorophenyl phenyl ether	7005-72-3	N	68.2	8.1	63.0	2.5	96.6	2.5	80.7	1.0	67.8	1.0
1,2-Dichlorobenzene	95-50-1	N	33.3	4.5	15.8	2.0	27.8	6.5	53.2	10.1	2.0	1.2
1,3-Dichlorobenzene	541-73-1	N	29.3	4.8	12.7	1.7	20.5	6.2	46.8	10.5	0.6	0.6
Diethyl phthalate	84-66-2	N	24.8	1.6	23.3	0.3	121.1	3.3	99.0	4.5	94.8	2.9
4,6-Dinitro-*o*-cresol	534-52-1	A	66.1	8.0	63.8	2.5	74.2	3.5	55.2	5.6	63.4	2.0
2,4-Dinitrotoluene	121-14-2	N	68.9	1.6	65.6	4.9	85.6	1.7	68.4	3.0	64.9	2.3
2,6-Dinitrotoluene	606-20-2	N	70.0	7.6	68.3	0.7	88.3	4.0	65.2	2.0	59.8	0.8
Heptachlor epoxide	1024-57-3	N	65.5	7.8	58.7	1.0	86.7	1.0	84.8	2.5	77.0	0.7
Hexachlorobenzene	118-74-1	N	62.1	8.8	56.5	1.2	95.8	2.5	89.3	1.2	78.1	4.4
Hexachlorobutadiene	87-68-3	N	55.8	8.3	41.0	2.7	63.4	4.1	76.9	8.4	12.5	4.6
Hexachlorocyclopentadiene	77-47-4	N	26.8	3.3	19.3	1.8	35.5	6.5	46.6	4.7	9.2	1.7
Hexachloroethane	67-72-1	N	28.4	3.8	15.5	1.6	31.1	7.4	57.9	10.4	1.4	1.2
5-Nitro-*o*-toluidine	99-55-8	B	52.6	26.7	64.6	4.7	74.7	4.7	27.9	4.0	34.0	4.0
Nitrobenzene	98-95-3	N	59.8	7.0	38.7	5.5	46.9	6.3	60.6	6.3	13.6	3.2
Phenol	108-95-2	A	51.6	2.4	52.0	3.3	65.6	3.4	65.5	2.1	50.0	8.1
1,2,4-Trichlorobenzene	120-82-1	N	66.7	5.5	49.9	4.0	73.4	3.6	84.0	7.0	20.0	3.2

[a] Percent recovery of analytes spiked at 200 mg/kg into NIST sediment SRM 1645
[b] Chemical Abstracts Service Registry Number
[c] Compound Type: A = Acid, B = Base, N = neutral
[d] Solvent system A = Methylene chloride
Solvent system B = Methylene chloride/Acetone (1/1)
Solvent system C = Hexane/Acetone (1/1)
Solvent system D = Methyl t-butyl ether
Solvent system E = Methyl t-butyl ether/Methanol (2/1)

TABLE 2
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

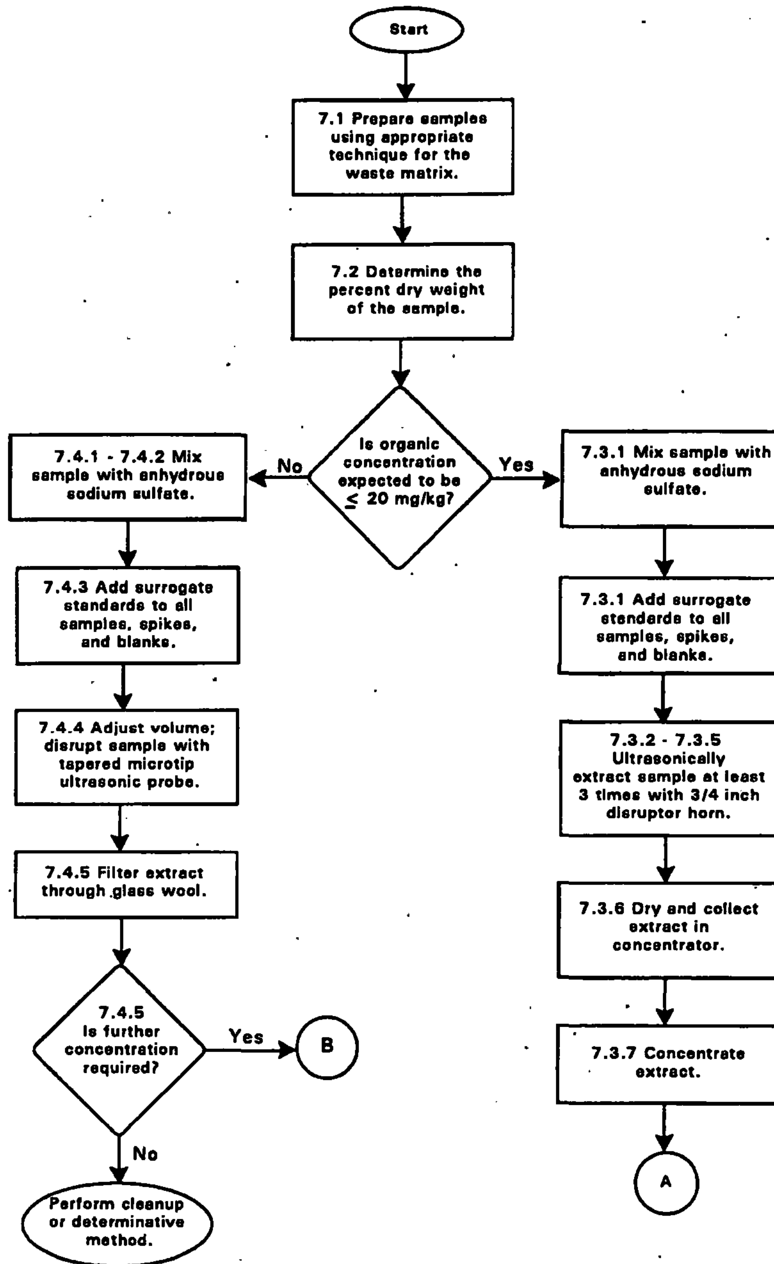
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	as received	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8091	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8111	as received	hexane	hexane	2.0	10.0
8121	as received	hexane	hexane	2.0	1.0
8141	as received	hexane	hexane	10.0	10.0
8270[c]	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0
8321	as received	methanol	-	-	1.0
8325	as received	methanol	-	-	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

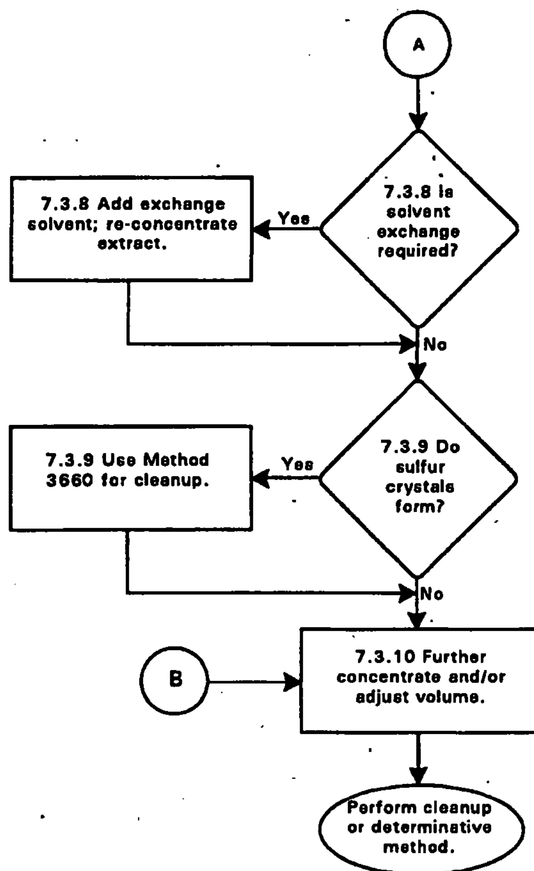
[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed by Method 8041, using a 1.0-mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5-mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3550B
ULTRASONIC EXTRACTION




A
7.3.8 Is solvent exchange required?
Yes
7.3.8 Add exchange solvent; re-concentrate extract.
No
7.3.9 Do sulfur crystals form?
Yes
7.3.9 Use Method 3660 for cleanup.
No
B
7.3.10 Further concentrate and/or adjust volume.
Perform cleanup or determinative method.

METHOD 3510C

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

1.3 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel.

2.2 The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Method 3510 is preferred over Method 3520 for the analysis of these classes of compounds. However, the recovery of phenols may be optimized by using Method 3520, and performing the initial extraction at the acid pH.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2-liter, with polytetrafluoroethylene (PTFE) stopcock.

4.2 Drying column - 20 mm ID Pyrex® chromatographic column with Pyrex® glass wool at bottom and a PTFE 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.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

NOTE: The following glassware is recommended for the purpose of solvent recovery during the concentration procedures requiring the use of Kuderna-Danish evaporative concentrators. Incorporation of this apparatus may be required by State or local municipality regulations that govern air emissions of volatile organics. EPA recommends the incorporation of this type of reclamation system as a method to implement an emissions reduction program. Solvent recovery is a means to conform with waste minimization and pollution prevention initiatives.

4.4 Solvent vapor recovery system (Kontes K-545000-1006 or K-547300-0000, Ace Glass 6614-30, or equivalent).

4.5 Boiling chips - Solvent-extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control (± 5°C). The bath should be used in a hood.

4.7 Vials - 2-mL, glass with PTFE-lined screw-caps or crimp tops.

4.8 pH indicator paper - pH range including the desired extraction pH.

4.9 Erlenmeyer flask - 250-mL.

4.10 Syringe - 5-mL.

4.11 Graduated cylinder - 1-liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall 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. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10 N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL. Other concentrations of hydroxide solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating to 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate. Other concentrations of acid solutions may be used to adjust sample pH, provided that the volume added does not appreciably change (e.g., <1%) the total sample volume.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4. Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents - All solvents must be pesticide quality or equivalent.

5.6.1 Methylene chloride, CH_2Cl_2, boiling point 39°C.

5.6.2 Hexane, C_6H_{14}, boiling point 68.7°C.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$, boiling point 82.3°C.

5.6.4 Cyclohexane, C_6H_{12}, boiling point 80.7°C.

5.6.5 Acetonitrile, CH_3CN, boiling point 81.6°C.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sect. 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample. Alternatively, if the entire contents of the sample bottle are to be extracted, mark the level of sample on the outside of the bottle. If high analyte concentrations are anticipated, a smaller sample volume may be taken and diluted to 1-L with organic-free reagent water, or samples may be collected in smaller sample bottles and the whole sample used.

7.2 Pipet 1.0 mL of the surrogate spiking solution into each sample in the graduated cylinder (or sample bottle) and mix well. (See Method 3500 and the determinative method to be used for details on the surrogate standard solution and matrix spiking solution).

7.2.1 For the sample in each batch (see Chapter One) selected for use as a matrix spike sample, add 1.0 mL of the matrix spiking standard.

7.2.2 If Method 3640, Gel-Permeation Cleanup, is to be employed, add twice the volume of the surrogate spiking solution and the matrix spiking standard, since half of the extract is not recovered from the GPC apparatus. (Alternatively, use 1.0 mL of the spiking solutions and concentrate the final extract to half the normal volume, e.g., 0.5 mL instead of 1.0 mL).

7.3 Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1, using 1:1 (v/v) sulfuric acid or 10 N sodium hydroxide. Lesser strengths of acid or base solution may be employed, provided that they do not result in a significant change (<1%) in the volume of sample extracted (see Secs. 5.3 and 5.5).

7.4 Quantitatively transfer the sample from the graduated cylinder (or sample bottle) to the separatory funnel. Use 60 mL of methylene chloride to rinse the cylinder (or bottle) and transfer this rinse solvent to the separatory funnel. If the sample was transferred directly from the sample bottle, refill the bottle to the mark made in Sec. 7.1 with water and then measure the volume of sample that was in the bottle.

7.5 Seal and shake the separatory funnel vigorously for 1 - 2 minutes with periodic venting to release excess pressure. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. The separatory funnel should be vented into a hood to avoid exposure of the analyst to solvent vapors.

7.6 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the 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 the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.7 Repeat the extraction two more times using fresh portions of solvent (Secs. 7.2 through 7.5). Combine the three solvent extracts.

7.8 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Secs. 7.2 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.9 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.10 Perform the concentration (if necessary) using the Kuderna-Danish Technique (Secs. 7.11.1 through 7.11.6).

7.11 K-D technique

7.11.1 Assemble a Kuderna-Danish (K-D) concentrator (Sec. 4.3) by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11.2 Attach the solvent vapor recovery glassware (condenser and collection device) (Sec. 4.4) to the Snyder column of the K-D apparatus following manufacturer's instructions.

7.11.3 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 Erlenmeyer flask, which contained the solvent extract, with 20 - 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11.4 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 (15 - 20°C above the boiling point of the solvent) 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 - 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.

7.11.5 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Alternatively, pour the exchange solvent into the top of the Snyder column while the concentrator remains on the water bath in Sec. 7.11.4. Concentrate the extract, as described in Sec. 7.11.4, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11.6 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1 - 2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Sec. 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.12.1) or nitrogen blowdown technique (7.12.2) is used to adjust the extract to the final volume required.

7.12.1 Micro-Snyder column technique

If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5 - 10 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 0.5 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, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or the exchange solvent, and adjust the final volume as indicated in Table 1, with solvent.

7.12.2 Nitrogen blowdown technique

7.12.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent to the final volume indicated in Table 1, using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce contaminants.

7.12.2.2 The internal wall of the tube must be rinsed several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube must be positioned to avoid water condensation (i.e., the solvent level should be below the level of the water bath). Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.13 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Sec. 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a PTFE-lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spikes, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

None.

TABLE 1
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

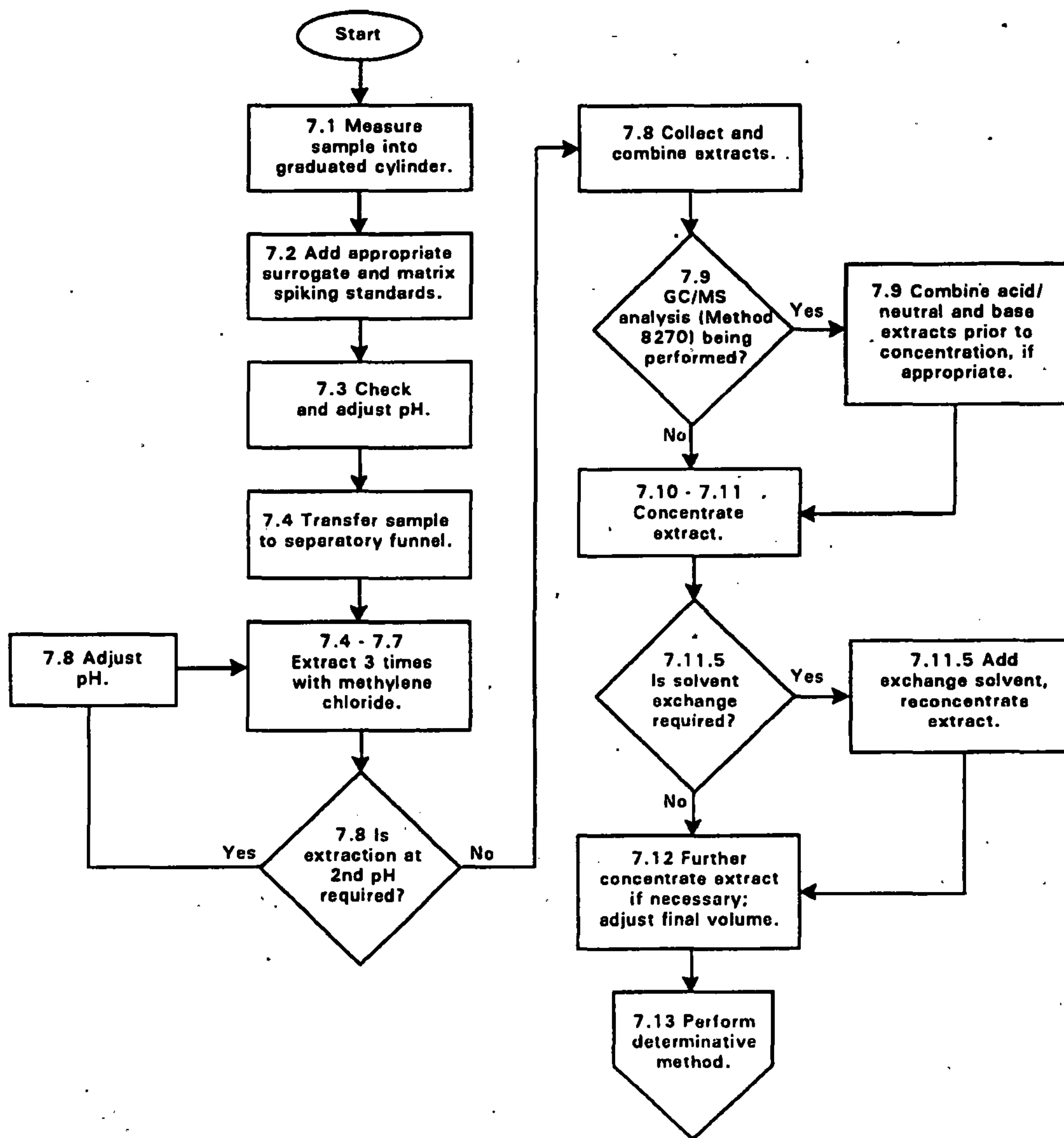
Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)[a]
8041	≤2	none	2-propanol	hexane	1.0	1.0, 0.5[b]
8061	5-7	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8082	5-9	none	hexane	hexane	10.0	10.0
8091	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8111	as received	none	hexane	hexane	2.0	10.0
8121	as received	none	hexane	hexane	2.0	1.0
8141	as received	none	hexane	hexane	10.0	10.0
8270[c,d]	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8325	7.0	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

[a] For methods where the suggested final extract volume is 10.0 mL, the volume may be reduced to as low as 1.0 mL to achieve lower detection limits.

[b] Phenols may be analyzed, by Method 8041, using a 1.0 mL 2-propanol extract by GC/FID. Method 8041 also contains an optional derivatization procedure for phenols which results in a 0.5 mL hexane extract to be analyzed by GC/ECD.

[c] The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

[d] Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Sec. 3.2).


Start
7.1 Measure sample into graduated cylinder.
7.2 Add appropriate surrogate and matrix spiking standards.
7.3 Check and adjust pH.
7.4 Transfer sample to separatory funnel.
7.8 Adjust pH.
7.4 - 7.7 Extract 3 times with methylene chloride.
7.8 Is extraction at 2nd pH required?
Yes
No
7.8 Collect and combine extracts.
7.9 GC/MS analysis (Method 8270) being performed?
Yes
No
7.9 Combine acid/ neutral and base extracts prior to concentration, if appropriate.
7.10 - 7.11 Concentrate extract.
7.11.5 Is solvent exchange required?
Yes
No
7.11.5 Add exchange solvent, reconcentrate extract.
7.12 Further concentrate extract if necessary; adjust final volume.
7.13 Perform determinative method.

Semivolatile Organic Compounds by Gas Chromatography Mass Spectrometry (GC/MS)

Method 8270, Revision 4, March 2001

Lab Manager: ______________________ **Date:** __________

QA Manager: ______________________ **Date:** __________

1. Applicable Matrix or Matrices

1.1. This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from solid waste matrices, soils, air sampling media and water samples.

2. Method Detection Limit (MDL)

2.1. The Estimated Quantitation limit (EQL), and hence, the method detection limit (MDL), of this method for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method.
EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

2.2. See Attachment (Table 6) for current MDL studies.

3. Scope and Application

3.1. This method cover the determination of a number of organic semivolatile compounds that are partitioned into an organic solvent and are suitable to gas chromatography. The compounds listed in Table 3 can be qualitatively and quantitatively determined using this method.

4. Summary of the Method

4.1. Samples are prepared for analysis by gas chromatography/mass spectrometry (GC/MS) by the appropriate sample preparation and, if necessary, sample cleanup procedures.

4.2. The semivolatiles compounds are introduced into the GC/MS by injecting the sample extract into gas chromatograph (GC) with a narrow-bore fused-silica capillary column. The GC column is temperature-programmed to separate the analytes, which are then detected with the mass spectrometer (MS) connected to the gas chromatograph.

4.3. Analytes eluted from the capillary column are introduced into the mass spectrometer via direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact spectra of authentic standards.

Quantitation is accomplished by comparing the response of a major (quantitiation) ion relative to an internal standard using a six-point calibration curve.

5. Definitions

5.1. Internal Standard (IS): A pure analyte(s) added to a sample, extract or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

5.2. Surrogate Analyte (SA): A pure analytes(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

5.3. Laboratory Duplicates (LD1 and LD2): Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation or storage procedures.

5.4. Method Blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The Method Blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

5.5. Laboratory Control Sample (LCS): An aliquot of reagent water or other clean matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

5.6. Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

5.7. Primary Dilution Standard Solution (PDS): A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

5.8. Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6. Interferences

7. Safety

7.1. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method.

7.2. The following parameter covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3´-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4´DDT. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

8. Materials and Equipment

8.1. Hewlett Packard 6890 gas chromatograph, Hewlett Packard 5793 mass selective detector with Hewlett Packard 7683 autosampler. The GC/MS unit is linked to a Hewlett Packard ChemStation Data System.

Mass spectrometer – Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for Decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in the Table 5 in Appendix when 50ng of the GC/MS tuning standard (DFTPP) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC

8.2. Capillary column: Alltech, EC-5 coated fused silica capillary column, 30 meters by 0.25´(0.32) mm ID with 0.25 µm film thickness.

9. Reagents and Standards

9.1. Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall 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.

9.2. Organic-free reagent water – All references to water in this method refer to organic-free reagent water.

9.3. Stock standard solutions (200 mg/L) – Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

Prepare stock standard solution (200 mg/L) by adding 1ml of stocks 9.3.1 to 9.3.8, 200µL of stock 9.3.9, 400µL of stock 9.3.10 to Full Volume of 10ml Methylene Chloride.

