EPA/600/R-96/036
November 1996

Guidance for Total Organics

Draft Final Report

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Contract Number 68-D4-0022
Work Assignment No. 08

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The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under EPA Contract 68-D4-0022 to Radian Corporation. It has been subjected to Agency review and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Abstract

This document provides guidance to those wishing to determine the total organics content of source samples. The preparation of air quality permit applications for waste combustion units require total organics data. This document identifies specific techniques to determine the total organics sampled from stationary sources. It describes the measurement of total organics from stack emissions and related field sampling efforts, combining the organics from three specific boiling point/vapor pressure classes: light hydrocarbons and volatile organics (boiling points $< 100°C$), semivolatile organics (boiling points 100°C to 300°C), and non-volatile organics (boiling points $> 300°C$). It describes methods for measuring and reporting the individual parameters. The document seeks to avoid the confusion about organics measurement and eliminate the misleading and non-descriptive titles often given to different facets of organics analysis. It also provides information about combining the component parts of the organics analysis results into a helpful description of the data. Knowing the amount of previously uncharacterized organic material enables more accurate risk assessment estimates to be made. Discussions of the specific methods and operating procedures are found in the appendices and references.

Contents

Appendices

Contents, Continued

List of Tables

List of Figures

Acknowledgments

This document was prepared for the US Environmental Protection Agency's National Exposure Research Laboratory (NERL) located in the Research Triangle Park, NC. The authors wish to thank those people who have made this work possible: Joan T. Bursey and Raymond G. Merrill of Radian Corporation, and Larry D. Johnson of EPA.

Acronyms and Abbreviations

AEERL - Air and Energy Engineering Research Laboratory, RTP

CH_4 - Methane

C_7 - Heptane

C_{17} - Heptadecane

Draft Method 0040 - "Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags"

Draft Method 3542 - "Extraction of Semivolatile Analytes Collected Using Modified Method 5 (Method 0010) Train"

EPA - Environmental Protection Agency

FID - Flame ionization detector

Field GC - Field gas chromatography, light organics collected in Tedlar® bags and analyzed in the field by GC/FID

GC - Gas chromatograph

GRAV - Gravimetric mass, nonvolatile organics with boiling point > 300°C

heptadecane - Straight chain hydrocarbon, saturated, 17 carbon atoms

heptane - Straight chain hydrocarbon, saturated, 7 carbon atoms

Level 1 - IERL (AEERL) Procedures Manual: Level 1 Environmental Assessment

m - Meter

Method 0010 - "SW-846, Method 0010, Modified Method 5 Sampling Train"

Method 8270 - "SW-846, Method 8270, Gas Chromatography/Mass Spectrometry for Semivolatile Organics: Capillary Column Technique"

Acronyms and Abbreviations, Continued

mL - Milliliter

μg - Microgram

μL - Microliter

m^3 - Cubic meter

MS - Mass spectrometry

NERL - National Exposure Research Laboratory

purge and trap - Analytical technique where the water sample is introduced to the instrument by gas purging, trapping of the gas, and desorption from the trap

QC - Quality control

RCRA - Resource Conservation and Recovery Act

Recoverable organics - Those organic compounds capable of being collected in a specific sampling train (Method 0010, Draft Method 0040) and subsequently analyzed

RTP - Research Triangle Park, North Carolina

semivolatile - Compound class between the volatile and non volatile compounds, generally defined by boiling point between 100°C and 300°C

SW-846 - Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846 Manual, 3rd Edition

Tedlar® - Trade name for sampling bag material used in direct collection of air samples

total organics - Combination of Field GC, TCO, and GRAV mass

TCO - Total chromatographable organics

volatiles - Volatile organic compounds with boiling points < 100°C

Section 1

Introduction/Background

The characterization of stationary source emissions requires screening and analysis procedures that identify components of several compound classes. The need to characterize emissions containing multiple organic compounds continues to increase. Revisions to the guidance for conducting risk assessments at Resource Conservation and Recovery Act (RCRA) hazardous waste combustion units have recently included the requirement that total organic carbon analysis be conducted.[1,2] The uncharacterized organic portion of organic emissions that have not been specifically identified and quantified by other methods must be measured. By knowing the amounts of previously uncharacterized organic material, more accurate risk assessment estimates can be made. The preparation of air quality permit applications for waste combustion units require total organics data.

This document describes the measurement of total organics from stack emissions and related field sampling efforts, combining the organics from three specific boiling point/vapor pressure classes: light hydrocarbons and volatile organics (bp $< 100°C$), semivolatile organics (bp 100°C-300°C), and nonvolatile organic compounds (bp $> 300°C$). The total organics measurements are not merely a mass measurement of carbon, soot, or particulate content alone. The combination of the three fractions and techniques gives the analyst specific identified organic compound classes and provides the means to analyze the components of each boiling point class.

Field gas chromatography (Field GC) with flame ionization detection (FID) of an integrated Tedlar® bag sample is recommended for organics of boiling points less than 100°C. Total chromatographable organic (TCO) analysis is recommended for compounds boiling between 100°C and 300°C. Finally, gravimetric (GRAV) techniques are appropriate for

compounds boiling at 300°C or higher. The summary of these three techniques is shown in Figure 1.

A combination of two sampling and four analytical techniques described in this document gives the investigator the approximate mass of all identified and unidentified "recoverable" organic material. The mass of organic material that remains after correction for the identified organic compounds found using RCRA SW-846 methods is the residual organic carbon and this quantity is used to estimate risk from unidentified organic emissions. A description of the measurement techniques is found in the following pages. Detailed discussions of methods and operating procedures are found in the references and appendices of this document.

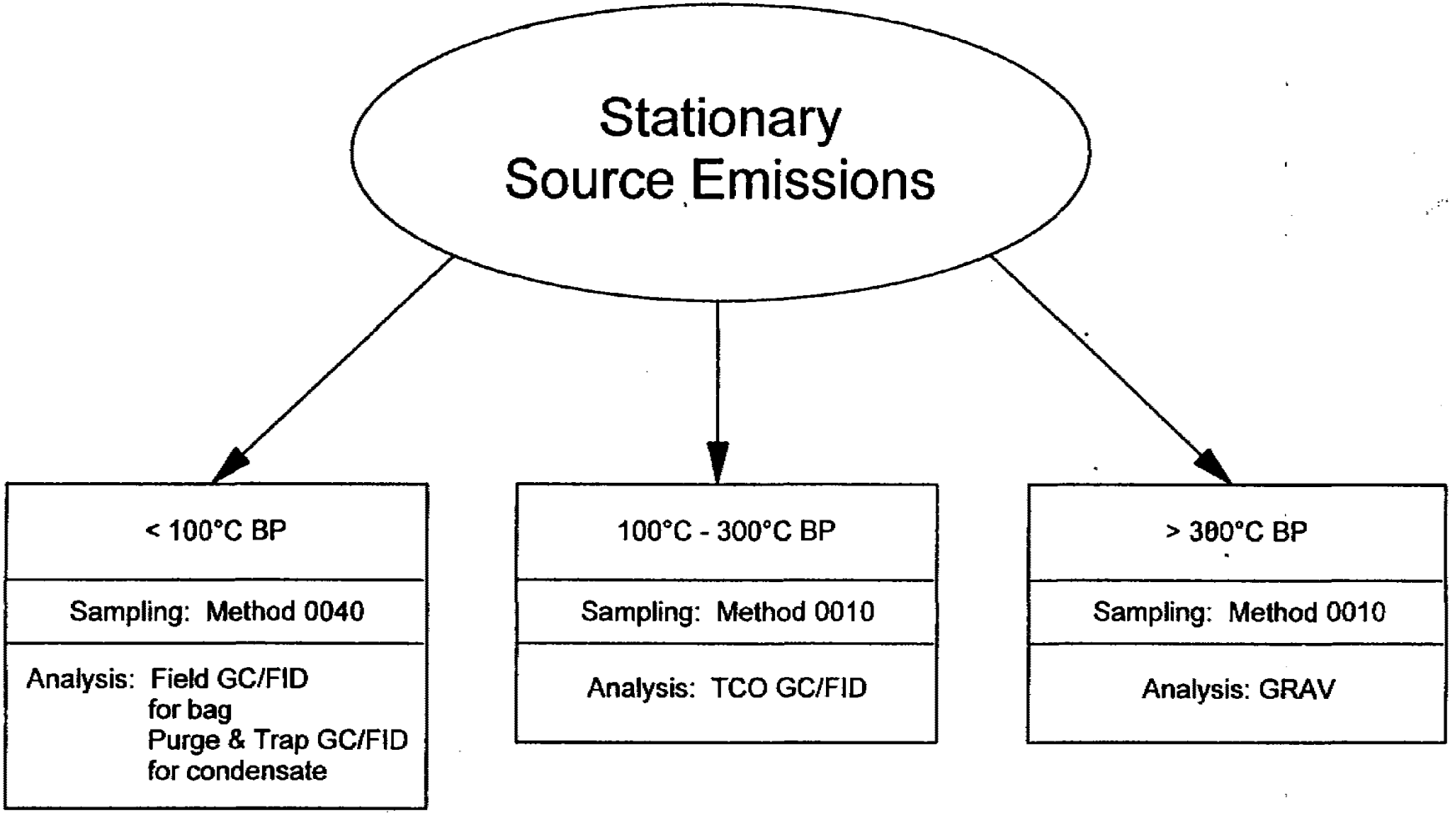


Figure 1. Stationary Source Emissions

Section 2

Method for Total Organics Measurement

The method for total organics measurement incorporates three distinct sets of analyses, described in the following sections:

- First, the volatile organics are collected and measured by a technique known as Field GC using bag sampling according to Draft Method 0040. Emphasis is made on the identification of methane, because methane may appear in significant quantities in stack sampling efforts and correct identification may be vital to subsequent analysis of risk assessment of the stationary source. In addition, the volatile organics collected in the condensate trap of Draft Method 0040 are analyzed by Purge and Trap GC/FID.

- Second, the semivolatile organic compounds are collected using Method 0010 and the dichloromethane extracts of the pooled components of the sampling train are determined by TCO GC/FID. The marker compounds are n-heptane (C_7) and n-heptadecane (C_{17}) because their boiling points are 98°C and 302°C, respectively.

- Finally, the non-volatile organics are determined by a gravimetric procedure known as GRAV from the same pooled dichloromethane extract of the Method 0010 train components as the semivolatile organic compounds.

The data from these four analytical determinations are collected and added to obtain a total organics value for the sample of choice, as shown in Table 1. The total value is then comparable from site to site or application to application, and the end-user or researcher can more easily compare total organics data from various sources.

This identification of known vs. unidentified organics is of benefit in subsequent risk assessment calculations.

Table 1. Total Organics Components

Component	Method		Units	Boiling Point Range	Vapor Pressure
	Sampling	Analysis			
Field GC, volatile organics	0040	GC/FID and Purge & Trap GC/FID	$\mu g/m^3$	< 100°C	> 40 mm at 22.3°C (> heptane)
TCO, semivolatile organics	0010	GC/FID	$\mu g/m^3$	100° C < BP < 300°C	1 mm Hg at 115°C > VP > 40 mm at 22.3°C
GRAV, non-volatile organics	0010	gravimetric	$\mu g/m^3$	> 300°C	< 1 mm Hg at 115°C (< heptadecane)
Total Organics = (Field GC + Purge and trap GC) + TCO + GRAV in units of $\mu g/m^3$					

Section 3

Field Gas Chromatography (Field GC) Method and Purge and Trap GC Method

The field GC portion of total organics is determined by field analysis of a bag sample by GC with a flame ionization detector (FID). This procedure is described in this document as Appendix A (SW-846 Method 8240 & 18) and in Appendix E (EPA Draft Method 0040). The identified range of organics for field GC is defined by boiling point range, in this case $< 100°$ C. The analysis procedures are normally performed in the field to minimize sample (compound) loss due to storage and shipping. Additionally, the condensate collected as a part of the Method 0040 sampling train is analyzed for low boiling organics by purge and trap GC/FID. The condensate fraction is normally transferred to a vial with no headspace and shipped to the laboratory for analysis.

Bag Sampling/Analysis

Compounds with boiling points below 100°C are sampled into Tedlar® bags and on site gas chromatographic analysis of the collected sample is preformed. The range of applicable compounds is very large: methane has a boiling point of -160°C, and hexane boils at 69°C. The reporting range for the methodology extends to 100°C. If a packed column is used to perform all of the gas chromatographic analysis, a very judicious selection of phase and analytical conditions must be made in order to achieve chromatographic resolution for methane at the same time as the total analysis time is limited to no more than 15-20 minutes. Some investigators prefer the use of two gas chromatographs, one with an appropriate column and conditions for C_1 - C_4 and the second with an appropriate column and conditions for the C_4 - C_6 range. A capillary column is needed to perform the analysis over the entire volatility range

with adequate resolution. A capillary column with a length of 60 m may be required to provide adequate resolution for the C_2-hydrocarbon isomers. The gas chromatographic analysis will primarily be separating compounds on the basis of boiling points, but in some cases the separation will be influenced by the polarity of the compounds. Numerous chromatographic conditions such as column temperature, ramp for temperature programming, duration of an isothermal hold, and temperature of any transfer line will all have to be optimized for the best chromatographic results. A flame ionization detector is needed to perform the analysis.

The gas chromatograph must be calibrated for quantitative analysis with a normal hydrocarbon curve. The curve is prepared using certified cylinders containing the n-alkanes from C_1 through C_6. A multipoint calibration of at least three points (in duplicate) is required. Calibration for methane (CH_4) must be performed carefully so that the quantity of methane can be determined accurately. Methane is often found in significant quantities when incinerator stacks are sampled, and it is essential to be able to identify the compound correctly and provide an accurate quantitative measurement when calculations of risk or regulatory significance are being performed. The certified C_1 - C_6 standard gas mixture is used to calibrate the field gas chromatograph and a point approximately in the middle of the calibration range should be analyzed at least once per day as a calibration check. The multipoint calibration is achieved either through the use of multiple cylinders at different concentrations or by the use of sample loops of varying sizes.

After full calibration, sample analysis is initiated when the sample container (the Tedlar® bag) is connected to the sampling valve and the sample gas is drawn through the valve and sample loop. When the valve is sufficiently purged, the valve is actuated and the contents of the loop are injected into the chromatograph. Simultaneously with the injection of the sample, the temperature programmer and integrator/data system data acquisition are started. Chromatograms and integrator/data system output are collected. Retention times and responses must agree to within 5 percent relative standard deviation with the calibration curve. Uniform FID response for varying compound classes is assumed in this methodology. The resulting quantitative results therefore tend to be biased low for compounds which are not

n-alkanes. In many, if not most, cases the species present are not identical to those used for calibration of the on-site chromatograph; an exact correspondence between standard peaks and the peaks observed in the sample chromatogram will not be achieved.

Purge and Trap Sampling/Analysis

Compounds with boiling points below 100°C are sampled by Draft Method 0040 and some of the compounds are collected in the condenser component of the sampling train. This condensate requires purge and trap gas chromatographic analysis of the collected water sample. The operating procedures for this methodology is included in this document as Appendix B. A gas chromatograph with an appropriate column and conditions for the C_5 - C_7 range is required. A capillary column with a length of 60 m may be needed to provide adequate resolution for smaller organic and hydrocarbon isomers. A flame ionization detector is needed to perform this analysis.

The purge and trap GC must be calibrated for quantitative analysis with a normal hydrocarbon curve. The curve is prepared using liquid alkane standards containing the n-alkanes from C_5 through C_7. A multipoint calibration of at least three points (in duplicate) is needed. The alkane mixture is used to calibrate the GC and a point approximately in the middle of the calibration range should be analyzed at least once per day as a calibration check. The multipoint calibration is achieved through the use of serial dilutions of the primary stock standard mixture in methanol solution.

After full calibration, sample analysis is initiated when an aliquot of the water sample in the volatile organic analysis (VOA) vial is transferred to the purge flask. An inert gas is bubbled through the aliquot and volatile components of the aliquot are transferred from the aqueous phase to the vapor phase and swept to the sorbent trap (VOCOL®, VOCARB®, or equivalent). When the sample is thoroughly purged from the vessel into the trap, the valve is actuated and the trap contents are desorbed by rapid heating onto the head of the GC column with the FID detector. The temperature programmer and integrator/data system data acquisition are started. Chromatograms and integrator/data system output are collected.

Uniform FID response for varying compound classes is assumed in this methodology. The lower boiling organic compounds are not expected to be found in the condensate solutions collected in a Draft Method 0040 sampling train. If compounds are found with retention times prior to the C_4 retention time, an appropriate response factor will be used to determine the concentration of those components and their values are reported as C_4 with the other organic results.

Section 4

Source Sampling and Sample Extract Preparation for TCO and GRAV

In order to obtain the sample required for TCO and GRAV analysis, the field sample must be collected in the appropriate manner. The sample is collected using the Semivolatile Organic Sampling Train, Method 0010, included in this document as Appendix F. This sampling method, also known as the Modified Method 5 Sampling Train, generates a set of sampling train components which must be carefully handled in order to preserve the compounds of interest.

The sampling train is disassembled and "broken-down" according to the specifications of Draft Method 3542, "Extraction of Semivolatile Analytes Collected Using Modified Method 5 (Method 0010) Train (Appendix G). There are, however, several exceptions to the method as written which must be observed in order to obtain valid data for total organics determinations. They are listed below:

- The component parts of the sampling train are normally collected in three parts: 1) particulate matter filter and front half rinse, 2) condensate and condensate rinse, and 3) XAD-2® and back half rinse. These components are combined into a single pooled extract for the purposes of total organics measurements. As in Method 3542, the three parts may be taken to final volumes of 5 mL each, but the three extracts are then combined and taken to a final pooled volume of no less than 5 mL. **Note**: At no time should any of the extracts (parts or pooled) be reduced to volumes less than 3 mL, or loss of semivolatile compounds may occur.

- Since the extracts for total organics determinations are analyzed by GC/FID and gravimetric techniques, none of the surrogates, isotopically-labeled standards, or internal standards associated with GC/MS analysis (Method 8270) should be added to the extractors or sample extracts. After the sampling train is disassembled, the components are rinsed and extracted normally, but without

the addition of surrogate compounds.

- The final pooled extract sample volume is recorded and an aliquot is used for the TCO GC/FID, while a duplicate aliquot is used in the GRAV measurements.

Section 5

Total Chromatographic Organic (TCO) Method

The TCO Method has been described in detail in the Level 1 Procedures Manual[3] and revised as an interim EPA/AEERL operating procedure (Appendix C). The identified range of organic compounds is defined by boiling point range, in this case 100-300°C. Compounds with boiling points between 100°C and 300°C are analyzed by GC with an FID detector after collection using a Method 0010 sampling train. The TCO procedure is carried out by analysis of a dichloromethane extract (a combination of the extracts from the three major components of the sampling train). The analysis is generally performed in the laboratory after extraction and compositing of the extracts of the individual components of the Method 0010 sampling train.

TCO Method

The TCO Method, in its current form, is a capillary GC/FID method quantifying chromatographable material in the 100°C to 300°C boiling point range. An aliquot of the Method 0010 dichloromethane extract is injected onto a capillary GC column with an FID detector, and the peak areas are summed over the retention time window that encompasses the TCO boiling point range. The entire analysis window is established by injecting C_7 and C_{17} as the reference peaks between which the TCO integration will occur.

Analysis may be performed using a capillary (preferred) or packed column GC. A non-polar or slightly polar column is used to provide adequate resolution and analysis in a total run time of approximately 45 minutes. A 15 to 30 m non-polar wide bore column (0.32 mm) has been found to be effective for TCO analysis. As a capillary or packed column procedure,

the GC/FID is operated in a manner consistent with the manufacturer's recommendations for gas flow, temperature zones, and injection volume. Analysis is performed most easily using a GC with a liquid autosampler, so that calibrations and sample injections can be performed in a consistent and automated fashion. The TCO value is determined from a calibration standard curve, generated with hydrocarbon standards which fall within the TCO range, specifically decane, dodecane, and tetradecane. An integrator or GC data system is used to record the data points as they are obtained from the injections of calibration standards and samples. The organics identified in the prescribed boiling point range are quantified and summed (totalled) to obtain the TCO portion of the total organics number. Reporting units are generally in terms of μg per sample, which is then converted to $\mu g/m^3$, based on the sampling volume. The GC used for TCO analysis is calibrated using dilutions of a specific hydrocarbon stock solution. A multipoint calibration of at least three different concentrations in duplicate is required for this procedure. After calibration has been performed, a daily quality control (QC) check sample is run to verify that the GC is performing correctly. The QC check sample is run with a standard in the middle of the working range of the GC calibration standards.

While it is understood that the compounds in this volatility and boiling point range might include compounds that are not hydrocarbons, the FID detector is seen as a good all-purpose detector for the quantification of the sample extracts.

Section 6

Gravimetric (GRAV) Method

The third component of the total organics measurement process is called gravimetric mass (GRAV). The GRAV Method has also been described in detail in the Level 1 Procedures Manual[3] and also revised as an interim EPA/AEERL operating procedure (Appendix D). The GRAV procedure is carried out by analysis of an aliquot of the same dichloromethane extract from the Method 0010 sampling train as was used for TCO determinations.

GRAV Method

The GRAV Method, in its current form, quantifies nonvolatile organic material with a boiling point greater than 300°C. A carefully measured aliquot of the Method 0010 dichloromethane extract is placed in a precleaned and preweighted aluminum weighing pan and allowed to dry in air at room temperature, then come to complete dryness in a room temperature desiccator, while exposure to dust and contaminants are minimized. The residue in the pan is weighed accurately, and the mass is recorded to determine the GRAV value. For this procedure, the three individual dichloromethane extracts from Method 0010 are pooled and reduced to a final volume of 5.0 mL. A volume of 1 mL of the pooled extract is used for the GRAV determinations, which are performed in duplicate. Other final extract and GRAV aliquot volumes may be used, but the sample extraction and concentration procedures of Method 3542 (Appendix G) should be followed closely to avoid loss of more volatile organics. The GRAV organics in the greater than 300°C range are measured on an analytical balance and recorded for the GRAV portion of the total organics number. This value, in μg, is converted to units of μg per sample, which is then divided by sample volume to obtain $\mu g/m^3$.

This sum is added to the previously determined TCO and field GC values to find the total organics value, in units of micrograms per m^3.

Section 7

References

1. Revised Draft of Risk Assessment Implementation Guidance for Hazardous Waste Combustion Facilities. Memorandum from Michael H. Shapiro, Office of Solid Waste. U. S. Environmental Protection Agency, May 5, 1994.

2. Johnson, Larry D., M. Rodney Midgett, Ruby H. James, Michael M. Thomason, and M. Lisa Manier. Screening Approach for Principal Organic Hazardous Constituents and Products of Incomplete Combustion. Journal of Air & Waste Management Association. Vol. 39, No. 5, May 1989.

3. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition). U.S. Environmental Protection Agency. EPA-600/7-78-201. October 1978.

Appendix A

Recommended Operating Procedure for Field Gas Chromatography

(From SW-846, Method 8240 and Method 18 - 40 CFR Part 60, Appendix A)

Disclaimer

This recommended operating procedure has been prepared for the sole use of the National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

Acknowledgements

Assisting in the preparation of this procedure, dated 4/95 as Work Assignment No. 8 were Joan T. Bursey and Robert Martz, Radian Corporation, Research Triangle Park, NC, under EPA contract 68-D4-0022. Merrill Jackson is the Project Officer for the EPA contract with Radian Corporation.

RECOMMENDED OPERATING PROCEDURE FOR FIELD GAS CHROMATOGRAPHY

A.1.0 INTRODUCTION

Field analyses are performed for samples that are subject to significant degradation if analysis is delayed even for the amount of time required to ship samples to a laboratory, or in situations where performing analysis in the field is preferable to handling and shipping samples such as Tedlar® bags. In determining Total Organics, field gas chromatography is performed to determine compounds in the C_1 - C_7 hydrocarbon range. This range encompasses alkanes, alkenes, cyclic compounds, and functionalized organic compounds. For example, methane, chloromethane, formaldehyde, and methanol are all C_1 compounds. The methodology is applicable to C_1 - C_7 hydrocarbons, organic compounds boiling in the range -160°C to 100°C. When performing field gas chromatographic analysis, species eluting in the specified boiling point range are quantified as n-alkanes. The sensitivity of the flame ionization detector varies from compound to compound, but n-alkanes as a class have a higher flame ionization response than other classes of compounds such as oxygenated or halogenated hydrocarbons. Therefore, using n-alkanes as calibrants and assuming equivalent responses for all other compounds in the appropriate boiling point range tends to bias results low. That is, if an alkane standard and a non-alkane peak have equivalent system responses, the non-alkane peak is assigned a quantitative value equivalent to the alkane. The non-alkane peak, however, has a poorer response to the flame ionization detector than the alkane. The amount of non-alkane required to produce the same response as an alkane may be several times higher than the amount of alkane, so the reported value shows a low bias.

A.2.0 SCOPE AND APPLICATION

This procedure defines the field gas chromatographic analysis of gaseous stationary source emissions sampled into a Tedlar® bag for C_1 - C_7 hydrocarbons, a

chromatographic elution range defining organic compounds boiling in the range of -160°C to 100°C.

A.3.0 SUMMARY OF METHOD

A gas sample contained in a Tedlar® bag is analyzed in the field by gas chromatography/flame ionization detection (GC/FID). The instrument is set up in the field with column and conditions appropriate for the analysis of C_1 - C_7 n-alkanes. Retention times are determined and calibration is performed with a certified gaseous standard of C_1 - C_7 alkanes in air or nitrogen. Compounds of interest are identified by retention times or retention time ranges and quantitative analysis is performed.

A.4.0 SAMPLE HANDLING AND PRESERVATION

Samples for this analysis are contained in Tedlar® bags. These samples should be analyzed as soon after acquisition as possible, preferably within two hours. Exposure to extremes of light and temperature should be avoided.

A.5.0 APPARATUS AND REAGENTS

A.5.1 Gas Chromatograph

The gas chromatograph to be used for this analysis must be capable of being moved into the field, with a flame ionization detector, temperature-controlled sample loops of varying sizes with a valve assembly, temperature-programmable oven, and an appropriate chromatographic column to obtain the resolution desired for the analysis.

A.5.2 Recorder/Integrator/Data System

A recorder is required. Appropriate parameters are 1 inch/min chart speed, 1 mV full scale, 1 sec full scale response time. An integrator is required. The function of

both the recorder and integrator may be superseded by a data system, if available. Parameters which should be specified and recorded in the instrument log include noise suppression, up-slope sensitivity, down-slope sensitivity, baseline reset delay, area threshold, front shoulder control, rear shoulder control, and data sampling frequency.

A.5.3 Columns

For the C_1 -C_4 hydrocarbons, a packed stainless steel SP-1000® column (6 ft x 1/8 inch outer diameter), or equivalent which can be calibrated over the specified hydrocarbon range is required. Some possible equivalent columns include PLOT® or TCEP® columns. If a PLOT column is used, this column could be used for the C_5 to C_7 hydrocarbon range as well. An alternative is to use a second gas chromatograph with a generic nonpolar packed or capillary column for the C_5 to C_7 range and a flame ionization detector.

A.5.4 Gas Standard

A certified n-alkane gas standard of C_1 - C_7 n-alkanes in air or nitrogen is required. The concentrations of the alkanes in the certified standard may range from 5 - 100 ppm. A multipoint calibration curve at different concentrations may be obtained by using sample loops of different sizes or multiple gas cylinders at different concentrations.

A.5.5 Cylinder Gases

Helium carrier gas, hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column is required. Fuel (hydrogen), as recommended by the manufacturer for operation of the flame ionization detector, and zero air, hydrocarbon free air for operation of the flame ionization detector, are required.

A.5.6 Regulators

Appropriate regulators are required for all gas cylinders for both support gases and for certified gaseous standards.

A.5.7 Teflon® Tubing

Diameter and length determined by requirements for connection of gas cylinder regulators and the gas chromatograph.

A.6.0 GAS CHROMATOGRAPH SETUP AND CHECK

The gas chromatograph must be completely calibrated at each new test site in the field. Whenever the gas chromatograph is set up, the following parameters must be verified for correct operation:

1) All support gas supplies must be at the proper pressure.

2) Verify that the carrier gas flow to the analytical column is correct (for a packed column, the gas flow rate should be 30 ± 2 mL/min; for a capillary column, flow rate will depend upon the column diameter and should be adjusted according to the manufacturer's specifications for the column). Flow rate is checked at the analytical column outlet after disconnection from the detector. The instrument must be at ambient temperature.

3) Verify that the hydrogen flow is appropriate for the operation of the flame ionization detector. The flow rate is checked at the control panel on the gas chromatograph.

4) Verify that the air flow is appropriate for the operation of the flame ionization detector. The air flow rate is checked at the gas control panel on the gas chromatograph.

5) Verify that the electrometer is functioning properly. The electrometer must be balanced and the bucking controls set as required.

6) Verify that recorder/integrator/data system are functioning properly.

A.7.0 CALIBRATION

To determine the temperature ranges for reporting the results of GC analyses for the C_1 - C_7 compounds, the gas chromatograph is given a normal boiling point - retention time calibration. The n-alkanes, their boiling points, and the data reporting ranges are shown below.

Compound	Boiling Point, °C	Reporting Range, °C	Report As
methane	-161	-160 to -100	C_1
ethane	-88	-100 to -50	C_2
propane	-42	-50 to 0	C_3
butane	0	0 to 30	C_4
pentane	36	30 to 60	C_5
hexane	69	60 to 90	C_6
heptane	98	90 to 98	C_7

To perform a multipoint calibration, connect the C_1 - C_7 certified standard gas cylinder to the sampling valve, and allow the gas to flow through the valve at a constant, low, and reproducible flow rate of 20 mL/min measured at the sample valve outlet using a bubble flowmeter. When the sample valve has purged (approximately 5 min), allow the sample loop pressure to equilibrate to atmospheric pressure and actuate the valve and inject the contents of the sample loop into the gas chromatograph. Simultaneously, start the integrator and/or data system and the temperature programmer, if used. Obtain chromatograms and integrator/data system output. Retention times and responses shall agree to within 5% relative standard deviation. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their mean value. The average value multiplied by the attenuation factor is then the calibration area value for the concentration.

The multipoint calibration must encompass at least three concentration levels, with each point analyzed at least in duplicate (a minimum of six calibration data points for each n-alkane). The different concentrations are achieved either by analysis of standards from cylinders at three different concentrations or by use of sample loops of different sizes with one certified gaseous standard. Prepare a plot of the concentration versus the calibration area values, perform a regression analysis, and draw the least squares line.

A.8.0 DAILY CALIBRATION CHECK

The C_1 - C_7 certified standard gas mixture will be injected and analyzed at the start of each day, at a concentration at approximately the midpoint of the calibration curve. Retention times and responses for each component should agree with the initial calibration data to within ± 10 percent. If the daily calibration check meets this specification, the full calibration need not be repeated.

A.9.0 ANALYSIS OF SAMPLES

If any doubt exists concerning the relationship between the stationary source sample GC peaks and the GC peaks obtained from calibration, a small amount of the calibration gas should be spiked with the sample in order to verify retention times.

To perform the analysis of gaseous samples, the chromatograph, recorder, integrator/data system must be set up according to the manufacturer's manuals and calibrated. Operating parameters should be confirmed. The operating parameters are to be listed on each chromatogram, and each recorder chart should be labeled. The sample bag should be connected to the gas sample valve, the sample loop purged with the sample, and the contents of the loop should be injected. The integrator/data system and recorder should be started simultaneously with injection.

If any doubt exists concerning the relationship between the stationary source sample GC peaks and the peaks obtained from analysis of the calibration standard, a small aliquot of the calibration gas should be spiked with the sample in order to verify retention times.

A.10.0 CALCULATIONS FOR C_1 - C_7 HYDROCARBONS

The calibration curve for the n-alkanes is constructed in the following manner:

1) For each alkane, the average retention time and relative standard deviation are calculated.

2) Plot boiling point of each alkane versus the average retention times (in seconds).

3) Draw the curve, manually or by computer.

4) On the curve, locate and record the retention times corresponding to the reporting ranges: -160°C to -100°C, -100°C to -50°C, -50°C to 0°C, 0°C - 30°C, 30°C to 60°C, 60°C to 90°C, and 90°C to 98°C.

5) Calculate average area response and relative standard deviations for the propane calibration standard.

6) Plot response (μV/sec) as ordinate versus concentration of the standard in mg/m^3 injected as abscissa. Draw in the curve. Perform least squares linear regression and obtain the slope ($\mu V/sec * m^3/mg$).

7) In each retention time range of the sample, sum up the peak areas.

8) Convert peak areas (μV / sec) to mg/m^3 by dividing by the proper response (slope factor).

9) Record the total concentration of material in each retention time range.

Appendix B

Recommended Operating Procedure for Purge and Trap Gas Chromatography With FID Detection

(From SW-846 Method 8240 and Draft Method 0040)

Disclaimer

This recommended operating procedure has been prepared for the sole use of the National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

Acknowledgements

Assisting in the preparation of this procedure, dated 4/95 as Work Assignment No. 8 were Joan T. Bursey and Robert Martz, Radian Corporation, Research Triangle Park, NC, under EPA contract 68-D4-0022. Merrill Jackson is the Project Officer for the EPA contract with Radian Corporation.

RECOMMENDED OPERATING PROCEDURE FOR PURGE AND TRAP GAS CHROMATOGRAPHY WITH FID DETECTION

B.1.0 INTRODUCTION

As a complement to the Field Gas Chromatography analysis of total organics, the condenser component of the Draft Method 0040 sampling train is analyzed using purge and trap techniques and an FID detector. In determining total organics, purge and trap gas chromatography is performed to determine compounds in the C_1 - C_7 hydrocarbon range. This range encompasses alkanes, alkenes, cyclic compounds, and functionalized organic compounds. For example, methane, chloromethane, formaldehyde, and methanol are all C_1 compounds. The methodology is applicable to C_1 - C_7 hydrocarbons, organic compounds boiling in the range -160°C to 100°C. In performing purge and trap gas chromatographic analysis, species eluting in the specified boiling point range are quantified as n-alkanes. The sensitivity of the flame ionization detector varies from compound to compound, but n-alkanes as a class have a higher flame ionization response than other classes of compounds such as oxygenated or halogenated hydrocarbons.

B.2.0 SCOPE AND APPLICATION

The field gas chromatographic analysis encompasses gaseous stationary source emissions sampled into a Tedlar® bag in the sampling train. Analysis is performed for the organic compounds boiling in the range of -160°C to 100°C. In Draft Method 0040, the condenser, the condensate trap and the sample line from trap to the Tedlar® bag are carefully rinsed and the combined water sample is transferred to a graduated cylinder. After carefully measuring the sample volume, the water sample is transferred to a 20 mL or 40 mL amber glass VOA vial with a Teflon® septum screw cap with zero void volume. VOA vials under zero headspace conditions may be stored on ice or in a refrigerated container until analysis. This procedure defines the gas chromatographic analysis of gaseous stationary source emissions sampled into the condensate component of a Draft Method 0040 train.

B.3.0 SUMMARY OF METHOD

The volatile compounds are introduced into the gas chromatograph (GC) by the purge and trap method. The components are separated via the GC and detected using a flame ionization detector (FID), which is used to provide quantitative information.

An inert gas is bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. The sorbent columns of choice are a VOCOL® or VOCARB 3000® design, or equivalent. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a GC column. The GC column is heated via a temperature program to elute the components, which are detected with an FID detector.

A volatile organic sample contained in a VOA vial is analyzed in the laboratory by gas chromatography/flame ionization detection (GC/FID). The instrument is set up with column and conditions appropriate for the analysis of C_4 - C_7 n-alkanes. Retention times are determined and calibration is performed with a liquid standard of C_5 - C_7 alkanes. Compounds of interest are identified by retention times or retention time ranges and quantitative analysis is performed.

B.4.0 SAMPLE HANDLING AND PRESERVATION

Samples for this analysis are transferred from the condenser vessel to VOA vials. These samples should be analyzed as soon after acquisition as possible, preferably within two weeks of collection. Samples are refrigerated without headspace in the vials until analysis. Exposure to extremes of light and temperature should be avoided.

