APPENDIX A

STANDARD OPERATING PROCEDURES

SUMMA CANISTER SAMPLING

SOP#: 1704
DATE: 07/27/95
REV. #: 0.1

1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe a procedure for sampling of volatile organic compounds (VOCs) in ambient air. The method is based on samples collected as whole air samples in Summa passivated stainless steel canisters. The VOCs are subsequently separated by gas chromatography (GC) and measured by mass-selective detector or multidetector techniques. This method presents procedures for sampling into canisters at final pressures both above and below atmospheric pressure (respectively referred to as pressurized and subatmospheric pressure sampling).

This method is applicable to specific VOCs that have been tested and determined to be stable when stored in pressurized and subatmospheric pressure canisters. The organic compounds that have been successfully collected in pressurized canisters by this method are listed in the Volatile Organic Compound Data Sheet (Appendix A). These compounds have been measured at the parts per billion by volume (ppbv) level.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent on site conditions, equipment limitations or limitations imposed by the procedure or other procedure limitations. In all instances, the ultimate procedures employed should be documented and associated with the final report.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

2.0 METHOD SUMMARY

Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. Both modes may also use a mass flow controller/vacuum pump arrangement to regulate flow. With the above configuration, a sample of ambient air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre-evacuated Summa passivated canister. Alternatively, subatmospheric pressure sampling may be performed using a fixed orifice, capillary, or adjustable micrometering valve in lieu of the mass flow controller/vacuum pump arrangement for taking grab samples or short duration time-integrated samples. Usually, the alternative types of flow controllers are appropriate only in situations where screening samples are taken to assess for future sampling activities.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to a laboratory for analysis. Upon receipt at the laboratory, the canister tag data is recorded. Sample holding times and expiration should be determined prior to initiating field activities.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned.

5.0 EQUIPMENT/APPARATUS

The following equipment/apparatus (Figure 1, Appendix B) is required:

5.1 Subatmospheric Pressure Sampling Equipment

1. VOC canister sampler - whole air sampler capable of filling an initially evacuated canister by action of the flow controlled pump from vacuum to near atmospheric pressure. (Andersen Samplers Inc., Model 87-100 or equivalent).

2. Sampling inlet line - stainless steel tubing to connect the sampler to the sample inlet.

3. Sample canister - leak-free stainless steel pressure vessels of desired volume with valve and Summa passivated interior surfaces (Scientific Instrumentation Specialist, Inc., ID 83843, Andersen Samplers, Inc., or equivalent).

4. Particulate matter filter - 2-µm sintered stainless steel in-line filter (Nupro Co., Model SS-2F-K4-2, or equivalent).

5. Chromatographic grade stainless steel tubing and fittings - for interconnections (Alltech Associates, Cat. #8125, or equivalent). All materials in contact with sample, analyte, and support gases should be chromatographic grade stainless steel.

6. Fixed orifice, capillary, or adjustable micrometering valve - used in lieu of the electronic flow controller/vacuum pump for grab samples or short duration time-integrated samples.

5.2 Pressurized Sampling Equipment

1. VOC canister sampler - whole air sampler capable of filling an initially evacuated canister by action of the flow controlled pump from vacuum to near atmospheric pressure. (Andersen Samplers Inc., Model 87-100).

2. Sampling inlet line - stainless steel tubing to connect the sampler to the sample inlet.

3. Sample canister - leak-free stainless steel pressure vessels of desired volume with valve and Summa passivated interior surfaces (Scientific Instrumentation Specialist, Inc., ID 83843, Andersen Samplers, Inc., or equivalent).

4. Particulate matter filter - 2-µm sintered stainless steel in-line filter (Nupro Co., Model SS-2F-K4-2, or equivalent).

5. Chromatographic grade stainless steel tubing and fittings - for interconnections (Alltech Associates, Cat. #8125, or equivalent). All materials in contact with sample, analyte, and support gases should be chromatographic grade stainless steel.

6.0 REAGENTS

This section is not applicable to this SOP.

7.0 PROCEDURE

7.1 Subatmospheric Pressure Sampling

7.1.1 Sampling Using a Fixed Orifice, Capillary, or Adjustable Micrometering Valve

1. Prior to sample collection, the appropriate information is completed on the Canister Sampling Field Data Sheet (Appendix C).

2. A canister, which is evacuated to 0.05 mm Hg and fitted with a flow restricting device, is opened to the atmosphere containing the VOCs to be sampled.