9.3.1. CLP Semi-volatiles B/N Mix#1, @ 2000 µg/mL, Absolute # 10001
9.3.2. CLP Semi-volatiles B/N Mix#2, @ 2000 µg/mL, Absolute # 10002
9.3.3. CLP Semi-volatiles Toxic Substances#1, @ 2000 µg/mL, Absolute # 10004
9.3.4. CLP Semi-volatiles Toxic Substances#2, @ 2000 µg/mL, Absolute # 10005
9.3.5. CLP Semi-volatiles Benzidines, @ 2000 µg/mL, Absolute # 10006
9.3.6. CLP Semi-volatiles PAH-Mix, @ 2000 µg/mL, Absolute # 10007
9.3.7. EPA 8270-Analytes Mix#8, @ 2000 µg/mL, Absolute # 100018
9.3.8. Pyridine Standard, @ 2000 µg/mL, Restek # 30409
9.3.9. Acid Surrogates @ 10.000 µg/mL Restek # 31063
9.3.10. B/N Surrogates @ 5000 µg/mL Restek # 31062

9.4. Internal standard solutions – The recommended internal standards are 1,4-dichlorobenzene-d_4 naphthalene-d_8, acenaphthalene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12} (see Table 4).

9.4.1. Semi-Volatile internal standard solution @4000µg/mL Restek # 31006

9.5. GC/MS tuning standard stock solution (1000µg/mL) containing decafluorotriphenylphosphine (DFTPP). The solution should also contain 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance.

9.5.1. The 50 ng/µL of DFTPP tuning solution is made by taking 50 µL of stock below and adding 950 µL of methylene chloride.

Semi-Volatiles Tuning Solution @ 1000 µg/mL Ultra GCM-150. Restek # 1378

9.6. Calibration standards – A minimum of five calibration standards should be prepared at five different concentrations. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in actual samples but should not exceed the working range of the GC/MS system. Each standard should contain each analyte for detection by this method. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

Six initial calibration standards are actually prepared according to the Table 1.

Table 1. Preparation of initial calibration standards

Concentration [µg/L]	Amount of 200ppm stock standard solution (see 9.3) [µL]	Amount of Methylene Chloride [µL]	Amount of internal standard solution (see 9.4) [µL]
5	25	965	10
10	50	940	10
25	125	865	10
50	250	740	10
75	375	615	10
100	500	490	10

9.6.1. Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the premixed certified solutions (or alternately, from the secondary dilution of stock standards – see 9.3).

The standard that is most commonly prepared for calibration verification is the 25 µg/L concentration made by adding 125 µL of 200 ppm standard stock solution (see 9.3), 10µL of SV-internal standard solution (see 9.4) to 865 µL of methylene chloride.

9.6.2. It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

9.7. Surrogate standards – the recommended surrogates are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and terphenyl-d_{14}. These are the surrogates used by the laboratory:

9.7.1. Acid Surrogates @ 10.000 µg/mL Restek # 31063
9.7.2. B/N Surrogates @ 5000 µg/mL Restek # 31062

Each sample undergoing GC/MS analysis must be spiked with 1 mL of each of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required

9.8. Matrix spike and laboratory control standards (LCS) - Matrix spiking standards should be prepared from semivolatile organic compounds, which are representative of the compounds being investigated. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

9.8.1. C-363 BNA Matrix Spike, NCI Solutions, Inc. is used in 8270 method, see Table 2

Table 2. Compounds present in BNA Matrix Spike Mix and their

concentrations.

Compound	Concentration [µg/mL]
4-Chloro-3-methylphenol	150
2-Chlorophenol	150
4-Nitrophenol	150
Pentachlorophenol	150
Phenol	150
Acenaphthene	100
1,4-Dichlorobenzene	100
2,4-Dinitrotoluene	100
N-Nitrosodi-n-propylamine	100
Pyrene	100
1,2,4-Trichlorobenzene	100

0.5 mL of this Matrix Spike solution is added into 1mL of a blank sample.

9.8.2. The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

9.8.3. If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required

9.9. Acetone, hexane, methylene chloride, isooctane, carbon disulfide, toluene and other appropriate solvents should be pesticides quality or equivalent.

10. Sample Collection, Preservation and Storage.

10.1. Sample extracts are stored at 4°C temperature, prior to analysis, in sealed vials (e.g. screw-caps vials or crimp-capped vials) equipped with unpierced PTFE-lined septa.

11. Quality Control

11.1. The GC/MS system must be tuned to meet the DFTPP specifications in Section 12.1 and 12.3.1

11.2. There must be an initial calibration of the GC/MS system as described in Section 12.2

11.3. The GC/MS system must meet the SPCC criteria described in Section 12.3.4 and the CCC criteria in Section 12.3.5 each 12 hours.

11.4. Initial Demonstration of Proficiency – Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever

new staff is trained or significant changes in instrumentation are made.

11.4.1. The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

Prepare a reference sample concentrate in methanol at a concentration such that the spike will provide a concentration in the clean matrix that is 10-50 times the MDL for each analyte in that matrix.

The concentration of the target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of the analyte is being evaluated relative to a regulatory limit or action level, the spike should be at or below the limit, or 1 – 5 times the background concentration (if historical data are available), whichever is higher. If historical data is not available, it is suggested that a background sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculations of recoveries.

11.4.2. To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds), e.g., organic-free reagent water for the aqueous matrix and organic-free sand or soil for the solid matrix.

11.4.3. Prepare the reference sample by adding 1.0 mL of the reference sample concentrate (see Section 11.4) to each of four 1-L aliquots of organic-free reagent water.

11.4.4. Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples.

11.4.5. Calculate the average recovery (x) in µg/L and the standard deviation of the recovery (s) in µg/L for each analyte of interest using the four results.

11.4.6. Single laboratory performance data are included in SW846 8270B, Table 7. Compare s and x for each analyte with the corresponding performance data. If s and x for all analytes of interest meet the appropriate acceptance criteria, then the system performance is acceptable and analysis of actual samples can begin. If any individual s value exceeds the precision limit or any individual x value falls outside the range for accuracy, then the system performance may be unacceptable for that analyte.

11.4.6.1. Locate and correct the source of the problem and repeat the test for all analytes of interest, beginning at Section 11.4.2.

11.4.6.2. Beginning at Section 11.4.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general

problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning at Section 11.4.2.

11.4.7. Even though the method contains performance data, the development of in-house acceptance limits is strongly recommended, and may be accomplished using the procedure below.

11.4.7.1. For each matrix spike sample analyzed, calculate the percent recovery of each matrix spike compound added to the sample using the calculation below.

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n} \times 100$$

where:

C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot

11.4.7.2. Calculate the average percent recovery (p) and the standard deviation (s) for each of the matrix spike compounds after analysis of 15-20 matrix spike samples of the same matrix using the equations below. Calculate the average percent recovery and the standard deviation of each of the surrogates after analysis of 15-20 field samples of the same matrix.

$$p = \sum_{i=1}^{n} p_i$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (p_i - p)^2}{n - 1}}$$

11.4.7.3. After the analysis of 15-20 matrix spike samples of a particular matrix (for matrix spike limits) or 15-20 field samples (for surrogate limits), calculate upper and lower control limits for each matrix spike or surrogate compound:

Upper control limit = p + 3s
Lower control limit = p – 3s

Calculate warning limits as:

Upper warning limit = p + 2s
Lower warning limit = p – 2s

These control limits approximate a 99% confidence interval around the mean recovery; while the warning limits approximate a 95% confidence interval.

11.5. Sample Quality Control for Preparation and Analysis – This includes the analysis of QC samples including a method blank, matrix spike, a duplicate and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample

11.5.1. Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

11.5.2. Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then the analyst may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the analyst should use a matrix spike and matrix spike duplicate pair.

11.5.2.1. Accuracy is estimated from the recovery of spiked analytes from the matrix of interest. Laboratory performance in a clean matrix is estimated from the recovery of analytes in the LCS. Calculate the recovery of each spiked analyte in the matrix spike, matrix spike duplicate and LCS according to the equation in Section 11.4.7.

11.5.2.2. If there is insufficient sample to do a duplicate or a matrix spike/matrix spike duplicate pair, the analyst should prepare a Laboratory Control Sample (LCS) and an LCS duplicate to determine the precision of the analysis. Precision (as RPD) is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where:
C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

11.5.3. A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentration as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. As a general rule, if any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for

recovery, the laboratory should determine if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Section 11.6) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either matrix spikes or surrogates alone.

11.5.4. Recommended QC acceptance criteria for matrix spike samples and LCS

It is necessary for the laboratory to develop single-laboratory performance data for accuracy and precision in the matrices of interest (see Section 11.4.7). Method performance in each matrix is monitored through the use of control charts.

For the LCS, the laboratory should use 70 – 130% as interim acceptance criteria for recoveries of spiked analytes until in-house limits are developed (see Section 11.4.7). Where in-house limits have been developed for matrix spike recoveries, the LCS results should fall within those limits, as the LCS is prepared in a clean matrix.

As a general rule, the recoveries of most compounds spiked into samples should fall within the range of 70 – 130%, and this range should be used as a guide in evaluating in-house performance. However, matrix spike recoveries and LCS recoveries may be affected by the spike-to-background ratio.

11.6. Surrogate recoveries – The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. Use the equations in Section 11.4.7.2 and the definitions in Section 11.4.7.3 to develop laboratory control limits.

11.6.1. Surrogate recovery is calculated as (This calculation is supported by the ChemStation data system if the compound is correctly identified as a surrogate in the method file and the resulting recovery will be present on the report.):

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

If recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

11.6.1.1. Examine the chromatograms for interfering peaks and integrated peak areas

11.6.1.2. Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample

11.6.1.3. If no instrument problem is found, the sample should be re-analyzed

11.6.1.4. If, upon re-analysis (in either Section 11.6.1.2 or 11.6.1.3) the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the reanalysis data to the data user. If holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

11.7. The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place

11.8. The laboratory regularly participates in relevant performance evaluation studies.

12. Calibration and standardization.

12.1. The GC/MS system must be hardware-tuned using a 50 ng injection of DFTPP solution. The analyses must not begin until the tuning criteria are met.

12.1.1. In the absence of specific recommendation on how to acquire the mass spectrum of DFTPP from the instrument manufacture, the following approach has been shown to be useful: Three scans (the peak apex scan and the scans immediately proceeding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan acquired no more than 20 scans prior to the elution of DFTPP. The background subtraction should be designed only to eliminate column bleed or instrument background ions. Do not subtract part of the DFTPP peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer

The approach used above (the average of the apex scan and the two scans immediately adjacent on both sides of the apex) is that used by the ChemStation during the "Autofind DFTPP" menu choice. The analyst may also evaluate the peak at various individual scans and over an average of scans by making the selections and using ChemStation to "Evaluate DFTPP."

12.1.2. Use the DFTPP mass intensity criteria in the Table 5, as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 525 or manufacturer's instructions), provided that the method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSD's, LCS's and blanks associated with a DFTPP analysis must use identical mass spectrometer instrument conditions

12.1.3. The GC/MS tuning standard solution should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20 %. 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 break off the first 6-12 in. of the capillary column. The use of a guard column between the injection port and the analytical column may help to prolong analytical column performance.

12.2. Initial calibration.

12.2.1. To prepare a calibration standard, follow the table in Section 9.6.

12.2.2. The internal standards selected in sec. 9.4 should permit most of the components of interest in a chromatogram to have retention times of 0.80 -1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as a primary ion for quantitation, see Table 3. If interferences are noted, use the next most intense ion as the quantitation ion (i.e. for 1,4-dichlorobenzene-d_4, use 152 m/z ion).

12.2.3. Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 – 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water. Tabulate the area response of the characteristic ions against the concentration for each target analyte and each internal standard (as indicated in Table 4). Calculate response factors (RF) for each target analyte relative to one of the internal standards as follows:

$$RF = \frac{(A_S)(C_{IS})}{(A_{IS})(C_S)}$$

where: A_S = Peak area (or height) of the analyte or surrogate.
A_{IS} = Peak area (or height) of the internal standard.
C_S = Concentration of the analyte or surrogate.
C_{IS} = Concentration of the internal standard.

The ChemStation data system software supports this calculation.

12.2.4. System performance check compounds (SPCCs).

12.2.4.1. A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatile the SPCC compounds are:

- N-Nitrosodi-n-propylamine,
- hexachloropentadiene,
- 2,4-dinitrophenol

- 4-nitrophenol.

These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.

12.2.4.2. Calculate the mean RF for each target analyte using the RF values calculated from the initial (a minimum of a 5-point) calibration curve. The minimum acceptable average RF for these compounds is 0.0500. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated. A system performance check should be made before this calibration curve is used.

12.2.5. Calibration check compounds (CCCs)

12.2.5.1. The purpose of the CCC is to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in sec.12.2.7.

12.2.5.2. Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \text{mean RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\text{mean RF}} \times 100$$

where:

Rf_i = RF for each of the calibration standards
mean RF = mean RF for each compound in the initial calibration
n = Number of calibration standards

12.2.5.3. The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. The CCCs are:

- Acenaphthene,
- 1,4-Dichlorobenzene,
- Hexachlorobutadiene,
- Diphenylamine,

- Di-n-octyl phthalate,
- Fluoranthene,
- Benzo(a)Pyrene,
- 4-Chloro-3-methylphenol,
- 2,4-Dichlorophenol,
- 2-Nitrophenol,
- Phenol,
- Pentachlorophenol,
- 2,4,6-Trichlorophenol..

12.2.5.4. If an RSD of greater than 30% is measure for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

12.2.6. Evaluation of retention times – The relative retention time (RRT) of each target analyte in each calibration standard should agree within 0.06 RRT units. Late-eluting target analytes usually have much better agreement.

12.2.7. Linearity of target analytes.

12.2.7.1. If the RSD of any target analytes is 15 % or less then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation

12.2.7.2. If the RSD of any target analyte is greater than 15 %, use one of the additional calibration options below. The ChemStation data system supports all of the models below except for Data Transformations

12.2.7.3. Calibration linearity

SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data, as described below. Given the limitations in instrument data systems, it is likely that the analyst will have to choose one model for all analytes in a particular method. (Multiple models are allowable for use with the ChemStation data system.) Both models can be applied to internal standard calibration data.

NOTE: The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

Whichever calibration model is employed, a unique analyte or surrogate concentration must fall within the calibration range. Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

NOTE: The following sections describe various options for initial calibration and provide the calibration acceptance criteria used to evaluate each option.

The criteria listed in these sections are designed for quantitation of trace level concentration of the analytes of interest. If data of lesser quality will satisfy project-specific data needs, then less stringent criteria may be employed, provided that they are documented and approved in a project-specific QA project plan.

The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met. The second approach is to use a *priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of the physics of the detector or specific manufacturer's recommendations.

12.2.7.3.1. Linear calibration using the average response factor

When calculated as described in Section 12.2.3, response factors are a measure of the slope of the calibration relationship and assume that the curve passes through the origin. Under ideal conditions, the factors will not vary with the concentration of the standard that is injected into the instrument. In practice, some variation is to be expected. However, when the variation measured as the relative standard deviation (RSD) is less than or equal to 15%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin.

NOTE: Linearity through zero is a statistical assumption and not a rationale for reporting results below the calibration range demonstrated by the analysis of the standards.

To evaluate the linearity of the initial calibration, calculate the mean RF, the standard deviation (SD), and the RSD as follows:

$$\text{mean RF} = \sum_{i=1}^{n} RF_i$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (RF_i - \text{mean RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\text{mean RF}} \times 100$$

If the RSD of the response factors is less than or equal to 15 % over the calibration range, then linearity through the origin may be assumed, and the average response factor may be used to determine sample concentrations

12.2.7.3.2. Given the potentially large numbers of analytes that may be

analyzed in some methods, it is likely that some analytes may exceed the 15% acceptance limit for the RSD for a given calibration. In those instances, the following steps are recommended, but not required.

The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Section 18 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 15 %, the analyst may wish to review the results (area counts, response factors and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. Changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

NOTE: As noted in Section 9.6, the method quantitiation limit is established by the concentration of the lowest standard analyzed during the initial calibration. Hence, narrowing the calibration range by changing the concentration of the lowest standard will, by definition, change the method quantitation limit. When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the analyst must ensure that the method quantitation limit is at least as low as the regulatory limit or action level

12.2.7.3.3. In those instances where the RSD for one or more analytes exceeds 15%, the initial calibration may still be acceptable if the following conditions are met:

12.2.7.3.3.1. The mean of the RSD values for all analytes in the calibration is less than or equal to 15 %. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes. If no analyte has an RSD above 15 %, then the mean RSD calculation need not be performed.

12.2.7.3.3.2. The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a

specific project. In other words, if the target analyte is part of the calibration standard, its RSD value is included in the evaluation.

12.2.7.3.3.3. The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 15% and the results of the mean RSD calculation.

NOTE: The analyst and the data user must be aware that the use of the approach listed in Section 12.2.7.3.2 (i.e., the average of all RSD values ≤15%) will lead to greater uncertainty for those analytes for which the RSD is greater than 15%. The analyst and the data user should review the associated quality control sample results carefully, with particular attention to the matrix spike and laboratory control sample results (see Sections 11.5.2 and 11.5.3), to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to employ one of the other calibration approaches (see Sections 12.2.7.4 and 12.2.7.5) or adjust the instrument operating conditions and/or the calibration range until the RSD is ≤ 15%.

12.2.7.3.4. If all of the conditions in Section 12.2.7.3.3 are met, then the average response factor may be used to determine sample concentration as described in Section 14.1.1.

12.2.7.4. Linear calibration using a least squares regression

If the RSD of the response factors is greater than 15 % over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on past experience or a *priori* knowledge of the instrument response. Further, at the discretion of the analyst, this approach also may be used for analytes that do meet the RSD limits in Section 12.2.7.3.1.

This is most easily achieved by performing a linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphic convention.

The analyst may also employ a weighted least squares regression if replicate multi-point calibrations have been performed, e.g., three 5-point curves. For all other instances, an appropriate unweighted least squares method should be used. When using a weighted linear least squares regression, the following weighting factor should be used:

$$\frac{1}{SD^2}$$

where SD is the standard deviation of the replicate results at each individual standard concentration. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

where:

y = Instrument response (peak area or height)
a = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = The intercept

The analyst should not force the line through the origin, but have the intercept calculated from the data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0,0) as a calibration point. The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

When a weighted linear least squares regression is employed, the regression equation becomes:

$$y = \frac{1}{SD^2}(ax + b)$$

which may be rearranged to solve for x, the concentration. Using internal standard quantitation, the regression equation is rearranged as shown below:

$$\frac{A_S C_{IS}}{A_{IS}} = aC_S + b$$

where:

A_S = Area (or height) of the peak for the target analyte in the sample
A_{IS} = Area (or height) of the peak for the internal standard
C_S = Concentration of the target analyte in the calibration standard
C_{IS} = Concentration of the internal standard
a = Slope of the line (also called the coefficient of C_s)
b = The intercept

In calculating sample concentrations by the internal standard method, the regression equation is rearranged to solve for the concentration of the target analyte (C_s) as shown below:

$$C_s = \frac{\frac{A_s C_{is}}{A_{is}} - b}{a}$$

12.2.7.5. Non-linear calibration

In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model may be employed.

NOTE: It is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentration or to avoid proper instrument maintenance. Thus, non-linear calibration should not be employed for methods or instruments previously shown to exhibit linear calibration for the analytes of interest.

When using a calibration model for quantitation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

As noted above, the model must be continuous. A curve is continuous when it has consecutive numerical values along the function, whether increasing or decreasing, and without having breaks in the function (i.e., the pen shall never leave the paper from the minimum to the maximum). The model must also be continuously differentiable, such that all derivatives of the function are continuous functions themselves, and monotonic, such that all tangent lines of the derivative to all of the points on the calibration curve have either only positive or negative slopes.

If the model is not a polynomial, it should not include more than four parameters, i.e.,

$$y = f(a, b, c, d, x)$$

where "f" indicates a function with up to four parameters.

In estimating model parameters for the calibration data, the instrumental response (y) must be treated as the dependent variable. Do not force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point. Model estimates from the regression must be used as calculated, i.e., if the model is a polynomial, the intercept is d and may not be set to 0. Weighting in a calibration model may significantly improve its accuracy.

The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches described above. Whereas this method employs a minimum of five standards for a linear (first order) calibration model, a quadratic (second order) model requires six standards, and a third order polynomial requires seven standards.

Most curve fitting programs will use some form of a least squares minimization to adjust the coefficients of the polynomial (a,b,c and d above) to obtain the polynomial that best fits the data. The "goodness of fit" of the polynomial equation is evaluated by calculating the weighted coefficient of the determination (COD).

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \text{mean } y)^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - Y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \text{mean } y)^2}$$

where:

y_{obs} = Observed response (area) for each concentration from each initial calibration standard
mean y = Mean observed response from the initial calibration
Y_i = Calculated (or predicted) response at each concentration from the initial calibration(s)
n = Total number of calibration points (i.e., 6 for a quadratic model; 7 for a third order model)
p = Number of adjustable parameters in the polynomial equation (i.e., 3 for a third order; 2 for a second order polynomial)

Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

As noted in Section 12.2.7.3, whichever of these options is employed, a unique analyte or surrogate concentration must fall within the calibration range. Analysts are advised to check both second and third order calibration models to ensure that this holds true (e.g., no parabolas or repeating functions in the calibration range). Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

12.2.7.6. Data transformations

An understanding of the fundamental behavior of the detector may be used to choose a data transformation that will then allow for a simple calibration model. For

example, the response of a flame photometric detector in the sulfur mode is known to be proportional to the square of the sulfur concentration. Therefore, using the data system to take the square root of the instrument response before integration or the square root of the peak height allows for a calibration factor approach rather than a polynomial calibration curve. Instrument response may be transformed prior to any calculations (including integration) subject to the following constraints:

12.2.7.6.1. Any parameters used in the transformation should be fixed for the calibration and all subsequent analyses and verifications until the next calibration.

12.2.7.6.2. The transformation model chosen should be consistent with the behavior of the instrument detector. All data transformations must be clearly defined and documented by the analyst and related back to the fundamental behavior of the detector. In other words, this approach may not be used in the absence of specific knowledge about the behavior of the detector, nor as a "shot in the dark" to describe the calibration.