B.5.0 APPARATUS AND REAGENTS

Apparatus and reagents needed to perform the purge and trap analysis techniques are summarized in the following paragraphs. Glassware, vials, laboratory refrigerators, compressed gas storage, and items customarily found in an analytical laboratory are assumed to be readily available.

B.5.1 Purge and trap device

The purge and trap device consists of three major components: a purge chamber for the water, a trap, and a desorber capable of rapidly heating the trap. The purge chamber should be designed to accept 5 mL samples of water with a water column of at least 3 cm. The purge gas must pass through the water column as finely divided bubbles, normally obtained by passing the gas through a medium porosity glass frit. The packing material for the trap should be a commercially available sorbent material (or combination of materials) capable of trapping and releasing low boiling (volatile) organic compounds. VOCOL® or VOCARB 3000® (Carbopack B and Carboxen® in series) sorbent packing materials, or an equivalent sorbent, are acceptable for the traps, providing they adequately trap and desorb the organic components of interest. The desorber should be capable of rapidly heating the trap to a temperature of at least 180°C for desorption.

B.5.2 Reagent water

Reagent water for this analysis is defined as water in which interferents are not observed at the method detection limit (MDL) of the parameters of interest. Purified water (carbon filtration or deionized distilled water) may be used. Alternatively, water may be boiled and subjected to a bubbled stream of inert gas, then sealed until used.

B.5.3 **Gas Chromatograph Setup**

For the C_1 -C_4 hydrocarbons, a packed stainless steel SP-1000® column (6 ft x 1/8 inch outer diameter), or equivalent which can be calibrated over the specified boiling point range is required. Some possible equivalent columns include PLOT® or TCEP® columns. If a PLOT column is used, this column could be used for the C_5 to C_7 hydrocarbon range as well. An alternative is to use a second gas chromatograph with a generic nonpolar packed or capillary column for the C_5 to C_7 range and a flame ionization detector.

The gas chromatograph must be completely calibrated for use. Whenever the gas chromatograph is set up, the following parameters must be verified for correct operation:

1) All support gas supplies must be at the proper pressure.

2) Verify that the carrier gas flow to the analytical column is correct (for a packed column, the gas flow rate should be 30 ± 2 mL/min; for a capillary column, flow rate will depend upon the column diameter and should be adjusted according to the manufacturer's specifications for the column). Flow rate is checked at the analytical column outlet after disconnection from the detector. The instrument must be at ambient temperature.

3) Verify that the hydrogen flow is appropriate for the operation of the flame ionization detector. The flow rate is checked at the control panel on the gas chromatograph.

4) Verify that the air flow is appropriate for the operation of the flame ionization detector. The air flow rate is checked at the gas control panel on the gas chromatograph.

5) Verify that the electrometer is functioning properly. The electrometer must be balanced and the bucking controls set as required.

6) Verify that recorder/integrator/data system are functioning properly.

B.5.4 **Regulators**

Appropriate regulators are required for all gas cylinders for detector and carrier gases.

B.5.5 **Liquid Standard**

A set of n-alkane liquid standards of C_5 - C_7 n-alkanes is required. The concentrations of the alkanes in the standard may range over several orders of magnitude within the working range of the GC/FID. A multipoint calibration curve at different concentrations may be obtained by using multiple dilutions of a stock standard solution.

Calibration standards should be prepared from secondary dilution of stock standards. The solutions should be prepared in methanol, with one of the concentrations at a level near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples (not exceeding the working range of the GC/FID system). Each standard should contain the straight chain hydrocarbons C_5 to C_7. The lower boiling organic compounds (C_1 to C_3) are not expected to be found in the condensate solutions collected in a Draft Method 0040 sampling train. If compounds are found with retention times prior to the C_4 retention time, an appropriate response factor will be used to determine the concentration of those components and their value reported as C_4 (butane) with the other organic results.

B.5.6 **Cylinder Gases**

Helium carrier gas, hydrocarbon free, as recommended by the manufacturer for operation of the detector and compatibility with the column. Fuel (hydrogen), as recommended by the manufacturer for operation of the flame ionization detector, and zero air, hydrocarbon free air for operation of the flame ionization detector, are required.

B.5.7 Recorder/Integrator/Data System

A recorder is required. Appropriate parameters are 1 inch/min chart speed, 1 mV full scale, 1 sec full scale response time. An integrator is required. The function of both the recorder and integrator may be superseded by a data system, if available. Parameters which should be specified and recorded in the instrument log include noise suppression, up-slope sensitivity, down-slope sensitivity, baseline reset delay, area threshold, front shoulder control, rear shoulder control, and data sampling frequency.

B.6.0 CALIBRATION

To determine the temperature ranges for reporting the results of GC analyses for the C_5 - C_7 compounds, the gas chromatograph is given a normal boiling point - retention time calibration. The n-alkanes, their boiling points, and the data reporting ranges are shown below.

Compound	Boiling Point, °C	Reporting Range, °C	Report As
methane	-161	-160 to -100	C_1
ethane	-88	-100 to -50	C_2
propane	-42	-50 to 0	C_3
butane	0	0 to 30	C_4
pentane	36	30 to 60	C_5
hexane	69	60 to 90	C_6
heptane	98	90 to 100	C_7

To perform a multipoint calibration for purge and trap analysis, the most practical method is to prepare liquid standards in methanol of the C_5 through C_7 alkanes by dilution of a primary stock. A set of dilutions is prepared, covering the working range of the instrument and the solutions are spiked directly into clean reagent water in VOA vials. The purge and trap system is activated to purge the standard from the purge

vessel into the trap. After trapping is complete, the desorber is activated (heated) and simultaneously the integrator and/or data system and the temperature programmer are started. Obtain chromatograms and integrator/data system output. Retention times and responses shall agree to within 5% relative standard deviation. Repeat the standard injection until two consecutive injections give area counts within 5 percent of their mean value. The average value multiplied by the attenuation factor is then the calibration area value for the concentration.

The multipoint calibration must encompass at least three concentration levels, with each point analyzed at least in duplicate (a minimum of six calibration data points for each n-alkane). The different concentrations are achieved by analysis of standards at three different concentrations of liquid standards of the C_5 through C_7 alkanes. Prepare a plot of the concentration versus the calibration area values, perform a regression analysis, and draw the least squares line.

B.7.0 DAILY CALIBRATION CHECK

A C_5 - C_7 standard mixture will be injected (purge and trap) and analyzed at the start of each day, at a concentration at approximately the midpoint of the calibration curve. Retention times and responses for each component should agree with the initial calibration data to within ± 10 percent. If the daily calibration check meets this specification, the full calibration need not be repeated.

B.8.0 ANALYSIS OF SAMPLES

If any doubt exists concerning the relationship between the stationary source sample GC peaks and the GC peaks obtained from calibration, a small amount of the calibration standard should be spiked with the sample in order to verify retention times.

To perform the analysis of condensate water samples, the chromatograph, recorder, integrator/data system must be set up according to the manufacturer's manuals and calibrated. Operating parameters should be confirmed. The operating parameters are to be listed on each chromatogram, and each recorder chart should be labeled. The sample vial should be correctly labeled and transferred to the purge vessel. After purging and trapping, the organics are desorbed onto the head of the GC column ("injection"). The integrator/data system and recorder should be started simultaneously with injection.

B.10.0 CALCULATIONS FOR C_5 - C_7 HYDROCARBONS

The calibration curve for the n-alkanes is constructed in the following manner:

1) For the alkanes C_5 through C_7, the average retention time and relative standard deviation are calculated.

2) Plot boiling point of each alkane versus the average retention times (in seconds).

3) Draw the curve, manually or by computer.

4) On the curve, locate and record the retention times corresponding to the reporting ranges: 0°C - 30°C, 30°C to 60°C, 60°C to 90°C, and 90°C to 100°C .

5) Calculate average area response and relative standard deviations for the hexane calibration standard.

6) Plot response (μV/sec) as ordinate versus concentration of the standard in mg/m^3 injected as abscissa. Draw in the curve. Perform least squares linear regression and obtain the slope (μV/sec * m^3/mg).

7) In each retention time range of the sample, sum up the peak areas.

8) Convert peak areas (μV / sec) to mg/m^3 by dividing by the proper response (slope factor).

9) Record the total concentration of material in each retention time range.

Appendix C

Recommended Operating Procedure for Total Chromatographable Organics (TCO) Analysis

(This document was originally prepared for the EPA/AEERL Laboratory in RTP, NC and developed and reviewed by the QA Program of AEERL, under the direction of Judith S. Ford, QA Manager of EPA/AEERL)

Disclaimer

This recommended operating procedure has been prepared for the sole use of the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

Acknowledgements

Assisting in the preparation of this procedure, dated 10/88 as Document No. AEERL/13, were Robert F. Martz, Acurex Corporation, Research Triangle Park, NC, under EPA Contract 68-02-4701 for on-site technical support to AEERL; and Joseph D. Evans and Anne E. Worth, Research Triangle Institute, Research Triangle Park, NC, under EPA Contract 68-02-4291 for Quality Assurance (QA) support to AEERL. Judith S. Ford, QA Manager for AEERL, is the Project Officer for the QA contract with Research Triangle Institute.

TABLE OF CONTENTS

LIST OF TABLES

SECTION C.1

INTRODUCTION

C.1.1 Scope

This method provides semi-quantitative data for organic compounds with boiling points between 100 and 300°C. Samples that might include organic compounds in this volatility range are organic liquids, solid sample extracts, aqueous extracts, extracts from Source Assessment Sampling System (SASS) and Modified Method 5 (MM5) train sorbent modules, and liquid chromatography (LC) fractions obtained from those samples. This method is based on separating the components of a gas or liquid mixture in a gas chromatography (GC) column and measuring the separated components with a suitable detector.

This upper end of applicability is limited by column overloading and detector saturation. Typical range is 1 to 20 mg/mL. The operating range can be extended by dilution of samples with solvent (e.g., dichloromethane). The sensitivity limit shall be determined by the minimum detectable concentration of standards.

C.1.2 Limitations

Recommended operating procedures (ROPs) describe non-routine or experimental research operations where some judgment in application may be warranted. ROPs may not be applicable to activities conducted by other research groups and should not be used in place of standard operating procedures. Use of ROPs must be accompanied by an understanding of their purpose and scope. Questions should be directed to AEERL or to project personnel listed in the Acknowledgments.

C.1.3 Definitions

- **Accuracy** - The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random and systematic error or bias components which are due to sampling and analytical operations; a data quality indicator.

- **Calibrate** - To determine, by measurement or comparison with another standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of calibration standards should bracket the range of planned measurements.

- **Calibration Standard** - A substance or reference material used to calibrate the instrument.

- **Method Blank** - A clean sample processed simultaneously with samples containing an analyte of interest through all steps of the analytical procedure.

- **Precision** - The degree of variation among individual measurements of the same property, usually obtained under similar conditions; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms.

- **Quality Control (QC) Sample** - A sample prepared from substances or materials of known composition and quantity. It is used to assess the performance of a measurement method or portions thereof. It is intended primarily for routine intralaboratory use in controlling precision and bias in the method. It should be prepared from, or be traceable to, a standard other than the calibration standard.

- **Reagent Blank** - A sample of reagent(s), without the target analyte, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine their contribution to error in the observed value.

SECTION C.2

STARTUP

C.2.1 Personnel Requirements

This ROP is written for individuals with a BS/BA degree in chemistry and at least two years experience in gas chromatography, or equivalent.

C.2.2 Facilities Requirements

This procedure requires a standard analytical chemistry laboratory with counter space, secured areas for compressed gas storage, and electricity to operate the equipment. Flasks, beakers, tubing, etc., customarily found in such a laboratory are also needed and assumed to be readily available. GC tools (e.g., wrenches, screwdrivers, and spare parts, etc.) also need to be available in the laboratory.

C.2.3 Safety Requirements

Routine safety precautions required in any analytical chemistry laboratory are applicable here. These include such measures as no smoking while in the laboratory; wearing safety glasses, lab coats, and gloves when handling samples; and handling organic solvents in a fume hood, etc. Compressed gases considered to be fuels (e.g., hydrogen) must be stored on a pad outside the confines of the laboratory. A safety shower, eye wash, first aid kit, and fire extinguisher must be readily available inside the laboratory.

C.2.4 Apparatus

C.2.4.1 Equipment Needed

- **Gas chromatography:** With packed column and/or capillary column capabilities, oven temperature controller, and flame ionization detector (FID) (e.g., Perkin Elmer Sigma 115 or Hewlett Packard 5890).
- **Autosampler (optional):** Capable of handling methylene chloride extracts and appropriate wash vials.
- **Autosampler vials (optional):** Clear glass with Teflon® faced crimp caps, typically 100 μL or 1 mL size.
- **Crimping tool (optional):** Used to secure caps on autosampler vials.

C.2.4.2 Reagents And Materials

- **Methylene chloride:** Burdick and Jackson or equivalent grade.
- **Syringe:** 5 μL or 10 μL, gas tight, for hand injections. Otherwise, 3 μL or 10 μL syringes are used for autosampler injections.
- **Pasteur pipettes:** Disposable, used for sample transfer.
- **Pipette bulbs:** 1 mL, amber.
- **Squeeze bottle:** Teflon®, 250 mL or equivalent, used for methylene chloride rinse of vials.

C.2.4.3 Maintenance

- **Glassware:** Clean all glassware used in the total chromatographable organics (TCO) analysis by the method described in Reference 1.
- **Gas Chromatograph:** Change the GC inlet septum daily; follow this with a column bakeout at 250°C for 20 minutes or, until the detector response is stable and all evidence of contamination is gone (no peaks), or run an injection of clean solvent to verify column contamination is eliminated. Repeat this

procedure during the run if evidence of septum failure appears (e.g., increasing peak elution time with each run, or major loss of sensitivity).

C.2.4.4 Theory Of FID Detector

Flame ionization detectors operate by burning organic compounds in the detector's flame. The burning process oxidizes the carbon atoms, producing electrons and positive ions. An anode and cathode on either side of the flame collect the charged particles, and the resulting current is proportional to the concentration of oxidized carbon in the sample. Instrument electronics convert the detector current to a voltage, which changes linearly with changes in analyte concentration.

C.2.5 Interferences

The analytical system shall be demonstrated to be free from internal contaminants on a daily basis by running a bakeout or a QC sample. A reagent blank must be run for each new batch of reagents used to determine that reagents are contaminant-free. This is verified by an instrument response less than the detection limit.

If duplicate runs of a sample show increasing concentration greater than 15% or if cross-contamination is suspected (e.g., high-level sample followed by a low-level sample), a reagent blank shall be run to verify no contamination in the system. If contamination is evident, the column shall be baked out at approximately 250°C for twenty minutes or until the detector is stable, and the blank check repeated.

SECTION C.3

OPERATION

C.3.1 Summary of Method

TCO analysis quantifies chromatographable material with boiling points in the range of 100° to 300°C. This analysis is applied to all samples that might contain compounds in this volatility and boiling point range.

For TCO analysis, a 0.9 to 3 μL portion of the extract is analyzed by gas chromatography using a flame ionization detector (FID). Column conditions are described in this document in tabular form in Table 3-1. The peak areas are converted to concentration values using quantitative calibration standards.

For more information, consult Lentzen et al., IERL Procedures Manual: Level 1 (Reference 1).

C.3.2 Samples/Sampling Procedures

Samples for TCO analysis arrive or are prepared as methylene chloride (or occasionally as methanol) extracts of environmental samples, filters, resins, or ambient sampling components. An aliquot of the extract is transferred to a TCO vial and loaded into the autosampler as required.

All samples will be stored in a refrigerator at or below 4°C to retard analyte degradation. Samples will be analyzed as soon as possible after sample receipt and preparation to avoid loss of sample due to volatilization and degradation.

TABLE C-1

INSTRUMENTAL OPERATING CONDITIONS FOR GAS CHROMATOGRAPHY

Column	Temperature Program	Injector	Detector	Carrier Gas	Split Injector (optional)	Injector Volume	Solvent
Fused Silica Capillary Column (15 meters, wide bore, typically DB-1 , DB-5, or equivalent)	40°C for 3 minutes 8°C/min increase to 250°C and hold for total run time of 45 minutes	300°	F.I.D. 300°	Helium 1-3 mL/min	10/1 split ratio	Not to exceed 3 μL (Typically 1 μL)	Dichloromethane (pesticide grade, distilled in glass or equivalent)
Packed Column (Methyl Silicone oil or equivalent 1/8 in. x 6 ft. steel)	50°C or 5 minutes 20°C/min increase to 250°C, then hold	300°	F.I.D. 300°	Helium at 30 mL/min	N/A	1-5 μL	Dichloromethane (pesticide grade, distilled in glass or equivalent)

C.3.3 Operation

Note: All glassware coming in contact with a sample shall be cleaned by Level 1 procedures (Ref. 1). Briefly, this entails sequential cleaning with soapy water, deionized water, 50:50 (V/V) nitric acid/sulfuric acid, deionized water, methyl alcohol, and methylene chloride, followed by oven drying.

Those steps that are only applicable to automatic injection are shown with an asterisk (*).

- Start up by the manufacturer's suggested method.
* • Replace septum on auto-sampler and column.
* • Ensure injection needle is in line with injection port. The autosampler needle should be manually "injected" through the injection port to verify alignment.
- Bakeout GC at 200°C for 20 minutes until FID response is stable and all evidence of column contamination is gone (no peaks), or run an injection of clean solvent as the first injection of the day to verify that column contamination is eliminated.
* • Load auto-sampler tray with samples.
* • Check the autosampler flush by placing the autosampler in manual mode and flushing a vial of clean solvent through the needle assembly.
* • Set auto-sampler to inject approximately 1 μL of samples. Capillary column can be damaged if too great a volume is injected.
- Run a QC standard using the specified conditions to verify that the system is operating properly. Check the TCO window (C_7 to C_{17}) to ensure the range has not changed. (Retention times may change with column aging.) The TCO window for calculations should be adjusted as required.
- Flush needle with solvent (dichloromethane) between injections.
- Run samples and collect data.
- Analyze data according to the method described in Section 3.4.

- After all analyses are complete, bakeout the column at 200°C for 20 minutes, or run clean solvent as a "sample."
- Shut down instrument by method suggested by manufacturer.

C.3.4 Analysis

The peak area (FID response/μL) is summed over the TCO range window and corresponding TCO value (mg/mL) is determined from the calibration curve. In the event that the TCO value is outside the linear working range, the sample shall be concentrated or diluted, depending on the requirements, and reanalyzed. If there is not enough sample to concentrate, the values are reported as found, and an appropriate qualifying statement is included in the analytical report.

It is important that the observed values of the total integrated area for samples be corrected by subtracting an appropriate solvent blank, prepared in the same manner as the samples.

SECTION C.4

TROUBLESHOOTING

C.4.1 Calibration

Quantitative calibration of the TCO procedure is accomplished by the use of mixtures of known concentration of the normal hydrocarbons decane, dodecane, and tetradecane. Retention time limits correspond to the TCO range of boiling points and are defined by the peak maxima for n-heptane (C_7, B.P. 98°C) and n-heptadecane (C_{17}, B.P. 303°C). Therefore, integration of detector response should begin at the retention time of C_7 and terminate at the retention time of C_{17}. The C_7 and C_{17} peaks are not included in this integration. By this procedure, the integrated area will cover material in the boiling range of approximately 100°C to 300°C. Calibrate the GC with dilutions of a stock solution, generating a response/concentration curve. The calibration curve must be 1 and must have a correlation coefficient greater than 0.97 to be acceptable. The preparation and dilution of the stock solution is described below:

- Weigh approximately 100 μL aliquots of each (heptane, decane, dodecane, tetradecane, and heptadecane, C_7, C_{10}, C_{12}, C_{14}, C_{17}) (99% + pure) into a 10 mL volumetric flask or septum-sealed vial. Weigh each hydrocarbon successively into the vial starting from least volatile to most volatile.

- Dilute the vial contents up to approximately 3 mL with dichloromethane.

- Transfer this quantitatively to a clean, 10 mL amber volumetric flask and add dichloromethane up to the 10 mL mark. This stock solution will have approximately 22 mg (C_7 to C_{12})/mL and 15 mg(C_{14} to C_{17})/mL. Several (at least three) dilutions of the stock solution are made to cover the linear working range.

C.4.2 Method Precision and Accuracy

Duplicate results by the same operator will be rejected if they differ by more than 15%. The result of a quality control sample, run daily, will be considered deficient if it differs by more than 15% from the preparation value. If this value falls outside the accepted range, the system must be evaluated for the probable cause, and a second standard run or a new calibration performed over the range of interest.

SECTION C.5

DATA REDUCTION

C.5.1 Calculations

The peak area (FID response/μL) is summed over the TCO window and a corresponding TCO value (mg/mL) is determined from the calibration curve.

- Construct the calibration line by fitting a linear regression equation to the results of the analysis of the calibration standard solution. The concentration of the standards must fall within the linear working range of the instrument and bracket the concentration of the sample. Use the C_{10} to C_{14} standards for calibration.

  Standard Calibration Equation:

  $$R_i = (M)\ C_i + (B) \qquad (1)$$

  Where R_i = FID Response (total C_{10} to C_{14} Peaks),
  C_i = Concentration mg/L (total of C_{10} to C_{14} standards),
  M = Slope of line, and
  B = Intercept of line.

- Calculate the TCO value for the sample (C_u, measured value) and blank (C_B, blank value) by summing the FID response over the TCO retention time span and calculating the concentration from the calibration equation.

  It is important that the observed values of the total integrated area for samples be corrected by subtracting an appropriate solvent blank prepared in the same manner as the samples. The sample is corrected for the blank:

  $$C_u \text{ corrected} = C_u \text{ measured} - C_B \qquad (2)$$

C.5.2 Data Reporting

The results of each TCO analysis should be reported as one number (in milligrams), corresponding to the quantity of material in the 100°C to 300°C boiling range in the original sample collected. If more information is available (e.g., cubic meters of gas sampled), the mg/sample value can then be easily converted to the required reporting units.

SECTION C.6

QUALITY ASSURANCE/QUALITY CONTROL

C.6.1 QC Checks

If evidence of septum failure appears (e.g., increasing peak elution time with each run or major loss of sensitivity), perform a column bakeout at 250°C for twenty minutes or until the FID response is stable and all evidence of contamination is gone (no peaks), or run an injection of clean solvent to verify that column contamination is eliminated.

C.6.2 QC Controls

Run a reagent sample for each new batch of reagent or lot of solvent used. If the analysis fails to show organic contaminants to be below detection limits under identical instrument operating conditions as used for samples, then the reagent shall be distilled in glass and retested, or the reagent batch will be unacceptable for TCO analyses.

Prepare a QC sample that is approximately mid-way in the linear working range. Run this QC sample daily to verify the performance of the GC. Determine the TCO value using the calibration curve and its value plotted compared to the theoretical value. If two runs of the QC sample differ by more than 15% of the actual value, prepare a new QC sample and repeat the test. If the new sample fails the test, determine if there is a loose column connection, septum, or altered split flow. After correction, run a new QC sample. If the new sample fails the test, re-calibrate the instrument and/or perform a column change if needed.

SECTION C.7

REFERENCES

1. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition). EPA 600/7-78/201, NTIS No. PB 293-795, pp. 140-142, October 1978.

Appendix D

Recommended Operating Procedure for Gravimetric (GRAV) Analysis of Organic Extracts

(This document was originally prepared for the EPA/AEERL Laboratory in RTP, NC and developed and reviewed by the QA Program of AEERL, under the direction of Judith S. Ford, QA Manager of EPA/AEERL)

Disclaimer

This recommended operating procedure has been prepared for the sole use of the Air and Energy Engineering Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and may not be specifically applicable to the activities of other organizations.

Acknowledgements

Assisting in the preparation of this procedure, dated 9/86 as Document No. AEERL/12, were Robert F. Martz, Acurex Corporation, Research Triangle Park, NC, under EPA Contract 68-02-4701 for on-site technical support to AEERL; and Monica Nees, Research Triangle Institute, Research Triangle Park, NC, under EPA Contract 68-02-4291 for Quality Assurance (QA) support to AEERL. Judith S. Ford, QA Manager for AEERL, is the Project Officer for the QA contract with Research Triangle Institute.

D.1.0 PROCEDURAL ELEMENTS

D.1.1 Scope and Application

Organic compounds with boiling points of 300°C and higher, after extraction with methylene chloride, evaporation of the solvent, and drying to constant weight, can be determined quantitatively by the gravimetric analysis described in the procedure.[1] This method is applicable to organic liquids, solid sample extracts, aqueous extracts, and extracts from the Source Assessment Sampling System (SASS) or Modified Method 5 train sorbent module. This analysis should be performed after enough of the sample extract has been concentrated to weigh accurately.[2] The suggested solvent is methylene chloride because of its good extraction properties and high volatility. Other solvents may give different results (e.g., methyl alcohol may extract polar compounds which would not be extracted with methylene chloride). All samples being dried to constant weight should be stored in a desiccator.

The range of applicability is limited by the sensitivity of the balance and the organic content of the sample. The balance must be accurate to $\pm$ 0.01 mg. If a sample of five milliliters is used for the analysis, then a sensitivity of 0.1 mg/5 mL or 0.002 mg/mL of sample can be achieved. This sensitivity can be improved by further concentration of more sample.

D.1.2 Definitions

- Method Blank: Provides a check on contamination resulting from sample preparation and measurement activities. Typically run in the laboratory after receipt of samples from the field by preparing a material known not to contain the target parameter. Addresses all chemicals and reagents used in a method.

- Reagent Blank: Provides information on contamination due to specific chemical reagents used during sample preparation, plus any background from the measurement system.

- Audit Sample: Has known "true values," but is flagged for the laboratory as a "performance evaluation (PE) sample." Provides information on performance, but this information must be tempered with the understanding that the sample may be given extra attention by the analyst. An internal PE sample is created by the in-house analytical laboratory, while an external PE sample is created outside of the analytical laboratory.

D.1.3 Interferences

Results may be biased due to contamination of the solvent, glassware, or both. A method blank (control) shall be run in duplicate for each lot of solvent and/or set of samples to provide a control check on the purity of the solvent and the glassware cleaning procedure. The method blank, consisting of a solvent sample from the same lot as that used to prepare samples, shall be prepared and concentrated in an identical manner.

Two reagent blanks shall be analyzed each day samples are run to ensure results which are not biased due to solvent contamination. The reagent blank shall be a solvent sample from the same lot used to prepare the samples and shall not be concentrated prior to analysis. To minimize error in weight due to moisture condensation, the pans containing the sample must appear visually dry before being placed in a desiccator in preparation for drying to constant weight.

D.1.4 Apparatus

(1) Analytical Balance: Capable of weighing 0.01 mg with an accuracy of $\pm$ 0.005 mg.

(2) Desiccating Cabinet: Seal-tight gasketed with gum rubber. (Desiccators which use silicone sealant shall not be used because of possible contamination of the sample. Silicone grease may interfere with subsequent analysis.)

(3) Oven: Capable of operation to 175°C.

(4) Fume Hood: Standard laboratory.

(5) Dust Cover, Plexiglass®, or equivalent: To protect samples drying in hood.

D.1.5 Reagents and Materials

(1) Disposable Aluminum Weighing Pans: Approximately 2" in diameter, 1/2" deep; crimped sides; weighing approximately 1.0 grams.

(2) Tweezers.

(3) Aluminum Foil

(4) Pipets: 1 to 5 mL (Class A Volumetric).

(5) Glass Beakers: 50 to 400 mL.

(6) Wash Bottles: Teflon® or equivalent.

(7) Deionized Water.

(8) Nitric Acid/Sulfuric Acid, 50:50 (V/V): Prepared from reagent-grade acids.

(9) Methylene Chloride: Burdick and Jackson or equivalent grade.

(10) Methyl Alcohol: Burdick and Jackson or equivalent grade.

(11) Drierite® and/or Silica Gel: New Drierite® or silica gel may be used as received. Used Drierite® or silica gel may be reactivated by drying it in an oven for at least two hours at 175°C.

D.1.6 Sample Handling

All apparatus that contacts either the concentrated or evaporated residue samples shall be glass, Teflon®, aluminum, or stainless steel. Evaporation of samples shall be carried out in an area free of airborne dust and organic vapors that could contaminate the samples.

Ordinarily, all glassware coming in contact with a sample, in either dilute or concentrated form, must be cleaned by complete Level 1 procedures.[2] Briefly, this cleaning procedure entails sequential cleaning with soapy water, deionized water, 50:50 (V/V) nitric acid:sulfuric acid, deionized water, methyl alcohol, and methylene chloride, followed by oven drying. The use of deionized water for cleaning glassware is critical when inorganic substances are being analyzed or heavy metal contaminants are present in high concentration in tap water.

This ROP, however, covers only the analysis of organic constituents. Tap water can be substituted for deionized water in glassware cleaning whenever the organic concentration exceeds 1 mg/sample as measured by this ROP. Experience has shown that tap water adds no measurable amount of organic contaminants to the method or reagent blanks under these conditions.

D.1.7 Sampling/Analysis Procedures

(1) Label aluminum sample pans on the underside using a ballpoint pen or other sharp object. Handle dishes only with clean tweezers.

(2) Clean the weighing pans by first rinsing them with deionized water, then dipping them successively into three beakers of methyl alcohol, methylene chloride, and, finally, methyl alcohol again.

(3) Dry the cleaned weighing pans to constant weight on a shelf lined with clean aluminum foil in an oven heated to at least 105°C. Cool the plans in a desiccator for a minimum of 4 to 8 hours or overnight.

(4) Weigh pans to constant weight to an accuracy of ± 0.01 mg, recording the pan tare weight.

(5) By pipet, transfer a 1.0 mL aliquot of the sample to the aluminum sample pan or use 1/10 of the concentrated sample. Aliquot size must never exceed 5 mL to avoid loss of sample through capillary action.

(6) Place the sample pan on a clean piece of aluminum foil in a clean fume hood. Shield the pan from dust with a Plexiglas® or other cover positioned to allow for adequate air circulation. Evaporate sample to visual dryness at room temperature. Solvent evaporation usually takes about 30 minutes.

(7) Place sample pan in desiccator over Drierite® and/or silica gel for at least 8 hours.

(8) Weigh sample pan at approximately 4-hour intervals until three successive values differ by no more than ± 0.03 mg. If the residue weight is less than 0.1 mg, concentrate more sample in the same sample pan. If there is insufficient sample remaining for this purpose, report the initial value obtained, along with an explanation.

D.1.8 Calculations

The gravimetric range organics (GRAV) is calculated in units of mg/sample as follows:

$$GRAV = \frac{(Sample\,Weight_{mg} + Pan\,Weight_{mg}) - (Pan\,Tare\,Weight_{mg})}{Aliquot\,Volume_{mL} / Total\,Concentration\,Sample\,Volume_{mL}}$$

The calculated GRAV weight is corrected for the method blank:

Corrected GRAV mass = Measured GRAV mass - Method Blank mass

D.1.9 Data Reporting

The results of the analysis are averaged and reported in units of mg organics/original sample.

D.1.10 Precision

Duplicate analyses shall be run by the same analyst and shall be rejected if results differ by more than 20% from the average. If insufficient material is present to rerun the sample, both values will be reported with a qualifying statement.

D.1.11 Accuracy

Dry sample weight should be at least 1 mg per analysis whenever possible. Accuracy of the analysis is $\pm$ 20% of actual value. A proficiency test should be performed by each analyst as described in Section 2.0.

D.2.0 QUALITY CONTROL ELEMENTS

- All operators should demonstrate proficiency with Gravimetric Analysis of Organic Extracts (GRAV) prior to sample analysis. In the proficiency testing, include a GRAV analysis of a reagent blank, a method blank, and an audit sample. The method or reagent blank shall be less than 5 mg/mL of sample. Results of the audit sample shall be within the precision and accuracy specifications outlined in this ROP.

- Two types of audit samples are used. The first contains 100 mg of eicosane [$CH_3(CH_2)_{18}CH_3$] in 250 mL of methylene chloride. Concentrate this solution to 10 mL in a manner identical to that used for sample preparation prior to GRAV analysis. The second type of audit sample can be either prepared in-house or received from an independent laboratory. An external audit sample must contain organic compounds with chain lengths of more than 18 carbons (and boiling points above 300°C) in sufficient concentration to be determined

accurately. Perform the GRAV analysis in duplicate as described in Section 1.7 of this procedure.

- Determine the GRAV value of duplicate method blanks for each new lot of solvent and/or set of samples. Run a method blank any time contamination is suspected. Prepare the blank using the same lot of reagent and the same concentration procedure as that used to prepare the samples. The solvent sample shall be a volume equivalent to that used for sample preparation. If the blank GRAV value is unusually high (i.e., 5 mg/mL of sample), find the cause of the contamination and repeat the method blank GRAV analysis.

- Analyze two reagent blanks for GRAV each day samples are run to ensure the results are not biased due to solvent contamination. The reagent blank shall consist of an aliquot of the solvent used to prepare the samples. If both reagent blank GRAV values are high (i.e., 2 mg/mL of sample), find the cause of the contamination and reanalyze samples and reagent blanks.

- Analyze all samples in duplicate. Samples are analyzed by the same analyst and must agree to within 20% of the average. In the event this condition is not met, repeat the analyses.

NOTE: If the conditions require the sample to be reanalyzed (e.g., high blank values or poor precision) and insufficient sample remains, then report the value obtained by the initial analysis and include a qualifying statement.

The following section (D.3.0, MicroGRAV) is a supplement to the original GRAV SOP, dated 9/86.[3]

D.3.0 MICROGRAV

The microGRAV technique allows the analyst to use a lighter gravimetric weigh pan and a smaller aliquot of sample extract to perform the extract weighings. All of the procedures used in traditional GRAV analysis are used with the following exceptions:

D.3.1 Reagents and Materials

(1) Weigh pans: Disposable weigh pans are constructed using heavy duty aluminum foil and a molding jig similar to the one shown in Figure D-1. The jig may be constructed of any inert material (nylon, plastic, Teflon®), providing it conforms to the general shape of the figure and the internal surfaces have generally rounded edges for ease of molding. The foil is cut into 2 inch circles or squares of foil, molded into shape by hand pressing, and the excess foil is cut away from the outer edges of the pan with a sharp knife or scissors. This produces pans weighing approximately 0.25 grams each, replacing the commercial 1 gram weigh pans.

(2) Pipets: Positive displacement pipets, fixed volume 250 μL or adjustable volume 100-250 μL are recommended (Rainin Pipetman® or equivalent with a Teflon® plunger internal to the pipet). Disposable tips are used as received from the manufacturer, one per sample extract.

D.3.2 Sampling/Analysis Procedures

(1) Label aluminum foil pans by marking on the underside using a dull pencil or toothpick. Use caution to avoid piercing through the pan.

(2) There is no need to clean the pans with solvent as long as they are kept from contact with excess dust or moisture. Experience has shown that the homemade pans are quite free of organic contamination indicated by the analysis of many solvent and dust blanks.