3. The pressure differential causes the sample to flow into the canister.

4. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-integrated samples (duration of 12 to 24 hours). The sampling duration depends on the degree to which the flow is restricted.

5. A critical orifice flow restrictor will have a decrease in the flow rate as the pressure approaches atmospheric.

6. Upon sample completion at the location, the appropriate information is recorded on the

Canister Sampling Field Data Sheet.

7.1.2 Sampling Using a Mass Flow Controller/Vacuum Pump Arrangement (Andersen Sampler Model 87-100)

1. Prior to sample collection the appropriate information is completed on the Canister Sampling Field Data Sheet (Appendix C).

2. A canister, which is evacuated to 0.05 mm Hg and connected in line with the sampler, is opened to the atmosphere containing the VOCs to be sampled.

3. A whole air sample is drawn into the system through a stainless steel inlet tube by a direct drive blower motor assembly.

4. A small portion of this whole air sample is pulled from the inlet tube by a specially modified inert vacuum pump in conjunction with a mass flow controller.

5. The initially evacuated canister is filled by action of the flow controlled pump to near atmospheric pressure.

6. A digital time-program is used to pre-select sample duration and start and stop times.

7. Upon sample completion at the location, the appropriate information is recorded on the Canister Sampling Field Data Sheet.

7.2 Pressurized Sampling

7.2.1 Sampling Using a Mass Flow Controller/Vacuum Pump Arrangement (Anderson Sampler Model 87-100)

1. Prior to sample commencement at the location, the appropriate information is completed on the Canister Sampling Field Data Sheet.

2. A canister, which is evacuated to 0.05 mm Hg and connected in line with the sampler, is opened to the atmosphere containing the VOCs to be sampled.

3. A whole air sample is drawn into the system through a stainless steel inlet tube by a direct drive blower motor assembly.

4. A small portion of this whole air sample is pulled from the inlet tube by a specially modified inert vacuum pump in conjunction with a mass flow controller.

5. The initially evacuated canister is filled by action of the flow controlled pump to a positive pressure not to exceed 25 psig.

6. A digital time-programmer is used to pre-select sample duration and start and stop times.

7. Upon sample completion at the location, the appropriate information is recorded on the Canister Sampling Field Data Sheet.

8.0 CALCULATIONS

1. A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling over the desired sample period. The flow rate can be calculated by:

$$F = \frac{(P)(V)}{(T)(60)}$$

where:

F	=	flow rate (cm^3/min)
P	=	final canister pressure, atmospheres absolute
V	=	volume of the canister (cm^3)
T	=	sample period (hours)

For example, if a 6-L canister is to be filled to 202 kPa (two atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{(2)(6000)}{(24)(60)} = 8.3 cm^3/\text{min}$$

2. If the canister pressure is increased, a dilution factor (DF) is calculated and recorded on the sampling data sheet.

$$DF = \frac{Ya}{Xa}$$

where:

Xa = canister pressure (kPa, psia) absolute before dilution.

Ya = canister pressure (kPa, psia) absolute after dilution.

After sample analysis, detected VOC concentrations are multiplied by the dilution factor to determine concentration in the sampled air.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

The following general quality assurance procedures apply:

1. All data must be documented on standard chain of custody records, field data sheets, or site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OSHA, and corporate health and safety practices. Specifically, pressurizing of Summa canisters should be performed in a well ventilated room, or preferably under a fume hood. Care must be taken not to exceed 40 psi in the canisters. Canisters are under pressure, albeit only 20-30 psi, and should not be dented or punctured. They should be stored in a cool dry place and always be placed in their plastic shipping boxes during transport and storage.