12.2.7.6.3. No transformations should be performed on areas or other results (e.g., the transformation must be applied to the instrument response itself).

12.2.7.6.4. When the transformed data are used to develop calibration factors, those factors must meet the acceptance criteria described in Section 12.2.7.3.1.

12.2.7.7. When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standards preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

12.3. GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

12.3.1. Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the DFTPP must meet the criteria given in the table in Appendix before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

12.3.2. The initial calibration curve for each compound of interest should be verified once every 12 hours prior to sample analysis using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Sections 12.3.4 and 12.3.5.

<u>NOTE</u>: The DFTPP and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

12.3.3. A method blank should be analyzed after the calibration standard, or at any

other time during the analytical shift to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

12.3.3.1. The results of the method blank should be:

12.3.3.1.1. Less than the laboratory's MDL for the analyte or less than the level of acceptable blank contamination specified in the approved quality assurance project plan.

12.3.3.1.2. Less than 5% of the regulatory limit associated with an analyte.

12.3.3.1.3. Or less than 5% of the sample result for the same analyte, whichever is greater.

12.3.3.1.4. If the method blank results do not meet the acceptance criteria above, then the analyst should take corrective action to locate and reduce the source of the contamination and to re-extract and reanalyze any samples associated with the contaminated method blank.

12.3.4. System Performance Check Compounds (SPCCs)

12.3.4.1. A system performance check must be made during each 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Section 12.3.4.2). This is the same check that is applied during the initial calibration.

12.3.4.2. If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

12.3.5. Calibration Check Compounds (CCCs)

12.3.5.1. After the system performance check is met, the CCCs listed in Section 12.2.6.3 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model.

12.3.5.1.1. Verification of linear calibrations

Calibration verification for linear calibration involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate %Drift or %Difference, depending on the model used.

$$\%Drift = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

where the calculated concentration is determined using the mean response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\%Difference = \frac{RF_V - \text{mean RF}}{\text{mean RF}} \times 100$$

where RF_V is the response factor from the analysis of the verification standard, and mean RF is the mean response factor from the initial calibration.

12.3.5.1.2. Verification of a non-linear calibration

Calibration verification of a non-linear calibration is performed using the percent drift calculation described in Section 12.3.5.1.1. It may also be appropriate to employ two standards at different concentrations to verify the calibration. In this instance, one standard should be near the inflection point in the curve. The choice of specific standards and concentrations is generally a method- or project-specific consideration

12.3.5.2. If the percent difference or drift for each CCC is less than or equal to 20 %, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20 % difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20 % difference criterion.

12.3.5.2.1. Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

12.3.5.3. Internal standard retention time – The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions an corrections must be made, as required.

12.3.5.4. Internal standard response – If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50 % to +100 %) from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the

system was malfunctioning is required.

13. Procedure

13.1. GC/MS conditions

13.1.1. GC operating conditions

Injector temperature:	260 °C
Transfer line temperature:	110 °C
Carrier gas (He) flow rate:	1.0 mL/min
Initial temperature:	40 °C, hold for 3 minutes
Temperature program:	20 °C/min to 140 °C, hold for 0 minutes
	15 °C/min to 330 °C
Final temperature:	260 °C, hold for 2 minutes
Injector:	Splitless
Injection volume:	1µL

13.1.2. MS operating conditions

Mass range:	35-550
Scan time:	5.41 scan/sec
Source temperature:	250 °C

13.2. GC/MS analysis of samples

13.2.1. It is highly recommended that the sample extracts be screened on a GC/FID or GC/PID using the same type of capillary column used in the GC/MS system. This will minimize contamination of the GC/MS system from unexpectedly high concentration of organic compounds. Sample screening is particularly important when this method is used to achieve low detection levels.

13.2.1.1. Currently, no screening methods are employed by this laboratory, but client histories are utilized. This information is available on the LIMS.

13.2.2. DFTPP tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

13.2.3. All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

13.2.4. Inject a 1µL aliquot of the sample extract into the GC/MS system, using the same operating conditions that were used for the calibration (see Section13.1).

13.2.5. If the response for any quantitation ion exceeds the initial calibration range of the GC/MS system, the sample extract must be diluted and reanalyzed. Additional internal standard must be added to the diluted extract to maintain the same concentration as in the calibration standards (40 ng/µL)

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks and standards to effectively check drifting method performance, poor injection execution and anticipate the need for system inspection and/or maintenance.

13.2.6. The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

13.3. Qualitative analysis

13.3.1. The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characterisitic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

13.3.1.1. The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time, such as that of the ChemStation data system, will be accepted as meeting this criterion.

13.3.1.2. The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

13.3.1.3. The relative intensities of the characteristic ions agree within 30 % of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50 % in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20 % and 80 %.)

13.3.1.4. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25 % of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.3.1.5. Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

13.3.1.6. Examination of extracted ion current profiles of appropriate ions can aid in selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

13.3.2. For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste diluting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

13.3.2.1. 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.

13.3.2.2. The relative intensities of the major ions should agree within ±20 %. (Example: For an ion with an abundance of 50 % in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70 %).

13.3.2.3. Molecular ions present in the reference spectrum should be present in the sample spectrum.

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

13.3.2.5. 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 peaks. Data system library reduction programs can sometimes create these discrepancies.

13.4. Quantitative analysis

13.4.1. Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

13.4.2. If the RSD of a compound's response factors is 15 % or less, then the concentration in the extract may be determined using the average response factor (mean RF) from initial calibration data (Section 14.1.1).

13.4.3. Where applicable, the concentration of any non-target analytes identified in the

sample (Section 13.3.2) should be estimated. The same formulae should be used with the following modifications: The areas A_S and A_{IS} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1.

13.4.4. The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14. Data Analysis and Calculations

14.1. The calculation of analyte and surrogate concentrations is completed by the ChemStation software using one of the equations below, depending upon the model used in the calibration.

14.1.1. Linear calibration:

14.1.1.1. Aqueous samples

$$\text{Concentration}\ (\mu g/mL) = \frac{(A_S)(C_{IS})(D)}{(A_{IS})(\text{meanRF})(V_S)}$$

where:
A_S = Area (or height) of the peak for the analyte in the sample
A_{IS} = Area (or height) of the peak for the internal standard
C_{IS} = Concentration of the internal standard in the concentrated sample extract or volume purged in µg/L
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D=1. The dilution factor is always dimensionless.
mean RF = Mean response factor from the initial calibration.
V_S = Volume of the aqueous sample extracted or purged (mL). If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL which is equivalent to µg/L.

14.1.1.2. Nonaqueous samples

$$\text{Concentration}\ (\mu g/kg) = \frac{(A_S)(C_{IS})(D)}{(A_{IS})(\text{mean RF})(W_S)}$$

where: A_S, A_{IS}, C_{IS}, D and mean RF are the same as for aqueous samples, and
W_S = weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in

units of ng/g which is equivalent to µg/kg.

14.1.1.3. If a linear calibration that does not pass through the origin has been employed, then the regression equation is rearranged as shown in Section 12.2.7.4

14.1.2. Calculations for a non-linear calibration curve

When a non-linear curve has been employed, the non-linear model is rearranged to solve for the concentration of the analyte in volume, and the concentration is converted to a sample concentration using the equation below.

$$Cs = \frac{(C_{ex})(V_t)}{(V_s)}$$

where:

C_S = Concentration in the sample
C_{ex} = Concentration in final extract
V_t = Total volume of the concentrated extract
V_S = Volume of the sample extracted

For solid samples, substitute the weight of the sample, W_S, for V_S.

The concentration of the analyte in the volume of the sample that is purged will be the same as in the original sample, except when dilutions are performed.

15. Method Performance

15.1. Initial Demonstration of Laboratory Accuracy and Precision Table 7

15.2. MDL Study Table 6

15.2.1. Method detection limits were calculated using the formula:

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

where:

$t_{(n-1,1-alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = Number of replicates
S = The standard deviation of the replicate analysis

16. Pollution Prevention

16.1. See the current revision of PSC SOP SA002.

17. Data Assessment and Acceptance Criteria for Quality Control Programs

17.1. A summary of the raw data, spike recovery form and a quality control form noting surrogate recoveries, internal standard responses and if the sample was run within the 12-hour time period from the last tune check are copied and put into the project folder after validation by a second analyst/supervisor.

17.2. The reported values are then entered into LIMS. Data is further validated in LIMS by a third analyst

17.3. Each of the chromatograms for the raw data are initialed by the analyst and saved according to the run date with all other GC/MS data for the particular volatiles instrument.

18. Corrective Actions for Out-Of-Control Data

18.1. Initial Calibration has some analytes that exceed the 15 % acceptance limit for the RSD – The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Section 18.2 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 15 %, the analyst may wish to review the results (area counts, response factors and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

18.2. Suggested chromatographic system maintenance

Corrective measures may involve any one or more of the following remedial actions. This list is by no means comprehensive and analysts should develop expertise in trouble shooting their specific instruments and analytical procedures. The manufacturers of chromatographic instruments, detectors, columns and accessories generally provide detailed information regarding the proper operation and limiting factors associated with their products. The importance of reading and reviewing this information cannot be over-emphasized.

18.2.1. Capillary GC columns

Routine maintenance may compel the analyst to clean and deactivate the glass injection port insert or replace it with a fresh insert that has been cleaned and deactivated with dichlorodimethylsilane. Cut off 0.5 – 1.0 m of the injector end of the column using a 90 ° cut. Place ferrule onto the column before cutting.

Exceptional maintenance may compel the analyst to replace gas traps and backflush the column with solvent, if appropriate, according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

18.2.2. Metal (GC) injector body

Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert. Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

Prepare a solution of deactivating agent (dichlorodimethylsilane) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution; serially rinse the injector body with toluene, methanol, acetone, hexane and methanol again. Reassemble the injector and replace the GC column.

NOTE: Due to the solvents (Toluene and acetone are common target compounds.) used in this procedure, this should only be used as a last resort to eliminate active sites. The final methanol rinse must be thorough enough to remove all traces of these solvents in the injection port.

18.3. Calibration verification

18.3.1. A system performance check must be made during each 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Section 12.2.4). If the minimum response factors

are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

18.3.2. If the percent difference or drift for each CCC is less than or equal to 20 % for the calibration verification, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20 % difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20 % difference criterion.

18.3.3. The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions an corrections must be made, as required.

18.3.4. If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50 % to +100 %) from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

18.4. If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the laboratory should determine if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Section 11.6) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either matrix spikes or surrogates alone.

18.5. If surrogate recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

18.5.1. Examine the chromatograms for interfering peaks and integrated peak areas.

18.5.2. Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample.

18.5.3. If no instrument problem is found, the sample should be re-analyzed.

18.5.4. If, upon re-analysis (in either Section 18.5.1 or 18.5.3) the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the reanalysis data to the data user. If

holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

18.6. The results of the method blank should be:

18.6.1. Less than the laboratory's MDL for the analyte or less than the level of acceptable blank contamination specified in the approved quality assurance project plan.

18.6.1.1. Less than 5 % of the regulatory limit associated with an analyte.

18.6.1.2. Or less than 5 % of the sample result for the same analyte, whichever is greater.

18.6.1.3. If the method blank results do not meet the acceptance criteria above, then the analyst should take corrective action to locate and reduce the source of the contamination and to re-extract and reanalyze any samples associated with the contaminated method blank.

18.7. Any sample result that falls above 10 % of the range of the calibration must be diluted to a value that falls within the calibration curve.

18.8. When a sample is analyzed that has saturated response from a compound, the samples immediately following that sample may contain responses for that compound above the detection limit, depending on the degree of saturation. It is up to the analyst's discretion and history of the client samples, if available, to determine if these results are representative of the sample or due to carryover and if the latter is true to proceed with reanalysis.

19. Contingencies for Handling Out-of-Control Data or Unacceptable Data

19.1. See Section 18

20. Waste Management

20.1. See the current revision of PSC SOP SA002.

21. References

21.1. SW846 8270B, Revision 3, December 1996 –SemiVolatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS)

21.2. SW846 8000B, Revision 2, December 1996 – Determinative Chromatographic Separations

MS002_02

Philip Analytical Services

Semi Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS)

In-Service Date: March 8, 2001

I certify that I have read, understood, and will abide by the procedures set forth in this Policy.

Laboratory Personnel Responsible for Implementation of this Policy include:

Signature/Date

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Attachment

Table 3.

Semi volatile compounds, which can be determined by this method. Compounds analyzed by our laboratory are indicated in bold.

Compounds	CAS No[a]	Primary Ion	Secondary Ion(s)
Acenaphthene	83-32-9	154	153,152
Acenaphthylene	208-96-8	152	151,153
Acetophenone	98-86-2	105	71,75,120
2-Acetylaminofluorene	53-96-3	181	180,223,152
1-Acetyl-2-thiourea	591-08-2	118	43,42,76
Aldrin	309-00-2	66	263,220
2-Aminoanthraquinone	117-79-3	223	167,195
Aminoazobenzene	60-09-3	197	92,120,65,77
4-Aminobiphenyl	92-67-1	169	168,170,115
3-Amino-9-ethylcarbazole	132-32-1	195	210,181
Anilazine	101-05-3	239	241,143,178,89
Aniline	62-53-3	93	66,65
o-Anisidine	90-04-0	108	80,123,52
Anthracene	120-12-7	178	176,179
Aramite	140-57-8	185	191,319,334,197,321
Aroclor 1016	12674-11-2	222	260,292
Aroclor 1221	11104-28-2	190	224,260
Aroclor 1232	11141-16-5	190	224,260
Aroclor 1242	53496-21-9	222	256,292
Aroclor 1248	12672-29-6	292	362,326
Aroclor 1254	11097-69-1	292	362,326
Aroclor 1260	11096-82-5	360	362,394
Azinphos-methyl	86-50-0	160	132, 93.104,105
Azobenzene	103-33-3	77	51,182,105
Barban	101-27-9	222	51,87,224,257,153
Benzidine	92-87-5	184	92,185
Benzoic acid	65-85-0	122	105,77
Benz(a)anthracene	56-55-3	228	229,226
Benzo(b)fluoranthene	205-99-2	252	253,125
Benzo(k)fluoranthene	207-08-9	252	253,125
Benzo(g,h,i)perylene	191-24-2	276	138,277
Benzo(a)pyrene	50-32-8	252	253,125
p-Benzoquinone	106-51-4	108	54,82,80
Benzyl alcohol	100-51-6	108	79,77
α-BHC	319-84-6	183	181,109
β-BHC	319-85-7	181	183,109
δ-BHC	319-86-8	183	181,109
γ-BHC	58-89-9	183	181,109
Bis(2-chloroethoxy)methane	111-91-1	93	95,123
Bis(2-chloroethyl) ether	111-44-4	93	63,95

Bis(2-chloroisopropyl) ether	108-60-1	45	77,121
Bis(2-ethylhexyl) phthalate	117-81-7	149	167,279
4-Bromophenyl phenyl ether	101-55-3	248	250,141
Bromoxynil	1689-84-5	277	279,88,275,168
Butyl benzyl phthalate	85-68-7	149	91,209
Captafol	2425-06-1	79	77,80,107
Captan	133-06-2	79	149,77,119,117
Carbaryl	63-25-2	144	115,116,201
Carbofuran	1563-66-2	164	149,131,122
Carbophenothion	786-19-6	157	97,121,342,159,199
Chlordane	57-74-9	373	375,377,371
Carbazole	86-74-8	167	166,168
Chlorfenvinphos	470-90-6	267	269,323,325,295
4-Chloroaniline	106-47-8	127	129,65,92
Chlorobenzilate	510-15-6	251	139,253,111,141
5-Chloro-2-methylaniline	95-79-4	106	141,140,77,89
4-Chloro-3-methylphenol	59-50-7	107	144,142
3-(Chloromethyl) pyridine hydrochloride	6959-48-4	92	127,129,65,39
1-Chloronaphthalene	90-13-1	162	127,164
2-Chloronaphthalene	91-58-7	162	127,164
2-Chlorophenol	95-57-8	128	64,130
4-Chloro-1,2-phenylenediamine	95-83-0	142	80,144
4-Chloro-1,3-phenylenediamine	5131-60-2	142	80,144
4-Chlorophenyl phenyl ether	7005-72-3	204	206,141
Chrysene	218-01-9	228	226,229
Coumaphos	56-72-4	362	226,210,364,97,109
p-Cresidine	120-71-8	122	94,137,77,93
Crotoxyphos	7700-17-6	127	105,193,166
2-Cyclohexyl-4,6-dinitro-phenol	131-89-5	231	185,41,193,266
4,4'-DDD	72-54-8	235	237,165
4,4'-DDE	72-55-9	146	248,176
4,4'-DDT	50-29-3	235	237,165
Demeton-O	298-03-3	88	89,60,61,115,171
Demeton-S	126-75-0	88	60,81,89,114,151
Diallate (cis or trans)	2303-16-4	86	234,43,70
2,4-Diaminotoluene	95-80-7	121	122,94,77,104
Dibenz(a,j)acridine	224-42-0	279	280,277,250
Dibenz(a,h)anthracene	53-70-3	278	139,279
Dibenzofuran	1332-64-9	168	139
Dibenzo(a,e)pyrene	192-65-4	302	151,150,300
1,2-Dibromo-3-chloropropane	96-12-8	157	155,75,159
Di-n-butyl phthalate	84-74-2	149	150,104
Dichlone	117-80-6	191	163,226,228,135,193
1,2-Dichlorobenzene	95-50-1	146	148,111
1,3-Dichlorobenzene	541-73-1	146	148,111
1,4-Dichlorobenzene	106-46-7	146	148,111
3,3'-Dichlorobenzidine	91-94-1	252	254,126
2,4-Dichlorophenol	120-83-2	162	164,98
2,6-Dichlorophenol	87-65-0	162	164,98

Dichlorovos	62-73-7	109	185,79,145
Dicrotophos	141-66-2	127	67,72,109,193,237
Dieldrin	60-57-1	79	263,279
Diethyl phthalate	84-66-2	149	177,150
Diethylstilbestrol	56-53-1	268	145,107,239,121,159
Diethyl sulfate	64-67-5	139	45,59,99,111,125
Dihydrosaffrole	56312-13-1	135	64,77
Dimethoate	60-51-5	87	93,125,143,229
3,3'-Dimethoxybenzidine	119-90-4	244	201,229,186
Dimethylaminoazobenzene	60-11-7	225	120,77,105,148,42
7,12-Dimethylbenz(a)-anthracene	57-97-6	256	241,239,120
3,3'-Dimethylbenzidine	119-93-7	212	106,196,180
þ,þ-Dimethylphenethylamine	122-09-8	58	91,65,42
2,4-Dimethylphenol	105-67-9	122	107,121
Dimethyl phthalate	131-11-3	163	194,164
1,2-Dinitrobenzene	528-29-0	168	50,63,74
1,3-Dinitrobenzene	99-65-0	168	75,50,76,92,122
1,4-Dinitrobenzene	100-25-4	168	75,50,76,92,122
4,6-Dinitro-2-methylphenol	534-52-1	198	51,105
2,4-Dinitrophenol	51-28-5	184	63,154
2,4-Dinitrotoluene	121-14-2	165	63,89
2,6-Dinitrotoluene	606-20-2	165	63,89
Dinocap	39300-45-3		
Dinoseb	88-85-7	211	163,147,117,240
Dioxathion	78-34-2	97	125,270,153
Diphenylamine	122-39-4	169	168,167
5,5-Diphenylhydantoin	57-41-0	180	104,252,223,209
1,2-Diphenylhydrazine	122-66-7	77	105,182
Di-n-octyl phthalate	117-84-0	149	167,43
Disulfoton	298-04-4	88	97,89,142,186
Endosulfan I	959-98-8	195	339,341
Endosulfan II	33213-65-9	337	339,341
Endosulfan sulfate	1031-07-8	272	387,422
Endrin	72-20-8	263	82,81
Endrin aldehyde	7421-93-4	67	345,250
Endrin ketone	53494-70-5	317	67,319
EPN	2104-64-5	157	169,185,141,323
Ethion	563-12-2	231	97,153,125,121
Ethyl carbamate	51-79-6	62	44,45,74
Ethyl methanesulfonate	62-50-0	79	109,97,45,65
Famphur	52-85-7	218	125,93,109,217
Fensulfothion	115-90-2	293	97,308,125,292
Fenthion	55-38-9	278	125,109,169,153
Fluchloralin	33245-39-5	306	63,326,328,264,65
Fluoranthene	206-44-0	202	101,203
Fluorene	86-73-7	166	165,167
2-Fluorobiphenyl (surr)	321-60-8	172	171
2-Fluorophenol (surr)	367-12-4	112	64
Heptachlor	76-44-8	100	272,274