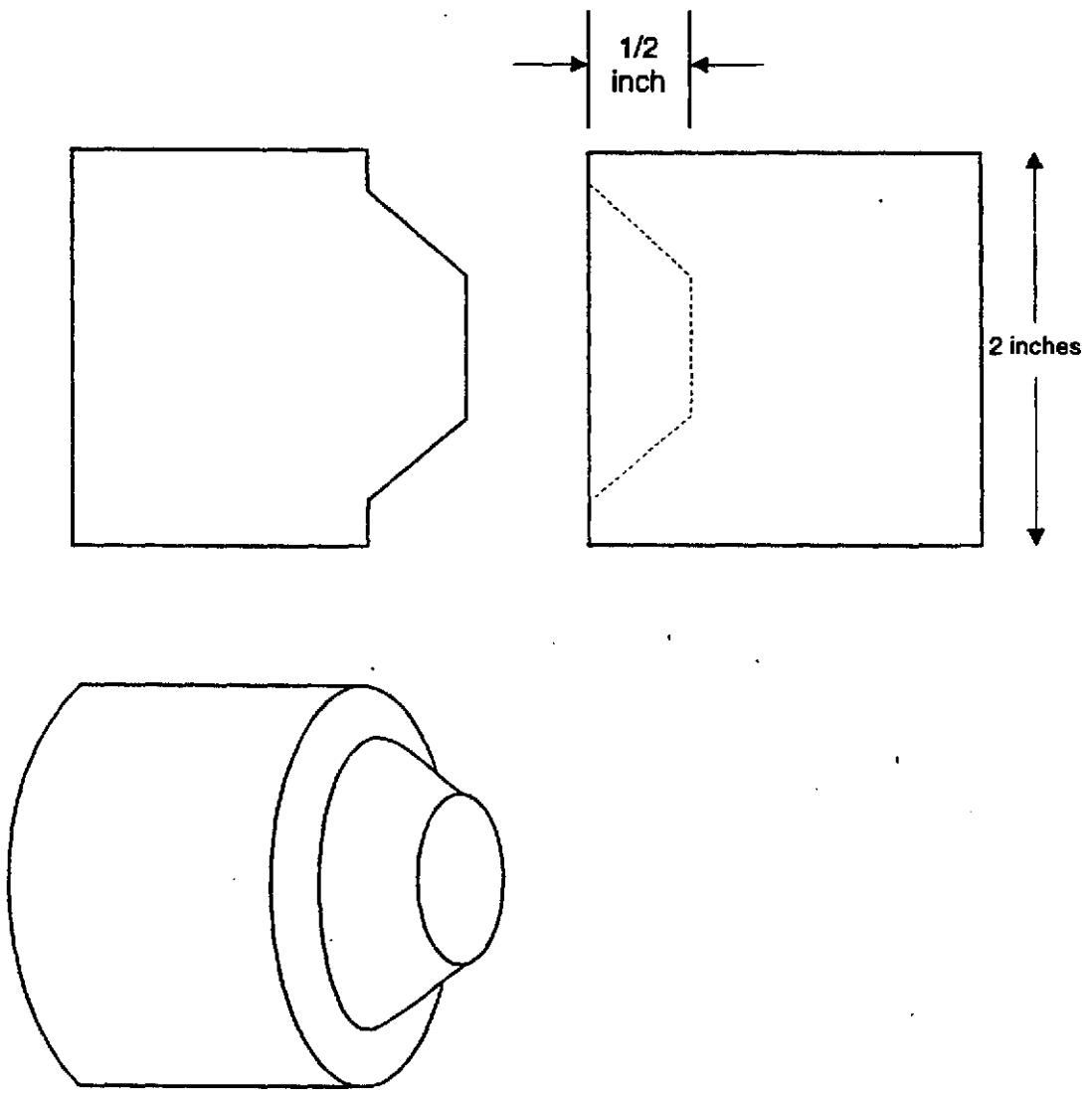


Figure D-1. Molding Jig for Construction of MicroGRAV Pans

(3) The pans are ready to use after molding and desiccating prior to tare weighing. No preheating or drying with an oven is necessary.

(4) Using a positive displacement disposable pipet, transfer a 0.250 mL aliquot of sample to the microGRAV pan. If necessary for a specialized application requiring larger aliquots, repeated transfers of 0.250 mL can be added to an individual pan, allowing the extract to air dry in the fume hood between transfers.

(5) All other procedures of microGRAV analysis are identical to the traditional GRAV techniques: carefully handle the pans with tweezers, air dry to visual dryness in a protective fume hood prior to desiccating, weigh the sample with a manual or digital microbalance, perform mass calculations, etc.

D.4.0 REFERENCES

1. Harris, J.C. et al. Laboratory Evaluation Level 1 Organic Analysis Procedure. EPA-600/S7-82-048, NTIS PB 82-239, pp. 30-36, March 1982.

2. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. IERL Procedures Manual: Level 1 Environmental Assessment (Second Edition). EPA-600/7-78-201, NTIS PB 293-795, pp. 26-142, October 1978.

3. Assisting in the preparation of this supplement, dated 9/91 were Robert F. Martz and David F. Natschke of Acurex Environmental Corporation, Research Triangle Park, NC, under EPA contract 68-02-4701 in support of the multi-laboratory Boise and Roanoke Integrated Air Cancer Program. James Dorsey and Raymond Steiber of EPA were the technical directive managers for the EPA contract with Acurex Environmental. Judith S. Ford was the EPA QA Manager of record for the AEERL contract.

Appendix E

EPA Draft Method 0040

Sampling of Principal Organic Hazardous Constituents from Combustion Sources Using Tedlar® Bags

(This is the latest draft version of Method 0040 from SW-846. The final version of the document when released supersedes this one and will be inserted in its place)

DRAFT METHOD 0040

1.0 SCOPE AND APPLICATION

1.1 Scope: This method establishes standardized test conditions and sample handling procedures for the collection by time integrated evacuated Tedlar® bag of volatile organic compounds from stationary sources, such as hazardous waste incinerators. This method also provides specific guidelines governing the use of Tedlar® bags for sample collection and storage.

1.2 Application

1.2.1 This method is applicable to the determination and speciation of volatile organic compounds contained in an effluent gas sample collected from stationary sources, such as hazardous waste incinerators and other combustion sources. Gas chromatography/ mass spectrometry (GC/MS) is the recommended analytical technique because of its unique ability to provide positive identification of compounds in complex mixtures like stack gas.

1.2.2 This method is not applicable to the collection of samples in areas where there is an explosion hazard. Substitution of intrinsically safe equipment or procedures for the equipment or procedures described in this method will not be sufficient to adapt this method for use in areas where there is an explosion hazard. Additional modifications to the sampling and analytical protocols may be required. No modification may be made to this method without prior approval from the appropriate regulatory personnel.

1.2.3 This method does not employ isokinetic sampling and therefore is not applicable to the collection of highly water soluble volatile organic compounds contained in an aerosol of water. This method uses either constant or proportional rate sampling, depending upon the extent of the variability of the emission flow rate.

1.2.4 This method is recommended only for use by either experienced sampling and analytical personnel or by persons under close supervision of such qualified personnel.

1.2.5 Applicable Compounds: Compounds for which this method can be considered shall meet the following criteria:

1. Boiling points < 121°C;

2. Source concentration below the respective condensation point.

3. Organic compounds that exhibit a loss in a Tedlar® bag of less than 20% over a 72-hour storage time during validation studies.

1.2.5.1 Candidate analytes (Table 1) were chosen on the basis of demonstrated stability in a Tedlar® bag (<20% degradation after 72 hours) in previous studies.[1] Condensation points (calculated from vapor pressure) at 20°C and estimated instrument detection limits (from SW-846 Method 5041) have been provided for each of the compounds. This method is not limited to these compounds. However, stability and recovery shall be demonstrated when compounds other than those listed in Table 1 are to be sampled.

1.2.6 Detection Limits and Source Considerations

1.2.6.1 The estimated detection limit of this method (Table 1) is compound specific and is in the range of 0.03 to 0.9ppm. Matrix effects may cause the individual compound detection limits to be higher.

1.2.6.2 Available stability data suggests that this method may not perform well in sampling streams containing polar and reactive compounds like methyl ethyl ketone,[1] formaldehyde,[2] methanol,[2] 1-butene,[3] and acetone[3]. The use of this method to sample these compounds needs to be evaluated before sampling.

1.2.7 Sample Hold Time: The time lapse between sampling and analysis shall not exceed 72 hours unless it can be justified by specific sample matrix stability data that meets the criteria of Section 1.2.5, #3. Stability in a Tedlar® bag shall be demonstrated by spiking analytes into inert gas in the laboratory and into stack gas in the field. The spiking level must be at least at the level found in the samples of the emissions matrix obtained during the pre-site survey. Compound recovery in both laboratory and field studies must be $\geq$ 80% after 72 hours for consideration of applicability. Extended hold times should be planned and approved by appropriate regulatory personnel before the test.

2.0 SUMMARY

2.1 Figure 1 shows a flow chart of the method. In this method, a representative sample is drawn from a source through a heated sample probe and filter. The sample then passes through a heated 3-way valve and into a condenser where the moisture and condensable components are removed; it is then collected in a Tedlar® bag held in a rigid, opaque container. The dry gas sample and the corresponding condensate are then transported together to a GC/MS. A mass spectrometer is most suited for the analysis and quantitation of complex mixtures of volatile organic compounds. The total amount of the analyte in the sample is determined by summing the individual amounts in the bag and the condensate.

2.2 **Common Problems:** Problems that can invalidate Tedlar® bag sampling data and techniques to remedy these problems are listed in Table 2.

3.0 INTERFERENCES

Major sources of interferences are:

1. Background hydrocarbon contamination of the Tedlar® bag arising from the bag material. Purging the bag with air or N_2 may reduce the hydrocarbon level. Exposure of the bag to direct sunlight will increase hydrocarbon levels.[4] The bag must be protected from exposure to sunlight by using an opaque container to house the bag during sampling and shipping.

2. Components of the source emissions other than the target compounds. Interferants may be differentiated from the target compounds during mass spectrometric analysis.

4.0 APPARATUS AND MATERIALS

4.1 Tedlar® Bag Sampling Train: A detailed schematic of the principal components of the sampling train is shown in Figure 2.

4.1.1 The sampling train (Figure 2) consists of a glass-lined probe, a heated glass or Teflon® filter holder and quartz filter attached to one of two inlets of a glass and Teflon® 3-way isolation valve (Figures 3 and 4). The second valve inlet is connected to a charcoal trap to filter incoming air when releasing system pressure after leak checks. The outlet of the isolation valve is connected to a glass, water-cooled, coil-type condenser and a glass condensate trap for removal and collection of condensable liquids present in the gas stream. A 1/4-in. OD x 1/8-in. ID Teflon® transfer line connects the condensate trap to a second 3-way isolation valve and the isolation valve to a Tedlar® bag contained in a rigid, air-tight container for sampling, storage, and shipping. The bag container is connected to a control console with 1/4-in. OD x 1/8-in. ID vacuum line by means of 1/4-in. Teflon® connectors at each end. A charcoal trap is placed in the vacuum line between the bag container and the control console to protect the console and sampling personnel from hazardous emissions in case of bag rupture during sampling.

4.1.2 The vacuum required to operate this system is provided by a leak-free diaphragm pump contained in the control console (Figure 5). When the pump is turned on, the space between the inner walls of the bag container and the Tedlar® bag is evacuated, placing the system under negative pressure to pull the sample through the sampling train and into the Tedlar® bag. The sampling train vacuum is monitored with a vacuum gauge installed in-line between the vacuum line and the coarse adjustment valve mounted in the control console.

4.1.3 Sample flow rate is regulated by adjusting the coarse and fine valves on the control console. The coarse adjustment valve controls the sample inlet volume and rate and isolates the vacuum line, vacuum gauge, and sample train from the pump and other console components during leak checks. Sample volume is measured with a calibrated dry gas meter contained in the control console. Sampling rate is monitored by a rotometer, contained in the control console, which is installed on the outlet side of the dry gas meter.

4.1.4 The source, probe, filter, and condenser temperatures are monitored by Type J or K thermocouples using the digital temperature readout in the control console. Probe heater temperature is regulated by the temperature controller provided in the control console (Figure 5).

4.1.5 The velocity pressure and temperature of the source gases are measured using a standard or S-type pitot tube connected to a manometer with 1/4-in. OD x 1/8-in. ID tubing, in accordance with EPA Method 2. The source velocity pressure and temperature must be monitored during sampling and the sampling rate adjusted proportionally to changes in the flue gas velocity (Section 7.5.1.2).

4.2 Sample Train Components:

4.2.1 Probe Assembly: The probe assembly consists of a length of heated and insulated borosilicate glass tube inside a length of stainless steel tubing. The probe temperature shall be maintained between 130°C (266°F) and 140°C (284°F) in order to prevent damage to Teflon® lines and to facilitate efficient cooling of the gases in the condenser. Water cooling of the stainless steel sheath will be necessary when the source temperature approaches or exceeds 140°C (284°F).

4.2.2 Particulate Filter: Particulate matter from the sample gas stream exiting the probe is collected on a quartz filter substrate in a heated 47-mm Teflon® or glass filter holder. Use clean filters in order to prevent sample contamination. The particulate matter itself is not analyzed or archived. However, removal of particulate matter provides a cleaner sample for analysis. All connections between the probe and particulate filter shall be heated to maintain the temperature between 130°C (266°F) and 140°C (284°F) so that compounds remain in the volatile phase. Heat-wrapped Teflon® unions with stainless steel nuts and Teflon® ferrules are recommended for all heated connections.

4.2.3 Isolation Valves: A typical isolation valve is shown in Figure 3. The isolation valves shall be constructed of Teflon® or glass with Teflon® stopcocks to provide gas tight seals without the use of sealing greases. The probe and bag isolation valves are of identical design and materials and are therefore interchangeable. The probe isolation valve provides for the attachment of a charcoal or similar purge trap to allow filtered ambient air to enter the train when returning the train to ambient pressure after leak checks. This valve directly connects the probe and filter assembly to the condenser inlet and must be heated to between 130°C (266°F) and 140°C (284°F). The bag isolation valve allows the bag to be opened for sampling or evacuation and isolated and sealed for leak checks or system purges.

4.2.4 Condenser: Use a jacketed, water-cooled, coil-type glass condenser with a volume of at least 125 milliliter (mL). The condenser shall have sufficient capacity to maintain the temperature of the sample gas stream between 20°C (68°F) and 4°C (39°F) to ensure proper removal and collection of condensable moisture in the effluent gas sample. The cooled sample gas stream temperature should not exceed ambient temperature. All condenser connections must form a leak-free, vacuum-tight seal without using sealing greases. Stainless steel fittings are not permitted, and Teflon® unions or washers with screw caps are recommended.

4.2.5 Condensate Trap: A glass Erlenmeyer distilling flask with threaded screw cap connections, Teflon® seals, and a minimum volume of 125 mL may be used to trap condensate. All connections on the condenser and trap shall be sized to accept 1/4-in. OD x 1/8-in. ID Teflon® or glass fittings. The stem from the condenser must be positioned to within 0.5-in from the bottom of the condensate trap.

4.2.6 Sample Transfer Lines and Connection Fittings: All sample transfer lines connecting components shall be less than 5 ft long and constructed of 1/4-in. OD x 1/8-in. ID Teflon® tubing or glass. All sample lines upstream of the condenser and condensate trap must be heated and the temperature maintained between 130°C (266°F) and 140°C (284°F). Use Teflon® fittings for connections between various train components to provide leak-free, vacuum-tight connections without the use of sealing grease. New tubing should be used for each separate test series or condition to prevent cross contamination of sample compounds.

4.2.7 Tedlar® Storage Bag: Choose a bag size according to the guidelines provided in Section 7.2.4. In order to minimize wall effects, the sample volume must fill at least 80% of the bag capacity. The recommended size range for bags is 25 L to 35 L. Small bags (< 25 L) are easier to store and transport but may have insufficient volume for proportional sampling. In addition, accurate volumetric measurement is difficult with smaller bags. Large bags (> 50 L) lack portability but may be required under certain conditions, such as during proportional sampling and for sampling sources requiring high sample rates.

4.2.8 Evacuated Container (Bag Container): Use any rigid, air-tight metal or plastic (e.g., PVC®/Polyethylene®/Nalgene®) drums or glass containers to house the Tedlar® bag during sampling, storage, and transport. The container must be constructed so that it can easily be assembled and disassembled (for bag removal). The container must be able to hold a negative pressure of at least 10 in. H_2O. The

bag container must be at least 20% smaller than the Tedlar® bag being used but must be large enough to hold the volume of sample required (e.g., for a sample size of 20 L, a 25-L Tedlar® bag inside a 20-L container provides sufficient volume without danger of overinflating the bag).

Containers must not have staples, sharp edges, or metal closures which might damage bags. The container should also be constructed of a material that shields the sample from exposure to sunlight to protect the bag contents from ultra-violet light. A viewing port or other means of observing the flexible bag during sampling is desirable. During storage and transport, the viewing port shall be covered with opaque material.

4.2.9 Vacuum Lines: Use Tygon®, Poly®, Nylon®, or similar tubing capable of maintaining at least 10-in. H_2O negative pressure without collapse as vacuum lines. Tubing should be 1/4-in. OD x 1/8-in. ID size to minimize volume and ensure compatibility of connection fittings throughout the train. Stainless steel fittings and valves may be used for vacuum line connections but may not be used in the sampling line.

4.2.10 Control Console (Meter System): The metering system required for this method is readily available in the form of a Volatile Organic Sampling Train (VOST, SW-846 Method 0030) control console/meter box (e.g., Nutech Model 280.01B) and shall consist of the components pictured in Figure 5.

4.2.10.1 Vacuum Gauge (Meter Pressure): Use a direct reading, mechanical vacuum gauge capable of measuring pressures of at least 15 in. Hg with 1-in. or smaller increments to monitor system vacuum during sampling and leak checking the bag, the container, and the sampling train.

4.2.10.2 Sample Flow Rate Adjustment Valves (Coarse and Fine): The coarse adjustment valve controls volume and rate of sample flow and isolates the control console from the sampling train and vacuum line during leak checks. The fine adjustment valve controls sample rate and system vacuum. Closing the valve (clockwise) increases train vacuum and sample flow rate. Opening the valve (counterclockwise) decreases train vacuum and sample flow rate.

4.2.10.3 Pump: Use a leak-free diaphragm pump or equivalent that is capable of pulling and maintaining a vacuum of at least 15 in. Hg and a flow rate of at least 1 liter per minute (Lpm).

4.2.10.4 Calibrated Dry Gas Meter: The control console contains a calibrated dry gas meter (Singer Model 802/American Meter Model 602 or equivalent) capable of reading 1 L per revolution with 0.1-L increments, and provides accurate measurement of the volume of the sample collected.

4.2.10.5 Flow Meter: Use a rotometer with a glass tube and a glass, Teflon®, or sapphire float ball of suitable range (0-5 Lpm) to measure the sample flow rate. The flow meter shall be accurate to within 5% over the selected range. A range of ± 25% of the desired sampling rate is suggested to ensure greater accuracy of readings and a better range for adjustment of the sampling rate (proportional to the source gas stream velocity). The rotometer is installed at the outlet of the dry gas meter in the console.

4.2.10.6 Thermocouples and Temperature Read Out Device: Use a sufficient number and length of type J or K thermocouples. The 10-channel (1 to 4 remote; 5 dry gas meter, 6 to 10 spares) digital thermocouple

read-out provided in the control console displays the source, probe, filter, and condenser temperatures.

4.2.10.7 Heat Controller: Use a rheostat or digital temperature controller (e.g., Fuji PYZ4 or equivalent) to regulate probe heat temperatures.

4.2.11 Pitot Tube Probe: Use a standard or S-type pitot tube must be used for pretest and post-test velocity traverses (as described in Section 2.1 of EPA Method 2) and to monitor flow so that the sampling rate can be regulated proportionally to the source gas velocity throughout the length of the sampling run.

4.2.12 Pressure Gauge (Manometer): Use a water- or oil-filled U-tube or incline manometer capable of measuring to at least 10 in. H_2O and accurate to within 0.1 in. H_2O for monitoring and measuring the source gas velocity (as described in Section 2.2 of EPA Method 2).

4.2.13 Barometer: Use an aneroid or other barometer capable of measuring atmospheric pressure to within 0.1 in. Hg of actual barometric pressure.

4.2.14 Charcoal Absorbent Traps: Use charcoal traps to absorb organic compounds in the atmosphere at the site. One charcoal trap is attached to the probe isolation valve and filters incoming air when releasing vacuum to prevent contamination of the train during leak checks. A second charcoal trap is located in the vacuum line and filters any gas exiting the sample train to protect sampling personnel in case of bag rupture. Any readily available, ready made charcoal tube similar to a VOST tube may be used.

4.2.15 Stopwatch: Use any stopwatch capable of measuring 1 second to time sample collection.

5.0 REAGENTS AND MATERIALS

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.

5.2 Reagents:

5.2.1 Water: Water used for sample train preparation shall be distilled and deionized. Water used for rinses during recovery of condensate shall be prepurged high performance liquid chromatography (HPLC) grade. Clean clear tap water may be used as condenser cooling water.

5.2.2 Nitric Acid (10%), HNO_3: All HNO_3 used must be reagent grade.

5.2.3 Charcoal: Use SKC petroleum-base or equivalent charcoal. A mesh size of 6-14 is recommended. New charcoal must be used for each run series or test condition and may be reused if reconditioned using the same criteria specified in VOST (SW-846, Method 0030), Section 3.2.

5.2.4 Methanol: Use spectrometric or equivalent grade methanol.

5.3 Field Spiking Standards: Appropriate cylinder gases containing the target components of interest in known concentrations (highest purity available) for field spiking must be obtained.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Pretest Preparation:

6.1.1 Glassware: Before sampling, prepare the glass components of the train as follows:

1. Clean with nonionic detergent (e.g., Alconox) and hot water in an ultrasonic bath.
2. Rinse three times with distilled and deionized water.
3. Rinse three times with 10% HNO_3.
4. Rinse three times with distilled and deionized water.
5. Dry in an oven heated to at least 130°C (266°F) for 2 hours.

6.1.2 Sample Lines and Bag Containers: Treat all Teflon® lines, fittings, and the sample bag containers as outlined in Section 6.1.1 following steps 1 through 4. Then air dry these components in an area free of organic compounds. Use clean Teflon® tubing for each test series or condition. Hand wash the bag containers.

6.1.3 Bag Cleaning Procedure: Ensure that all bags are clean before using them for sampling. First, flush each bag three times with high purity nitrogen (N_2; 99.998%). Then fill each bag with the N_2 and analyze the bag contents at the highest sensitivity setting using the same analysis technique as will be used for analyzing samples. Analyze one analytical system blank each day before constructing the calibration curve by taking the gas chromatograph through its analytical program with no sample injection. Perform an analytical system blank again if carryover between samples is indicated. Other, less stringent methods of cleaning and analysis may be used at the risk of overlooking important contaminants. An acceptable level of contamination will be a response less than five times the instrument detection limit

or half of the level of concern, whichever is less. Repeat the nitrogen flush as necessary until the acceptable level has been reached. No bag shall be used until it has been satisfactorily cleaned.

6.2 **Sample Bag Storage and Transport Procedures**: To ensure sampling integrity, perform sample recovery in a manner that prevents contamination of the bag sample. Protect the bag from sharp objects, direct sunlight and low ambient temperatures (below 0°C) that could cause condensation of any of the analytes. Store the bag samples in an area that has restricted access to prevent damage to or tampering with the sample before analysis. Analyze the bag samples within 72 hours of sample collection unless it can be shown that significant (>20%) sample degradation does not occur over a longer period of sample storage. Upon completion of the testing and sample recovery, check all the data forms for completeness and the sample bags for proper identification. Store the bags in rigid, opaque containers during all sampling, storage and transport procedures. Ship the bags using ground transportation. Follow all hazardous materials shipping procedures.

6.3 **Condensate Storage and Transport Procedures**: To ensure sampling integrity, perform sample recovery in a manner that prevents contamination of the condensate (Section 7.6.5). Store the condensate in 40 mL vials under head-space free conditions. Place the vials in ice or in a refrigerated container at 4°C (± 2°C) [39°F (± 4°F)] immediately following recovery and during transport for analysis. In addition, store the vials in an area that has restricted access to prevent damage to or tampering with the sample before analysis. Upon completion of the testing and sample recovery, check all the data forms for completeness and the condensate samples for proper identification. Ship the condensate samples using ground transportation. Follow all hazardous materials shipping procedures.

7.0 PROCEDURE

7.1 Pretest Survey:

7.1.1 Perform a pretest survey for each source to be tested. The purpose of the survey is to obtain source information to select the appropriate sampling and analysis parameters for that source. Potential interferences may be detected and resolved during the survey. When necessary information about the source cannot be obtained, collection and analysis of actual source samples may be required.

7.1.2 The following information must be collected during a survey before a test can be conducted. The information can be collected from literature surveys and source personnel, but an actual on-site inspection is recommended. A copy of the survey results must be forwarded to the chemist performing the sample analyses.

7.1.2.1 Determine whether the sampling site is in a potentially explosive atmosphere. If the sample site is located in an explosive atmosphere, use other, instrinsically safe test methods. This method is never to be used in a potentially explosive atmosphere (Section 1.2.2).

7.1.2.2 Measure and record the stack dimensions on a data sheet similar to the data sheet shown in Figure 6. Select the sampling site and the gaseous sampling points according to EPA Method 1 or as specified by the regulatory personnel.

7.1.2.3 Determine the stack pressure, temperature, and the range of velocity pressures using EPA Method 2.

7.1.2.4 Determine the stack gas moisture content (Section 7.7.7) using EPA Approximation Method 4 or its alternatives. Perform the determination when process operations are as they will be during final sampling. If the process uses and emits ambient air, use a sling psychrometer to measure the moisture content of the ambient air in the area of process air uptake.

7.1.2.5 Select a condensate collection system with a minimum volume of 50 mL. Select a sampling rate and volume that will yield a total condensate catch at or below 50 mL, to allow recovery of the condensate into volatile organic analysis (VOA) vials with minimum dead space.

7.1.2.6 In accordance with EPA Method 1, select a suitable probe liner and probe length as determined by the temperature and dimensions of the source. Determine the point within the stack that represents an average flow and temperature of the stack. Mark the probe at the determined distance to provide a reference point. For sample collection, insert the probe into the duct to the predetermined point to ensure proper probe placement and collection of a representative sample.

7.1.2.7 Determine whether the source has a constant or variable gas flow rate. The flow rate may be considered constant if the variation over the sampling period is no more than 20%. If the process is constant, use a constant sampling rate (Section 7.5.1.1). If the process is not constant, use proportional sampling (Section 7.5.1.2).

7.1.2.8 Determine approximate levels of target compounds by collecting a pretest bag sample for analysis. This information is needed to establish parameters for the analytical system.

7.1.2.9 Check the sampling site to ensure that adequate electrical service is available.

7.1.2.10 Follow all guidelines in the health and safety plan for the test. Use appropriate safety equipment as required by conditions at the sampling site (e.g., respirator, ear and eye protection, and a safety belt) (Section 7.1.2.8).

7.2 Pretest Procedures

7.2.1 Assembly: Assemble the train according to the diagram in Figure 2. Adjust the probe, filter, and valve heater controls to maintain a temperature between 130°C (266°F) and 140°C (284°F), circulate cooling water from an ice bath to the condenser until the temperature is stabilized at or below 20°C. Allow the probe, filter, valve, and condenser temperatures to stabilize before sampling. Mark the probe, pitot tube, and thermocouple assembly with the proper sampling points as determined in accordance with EPA Method 1. Before sampling, insert the pitot tube and thermocouple probe into the stack, to allow the thermocouple readings to stabilize.

7.2.2 Preliminary Velocity and Temperature Traverse: While the probe, filter, valve, and condenser temperatures are stabilizing, perform a preliminary velocity/temperature traverse in accordance with EPA Methods 1 and 2. Record the velocity (ΔP) and temperature (T, °C) at each point to determine a point of average flow and velocity and measure the static pressure at that point. Determine the average velocity head (ΔP_{avg}) and range of fluctuation.

7.2.3 Determination of Moisture Content: Determine the moisture content of the gas stream being sampled before (Section 7.1.2.4) or during actual

sampling. For combustion or water controlled processes (wet electrostatic precipitators and scrubbers), obtain moisture content of the flue gas during test conditions from plant personnel or by direct measurement using EPA Method 4.

7.2.4 Criteria for Selection of Sample Volume and Flow Rate: The flow rate should fill the bag to at least 80% of its capacity during the sampling period. The following criteria should be met:

1. Minimum stack sampling time for each run should be 1 h. Data from less than 1 h of sample collection would be an invalid test run. Two hours of stack sampling time is recommended as optimal.[5]

2. The minimum sample volume shall be no less than 15 L.

3. The minimum allowed sample flow rate shall be 250 mL/min.

Typically the average sampling flow rate is about 0.5 L/min which will yield approximately 30 L of sample collected per hour.

7.2.4.1 Mass Emission Rate Determination: Determine whether the final result will be presented on a concentration or mass emission basis before sampling. If results will be presented on a concentration basis, only the concentrations of the target analytes and the stack gas moisture content need to be measured. If the mass emission rate of any compound is to be presented, the volumetric flow rate of the stack gas must also be determined. The volumetric flow rate may be determined by performing a temperature and velocity traverse in accordance with EPA Methods 1 and 2, with actual sample collection.

7.3 Leak Check Procedures

7.3.1 Bag Evacuation and Bag Leak Check Procedure: Before sampling, ensure that the Tedlar® bag is fully evacuated and leak free.

7.3.1.1 Assemble the sample train as illustrated in Figure 2 and described in Section 4.1.1, ensuring that all connections are tight.

7.3.1.2 Turn the probe isolation valve to position 1 and turn the bag isolation valve to position 1 (Figure 4).

7.3.1.3 Disconnect the vacuum line from the bag container (the quick connect has a valve to seal the line; Figure 2) and turn on the pump in the control console (Figure 5).

7.3.1.4 Open the coarse adjustment valve and adjust the fine adjustment valve on the control console (Figure 5) until the vacuum gauge reads 5 in. Hg.

7.3.1.5 Turn the bag isolation valve to position 3 (Figure 4) and open the coarse valve completely to obtain maximum flow rate.

7.3.1.6 Observe the dry gas meter and rotometer as the bag is evacuated. The bag is completely evacuated when no flow is indicated on the dry gas meter and the vacuum rises to 5 in. Hg (Figure 5).

7.3.1.7 Allow the rotometer float ball to drop to zero. Time and record the leak rate using one of the following procedures.

7.3.1.7.1 Timed Leak Rate (measured in liters per minute) - Observe the leak rate indicated on the dry gas meter and time for 1 min. The leak rate must be less than 4% of the sample rate (e.g., 0.02 Lpm for a sample rate of 1 Lpm).

7.3.1.7.2 Timed Pressure Loss Rate (measured in inches Hg drop per minute) - Close both the coarse and fine adjustment valves and turn off the pump. Observe the vacuum gauge and time the pressure drop. The leak rate must be less than or equal to 0.1 in. Hg/min.

7.3.1.8 If all connections are found to be leak tight and the leak rate cannot meet the set criteria, discard the bag and test another clean bag.

7.3.1.9 Turn the bag isolation valve to position 1 (Figure 4) to seal the evacuated bag.

7.3.1.10 Turn off the pump and turn the probe isolation valve to position 3 (Figure 4) allowing the train to return to ambient pressure.

7.3.1.11 Return the probe isolation valve to position 1, seal the end of the probe and reconnect the vacuum line to the bag container (Figures 2 and 4).

7.3.2 Pretest Leak Check

7.3.2.1 Before sampling and immediately after evacuating and leak checking the bag, perform a pretest leak check of the sampling train.

7.3.2.2 Ensure that the bag isolation valve is in position 1 (Figure 4) and the end of the probe is sealed.

7.3.2.3 Turn the probe isolation valve to position 2 (Figure 4), turn the pump on, and open the coarse adjustment valve (Figure 5).

7.3.2.4 Allow the sample train to evacuate and adjust the fine adjustment valve to increase the vacuum to 5 in. Hg (Figure 5).

7.3.2.5 When the rotometer drops to zero and the dry gas meter slows to a stop, time and record the leak rate following the procedures outlined in Section 7.3.1.7.

7.3.2.6 If the leak rate is greater than 0.1 in Hg/min or 4% of the sampling rate, check all connections, valves, and the probe seal for tightness. Any leak found must be corrected and the leak check repeated before sampling collection begins.

7.3.2.7 After completing a satisfactory leak check, return the sampling train to ambient pressure by turning the probe isolation valve to position 3 (Figure 4) and turning off the pump (Figure 4).

7.3.2.8 When the vacuum gauge drops to zero, immediately turn the probe isolation valve to position 1 (Figure 4).

7.3.3 Post-test Leak Check

7.3.3.1 A post-test leak check must be performed after each bag sample is collected, before changing the bag and container for the next sample.

7.3.3.2 Ensure that the bag and probe isolation valves are in position 1 (Figure 4) and the pump is turned off when sample collection is completed.

7.3.3.3 Remove the probe from the stack and seal the end of the probe with a leak-tight seal. Check all connections and train components for looseness or breakage. Do not tighten any connections. Record any abnormal conditions.

7.3.3.4 Turn the probe isolation valve to position 2 (Figure 4) and disconnect the quick connectors on the bag isolation valve return line from the tee on the vacuum line (Figure 2).

7.3.3.5 Turn on the pump and adjust the fine adjustment valve until the train vacuum reaches at least 1 in. Hg above the highest vacuum attained during sample collection. Time and record the leak rate as previously outlined in Section 7.3.1.7.

7.3.3.6 If the leak rate is less than 4% of the sample rate or 0.1 in. Hg/min., the sample is considered valid (Section 7.3.1.7.1 and 7.3.1.7.2).

7.3.3.7 Return the sample train to ambient pressure (Sections 7.3.2.7 and 7.3.2.8) and disconnect the sample and vacuum lines from the bag and container to prepare the train for the next sample.

7.3.3.8 If the post-test leak check proves invalid, discard the invalid sample. Attach a new Tedlar® bag, evacuate and leak check the bag, and repeat the sample collection.

7.4 Preparation for Sample Collection

7.4.1 Perform the pretest leak checks outlined in Section 7.3.

7.4.2 Remove the seal from the end of the probe and insert the probe into the stack to the point of average velocity and temperature and constant flow.

7.4.3 Purge the sampling train (probe, valve, and filter assembly ONLY) using the following procedures:

1. Cap the inlet side of the charcoal purge trap connected to the probe isolation valve tee using a 1/4 in. cap and plug with Teflon® ferrules for an air-tight seal (Figure 2).

2. Disconnect the vacuum line quick connect from the rigid bag container (the quick connect has a valve to seal the line).

3. Disconnect the return line connected to the bag isolation valve from the quick connect at the vacuum line tee (Figure 2).

4. Connect the purge line from the probe isolation valve tee to the vacuum line tee using the quick connects (Figure 2).

5. Ensure that the bag isolation valve is in position 1 (Figure 4), turn on the pump, and turn the probe isolation valve to position 2 (Figure 4).

6. Draw at least eight times the sample volume of flue gas, or purge for at least 10 minutes, whichever is greater.

NOTE: A three-way valve may be used in place of the purge quick connects at the vacuum line tee.

7.4.4 Adjust the sample flow rate to the desired setting and check all temperature and flow readings during the purge to ensure proper settings.

7.4.5 Purge the sampling train before and between the collection of each sample during the test run.

7.4.6 Label each bag/container and VOA vial clearly, uniquely, and consistently with its corresponding data form and run. Follow appropriate traceability requirements as defined by the regulatory personnel.

7.5 **Sample Collection:** Start sample collection after the pretest leak check (Section 7.3.2) and the system purge (Section 7.4). Collect the sample using proportional rate sampling if the pretest survey measurements (Section 7.1.2.7) show that the emission flow rate varies by more than 20% over the sampling period. Otherwise, use constant rate sampling. Prepare for sample collection for either method by turning the bag isolation valve to position 2 (Figure 4) while the pump is still running from the system purge.

If a viewing port has been incorporated in the bag container design, visually inspect the Tedlar® bag frequently during the sampling run to ensure that it is filling properly and that a sufficient sample volume is collected. This frequent inspection will also help prevent overfilling and bursting the bag during sampling.

7.5.1. Constant Rate Sampling:

1. Place the end of the probe at a point within the duct determined to have the average velocity and temperature and a constant flow rate.

2. Record the start volume from the dry gas meter and begin timing the sample period.

3. Take flue gas velocity and temperature readings using either EPA Method 2A for smaller ducts (<24 inches) with a remote pitot tube and thermocouple or EPA Method 2 for larger ducts (>24 inches). Utilizing a sample probe with pitot tubes and thermocouples attached will generally ease sampling and will provide a direct means to monitor flue gas velocity and temperature at the sample probe inlet.

4. Record all required data upon starting, and at intervals of no more than 5 minutes on the field sampling data form (Figure 7).