12.0 REFERENCES

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APPENDIX A

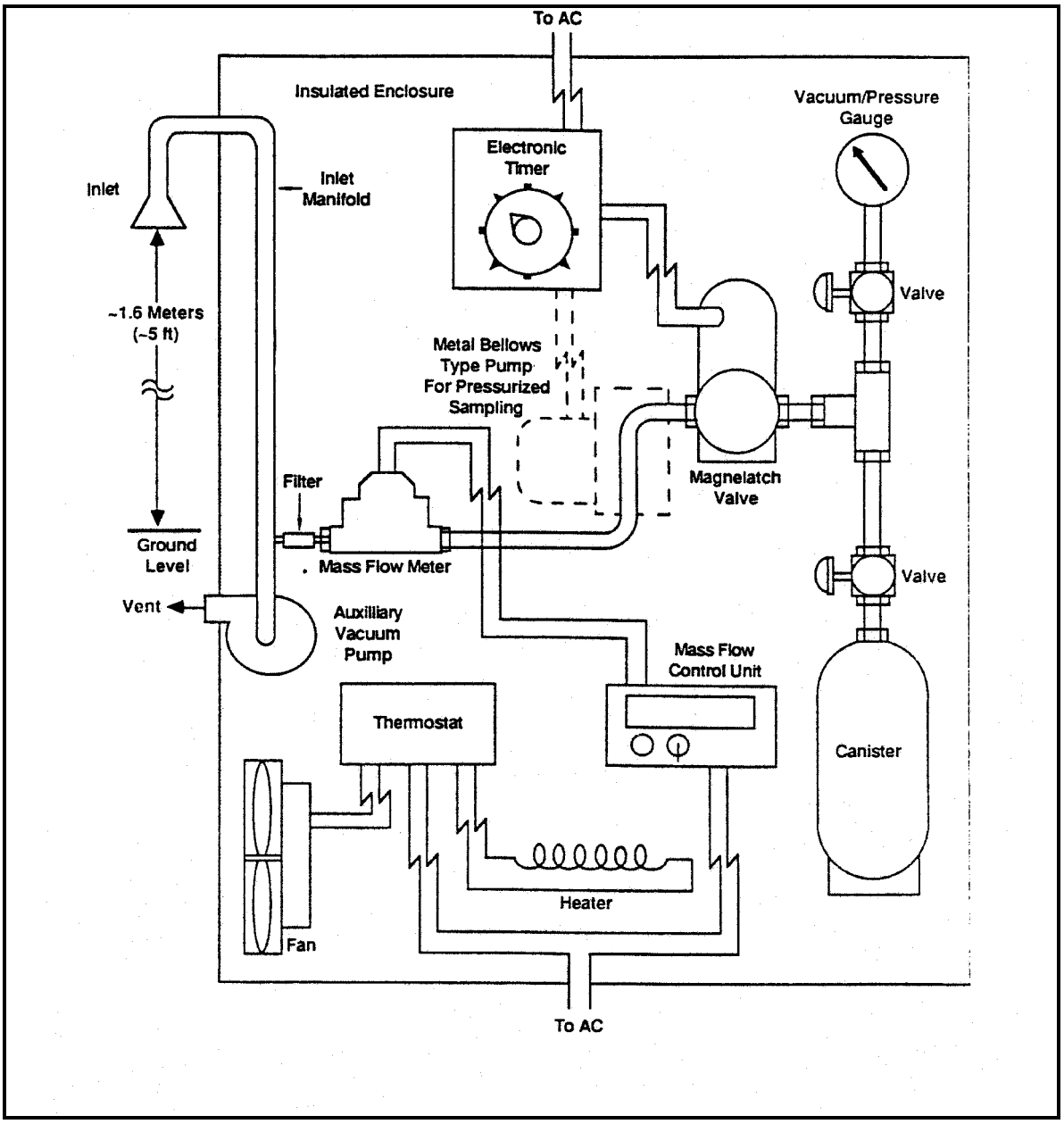
Volatile Organic Compound Data Sheet

TABLE 1. VOLATILE ORGANIC COMPOUND DATA SHEET

COMPOUND (SYNONYM)	FORMULA	MOLECULAR WEIGHT	BOILING POINT (°C)	MELTING POINT (°C)	CAS NUMBER
Freon 12 (Dichlorodifluoromethane)	Cl_2CF_2	120.91	-29.8	-158.0	
Methyl chloride (Chloromethane)	CH_3Cl	50.49	-24.2	-97.1	74-87-3
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	$ClCF_2CClF_2$	170.93	4.1	-94.0	
Vinyl chloride (Chloroethylene)	$CH_2=CHCl$	62.50	-13.4	-1538.0	75-01-4
Methyl bromide (Bromomethane)	CH_3Br	94.94	3.6	-93.6	74-83-9
Ethyl chloride (Chloroethane)	CH_3CH_2Cl	64.52	12.3	-136.4	75-00-3
Freon 11 (Trichlorofluoromethane)	CCl_3F	137.38	23.7	-111.0	
Vinylidene chloride (1,1-Dichloroethene)	$C_2H_2Cl_2$	96.95	31.7	-122.5	75-35-4
Dichloromethane (Methylene chloride)	CH_2Cl_2	84.94	39.8	-95.1	75-09-2
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF_2ClCCl_2F	187.38	47.7	-36.4	
1,1-Dichloroethane (Ethylidene chloride)	CH_3CHCl_2	98.96	57.3	-97.0	74-34-3
cis-1,2-Dichloroethylene	$CHCl=CHCl$	96.94	60.3	-80.5	
Chloroform (Trichloromethane)	$CHCl_3$	119.38	61.7	-63.5	67-66-3
1,2-Dichloroethane (Ethylene dichloride)	$ClCH_2CH_2Cl$	98.96	83.5	-35.3	107-06-2
Methyl chloroform (1,1,1-Trichloroethane)	CH_3CCl_3	133.41	74.1	-30.4	71-55-6
Benzene (Cyclohexatriene)	C_6H_6	78.12	80.1	5.5	71-43-2
Carbon tetrachloride (Tetrachloromethane)	CCl_4	153.82	76.5	-23.0	56-23-5
1,2-Dichloropropane (Propylene dichloride)	$CH_3CHClCH_2Cl$	112.99	96.4	-100.4	78-87-5
Trichloroethylene (Trichloroethene)	$ClCH=CCl_2$	131.29	87	-73.0	79-01-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	$CH_3CCl=CHCl$	110.97	76		
trans-1,3-Dichloropropene (cis-1,3-Dichloropropylene)	$ClCH_2CH=CHCl$	110.97	112.0		
1,1,2-Trichloroethane (Vinyl trichloride)	$CH_2ClCHCl_2$	133.41	113.8	-36.5	79-00-5