Heptachlor epoxide	1024-57-3	353	355,351
Hexachlorobenzene	118-74-1	284	142,249
Hexachlorobutadiene	87-68-3	225	223,227
Hexachlorocyclopentadiene	77-47-4	237	235,272
Hexachloroethane	67-72-1	117	201,199
Hexachlorophene	70-30-4	196	198,209,211,406,408
Hexachloropropene	1888-71-7	213	211,215,117,106,141
Hexamethylphosphoramide	680-31-9	135	44,179,92,42
Hydroquinone	123-31-9	110	81,55,53
Indeno(1,2,3-cd)pyrene	193-39-5	276	138,227
Isodrin	465-73-6	193	66,195,263,265,147
Isophorone	78-59-1	82	95,138
Isosafrole	120-58-1	162	131,104,77,51
Kepone	143-50-0	272	274,237,178,143,270
Leptophos	21609-90-5	171	377,375,77,155,139
Malathion	121-75-5	173	125,127,93,158
Maleic anhydride	108-31-6	54	98,53,44
Mestranol	72-33-3	277	310,174,147,242
Methapyrilene	91-80-5	97	50,191,71
Methoxychlor	72-43-5	227	228,152,114,274,212
3-Methylcholanthrene	56-49-5	268	252,253,126,134,113
4,4'-Methylenebis(2-chloroaniline)	101-14-4	231	266,268,140,195
4,4'-Methylenebis (N,N-dimethylaniline)	101-61-1	254	253,134,126,210
Methyl methanesulfonate	66-27-3	80	79,65,95
2-Methylnaphthalene	91-57-6	142	141
Methyl parathion	298-00-0	109	125,263,79,93
2-Methylphenol	95-48-7	107	108,77,79,90
3-Methylphenol	108-39-4	107	108,77,79,90
4-Methylphenol	106-44-5	107	108,77,79,90
Mevinphos	7786-34-7	127	192,109.67,164
Mexacarbate	315-18-4	165	150,134,164,222
Mirex	2385-85-5	272	237,274,270,239,235
Monocrotophos	6923-22-4	127	192,67,97,109
Naled	300-76-5	109	145,147,301,79,189
Naphthalene	91-20-3	128	129,127
1,4-Naphthoquinone	13015-4	158	104,102,76,50,130
1-Naphthylamine	134-32-7	143	115,89,63
2-Naphthylamine	91-59-8	143	115,116
Nicotine	54-11-5	84	133,161,162
5-Nitroacenaphthene	602-87-9	199	152,169,141,115
2-Nitroaniline	88-74-4	65	92,138
3-Nitroaniline	99-09-2	138	80,123,52
4-Nitroaniline	100-01-6	138	65,108,92,80,39
5-Nitro-o-anisidine	99-59-2	168	79,52,138,153,77
Nitrobenzene	98-95-3	77	123,65
Nitrobenzene-d_5 (surr)		82	128,54
4-Nitrobiphenyl	92-93-3	199	152,141,169,151
Nitrofen	1836-75-5	283	285,202,139,253
2-Nitrophenol	88-75-5	139	109,65

4-Nitrophenol	100-02-7	139	109,65
5-Nitro-o-toluidine	99-55-8	152	77,79,106,94
4-Nitroquinoline-1-oxide	56-57-5	174	101,128,75,116
N-Nitrosodi-n-butylamine	924-16-3	84	57,41,116,158
N-Nitrosodiethylamine	55-18-5	102	42,57,44,56
N-Nitrosodimethylamine	62-75-9	42	74,44
N-Nitrosomethylethylamine	10595-95-6	88	42,43,56
N-Nitrosodiphenylamine	86-30-6	162	104,77,103,135
N-Nitrosodi-n-propylamine	621-64-7	70	42,101,130
N-Nitrosomorpholine	59-89-2	56	116,30,86
N-Nitrosopiperidine	100-75-4	114	42,55,56,41
N-Nitrosopyrrolidine	930-55-2	100	41,42,68,69
Octamethyl pyrophosphoramide	152-16-9	135	44,199,286,153,243
4,4'-Oxydianiline	101-80-4	200	108,171,80,65
Parathion	56-38-2	109	97,291,139,155
Pentachlorobenzene	608-93-5	250	252,108,248,215,254
Pentachloronitrobenzene	82-68-8	237	142,214,249,295,265
Pentachlorophenol	87-86-5	266	264,268
Phenacetin	62-44-2	108	180,179,109,137,80
Phenanthrene	85-01-8	178	179,176
Phenobarbital	50-06-6	204	117,232,146,161
Phenol	108-95-2	94	65,66
Phenol-d_6 (surr)	106-50-3	99	42,71
1,4-Phenylenediamine	298-02-2	108	80,53,54,52
Phorate	2310-17-0	75	121,97,93,260
Phosmet	732-11-6	160	77,93,317,76
Phosalone	732-11-6	182	184,367,121,379
Phosphamidon	13171-21-6	127	264,72,109,138
Phthalic anhydride	85-44-9	104	76,50,148
2-Picoline (2-Methylpyridine)	109-06-8	93	66,92
Piperonyl sulfoxide	120-62-7	162	135,105,77
Pronamide	23950-58-5	173	175,145,109,147
Propylthiouracil	51-52-5	170	142,114,83
Pyrene	129-00-0	202	200,203
Pyridine	110-86-1	79	52,51
Resorcinol	108-46-3	110	81,82,53,69
Safrole	94-59-7	162	104,77,103,135
Strychnine	57-24-9	334	334,335,333
Sulfallate	95-06-7	188	88,72,60,44
Terbufos	13071-79-9	231	57,97,153,103
Terphenyl-d_{14}(surr)	1718-51-0	244	122,212
1,2,4,5-Tetrachlorobenzene	95-94-3	216	214,179,108,143,218
2,3,4,6-Tetrachlorophenol	58-90-2	232	131,230,166,234,168
Tetrachlorvinphos	961-11-5	329	109,331,333
Tetraethyl dithiopyrophosphate (Sulfotep)	3689-24-5	322	202,97,266
Tetraethyl pyrophosphate	107-49-3	99	155,127,81,109
Thionazine	297-97-2	107	96,97,143,79,68
Thiophenol (Benzenethiol)	108-98-5	110	66,109,84
Toluene diisocyanate	584-84-9	174	145,173,146,132,91

o-Toluidine	95-53-4	106	107,77,79,90
Toxaphene	8001-35-2	159	231,233
2,4,6-Tribromophenol (surr)	118-79-6	330	332,141
1,2,4-Trichlorobenzene	120-82-1	180	182,145
2,4,5-Trichlorophenol	95-95-4	196	198,97,132,99
2,4,6-Trichlorophenol	88-06-2	196	198,200
Trifluralin	1582-09-8	306	43,264,41,290
2,4,5-Trimethylaniline	137-17-7	120	135,134,91,77
Trimethyl phosphate	512-56-1	110	79,95,109,140
1,3,5-Trinitrobenzene	99-35-4	127	67,72,109,193,237
Tris(2,3-dibromopropyl) phosphate	126-72-7	201	137,119,217,219,199
Tri-p-tolyl phosphate	78-32-0	368	367,107,165,198
O,O,O-Triethyl phosphorothioate	126-68-1	29	121, 65,93

[a] Chemical Abstract Service Registry Number

Table 4.

Semi volatile internal standards with corresponding analytes assigned for quantitation.

1,4-Dichlorobenzene-d_4	**Naphthalene-d_8**	**Acenaphthene-d_{10}**
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl) ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl) ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr)
4-Methylphenol	Nitrobenzene-d_5 (surr)	Hexachlorocyclopentadiene
N-Nitrosodimethylamine	2-Nitrophenol	1-Naphthylamine
N-Nitroso-di-n-propyl-amine	N-Nitrosodi-n-butylamine	2-Naphthylamine
Phenol	N-Nitrosopiperidine	2-Nitroaniline
Phenol-d_6 (surr)	1,2,4-Trichlorobenzene	3-Nitroaniline
2-Picoline		4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl) phthalate	Benzo(g,h,i)- perylene
Di-n-butyl phthalate	Butyl benzyl phthalate	Benzo(a)pyrene
4,6-Dinitro-2-methyl- phenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)-anthracene
Fluoranthene	p-Dimethylaminoazobenzene	
Hexachlorobenzene	Pyrene	
N-Nitrosodiphenylamine	Terphenyl-d_{14} (surr)	
Pentachlorophenol	7,12-Dimethylbenz(a)anthracene	
Pentachloronitrobenzene	Di-n-octyl phthalate	
Phenacetin	Indeno(1,2,3-cd) pyrene	
Phenanthrene	3-Methylchol-anthrene	
Pronamide		

(surr) = surrogate

Table 5.

DFTPP key ions and ion abundance criteria [a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% 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 less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a] Data taken from Reference 21.1

Table 6. MDL

Table 7. Single Laboratory Performance Data

MS004_05
February 27, 2001

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS)

SW846-8260B Revision 2

Lab Manager________________________ **Date**____________

QA Manager________________________ **Date**____________

Applicable Matrices

1.1 This method is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils and sediments.

2 Method Detection Limit

2.1 The Estimated Quantitation limit (EQL), and hence, the method detection limit (MDL), of this method for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes and 5 µg/L for ground water. Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

2.2 The in-house laboratory MDLs for both soils and waters determined on February 23 and 24 and July 4 of the year 2000 and January 12, 14 and 15 of the year 2000, respectively, are listed in Attachment 2.

2.3 The in-house Practical Quantitation Limits (PQLs) for both soils and waters determined on February 23 and 24 and July 4 of the year 2000 and January 12, 14 and 15 of the year 2000, respectively, are listed in Attachment 2.

3 Scope and Application

3.1 There are various techniques by which these compounds may be introduced into the GC/MS system. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes, and this is the technique most commonly used at this laboratory. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030 and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

3.2 This method can be used to quantitate most organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers and sulfides.

3.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

4 Summary of Method

4.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Section 3.1). The analytes are introduced directly to a narrow-bore capillary column for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC) .

4.1.1 The method states that the analytes are to introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary column for analysis. Both GC/MS Volatiles systems currently have narrow-bore columns installed. Due to developments in technology, the early eluting analytes show no evidence of needing to be "refocused" as suggested in Section 4.1 although the Tekmar 3100 unit set up in tandem to one of the GC/MS Volatile systems is equipped for cryogenic interface.

4.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a direct connection. (Wide-bore capillary columns normally require a jet separator, but since the laboratory employs the use of narrow-bore capillary columns, they may be directly interfaced to the ion source.) Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electon impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration.

5 Definitions

5.1 Internal Standard (IS): A pure analyte(s) added to a sample, extract or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component.

5.2 Surrogate Analyte (SA): A pure analytes(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

5.3 Laboratory Duplicates (LD1 and LD2): Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation or storage procedures.

5.4 Trip Blank: An aliquot of organic-free reagent water that is placed in a sample container in the laboratory and is transported to the sampling site and returned to the laboratory without being opened. This serves as a check on sample contamination originating from sample transport, shipping and from the site conditions.

5.5 Method Blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The Method Blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

5.6 Laboratory Control Sample (LCS): An aliquot of reagent water or other clean matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

5.7 Laboratory Fortified Sample Matrix (LFM): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

5.8 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

5.9 Primary Dilution Standard Solution (PDS): A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

5.10 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6 Interferences

6.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explain this in text accompanying the uncorrected data.

6.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringe with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

6.2.1 Currently only one rinse of organic-free reagent water of the purging apparatus and sample syringe is used. Two rinses has shown not to be necessary with the current instrumentation. Also, analyst discretion and client sample history is used to determine if the presence of a compound in a sample immediately following a sample with a high concentration of this compound is actually representative of sample composition or is the result of cross-contamination. If there is any doubt as to whether the compound is actually present in the sample, the sample is re-analyzed.

6.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning or replacement of the sample pathway. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

6.3.1 Currently, no screening methods are employed by this laboratory, but client histories are utilized. This information is available on the LIMS.

6.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free reagent water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

6.4.1 Usually only a 5-mL purge is employed and the rinsing procedure followed is that in Section 6.2.1.

6.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

6.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared

from organic-free reagent water and carried through the sampling, handling and storage protocols can serve as a check on such contamination.

6.7 Use of sensitive mass spectrometers to achieve lower detection levels will increase the potential to detect laboratory contaminants as interferences.

6.8 Direct injection – Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

6.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

6 Safety

7.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method.

7.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

8 Materials and Equipment

8.1 Purge-and-trap device for aqueous samples – Described in Method 5030.

8.2 Purge-and-trap device for solid samples – Described in Method 5035.

8.3 The equipment listed below is not currently employed by the laboratory due to the fact that the matrices it is required for are not analyzed by the laboratory.

8.3.1 Automated static headspace device for solid samples – Described in Method 5021.

8.3.2 Azeotropic distillation apparatus for aqueous and solid samples – Described in Method 5031.

8.3.3 Vacuum distillation apparatus for aqueous, solid and tissue samples – Described in Method 5032.

8.3.4 Desorption device for air trapping media for air samples – Described in Method 5041.

8.3.5 Air sampling loop for sampling from Tedlar® bags for air samples – Described in Method 0040.

8.4 Injection port liners (Restek Catalog # 20973 or equivalent)

8.4.1 For direct injection, injection port liners HP Catalog #18740-80200, or equivalent) – modified by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven. The column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

8.5 Gas chromatograph/mass spectrometer/data system

8.5.1 Gas chromatograph – An analytical system complete with a temperature programmable gas chromatograph suitable for split/splitless injection with appropriate interface for sample introduction device. The system includes all required accessories including analytical columns and gases. HP 6890 gas chromatographs are used in the laboratory.

8.5.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

8.5.1.1.1 The HP 6890 is equipped with an Electronic Pressure Controller (EPC) which accomplishes this.

8.5.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore a subambient oven controller may be necessary.

8.5.1.2.1 It is not necessary to achieve a temperature this low for the columns employed.

8.5.1.3 The narrow-bore capillary column is directly coupled to the source. If wide-bore capillary columns were employed, the column would need to be interfaced through a jet separator to the source.

8.5.1.4 Capillary pre-column interface – This device is the interface between the sample introduction device and the capillary gas

chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical column.

8.5.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer.

8.5.1.5.1 Due to developments in technology, the early eluting analytes show no evidence of needing to be "refocused" via a technique such as cryofocussing (See Sections 8.5.1.4 and 8.5.1.5), therefore, the capillary pre-column interface and the liquid nitrogen as discussed in Sections 8.5.1.4 and 8.5.1.5 are not currently employed in the laboratory.

8.5.2 Gas chromatographic columns

8.5.2.1 Hewlett Packard, HP-VOC, 60 m, 0.20 mm ID, 1.1 μm film thickness (Catalog # 19091R-306)

8.5.2.2 Restek, Rtx-502.2, 60m, 0.25 mm ID, 1.4 μm film thickness (Catalog #19016)

8.5.3 Mass spectrometer – Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in the table below when 5-50ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

Mass (m/z)	Relative Abundance Criteria
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base Peak, 100% Relative Abundance
96	5 to 9 % of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95

175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in the above table when 5 or 50 ng of BFB are introduced.

HP 5973 mass spectrometers in the EI mode are used in the laboratory.

8.6 GC/MS interface – Some alternatives may be used to interface the GC to the mass spectrometer.

8.6.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 – 0.32 mm ID columns and is what is employed in the laboratory.

8.6.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface is used with a 0.53 mm ID column.

8.6.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Section 11 can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

8.7 Data system – A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. 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 Extract 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.

8.7.1 All of these features are available on the two HP workstations which are equipped with HP ChemStation software and are interfaced with both the gas chromatographs and mass spectrometers.

8.8 Microsyringes – 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

8.9 Syringe valve – Two-way, with Luer ends (three each).

8.10 Syringes – 5-, 10-, or 25-mL, gas-tight with shutoff valve.

8.11 Balance – Analytical, capable of weighing 0.0001 g and top-loading, capable of weighing 0.1 g.

8.11.1 The more accurate balance is employed for the making of standards from neats.

8.12 Sample Containers – 40 mL screw cap vials each equipped with a Teflon-faced silicone septum.

8.13 Glass scintillation vials – 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

8.14 Vials – 2-mL, for GC autosampler.

8.15 Disposable pipets – Pasteur

8.16 Volumetric flasks, Class A – 5-mL, 10-mL, 50-mL and 100-mL, with ground-glass stoppers.

8.17 Spatula – Stainless steel.

8.18 Magnetic stir bars.

9 Reagents and Standards

9.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall 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.

9.2 Organic-free reagent water – All references to water in this method refer to organic-free reagent water, as defined below.

9.2.1 For volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently,

while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

9.2.2 A MilliQ water purification system is used to generate organic free-reagent water at the laboratory.

9.3 Methanol, CH_3OH – Pesticide quality or equivalent, demonstrated to be free of analytes. Purge-and-trap grade methanol is utilized by the laboratory. Store apart from other solvents.

9.4 Reagent hexadecane – Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

9.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ – Free of interferences at the detection limit of the target analytes.

9.6 Sodium thiosulfate – ACS reagent grade, granular.

9.7 Sodium bisulfate, $NaHSO_4$

9.8 Hydrochloric acid (1:1 v/v), HCl – Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

9.9 Sulfuric Acid, H_2SO_4

9.10 Stock solutions – The routinely used stock solutions are purchased as certified solutions. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

9.10.1 UltraScientific Catalog # AMN-623 – Acrolein and Acrolynitrile stock

9.10.2 Restek Catalog # 30265 – 2-Chloroethyl vinyl ether stock

9.10.3 Restek Catalog #30202A – 524 Mix #7A

9.10.4 Restek Catalog #30203 – 524 Mix #8

9.10.5 Restek Catalog #30431 – 502.2 MEGA2000

9.10.6 Restek Catalog #30042 – 502.2 Mix #1

9.10.7 Alternatively, stock solutions may be prepared from pure standard materials. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

9.10.7.1 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 0.0001 mg.

9.10.7.2 Add the assayed reference material, as describe below.

9.10.7.2.1 Liquids – 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 alcohol without contacting the neck of the flask.

9.10.7.2.2 Gases – To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

9.10.7.3 Reweigh, dilute to volume, stopper and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compounds purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.

9.10.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store with minimal headspace and protected from light at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

9.10.7.5 Frequency of Standard Preparation

9.10.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

9.10.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented.

9.10.7.5.3 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichlorodifluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration.

9.10.7.5.3.1 Before removing the cylinder shipping cap, be sure the valve is completely close (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

9.10.7.5.3.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

9.10.7.5.3.3 Transfer half the working standard containing other analytes, internal standards and surrogates to the purge apparatus.

9.10.7.5.3.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence.

9.10.7.5.3.4.1 Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

9.10.7.5.3.4.2 Make sure the on/off valve on the syringe is in the open position.

9.10.7.5.3.4.3 Slowly open the valve on the cylinder and withdraw a full syringe volume.

9.10.7.5.3.4.4 Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

9.10.7.5.3.4.5 Expel the gas from the syringe into a well-ventilated area.

9.10.7.5.3.4.6 Repeat steps 9.10.7.5.3.4.1 through 9.10.7.5.3.4.5 one more time to fully purge the fitting.

9.10.7.5.3.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 9.10.7.5.3.4.1 through 9.10.7.5.3.4.5. Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

9.10.7.5.3.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30psi.

9.10.7.5.3.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

<u>NOTE</u>: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

9.10.7.5.3.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve lines.

9.10.7.5.3.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

9.10.7.5.3.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

9.10.7.5.3.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

9.11 Secondary dilution standards – Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Section 9.10.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

9.12 Surrogate standards – The recommended surrogates are toluene-d8, 4-bromofluorobenzene, 1,2-dichloroethane-d4 and dibromofluoromethane. These are the surrogates used by the laboratory. Other compounds may be used as surrogates, depending upon the analysis requirements. If using pure standard materials, a stock surrogate solution in methanol should be prepared as described in Section 9.10.7, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

9.13 Internal standards – The recommended internal standards are fluorobenzene, chlorobenzene-d5 and 1,4-dichlorobenzene-d4. These three internal standards plus 1,4-difluorobenzene are the internal standards used by the laboratory. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. If using pure standard materials, a stock internal standard solution in methanol should be prepared as described in Section 9.10.7. Prepare a secondary dilution standard in methanol using the procedures described in Section 9.11. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µl of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration standard.

9.13.1 The internal standards and surrogate standards are combined in the same solution by making a secondary dilution of the two purchased stocks below.

Restek Catalog #30074 – 8260 Internal Standard Mix

Restek Catalog #30240 – 8260A Surrogate Mix

Following the procedure in Section 9.11, 1.0 mL of each of these solutions is brought to a final volume of 10 mL with methanol. This results in a concentration of 250 µg/mL for each of the internal standards and surrogates. A 1.0 µL aliquot of this solution is added to all calibration standards, QC samples and client samples for the equivalent of a 50 µg/L concentration.

9.14 4-Bromofluorobenzene (BFB) standard – A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

9.14.1 The BFB standard is made by introducing 100 µL of the stock below into a 10-mL volumetric flask partially filled with methanol following the procedure in Section 9.11. The flask is then filled to final volume.

Restek Catalog #30082 – BFB Standard

Adding 4 µL of this solution to a 40-mL vial filled with reagent water equates to a concentration of 50 ng/5 mL.

9.15 Calibration standards – There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

9.15.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the premixed certified solutions (or alternately, from the secondary dilution of stock standards – see Sections 9.10.7 and 9.11). Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

Seven initial calibration standards are actually prepared according to the table below.

Concentration	Amount of each of the premixed certified solutions (See Secs. 9.10.2 through 9.10.6)	Final Volume of Reagent Water
5 µg/L	0.5 µL	200 mL
25 µg/L	2.5 µL	200 mL
50 µg/L	5 µL	200 mL
70 µg/L	3.5 µL	100 mL
100 µg/L	5 µL	100 mL
160 µg/L	8 µL	100 mL
200 µg/L	10 µL	100 mL

NOTE: The concentration is that for all analytes in the mixes except for Xylenes. Due to the coelution of the isomeric pair m-Xylene and p-Xylene, the combined concentration of

m- & p-Xylene is actually double that of the concentrations listed here.

9.15.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the premixed certified solutions (or alternately, from the secondary dilution of stock standards – see Sections 9.10.7 and 9.11). Prepare these solutions in organic-free reagent water. See Section 12.3 for guidance on calibration verification.

9.15.2.1 The standard that is most commonly prepared for calibration verification is the 50 µg/L concentration made by adding 5 µL of each of the premixed certified solutions (see Sections 9.10.2 through 9.10.6) to a 200-mL volumetric flask filled to the mark with organic-free reagent water.

9.15.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

9.15.4 The calibration standards must also contain the internal standards chosen for the analysis.

9.16 Matrix spiking and laboratory control sample (LCS) standards – Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

9.16.1 The matrix spike and laboratory control spiking standard is made by introducing 500 µL of the stock below into a 5-mL volumetric flask partially filled with methanol following the procedure in Section 9.11. The flask is then filled to final volume.

Restek Catalog #30005 – VOA Matrix Spike Mix

Adding 8 µL of this solution to a 40-mL vial filled with sample or reagent water equates to a concentration of 50 µg/L of each of the compounds listed in Section 9.16. Or, in the case of soils, adding 1 µL of this solution to 5 g of sample or 5 g of reagent water equates to a concentration of 50 µg/kg of each of the compounds listed in Section 9.16.

9.16.2 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 μg/10.0 mL.