5. Adjust the sample flow rate and sampling train heating systems to the correct levels, after every velocity and temperature reading. The tester must closely monitor the sample train and control console to ensure that the sample flow rate does not vary by more than 20% during any 5-minute period.

7.5.2. Proportional Sampling:

1. Position the probe in the center of the stack.

2. Record the start volume from the dry gas meter and begin timing the sample period.

3. Monitor the velocity head during sampling as described in Section 4.1.5 and maintain a constant proportion between the sample flow rate and the flow rate in the duct. The flow rate to be used during sampling (Section 7.2.2) is calculated using the proportional sample rate equation in Section 7.8.4. With this equation and the sample rate assigned to the average flow rate, the rotometer setting can be determined after each velocity reading and the sample rate set accordingly.

4. Record all required data upon starting, and at intervals of no more than 5 minutes on the field sampling data form (Figure 7).

7.5.1.3 Single-Point Sampling: Collect samples from a single point within the duct as described in Sections 7.5.1.1 and 7.5.1.2, unless multipoint sampling has been determined necessary (Section 7.5.1.4).

7.5.1.4 Multipoint Sampling: Perform multipoint integrated sampling only in a case where there is a possibility of effluent stratification. Stratification of gases is less likely than of particulates. If however, multipoint sampling is required, determine the necessary number of sample points in accordance with EPA Methods 1 and 2.

7.6 Post-test Procedures:

7.6.1 Record the final volume from the dry gas meter at the end of each sample collection period.

7.6.2 Perform a post-test leak check as described in Section 7.3.3.

7.6.3 Inspect the field sampling data form (Figure 7) and sample identification labels for accuracy and completeness.

7.6.4 Replace the particulate filter after each sample.

7.6.5 Condensate Recovery: The condensate collected during sampling must be recovered separately for each individual bag sample collected, using the following procedures.

7.6.5.1 Carefully remove the condensate trap, the condenser and the sample line (from the trap to the bag) from the sample train. Pour the contents of the condensate trap into a clean measuring cylinder.

7.6.5.2 Rinse the condenser, the condensate trap and the sample three times with 10 mL of HPLC grade water and add the rinsings to the measuring cylinder containing the condensate. Record the final volume of the condensate and rinse mixture on the field sampling data form (Figure 7). High moisture sources (such as those with wet control devices) may require a 150-mL or 200mL measuring cylinder while low moisture sources (such as some rotary kilns and pyrolytic incinerators) may require only a 100-mL size.

7.6.5.3 Pour the contents of the measuring cylinder into a 20- or 40-mL amber glass VOA vial with a Teflon® septum screw cap. Fill the vial until the liquid level rises above the top of the vial and cap tightly. The vial should contain zero void volume (i.e., no air bubbles). Discard any excess condensate into a separate container for storage and transport for proper disposal.

7.6.5.4 Label each vial by using wrap around labels. Labels can be preprinted or can be filled out on site.

7.7 **Analytical Approach:** The following description provides general guidelines to the analytical approach rather than a comprehensive analytical protocol. The primary analytical tool recommended for the measurement of volatile organic compounds in source emissions is GC/MS using fused-silica capillary GC columns. Prescreening of the sample by gas chromatography with either flame ionization (GC/FID) or electron capture detection (GC/ECD) is recommended because it may not only be cost effective, but will also yield information regarding the complexity and concentration level of the sample. If the smallest feasible injection loop saturates the analytical system, dilutions of the sample can be made into Tedlar® bags using pure N_2 (99.998%) as diluent. Calculate the concentration of the volatile organic compounds in the gaseous emissions by using the equations (14-18) in Section 7.8.10.

7.7.1 **Analysis of gaseous components:** Introduce the gases into the gas chromatograph through the use of a sample loop. Use a cryogenic trap if sample concentration before analysis if necessary.

For most purposes, electron ionization (EI) mass spectra will be collected because a majority of the volatile organic compounds give characteristic EI spectra. Also, EI spectra are compatible with the NIST Library of Mass Spectra and other

mass spectral references, which aid in the identification process for other components in the incinerator process streams.

To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions can be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification. For descriptions of GC conditions, MS conditions, internal standard usage, and quantitative and quantitative identification, refer to the SW-846 Method 8240.

7.7.2 Analysis of condensates: Refer to the SW-846 Method 8240 to analyze condensate samples by using the purge and trap technique or by direct aqueous injection. Use direct solvent injection if an organic phase is present distinct from the aqueous phase. Use dilution as necessary to prevent saturation of the analytical system.

7.8 Calculations:

7.8.1 Carry out all calculations for determining the concentrations and emission rates of the target compounds. Round off figures after final calculations to three significant figures.

7.8.2 Nomenclature

A = Stack/source cross sectional area, m^2 (ft^2)

A_B = Amount of volatile organic compound in bag (ng)

A_c = Amount of volatile organic compound in condensate (ng)

A_{vol} = Amount of volatile organic compound in analytical sample (ng)

A_T = Total amount of volatile organic compound (ng), $A_B + A_C$

B_{ws} = Water vapor in the gas stream, proportion by volume (x 100 = % H_2O)

C_p = Type S pitot tube coefficient (nominally 0.84 $\pm$ 0.02), dimensionless.

$C_{Emission}$ = Concentration of volatile organic compound in emissions (ng/mL)

C_{vol} = Concentration of volatile organic compound per volume sampled (ng/mL)

C_{spike} = Concentration of spiking standard in the Tedlar® bag (ng/mL or μg/L)

C_{stock} = Concentration of spike standard in the stack/audit cylinder.

$DV_{eff(std)}$ = Volumetric flow rate of exhaust gas, L/min, ft^3/m.

K_p = Pitot tube constant,

$$34.97\,\text{m/sec}\left[\frac{(\frac{g}{gmole})(mmHg)}{(K)(mmH_2O)}\right]^{1/2}$$

$$85.49\,\text{ft/sec}\left[\frac{(\frac{lb}{lbmole})(inHg)}{(^{o}R)(inH_2O)}\right]^{1/2}$$

L_a = Maximum acceptable leakage rate for a leak check, either pretest or following a component change; equal to 0.00057 L (0.02 ft^3/min) or 4% of the average sampling rate, whichever is less.

LDL_{vol} = Lower detectable amount of volatile organic compound in entire sampling train.

L_i = Individual leakage rate observed during the leak check conducted before to the "i^{th}" component change (i = 1, 2, 3...n) L/min.

L_p = Leakage rate observed during the post-test leak check, L/min.

Max $Mass_{vol}$ = Maximum allowable mass flow rate (g/hr [lb/hr]) of volatile organic compound emitted from the combustion source.

Max $Conc_{vol}$ = Maximum anticipated concentration of the volatile organic compound in the exhaust gas stream, g/m^3 (lb ft^3).

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_{fd} = Dry mole fraction of the flue gas.

M_s = Wet molecular weight of the flue gas.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_g = Flue gas static pressure, mm H_2O (in. H_2O).

P_k = Specific gravity of mercury (13.6)

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

Q_m = Average sampling rate, L/min.

Q_s = Calculated sampling rate, L/min.

Q_{sd} = Volumetric air flow rate, (L/min, ft^3/min).

R	=	Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).
T_m	=	Absolute average dry gas meter temperature, K (°R).
T_s	=	Absolute average stack gas temperature, K (°R).
T_{std}	=	Standard absolute temperature, 293K (528°R).
V_A	=	Analytical sample volume (mL).
V_B	=	Bag volume (mL).
V_i	=	Concentration of volatile organic compound (wt %) introduced into the combustion process.
V_i conc	=	Anticipated concentration of the volatile organic compound in the exhaust gas stream, g/L (lb/ft^3).
V_{lc}	=	Total volume of liquid collected in the condensate knockout trap.
V_m	=	Volume of gas sample as measured by dry gas meter, L.
$V_{m(std)}$	=	Volume of gas sample measured by dry gas meter, corrected to standard conditions, L.
V_{spike}	=	Volume of gaseous or liquid spiking standard (mL)
V_{TBC}	=	Minimum dry standard volume to be collected at dry gas meter.
V_T	=	Train sample volume (mL)
$V_{w(std)}$	=	Volume of water vapor in the gas sample, corrected to standard conditions, L (ft^3).
V_s	=	Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).
WF	=	Mass flow rate of waste feed per hour, g/hr (lb/hr).
γ	=	Dry gas meter calibration factor, dimensionless.

ΔH = Average pressure differential of orifice meter, inches H_2O.

ΔP = Actual velocity pressure, mm (in.) H_2O.

ΔP_{avg} = Average velocity pressure, mm (in.) H_2O.

ρw = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_1 = Sampling time interval from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

60 = Second/minute conversion.

100 = Conversion to percent.

7.8.3 Conversion Factors:

From	To	Multiply by
ft^3	L	0.02832

7.8.4 Proportional Sample Rate Calculation. The flow rate to be used during sampling when the velocity head varies from the average is calculated using the following equation.

$$Q_s = Q_m \frac{\sqrt{\Delta P}}{\sqrt{\Delta P_{Avg}}} \quad (1)$$

7.8.5 Dry Gas Volume: Correct the sample measured by the dry gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using the following equation:

$$V_{m(std)} = V_m \gamma \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}} = K_1 V_m \gamma \frac{P_{bar} + \Delta H/13.6}{T_m} \qquad (2)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or

K_1 = 17.64°R/in. Hg for English units.

Equation 2 can be used as written, unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted before component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 2 must be modified as follows (with the approval of the appropriate regulatory personnel):

a. Case I (no component change made during sampling run): Replace V_m in Equation 2 with the expression:

$$V_m - [(L_p - L_a)]\,\theta$$

b. Case II (one or more component changes made during the sampling run): Replace V_m in Equation 2 with the expression:

$$V_m - \left[\sum_{i=1}^{n} (L_i - L_a)\theta_1\right] - (L_p - L_a)\theta_p$$

and substitute only for those leakage rates (L_i or L_p) that exceed L_a.

7.8.6 Volume of Water Vapor:

$$V_{w(std)} = V_{lc} \frac{\rho_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \quad (3)$$

where:

K_2 = 0.001333 m^3/mL for metric units, or

K_2 = 0.04707 ft^3/mL for English units.

7.8.7 Moisture Content:

$$B_{ws} = \frac{V_{w\ (std)}}{V_{m\ (std)} + V_{w\ (std)}} \quad (4)$$

7.8.8 Volumetric Flow Rate Equations:

7.8.8.1 Static Pressure

$$P_s = P_{Bar} + \left[\frac{P_g}{P_k}\right] \quad (5)$$

7.8.8.2 Dry Molecular Weight

$$M_d = (\%\ CO_2 \times 0.44) + (\%\ O_2 \times 0.32) + [(\%\ CO + \%\ N_2) \times 0.28] \quad (6)$$

7.8.8.3 Dry Mole Fraction

$$M_{fd} = 1 - B_{ws} \quad (7)$$

7.8.8.4 Wet Molecular Weight

$$M_s = (M_d \times M_{fd}) + (18 \times B_{ws}) \quad (8)$$

7.8.8.5 Flue Gas Velocity

$$V_s = k_p C_p \left(\sqrt{\Delta \bar{P}}\right)_{avg} \left[\frac{\sqrt{T_{s(avg)}}}{M_s P_s}\right] \quad (9)$$

7.8.8.6 Volumetric Flow Rate

$$DV_{eff(std)} = 60 V_s M_{fd} A \left[\frac{T_{std}}{T_{s(avg)}}\right] \times \left[\frac{P_s}{P_{std}}\right] \quad (10)$$

7.8.9 Concentration of a volatile organic compound in the gaseous emissions of a combustion process:

7.8.9.1 Divide the amount of volatile organic compound determined through analysis by the volume of sample introduced into the analytical system to obtain concentration of the volatile organic compound in the bag or the condensate.

$$C_{vol} = \frac{A_{vol}}{V_A} \quad (11)$$

7.8.9.2 Multiply the concentration of the volatile organic compound (ng/mL) by the sample volume (bag or condensate) to determine the amount of the volatile organic compound in the bag or condensate.

$$A_B = C_{vol} \times V_B \quad (12)$$

or

$$A_C = C_{vol} \times V_{lc} \quad (13)$$

7.8.9.3 Sum the amount of volatile organic compound found in all samples associated with a single train.

$$A_T = A_B + A_C \quad (14)$$

7.8.9.4 Divide the total amount found by the volume of stack gas sampled to determine the concentration of the volatile organic compound in the gaseous emissions.

$$\frac{A_T}{V_T} = C_{Emission} \quad (15)$$

7.8.10 Concentration of the spiking standard in the Tedlar® bag:

$$C_{spike} = \frac{V_{spike} \times C_{stock}}{V_B} \quad (16)$$

7.8.11 Recovery of the spiking standard from the Tedlar® bag sample:

$$\% \text{ Recovery} = \frac{C_{vol}}{C_{spike}} \times 100 \quad (17)$$

8.0 QUALITY CONTROL

8.1 Quality Assurnace/Quality Control Requirements Before Sampling

8.1.1 Pitot Tube Probe: Before sampling, assemble and calibrate the pitot tube probe (described in Section 4.2.11) in accordance with the EPA Method 2. Leak check to ± 10 in. H_2O. The pitot tube assembly must be leak free (0.00 in. H_2O in 1 minute).

8.1.2 Pressure Gauge (Manometer): Calibrate the pressure gauge (described in Section 4.2.12) in accordance with the EPA Method 2. Leak check the pitot tubes, pressure gauge, and pitot tube lines simultaneously, as a unit, before the velocity traverse.

8.1.3 Thermocouple and Temperature Readout Device: Calibrate these devices (desribed in Section 4.2.10.6) within 30 days of sampling and in accordance with the EPA Method 2. The thermocouple and temperature read out must be accurate to ± 1°C (± 2°F).

8.1.4 Metering System: Calibrate the dry gas meter contained in the control console in accordance with the procedures outlined in Section 5.3 of EPA Method 5. Calibrate the meter at a flow rate appropriate for the sampling rate used during the test.

8.1.5 Probe Heater: Calibrate the probe heater before sampling collection following procedures outlined in Section 5.5 of EPA Method 5.

8.1.6 Barometer: Adjust the barometer daily and before each test series to ± 0.1 in. (25 mm) Hg of the corrected barometric pressure reported by a National Weather Service Station located nearby and at the same altitude above sea level.

8.2 Number of Sampling Runs: The number of sampling runs to be performed shall be determined by the appropriate regulatory personnel. At least two runs (two hours of stack sampling time) are recommended for each test series to provide minimal statistical data.

Ensure that all compounds on the analyte list have been validated for this method prior to sampling. Perform validation as required in accordance with the EPA Method 301.[6]

8.3 Blanks and Field Spikes: Field, trip and laboratory blanks, contamination checks and field spiked samples are required to monitor the performance of the sampling method and to provide the required information to take corrective action if problems are observed in the laboratory operations or in field sampling activities.

8.3.1 Field blanks: Take at least one field blank sample daily and per source. Collect high purity air or N_2 (99.998%) from a compressed gas cylinder in the same manner as source emissions. Draw the air or nitrogen gas through the sampling system and into the bag. Field blank samples shall consist of the condensate and a bag sample. Transport and analyze this blank sample along with the stack gas samples. When the field bland values are greater than 20% of the stack values, flag the data. Report the field blank values with the stack gas results.

8.3.2 Trip Blanks: Take at least two Tedlar® bags labeled "trip blanks" and filled with an inert gas to the sampling site. These bags will be treated like any other samples except that they will not be opened during storage at the site. These bags will be subsequently analyzed to monitor potential contamination which may occur during storage and shipment.

8.3.3 Laboratory Blanks: Leave two Tedlar® bags labeled "laboratory blanks: in the laboratory using the method of storage that is used for field samples. If the field and trip blanks contain high concentrations of contaminants (i.e., greater than five times the detection limit of particular analyte), the laboratory blank shall be analyzed to identify the source of contamination.

8.3.4. Tedlar® Bag Contamination Checks: The use of new bags for each test series is recommended. All bags must be cleaned and checked for contamination before being used for sampling (Section 6.1.3).

8.3.5. Field Spike Samples: Take at least one field spike sample per 10 field samples, or a minimum number of one field spike per test. Spike the chosen bag sample with a known mixture (gaseous or liquid) of all the target pollutants using either gaseous or liquid injection into the bag. Transport and analyze the spiked sample with the stack gas samples. Report the spike sample recoveries with the source test results. The compound recoveries in the spiked sample must be greater than 80% and less than 120%. Use Equation 17 in Section 7.8.11 to calculate spiking compound recovery.

The spiking level should be at least the level anticipated in the emissions matrix. Use Equation 16 in Section 7.8.10 to calculate the spiking level. The syringe volume for the gaseous injection should not exceed 200 mL to minimize leakage through the septum after injection. For liquid injections, the volume injected must not exceed 1 mL to ensure complete volatilization. The final volume of the spiked gas must not exceed 1% of the total sample volume. Use the ideal gas equation to calculate the volume of gas generated by a liquid injection into the bag.

8.3.5.1 Procedure for the Injection of Gaseous or Liquid Standards:

1. Obtain spiking stock that is sufficiently concentrated to spike a Tedlar® sample without exceeding 1% volume limit. Select appropriate analyzes, analyte homologs, or isotopically labeled analogs in cylinders or SUMMA® canisters for gaseous injections or neat liquids or methanol solutions for liquid injections.

2. Install an injection port that consists of a Swagelok® tee fitting with a septum, in the sample line just before the 1/4-in. quick connector on the Tedlar® bag (Figure 2). Locate this port as close the bag as possible to minimize wall effects. Use a new septum for each sampling run that involves spiking.

3. Perform a leak test as described in Section 7.3 with the injection port in line.

4. Start sampling the stack as described in Sections 7.4 and 7.5.

5. In preparation for injection, clean the syringe by flushing three times with an inert gas (high purity N_2, 99.998%) for gaseous injections, or with methanol for liquid injections. Then flush the syringe three times with the gaseous or liquid spiking standard.

6. After half an hour of sample collection, take up the desired volume of the spiking standard into the syringe (for gases, allow

the standard to equilibrate to atmospheric pressure) and inject it through the septum into the bag without interruping the sampoing procedure. All apparatus upstream of the bag should be under slight negative pressure.

8.4 Performance Audits: Conduct performance audits to evaluate quantitatively the quality of data produced by the total measurement system (sample collection, sample analysis, and data processing). Accuracy (% recovery) must be greater than 50% and less than 150 percent. Precision (% relative standard deviation) must be less than 50 percent. Better performance must be achieved routinely.

9.0 METHOD PERFORMANCE

9.1 Method Performance Evaluation: Evaluation of analytical procedures for a selected series of compounds shall include the sample preparation procedures and each associated analytical determination. Challenge the analytical procedures by spiking the test compounds at appropriate levels carried through the procedures.

9.2 Method Detection Limit: Determine the overall method detection limits (lower and upper) on a compound-by-compound basis according to the 40 CFR Part 136b for the determination of the detection limit.[7] Different compounds may exhibit different collection efficiencies as well as instrumental minimum detection limit.

9.3 Method Precision and Bias: Determine the overall method precision and bias (in accordance with the EPA Method 301[6]) on a compound-by-compound basis at a given concentration level. Include in the method precision value a combined variability due to sampling and instrumental analysis. The method bias is dependent upon the collection efficiency of the train components.

No evaluation and validation data are available for this method.

10.0 REFERENCES

1. Howe, G.B., B.A. Pate, and R.K.M. Jayanty, "Stability of Volatile Principal Organic Hazardous Constituents (POHCs) in Tedlar® Bags," Research Triangle Institute Report to the EPA, Contract No. 68-02-4550, 1991.

2. Andino, J.M., and J. W. Butler, "A Study of the Stability of Methanol-Fueled Vehicle Emissions in Tedlar® Bags", *Environ. Sci. Technol.* 1991, 25(9), 1644-1646.

3. Posner, J.C., and W.J. Woodfin, "Sampling with Gas Bags I: Loses of Analyte with Time," Appendix L Industrial Hygiene, 1986, (4), 163-168.

4. Seila, R.L., W.A. Lonneman, and S.A. Meeks, "Evaluation of Polyvinyl Fluoride as a Container Material for Air Pollution Samples," J.Environ. Sci. Health., 1976, 2, 121-130.

5. U.S. Environmental Protection Agency, Hazardous Waste Incineration Measurement Guidance Manual, Volume III of the Hazardous Waste Incineration Guidence Series, EPA/625/6-89/021, p5.

6. U.S. Environmental Protection Agency, Method 301, "Protocol for the Field Validation of Emission Concentrations from Stationary sources", EPA 450/4-90-015, February 1991.

7. U.S. Environmental Protection Agency, 40 CFR Part 136, Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit".

11.0 BIBLIOGRAPHY

Test Methods for Evaluating Solid Waste, 3rd ed., SW-846. U.S. Environmental Protection Agency. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, D.C., 1987.

U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Methods 1, 2, 3, 4, 5, 18 and 25.

Table 1

Compounds For Which Applicability of the Method Has Been Demonstrated

Compound	CAS No.	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Instrument Detection Limit[a] (ppm)
Dichlorodifluoromethane	75718	-30	Gas	0.20
Vinyl chloride	75014	-19	Gas	0.11
1,3-Butadiene	106990	-4	Gas	0.90
1,2-Dichlor-1,1,2,2-tetrafluoroethane	76142	4	Gas	0.14
Methyl bromide	74839	4	Gas	0.14
Trichlorofluoromethane	353548	24	88	0.18
Vinylidene chloride	75354	31	22	0.07
Methylene chloride	75092	40	44	0.05
1,1,2-Trichlorotrifluoroethane	76131	48	37	0.13
Chloroform	67663	61	21	0.04
1,1,1-Trichloroethane	71556	75	13	0.03
Carbon tetrachloride	56235	77	11	0.03
Benzene	71432	80	10	0.16
Trichloroethylene	79016	87	8	0.04
1,2-Dichloropropane	78875	96	5	0.05
Toluene	108883	111	3	0.08
Tetrachloroethylene	127184	121	2	0.03

[a]Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits

Table 2

Problems That Can Invalidate Tedlar® Bag Sampling Data and Suggested Remedies

	Problem	Remedy
1.	Condensation of the gases or water vapor in the bag	Sample below the condensation point of the analytes; lower the temperature in the condensate trap.
2.	Leaks developing in the bag during testing, transport, and/or analysis	Use double sealed bags; perform additional sampling runs; protect the bags from sharp objects by sampling and shipping in rigid, opaque containers; ship the bags in the same containers used during sampling.
3.	Hydrocarbon contamination	Minimize exposure of the bag to heat and direct light, by sampling and shipping in rigid, opaque containers; purge the bags with ultrapure N_2 in the laboratory and establish through analysis that the hydrocarbon levels are acceptable; use the bags only once.

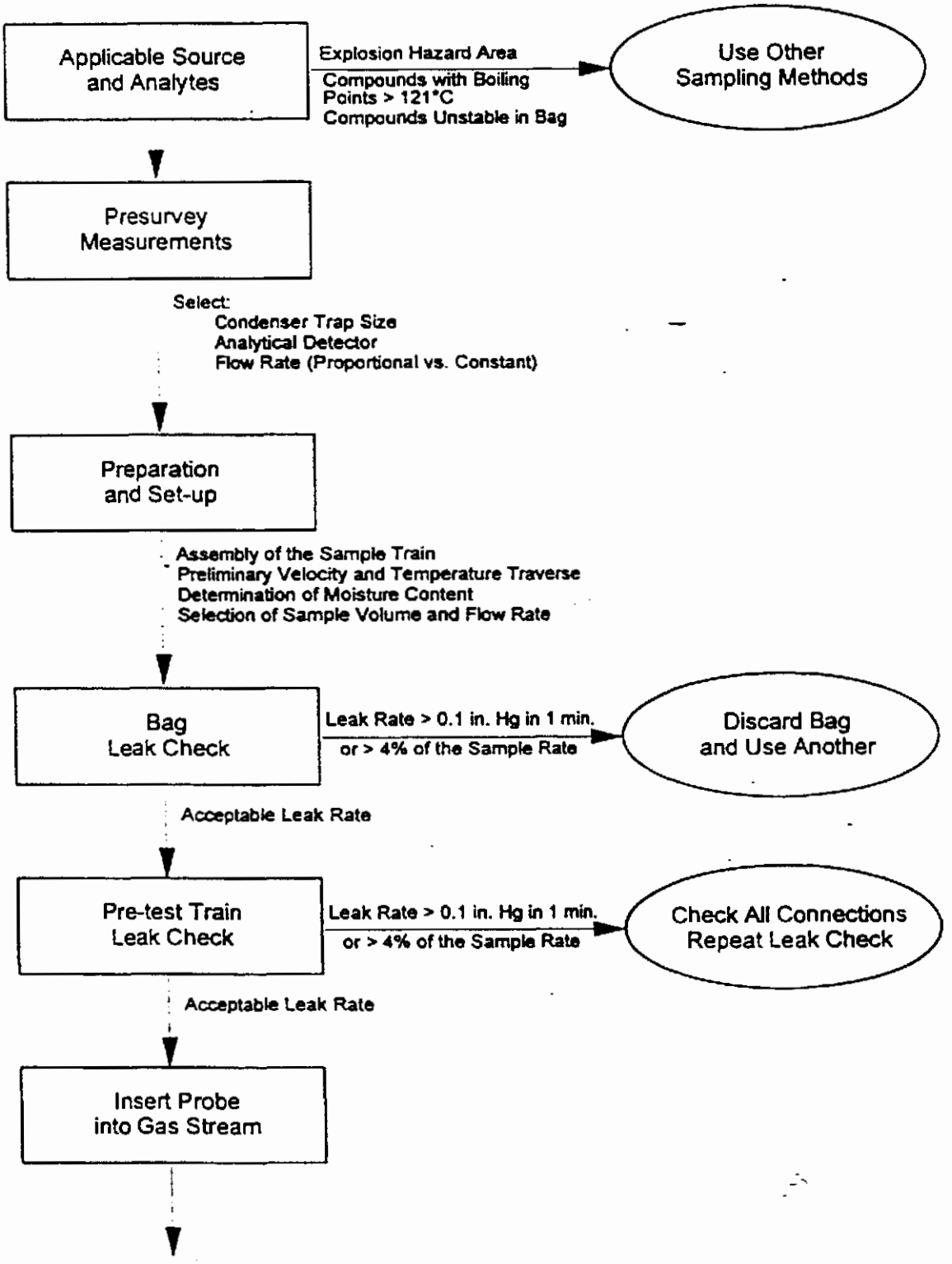


Figure 1. Outline of Method 0040

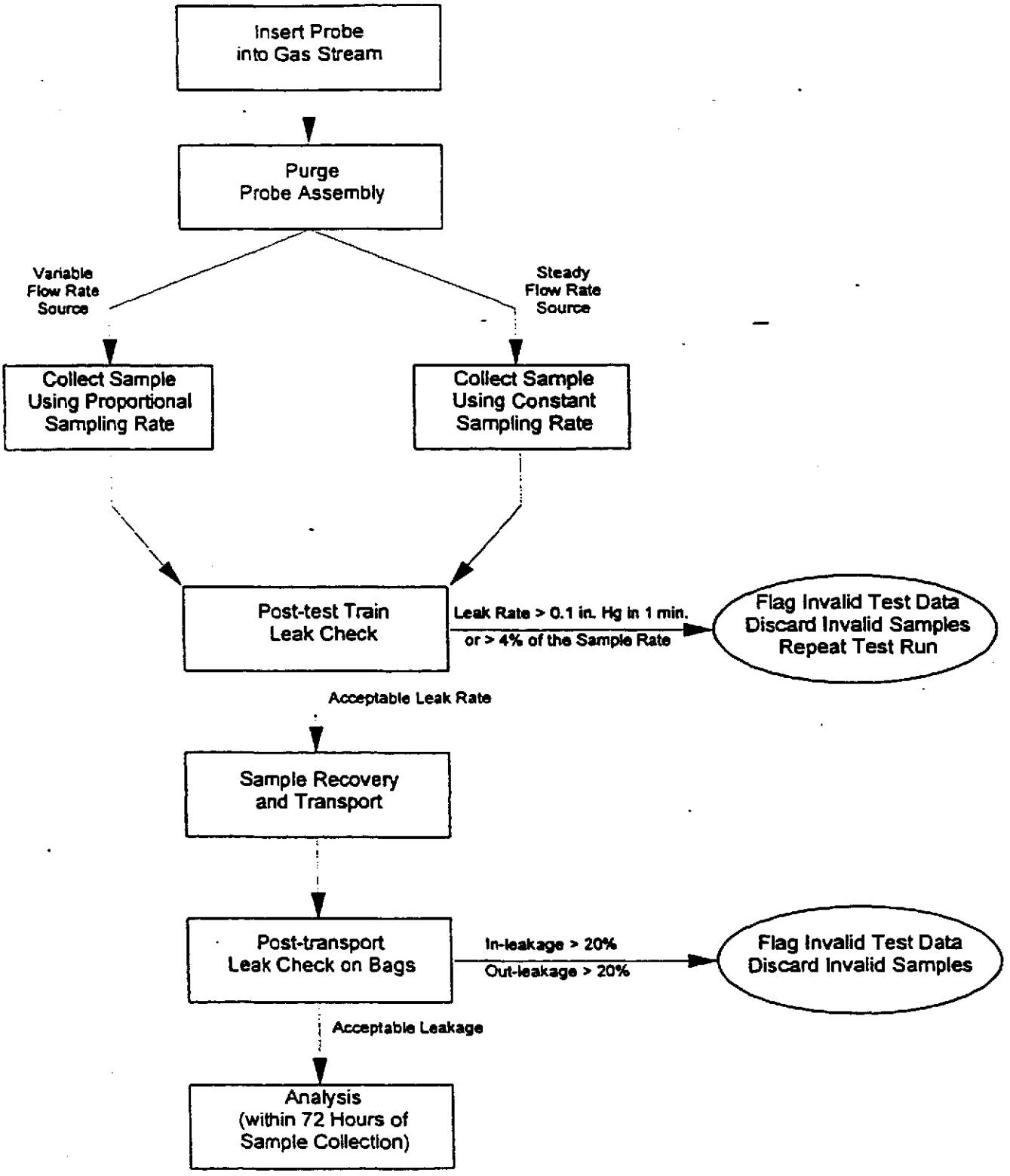


Figure 1. Continued

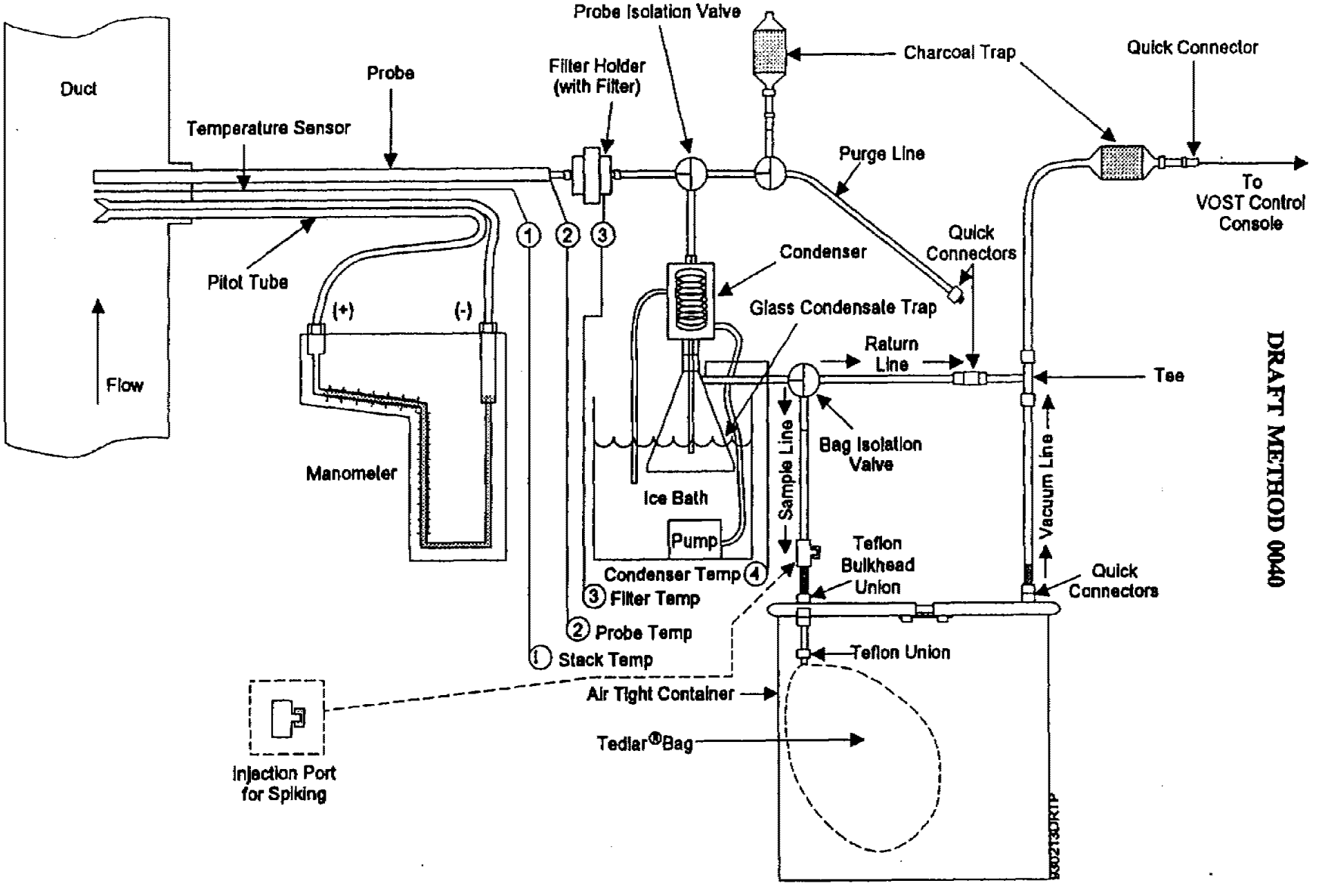
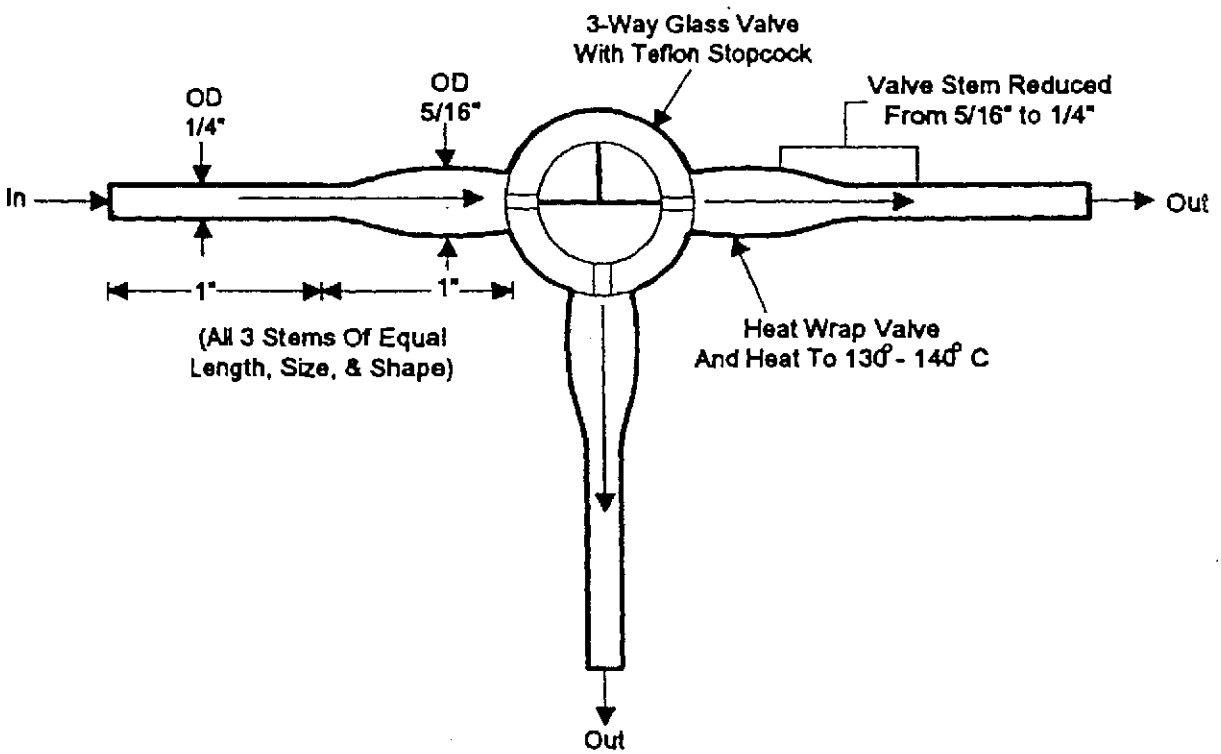
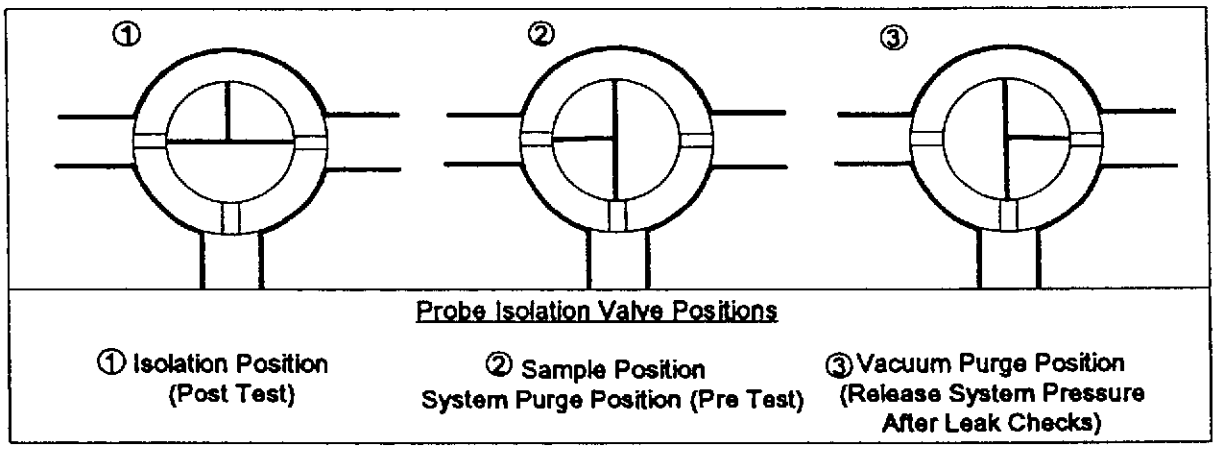