9.16.3 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

9.16.4 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

10 Sample Collection, Preservation and Storage

10.1 Standard 40-mL glass screw cap VOA vials with Teflon lined silicone septa may be used for liquid matrices. Special 40-mL VOA vials for purge and trap of solid samples, if a system requiring a septum at both ends of the vial, are described in Method 5035. (The Archon autosampler only requires a septum at one end of the vial.) Although the referenced methods are currently not employed by the laboratory, the following information is included for possible future reference. VOA vials for headspace analysis of solid samples are described in Method 5021. Standard 125-mL widemouth glass containers may be used for Methods 5031 and 5032. However, the sampling procedures described in Method 5035 may minimize sample preparation analyte loss better than the procedures described in Methods 5031 and 5032.

The vials and septa should either be purchased pre-cleaned from the manufacturer or washed with soap and water and rinsed with distilled deionized water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100°C for approximately one hour.

NOTE: Do not heat the septa for extended periods of time (i.e., more than one hour) because the silicone begins to slowly degrade at 105°C.

When collecting the samples, liquids and solids should be introduced into the vials gently to reduce agitation which might drive off volatile compounds.

In general, liquid samples should be poured into the vial without introducing any air bubbles within the vial as it is being filled. Should bubbling occur as a result of violent pouring, the sample must be poured out and the vial refilled. The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed and the vial inverted, no headspace is visible. The samples should be hermetically sealed in the vial at the time of sampling and must not be opened prior to analysis to preserve their integrity.

10.1.1 Due to differing solubility and diffusion properties of gases in LIQUID matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro bubbles and should not invalidate a sample for volatiles analysis.

10.1.2 The presence of a macro bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The later case is usually accompanied by a buildup of pressure within the vial (e.g., carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Ci, unpublished data) indicate that "pea-size" bubbles (i.e., bubbles not exceeding ¼ inch or 6 mm in diameter) did not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

10.2 Immediately prior to analysis of liquid samples, the aliquot to be analyzed should be taken from the vial using the instructions from the appropriate sample introduction technique:

10.2.1 The Archon autosampler will remove volumes between 5 and 25 mL from the 40 mL vials.

10.2.2 For smaller analysis volumes, i.e., in the case of very large dilutions, a gas-tight syringe may be inserted directly through the septum of the vial to withdraw the sample.

10.2.3 For larger analysis volumes that cannot be removed using the Archon autosampler (i.e., if more than 5 mm of sediment is at the bottom of the vial), the sample may be carefully poured into the syringe barrel. Opening a volatile sample to pour a sample into a syringe destroys the validity of the sample for future analysis. Therefore, if there is only one VOA vial, it is strongly recommended that the analyst fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly.

10.2.4 If these guidelines are not followed, the validity of the data generated from the samples may be suspect.

10.3 VOA vials for samples with solid or semi-solid matrices (e.g., sludges) should be filled according to the guidance given in the appropriate 5000 series sample introduction method to be used. When 125-mL wide mouth glass containers are used, the containers should be filled as completely as possible. The 125-mL vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. A minimum of two vials should also be filled per sample location.

10.4 At least two VOA vials should be filled and labeled immediately at the point at which the sample is collected. They should NOT be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. The two vials from each sampling location should then be sealed in separate plastic bags to prevent cross-contamination between samples, particularly if the sampled waste is suspected of containing high levels of volatile organics. (Activated carbon may also be included in the bags to prevent cross-contamination from highly contaminated samples.) VOA samples may also be contaminated by diffusion of volatile organics through the septum during shipment and storage. To monitor possible contamination, a trip blank prepared from organic-free reagent water should be carried throughout the sampling, storage and shipping process.

10.5 Sample Storage – The sample storage area must be free of organic solvent vapors and direct intense light.

10.5.1 For samples for Method 5035, e.g., solids, store samples at 4°C until analysis. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

10.5.2 For samples for Method 5030, e.g., aqueous samples with no residual chlorine present, adjust pH to less than 2 with H_2SO_4, HCl or solid $NaHSO_4$. Store samples at 4°C until analysis. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

10.5.3 For samples for Method 5030 that do contain residual chlorine, collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Adjust pH to less than 2 with H_2SO_4, HCl or solid $NaHSO_4$.

10.5.4 For samples for Method 5030 that are to be analyzed for acrolein and acrylonitrile, adjust pH to 4 – 5. Store samples at 4°C until analysis. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

11 Quality Control

11.1 The GC/MS system must be tuned to meet the BFB specifications in Section 12.1 and 12.3.1.

11.2 There must be an initial calibration of the GC/MS system as described in Section 12.2.

11.3 The GC/MS system must meet the SPCC criteria described in Section 12.3.4 and the CCC criteria in Section 12.3.5 each 12 hours.

11.4 Initial Demonstration of Proficiency – Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

11.4.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

Prepare a reference sample concentrate in methanol at a concentration such that the spike will provide a concentration in the clean matrix that is 10-50 times the MDL for each analyte in that matrix.

The concentration of the target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of the analyte is being evaluated relative to a regulatory limit or action level, the spike should be at or below the limit, or 1 – 5 times the background concentration (if historical data are available), whichever is higher. If historical data is not available, it is suggested that a background sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculations of recoveries.

11.4.2 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds), e.g., organic-free reagent water for the aqueous matrix and organic-free sand or soil for the solid matrix.

11.4.3 Prepare the reference sample by adding 400 µL of the reference sample concentrate (see Section 11.4.1) to 200 mL of organic-free reagent water. Transfer this solution immediately to 40-mL vials when validating water analysis performance by Method 5030. When validating soil analysis performance by Method 5035, transfer this solution in 5 mL aliquots into 40-mL vials each containing 5 g of sand place in a muffle furnace at 550°C for four hours.

11.4.4 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples.

11.4.5 Calculate the average recovery (x) in μg/L and the standard deviation of the recovery (s) in μg/L for each analyte of interest using the four results.

11.4.6 Single laboratory performance data are included in SW846 8260B, Table 7. Compare s and x for each analyte with the corresponding performance data. If s and x for all analytes of interest meet the appropriate acceptance criteria, then the system performance is acceptable and analysis of actual samples can begin. If any individual s value exceeds the precision limit or any individual x value falls outside the range for accuracy, then the system performance may be unacceptable for that analyte.

11.4.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest, beginning at Section 11.4.2.

11.4.6.2 Beginning at Section 11.4.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning at Section 11.4.2.

11.4.7 Even though the method contains performance data, the development of in-house acceptance limits is strongly recommended, and may be accomplished using the procedure below.

11.4.7.1 For each matrix spike sample analyzed, calculate the percent recovery of each matrix spike compound added to the sample using the calculation below.

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n} \times 100$$

where:
C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot

11.4.7.2 Calculate the average percent recovery (p) and the standard deviation (s) for each of the matrix spike compounds after

analysis of 15-20 matrix spike samples of the same matrix using the equations below. Calculate the average percent recovery and the standard deviation of each of the surrogates after analysis of 15-20 field samples of the same matrix.

$$p = \sum_{i=1}^{n} p_i$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n} (p_i - p)^2}{n - 1}}$$

11.4.7.3 After the analysis of 15-20 matrix spike samples of a particular matrix (for matrix spike limits) or 15-20 field samples (for surrogate limits), calculate upper and lower control limits for each matrix spike or surrogate compound:

Upper control limit = p + 3s
Lower control limit = p – 3s

Calculate warning limits as:

Upper warning limit = p + 2s
Lower warning limit = p – 2s

These control limits approximate a 99% confidence interval around the mean recovery, while the warning limits approximate a 95% confidence interval.

11.4.8 Sample Quality Control for Preparation and Analysis – This includes the analysis of QC samples including a method blank, matrix spike, a duplicate and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

11.4.8.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

11.4.8.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then the analyst may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the analyst should use a matrix spike and matrix spike duplicate pair.

11.4.8.2.1 Accuracy is estimated from the recovery of spiked analytes from the matrix of interest. Laboratory performance in a clean matrix is estimated from the recovery of analytes in the LCS. Calculate the recovery of each spiked analyte in the matrix spike, matrix spike duplicate and LCS according to the equation in Section 11.4.7.1.

11.4.8.2.2 If there is insufficient sample to do a duplicate or a matrix spike/matrix spike duplicate pair, the analyst should prepare a Laboratory Control Sample (LCS) and an LCS duplicate to determine the precision of the analysis. Precision (as RPD) is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

11.4.8.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentration as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. As a general rule, if any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the laboratory should determine if there is a matrix effect or a laboratory

performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Section 11.5) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either matrix spikes or surrogates alone.

11.4.8.4 Recommended QC acceptance criteria for matrix spike samples and LCS

It is necessary for the laboratory to develop single-laboratory performance data for accuracy and precision in the matrices of interest (see Section 11.4.7). Method performance in each matrix is monitored through the use of control charts.

For the LCS, the laboratory should use 70 – 130% as interim acceptance criteria for recoveries of spiked analytes until in-house limits are developed (see Section 11.4.7). Where in-house limits have been developed for matrix spike recoveries, the LCS results should fall within those limits, as the LCS is prepared in a clean matrix.

As a general rule, the recoveries of most compounds spiked into samples should fall within the range of 70 – 130%, and this range should be used as a guide in evaluating in-house performance. However, matrix spike recoveries and LCS recoveries may be affected by the spike-to-background ratio.

11.5 Surrogate recoveries – The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. Use the equations in Section 11.4.7.2 and the definitions in Section 11.4.7.3 to develop laboratory control limits.

11.5.1 Surrogate recovery is calculated as (This calculation is supported by the ChemStation data system if the compound is correctly identified as a surrogate in the method file and the resulting recovery will be present on the report.):

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

If recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

11.5.1.1 Examine the chromatograms for interfering peaks and integrated peak areas.

11.5.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample.

11.5.1.3 If no instrument problem is found, the sample should be re-analyzed.

11.5.1.4 If, upon re-analysis (in either Section 11.5.1.2 or 11.5.1.3) the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the reanalysis data to the data user. If holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

11.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

11.7 The laboratory regularly participates in relevant performance evaluation studies.

12 Calibration and Standardization

12.1 Each GC/MS system must be hardware-tuned to meet the criteria in the table in Section 8.5.3 for a 5-50 ng injection or purging of 4-bromofluorobenzene. Analyses must not begin until these criteria are met.

12.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may 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 no more than 20 scans prior to the elution of BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

12.1.1.1 The approach used above (the average of the apex scan and the two scans immediately adjacent on both sides of the apex) is that used by the ChemStation during the "Autofind BFB" menu choice. The analyst may also evaluate the peak at various individual scans and over an average of scans by making the selections and using ChemStation to "Evaluate BFB."

12.1.2 Use the BFB mass intensity criteria in the table in Section 8.5.3 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2 or manufacturer's instructions), provided that the method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

12.2 Initial calibration

12.2.1 Set up the sample introduction system as outlined in the method of choice (see Section 13.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (See Section 9.15). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed. A 5 mL purge is traditionally employed for Method 5030 in this laboratory.

12.2.1.1 To prepare a calibration standard, follow the table in Section 9.15.1. Add the appropriate volume of each of the premixed certified solutions to the specified volume volumetric flask filled to the mark with organic-free reagent water. Use a microsyringe and rapidly inject the alcoholic standard 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. If preparing standards for Method 5030, discard the contents contained in the neck of the flask and pour off the remaining solution into 40 mL vials and cap securely. Make sure that no headspace is present in the vials. If preparing standards for Method 5035, discard the contents contained in the neck of the flask and remove 5 mL aliquots from the volumetric flask and transfer to 40-mL vials containing magnetic stir bars. Aqueous standards are not stable and should be prepared daily.

12.2.1.2 The internal standards listed in Section 9.13 should permit most of the components of interest in a chromatogram to have retention times of 0.80 – 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation as specified in SW846 8260B, Table 5. If interferences are noted, use the next most intense ion as the quantitation ion.

12.2.1.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

12.2.2 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 – 2 μL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

12.2.3 Tabulate the area response of the characteristic ions against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured.

12.2.4 The RF is calculated as follows.

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

where: A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

The ChemStation data system software supports this calculation.

12.2.5 System performance check compounds (SPCCs) – Calculate the mean RF for each target analyte using the RF values calculated from the initial (a minimum of a 5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

12.2.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

12.2.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

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

12.2.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

12.2.6 Calibration check compounds (CCCs)

12.2.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Section 12.2.8.

12.2.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \text{mean RF})^2}{n-1}} \qquad RSD = \frac{SD}{\text{mean RF}} \times 100$$

where: Rf_i = RF for each of the calibration standards
mean RF = mean RF for each compound in the initial calibration
n = Number of calibration standards

12.2.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project and therefore not included in the calibration standards, refer to Section 12.2.8.1. The CCCs are:

1,1-Dichloroethene
Chloroform
1,2-Dichloropropane
Toluene
Ethylbenzene
Vinyl chloride

12.2.6.4 If an RSD of greater than 30% is measure for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

12.2.7 Evaluation of retention times – The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

12.2.8 Linearity of target analytes

12.2.8.1 If the RSD of any target analyte is 15% or less then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Section 14.1.1).

12.2.8.2 If the RSD of any target analyte is greater than 15%, use one of the additional calibration options below. The ChemStation data system supports all of the models below except for Data Transformations (Section 12.2.8.3.4).

12.2.8.3 Calibration linearity

SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data, as described below. Given the limitations in instrument data systems, it is likely that the analyst will have to choose one model for all analytes in a particular method. (Multiple models are allowable for use with the ChemStation data system.) Both models can be applied to internal standard calibration data.

NOTE: The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear

calibration to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

Whichever calibration model is employed, a unique analyte or surrogate concentration must fall within the calibration range. Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

NOTE: The following sections describe various options for initial calibration and provide the calibration acceptance criteria used to evaluate each option. The criteria listed in these sections are designed for quantitation of trace level concentration of the analytes of interest. If data of lesser quality will satisfy project-specific data needs, then less stringent criteria may be employed, provided that they are documented and approved in a project-specific QA project plan.

The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met. The second approach is to use a *priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of the physics of the detector or specific manufacturer's recommendations.

12.2.8.3.1 Linear calibration using the average response factor

When calculated as described in Section 12.2.4, response factors are a measure of the slope of the calibration relationship and assume that the curve passes through the origin. Under ideal conditions, the factors will not vary with the concentration of the standard that is injected into the instrument. In practice, some variation is to be expected. However, when the variation measured as the relative standard deviation (RSD) is less than or equal to 15%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin.

NOTE: Linearity through zero is a statistical assumption and not a rationale for reporting results below the calibration range demonstrated by the analysis of the standards.

To evaluate the linearity of the initial calibration, calculate the mean RF, the standard deviation (SD), and the RSD as follows:

$$\text{mean RF} = \sum_{i=1}^{n} RF_i$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \text{mean RF})^2}{n-1}}$$

$$RSD = \frac{SD}{\text{mean RF}} \times 100$$

If the RSD of the response factors is less than or equal to 15% over the calibration range, then linearity through the origin may be assumed, and the average response factor may be used to determine sample concentrations.

12.2.8.3.1.1 Given the potentially large numbers of analytes that may be analyzed in some methods, it is likely that some analytes may exceed the 15% acceptance limit for the RSD for a given calibration. In those instances, the following steps are recommended, but not required.

The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Section 18.1.1 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 15%, the analyst may wish to review the results (area counts, response factors and

RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. Changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

NOTE: As noted in Section 9.15.1, the method quantitiation limit is established by the concentration of the lowest standard analyzed during the initial calibration. Hence, narrowing the calibration range by changing the concentration of the lowest standard will, by definition, change the method quantitation limit. When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the analyst must ensure that the method quantitation limit is at least as low as the regulatory limit or action level.

12.2.8.3.1.2 In those instances where the RSD for one or more analytes exceeds 15%, the initial calibration may still be acceptable if the following conditions are met:

12.2.8.3.1.2.1 The mean of the RSD values for all analytes in the calibration is less than or equal to 15%. The mean RSD is calculated by summing the RSD value for each analyte and dividing by

the total number of analytes. If no analyte has an RSD above 15%, then the mean RSD calculation need not be performed.

12.2.8.3.1.2.2 The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the target analyte is part of the calibration standard, its RSD value is included in the evaluation.

12.2.8.3.1.2.3 The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 15% and the results of the mean RSD calculation.

NOTE: The analyst and the data user must be aware that the use of the approach listed in Section12.2.8.3.1.2.1 (i.e., the average of all RSD values ≤15%) will lead to greater uncertainty for those analytes for which the RSD is greater than 15%. The analyst and the data user should review the associated quality control sample results carefully, with particular attention to the matrix spike and laboratory control sample results (see Sections 11.4.8.2 and 11.4.8.3), to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to employ one of the other calibration approaches (see Sections 12.2.8.3.2 and 12.2.8.3.4) or adjust the instrument operating conditions and/or the calibration range until the RSD is ≤15%.

12.2.8.3.1.3 If all of the conditions in Section 12.2.8.3.1.2 are met, then the average response factor may be used to determine sample concentration as described in Section 14.1.1.

12.2.8.3.2 Linear calibration using a least squares regression

If the RSD of the response factors is greater than 15% over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on past experience or a *priori* knowledge of the instrument response. Further, at the discretion of the analyst, this approach also may be used for analytes that do meet the RSD limits in Section 12.2.8.3.1.

This is most easily achieved by performing a linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphic convention.

The analyst may also employ a weighted least squares regression if replicate multi-point calibrations have been performed, e.g., three 5-point curves. For all other instances, an appropriate unweighted least squares method should be used. When using a weighted linear least squares regression, the following weighting factor should be used:

$$\frac{1}{SD^2}$$

where SD is the standard deviation of the replicate results at each individual standard concentration. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

where:

y = Instrument response (peak area or height)
a = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = The intercept

The analyst should not force the line through the origin, but have the intercept calculated from the data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0,0) as a calibration point. The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

When a weighted linear least squares regression is employed, the regression equation becomes:

$$y = \frac{1}{SD^2}(ax + b)$$

which may be rearranged to solve for x, the concentration. Using internal standard quatitation, the regression equation is rearranged as shown below:

$$\frac{A_S C_{IS}}{A_{IS}} = aC_S + b$$

where:

- A_S = Area (or height) of the peak for the target analyte in the sample
- A_{IS} = Area (or height) of the peak for the internal standard
- C_S = Concentration of the target analyte in the calibration standard
- C_{IS} = Concentration of the internal standard
- a = Slope of the line (also called the coefficient of C_s)
- b = The intercept

In calculating sample concentrations by the internal standard method, the regression equation is rearranged to solve for the concentration of the target analyte (C_s) as shown below:

$$C_s = \frac{\frac{A_s C_{is}}{A_{is}} - b}{a}$$

12.2.8.3.3 Non-linear calibration

In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model may be employed.

NOTE: It is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentration or to avoid proper instrument maintenance. Thus, non-linear calibration should not be employed for methods or instruments previously shown to exhibit linear calibration for the analytes of interest.

When using a calibration model for quantiation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

As noted above, the model must be continuous. A curve is continuous when it has consecutive numerical values along the function, whether increasing or decreasing, and without having breaks in the function (i.e., the pen shall never leave the paper from the minimum to the maximum). The model must also be continuously differentiable, such that all derivatives of the function are continuous functions themselves, and monotonic, such that all tangent lines of the derivative to all of the points on the calibration curve have either only positive or negative slopes.

If the model is not a polynomial, it should not include more than four parameters, i.e.,

$$y = f(a,b,c,d,x)$$

where "f" indicates a function with up to four parameters.

In estimating model parameters for the calibration data, the instrumental response (y) must be treated as the dependent variable. Do not force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point. Model estimates from the regression must be used as calculated, i.e., if the model is a polynomial, the intercept is d and may not be set to 0. Weighting in a calibration model may significantly improve its accuracy.

The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches described above. Whereas this method employs a minimum of five standards for a linear (first order) calibration model, a quadratic (second order) model requires six standards, and a third order polynomial requires seven standards.

Most curve fitting programs will use some form of a least squares minimization to adjust the coefficients of the polynomial (a,b,c and d above) to obtain the polynomial that best fits the data. The "goodness of fit" of the polynomial equation is evaluated by calculating the weighted coefficient of the determination (COD).

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \text{mean } y)^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - Y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \text{mean } y)^2}$$

where:

y_{obs} = Observed response (area) for each concentration from each initial calibration standard

mean y = Mean observed response from the initial calibration

Y_i = Calculated (or predicted) response at each concentration from the initial calibration(s)

n = Total number of calibration points (i.e., 6 for a quadratic model; 7 for a third order model)

p = Number of adjustable parameters in the polynomial equation (i.e., 3 for a third order; 2 for a second order polynomial)

Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

As noted in Section 12.2.8.3, whichever of these options is employed, a unique analyte or surrogate concentration must fall within the calibration range. Analysts are advised to check both second and third order calibration models to ensure that this holds true (e.g., no parabolas or repeating functions in the calibration range). Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

12.2.8.3.4 Data transformations

An understanding of the fundamental behavior of the detector may be used to choose a data transformation that will then allow for a simple calibration model. For example, the response of a flame photometric detector in the sulfur mode is known to be proportional to the square of the sulfur concentration. Therefore, using the data system to take the square root of the instrument response before integration or the square root of the peak height allows for a calibration factor approach rather than a polynomial calibration curve. Instrument response may be transformed prior to any calculations (including integration) subject to the following constraints:

12.2.8.3.4.1 Any parameters used in the transformation should be fixed for the calibration and all subsequent analyses and verifications until the next calibration.

12.2.8.3.4.2 The transformation model chosen should be consistent with the behavior of the instrument detector. All data transformations must be clearly defined and documented by the analyst and related back to the fundamental behavior of the detector. In other words, this approach may not be used in the absence of specific knowledge about the behavior of the detector, nor as a "shot in the dark" to describe the calibration.

12.2.8.3.4.3 No transformations should be performed on areas or other results (e.g., the transformation must be applied to the instrument response itself).

12.2.8.3.4.4 When the transformed data are used to develop calibration factors, those factors must meet the acceptance criteria described in Section 12.2.8.3.1.

12.2.8.4 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standards preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

12.3 GC/MS calibration verification – Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

12.3.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in the table in Section 8.5.3 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

12.3.2 The initial calibration curve (Section 12.2) for each compound of interest should be verified once every 12 hours prior to sample analysis using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibration range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Sections 12.3.4 and 12.3.5.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

12.3.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples.

12.3.3.1 The results of the method blank should be:

12.3.3.1.1 Less than the laboratory's MDL for the analyte or less than the level of acceptable blank contamination specified in the approved quality assurance project plan.

12.3.3.1.2 Less than 5% of the regulatory limit associated with an analyte.

12.3.3.1.3 Or less than 5% of the sample result for the same analyte ,whichever is greater.

12.3.3.1.4 If the method blank results do not meet the acceptance criteria above, then the analyst should take corrective action to locate and reduce the source of the contamination and to re-extract and reanalyze any samples associated with the contaminated method blank.

12.3.4 System Performance Check Compounds (SPCCs)

12.3.4.1 A system performance check must be made during each 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Section 12.2.5.4). This is the same check that is applied during the initial calibration.

12.3.4.2 If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

12.3.5 Calibration Check Compounds (CCCs)

12.3.5.1 After the system performance check is met, the CCCs listed in Section 12.2.6.3 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model.

12.3.5.1.1 Verification of linear calibrations

Calibration verification for linear calibration involves the calculation of the percent drift or the percent difference of the instrument response between the initial

calibration and each subsequent analysis of the verification standard. Use the equations below to calculate %Drift or %Difference, depending on the model used.

$$\%Drift = \frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times$$

where the calculated concentration is determined using the mean response factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\%Difference = \frac{RF_V - \text{mean RF}}{\text{mean RF}} \times 100$$

where RF_V is the response factor from the analysis of the verification standard, and mean RF is the mean response factor from the initial calibration.

12.3.5.1.2 Verification of a non-linear calibration

Calibration verification of a non-linear calibration is performed using the percent drift calculation described in Section 12.3.5.1.1. It may also be appropriate to employ two standards at different concentrations to verify the calibration. In this instance, one standard should be near the inflection point in the curve. The choice of specific standards and concentrations is generally a method- or project-specific consideration.

12.3.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference criterion.

12.3.5.2.1 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

12.3.5.3 Internal standard retention time – The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions an corrections must be made, as required.

12.3.5.4 Internal standard response – If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

13 Procedure

13.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

13.1.1 Direct injection – This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

13.1.2 Purge-and-trap – This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides for techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030. The purge-and-trap technique is the one employed by the laboratory for sample introduction.

13.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid

samples is performed at 40°C to improve purging efficiency. There is no heated purge for soils performed in the laboratory at this time.

13.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

13.1.3 Vacuum distillation – This technique may be used for the introduction of volatile organics from aqueous, solid or tissue samples (Method 5032) into the GC/MS system.

13.1.4 Automated static headspace – This technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

13.1.5 Cartridge desorption – This technique may be used for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

13.2 GC/MS conditions

13.2.1 Gas chromatograph operating conditions

Injector temperature:	220°C
Transfer line temperature:	110°C
Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	40°C, hold for 5 minutes
Temperature program:	4°C/min to 50°C, hold for 0 minutes 10°C/min to 260°C
Final temperature:	260°C, hold for 4 minutes
Split ratio:	36.2:1

13.2.2 Mass spectrometer operating conditions

Mass range:	35 – 260 amu
Scan time:	3.25 scan/sec
Source temperature:	250°C

13.3 GC/MS analysis of samples

13.3.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentration of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021) or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when this method is used to achieve low detection levels.

13.3.1.1 Currently, no screening methods are employed by this laboratory, but client histories are utilized. This information is available on the LIMS.

13.3.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

13.3.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

13.3.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

13.3.4.1 The above procedure would be utilized for manual introduction of the sample into the purging vessel. Since most clients provide more than one vial for analysis and this analysis is completed via the Archon autosampler, the above information is more important for consideration with regards to performing dilutions. If more than one dilution is required from only one vial for analysis, simultaneously prepare both dilutions manually in separate volumetric flasks (Section 13.3.6.2).

13.3.5 The Archon waits for a signal from the purge-and-trap device that the trap is at ambient temperature (40°C). When the ready signal is received by the Archon, a 5 mL portion is removed directly from a 40 mL vial by

the Archon sample syringe. While still in the syringe, 1 µL of the internal standard/surrogate standard mixture is added to the sample. The sample is then introduced into the purge vessel on the purge-and-trap device.

13.3.5.1 If manual analysis is required due to sample matrix (if more than 5 mm of sediment is at the bottom of the vial) or the number of vials provided for analysis, remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe and adjust the final volume to 25.0 mL.

13.3.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays until the diluted sample is in a zero-headspace container.

13.3.6.1 Dilutions up to 100x can be made by the Archon. The pre-programmed dilutions allowable by this unit are 2, 5, 10, 20, 50 and 100x. These dilutions are performed by the Archon removing the appropriate volume required by the dilution directly from the filled sample vial and adding the necessary amount of the blank/rinse water to make the dilution in the Archon syringe. While still in the syringe, 1 µL of the internal standard/surrogate standard mixture is added to the sample. The sample is then introduced into the purge vessel on the purge-and-trap device.

13.3.6.2 Dilutions may also be made in volumetric flasks (50-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

13.3.6.3 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

13.3.6.4 Inject the proper aliquot of sample from the sample vial into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert and shake three times. Repeat the above procedure for additional dilutions.

13.3.6.5 Discard the contents contained in the neck of the flask and pour off the remaining solution into 40-mL vials and cap securely. Make sure that no headspace is present in the vials.

13.3.6.6 This diluted sample is placed in the Archon and proceeds from Section 13.3.5.

13.3.7 Compositing aqueous samples prior to GC/MS analysis

13.3.7.1 Flask compositing – This is the procedure most often used in the laboratory.

13.3.7.1.1 In the flask compositing procedure, a 300- to 500-mL round bottom flask is immersed in an ice bath. The individual VOA grab samples, maintained at 0-4°C, are slowly poured into the round bottom flask. The flask is swirled slowly to mix the individual grab samples. After mixing, multiple aliquots of the composited sample are poured into VOA vials and sealed for subsequent analysis. An aliquot can also be poured into a syringe for immediate analysis.

13.3.7.2 Syringe compositing

13.3.7.2.1 Add 5 mL of each sample (up to 5 samples are allowed to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

13.3.7.2.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

13.3.7.2.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

13.3.7.2.4 Once all the aliquots have been combined in the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Section 13.1).

13.3.7.2.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

13.3.7.3 Before placing in the Archon, if preparing matrix spikes for Method 5030, inject 8μL of the Matrix Spiking Solution (Section 9.16.1) through the septum of the filled 40-mL sample vial. If preparing matrix spikes for Method 5035, inject 1μL of the Matrix Spiking Solution (Section 9.16.1) through the septum of the vial containing the aliquot of sample to be spiked.

13.3.7.3.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. If preparing an LCS for Method 5030, inject 8μL of the Matrix Spiking Solution (Section 9.16.1) through the septum of a 40-mL vial filled with organic-free reagent water. If preparing matrix spikes for Method 5035, inject 1μL of the Matrix Spiking Solution (Section 9.16.1) through the septum of a vial containing an amount of organic-free reagent water equivalent to the amount of sample usually analyzed (5g).

13.3.7.4 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

13.3.8 Analyze the sample following the procedure in the introduction method of choice.

13.3.8.1 For direct injection, inject 1 to 2 μL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

13.3.8.2 The concentration of the internal standards, surrogates and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 μL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks and standards to effectively check drifting method performance, poor injection execution and anticipate the need for system inspection and/or maintenance.

13.3.9 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

13.3.9.1 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, the samples immediately following that sample may contain responses for that compound above the detection limit, depending on the degree of saturation. It is up to the analyst's discretion and history of the client samples, if available, to determine if these results are representative of the sample or due to carryover and if the latter is true to proceed with reanalysis.

13.3.9.1.1The method states that when a sample is analyzed that has saturated response from a compound, this analysis must be followed by the analysis of organic-free reagent water. If the blank analysis is not free of interferences, the system must be decontaminated. Samples analysis may not resume until a blank can meet the organic-free reagent water criteria specified in 9.2.1. This has shown not to be necessary with the current instrumentation and instead, the procedure in Section 13.3.9.1 is followed.

13.3.9.1.2All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

13.3.9.2 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound indentification unless multiple ions are monitored for each compound.

13.4 Qualitative analysis

13.4.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characterisitic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if

less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

13.4.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time, such as that of the ChemStation data system, will be accepted as meeting this criterion.

13.4.1.2 The relative retention time (RRT) of the sample component is within ±0.06 RRT units of the RRT of the standard component.

13.4.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

13.4.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13.4.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

13.4.1.6 Examination of extracted ion current profiles of approprate ions can aid in selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

13.4.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be

determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste diluting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

13.4.2.1 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.

13.4.2.2 The relative intensities of the major ions should agree within ±20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

13.4.2.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

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

13.4.2.5 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 peaks. Data system library reduction programs can sometimes create these discrepancies.

13.4.3 Quantitative analysis

13.4.3.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

13.4.3.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor (mean RF) from initial calibration data (Section 14.1.1).

13.4.3.3 Where applicable, the concentration of any non-target analytes identified in the sample (Section 13.4.2) should be estimated.

The same formulae should be used with the following modifications: The areas A_S and A_{IS} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1.

13.4.3.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

14 Data Analysis and Calculations

14.1 The calculation of analyte and surrogate concentrations is completed by the ChemStation software using one of the equations below, depending upon the model used in the calibration.

14.1.1 Linear calibration:

14.1.1.1 Aqueous samples

$$\text{Concentration}\,(\mu g/mL) = \frac{(A_S)(C_{IS})(D)}{(A_{IS})(\text{meanRF})(V_S)}$$

where:
A_S = Area (or height) of the peak for the analyte in the sample
A_{IS} = Area (or height) of the peak for the internal standard
C_{IS} = Concentration of the internal standard in the concentrated sample extract or volume purged in µg/L
D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D=1. The dilution factor is always dimensionless.
mean RF = Mean response factor from the initial calibration.
V_S = Volume of the aqueous sample extracted or purged (mL). If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL which is equivalent to µg/L.

14.1.1.2 Nonaqueous samples

$$\text{Concentration}\,(\mu g/kg) = \frac{(A_S)(C_{IS})(D)}{(A_{IS})(\text{mean RF})(W_S)}$$

where: A_S, A_{IS}, C_{IS}, D and mean RF are the same as for aqueous samples, and
W_S = weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/g which is equivalent to µg/kg.

14.1.1.3 If a linear calibration that does not pass through the origin has been employed, then the regression equation is rearranged as shown in Section 12.2.8.3.2.

14.1.2 Calculations for a non-linear calibration curve

When a non-linear curve has been employed, the non-linear model is rearrange to solve for the concentration of the analyte in the purge volume, and the concentration is converted to a sample concentration in using the equation below.

$$C_S = \frac{(C_p)(V_t)}{(V_S)}$$

where: C_S = Concentration in the sample
C_p = Concentration in the purged volume
V_t = Total volume purged
V_S = Volume of the sample purged

For solid samples, substitute the weight of the sample, W_S, for V_S.

The concentration of the analyte in the volume of the sample that is purged will be the same as in the original sample, except when dilutions are performed.

15 Method Performance

15.1 Initial Demonstration of Laboratory Accuracy and Precision Attachment 1

15.2 MDL Study Attachment 2

15.2.1 Method detection limits were calculated using the formula:

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

where: $t_{(n-1,1-alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = Number of replicates
S = The standard deviation of the replicate analysis

16 Pollution Prevention

16.1 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment.

17 Data Assessment and Acceptance Criteria for Quality Control Programs

17.1 A summary of the raw data, spike recovery form and a quality control form noting surrogate recoveries, internal standard responses and if the sample was run within the 12-hour time period from the last tune check are copied and put into the project folder after validation by a second analyst/supervisor.

17.2 The reported values are then entered into LIMS. Data is further validated in LIMS by a third analyst.

17.3 Each of the chromatograms for the raw data are initialed by the analyst and saved according to the run date with all other GC/MS data for the particular volatiles instrument.

18 Corrective Actions for Out-Of-Control Data

18.1 Initial Calibration has some analytes that exceed the 15% acceptance limit for the RSD – The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Section 18.1.1 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 15%, the analyst may wish to review the results (area counts, response factors and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity

can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

18.1.1 Suggested chromatographic system maintenance

Corrective measures may involve any one or more of the following remedial actions. This list is by no means comprehensive and analysts should develop expertise in trouble shooting their specific instruments and analytical procedures. The manufacturers of chromatographic instruments, detectors, columns and accessories generally provide detailed information regarding the proper operation and limiting factors associated with their products. The importance of reading and reviewing this information cannot be over-emphasized.

18.1.1.1 Capillary GC columns

Routine maintenance may compel the analyst to clean and deactivate the glass injection port insert or replace it with a fresh insert that has been cleaned and deactivated with dichlorodimethylsilane. Cut off 0.5 – 1.0 m of the injector end of the column using a 90° cut. Place ferrule onto the column before cutting.

Exceptional maintenance may compel the analyst to replace gas traps and backflush the column with solvent, if appropriate, according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

18.1.1.2 Metal (GC) injector body

Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert. Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

Prepare a solution of deactivating agent (dichlorodimethylsilane) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, hexane and methanol again. Reassemble the injector and replace the GC column.

NOTE: Due to the solvents (Toluene and acetone are common target compounds.) used in this procedure, this should only be used as a last resort to eliminate active sites. The final methanol rinse must be thorough enough to remove all traces of these solvents in the injection port.

18.2 Calibration verification

18.2.1 A system performance check must be made during each 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Section 12.2.5.4). If the minimum response factors are not met, the system must be evaluated and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

18.2.2 If the percent difference or drift for each CCC is less than or equal to 20% for the calibration verification, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift) for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference criterion.

18.2.3 The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions an corrections must be made, as required.

18.2.4 If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to +100%) from that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

18.3 If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the laboratory should determine if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Section 11.5) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either matrix spikes or surrogates alone.

18.4 If surrogate recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

18.4.1 Examine the chromatograms for interfering peaks and integrated peak areas.

18.4.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample.

18.4.3 If no instrument problem is found, the sample should be re-analyzed.

18.4.4 If, upon re-analysis (in either Section 18.4.1 or 18.4.3) the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the reanalysis data to the data user. If holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

18.5 The results of the method blank should be:

18.5.1 Less than the laboratory's MDL for the analyte or less than the level of acceptable blank contamination specified in the approved quality assurance project plan.

18.5.1.1 Less than 5% of the regulatory limit associated with an analyte.

18.5.1.2 Or less than 5% of the sample result for the same analyte ,whichever is greater.

18.5.1.3 If the method blank results do not meet the acceptance criteria above, then the analyst should take corrective action to locate and reduce the source of the contamination and to re-extract and reanalyze any samples associated with the contaminated method blank.

18.6 Any sample result that falls above 10% of the range of the calibration must be diluted to a value that falls within the calibration curve.

18.7 When a sample is analyzed that has saturated response from a compound, the samples immediately following that sample may contain responses for that compound above the detection limit, depending on the degree of saturation. It is up to the analyst's discretion and history of the client samples, if available, to determine if these results are representative of the sample or due to carryover and if the latter is true to proceed with reanalysis.

19 Contingencies for Handling Out-of-Control Data or Unacceptable Data

19.1 See Section 18.

20 Waste Management

20.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected.

21 References

21.1 SW846 8260B, Revision 2, December 1996 – Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS)

21.2 SW846 8000B, Revision 2, December 1996 – Determinative Chromatographic Separations

21.3 Chapter Four, Revision 3, December 1996 – Organic Analytes

MS004_05

Philip Analytical Services

Volatile Organic Compounds By Gas Chromatography/Mass Spectrometry (GC/MS)

In-Service Date: February 27, 2001

I certify that I have read, understood, and will abide by the procedures set forth in this Policy.

Laboratory Personnel Responsible for Implementation of this Policy include:

Signature/Date

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GC016_05
April 23, 2001

AROMATIC AND HALOGENATED VOLATILES BY GAS CHROMATOGRAPHY USING PHOTOIONIZATION AND/OR ELECTROLYTIC CONDUCTIVITY DETECTORS

SW846-8021B Revision 2

Lab Manager________________________________ Date______________

QA Manager________________________________ Date______________

1 Applicable Matrices

1.1 This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils and sediments.

2 Method Detection Limit

2.1 Method detection limits (MDLs) are compound dependent and vary with purging efficiency and concentration. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 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 in sufficient amounts. Determination of some structural isomers (i.e., Xylenes) may be hampered by coelution.

2.2 The in-house laboratory MDLs for both soils and waters determined on August 3, 2000 and October 18, 2000 , respectively, are listed in Attachment 2.

2.3 The in-house Practical Quantitation Limits (PQLs) for both soils and waters determined on August 3, 2000 and October 18, 2000, respectively, are listed in Attachment 2.

3 Scope and Application

3.1 This method is used to determine volatile organic compounds in a variety of solid waste matrices.

3.2 The estimated quantitation limit (EQL) for an individual compound is approximately 1 µg/kg (wet weight) for soil/sediment samples, 0.1 mg/kg (wet weight) for wastes, and 1 µg/L for ground water. EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

3.3 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs for measurement of purgeable organics at low µg/L concentrations and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

3.4 Other non-RCRA compounds which are amenable to analysis by this method include:

Analyte	CAS No.
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
2-Chlorotoluene	95-49-8
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
n-Propylbenzene	103-65-1
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8

4 Summary of Method

4.1 This method provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. Samples can be analyzed using direct injection (Method 3585 for oily matrices) or purge-and-trap (Method 5030/5035), headspace (Method 5021) or vacuum distillation (Method 5032). Groundwater samples may be analyzed using Method 5030, Method 5021 or Method 5032. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series. The GC system may also be set up to use a single detector when an analyst is looking for only halogenated compounds (HECD) or aromatic compounds (PID).

4.2 Tentative identifications are obtained by analyzing standards under the same conditions used for sample and comparing resultant GC retention times. Confirmatory information can be gained by comparing the relative response from the two detectors. Concentrations of the identified components are measured by relating the response produced for that compound in the sample to the response produced by that same compound in the standards.

5 Definitions

5.1 Surrogate Analyte (SA): A pure analytes(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

5.2 Laboratory Duplicates (LD1 and LD2): Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analysis of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation or storage procedures.

5.3 Trip Blank: An aliquot of organic-free reagent water that is placed in a sample container in the laboratory and is transported to the sampling site and returned to the laboratory without being opened. This serves as a check on sample contamination originating from sample transport, shipping and from the site conditions.

5.4 Method Blank: An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards and surrogates that are used with other samples. The Method Blank is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

5.5 Laboratory Control Sample (LCS): An aliquot of reagent water or other clean matrix to which known quantities of the method analytes are added in the laboratory. The LCS is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

5.6 Laboratory Fortified Sample Matrix (LFM): An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

5.7 Stock Standard Solution (SSS): A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

5.8 Primary Dilution Standard Solution (PDS): A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

5.9 Calibration Standard (CAL): A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

6 Interferences

6.1 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

6.2 Sulfur dioxide is a potential interferant in the analysis for vinyl chloride.

7 Safety

7.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst.

7.2 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

8 Materials and Equipment

8.1 Sample introduction apparatus – Tekmar LSC-2 sample concentrator

8.2 Gas Chromatograph – capable of temperature programming; equipped with variable-constant differential flow controllers, photoionization and electrolytic conductivity detectors connected with a short piece of uncoated capillary tubing,

0.32-0.5 mm ID, and data system. An HP 5890 Series II gas chromatograph is utilized in the laboratory. HP Chemserver serves as the data system.

8.2.1 Column – Restek RTX 502.2, 105 meter fused silica, 0.52 mm diameter, 3.0µm DF. Due to the column employed, it is not necessary to achieve subambient temperatures.

8.2.2 Photoionization detector (PID) – OI Analytical Model 4430

8.2.3 Electrolytic conductivity detector (HECD or ELCD) – OI Analytical Model 4420

8.3 Syringes – 5 mL glass hypodermic with Luer-Lok tips

8.4 Syringe valves – 2-way with Luer ends [polytetrafluoroethylene (PTFE) or Kel-F]

8.5 Microsyringe – 10µL, 25 µL, 100 µL

8.6 Syringes – 0.50, 1.0 and 5 mL, gas-tight with shut-off valve

8.7 Bottle – 15 mL, PTFE-lined with screw-cap or crimp top

8.8 Analytical balance – 0.0001 g

8.9 Volumetric flasks, Class A – appropriate sizes with ground glass stoppers

9 Reagents and Standards

9.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall 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.

9.2 Organic-free reagent water – All references to water in this method refer to organic-free reagent water, as defined below.

9.2.1 For volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

9.2.2 A MilliQ water purification system is used to generate organic-free reagent water at the laboratory.

9.3 Methanol, CH_3OH – Pesticide quality or equivalent, demonstrated to be free of analytes. Purge-and-trap grade methanol is utilized by the laboratory. Store apart from other solvents.

9.4 Stock solutions – The routinely used stock solutions are purchased as certified solutions. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

9.4.1 Restek Catalog #30265 – 2-Chloroethyl vinyl ether stock

9.4.2 Restek Catalog #30432 – 502.2 CAL 200 MEGA MIX

9.4.3 Restek Catalog #30439 – 502.2 Mix #1A

9.4.4 Alternatively, stock solutions may be prepared from pure standard materials. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

9.4.4.1 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. Weigh to the nearest 0.1 mg.

9.4.4.2 Add the assayed reference material, as describe below.

- Liquids – 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 alcohol without contacting the neck of the flask.

- Gases – To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

9.4.4.3 Reweigh, dilute to volume, stopper and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the 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.

9.4.4.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store with minimal headspace and protected from light at -10°C to -20°C or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

9.4.4.5 Frequency of Standard Preparation

- Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

- Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

9.5 Prepare secondary dilution standards, using stock standard solutions, in methanol, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 9.6.1 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Secondary standards for gases

should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Section 9.4.4.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

9.6 Calibration standards – There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

9.6.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the premixed certified solutions (or alternately, from the secondary dilution of stock standards – see Sections 9.4.4 and 9.5). Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

Seven initial calibration standards are actually prepared according to the table below.