Figure 2. Schematic of the Method 0040 Sampling Train



950049-LN-DRTP

Figure 3. Isolation Valve Design



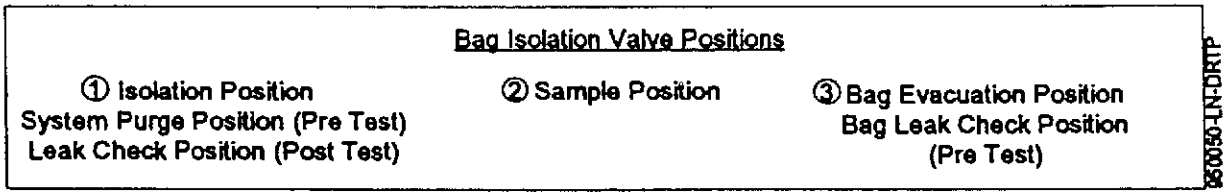


Figure 4. Valve Operation

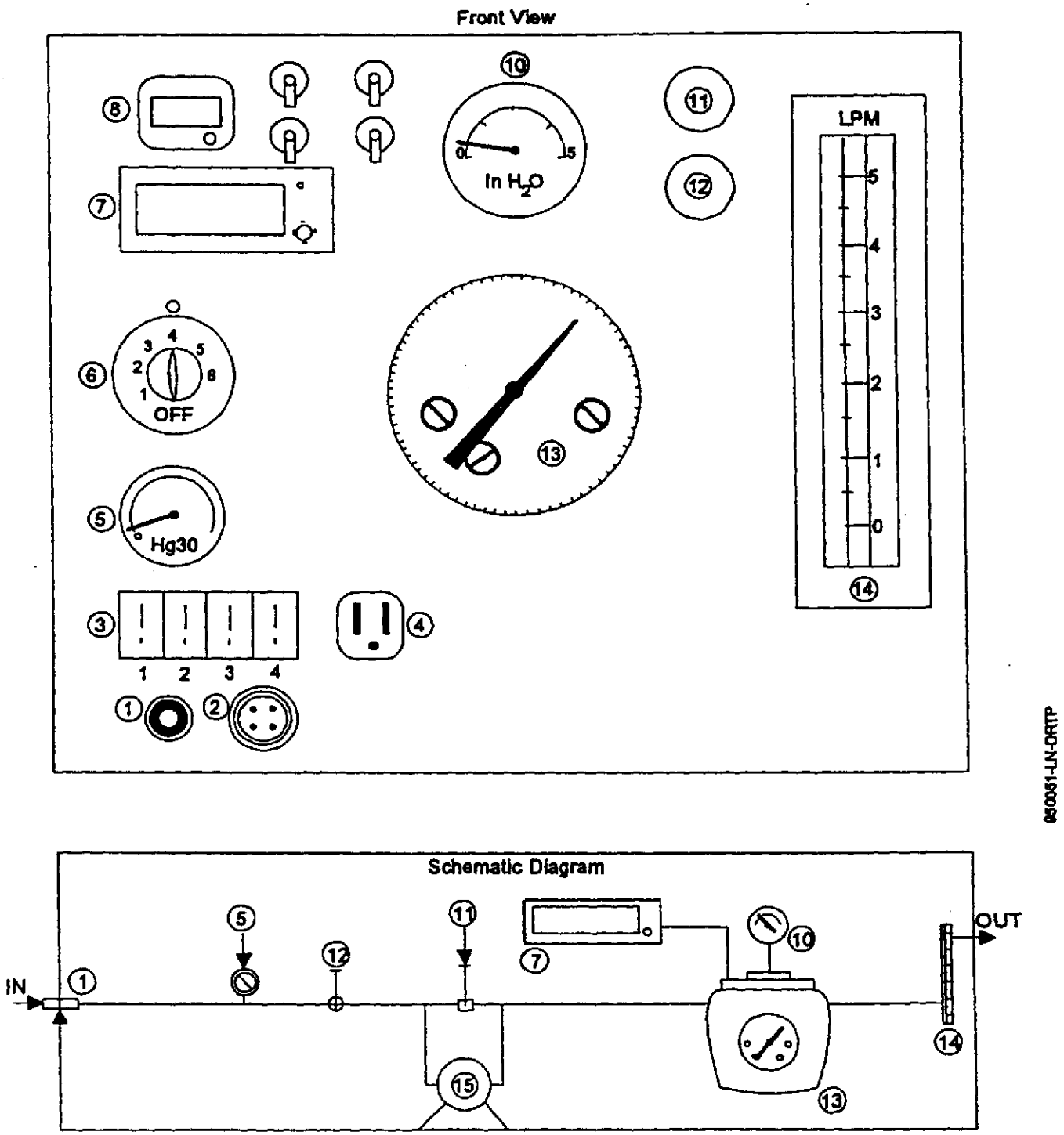


Figure 5. Diagram of a Control Console

Control Console Components

1. 1/4 in. S.S. Quick Connect - Vacuum line inlet from sample train (to bag container).

2. Amphenol Receptacle - provides power through umbilical to probe heat & water pump.

3. Thermocouple Receptacles - 4 thermocouple inlets for:
   1. Stack Temperature
   2. Probe Temperature
   3. Condenser Temperature
   4. Ambient Temperature

4. 110 VAC Receptacle - auxiliary power for isolation valve heat.

5. Vacuum Gauge - 0-30 in. Hg.

6. Heat Controller

7. Digital Thermocouple Read Out - 10 channel (displays temperature readings during sampling)
   - (1-4 remote as listed above)
   - (5 dry gas meter temperature)
   - (6-10 spares)

8. Timer (optional)

9. Power Switches - control (on/off)
   1. Main power - with separate switches for each.
   2. Sample pump
   3. Water pump
   4. Timer

10. Meter pressure Gauge - (inches water column)

11. Fine Adjustment (Bypass) Valve

12. Coarse Adjustment (on/off) Valve

13. Dry Gas Meter

14. Rotometer (Flow Meter)

15. Charcoal Trap (Optional)

Figure 5. Continued

1. Name of Company _____ Date _____
   Address _____
   _____
   _____
   Contacts _____ Phone _____

   Process to be sampled _____
   _____
   Duct or vent to be sampled _____
   _____
II. Process description _____
   _____
   Raw Material _____
   _____
   Products _____
   _____

   Operating cycle
   Check: Batch _____ Continuous _____ Cyclic _____
   Timing of batch or cycle _____
   Best time to test _____
III. Sampling site
   A. Description
   Site description _____
   Duct shape and size _____
   Materials _____
   Wall thickness _____ inches
   Upstream distance _____ inches _____ diameter
   Downstream distance _____ inches _____ diameter
   Size of port _____

Figure 6. Pretest Survey Data Form

Temperature _____ °C Data Source _____

Velocity _____ Data Source _____

Static pressure _____ inches H_2O Data Source _____

Moisture content _____ % Data Source _____

Particulate content _____ Data Source _____

Gaseous components

N_2	_____ %	Hydrocarbons	_____ ppm
O_2	_____ %	_____	_____ ppm
CO	_____ %	_____	_____ ppm
CO_2	_____ %	_____	_____ ppm
SO_2	_____ %	_____	_____ ppm

Hydrocarbon components

_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm
_____	_____ ppm

C. Sampling considerations

Location to set up GC _____

Power available at duct _____

Plant entry requirements _____

Security agreements _____

Potential problems _____

Site diagrams (Attach additional sheets if required).

Figure 6. Continued

Plant		Dilution system: (dynamic)	
City		emission flowsetting	
Operator		diluent flowsetting	(in.) Hg
Date		Dilution system: (statis)	
Run Number		emission flowsetting	
Stack dia. (in.)		Final leak check	(cfm)
Sample box number		Vacuum during leak check	(in. H_2O)
Pitot tube (C_p)		Sampling point location	
Static press	(in.) H_2O	Total concensate volume	mL
Flowmeter calib (Y)		VOA vial size	mL
Average (ΔP)	in. H_2O	VOA vial number	
Initial flowmeter setting	liters	Tedlar® bag volume	liters
Average stack temp	°C	Container volume	liters
Barometric pressure		Container number	

Figure 7. Field Sampling Data Form

Appendix F

SW-846, Method 0010

Modified Method 5 Sampling Train

(This is the latest version of Method 0010 from SW-846. The final version of the document when released supersedes this one and will be inserted in its place)

METHOD 0010

MODIFIED METHOD 5 SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semivolatile Principal Organic Hazardous Compounds (POHCs) from incineration systems (PHS, 1967). This method also may be used to determine particulate emission rates from stationary sources as per EPA Method 5 (see References at the end of this method).

2.0 SUMMARY OF METHOD

2.1 Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species. Semivolatile species are defined as compounds with boiling points $> 100°C$.

2.2 Comprehensive chemical analyses of the collected sample are conducted to determine the concentration and identity of the organic materials.

3.0 INTERFERENCES

3.1 Oxides of nitrogen (NO_x) are possible interferents in the determination of certain water-soluble compounds such as dioxane, phenol, and urethane; reaction of these compounds with NO_x in the presence of moisture will reduce their concentration. Other possibilities that could result in positive or negative bias are (1) stability of the compounds in methylene chloride, (2) the formation of water-soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water-soluble compounds from aqueous media. Use of two or more ions per compound for qualitative and quantitative analysis can overcome interference at one mass. These concerns should be addressed on a compound-by-compound basis before using this method.

4.0 APPARATUS AND MATERIALS

4.1 Sampling Train:

4.1.1 A schematic of the sampling train used in this method is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment is identical to that used in EPA Method 5 determinations. The new components required are a condenser coil and a sorbent module, which are used to collect semivolatile organic materials that pass through the glass- or quartz-fiber filter in the gas phase.

4.1.2 Construction details for the basic train components are given in APTD-0581 (see Martin, 1971, in Section 13.0, References); commercial models of this equipment are also available. Specifications for the sorbent module are provided in the following subsections. Additionally, the following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

4.1.3 Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (see Rom, 1972, in Section 13.0, References). As correct usage is important in obtaining valid results, all users should refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

4.1.3.1 Probe nozzle: Stainless steel (316) or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design and constructed from seamless tubing (if made of stainless steel). Other construction materials may be considered for particular applications. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Paragraph 9.1.

4.1.3.2 Probe liner: Borosilicate or quartz-glass tubing with a heating system capable of maintaining a gas temperature of 120 ± 14°C (248 ± 25°F) at the exit end during sampling. (The tester may opt to operate the equipment at a temperature lower than that specified.) Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) are considered acceptable. Either borosilicate or quartz-glass probe liners may be used for stack temperatures up to about 480°C (900°F). Quartz liners shall be used for temperatures between 480 and 900°C (900 and 1650°F). [The softening temperature for borosilicate is 820°C

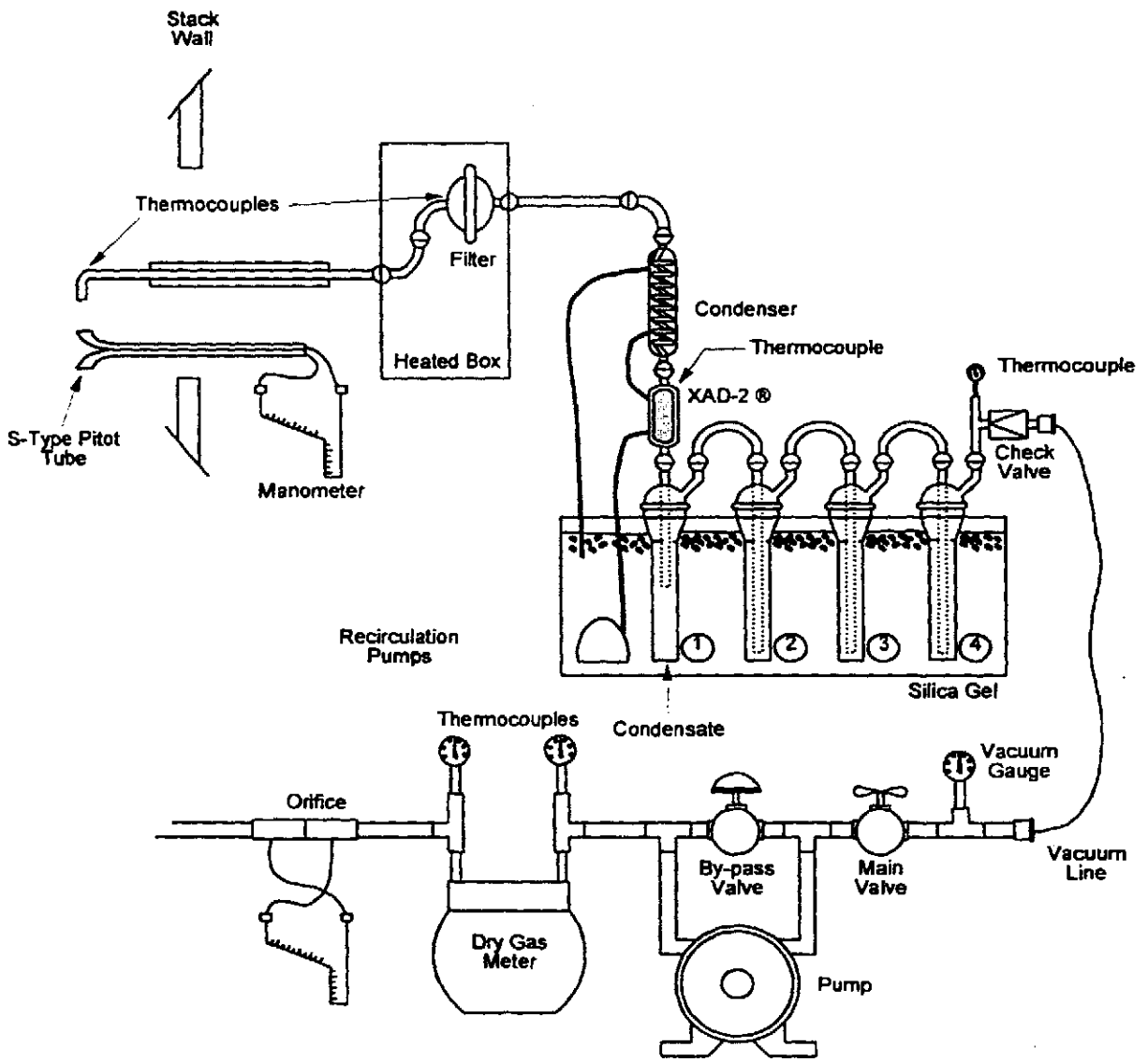


Figure 1. Modified Method 5 Sampling Train

(1508°F), and for quartz 1500°C (2732°F).] Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500°C.

4.1.3.3 Pitot tube: Type S, as described in Section 2.1 of EPA Method 2, or other appropriate devices (Vollaro, 1976). The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.

4.1.3.4 Differential pressure gauge: Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity-head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.3.5 Filter holder: Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of materials that will not introduce organic material into the gas stream at the temperature at which the filter holder will be maintained. The gasket shall be constructed of Teflon® or materials of equal or better characteristics. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

4.1.3.6 Filter heating system: Any heating system capable of maintaining a temperature of 120 ± 14°C (248 ± 25°F) around the filter holder during sampling. Other temperatures may be appropriate for particular applications. Alternatively, the tester may opt to operate the equipment at temperatures other than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

4.1.3.7 Organic sampling module: This unit consists of three sections, including a gas-conditioning section, a sorbent trap, and a condensate knockout trap. The gas-conditioning system shall be capable of conditioning the gas, leaving the back half of the filter holder to a temperature not exceeding 20°C (68°F). The sorbent trap shall be sized to contain approximately 20 g of porous polymeric resin (Rohm and Haas XAD-2 or equivalent) and shall be jacketed to maintain the internal gas temperature at 17 ± 3°C (62.5 ± 5.4°F). The most commonly used coolant is ice water from the impinger ice-water bath, constantly circulated through the outer jacket, using rubber or plastic tubing and

a peristaltic pump. The sorbent trap should be outfitted with a glass well or depression, appropriately sized to accommodate a small thermocouple in the trap for monitoring the gas entry temperature. The condensate knockout trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate formed vertically downward from the conditioning section, through the adsorbent media, and into the condensate knockout trap. The knockout trap is usually similar in appearance to an empty impinger directly underneath the sorbent module; it may be oversized but should have a shortened center stem (at a minimum, one-half the length of the normal impinger stems) to collect a large volume of condensate without bubbling and overflowing into the impinger train. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, Teflon®, or other inert materials. Commercial versions of the complete organic module are not currently available, but may be assembled from commercially available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 2 and 3 (the thermocouple well is shown in Figure 2).

4.1.3.8 Impinger train: To determine the stack-gas moisture content, four 500-mL impingers, connected in series with leak-free ground-glass joints, follow the knockout trap. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (½-in.) I.D. glass tube extending about 1.3 cm (½ in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith Design with the standard tip. The first and second impingers shall contain known quantities of water or appropriate trapping solution. The third shall be empty or charged with a caustic solution, should the stack gas contain hydrochloric acid (HCl). The fourth shall contain a known weight of silica gel or equivalent desiccant.

4.1.3.9 Metering system: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates. Sampling trains using metering systems designed for flow rates higher than those described in APTD-0581 and APTD-0576 may be used, provided that the specifications of this method are met.

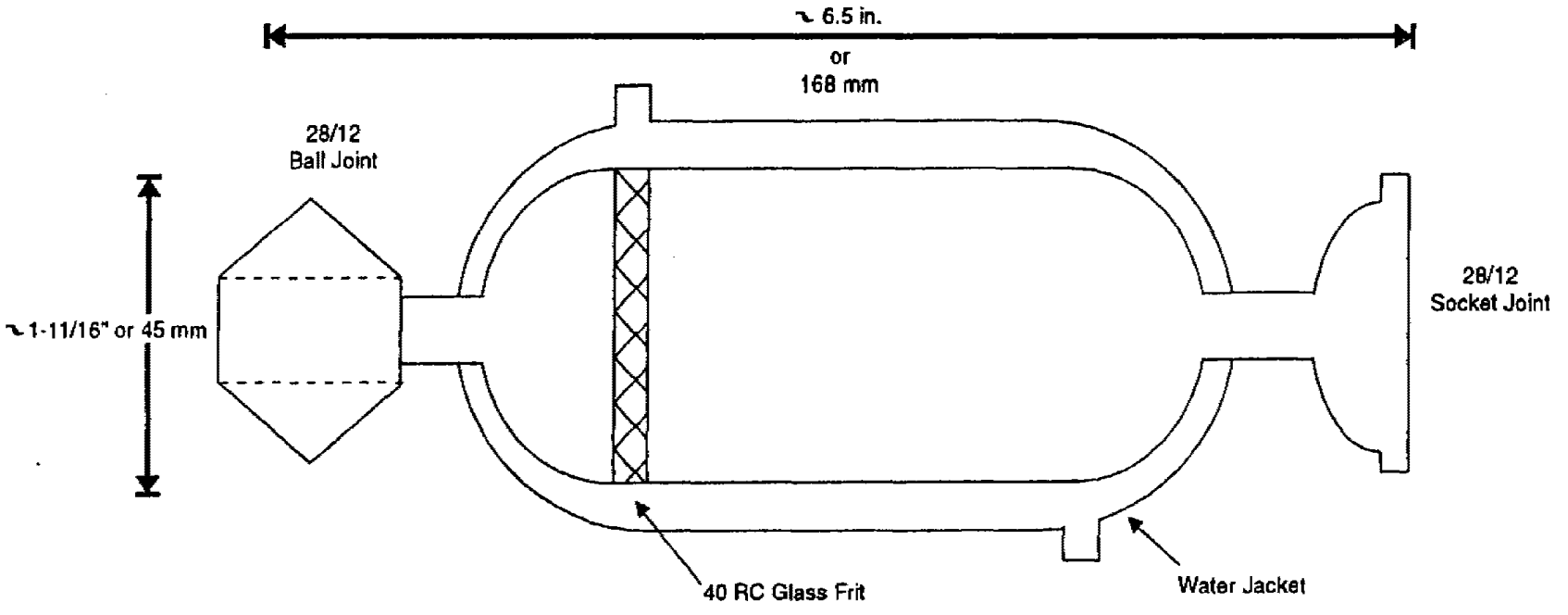


Figure 2. Adsorbent Sampling System

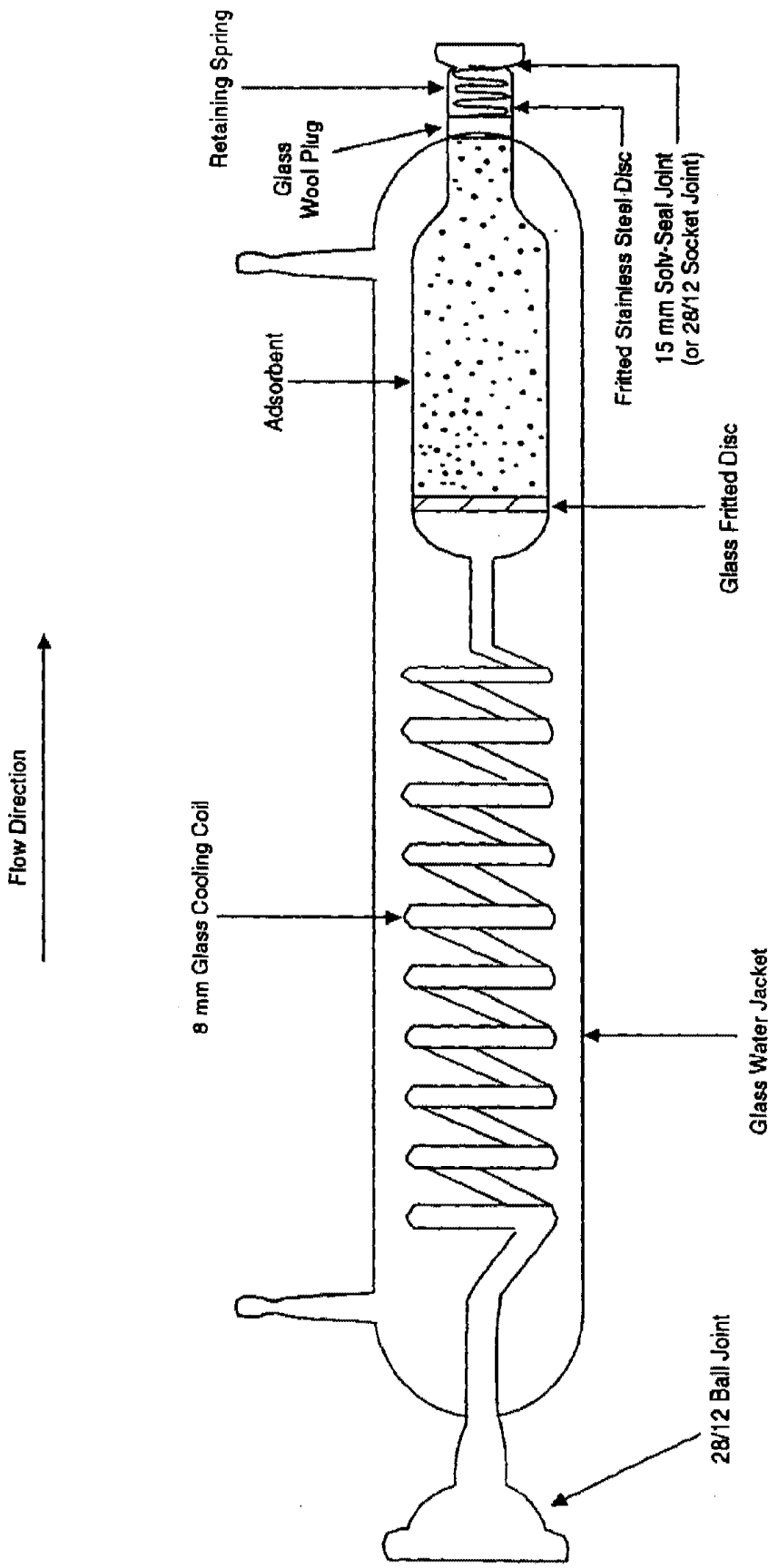


Figure 3. Adsorbent Sampling System

4.1.3.10 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30-m (100 ft) elevation increase (vice versa for elevation decrease).

4.1.3.11 Gas density determination equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2), and gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see EPA Method 2, Figure 2-7). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

4.1.3.12 Calibration/field-preparation record: A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures (i.e., filter and silica gel tare weights, clean XAD-2, quality assurance/quality control check results, dry-gas meter, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

4.2 Sample Recovery:

4.2.1 **Probe liner:** Probe nozzle and organic module conditioning section brushes; nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon®, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the organic module conditioning section.

4.2.2 **Wash bottles:** Three. Teflon® or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

4.2.3 **Glass sample storage containers:** Chemically resistant, borosilicate amber and clear glass bottles, 500-mL or 1,000-mL. Bottles should be tinted to prevent action of light on sample. Screw-cap liners shall be either Teflon® or

constructed so as to be leak-free and resistant to chemical attack by organic recovery solvents. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

4.2.4 Petri dishes: Glass, sealed around the circumference with wide (1-in.) Teflon® tape, for storage and transport of filter samples.

4.2.5 Graduated cylinder and/or balances: To measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory triple-beam balances capable of weighing to ±0.5 g or better are required.

4.2.6 Plastic storage containers: Screw-cap polypropylene or polyethylene containers to store silica gel.

4.2.7 Funnel and rubber policeman: To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

4.2.8 Funnels: Glass, to aid in sample recovery.

4.3 Filters: Glass- or quartz-fiber filters, without organic binder, exhibiting at least 99.95% efficiency (<0.05% penetration) on 0.3-um dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reeve Angel 934 AH or Schleicher and Schwell #3 filters work well under these conditions.

4.4 Crushed Ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending on ambient air temperature.

4.5 Stopcock grease: Solvent-insoluble, heat-stable silicone grease. Use of silicone grease upstream of the module is not permitted, and amounts used on components located downstream of the organic module shall be minimized. Silicone grease usage is not necessary if screw-on connectors and Teflon® sleeves or ground-glass joints are used.

4.6 Glass wool: Used to plug the unfritted end of the sorbent module. The glass-wool fiber should be solvent-extracted with methylene chloride in a Soxhlet extractor for 12 hr and air-dried prior to use.

5.0 REAGENTS

5.1 Adsorbent resin: Porous polymeric resin (XAD-2 or equivalent) is recommended. These resins shall be cleaned prior to their use for sample collection. Appendix A of this method should be consulted to determine appropriate precleaning procedure. For best results, resin used should not exhibit a blank of higher than 4 mg/kg of

total chromatographable organics (TCO) (see Appendix B) prior to use. Once cleaned, resin should be stored in an airtight, wide-mouth amber glass container with a Teflon®-lined cap or placed in one of the glass sorbent modules tightly sealed with Teflon® film and elastic bands. The resin should be used within 4 wk of the preparation.

5.2 Silica gel: Indicating type, 6-16 mesh. If previously used, dry at 175°C (350°F) for 2 hr before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

5.3 Impinger solutions: Distilled organic-free water (Type II) shall be used, unless sampling is intended to quantify a particular inorganic gaseous species. If sampling is intended to quantify the concentration of additional species, the impinger solution of choice shall be subject to Administrator approval. This water should be prescreened for any compounds of interest. One hundred mL will be added to the specified impinger; the third impinger in the train may be charged with a basic solution (1 N sodium hydroxide or sodium acetate) to protect the sampling pump from acidic gases. Sodium acetate should be used when large sample volumes are anticipated because sodium hydroxide will react with carbon dioxide in aqueous media to form sodium carbonate, which may possibly plug the impinger.

5.4 Sample recovery reagents:

5.4.1 **Methylene chloride:** Distilled-in-glass grade is required for sample recovery and cleanup (see Note to 5.4.2 below).

5.4.2 **Methyl alcohol:** Distilled-in-glass grade is required for sample recovery and cleanup.

NOTE: Organic solvents from metal containers may have a high-residue blank and should not be used. Sometimes suppliers transfer solvents from metal to glass bottles; thus blanks shall be run prior to field use and only solvents with low blank value (<0.001%) shall be used.

5.4.3 **Water:** Water (Type II) shall be used for rinsing the organic module and condenser component.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Because of complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

6.2 Laboratory preparation:

6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.

6.2.2 Weigh several 200- to 300-g portions of silica gel in airtight containers to the nearest 0.5 g. Record on each container the total weight of the silica gel plus containers. As an alternative to preweighing the silica gel, it may instead be weighed directly in the impinger or sampling holder just prior to train assembly.

6.2.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass Petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

6.2.4 Desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hr, and weigh at intervals of at least 6 hr to a constant weight (i.e., <0.5-mg change from previous weighing), recording results to the nearest 0.1 mg. During each weighing the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above 50%. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2-3 hr, desiccated for 2 hr, and weighed.

6.3 Preliminary field determinations:

6.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see EPA Method 2, Section 3.1) be performed. Determine the stack-gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack-gas dry molecular weight, as described in EPA Method 2, Section 3.6. If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

6.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of EPA Method 2.)

6.3.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

6.3.4 A minimum of 3 dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHCs from incineration systems. Additional sample volume shall be collected as necessitated by analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Section 10.0.

6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min.

6.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-sample volumes. In these cases, the Administrator's approval must first be obtained.

6.4 Preparation of collection train:

6.4.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon® film or aluminum foil until just prior to assembly or until sampling is about to begin.

6.4.2 Fill the sorbent trap section of the organic module with approximately 20 g of clean adsorbent resin. While filling, ensure that the trap packs uniformly, to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, which will cause clinging to trap walls. This may be minimized by filling the trap in the presence of an antistatic device. Commercial antistatic devices include Model-204 and Model-210 manufactured by the 3M Company, St. Paul, Minnesota.

6.4.3 If an impinger train is used to collect moisture, place 100 mL of water in each of the first two impingers, leave the third impinger empty (or charge with caustic solution, as necessary), and transfer approximately 200-300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

6.4.4 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

6.4.5 When glass liners are used, install the selected nozzle using a Viton-A O-ring when stack temperatures are $<260°C$ (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems utilizing either 316 stainless steel or Teflon® ferrules may be used. When metal liners are used, install the nozzle as above, or by a leak-free direct mechanical connection. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

6.4.6 Set up the train as in Figure 1. During assembly, do not use any silicone grease on ground-glass joints that are located upstream of the organic module. A very light coating of silicone grease may be used on all ground-glass joints that are located downstream of the organic module, but it should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone-grease contamination. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack. The organic module condenser must be maintained at a temperature of 17 ± 3°C. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

6.4.7 Place crushed ice around the impingers and the organic module condensate knockout.

6.4.8 Turn on the sorbent module and condenser coil coolant recirculating pump and begin monitoring the sorbent module gas entry temperature. Ensure proper sorbent module gas entry temperature before proceeding and again before any sampling is initiated. It is extremely important that the XAD-2 resin temperature never exceed 50°C (122°F), because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C (68°F) for efficient capture of the semivolatile species of interest.

6.4.9 Turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize.

6.5 Leak-check procedures

6.5.1 Pre-test leak-check:

6.5.1.1 Because the number of additional intercomponent connections in the Semi-VOST train (over the M5 Train) increases the possibility of leakage, a pre-test leak-check is required.

6.5.1.2 After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton-A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum.
(NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.)

6.5.1.3 If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a

carbon-filled leak-check impinger (shown in Figure 4) to the inlet of the filter holder (cyclone, if applicable) and then plugging the inlet and pulling a 381-mm Hg (15-in. Hg) vacuum. (Again, a lower vacuum may be used, provided that it is not exceeded during the test.) Then, connect the probe to the train and leak-check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 381-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or >0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

6.5.1.4 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with the fine-adjust valve fully open and coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve; this will cause water to back up into the organic module. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

6.5.1.5 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable). When the vacuum drops to 127 mm (5 in.) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed. This prevents the water in the impingers from being forced backward into the organic module and silica gel from being entrained backward into the third impinger.

6.5.2 Leak-checks during sampling run:

6.5.2.1 If, during the sampling run, a component (e.g., filter assembly, impinger, or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Paragraph 6.5.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester shall void the sampling run. (It should be noted that any "correction" of the sample volume by calculation reduces the integrity of the generated pollutant concentration data and must be avoided.)

6.5.2.2 Immediately after a component change, and before sampling is reinitiated, a leak-check similar to a pre-test leak-check must also be conducted.

CROSS SECTIONAL VIEW
Leak Testing Apparatus

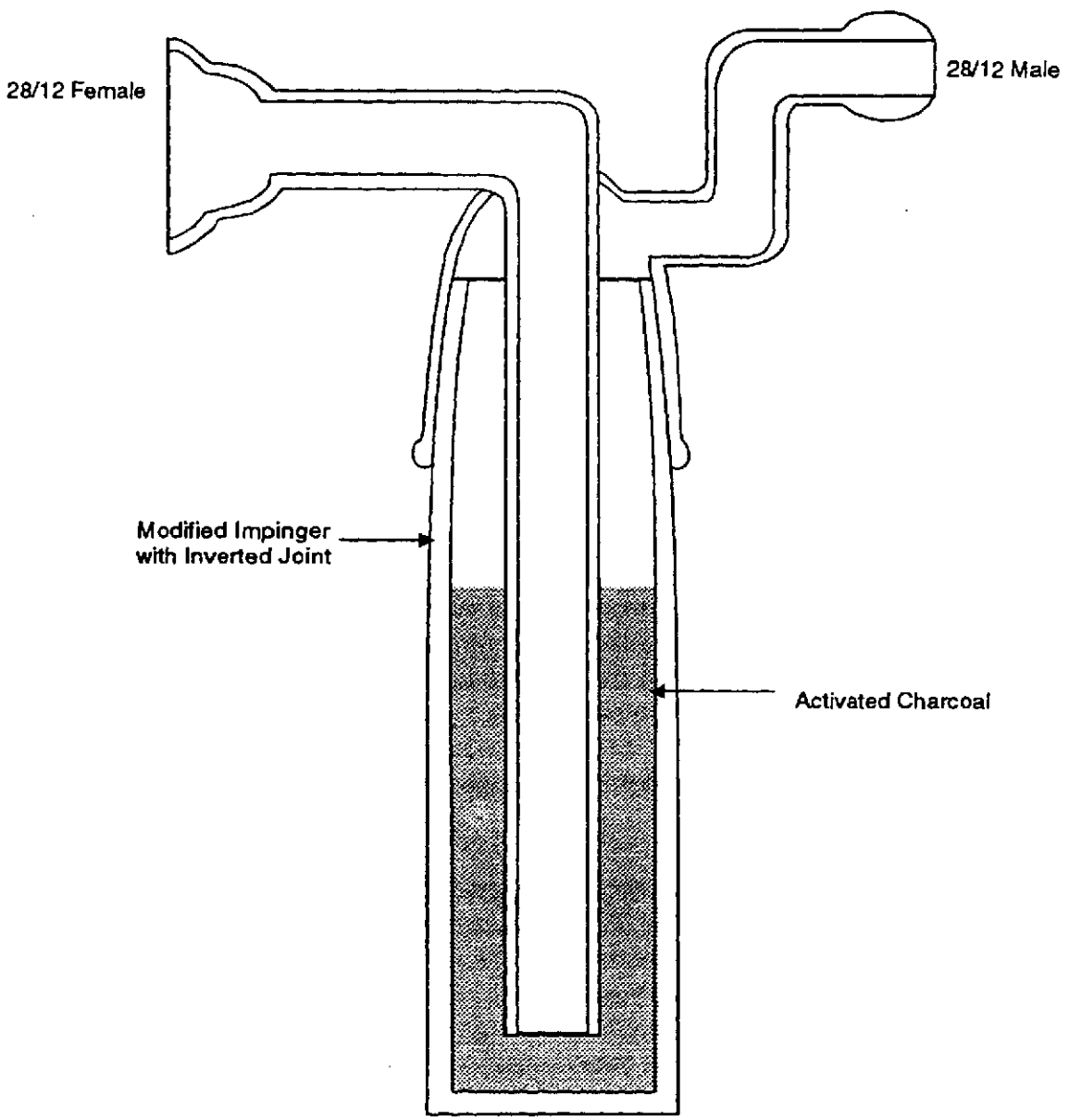


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Figure 4. Leak-check Impinger

6.5.3 Post-test leak-check:

6.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedures as the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate, correct the sample volume (as shown in the calculation section of this method), and consider the data obtained of questionable reliability, or void the sampling run.

6.6 Sampling-train operation:

6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter of 120 ± 14°C (248 ± 25°F) and a gas temperature entering the sorbent trap at a maximum of 20°C (68°F).

6.6.2 For each run, record the data required on a data sheet such as the one shown in Figure 5. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity-head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may draft due to vibrations and temperature changes, make periodic checks during the traverse.

6.6.3 Clean the stack access ports prior to the test run to eliminate the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are at the specified temperature, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot-tube coefficient is 0.84 ± 0.02 and the stack-gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 details the procedure for using the nomographs. If the stack-gas molecular weight and the pitot-tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps (Shigehara, 1974) are taken to compensate for the deviations.

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Plant _____

Location _____

Operator _____

Date _____

Run No. _____

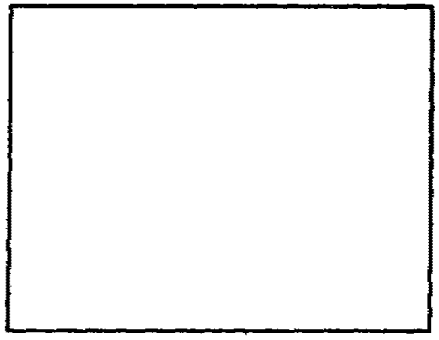
Sample Box No. _____

Meter Box No. _____

Meter H _____

C Factor _____

Pitot Tube Coefficient Cp _____



Schematic of Stack Cross Section

Ambient Temperature _____

Barometric Pressure _____

Assumed Moisture _____

Probe Length, m (ft) _____

Nozzle Identification No. _____

Avg. Calibrated Nozzle Diameter, cm (in) _____

Probe Heater Setting _____

Leak Rate, m /min (cfm) _____

Probe Liner Material _____

Static Pressure _____

Filter No. _____

Traverse Point Number	Sampling Time (θ) min.	Vacuum mm Hg (in. Hg)	Stack Temperature (T_s) °C(F)	Velocity Head (P_s) mm (in) H_2O	Pressure Differential Across Orifice Meter mm (H_2O) in (H_2O)	Gas Sample Volume m_s (ft)	Gas Sample Temp. At Dry Gas Meter		Filter Holder Temperature °C(°F)	Temperature of Gas Entering Sorbent Trap °C(°F)	Temperature of Gas Leaving Condenser or Last Impinger
							Inlet °C(°F)	Outlet °C(°F)			
Total							Avg.	Avg.			
Average											

Figure 5. Particulate Field Data

0010-17

Revision: 0
Date: September 1986

6.6.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack, to prevent water from backing into the organic module. If necessary, the pump may be turned on with the coarse-adjust valve closed.

6.6.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

6.6.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

6.6.7 During the test run, make periodic adjustments to keep the temperature around the filter holder and the organic module at the proper levels; add more ice and, if necessary, salt to maintain a temperature of $<20°C$ (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

6.6.8 If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. Using another complete filter holder/sorbent trap assembly is recommended, rather than attempting to change the filter and resin themselves. After a new filter/sorbent trap assembly is installed, conduct a leak-check. The total particulate weight shall include the summation of all filter assembly catches.

6.6.9 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

6.6.10 Note that when two or more trains are used, separate analysis of the front-half (if applicable) organic-module and impinger (if applicable) catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the front-half catches from the individual trains may be combined (as may the impinger catches), and one analysis of front-half catch and one analysis of impinger catch may be performed.

6.6.11 At the end of the sample run, turn off the coarse-adjust valve, remove

the probe and nozzle from the stack, turn off the pump, record the final dry-gas meter reading, and conduct a post-test leak-check. Also, leak-check the pitot lines as described in EPA Method 2. The lines must pass this leak-check in order to validate the velocity-head data.

6.6.12 Calculate percent isokineticity (see Section 10.8) to determine whether the run was valid or another test run should be made.

7.0 SAMPLE RECOVERY

7.1 Preparation:

7.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the sorbent module.

7.1.2 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

7.1.3 Cap the filter-holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas-conditioning section. Cap all organic module openings. Disconnect the organic-module knockout trap from the impinger train inlet and cap both of these openings. Ground-glass stoppers, Teflon® caps, or caps of other inert materials may be used to seal all openings.

7.1.4 Transfer the probe, the filter, the organic-module components, and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

7.1.5 Save a portion of all washing solutions (methanol/methylene chloride, Type II water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, prelabeled glass sample container.

7.1.6 Inspect the train prior to and during disassembly and note any abnormal conditions.

7.2 Sample containers:

7.2.1 Container no. 1: Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use a pair (or pairs) of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter-holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with 1-in.-wide Teflon® tape around the circumference of the lid.

7.2.2 Container no. 2: Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components first with methanol/methylene chloride (1:1 v/v) into a glass container. Distilled water may also be used. Retain a water and solvent blank and analyze in the same manner as the samples. Perform rinses as follows:

7.2.2.1 Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles, then make a final rinse of the inside surface with the solvent mix. Brush and rinse the inside parts of the Swagelok fitting with the solvent mix in a similar way until no visible particles remain.

7.2.2.2 Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container.

7.2.2.3 Follow the solvent rinse with a probe brush. Hold the probe in an inclined position and squirt solvent into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any solvent and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above-prescribed manner at least six times (metal probes have small crevices in which particulate matter can be entrapped). Rinse the brush with solvent and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe as described above.

7.2.2.4 It is recommended that two people work together to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

7.2.2.5 Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (1:1 v/v) mixture. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that solvent will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

7.2.3 **Container no. 3:** The sorbent trap section of the organic module may be used as a sample transport container, or the spent resin may be transferred to a separate glass bottle for shipment. If the sorbent trap itself is used as the transport container, both ends should be sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon® caps may be used. The sorbent trap should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If a separate bottle is used, the spent resin should be quantitatively transferred from the trap into the clean bottle. Resin that adheres to the walls of the trap should be recovered using a rubber policeman or spatula and added to this bottle.

7.2.4 **Container no. 4:** Measure the volume of condensate collected in the condensate knockout section of the organic module to within $\pm$ 1 mL by using a graduated cylinder or by weighing to within $\pm$ 0.5 g using a triple-beam balance. Record the volume or weight of liquid present, and note any discoloration or film in the liquid catch. Transfer this liquid to a prelabeled glass sample container. Inspect the back half of the filter housing and the gas-conditioning section of the organic module. If condensate is observed, transfer it to a graduated or weighing bottle and measure the volume, as described above. Add this material to the condensate knockout-trap catch.

7.2.5 **Container no. 5:** All sampling train components located between the high-efficiency glass- or quartz-fiber filter and the first wet impinger of the final condenser system (including the heated Teflon® line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/methylene chloride (1:1 v/v) and the rinsings combined. This rinse shall be separated from the condensate. If the spent resin is transferred from the sorbent trap to a separate sample container for transport,

the sorbent trap shall be thoroughly rinsed until all sample-wetted surfaces appear clean. Visible films should be removed by brushing. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to this container.

7.2.6 Container no. 6: Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weight the container and its contents to 0.5 g or better.

7.3 Impinger water:

7.3.1 Make a notation of any color or film in the liquid catch. Measure the liquid in the first three impingers to within $\pm$ 1 mL by using a graduated cylinder or by weighing it to within $\pm$ 0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

7.3.2 Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Paragraph 4.1.3.7). Amber glass containers should be used for storage of impinger catch, if required.

7.3.3 If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

7.4 Sample preparation for shipment: Prior to the shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon® tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

8.0 ANALYSIS

8.1 Sample preparation:

8.1.1 General: The preparation steps for all samples will result in a finite volume of concentrated solvent. The final sample volume (usually in the 1- to 10-mL range) is then subjected to analysis by GC/MS. All samples should be inspected and the appearance documented. All samples are to be spiked with surrogate standards as received from the field prior to any sample

manipulations. The spike should be at a level equivalent to 10 times the MDL when the solvent is reduced in volume to the desired level (i.e., 10 mL). The spiking compounds should be the stable isotopically labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis of the compounds of interest. Suggested surrogate spiking compounds are: deuterated napthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon-13-labeled pentachlorophenol.

8.1.2 Condensate: The "condensate" is the moisture collected in the first impinger following the XAD-2 module. Spike the condensate with the surrogate standards. The volume is measured and recorded and then transferred to a separatory funnel. The pH is to be adjusted to pH 2 with 6 N sulfuric acid, if necessary. The sample container and graduated cylinder are sequentially rinsed with three successive 10-mL aliquots of the extraction solvent and added to the separatory funnel. The ratio of solvent to aqueous sample should be maintained at 1:3. Extract the sample by vigorously shaking the separatory funnel for 5 min. After complete separation of the phases, remove the solvent and transfer to a Kuderna-Danish concentrator (K-D), filtering through a bed of precleaned, dry sodium sulfate. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 N sodium hydroxide and reextract combining the acid and base extracts. Rinse the sodium sulfate into the K-D with fresh solvent and discard the desiccant. Add Teflon® boiling chips and concentrate to 10 mL by reducing the volume to slightly less than 10 mL and then bringing to volume with fresh solvent. In order to achieve the necessary detection limit, the sample volume can be further reduced to 1 mL by using a micro column K-D or nitrogen blow-down. Should the sample start to exhibit precipitation, the concentration step should be stopped and the sample redissolved with fresh solvent taking the volume to some finite amount. After adding a standard (for the purpose of quantitation by GC/MS), the sample is ready for analysis, as discussed in Paragraph 8.2.

8.1.3 Impinger: Spike the sample with the surrogate standards; measure and record the volume and transfer to a separatory funnel. Proceed as described in Paragraph 8.1.2.

8.1.4 XAD-2: Spike the resin directly with the surrogate standards. Transfer the resin to the all-glass thimbles by the following procedure (care should be taken so as not to contaminate the thimble by touching it with anything other than tweezers or other solvent-rinsed mechanical holding devices). Suspend the XAD-2 module directly over the thimble. The glass frit of the module (see Figure 2) should be in the up position. The thimble is contained in a clean beaker, which will serve to catch the solvent rinses. Using a Teflon® squeeze bottle, flush the XAD-2 into the thimble. Thoroughly rinse the glass module with solvent into the beaker containing the thimble. Add the

XAD-2 glass-wool plug to the thimble. Cover the XAD-2 in the thimble with a precleaned glass-wool plug sufficient to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. If a question arises concerning the completeness of the extraction, a second extraction, without a spike, is advised. The thimble is placed in the extractor and the rinse solvent contained in the beaker is added to the solvent reservoir. Additional solvent is added to make the reservoir approximately two-thirds full. Add Teflon® boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5-6 times per hr. Extract the resin for 16 hr. Transfer the solvent and three 10-mL rinses of the reservoir to a K-D and concentrate as described in Paragraph 8.1.2.

8.1.5 Particulate filter (and cyclone catch): If particulate loading is to be determined, weigh the filter (and cyclone catch, if applicable). The particulate filter (and cyclone catch, if applicable) is transferred to the glass thimble and extracted simultaneously with the XAD-2 resin.

8.1.6 Train solvent rinses: All train rinses (i.e., probe, impinger, filter housing) using the extraction solvent and methanol are returned to the laboratory as a single sample. If the rinses are contained in more than one container, the intended spike is divided equally among the containers proportioned from a single syringe volume. Transfer the rinse to a separatory funnel and add a sufficient amount of organic-free water so that the methylene chloride becomes immiscible and its volume no longer increases with the addition of more water. The extraction and concentrations steps are then performed as described in Paragraph 8.1.2.

8.2 Sample analysis:

8.2.1 The primary analytical tool for the measurement of emissions from hazardous waste incinerators is GC/MS using fused-silica capillary GC columns, as described in Method 8270 in Chapter Four of this manual. Because of the nature of GS/MS instrumentation and the cost associated with sample analysis, prescreening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture (GC/ECD) is encouraged. Information regarding the complexity and concentration level of a sample prior to GC/MS analysis can be of enormous help. This information can be obtained by using either capillary columns or less expensive packed columns. However, the FID screen should be performed with a column similar to that used with the GS/MS. Keep in mind that GC/FID has a slightly lower detection limit than GS/MS and, therefore, that the concentration of the sample can be adjusted either up or down prior to analysis by GC/MS.

8.2.2 The mass spectrometer will be operated in a full scan (40-450) mode for most of the analyses. The range for which data are required in a GS/MS run will be sufficiently broad to encompass the major ions, as listed in Chapter Four, Method 8270, for each of the designated POHCs in an incinerator effluent analysis.

8.2.3 For most purposes, electron ionization (EI) spectra will be collected because a majority of the POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

8.2.4 To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions will be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound descriptions of GC conditions, MS conditions, and quantitative identification. Refer to Chapter Four, Method 8270, for complete descriptions of GC conditions, MS conditions, and qualitative and quantitative identification.

9.0 CALIBRATION

9.1 Probe nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

9.2 Pitot tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented, or corroded and if it meets design and intercomponent spacing specifications.

9.3 Metering system:

9.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: Make a 10-min calibration run at 0.00057 m^3/min

(0.02 cfm); at the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

9.3.2 After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

9.3.3 Leak-check of metering system: That portion of the sampling train from the pump to the orifice meter (see Figure 1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 6): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13-18 cm (5-7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

NOTE: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series shall be voided or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

9.4 Probe heater: The probe-heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

9.5 Temperature gauges: Each thermocouple must be permanently and uniquely marked on the casting; all mercury-in-glass reference thermometers must conform to ASTM E-1 63C or 63F specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change >1.5%.

9.5.1 Impinger, organic module, and dry-gas meter thermocouples: For the thermocouples used to measure the temperature of the gas leaving the impinger train and the XAD-2 resin bed, three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ± 2°C (3.6°F) with those of the absolute value of the

reference thermometer.

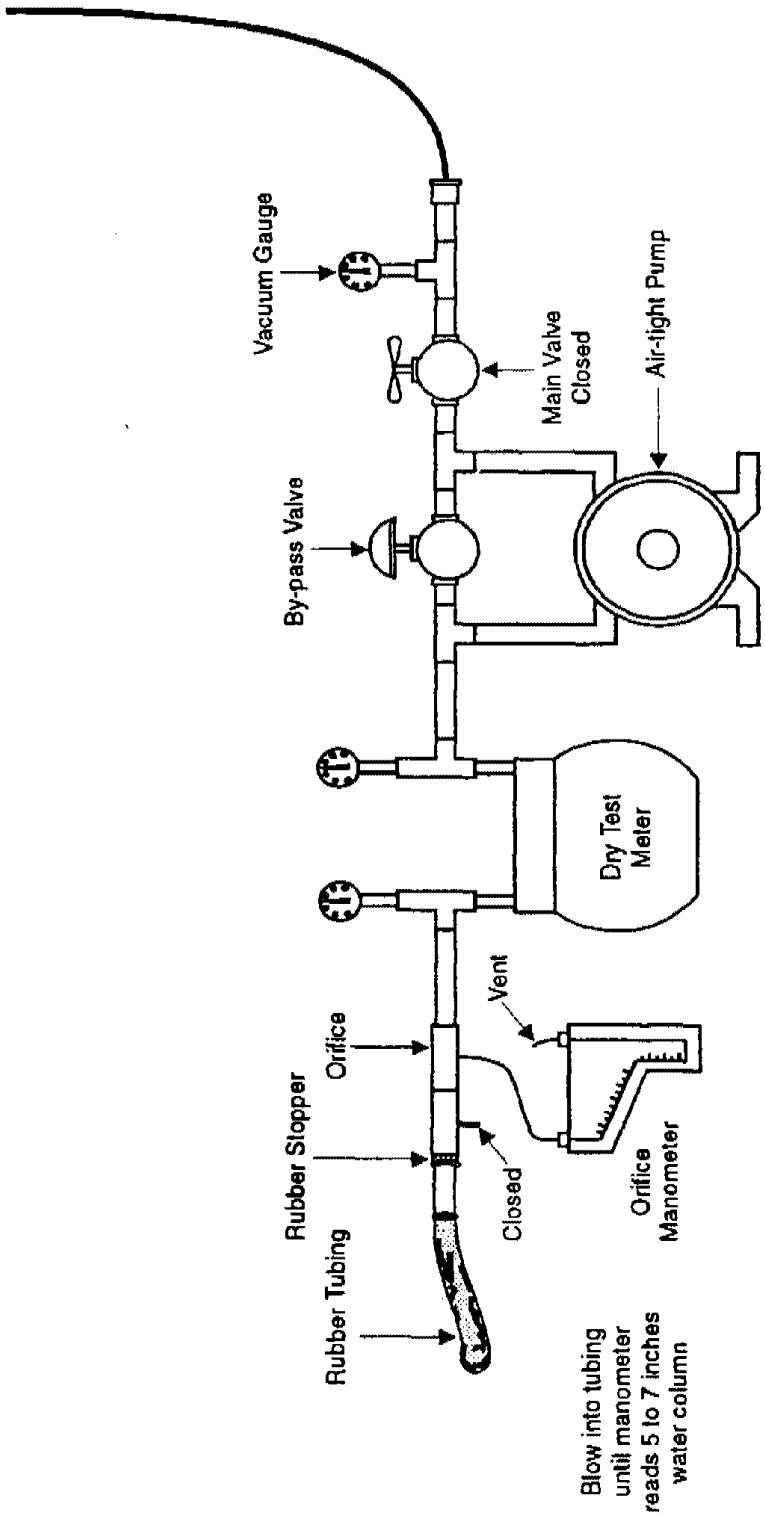


Figure 6. Leak-check of Meter Box

9.5.2 Probe and stack thermocouple: For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures must be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

9.6 Barometer: Adjust the barometer initially and before each test series to agree to within ± 25 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

9.7 Triple-beam balance: Calibrate the triple-beam balance before each test series, using Class-S standard weights; the weights must be within ± 0.5% of the standards, or the balance must be adjusted to meet these limits.

10.0 CALCULATIONS

10.1 Carry out calculations. Round off figures after the final calculation to the correct number of significant figures.

10.2 Nomenclature:

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak-check conducted prior to the "i^{th}" component change (i = 1, 2, 3...n) m^3/min (cfm).

L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).

M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack-gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry-gas meter temperature (see Figure 6), K (°R).

T_s = Absolute average stack-gas temperature (see Figure 6), K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, the impingers, and silica gel, mL.

V_m = Volume of gas sample as measured by dry-gas meter, dscm (dscf).

$V_{m(std)}$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

V_s = Stack-gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

γ = Dry-gas-meter calibration factor, dimensionless.

ΔH = Average pressure differential across the orifice meter (see Figure 2), mm H_20 (in. H_20).

ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).

θ = Total sampling time, min.

θ_1 = Sampling time interval from the beginning of a run until the first component change, min.

θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = sec/min.

100 = Conversion to percent.

10.3 Average dry-gas-meter temperature and average orifice pressure drop: See data sheet (Figure 5, above).

10.4 Dry-gas volume: Correct the sample measured by the dry-gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation 1:

$$V_{m(std)} = V_m \gamma \frac{T_{std}}{T_m} \frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}} = K_1 V_m \gamma \frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m} \quad (1)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or
K_1 = 17.64°R/in. Hg for English units.

It should be noted that Equation 1 can be used as written, unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation 1 must be modified as follows:

a. Case I (no component changes made during sampling run): Replace V_m in Equation 1 with the expression:

$$V_m - (L_p - L_a)$$

b. Case II (one or more component changes made during the sampling run): Replace V_m in Equation 1 by the expression:

$$V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\theta_1 - (L_p - L_a)\theta_p$$

and substitute only for those leakage rates (L_1 or L_p) that exceed L_a.

10.5 Volume of water vapor:

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{lc} \qquad (2)$$

where:

K_2 = 0.001333 m^3/mL for metric units, or
K_2 = 0.04707 ft^3/mL for English units.

10.6 Moisture content:

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad (3)$$

NOTE: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 3) and a second from the assumption of saturated conditions. The lower of the two values of B_w shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note to Section 1.2 of Method 4. For the purposes of this method, the average stack-gas temperature from Figure 6 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 1°C (2°F).

10.7 Conversion factors:

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

10.8 Isokinetic variation:

10.8.1 Calculation from raw data:

$$I = \frac{100\ T_s \left[K_3 F_{lc} + \left(\frac{V_m}{T_m} \right) \left(P_{bar} + \frac{\Delta H}{13.6} \right) \right]}{60 \theta V_s P_s A_n} \qquad (4)$$

where:

K_3 = 0.003454 mm Hg-m^3 for metric units, or
K_3 = 0.002669 in. Hg-ft^3/mL-°R for English units.

10.8.2 Calculation for intermediate values:

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \theta A_n P_s 60 (1 - B_{ws})}$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1 - B_{ws})} \qquad (6)$$

where:

K_4 = 4.320 for metric units, or
K_4 = 0.09450 for English units.

10.8.3 Acceptable results: If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90%, the Administrator may opt to accept the results.

10.9 To determine the minimum sample volume that shall be collected, the following sequence of calculations shall be used.

10.9.1 From prior analysis of the waste feed, the concentration of POHCs introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of POHC allowed to be present in the effluent. This may be expressed as:

$$\frac{(WF)\ (POHC_i\ conc)}{100}\ \frac{(100-\%DRE)}{100} + Max\ POHC_i\ Mass \qquad (7)$$

where:

WF = mass flow rate of waste feed per hr, g/hr (lb/hr).

$POHC_i$ = concentration of Principal Organic Hazardous Compound (wt %) introduced into the combustion process.

DRE = percent Destruction and Removal Efficiency required.

Max POHC = mass flow rate (g/hr [lb/hr]) of POHC emitted from the combustion source.

10.9.2 The average discharge concentration of the POHC in the effluent gas is determined by comparing the Max POHC with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary Method 1-4 determinations:

$$\frac{Max\ POHC_i\ Mass}{DV_{eff(std)}} = Max\ POHC_i\ conc \qquad (8)$$

where:

$DV_{eff(std)}$ = volumetric flow rate of exhaust gas, dscm (dscf).

$POHC_i$ conc = anticipated concentration of the POHC in the exhaust gas stream, g/dscm (lb/dscf).

10.9.3 In making this calculation, it is recommended that a safety margin of at least ten be included:

$$\frac{LDL_{POHC} \times 10}{POHC_i \text{ conc}} = V_{TBC} \qquad (9)$$

where:

LDL_{POHC} = detectable amount of POHC in entire sampling train.
NOTE: The whole extract from an XAD-2 cartridge is seldom, if ever, injected at once. Therefore, if aliquoting factors are involved, the LDL_{POHC} is not the same as the analytical (or column) detection limit.

V_{TBC} = minimum dry standard volume to be collected at dry-gas meter.

10.10 <u>Concentration of any given POHC in the gaseous emissions of a combustion process:</u>

1) Multiply the concentration of the POHC as determined in Method 8270 by the final concentration volume, typically 10 mL.

C_{POHC} (μg/mL) x sample volume (mL) = amount (μg) of POHC in sample (9)

where:

C_{POHC} = concentration of POHC as analyzed by Method 8270.

2) Sum the amount of POHC found in all samples associated with a single train.

Total (μg) = XAD-2 (μg) + condensate (μg) + rinses (μg) + impinger (μg) (10)

3) Divide the total μg found by the volume of stack gas sampled (m^3).

(Total μg)/(train sample volume) = concentration of POHC ($\mu g/m^3$) (11)

11.0 QUALITY CONTROL

11.1 <u>Sampling</u>: See EPA Manual 600/4-77-027b for Method 5 quality control.

11.2 <u>Analysis</u>: The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, incorporation of stable labeled surrogate compounds, quantitation versus stable labeled internal standards, capillary column

performance checks, and external performance tests. The surrogate spiking compounds selected for a particular analysis are used as primary indicators of the quality of the analytical data for a wide range of compounds and a variety of sample matrices. The assessment of combustion data, positive identification, and quantitation of the selected compounds are dependent on the integrity of the samples received and the precision and accuracy of the analytical methods employed. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

11.2.1 Field Blanks: Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, unused filters, and resin cartridges. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

11.2.2 Method Blanks: A method blank must be prepared for each set of analytical operations to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.2.3 Refer to Method 8270 for additional quality control considerations.

12.0 METHOD PERFORMANCE

12.1 Method performance evaluation: Evaluation of analytical procedures for a selected series of compounds must include the sample-preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

12.2 Method detection limit: The overall method detection limits (low and upper) must be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrumental minimum detection limit (MDL). The method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (breakthrough).

12.3 Method precision and bias: The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. From evaluation studies to date using a

dynamic spiking system, method biases of -13% and -16% have been determined for toluene and 1,1,2,2-tetrachloroethane, respectively. A precision of 19.9% was calculated from a field test data set representing seven degrees of freedom that resulted from a series of paired, unspiked Semivolatile Organic Sampling trains (Semi-VOST) sampling emissions from a hazardous waste incinerator.

13.0 REFERENCES

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METHOD 0010

APPENDIX A

PREPARATION OF XAD-2 SORBENT RESIN

1.0 SCOPE AND APPLICATION

1.1 XAD-2 resin as supplied by the manufacturer is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions, followed by careful drying.

2.0 EXTRACTION

2.1 **Method 1:** The procedure may be carried out in a giant Soxhlet extractor. An all-glass thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass-wool plug and stainless steel screen because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with Type II water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with H_2O for 8 hr.
Methyl alcohol	Extract for 22 hr.
Methylene chloride	Extract for 22 hr.
Methylene chloride (fresh)	Extract for 22 hr.

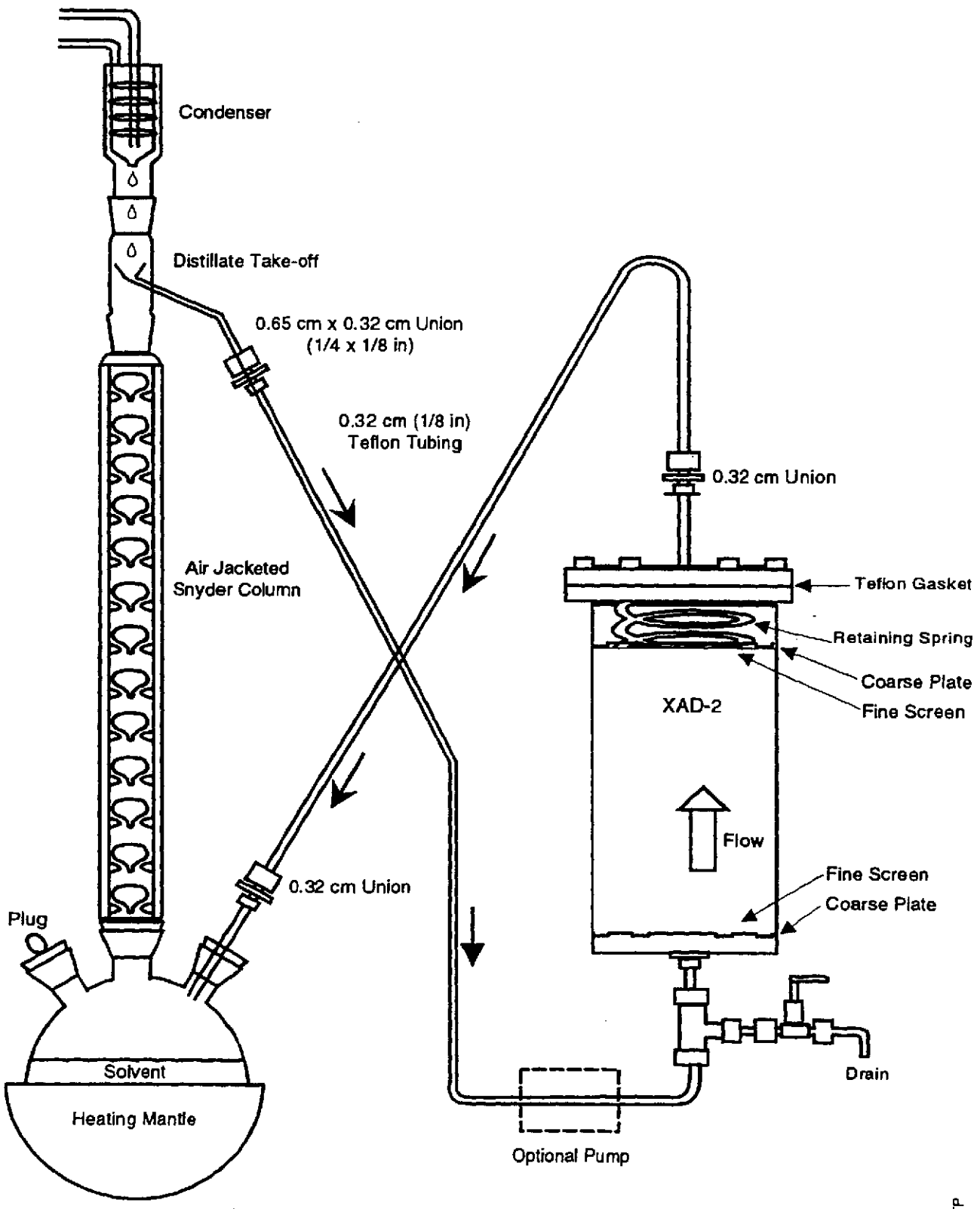


Figure A-1. XAD-2 Cleanup Extraction Apparatus

2.2 Method 2:

2.2.1 As an alternative to Soxhlet extraction, a continuous extractor has been fabricated for the extraction sequence. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure A-1 contains about 500 g of finished XAD-2. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2 is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3-liter in this case) to hold solvent equal to twice the dead volume of the XAD-2 canister. Solvent is refluxed through the Snyder column, and the distillate is continuously cycled up through the XAD-2 for extraction and returned to the flask. The flow is maintained upward through the XAD-2 to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

2.2.2 Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore the aqueous rinse is accomplished by simply flushing the canister with about 20 liters of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

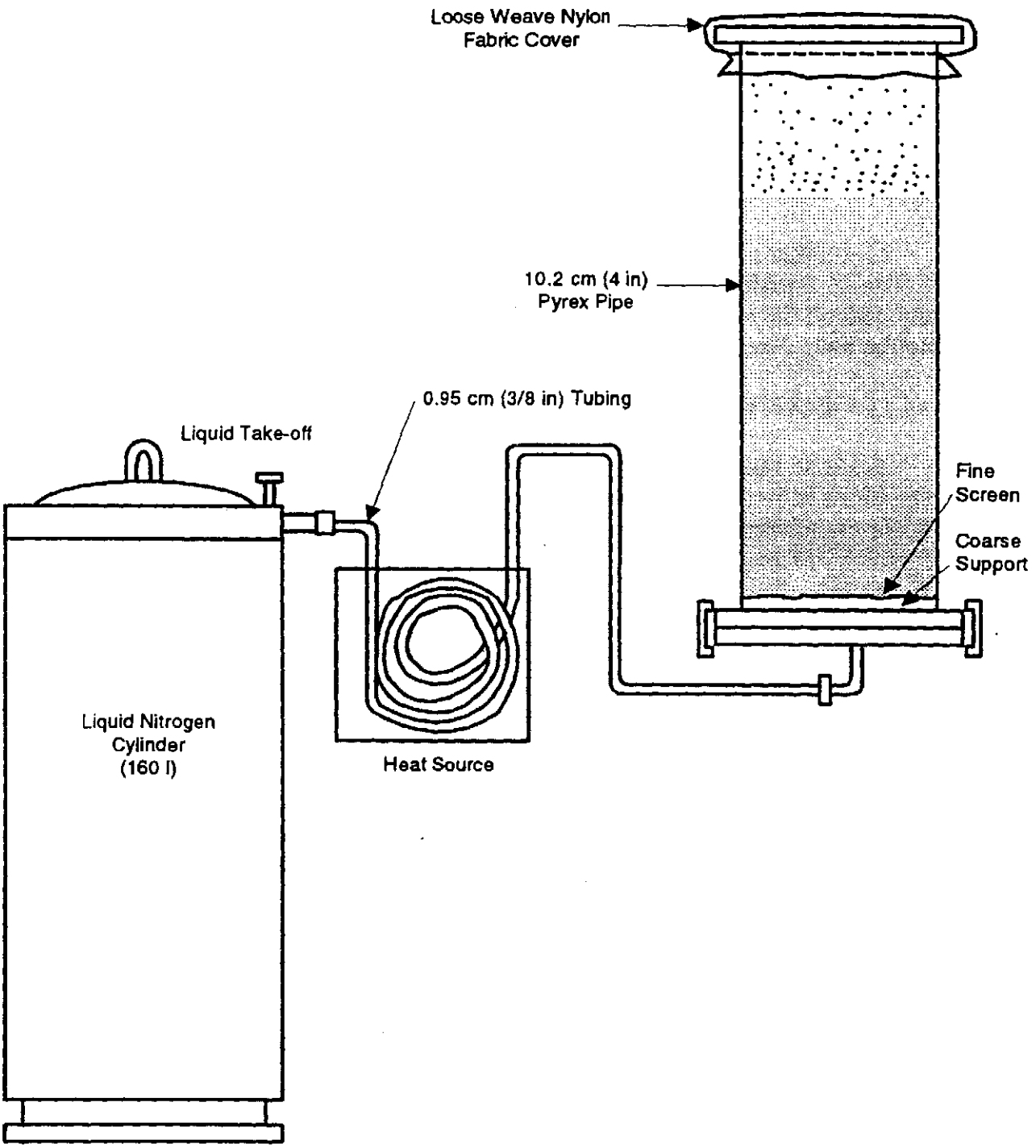
2.2.3 After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hr period is normally sufficient for each extraction.