Concentration	Amount of each of the premixed certified solutions (See Secs. 9.4.1 through 9.4.3)	Final Volume of Reagent Water
1 µg/L	0.5 µL	100 mL
2 µg/L	1 µL	100 mL
5 µg/L	2.5 µL	00 mL
10 µg/L	5 µL	100 mL
20 µg/L	10 µL	100 mL
30 µg/L	15 µL	100 mL
40 µg/L	20 µL	100 mL

NOTE: The concentration is that for all analytes in the mixes except for Xylenes. Due to the coelution of the isomeric pair m-Xylene and p-Xylene, the combined concentration of m- & p-Xylene is actually double that of the concentrations listed here.

9.6.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the premixed certified solutions (or alternately, from the secondary dilution of stock standards – see Sections 9.4.4 and 9.5). Prepare these solutions in organic-free reagent water. See Section 12.2 for guidance on calibration verification.

9.6.2.1 The standard that is most commonly prepared for calibration verification is the 20 µg/L concentration made by adding 10 µL of each of the premixed certified solutions (see Sections 9.4.1 through 9.4.3) to a 100-mL volumetric flask filled to the mark with organic-free reagent water.

9.6.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

9.6.4 In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

9.6.4.1 Use a 25 µL micro syringe.

9.6.4.2 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

9.6.4.3 Mix aqueous standards by inverting the flask three times.

9.6.4.4 Fill the vial from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

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

9.6.4.6 Standards should be stored and handled according to guidance in Sections 9.4.4.4 and 9.4.4.5.

9.7 Surrogate standards – The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and reagent blank with two or more surrogate compounds. The surrogates used are 1-chloro-2-fluorobenzene, 2-bromochlorobenzene and 1,4-dichlorobutane.

The surrogate spiking solution is prepared by making a secondary dilution of the two purchased stocks below.

Restek Catalog #30040 – 502.2 Internal Standard Mix #1

Restek Catalog #30086 – 8021 Surrogate Mix

Following the procedure in Section 9.5, 250 μL of Restek Catalog #30040 and 334 μL of Restek Catalog #30086 are brought to a final volume of 10 mL with methanol. This results in a concentration of 50 μg/mL for each of the surrogates. A 20 μL aliquot of this solution is added to all calibration standards, QC samples and client samples for the equivalent of a 10 μg/L concentration.

10 Sample Collection, Preservation and Storage

10.1 Standard 40-mL glass screw cap VOA vials with Teflon lined silicone septa may be used for liquid matrices. Special 40-mL VOA vials for purge and trap of solid samples, if a system requiring a septum at both ends of the vial, are described in Method 5035. (The PTA-30 autosampler only requires a septum at one end of the vial.) Although the referenced methods are currently not employed by the laboratory, the following information is included for possible future reference. VOA vials for headspace analysis of solid samples are described in Method 5021. Standard 125-mL widemouth glass containers may be used for Methods 5031 and 5032. However, the sampling procedures described in Method 5035 may minimize sample preparation analyte loss better than the procedures described in Methods 5031 and 5032.

The vials and septa should either be purchased pre-cleaned from the manufacturer or washed with soap and water and rinsed with distilled deionized water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100°C for approximately one hour.

NOTE: Do not heat the septa for extended periods of time (i.e., more than one hour) because the silicone begins to slowly degrade at 105°C.

When collecting the samples, liquids and solids should be introduced into the vials gently to reduce agitation which might drive off volatile compounds.

In general, liquid samples should be poured into the vial without introducing any air bubbles within the vial as it is being filled. Should bubbling occur as a result of violent pouring, the sample must be poured out and the vial refilled. The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed and the vial inverted, no headspace is visible. The samples should be hermetically sealed in the vial at the time of sampling and must not be opened prior to analysis to preserve their integrity.

10.1.1 Due to differing solubility and diffusion properties of gases in LIQUID matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro bubbles and should not invalidate a sample for volatiles analysis.

10.1.2 The presence of a macro bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The later case is usually accompanied by a buildup of pressure within the vial (e.g., carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Ci, unpublished data) indicate that "pea-size" bubbles (i.e., bubbles not exceeding ¼ inch or 6 mm in diameter) did not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

10.2 Immediately prior to analysis of liquid samples, the aliquot to be analyzed should be taken from the vial using the instructions from the appropriate sample introduction technique:

10.2.1 The PTA-30 autosampler will remove volumes of 5 mLs from the 40 mL vials.

10.2.2 For smaller analysis volumes, i.e., in the case of very large dilutions, a gas-tight syringe may be inserted directly through the septum of the vial to withdraw the sample.

10.2.3 For larger analysis volumes that cannot be removed using the PTA-30 autosampler (i.e., if more than 5 mm of sediment is at the bottom of the vial), the sample may be carefully poured into the syringe barrel. Opening a volatile sample to pour a sample into a syringe destroys the validity of the sample for future analysis. Therefore, if there is only one VOA vial, it is strongly recommended that the analyst fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time as the analyst has determined that the first sample has been analyzed properly.

10.2.4 If these guidelines are not followed, the validity of the data generated from the samples may be suspect.

10.3 VOA vials for samples with solid or semi-solid matrices (e.g., sludges) should be filled according to the guidance given in the appropriate 5000 series sample introduction method to be used. When 125-mL wide mouth glass containers are used, the containers should be filled as completely as possible. The 125-mL vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. A minimum of two vials should also be filled per sample location.

10.4 At least two VOA vials should be filled and labeled immediately at the point at which the sample is collected. They should NOT be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. The two vials from each sampling location should then be sealed in separate plastic bags to prevent cross-contamination between samples, particularly if the sampled waste is suspected of containing high levels of volatile organics. (Activated carbon may also be included in the bags to prevent cross-contamination from highly contaminated samples.) VOA samples may also be contaminated by diffusion of volatile organics through the septum during shipment and storage. To monitor possible contamination, a trip blank prepared from organic-free reagent water should be carried throughout the sampling, storage and shipping process.

10.5 Sample Storage – The sample storage area must be free of organic solvent vapors and direct intense light.

10.5.1 For samples for Method 5035, e.g., solids, store samples at 4°C until analysis. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

10.5.2 For samples for Method 5030, e.g., aqueous samples with no residual chlorine present, adjust pH to less than 2 with H_2SO_4, HCl or solid $NaHSO_4$. Store samples at 4°C until analysis. Analyze all samples within 14 days of collection. Samples not analyzed within this period must be discarded and replaced.

10.5.3 For samples for Method 5030 that do contain residual chlorine, collect sample in a 125-mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40-mL VOA vial. Adjust pH to less than 2 with H_2SO_4, HCl or solid $NaHSO_4$.

11 Quality Control

11.1 Initial Demonstration of Proficiency – Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made.

11.1.1 The reference samples are prepared from a spiking solution containing each analyte of interest. The reference sample concentrate (spiking solution) may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the reference sample

concentrate must be made using stock standards prepared independently from those used for calibration.

Prepare a reference sample concentrate in methanol at a concentration such that the spike will provide a concentration in the clean matrix that is 10-50 times the MDL for each analyte in that matrix.

The concentration of the target analytes in the reference sample may be adjusted to more accurately reflect the concentrations that will be analyzed by the laboratory. If the concentration of the analyte is being evaluated relative to a regulatory limit or action level, the spike should be at or below the limit, or 1 – 5 times the background concentration (if historical data are available), whichever is higher. If historical data is not available, it is suggested that a background sample of the same matrix from the site be submitted for matrix spiking purposes to ensure that high concentrations of target analytes and/or interferences will not prevent calculations of recoveries.

11.1.2 To evaluate the performance of the total analytical process, the reference samples must be handled in exactly the same manner as actual samples. Use a clean matrix for spiking purposes (one that does not have any target or interference compounds), e.g., organic-free reagent water for the aqueous matrix and organic-free sand or soil for the solid matrix.

11.1.3 Prepare the reference sample by adding 400 µL of the reference sample concentrate (see Section 11.1.1) to 200 mL of organic-free reagent water. Transfer this solution immediately to 40-mL vials when validating water analysis performance by Method 5030. When validating soil analysis performance by Method 5035, transfer this solution in 5 mL aliquots into 40-mL vials each containing 5 g of sand placed in a muffle furnace at 550°C for four hours.

11.1.4 Analyze at least four replicate aliquots of the well-mixed reference samples by the same procedures used to analyze actual samples.

11.1.5 Calculate the average recovery (x) in µg/L and the standard deviation of the recovery (s) in µg/L for each analyte of interest using the four results.

11.1.6 Single laboratory performance data are included in SW846 8021B, Table 2. Compare s and x for each analyte with the corresponding performance data. If s and x for all analytes of interest meet the appropriate acceptance criteria, then the system performance is acceptable and analysis of actual samples can begin. If any individual s value exceeds the precision limit or any individual x value falls outside the range for accuracy, then the system performance may be unacceptable for that analyte.

11.1.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest, beginning at Section 11.1.2.

11.1.6.2 Beginning at Section 11.1.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning at Section 11.1.2.

11.1.7 Even though the method contains performance data, the development of in-house acceptance limits is strongly recommended, and may be accomplished using the procedure below.

11.1.7.1 For each matrix spike sample analyzed, calculate the percent recovery of each matrix spike compound added to the sample using the calculation below.

$$\text{Recovery} = \%R = \frac{C_s - C_u}{C_n} \times 100$$

where: C_s = Measured concentration of the spiked sample aliquot
C_u = Measured concentration of the unspiked sample aliquot
C_n = Nominal (theoretical) concentration increase that results from spiking the sample, or the nominal concentration of the spiked aliquot

11.1.7.2 Calculate the average percent recovery (p) and the standard deviation (s) for each of the matrix spike compounds after analysis of 15-20 matrix spike samples of the same matrix using the equations below. Calculate the average percent recovery and the standard deviation of each of the surrogates after analysis of 15-20 field samples of the same matrix.

$$p = \sum_{i=1}^{n} p_i$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(p_i - p)^2}{n-1}}$$

11.1.7.3 After the analysis of 15-20 matrix spike samples of a particular matrix (for matrix spike limits) or 15-20 field samples (for surrogate limits), calculate upper and lower control limits for each matrix spike or surrogate compound:

Upper control limit = p + 3s
Lower control limit = p – 3s

Calculate warning limits as:

Upper warning limit = p + 2s
Lower warning limit = p – 2s

These control limits approximate a 99% confidence interval around the mean recovery, while the warning limits approximate a 95% confidence interval.

11.2 Sample Quality Control for Preparation and Analysis – This includes the analysis of QC samples including a method blank, matrix spike, a duplicate and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

11.2.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

11.2.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then the analyst may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, the analyst should use a matrix spike and matrix spike duplicate pair.

11.2.2.1 Accuracy is estimated from the recovery of spiked analytes from the matrix of interest. Laboratory performance in a clean matrix is estimated from the recovery of analytes in the LCS. Calculate the recovery of each spiked analyte in the matrix spike, matrix spike duplicate and LCS according to the equation in Section 11.1.7.1.

11.2.2.2 If there is insufficient sample to do a duplicate or a matrix spike/matrix spike duplicate pair, the analyst should prepare a Laboratory Control Sample (LCS) and an LCS duplicate to determine the precision of the analysis. Precision (as RPD) is calculated as follows:

$$RPD = \frac{|C_1 - C_2|}{\left(\frac{C_1 + C_2}{2}\right)} \times 100$$

where: C_1 = Measured concentration of the first sample aliquot
C_2 = Measured concentration of the second sample aliquot

11.2.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentration as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix. As a general rule, if any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the laboratory should determine if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Section 11.3) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either matrix spikes or surrogates alone.

11.2.4 Recommended QC acceptance criteria for matrix spike samples and LCS

It is necessary for the laboratory to develop single-laboratory performance data for accuracy and precision in the matrices of interest (see Section 11.1.7). Method performance in each matrix is monitored through the use of control charts.

For the LCS, the laboratory should use 70 – 130% as interim acceptance criteria for recoveries of spiked analytes until in-house limits are developed (see Section 11.1.7). Where in-house limits have been developed for matrix spike recoveries, the LCS results should fall within those limits, as the LCS is prepared in a clean matrix.

As a general rule, the recoveries of most compounds spiked into samples should fall within the range of 70 – 130%, and this range should be used as a guide in evaluating in-house performance. However, matrix spike recoveries and LCS recoveries may be affected by the spike-to-background ratio.

11.3 Surrogate recoveries – The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. Use the equations in Section 11.1.7.2 and the definitions in Section 11.1.7.3 to develop laboratory control limits.

11.3.1 Surrogate recovery is calculated as:

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

If recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

11.3.1.1 Examine the chromatograms for interfering peaks and integrated peak areas.

11.3.1.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample.

11.3.1.3 If no instrument problem is found, the sample should be re-analyzed.

11.3.1.4 If, upon re-analysis (in either Section 11.3.1.2 or 11.3.1.3) the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the reanalysis data to the data user. If holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

11.4 Retention time windows

Retention time windows are crucial to the identification of target compounds. Absolute retention times are used for compound identification in all GC methods that do *not* employ internal standard calibration. Retention time windows are established to compensate for minor shifts in absolute retention times as a result of sample loadings and normal chromatographic variability. The width of the retention time window should be carefully established to minimize the occurrence of both false positive and false negative results. Tight retention time windows may result in false negatives and/or may cause unnecessary

reanalysis of samples when surrogates or spiked compounds are erroneously not identified. Overly wide retention time windows may result in false positive results that cannot be confirmed upon further analysis.

11.4.1 Before establishing retention time windows, make sure that the chromatographic system is operating reliably and that the system conditions have been optimized for the target analytes and surrogates in the sample matrix to be analyzed. Analyze the initial calibration standards.

11.4.2 Record the retention time for each single component and surrogate to three decimal places (e.g., 0.007). Calculate the mean and standard deviation of the absolute retention times for each analyte and surrogate.

11.4.3 If the standard deviation of the retention times for a target compound is 0.000 (i.e., no difference between the absolute retention times), then the laboratory may either collect data from additional injections of standards or use a default standard deviation of 0.01 minutes. (Recording retention times to three decimal places rather than only two should minimize the instances in which the standard deviation is calculated as 0.000.)

11.4.4 The width of the retention time window for each analyte and surrogate is defined as ±3 times the standard deviation of the mean absolute retention time established during the series of standard analyses. If the default standard deviation in Section 11.4.3 is employed, the width of the window will be 0.03 minutes.

11.4.5 Establish the center of the retention time window for each analyte and surrogate by using the absolute retention time for each analyte and surrogate from the calibration verification standard at the beginning of the analytical shift. For samples run during the same shift as an initial calibration, use the retention time of the mid-point standard of the initial calibration.

11.4.6 Calculate absolute retention time windows for each analyte and surrogate on each chromatographic column and instrument. New retention time windows must be established when a new GC column is installed. The retention time windows should be reported with the analysis results in support of the identifications made.

11.4.7 If the instrument data system is not capable of employing compound-specific retention time windows, then the analyst may choose the widest window and apply it to all compounds.

11.4.8 The surrogates are added to each sample, blank and QC sample and are also contained in each calibration standard. Although the surrogates may be diluted out of certain sample extracts, their retention times in the calibration standards may be useful in tracking retention time shifts.

Whenever the observed retention time of a surrogate is outside the established retention time window, it is advisable to determine the cause and correct the problem before continuing the analyses.

11.5 The laboratory regularly participates in relevant performance evaluation studies.

12 Calibration and Standardization

12.1 Initial Calibration

Calibration must take place using the same sample introduction method that will be used to analyze actual samples (Section 13.3.1).

12.1.1 To prepare a calibration standard, follow the table in Section 9.6.1. Add the appropriate volume of each of the premixed certified solutions to the specified volume volumetric flask filled to the mark with organic-free reagent water. Use a microsyringe and rapidly inject the alcoholic standard 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. If preparing standards for Method 5030, discard the contents contained in the neck of the flask and pour off the remaining solution into 40 mL vials and cap securely. Make sure that no headspace is present in the vials. If preparing standards for Method 5035, discard the contents contained in the neck of the flask and remove 5 mL aliquots from the volumetric flask and transfer to 40-mL vials containing magnetic stir bars. Aqueous standards are not stable and should be prepared daily.

12.1.1.1 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

12.1.2 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 – 2 μL into the GC system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC system to water.

12.1.3 The ratio of the detector response to the amount (mass) of analyte in the calibration standard is defined as the calibration factor (CF).

$$CF = \frac{\text{Peak Area (or Height) of the Compound in the Standard}}{\text{Concentration of the Standard}}$$

12.1.4 Calibration linearity

SW-846 chromatographic methods allow the use of both linear and non-linear models for the calibration data, as described below. Given the

limitations in instrument data systems, it is likely that the analyst will have to choose one model for all analytes in a particular method. (Multiple models are allowable for use with the Chemserver data system.)

NOTE: The option for non-linear calibration may be necessary to achieve low detection limits or to address specific instrumental techniques. However, it is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentrations or to avoid proper instrument maintenance.

Whichever calibration model is employed, a unique analyte or surrogate concentration must fall within the calibration range. Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

NOTE: The following sections describe various options for initial calibration and provide the calibration acceptance criteria used to evaluate each option. The criteria listed in these sections are designed for quantitation of trace level concentration of the analytes of interest. If data of lesser quality will satisfy project-specific data needs, then less stringent criteria may be employed, provided that they are documented and approved in a project-specific QA project plan.

The choice of a specific calibration model should be made in one of two ways. The first is to begin with the simplest approach, the linear model through the origin, and progressing through the other options until the calibration acceptance criteria are met. The second approach is to use a *priori* knowledge of the detector response to choose the calibration model. Such knowledge may come from previous experience, knowledge of the physics of the detector or specific manufacturer's recommendations.

12.1.4.1 Linear calibration using the average calibration factor

When calculated as described in Section 12.1.3, calibration factors are a measure of the slope of the calibration relationship and assume that the curve passes through the origin. Under ideal conditions, the factors will not vary with the concentration of the standard that is injected into the instrument. In practice, some variation is to be expected. However, when the variation measured as the relative standard deviation (RSD) is less than or equal to 20%, the use of the linear model is generally appropriate, and the calibration curve can be assumed to be linear and to pass through the origin.

NOTE: Linearity through zero is a statistical assumption and not a rationale for reporting results below the calibration range demonstrated by the analysis of the standards.

To evaluate the linearity of the initial calibration, calculate the mean CF, the standard deviation (SD), and the RSD as follows:

$$\text{mean CF} = \sum_{i=1}^{n} CF_i$$

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(CF_i - \text{mean CF})^2}{n-1}}$$

$$RSD = \frac{SD}{\text{mean CF}} \times 100$$

If the RSD of the calibration factors is less than or equal to 20% over the calibration range, then linearity through the origin may be assumed, and the average response factor may be used to determine sample concentrations.

12.1.4.2 Given the potentially large numbers of analytes that may be analyzed in some methods, it is likely that some analytes may exceed the 20% acceptance limit for the RSD for a given calibration. In those instances, the following steps are recommended, but not required.

The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Section 18.1.1 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 20%, the analyst may wish to review the results (area counts, calibration factors and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD

recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. Changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

NOTE: As noted in Section 9.6.1, the method quantitiation limit is established by the concentration of the lowest standard analyzed during the initial calibration. Hence, narrowing the calibration range by changing the concentration of the lowest standard will, by definition, change the method quantitation limit. When the purpose of the analysis is to demonstrate compliance with a specific regulatory limit or action level, the analyst must ensure that the method quantitation limit is at least as low as the regulatory limit or action level.

- In those instances where the RSD for one or more analytes exceeds 20%, the initial calibration may still be acceptable if the following conditions are met:
- The mean of the RSD values for all analytes in the calibration is less than or equal to 20%. The mean RSD is calculated by summing the RSD value for each analyte and dividing by the total number of analytes. If no analyte has an RSD above 20%, then the mean RSD calculation need not be performed.
- The mean RSD criterion applies to all analytes in the standards, regardless of whether or not they are of interest for a specific project. In other words, if the target analyte is part of the calibration standard, its RSD value is included in the evaluation.
- The data user must be provided with either a summary of the initial calibration data or a specific list of those compounds for which the RSD exceeded 20% and the results of the mean RSD calculation.

NOTE: The analyst and the data user must be aware that the use of the average of all RSD values ≤20% will lead to greater uncertainty for those analytes for which the RSD is greater than 20%. The analyst and the data user should review the associated quality control sample results carefully, with particular attention to the matrix spike and laboratory control sample results (see Sections 11.2.2 and 11.2.3), to determine if the calibration linearity poses a significant concern. If this approach is not acceptable for a particular application, then the analyst may need to employ one of the other calibration approaches (see Sections 12.1.4.3 through 12.1.4.5) or adjust the instrument operating conditions and/or the calibration range until the RSD is ≤20%.

If the average of all RSD values ≤20%, then the average calibration factor may be used to determine sample concentration as described in Section 14.1.1.

12.1.4.3 Linear calibration using a least squares regression

If the RSD of the calibration factors is greater than 20% over the calibration range, then linearity through the origin cannot be assumed. If this is the case, the analyst may employ a regression equation that does not pass through the origin. This approach may also be employed based on past experience or a *priori* knowledge of the instrument response. Further, at the discretion of the analyst, this approach also may be used for analytes that do meet the RSD limit of 20%.

This is most easily achieved by performing a linear regression of the instrument response versus the concentration of the standards. Make certain that the instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). This is a statistical requirement and is not simply a graphic convention.

The analyst may also employ a weighted least squares regression if replicate multi-point calibrations have been performed, e.g., three 5-point curves. For all other instances, an appropriate unweighted least squares method should be used. When using a weighted linear least squares regression, the following weighting factor should be used:

$$\frac{1}{SD^2}$$

where SD is the standard deviation of the replicate results at each individual standard concentration. The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = ax + b$$

where:

y = Instrument response (peak area or height)
a = Slope of the line (also called the coefficient of x)
x = Concentration of the calibration standard
b = The intercept

The analyst should not force the line through the origin, but have the intercept calculated from the data points. Otherwise, the problems noted with the RSD value will occur, i.e., a line through the origin will not meet the QC specifications. In addition, do not include the origin (0,0) as a calibration point. The use of a linear regression may not be used as a rationale for reporting results below the calibration range demonstrated by the analysis of the standards. The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. In order to be used for quantitative purposes, r must be greater than or equal to 0.99.

When a weighted linear least squares regression is employed, the regression equation becomes:

$$y = \frac{1}{SD^2}(ax + b).$$

12.1.4.4 Non-linear calibration

In situations where the analyst knows that the instrument response does not follow a linear model over a sufficiently wide working range, or when the other approaches described here have not met the acceptance criteria, a non-linear calibration model may be employed.

NOTE: It is not EPA's intent to allow non-linear calibration to be used to compensate for detector saturation at higher concentration or to avoid proper instrument maintenance. Thus, non-linear calibration should not be employed for methods or instruments previously shown to exhibit linear calibration for the analytes of interest.

When using a calibration model for quantiation, the curve must be continuous, continuously differentiable and monotonic over the calibration range. The model chosen should have no more than four parameters, i.e., if the model is polynomial, it may be no more than third order as in the equation:

$$y = ax^3 + bx^2 + cx + d$$

As noted above, the model must be continuous. A curve is continuous when it has consecutive numerical values along the function, whether increasing or decreasing, and without having breaks in the function (i.e., the pen shall never leave the paper from the minimum to the maximum). The model must also be continuously differentiable, such that all derivatives of the function are continuous functions themselves, and monotonic, such that all tangent lines of the derivative to all of the points on the calibration curve have either only positive or negative slopes.

If the model is not a polynomial, it should not include more than four parameters, i.e.,

$$y = f(a,b,c,d,x)$$

where "f" indicates a function with up to four parameters.

In estimating model parameters for the calibration data, the instrumental response (y) must be treated as the dependent variable. Do not force the line through the origin, i.e., do not set the intercept as 0, and do not include the origin (0,0) as a calibration point. Model estimates from the regression must be used as calculated, i.e., if the model is a polynomial, the intercept is d and may not be set to 0. Weighting in a calibration model may significantly improve its accuracy.

The statistical considerations in developing a non-linear calibration model require more data than the more traditional linear approaches described above. Whereas this method employs a minimum of five standards for a linear (first order) calibration model, a quadratic (second order) model requires six standards, and a third order polynomial requires seven standards.

Most curve fitting programs will use some form of a least squares minimization to adjust the coefficients of the polynomial (a,b,c and d above) to obtain the polynomial that best fits the data. The "goodness of fit" of the polynomial

equation is evaluated by calculating the weighted coefficient of the determination (COD).

$$COD = \frac{\sum_{i=1}^{n}(y_{obs} - \text{mean } y)^2 - \left(\frac{n-1}{n-p}\right)\sum_{i=1}^{n}(y_{obs} - Y_i)^2}{\sum_{i=1}^{n}(y_{obs} - \text{mean } y)^2}$$

where:

y_{obs} = Observed response (area) for each concentration from each initial calibration standard

mean y = Mean observed response from the initial calibration

Y_i = Calculated (or predicted) response at each concentration from the initial calibration(s)

n = Total number of calibration points (i.e., 6 for a quadratic model; 7 for a third order model)

p = Number of adjustable parameters in the polynomial equation (i.e., 3 for a third order; 2 for a second order polynomial)

Under ideal conditions, with a "perfect" fit of the model to the data, the coefficient of the determination will equal 1.0. In order to be an acceptable non-linear calibration, the COD must be greater than or equal to 0.99.

As noted in Section 12.1.4, whichever of these options is employed, a unique analyte or surrogate concentration must fall within the calibration range. Analysts are advised to check both second and third order calibration models to ensure that this holds true (e.g., no parabolas or repeating functions in the calibration range). Samples with concentrations that exceed the calibration range must be diluted to fall within the range.

12.1.4.5 Data transformations

An understanding of the fundamental behavior of the detector may be used to choose a data transformation that will then allow for a simple calibration model. For example, the response of a flame photometric detector in the sulfur mode is known to be proportional to the square of the sulfur concentration. Therefore, using the data system to take the square root of the instrument response before integration or the square root of the peak height allows for a calibration factor approach rather than a polynomial calibration curve. Instrument response may be transformed prior to any

calculations (including integration) subject to the following constraints:

- Any parameters used in the transformation should be fixed for the calibration and all subsequent analyses and verifications until the next calibration.
- The transformation model chosen should be consistent with the behavior of the instrument detector. All data transformations must be clearly defined and documented by the analyst and related back to the fundamental behavior of the detector. In other words, this approach may not be used in the absence of specific knowledge about the behavior of the detector, nor as a "shot in the dark" to describe the calibration.
- No transformations should be performed on areas or other results (e.g., the transformation must be applied to the instrument response itself).
- When the transformed data are used to develop calibration factors, those factors meet the acceptance criteria of the average of all RSD values ≤20%.

12.1.5 When the RSD exceeds 20%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standards preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

12.2 Calibration verification

The calibration relationship established during the initial calibration (Section 12.1) must be verified at periodic intervals.

The initial calibration must be verified at the beginning of each 12-hour analytical shift and again after every 10 samples during which samples are analyzed. The 12-hour analytical shift begins with the injection of the calibration verification standard. The shift ends after the completion of the analysis of the last sample or standard that can be injected within 12 hours of the beginning of the shift.

If the response calculated concentration of an analyte is within ±15%

of the response obtained during the initial calibration, then the initial calibration is considered still valid, and the analyst may continue to use the CF values from the initial calibration to quantitate sample results.

If the calculated concentration for any analyte varies from the mean response obtained during the initial calibration by more than ±15%, then the initial calibration relationship may no longer be valid.

In keeping with the approach described for initial calibration in Section 12.1, if the average of the responses for all analytes is within 15%, then the calibration has been verified. However, the average must include all analytes in the calibration, regardless of whether they are target analytes for a specific project, and the data user must be provided with the calibration verification data or a list of those analytes that exceeded the 15% limit. The effect of using the average of the response for all analytes for calibration verification will be similar to that for the initial calibration – namely, that the quanititative results for those analytes where the difference is greater than 15% will include a greater uncertainty.

If the calibration does not meet the 15% limit (either on the basis of each compound or the average across all compounds), check the instrument operating conditions and if necessary, restore them to the original settings and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared.

NOTE: For target compounds that boil below 30°C at 1 atm pressure (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane and vinyl chloride), analysts may use a calibration verification acceptance criteria of within ±20 % difference from the initial calibration response.

12.2.1 Verification of linear calibrations

Calibration verification for linear calibrations involves the calculation of the percent drift or the percent difference of the instrument response between the initial calibration and each subsequent analysis of the verification standard. Use the equations below to calculate % Drift or % Difference.

$$\%\,\text{Drift} = \frac{\text{Calculated concentration - Theoretical concentration}}{\text{Theoretical concentration}} \times 100$$

where the calculated concentration is determined using the mean calibration factor from the initial calibration and the theoretical concentration is the concentration at which the standard was prepared.

$$\% \text{ Difference} = \frac{CF_v - \text{mean CF}}{\text{mean CF}} \times 100$$

where CF_v is the calibration factor from the analysis of the verification standard and mean CF is the mean calibration factor from the initial calibration. The % difference or % drift calculated for the calibration verification standard must be within ±15% for each analyte or averaged across all analytes be (see Section 12.2) before any sample analyses may take place.

12.2.2 Verification of a non-linear calibration

Calibration verification of a non-linear calibration is performed using the percent drift calculation described in Section 12.2.1. The % drift calculated for the calibration verification standard must be within ±15% for each analyte, or averaged across all analytes (see Section 12.2) before any sample analyses may take place. It may also be helpful to employ two standards at different concentrations to verify the calibration. In this instance, one standard should be near the inflection point in the curve.

12.2.3 Regardless of whether a linear of non-linear calibration model is used, if either the percent drift or percent difference criterion is not met, then no sample analyses may take place until the calibration has been verified or a new initial calibration is performed that meets the specifications in Section 12.1. If the calibration cannot be verified after the analysis of a single verification standard, then adjust the instrument operating conditions and/or perform instrument maintenance (see Section 18.1.1) and analyze another aliquot of the verification standard. If the calibration cannot be verified with the second standard, then a new initial calibration must be performed.

12.2.4 All target analytes and surrogates, including those reported as non-detects, must be included in a periodic calibration for purposes of retention time confirmation and to demonstrate that calibration verification criteria are being met.

12.2.5 Calibration verification may be performed using both high and low concentration standards from time to time. This is particularly true for the ELCD. This detector drifts, and periodic use of the high and low concentration standards serves as a further check on the initial calibration. The concentrations of these standards should generally reflect those observed in samples.

12.2.6 Samples must be bracketed by periodic analyses of standards that meet the QC acceptance criteria (e.g., calibration and retention time). Therefore, more frequent analyses of standards will minimize the number

of samples that would have to be reinjected if the QC limits are violated for the standard analysis. The results from these bracketing standards must meet the calibration verification criteria in Section 12.2.1 or 12.2.2 and the retention time criteria in Section 11.4. However, if the standard analyzed after a group of samples exhibits a response for an analyte that is above the acceptance limit and the analyte was not detected in any of the previous samples during the analytical shift, then the samples do not need to be reanalyzed as the verification standard has demonstrated that the analyte would have been detected were it present.

13 Procedure

13.1 Volatile compounds are introduced into the gas chromatograph either by direct injection (Method 3585 for oily matrices) or purge-and-trap (Methods 5030/5035), headspace (Method 5021), or by vacuum distillation (Method 5032). Methods 5030, 5021 or 5032 may be used directly on groundwater samples. Methods 5035, 5021 or 5032 may be used for low concentration contaminated soils and sediments. For high-concentration soils or sediments (>200 μg/kg), methanolic extraction, as described in 5035, may be necessary prior to purge-and-trap analysis. For guidance on the dilution of oily waste samples for direct injection refer to Method 3585.

13.2 Set up the gas chromatograph system so that the photoionization detector (PID) is in series with the electrolytic conductivity detector (HECD).

NOTE: Use of the dual detector system is not a requirement of the method. The GC system may also be set up to use a single detector when the analyst is looking for just halogenated compounds (using the HECD) or for just aromatic compounds (using the PID).

13.2.1 Oven settings

Carrier gas (Helium) Flow rate:	6 mL/min
Temperature program	
Initial temperature:	35°C, hold for 10 minutes
Program:	35°C to 200°C at 4°C/min
Final temperature:	200°C, hold for 9 minutes
Inlet temperature:	210°C
Detector base temperature:	200°C

13.2.2 The carrier gas flow is augmented with an additional 30 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors.

13.2.3 These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step.

13.3 Gas chromatographic analysis

13.3.1 Introduce volatile compounds into the gas chromatograph using either Methods 5030/5035 (purge-and-trap method) or the direct injection method (see Section 13.3.1.1), by Method 5021 (headspace) or by Method 5032 (vacuum distillation).

13.3.1.1 Direct injection – 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 (approximately 10,000 µg/L), therefore, it is only permitted where concentrations in excess of 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).

13.3.1.2 Refer to Method 3585 for guidance on the dilution and direct injection of waste oil samples.

13.3.2 All analyses, including field samples, matrix spike samples, matrix spike duplicates, laboratory control samples, method blanks and other QC samples are performed during an analysis sequence. The sequence begins with instrument calibration, which is followed by the analysis of samples. Verification of calibration and retention times is necessary after no less than every 10 samples. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded. It is necessary that a calibration verification standard be run at the end of the sequence to bracket the sample analyses. If critieria are exceeded, corrective action must be taken (see Section 18.1.1) to restore the system and/or a new calibration curve must be prepared for that compound and the samples must be reanalyzed.

13.3.3 Sample concentrations are calculated by comparing sample responses with the initial calibration of the system (Section 12.1.4). If sample response exceeds the limit of the initial calibration range, dilute the samples and reanalyze. Samples should be diluted so that all peaks are on scale, as overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure that all peaks are on scale over a 100-fold range, is acceptable as long as calibration limits are not exceeded. When overlapping peaks cause errors in peak area integration, the use of peak height measurements is recommended.

13.3.4 When there are a large number of target analytes, it may be difficult to fully resolve these compounds.

13.4 Compound identification

Tentative identification of an analyte occurs when a peak from a sample falls within the daily retention time window. Confirmation is necessary when the composition of samples is not well characterized. Confirmation techniques include analysis on a second column with dissimilar stationary phase or by an alternate detector.

When confirmation is made on a second column, that analysis should meet all of the QC criteria described above for calibration, retention times, etc.

Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

Many chromatographic interferences result from co-elution of one or more compounds with the analyte of interest, or may be the result of the presence of a non-analyte peak in the retention time window of an analyte. Such co-elution problems affect quantitation as well as identification, and may result in poor agreement between the quantitative results from two dissimilar columns. Therefore, even when the identification has been confirmed on a dissimilar column, the analyst should evaluate the agreement of the quantitative results on both columns.

NOTE: In most cases, samples run by this method are from a well-known source, therefore, the history of client results for target compounds is documented and confirmation is not necessary.

14 Data Analysis and Calculations

14.1 The calculation of analyte and surrogate concentrations is completed by the Chemserver software using one of the equations below, depending upon the model used in the calibration.

14.1.1 Linear calibration:

14.1.1.1 Aqueous samples

$$\text{Concentration } (\mu g/mL) = \frac{(A_s)(D)}{(\text{meanCF})(V_s)}$$

where: A_S = Area (or height) of the peak for the analyte in the sample

D = Dilution factor, if the sample or extract was diluted prior to analysis. If no dilution was made, D=1. The dilution factor is always dimensionless.

mean CF = Mean calibration factor from the initial calibration.

V_S = Volume of the aqueous sample extracted or purged (mL). If units of liters are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/mL which is equivalent to µg/L.

14.1.1.2 Nonaqueous samples

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(D)}{(\text{mean CF})(W_s)}$$

where: A_S, D and mean CF are the same as for aqueous samples, and

W_S = weight of sample extracted (g). Either a dry weight or wet weight may be used, depending upon the specific application of the data. If units of kilograms are used for this term, multiply the results by 1000.

Using the units specified here for these terms will result in a concentration in units of ng/g which is equivalent to µg/kg.

Where a volume of methanol extract is added to organic-free reagent water and purged, V_T is the total volume of the methanol extract and V_I is the volume of methanol extract that is added to the 5 mL of organic-free reagent water. The concentration is then calculated using the equation below.

$$\text{Concentration } (\mu g/kg) = \frac{(A_s)(V_T)(D)}{(\text{mean CF})(V_I)(W_s)}$$

14.1.1.3 If a linear calibration that does not pass through the origin has been employed, then the regression equation is rearranged as shown in Section 12.1.4.3, and the concentration of the analyte is calculated from the area response (Y), the slope (a) and the intercept (b). When using this form of linear calibration, it is the analyst's responsibility to ensure that the calculations take into account the volume or weight of the original sample, the dilution factor (if any) and dry weight (as applicable). One approach to this calculation is to perform the original linear regression using the concentration of the analyte in the final volume purged. The concentration of the analyte in the sample may then be calculated as follows:

$$C_S = \frac{(C_{ex})(V_T)}{(V_S)}$$

where:

C_s = Concentration in the sample
C_{ex} = Concentration in the final volume purged
V_T = Total volume of the concentrated extract
V_S = Volume of the sample purged

For solid samples, substitute the weight of the sample, W_S, for V_S.

The concentration of the analyte in the volume of the sample that is purged will be the same as in the original sample, except when dilutions are performed.

15 Method Performance

15.1 Initial Demonstration of Laboratory Accuracy and Precision — Attachment 1

15.2 MDL Study — Attachment 2

15.2.1 Method detection limits were calculated using the formula:

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

where: $t_{(n-1,1-alpha=0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom
n = Number of replicates
S = The standard deviation of the replicate analysis

16 Pollution Prevention

16.1 No solvents are utilized in this method except the extremely small volumes of methanol needed to make calibration standards. The only other chemicals used in this method are the neat materials in preparing standards and sample preservatives. All are used in extremely small amounts and pose no threat to the environment.

17 Data Assessment and Acceptance Criteria for Quality Control Programs

17.1 A summary of the raw data is copied and put into the project folder after validation by a second analyst/supervisor.

17.2 The reported values are then entered into LIMS. Data is further validated in LIMS by a third analyst.

17.3 Each of the chromatograms for the raw data are initialed by the analyst and saved according to the run date with all other GC data for the particular volatiles instrument.

18 Corrective Actions for Out-Of-Control Data

18.1 Initial Calibration has some analytes that exceed the 20% acceptance limit for the RSD – The first step is generally to check the instrument operating conditions. The suggested maintenance procedures in Section 18.1.1 may be useful in guiding such adjustments. This option will apply in those instances where a linear instrument response is expected. It may involve some trade-offs to optimize performance across all target analytes. For instance, changes to the operating conditions necessary to achieve linearity for problem compounds may cause the RSD for other compounds to increase, but as long as all analytes meet the RSD limits for linearity, the calibration is acceptable.

If the RSD for any analyte is greater than 20%, the analyst may wish to review the results (area counts, calibration factors and RSD) for those analytes to ensure that the problem is not associated with just one of the initial calibration standards. If the problem appears to be associated with a single standard, that one standard may be reanalyzed and the RSD recalculated. Replacing the standard may be necessary in some cases.

A third alternative is to narrow the calibration range by replacing one or more of the calibration standards with standards that cover a narrower range. If linearity can be achieved using a narrower calibration range, document the calibration linearity, and proceed with analyses. The changes to the upper end of the calibration range will affect the need to dilute samples above the range, while changes to the lower end will affect the overall sensitivity of the method. Consider the regulatory limits or action levels associated with the target analytes when adjusting the lower end of the range.

18.1.1 Suggested chromatographic system maintenance

Corrective measures may involve any one or more of the following remedial actions. This list is by no means comprehensive and analysts should develop expertise in trouble shooting their specific instruments and analytical procedures. The manufacturers of chromatographic instruments, detectors, columns and accessories generally provide detailed information regarding the proper operation and limiting factors associated with their products. The importance of reading and reviewing this information cannot be over-emphasized.

18.1.1.1 Capillary GC columns

Routine maintenance may compel the analyst to clean and deactivate the glass injection port insert or replace it with a

fresh insert that has been cleaned and deactivated with dichlorodimethylsilane. Cut off 0.5 – 1.0 m of the injector end of the column using a 90° cut. Place ferrule onto the column before cutting.

Exceptional maintenance may compel the analyst to replace gas traps and backflush the column with solvent, if appropriate, according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

18.1.1.2 Metal (GC) injector body

Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert. Lower the injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene, catching the rinsate in the beaker.

Prepare a solution of deactivating agent (dichlorodimethylsilane) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, hexane and methanol again. Reassemble the injector and replace the GC column.

NOTE: Due to the solvents (Toluene and acetone are common target compounds.) used in this procedure, this should only be used as a last resort to eliminate active sites. The final methanol rinse must be thorough enough to remove all traces of these solvents in the injection port.

18.2 Calibration verification

18.2.1 If the percent difference or drift for each target compound is less than or equal to 15% for the calibration verification, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 15% difference or drift) for any one target compound, then corrective action must be taken prior to the analysis of samples.

18.3 If any individual percent recovery in the matrix spike (or matrix spike duplicate) falls outside the designated range for recovery, the laboratory should determine if there is a matrix effect or a laboratory performance problem. A matrix effect is indicated if the LCS data are within limits but the matrix spike data exceed the limits. The surrogate recovery data (Section 11.3) should also be used to evaluate the data. Recoveries of both matrix spike compounds and surrogates that are outside of the acceptance limits suggest more pervasive analytical problems than problems with the recoveries of either matrix spikes or surrogates alone.

18.4 If surrogate recovery is not within in-house surrogate recovery limits, the following procedures are necessary.

18.4.1 Examine the chromatograms for interfering peaks and integrated peak areas.

18.4.2 Check instrument performance. If an instrument performance problem is identified, correct the problem and re-analyze the sample.

18.4.3 If no instrument problem is found, the sample should be re-analyzed.

18.4.4 If, upon re-analysis (in either Section 18.4.1 or 18.4.3) the recovery is again not within limits, report the data as an "estimated concentration." If the recovery is within the limits in the re-analysis, provide the reanalysis data to the data user. If holding time for the method has expired prior to the re-analysis, provide both the original and re-analysis results to the data user, and note the holding time problem.

18.5 The results of the method blank should be:

18.5.1 Less than the laboratory's MDL for the analyte or less than the level of acceptable blank contamination specified in the approved quality assurance project plan.

18.5.1.1 Less than 5% of the regulatory limit associated with an analyte.

18.5.1.2 Or less than 5% of the sample result for the same analyte, whichever is greater.

18.5.1.3 If the method blank results do not meet the acceptance criteria above, then the analyst should take corrective action to locate and reduce the source of the contamination and to re-extract and reanalyze any samples associated with the contaminated method blank.

18.6 Any sample result that falls above 10% of the range of the calibration must be diluted to a value that falls within the calibration curve.

18.7 When a sample is analyzed that has saturated response from a compound, the samples immediately following that sample may contain responses for that compound above the detection limit, depending on the degree of saturation. It is up to the analyst's discretion and history of the client samples, if available, to determine if these results are representative of the sample or due to carryover and if the latter is true to proceed with reanalysis.

19 Contingencies for Handling Out-of-Control Data or Unacceptable Data

19.1 See Section 18.

20 Waste Management

20.1 There are no waste management issues involved with this method. Due to the nature of this method, the discarded samples are chemically less contaminated than when they were collected.

21 References

21.1 SW846 8021B, Revision 2, December 1996 – Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoioniziation and/or Electrolytic Conductivity Detectors

21.2 SW846 8000B, Revision 2, December 1996 – Determinative Chromatographic Separations

21.3 Chapter Four, Revision 3, December 1996 – Organic Analytes

GC016_05

Philip Analytical Services

Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors

In-Service Date: April 23, 2001

I certify that I have read, understood, and will abide by the procedures set forth in this Policy.

Laboratory Personnel Responsible for Implementation of this Policy include:

Signature/Date

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