2.2.4 All materials of construction are glass, Teflon®, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

3.0 DRYING

3.1 After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proved to be the fastest and most reliable drying method.

3.2 A simple column with suitable retainers, as shown in Figure A-2, will serve as a satisfactory column. A 10.2-cm (4-in.) Pyrex® pipe, 0.6 m (2 ft) long will hold all of the XAD-2 from the extractor shown in Figure A-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.



950198D-ja-RTP

Figure A-2. XAD-2 Fluidized-bed Drying Apparatus

3.3 Method 1: The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has routinely proved to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight by consuming a full 160-liter cylinder of liquid nitrogen.

3.4 Method 2: As a second choice, high-purity tank nitrogen may be used to dry the XAD-2. The high purity nitrogen must be passed through a bed of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

4.0 QUALITY CONTROL PROCEDURES

4.1 For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be reextracted if the residual extractable organics are >20 μg/mL by TCO analysis or the gravimetric residue is >0.5 mg/20 g XAD-2 extracted. (See also Section 5.1, Method 0010.)

4.2 Four control procedures are used with the final XAD-2 to check for (1) residual methylene chloride, (2) extractable organics (TCO), (3) specific compounds of interest as determined by GC/MS, as described in Section 4.5 below, and (4) residue (GRAV).

4.3 Procedure for residual methylene chloride:

4.3.1 **Description:** A 1 $\pm$ 0.1-g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five μL of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared with a reference standard. The reference solution consists of 2.5 μL of methylene chloride in 100mL of toluene, simulating 100 μg of residual methylene chloride on the resin. The acceptable maximum content is 1,000 μg/g resin.

4.3.2 **Experimental:** The gas chromatograph conditions are as follows:

6-ft x 1/8-in. Stainless steel column containing 10% OV-101 on 100/120 Supelcoport;

Helium carrier at 30 mL/min;

FID operated on 4 x 10^{-11} A/mV;

Injection port temperature: 250°C;

Detector temperature: 305°C;

Program: 30°C (4 min) 40°C/min 250°C (hold); and

Program terminated at 1,000 sec.

4.4 Procedure for residual extractable organics:

4.4.1 **Description:** A 20 ± 0.1-g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned glass wool. (Note that 20 g of resin will fill a thimble, and the resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 hr with 200-mL of pesticide-grade methylene chloride (Burdick and Jackson pesticide-grade or equivalent purity). The 200-mL extract is reduced in volume to 10-mL using a Kuderna-Danish concentrator and/or a nitrogen evaporation stream. Five μL of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain >20 μg/mL of TCO extracted from the XAD-2. This is equivalent to 10 μg/g of TCO in the XAD-2 and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2 module. Care should be taken to correct the TCO data for a solvent blank prepared (200 mL reduced to 10 mL) in a similar manner.

4.4.2 **Experimental:** Use the TCO analysis conditions described in the revised Level 1 manual (EPA 600/7-78-201).

4.5 GC/MS Screen: The extract, as prepared in paragraph 4.4.1, is subjected to GC/MS analysis for each of the individual compounds of interest. The GC/MS procedure is described in Chapter Four, Method 8270. The extract is screened at the MDL of each compound. The presence of any compound at a concentration >25 μg/mL in the concentrated extract will require the XAD-2 to be recleaned by repeating the methylene chloride step.

4.6 Methodology for residual gravimetric determination: After the TCO value and GC/MS data are obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be <0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criterion. This level corresponds to 25 μg/g in the XAD-2, or about 3.25 mg in a resin charge of 130 g.

METHOD 0010

APPENDIX B

TOTAL CHROMATOGRAPHABLE ORGANIC MATERIAL ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 In this procedure, gas chromatography is used to determine the quantity of lower boiling hydrocarbons (boiling points between 90° and 300°C) in the concentrates of all organic solvent rinses, XAD-2 resin and LC fractions - when Method 1 is used (see References, Method 0010) - encountered in Level 1 environmental sample analyses. Data obtained using this procedure serve a twofold purpose. First, the total quantity of the lower boiling hydrocarbons in the sample is determined. Then, whenever the hydrocarbon concentrations in the original concentrates exceed 75 $\mu g/m^3$, the chromatography results are reexamined to determine the amounts of individual species.

The extent of compound identification is limited to representing all materials as normal alkanes based upon comparison of boiling points. Thus the method is not qualitative. In a similar manner, the analysis is semiquantitative; calibrations are prepared using only one hydrocarbon. They are replicated but samples routinely are not.

1.2 Application: This procedure applies solely to the Level 1 C7-C16 gas chromatographic analysis of concentrates of organic extracts, neat liquids, and of LC fractions. Throughout the procedure it is assumed the analyst has been given a properly prepared sample.

1.3 Sensitivity: The sensitivity of this procedure, defined as the slope of a plot of response versus concentration, is dependent on the instrument and must be verified regularly. TRW experience indicates the nominal range is of the order of 77 $\mu V \cdot V \cdot sec \cdot \mu L/ng$ of n-heptane and 79 $\mu V \cdot sec \cdot \mu l/ng$ of n-hexadecane. The instrument is capable of perhaps one-hundredfold greater sensitivity. The level specified here is sufficient for Level 1 analysis.

1.4 Detection limit: The detection limit of this procedure as written is 1.3 $ng/\mu L$ for a 1 μL injection of n-decane. This limit is arbitrarily based on defining the minimum detectable response as 100 $\mu v \cdot sec$. This is an easier operational definition than defining the minimum detection limit to be that amount of material which yields a signal twice the noise level.

1.5 Range: The range of the procedure will be concentrations of 1.3 $ng/\mu L$ and greater.

1.6 Limitations:

1.6.1 Reporting limitations: It should be noted that a typical environmental sample will contain compounds which (a) will not elute in the specified boiling ranges and thus will not be reported, and/or (b) will not elute from the column at all and thus will not be reported. Consequently, the organic content of the sample as reported is a lower bound and should be regarded as such.

1.6.2 Calibration limitations: Quantitation is based on calibration with n-decane. Data should therefore be reported as, e.g., mg C8/m^3 as n-decane. Since response varies linearly with carbon number (over a wide range the assumption may involve a 20% error), it is clear that heptane (C7) detected in a sample and quantitated as decane will be overestimated. Likewise, hexadecane (C16) quantitated as decane will be underestimated. From previous data, it is estimated the error involved is on the order of 6-7%.

1.6.3 Detection limitations: The sensitivity of the flame ionization detector varies from compound to compound. However, n-alkanes have a greater response than other classes. Consequently, using an n-alkane as a calibrant and assuming equal responses of all other compounds tends to give low reported values.

2.0 SUMMARY OF METHOD

2.1 A mL aliquot of all 10-mL concentrates is disbursed for GC-TCO analysis. With boiling point-retention time and response-amount calibration curves, the data (peak retention times and peak areas) are interpreted by first summing peak areas in the ranges obtained from the boiling point-retention time calibration. Then, with the response-amount calibration curve, the area sums are converted to amounts of material in the reported boiling point ranges.

2.2 After the instrument is set up, the boiling point-retention time calibration is effected by injecting a mixture of n-C7 through n-C16 hydrocarbons and operating the standard temperature program. Response-quantity calibrations are accomplished by injecting n-decane in n-pentane standards and performing the standard temperature program.

2.3 Definitions

2.3.1 GC: Gas chromatography or gas chromatograph.

2.3.2 C7-C16 n-alkanes: Heptane through hexadecane.

2.3.3 GCA temperature program: 4 min isothermal at 60°C, 10°C/min from 60° to 220°C.

2.3.4 **TRW temperature program:** 5 min isothermal at room temperature, 15°C/min from 30° to 250°C.

3.0 INTERFERENCES

Not applicable.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: This procedure is intended for use on a Varian 1860 gas chromatograph, equipped with dual flame ionization detectors and a linear temperature programmer. Any equivalent instrument can be used provided that electrometer settings, etc., be changed appropriately.

4.2 Gases:

4.2.1 **Helium:** Minimum quality is reactor grade. A 4A or 13X molecular sieve drying tube is required. A filter must be placed between the trap and the instrument. The trap should be recharged after every third tank of helium.

4.2.2 **Air:** Zero grade is satisfactory.

4.2.3 **Hydrogen:** Zero grade.

4.3 Syringe: Syringes are Hamilton 701N, 10 μL, or equivalent.

4.4 Septa: Septa will be of such quality as to produce very low bleed during the temperature program. An appropriate septum is Supelco Microsep 138, which is Teflon®-backed. If septum bleed cannot be reduced to a negligible level, it will be necessary to install septum swingers on the instrument.

4.5 Recorder: The recorder of this procedure must be capable of not less than 1 mV full-scale display, a 1-sec time constant and 0.5 in. per min chart rate.

4.6 Integrator: An integrator is required. Peak area measurement by hand is satisfactory but too time-consuming. If manual integration is required, the method of "height times width at half height" is used.

4.7 Columns:

4.7.1 **Preferred column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-101 on 100/120 mesh Supelcoport.

4.7.2 **Alternate column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-1 (or other silicon phase) on 100/120 mesh Supelcoport.

4.8 Syringe cleaner: Hamilton syringe cleaner or equivalent connected to a suitable vacuum source.

5.0 REAGENTS

5.1 Pentane: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for standards and for syringe cleaning.

5.2 Methylene chloride: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for syringe cleaning.

6.0 SAMPLING HANDLING AND PRESERVATION

6.1 The extracts are concentrated in a Kuderna-Danish evaporator to a volume less than 10 mL. The concentrate is then quantitatively transferred to a 10 mL volumetric flask and diluted to volume. A 1-mL aliquot is taken for both this analysis and possible subsequent GC/MS analysis and set aside in the sample bank. For each GC-TCO analysis, obtain the sample sufficiently in advance to allow it to warm to room temperature. For example, after one analysis is started, return that sample to the sample bank and take the next sample.

7.0 PROCEDURES

7.1 Setup and checkout: Each day, the operator will verify the following:

7.1.1 That supplies of carrier gas, air and hydrogen are sufficient, i.e., that each tank contains > 100 psig.

7.1.2 That, after replacement of any gas cylinder, all connections leading to the chromatograph have been leak-checked.

7.1.3 That the carrier gas flow rate is 30 ± 2 mL/min, the hydrogen flow rate is 30 ± 2 mL/min, and the air flow rate is 300 ± 20 mL/min.

7.1.4 That the electrometer is functioning properly.

7.1.5 That the recorder and integrator are functioning properly.

7.1.6 That the septa have been leak-checked (leak-checking is effected by placing the soap bubble flow meter inlet tube over the injection port adaptors), and that no septum will be used for more than 20 injections.

7.1.7 That the list of samples to be run is ready.

7.2 Retention time calibration:

7.2.1 To obtain the temperature ranges for reporting the results of the analyses, the chromatograph is given a normal boiling point-retention time calibration. The n-alkanes, their boiling points, and data reporting ranges are given in the table below:

	NBP, °C	Reporting Range, °C	Report As
n-heptane	89	90-110	C7
n-octane	126	110-140	C8
n-nonane	151	140-160	C9
n-decane	174	160-180	C10
n-undecane	194	180-200	C11
n-dodecane	214	200-220	C12
n-tridecane	234	220-240	C13
n-tetradecane	252	240-260	C14
n-pentadecane	270	260-280	C15
n-hexadecane	288	280-300	C16

7.2.2 Preparation of standards: Preparing a mixture of the C7-C16 alkanes is required. There are two approaches: (1) use of a standards kit (e.g., Polyscience Kit) containing bottles of mixtures of selected n-alkanes which may be combined to produce a C7-C16 standard; or (2) use of bottles of the individual C7-C16 alkanes from which accurately known volumes may be taken and combined to give a C7-C16 mixture.

7.2.3 Procedure for retention time calibration: This calibration is performed at the start of an analytical program; the mixture is chromatographed at the start of each day. To attain the required retention time precision, both the carrier gas flow rate and the temperature program specifications must be observed. Details of the procedure depend on the instrument being used. The general procedure is as follows:

7.2.3.1 Set the programmer upper limit at 250°C. If this setting does not produce a column temperature of 250°C, find the correct setting.

7.2.3.2 Set the programmer lower limit at 30°C.

7.2.3.3 Verify that the instrument and samples are at room temperature.

7.2.3.4 Inject 1 μL of the n-alkane mixture.

7.2.3.5 Start the integrator and recorder.

7.2.3.6 Allow the instrument to run isothermically at room temperature for five minutes.

7.2.3.7 Shut the oven door.

7.2.3.8 Change the mode to Automatic and start the temperature program.

7.2.3.9 Repeat steps 1-9 a sufficient number of times so that the relative standard deviation of the retention times for each peak is $<5\%$.

7.3 Response calibration:

7.3.1 For the purpose of a Level 1 analysis, response-quantity calibration with n-decane is adequate. A 10-μL volume of n-decane is injected into a tared 10 mL volumetric flask. The weight injected is obtained and the flask is diluted to the mark with n-pentane. This standard contains about 730 ng n-decane per μL n-pentane. The exact concentration depends on temperature, so that a weight is required. Two serial tenfold dilutions are made from this standard, giving standards at about 730, 73, and 7.3 ng n-decane per μL n-pentane, respectively.

7.3.2 **Procedure for response calibration:** This calibration is performed at the start of an analytical program and monthly thereafter. The most concentrated standard is injected once each day. Any change in calibration necessitates a full calibration with new standards. Standards are stored in the refrigerator locker and are made up monthly.

7.3.2.1 Verify that the instrument is set up properly.

7.3.2.2 Set electrometer at 1 x 10^{-10} A/mV.

7.3.2.3 Inject 1 μL of the highest concentration standard.

7.3.2.4 Run standard temperature program as specified above.

7.3.2.5 Clean syringe.

7.3.2.6 Make repeated injections of all three standards until the relative

standard deviations of the areas of each standard are ≤5%.

7.4 Sample analysis procedure:

7.4.1 The following apparatus is required:

7.4.1.1 Gas chromatograph set up and working.

7.4.1.2 Recorder, integrator working.

7.4.1.3 Syringe and syringe cleaning apparatus.

7.4.1.4 Parameters: Electrometer setting is 1 x 10^{-10} A/mV; recorder is set at 0.5 in./min and 1 mV full-scale.

7.4.2 Steps in the procedure are:

7.4.2.1 Label chromatogram with the data, sample number, etc.

7.4.2.2 Inject sample.

7.4.2.3 Start integrator and recorder.

7.4.2.4 After isothermal operation for 5 min, begin temperature program.

7.4.2.5 Clean syringe.

7.4.2.6 Return sample; obtain new sample.

7.4.2.7 When analysis is finished, allow instrument to cool. Turn chromatogram and integrator output and data sheet over to data analyst.

7.5 Syringe cleaning procedure:

7.5.1 Remove plunger from syringe.

7.5.2 Insert syringe into cleaner; turn on aspirator.

7.5.3 Fill pipet with pentane; run pentane through syringe.

7.5.4 Repeat with methylene chloride from a separate pipet.

7.5.5 Flush plunger with pentane followed by methylene chloride.

7.5.6 Repeat with methylene chloride.

7.6 Sample analysis decision criterion: The data from the TCO analyses of organic extract and rinse concentrates are first used to calculate the total concentration of C7-C16 hydrocarbon-equivalents (Paragraph 7.7.3) in the sample with respect to the volume of air actually sampled, i.e., $\mu g/m^3$. On this basis, a decision is made both on whether to calculate the quantity of each n-alkane equivalent present and on which analytical procedural pathway will be followed. If the total organic content is great enough to warrant continuing the analysis-- $>500\ \mu g/m^3$ --a TCO of less than 75 $\mu g/m^3$ will require only LC fractionation and gravimetric determinations and IR spectra to be obtained on each fraction. If the TCO is greater than 75 $\mu g/m^3$, then the first seven LC fractions of each sample will be reanalμzed using this same gas chromatographic technique.

7.7 Calculations:

7.7.1 **Boiling Point - Retention Time Calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.1.1 Average the retention times and calculate relative standard deviations for each n-hydrocarbon.

7.7.1.2 Plot average retention times as abscissae versus normal boiling points as ordinates.

7.7.1.3 Draw in calibration curve.

7.7.1.4 Locate and record retention times corresponding to boiling ranges 90-100, 110-140, 140-160, 160-180, 180-200, 200-220, 220-240, 240-260, 260-280, 280-300°C.

7.7.2 **Response-amount calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.2.1 Average the area responses of each standard and calculate relative standard deviations.

7.7.2.2 Plot response ($\mu v \cdot sec$) as ordinate versus ng/μL as abscissa.

7.7.2.3 Draw in the curve. Perform least squares regression and obtain slope ($\mu V \cdot sec \cdot \mu L/ng$).

7.7.3 **Total C7-C16 hydrocarbons analysis:** The required data for this calculation are on the chromatogram and on the data sheet. The data reduction is

performed as follows:

7.7.3.1 Sum the areas of all peaks within the retention time range of interest.

7.7.3.2 Convert this area (μV·sec) to ng/μL by dividing by the weight response for n-decane (μV·sec·μL/ng).

7.7.3.3 Multiply this weight by the total concentrate volume (10 mL) to get the weight of the C7-C16 hydrocarbons in the sample.

7.7.3.4 Using the volume of gas sampled or the total weight of sample acquired, convert the result of Step 7.7.3.3 above to $\mu g/m^3$.

7.7.3.5 If the value of total C7-C16 hydrocarbons from Step 7.7.3.4 above exceeds 75 $\mu g/m^3$, calculate individual hydrocarbon concentrations in accordance with the instructions in Paragraph 7.7.5.5 below.

7.7.4 Individual C7-C16 n-Alkane Equivalent Analysis: The required data from the analyses are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.4.1 Sum the areas of peaks in the proper retention time ranges.

7.7.4.2 Convert areas (μV·sec) to ng/μL by dividing by the proper weight response (μV·sec·μL/ng).

7.7.4.3 Multiply each weight by total concentrate volume (10 mL) to get weight of species in each range of the sample.

7.7.4.4 Using the volume of gas sampled on the total weight of sample acquired, convert the result of Step 7.7.4.3 above to $\mu g/m^3$.

8.0 QUALITY CONTROL

8.1 Appropriate QC is found in the pertinent procedures throughout the method.

9.0 METHOD PERFORMANCE

9.1 Even relatively comprehensive error propagation analysis is beyond the scope of this procedure. With reasonable care, peak area reproducibility of a standard should be of the order of 1% RSD. The relative standard deviation of the sum of all peaks in a fairly complex waste might be of the order of 5-10%. Accuracy is more difficult to assess. With good analytical technique, accuracy and precision should be of the order of 10-20%.

10.0 REFERENCES

1.0 Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedure Manual for Sampling and Analysis, Interagency Energy/Environmental R&D Program, Industrial Environmental Research Laboratory, Research Triangle Park, NC 27711, EPA-600/7-79-029a, January 1979.

Appendix G

Method 3542

Preparation of Modified Method 5 (SW-846, Method 0010) Train Components for Analysis by SW-846 Method 8270

(This is the latest draft version of Method 3542 from SW-846. The final version of the document when released supersedes this one and will be inserted in its place)

METHOD 3542

PREPARATION OF MODIFIED METHOD 5 (SW-846 METHOD 0010) TRAIN COMPONENTS FOR ANALYSIS BY SW-846 METHOD 8270

1.0 SCOPE AND APPLICATION

1.1 This method describes the extraction of semivolatile organic compounds from samples collected by the EPA SW-846 Method 0010. This method replaces Section 8.1 of SW-846 Method 0010 (Modified Method 5 Sampling Train, also known as SemiVOST) and Sections 7.1 and 7.2 of SW-846 Method 8270 (Gas Chromatography/ Mass Spectrometry for Semivolatile Organics: Capillary Column Technique), which deal with sample preparation. These sections discuss sample preparation procedures. Section 8.1 of Method 0010 addresses preparation of Method 0010 train components for analysis with very little detail. Sections 7.1 and 7.2 of Method 8270 address preparation of water, soil/sediment, and water matrices. Analytical procedures described in Section 7.3 of Method 8270 are relevant, with the exception that the final volume of the extracts of the Method 0010 train components must be 5 mL, with surrogate compound concentrations as indicated in this method.

Although this sample preparation technique is intended primarily for gas chromatography/mass spectrometric (GC/MS) analysis following Method 8270, the extracts prepared according to this method may be used with other analytical methods. The Method 0010 sampling train collects semivolatile organic compounds with boiling points above 100°C. Some of these semivolatile organic compounds may not be amenable to gas chromatography and will require the application of high performance liquid chromatography (HPLC) for quantitative analysis. The use of HPLC coupled with mass spectrometry (HPLC/MS) is an analytical technique that may also be applied. A solvent exchange from methylene chloride to a more polar solvent such as acetonitrile or extraction with a solvent other than methylene chloride will probably be required for successful application of HPLC techniques. Some semivolatile analytes may require derivatization for successful GC/MS analysis.

1.2 This method is restricted to use by or under the supervision of analysts experienced in the extraction and concentration of semivolatile organic compounds from the components of Method 0010 trains. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Samples generated by the Method 0010 Sampling Train (Method 0010 Sampling Train, Figure 2-1) are separated into six parts:

1. a particulate matter filter (labeled in Method 0010 as Container No. 1);
2. a front half rinse (labeled in Method 0010 as Container No. 2);
3. condenser rinse and rinse of all sampling train components located between the filter and the sorbent module (labeled in Method 0010 as Container No. 5);
4. sorbent trap section of the organic module (labeled in Method 0010 as Container No. 3);
5. any condensate and condensate rinse (labeled in Method 0010 as Container No. 4); and
6. silica gel (labeled in Method 0010 as Container No. 6).

The six parts recovered from the Method 0010 sampling train yield three 5 mL extracts to be analyzed according to the analytical procedures of Method 8270. The particulate matter filter is extracted by Soxhlet (SW-846 Method 3540, with exceptions as noted). The front half rinse is filtered, and any filtrate is added to the particulate matter filter for Soxhlet extraction. The front half rinse is a 50:50 mixture of methanol and methylene chloride generated by rinsing the probe and the front half of the filter holder in the Method 0010 train. The front half rinse is extracted with methylene chloride by separatory funnel (SW-846 Method 3510, with exceptions as noted) after sufficient HPLC-grade water (or equivalent) has been added to make the methylene chloride separate as a distinct phase from the methanol/water. The extracts from the filter and front half rinse are combined, moisture is removed by filtering through anhydrous sodium sulfate (Na_2SO_4), and the combined extract is concentrated using a Kuderna-Danish (K-D) sample concentrator (SW-846 Method 3540)

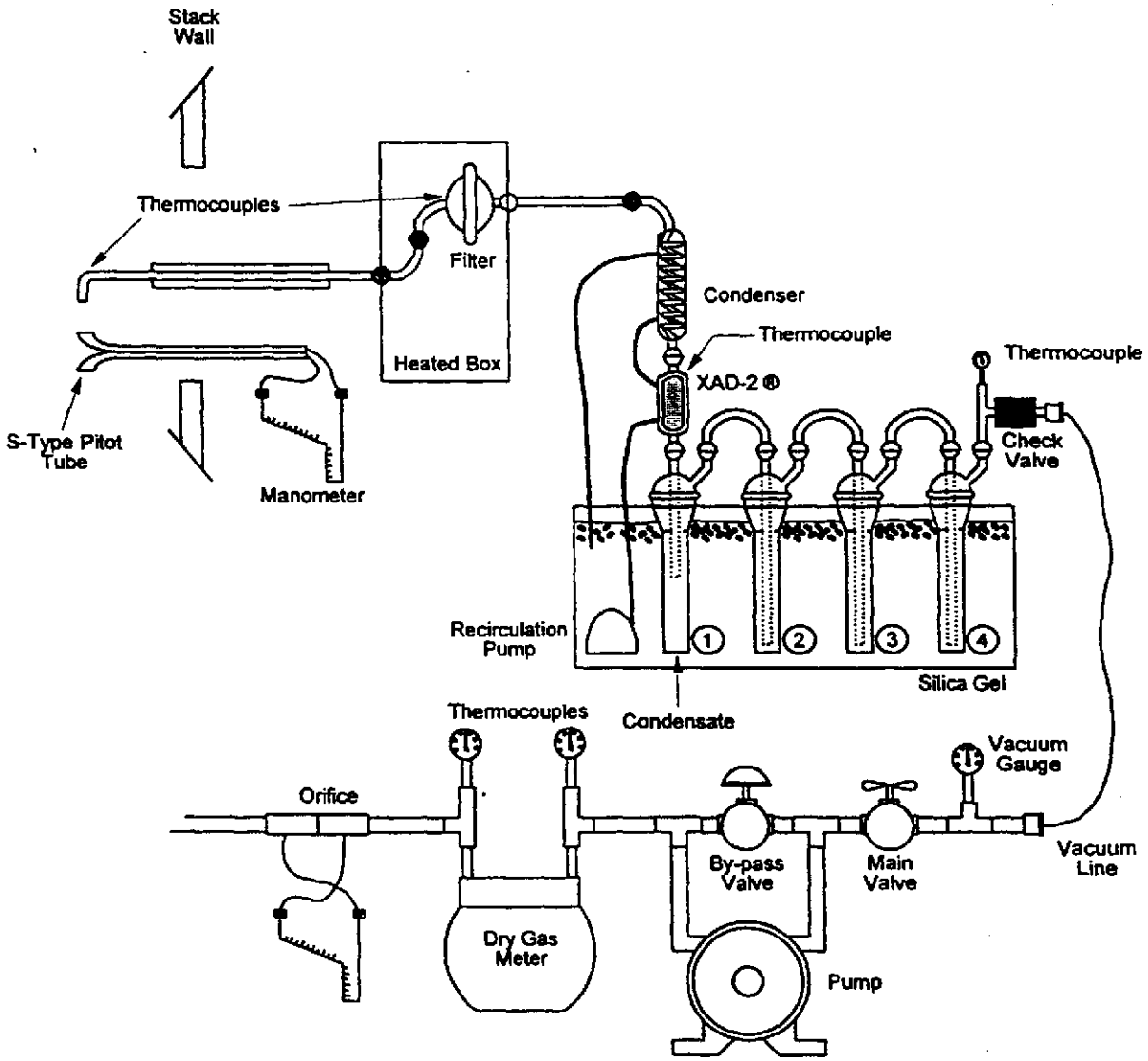


Figure 2-1. Method 0010 Sampling Train.

to a final volume of 5 mL. The final sample concentration to 5 mL can be performed more accurately by reducing the volume of the sample using a gentle stream of nitrogen or by using a micro-K-D. The condensate and condensate rinse fractions consist of the aqueous contents of the first impinger of the Method 0010 sampling train and the 50:50 methanol/methylene chloride rinse of the first impinger of the Method 0010 sampling train. The condensate and condensate rinse fractions are combined and extracted with methylene chloride using a separatory funnel after sufficient HPLC-grade water (or equivalent) has been added to make the methylene chloride separate from the methanol/water following the procedures of SW-846 Method 3510 (with exceptions as noted). After an initial methylene chloride extraction without pH adjustment, the pH of the combined condensate/condensate rinse fraction is determined. If the condensate/condensate rinse fraction is acid (pH $<$ 7), the pH is adjusted to a level less than 2 and the methylene chloride extraction is repeated. The pH of the condensate/condensate rinse fraction is then made basic (pH $>$ 12), and the methylene chloride extraction is repeated. The methylene chloride extracts are combined, and moisture is removed by filtration through a bed of anhydrous Na_2SO_4. If the condensate/condensate rinse fraction is found to be basic after the initial methylene chloride extraction, the pH adjustment sequence is reversed: a basic extraction is performed prior to an acid extraction, the methylene chloride extracts are combined, the moisture is removed, and the extract is concentrated to a volume of 5 mL. The XAD-2® sampling module is combined with the filter holder back half rinse and the 50:50 methylene chloride/methanol condenser rinse and extracted by Soxhlet (SW-846 Method 3540, with exceptions as noted). Water is added to the extract to ensure the separation of methanol/water from the methylene chloride, and a water extraction of the methylene chloride extract is performed. Moisture is removed from the methylene chloride extract, which is then concentrated to a final volume of 5 mL for analysis. The contents of the remaining impingers are usually archived, but may be extracted by separatory funnel. The silica gel is reused after regeneration by heating to remove moisture. The overall sample preparation scheme is shown in Figure 2-2.

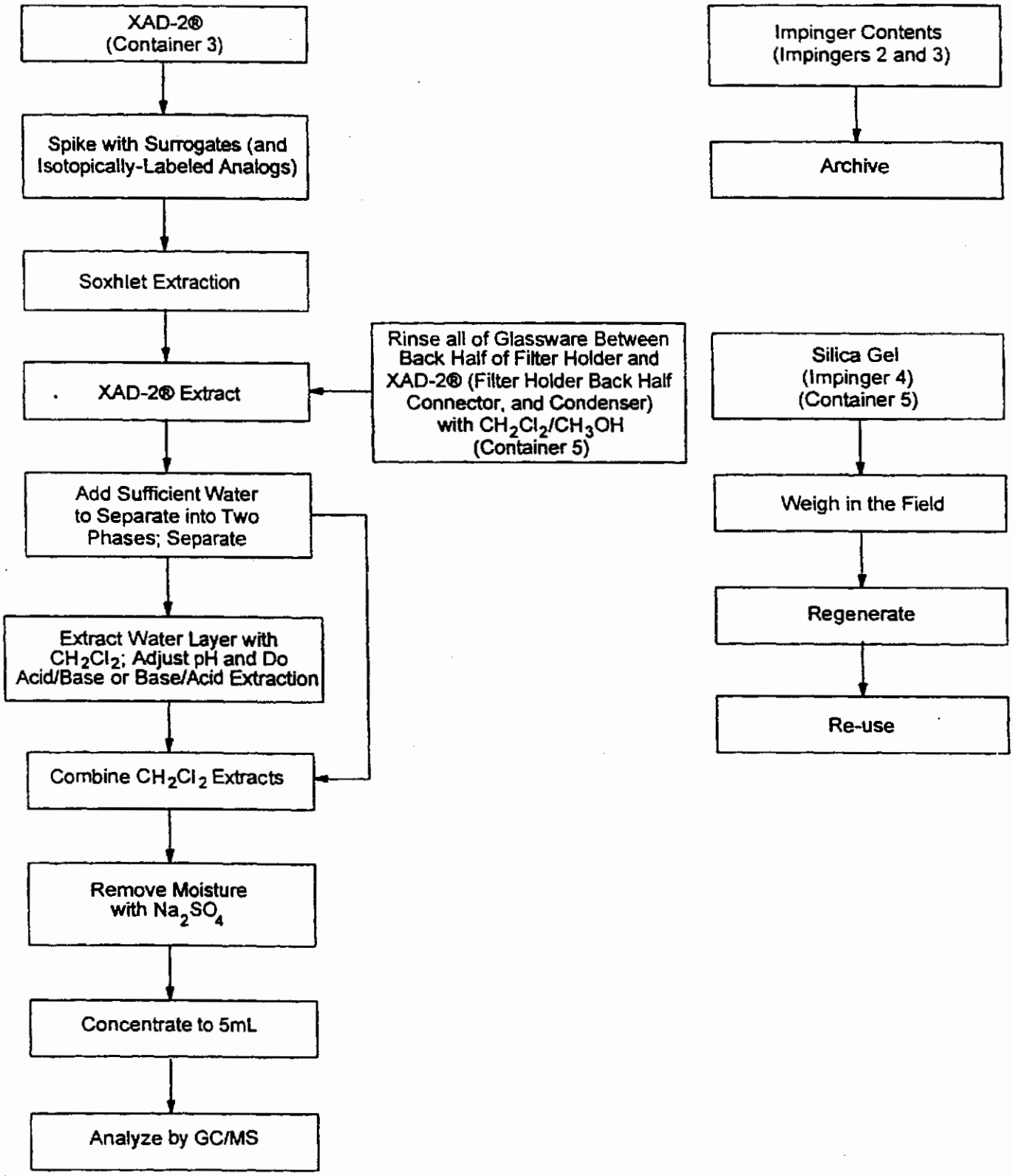


Figure 2-2. Sample Preparation Scheme for Method 0010 Train Components.

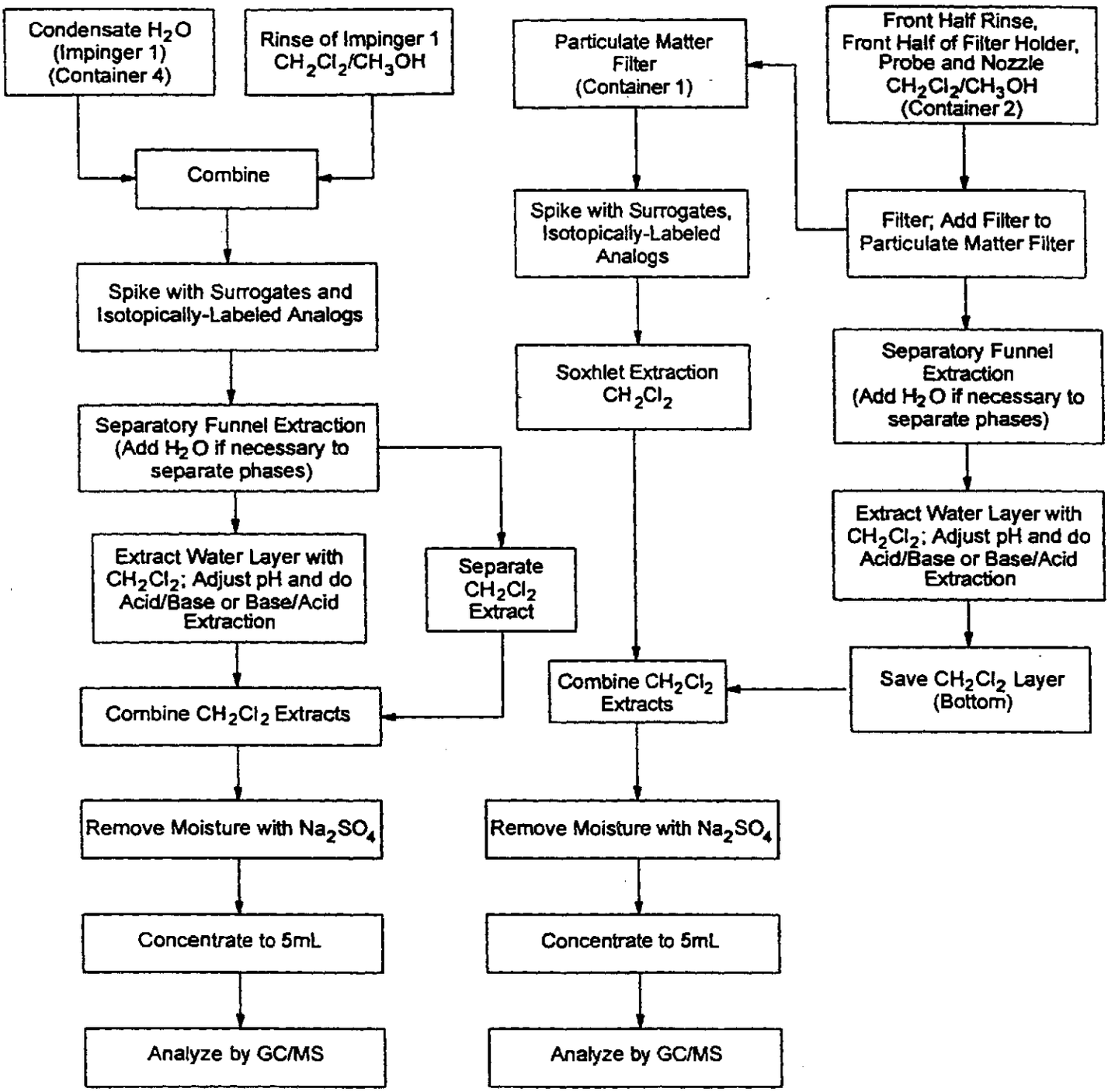


Figure 2-2. Continued

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by preparing and analyzing laboratory method (or reagent) blanks.

3.1.1 Glassware must be cleaned thoroughly before using. The glassware should be washed with laboratory detergent in hot water followed by rinsing with tap water and distilled water. The glassware may be cleaned by baking in a glassware oven at 400°C for at least one hour. After the glassware has cooled, the glassware should be rinsed three times with methanol and three times with methylene chloride. Volumetric glassware should not be heated to 400°C. Rather, after washing and rinsing, volumetric glassware may be rinsed with methanol followed by methylene chloride and allowed to dry in air.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems in sample analysis.

3.2 Matrix interferences in the analysis may be caused by components of the sampling matrix that are extracted from the samples. If matrix interferences interfere with the analysis, sample cleanup procedures (e.g., SW-846 Method 3620 or Method 3610) may be employed to remove or mitigate the interferences.

4.0 APPARATUS AND MATERIALS

4.1 **Soxhlet Extractor.** 40-mm I.D., with 500-mL round bottom flask and condenser.

4.2 **Boiling Chips.** Teflon®, solvent rinsed with methylene chloride, approximately 10/40 mesh.

4.3 **Forceps.** Rinsed with methylene chloride before use.

4.4 **Separatory Funnel.** 250 mL or larger, with Teflon® stopcock.

4.5 **Amber Glass Jar.** 500 mL with Teflon®-lined screw cap.

4.6 **Glass Funnel.** Long stem.

4.7 **Kuderna-Danish (K-D) Apparatus.**

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

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

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

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

4.8 Glass Wool. Non-silanized, pre-cleaned by Soxhlet extraction with methylene chloride. Air dry, store in pre-cleaned 500 mL jar.

4.9 Vials. 7-10 mL capacity, calibrated (calibrated centrifuge tubes may also be used).

4.10 Heating Mantle. Rheostat-controlled.

4.11 Water Bath. Heated, with concentric ring cover, capable of temperature control 80°C ± 5°C. The water bath should be used in a hood.

4.12 Gas-tight Syringe. 5-mL to 10-mL capacity. Gas-tight syringes have a glass barrel, with a Teflon® plunger to form an effective seal. The lack of contact with metal and the sealing properties make these syringes very useful for transferring liquid solutions.

4.13 Nitrogen Blowdown Apparatus. Analytical evaporator such as The Meyer N-EVAP Model 111 (Organomation Associates Inc., South Berlin, MA 01549) or equivalent.

4.14 Filter. Glass- or quart-fiber filters, without organic binder. The filters should be the same as those used in the Method 0010 sampling train.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, 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 sufficient purity to permit its use without compromising the integrity of the sample.

5.2 Methanol. Pesticide quality or equivalent.

5.3 Methylene Chloride. Pesticide quality or equivalent.

5.4 Reagent Water. Reagent water is defined as water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest. The cleanliness of the reagent water is determined by extracting 200 mL of reagent water three times with methylene chloride. The methylene chloride extracts are combined, moisture is removed by filtration through Na_2SO_4, the extract is concentrated to 5 mL, and GC/MS analysis is preformed.

5.4.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 400 to 500 g of activated carbon (Calgon Corporation, Filtrasorb-300 or equivalent).

5.4.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

5.5 Sodium Hydroxide Solution (10 Molar): Dissolve 40 g of sodium hydroxide (NaOH, ACS reagent grade) in reagent water and dilute to 100 mL.

5.6 Sulfuric Acid (H_2SO_4) (9 Molar). Slowly add 50 mL of concentrated 18 M H_2SO_4 (ACS reagent grade, specific gravity 1.84) to 50 mL of reagent water.

5.7 Sodium sulfate (Na_2SO_4). ACS, reagent grade, granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

5.8 Surrogate Stock Solution. Either surrogate standards (e.g., the surrogate standards used in Method 8270) or isotopically-labeled analogs of the compounds of interest must be spiked into the Method 0010 train components prior to extraction. Both surrogate standards and isotopically-labeled analogs may be used, if desired. A surrogate standard (i.e., a compound not expected to occur in an environmental sample but chemically similar to analytes) should be added to each sample, blank, and method spike just prior to extraction. The recovery of the surrogate standard is used to monitor for unusual matrix effects or sample processing errors. Normally three or more surrogate standards are added for each analyte group. The surrogate stock solution may be prepared from pure standard materials or purchased as a certified solution. Prepare the stock solution in methylene chloride, using assayed liquids or solids, as appropriate.

5.8.1 The following compounds are the surrogate standards recommended in SW-846 Method 8270:

Acid	Base/Neutral
2-Fluorophenol	2-Fluorobiphenyl
2,4,6-Tribromophenol	Nitrobenzene-d_5
Phenol-d_6	Terphenyl-d_{14}

5.8.2 Prepare a surrogate standard stock solution in methylene chloride that contains the surrogate compounds at a concentration of 5000 μg/mL for the acidic compounds, and 2500 μg/mL for base/neutral compounds. Prepare the stock

surrogate solution by accurately weighing 0.50 ± 0.05 g each of 2-fluorobiphenyl, p-terphenyl-d_{14}, and nitrobenzene-d_5, and 1.00 ± 0.05 g each of 2,4,6-tribromophenol, phenol-d_6, and 2-fluorophenol. Dissolve the materials in methylene chloride and dilute to volume in a 200 mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.8.3 Transfer the stock solution into Teflon®-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation or evaporation, especially just prior to preparing spiking solutions. Allow solutions to come to room temperature before use.

5.8.4 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.9 Surrogate Standard Spiking Solution. Prepare a surrogate standard spiking solution by transferring a 10-mL aliquot of the surrogate stock solution (using a 10-mL volumetric pipet) into a 50-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to a final volume of 50 mL with methylene chloride.

5.9.1 Transfer the surrogate standard spiking solution into Teflon®-sealed screw-cap bottles appropriately sized to minimize headspace. Store at 4°C and protect from light. Spiking solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use.

5.9.2 Surrogate standard spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

5.10 Isotopically-Labeled Analog Stock Solution. Either surrogate standards (e.g., the surrogate standards used in Method 8270) or isotopically-labeled analogs of the compounds of interest must be spiked into the Method 0010 train components prior to extraction. Both surrogate standards and isotopically-labeled analogs may be used, if desired. The use of isotopically-labeled analogs is optional but highly recommended. Common isotopic labels which are used include deuterium and carbon-13; homologs and fluorinated analogs of the compounds of interest may also be used. To assess extraction efficiency, use of an isotopically-labeled analog of the compound of interest is essential. The isotopically-labeled analog is spiked into the matrix immediately prior to extraction, and losses of the spiked compound can be attributed to the sample extraction/ concentration process. An isotopically-labeled analog stock solution can be made from pure standard materials or purchased as a certified solution. Even though the use of isotopically-labeled analogs is optional, each compound to be quantified must be represented by a specific recovery standard, whether in the surrogate standard mixture (Section 5.8) or in a separate spike.

5.10.1 Prepare an isotopically-labeled analog stock solution by accurately weighing approximately 0.250 g of each of the materials to be used. Dissolve in methylene chloride and dilute to volume with methylene chloride in a 200-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.10.2 Transfer the stock solution into Teflon®-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation, evaporation, or isotope exchange, especially just prior to preparing spiking solutions from them. Allow solution to come to room temperature before use.

5.10.3 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.11 Isotopically-Labeled Analog Spiking Solution

5.11.1 Prepare the isotopically-labeled analog standard by transferring a 10-mL aliquot of the stock isotopically-labeled analog stock solution (using a 10-mL volumetric pipet) into a 50-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to volume with methylene chloride. The concentration of the spiking solution should allow the isotopically-labeled analogs to be observed in the final sample in approximately the middle of the calibration range for the gas chromatograph/mass spectrometer, assuming 100% recovery.

5.11.2 Transfer the solution into Teflon®-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Spiking solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use. Allow solutions to come to room temperature prior to use.

5.11.3 Spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

5.12 Stock Method Spike Solution: A method spike consists of a spike of a clean matrix (i.e., clean, dry XAD-2®, clean, dry filter, or water) with a solution containing the compounds of interest (the method spike solution). The compound recoveries obtained from a method spike demonstrate that the compounds of interest can be recovered from the matrix, and aid in elucidating the effects of the field matrix. The method spike solution can be made from pure standard materials or purchased as certified solutions. The compounds of interest for the field test should be used as components of the method spike solution. A method spike is generated by spiking clean XAD-2® or clean reagent grade water.

5.12.1 Prepare a stock method spike solution by accurately weighing 0.05 g each of the compounds of interest. Dissolve the materials in methylene chloride and dilute to volume in a 50-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock solution.

5.12.2 Transfer the stock method spike solution into Teflon®-sealed screw-cap bottles sized to minimize headspace. Store at 4°C and protect from light. Stock solutions should be checked regularly for signs of degradation or evaporation, especially just prior to preparing spiking solutions from them.

5.12.3 Stock solutions should be replaced after one year, or sooner if analysis indicates a problem.

5.13 Method Spike Standard Solution

5.13.1 Prepare the method spike standard solution by transferring a 25-mL aliquot of the stock method spike solution (using a 25-mL volumetric pipet) into a 100-mL volumetric flask containing approximately 20 mL of methylene chloride. Dilute to volume with methylene chloride.

5.13.2 Transfer the method spike standard solution into Teflon®-lined screw-cap bottles appropriately sized to minimize headspace. Store at 4°C and protect from light. Spiking solutions should be checked regularly for signs of degradation or evaporation, especially just prior to use.

5.13.3 Spiking solutions should be replaced after six months, or sooner if analysis indicates a problem.

6.0 SAMPLE HANDLING

6.1 The six components from each Method 0010 sampling train (Figure 2-1) must be stored at 4°C between the time of sampling and extraction. Each sample should be extracted within 14 days of collection and must be analyzed within 40 days of extraction. The extracted sample must be stored at 4°C.

7.0 SAMPLE PREPARATION

7.1 The sample preparation procedure for the six parts of the Method 0010 train will result in three sample extracts for analysis:

1. Particulate Matter Filter and Front Half Rinse;
2. Condensate and Condensate Rinse; and
3. XAD-2® and Condenser/Back Half Rinse.

7.2 Particulate Matter Filter and Front Half Rinse.

7.2.1 Filter. The filter is identified as Container No. 1 in Method 0010.

7.2.1.1 Using clean forceps, place about 10 Teflon® boiling chips into the bottom of the round bottom flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

7.2.1.2 Using a clean syringe or volumetric pipet, add a 1-mL aliquot of the surrogate standard spiking solution (Section 5.9) to the filter. If isotopically-labeled analogs are being used, the isotopically-labeled analog solution (Section 5.11) may be added at this time. If a Method Spike is being prepared, the Method Spike Solution (Section 5.13) may be added at this time.

To ensure proper filter spiking, use a volume of approximately 1 mL of spiking solution. Leave the filter in the petri dish, particulate material on top, for spiking. Spike the 1 mL of spiking solution uniformly onto the particulate-coated surface of the filter in the petri dish by spotting small

volumes at multiple filter locations, using a syringe. Repeat the spiking process with isotopically-labeled standards or method spike solution, if these solutions are being used.

7.2.1.3 Using clean forceps, place the Particulate Matter Filter into a glass thimble and position the glass thimble in the Soxhlet extractor, making sure that the filter will be completely submerged in the methylene chloride with each cycle of the Soxhlet extractor. Place a piece of pre-cleaned unsilanized glass wool on top of the filter in the Soxhlet extractor to keep the filter in place. Rinse the petri dish three times with methylene chloride and add rinses to the Soxhlet.

The Front Half Rinse (Container No. 2) may contain particulate material which has been removed from the probe. This particulate material should be extracted with the filter. To separate particulate matter from the Front Half Rinse, filter the Front Half Rinse. To avoid introducing any contamination, use the same type of filter which has been used in the Method 0010 train, from the same lot as the filter in the Method 0010 train. Filter the Front Half Rinse, rinse Container No. 2 three times with 10 mL aliquots of methylene chloride, and filter the methylene chloride rinses. Transfer the filter with any particulate matter to the Soxhlet extractor with the original filter from the Method 0010 train. Extract the two filters together. Return the liquid portion of Container No. 2 to its orignial container for subsequent extraction or, alternatively, the Front Half Rinse can be filtered directly into a separatory funnel for extraction of the liquid portion of the Front Half Rinse.

7.2.1.4 Slowly add methylene chloride to the Soxhlet extractor containing the two filters through the Soxhlet (with condenser removed),

allowing the Soxhlet to cycle. Add sufficient solvent to fill the round bottom flask approximately half full and submerge the thimble containing the filters.

7.2.1.5 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet to a condenser, making sure that the coolant is flowing through the condenser.

7.2.1.6 Allow the sample to extract for 18 hours, cycling approximately once every thirty minutes.

7.2.1.7 After cooling, disconnect the extractor from the condenser. Tilt the Soxhlet slightly until the remaining solvent has drained into the round bottom flask.

7.2.1.8 Transfer the extract from the round bottom flask into a 500-mL amber glass bottle with Teflon®-lined screw cap. The bottle should have been rinsed three times each with methanol and methylene chloride. Rinse the round bottom flask three times with approximately 10-mL aliquots of methylene chloride and transfer the rinses to the amber bottle. Store the filter extract at 4°C until extraction of the filtered Front Half Rinse has been completed.

7.2.2 Front Half Rinse. The Front Half Rinse is identified as Container No. 2 in Method 0010.

7.2.2.1 Transfer the liquid contents of the filtered Front Half Rinse sample to a separatory funnel of appropriate size for the volume of the sample (a typical Front Half Rinse sample is 200 to 300 mL). Rinse the sample

container three times with 10-mL aliquots of methylene chloride, transferring the rinses to the separatory funnel after each rinse.

7.2.2.2 Because the Front Half Rinse sample consists of a mixture of methanol and methylene chloride, sufficient reagent grade water must be added to the separatory funnel to cause the organic and aqueous/methanol phases to separate into two distinct layers. The methylene chloride layer will be at the bottom of the separatory funnel. Continue to add water until the bottom layer (methylene chloride) does not increase in volume. An increase in volume can be monitored by marking the separatory funnel at the position of the phase separation.

NOTE: The Front Half Rinse is not spiked with any surrogate, isotopic analog, or method spike solutions because the extract from the Front Half Rinse is combined with the extract from the Particulate Matter Filter sample.

7.2.2.3 Add additional methylene chloride, if necessary, so that the ratio of water/methanol to methylene chloride is approximately 3:1. Add sodium hydroxide (Section 5.5) until pH of the water layer is > 11 (but < 14). Use wide-range pH paper to determine pH. Shake vigorously for 2 minutes with rapid arm motion, with periodic venting to release excess pressure. Allow the organic layer to separate for at least 10 minutes. Collect the methylene chloride extract in a 500-mL amber glass bottle with Teflon®-lined screw cap, which has been rinsed three times each with methanol and methylene chloride.

7.2.2.4 Add a second volume of methylene chloride (approximately the same volume as the first extraction) to the separatory funnel and repeat the

extraction procedure, combining the methylene chloride extracts in the amber bottle.

7.2.2.5 Perform a third extraction in the same manner.

7.2.2.6 Acidify the water to a pH <2 (but > 0) with sulfuric acid (Section 5.6) and repeat Section 7.2.2.4 three times. Measure pH with wide-range pH paper.

7.2.3 Concentration of Filter and Front Half Rinse Extracts. The combined extracts and rinses of extract storage bottles will have a total volume of 1 liter or more.

7.2.3.1 Assemble a Kuderna-Danish concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask with clips or springs. Using a clean pair of forceps, place about 5 Teflon® boiling chips into the concentrator tube. If the volume of extract to be concentrated is greater than 500 mL, repeat the concentration as many times as required using the same 500-mL evaporative flask and systematically adding remaining extract. If repeated concentrations are performed, use new boiling chips each time.

7.2.3.2 Using a clean pair of forceps, place a small portion of precleaned unsilanized glass wool in the bottom of a long stem funnel, and pour a 1-inch layer of cleaned sodium sulfate (Section 5.7) on top of the glass wool (use more sodium sulfate, if possible; fill the funnel to within approximately 0.5 inch of the top).

7.2.3.3 Rinse the sodium sulfate contained in the funnel three times with methylene chloride; discard the rinses. Support the funnel in a ring or clamp above the flask to prevent tipping.

7.2.3.4 Place the funnel into the upper opening of the K-D flask and slowly pour extracts from the Filter and Front Half Rinse through the sodium sulfate. Rinse the amber jars containing the extracts three times, using approximately 10 mL of methylene chloride each time. Add the rinses to the funnel. Rinse the sodium sulfate with methylene chloride to complete the transfer.

NOTE: During this process, monitor the condition of the sodium sulfate to determine that the bed of sodium sulfate is not solidifying and exceeding its drying capacity. If the sodium sulfate bed can be stirred and is still free-flowing, effective moisture removal from the extracts is occurring. If the sodium sulfate bed has begun to solidify, do not add more extract. Replace the sodium sulfate bed, re-dry the contents of the K-D flask, and continue drying the extracts.

7.2.3.5 Attach a three-ball macro Snyder column to the evaporative flask. Prewet the Snyder column by adding about 2 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-85°C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 20 to 30 minutes. Rinse sides of K-D during concentration with a small volume of methylene chloride. When the apparent volume of the liquid reaches 6-8 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 10 minutes.

NOTE: Never let the extract in the concentrator tube go to dryness even though additional solvent is present in the upper portion of the K-D apparatus.

NOTE: If the sample concentration is not completed within the anticipated period of time, check the temperature of the water bath and check the composition of the sample. If the methanol has not been completely removed from the methylene chloride extract by the procedures described in Sections 7.2.2.2 and 7.2.2.3, residual methanol will concentrate far slower than a methylene chloride extract and analytes will be lost in the concentration step. A sample containing methanol which has been concentrating for a prolonged period of time cannot be recovered, but extracts which contain residual methanol and have not yet been concentrated can be recovered by performing the procedures in Sections 7.2.2.2 and 7.2.2.3 again.

7.2.3.6 Remove the Snyder column and evaporative flask. With a clean pair of forceps, add two new Teflon® boiling chips to the concentrator tube. Attach a two-ball micro Snyder column to the concentrator tube. Prewet the Snyder column with about 0.5 mL of methylene chloride. Place the K-D apparatus on the hot water bath so that the concentrator tube is partially immersed in hot water, supporting the tube with a clamp. When the apparent volume of the liquid reaches 4-5 mL, remove the K-D apparatus from the water bath and allow the apparatus to cool and drain for at least 10 minutes. If the volume is greater than 5 mL, add a new boiling chip to the concentrator tube, prewet the Snyder column, and concentrate again on the hot water bath. Transfer the extract to a calibrated vial or centrifuge tube, rinse concentrator tube with a minimum volume of methylene chloride and add rinses to the vial, and add methylene chloride, if necessary, to attain a final volume of 5 mL.

Alternatively, the final concentration may be performed by blowing the surface of the solvent with a gentle stream of nitrogen using a glass disposable pipet to direct the stream of nitrogen. When the nitrogen blowdown technique is used, care must be taken to carefully rinse the sides of the vessel using a minimum quantity of methylene chloride to ensure that analytes are in the methylene chloride solution, not deposited on the sides of the glass container. Perform the blowdown procedure in a calibrated vial or centrifuge tube which does not contain boiling chips. The final extract volume must be 5 mL.

7.2.3.7 Transfer the extract to a 10-mL glass storage vial with a Teflon®-lined screw cap. Label the extract as Front Half Rinse and Particulate Filter, and store at 4°C until analysis (Section 7.3 and following Sections, Method 8270). Mark the liquid level on the vial to monitor solvent evaporation during storage.

7.3 Condensate and Condensate Rinse. The Condensate is identified as Container No. 4 in Method 0010; the Condensate Rinse is Container No. 5.

7.3.1 Transfer the contents of both the Condensate and the Condensate Rinse samples to a clean separatory funnel (expected volume of both containers is approximately 500 mL). Rinse each of the sample containers with three aliquots of methylene chloride (approximately 10 mL each), transferring the rinses to the separatory funnel.

7.3.2 Using a clean syringe or volumetric pipet, add a 1-mL aliquot of the surrogate standard (Section 5.9) to the liquid in the separatory funnel. If isotopically-labeled analogs are being used, the isotopically-labeled analog solution (Section 5.11) should be added to the separatory funnel.

7.3.3 Perform an initial methylene chloride extraction of the combined Condensate/Condensate Rinse which has been spiked with appropriate spiking solution(s). Add water as needed to ensure separation of phases. After the initial methylene chloride extraction, check the pH of the Condensate/Condensate Rinse solution with wide-range pH paper. If the solution is acidic (pH < 7), add acid until the pH is < 2 but > 0 and perform another methylene chloride extraction. Then make the Condensate/Condensate Rinse solution basic (pH > 11 but < 14) and perform another methylene chloride extraction. Combine methylene chloride extracts, remove moisture, and concentrate for analysis. If, after the initial methylene chloride extraction, the Condensate/Condensate Rinse solution is basic, increase pH until the pH is > 11 but < 14, and perform another methylene chloride extraction. Then make the Condensate/Condensate Rinse solution acidic (pH < 2 but > 0) and perform another methylene chloride extraction. Combine the methylene chloride extracts, remove moisture, and concentrate the extract for analysis. Refer to Section 7.2.2.2 and following sections for extraction and concentration of the Condensate/Condensate Rinse extract.

7.4 XAD-2®

The sorbent trap section of the organic module is identified as Container No. 3 in Method 0010. The sorbent trap section of the organic module shall be used as a sample transport container.

7.4.1 Using clean forceps, place about 10 Teflon® boiling chips in the bottom of the round bottom flask of the Soxhlet extractor and connect the Soxhlet extractor to the round bottom flask.

7.4.2 Transfer the XAD-2® to the extraction thimble. Remove the glass wool plug from the XAD-2® trap and add to the thimble of the Soxhlet extractor. If

ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor. If the XAD-2® is dry (i.e., free-flowing), pour the XAD-2® directly into the thimble (or directly into the Soxhlet extractor) and rinse the trap with methylene chloride, adding the rinses to the round bottom flask. If the XAD-2® is wet, removal from the trap may be difficult. To accomplish the transfer, flush the resin from the trap using a Teflon® wash bottle containing methylene chloride. Alternatively, acidic water (pH < 2) can be used to wash the walls of the XAD-2® trap. Collect the resin and solvent in a clean 500-mL beaker. Transfer the XAD-2®/methylene chloride from the beaker to the extraction thimble, taking care that no solvent is lost. Alternatively, the XAD-2® can be transferred directly to the Soxhlet extractor and the methylene chloride rinse and transfer solvent allowed to drain through the XAD-2® to the round bottom flask. Rinse the beaker several times with methylene chloride, pouring the rinses through the XAD-2® bed once the extraction thimble is in the Soxhlet extractor. Be sure that a glass wool plug is in place above the XAD-2® to ensure that the XAD-2® does not float out of the thimble.

NOTE: Under no circumstances should methanol or acetone be used to transfer the resin.

Alternative approaches to transfer of XAD-2® from the trap to the extraction thimble are discussed below.

The wet XAD-2® may be transferred from the sampling module to a piece of cleaned aluminum foil by inverting the trap (glass frit up) and tapping the trap on a solid surface covered with the cleaned aluminum foil. This process is slow and may result in breakage of the sampling module. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with

methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor. After the majority of the XAD-2® has been removed from the trap by tapping, the XAD-2® on the aluminum foil may be transferred to the extraction thimble. The sampling module should be rinsed with methylene chloride to flush the remaining XAD-2® particles adhering to the glass wall into the extraction thimble. After all XAD-2® has been transferred into the Soxhlet thimble, add a plug of glass wool to the top of the XAD-2® to hold the resin in place.

Alternatively, the XAD-2® can be transferred directly to the Soxhlet extractor and the methylene chloride rinse and transfer solvent allowed to drain through the XAD-2® to the round bottom flask. If ground glass stoppers are used to seal the sorbent trap during shipment, these ground glass stoppers should be rinsed with methylene chloride and the rinsate added to the round bottom flask of the Soxhlet extractor. To remove the XAD-2® from the sampling module, remove the glass wool from the end of the XAD-2® sampling module. Place this glass wool in the Soxhlet extractor to ensure thorough extraction of the glass wool. If the XAD-® is being transferred directly to the Soxhlet extractor, place a small piece of pre-cleaned glass wool in the side-arm of the Soxhlet extractor to ensure that no XAD-2® enters the side-arm of the Soxhlet extractor. Invert the XAD-2® sampling module (glass frit up) over an extraction thimble contained in a beaker, or directly over the Soxhlet extractor with pre-cleaned glass wool in the bottom, as shown in Figure 7-1. Add approximately 5 to 10 mL of methylene chloride above the glass frit of the sampling module. Connect a rubber pipet filler bulb with check valve that has been fitted with a ball joint to the XAD-2® sampling module. Using air pressure created by squeezing the bulb, gently but firmly push the methylene chloride through the frit, forcing the XAD-2® out of the sampling module. Avoid allowing methylene chloride to be pulled up into the bulb, since the sample will be compromised if methylene chloride is pulled up into the bulb and allowed to become part of the extract. This process will need to be repeated 3 to 5 times. Use a Teflon® wash bottle containing methylene chloride to

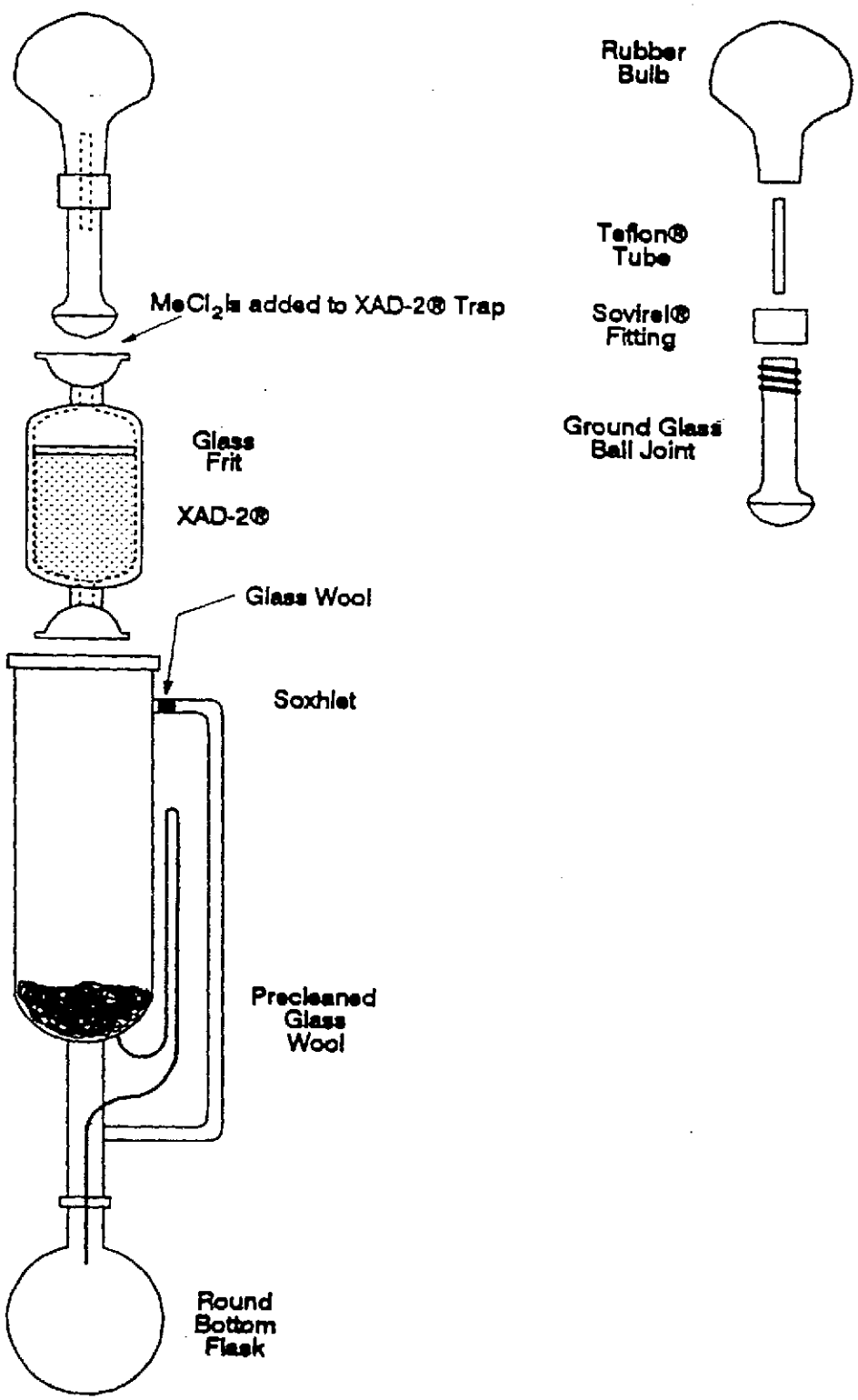


Figure 7-1. Transfer of Wet XAD-2®.

rinse the walls of the sampling module to transfer XAD-2® which has been retained on the walls of the sampling module after transfer of XAD-2® to the Soxhlet. A methylene chloride rinse of the walls will not remove all of the XAD-2®, but after 3 to 5 rinses of the walls of the sampling module, no more than a monolayer of XAD-2® particles should be retained. If more than a monolayer of XAD-2® remains, additional rinses are required.

NOTE: Under no conditions should methanol or acetone be used in the transfer of the XAD-2®.

7.4.3 With the XAD-2® in the Soxhlet extractor and glass wool on top of the XAD-2®, use a clean syringe or volumetric pipet to add a 1-mL aliquot of the surrogate standard spiking solution to the XAD-2®. Be sure that the needle of the syringe penetrates the XAD-2® bed to a depth of at least 0.5 in. If isotopically-labeled standard solution or method spike solution is being used, these solutions should be spiked at this time.

7.4.4 Container No. 5 contains the methylene chloride/methanol rinse of the condenser and all train components from the back half of the filter holder to the XAD-2® sampling module. These rinses consist of 50:50 methanol:methylene chloride. Transfer the contents of Container No. 5 to a separatory funnel and rinse the Container with three 10 mL aliquots of methylene chloride. Add the rinses to the separatory funnel. Sufficient reagent water must be added to the separatory funnel to cause the organic and aqueous phases to separate into two distinct layers. Refer to Section 7.2.2.2 and following sections for preparation of a methylene chloride extract from Container No. 5. Add the methylene chloride layer from the separatory funnel directly to the Soxhlet extractor containing the XAD-2® or collect the methylene chloride extract in a container and transfer from this container to the Soxhlet containing the XAD-2®. Pour the methylene chloride extract of the Condenser and

Back Half Rinses through the XAD-2® in the Soxhlet extractor; rinse the container or separatory funnel 3 times with approximately 10 mL aliquots of methylene chloride and add the rinses to the Soxhlet.

7.4.4 Add additional methylene chloride to the Soxhlet extractor, if necessary, pouring approximately 300-400 mL through the XAD-2® bed so that the round bottom flask is approximately half-full and the XAD-2® bed is covered.

7.4.5 Place a heating mantle under the round bottom flask and connect the upper joint of the Soxhlet extractor to a condenser.

NOTE: Start the extraction process immediately after spiking is completed to ensure that no volatilization of organic compounds from the resin or any spiking solutions occurs before the extraction process is started.

7.4.6 Allow the sample to extract for at least 18 hours but not more than 24 hours, cycling once every 25-30 minutes.

NOTE: Be sure that cooling water for the condensers is cold and circulating. Watch the extractor through two or three cycles to ensure that the extractor is working properly.

7.4.7 After the Soxhlet extractor has been cooled, disconnect the extractor from the condenser and tilt the extractor slightly until the remaining solvent in the Soxhlet has drained into the round bottom flask.

7.4.8 Inspect the contents of the round bottom flask to determine whether there is a visible water layer on top of the methylene chloride. If no water layer is observed, transfer the extract into a 500-mL amber glass bottle with Teflon®-lined

screw cap for storage (Section 7.2.1.8), or proceed directly with removal of moisture and concentration of the extract (Section 7.2.3.1). If a water layer is observed in the Soxhlet round bottom flask, transfer the contents to a separatory funnel, rinsing the round bottom flask three times with methylene chloride and adding the rinsings to the separatory funnel. Drain the methylene chloride from the separatory funnel and store in an amber glass bottle. Then perform an acid/base extraction of the water layer remaining in the separatory funnel (Section 7.3.3). Add the methylene chloride extract from the acid/base extraction to the methylene chloride extract from the round bottom flask in the amber glass jar. Store the extract in the amber glass bottle at 4°C for subsequent removal of moisture and concentration following the steps outlined in Section 7.2.3.1.

8.0 QUALITY CONTROL

8.1 A method blank consists of a clean filter, clean dry XAD-2®, or reagent water, which is spiked with surrogate standards prior to extraction. The method blank is extracted and concentrated using the same procedures as the corresponding sample matrix. One method blank is extracted and analyzed for every ten samples.

8.2 A method spike consists of a clean filter, XAD-2®, or reagent water, which is spiked with surrogate standards, isotopically-labeled standards if used, and method spike solution (if used) prior to extraction. The method spike is extracted and concentrated using the same procedures as the corresponding sample matrix. At least one method spike is extracted and analyzed for every matrix, with a frequency of one method spike for every twenty samples.

9.0 METHOD PERFORMANCE

9.1 Method Performance Evaluation. Evaluation of analytical procedures for a selected series of compounds must include the sample preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through all the procedures.

9.2 Method Detection Limits. The overall method detection limits (lower and upper) must be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrument minimum detection limit. The method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (breakthrough).

9.3 Method Precision and Bias. The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. The surrogate recoveries shown below represent mean recoveries for surrogates in all Method 0010 matrices in a field dynamic spiking study.

Compound	Mean Recovery	Standard Deviation	Relative Standard Deviation Percent
2-fluorophenol	74.6	28.6	38.3
phenol-d_5	77.8	27.7	35.6
nitrobenzene-d_5	65.6	32.5	49.6
2-fluorobiphenyl	75.9	30.3	39.9
2,4,6-tribromophenol	67.0	34.0	50.7
terphenyl-d_{14}	78.6	32.4	41.3

10.0 REFERENCES

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TECHNICAL REPORT DATA

1. REPORT NO.	2.	PB97-118533
EPA/600/R-96/036		

4. TITLE AND SUBTITLE	5. REPORT DATE
Guidance for Total Organics	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Robert F. Martz, Easter A. Coppedge, Larry D. Johnson	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Radian Corporation P.O. Box 13000 Research Triangle Park, NC 27709	11. CONTRACT/GRANT NO. 68-D4-0022
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
National Exposure Research Laboratory Office Of Research and Development U. S. Environmental Protection Agency Research Triangle Park, NC 27711	Published Report 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This document provides guidance to those wishing to determine the total organics content of source samples. Writers of air quality permit applications for waste combustion units require total organics data for their assessments. This document identifies specific techniques to determine the total organics sampled from stationary sources. It describes the measurement of total organics from stack emissions and related field sampling efforts, combining the organics from three specific boiling point/vapor pressure classes: light hydrocarbons and volatile organics (boiling points <100°C), semivolatile organics (boiling points 100°C to 300°C), and non-volatile organic compounds (boiling points >300°C). It describes methods for measuring and reporting the individual parameters. The document seeks to avoid the confusion about organics measurement and eliminate the misleading and non-descriptive titles often given to different facets of organics analysis. It also provides information about combining the component parts of the organics analysis results into a helpful description of the data. Knowing the amount of previously uncharacterized organic material enables more accurate risk assessment estimates to be made. Discussions of the specific methods and operating procedures are found in the appendices and references.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/ OPEN ENDED TERMS	c. COSATI

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	223
	20. SECURITY CLASS *(This Page)*	22. PRICE
	UNCLASSIFIED	