Toluene (Methyl benzene)	$C_6H_5CH_3$	92.15	110.6	-95.0	108-88-3
1,2-Dibromoethane (Ethylene dibromide)	$BrCH_2CH_2Br$	187.88	131.3	9.8	106-93-4
Tetrachloroethylene (Perchloroethylene)	$Cl_2C=CCl_2$	165.83	121.1	-19.0	127-18-4
Chlorobenzene (Phenyl chloride)	C_6H_5Cl	112.56	132.0	-45.6	108-90-7
Ethylbenzene	$C_6H_5C_2H_5$	106.17	136.2	-95.0	100-41-4
m-Xylene (1,3-Dimethylbenzene)	$1,3-(CH_3)_2C_6H_4$	106.17	139.1	-47.9	
p-Xylene (1,4-Dimethylxylene)	$1,4-(CH_3)_2C_6H_4$	106.17	138.3	13.3	
Styrene (Vinyl benzene)	$C_6H_5CH=CH_2$	104.16	145.2	-30.6	100-42-5
1,1,2,2-Tetrachloroethane	$CHCl_2CHCl_2$	167.85	146.2	-36.0	79-34-5
o-Xylene (1,2-Dimethylbenzene)	$1,2-(CH_3)_2C_6H_4$	106.17	144.4	-25.2	
1,3,5-Trimethylbenzene (Mesitylene)	$1,3,5-(CH_3)_3C_6H_6$	120.20	164.7	-44.7	108-67-8
1,2,4-Trimethylbenzene (Pseudocumene)	$1,2,4-(CH_3)_3C_6H_6$	120.20	169.3	-43.8	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	$1,3-Cl_2C_6H_4$	147.01	173.0	-24.7	541-73-1
Benzyl chloride (α-Chlorotoluene)	$C_6H_5CH_2Cl$	126.59	179.3	-39.0	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	$1,2-Cl_2C_6H_4$	147.01	180.5	-17.0	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	$1,4-Cl_2C_6H_4$	147.01	174.0	53.1	106-46-7
1,2,4-Trichlorobenzene	$1,2,4-Cl_3C_6H_3$	181.45	213.5	17.0	120-82-1
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)					

APPENDIX B

FIGURE 1. Subatmospheric/Pressurized Sampling Equipment



APPENDIX C

Canister Sampling Field Data Sheet

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SUMMA AIR SAMPLING WORK SHEET

Site: _____ Site#: _____
Samplers: _____ Work Assignment Manager: _____
Date: _____ Project Leader: _____

Sample #					
Location					
SUMMA ID					
Orifice Used					
Analysis/Method					
Time (Start)					
Time (Stop)					
Total Time					
SUMMA WENT TO AMBIENT	YES/NO	YES/NO	YES/NO	YES/NO	YES/NO
Pressure Gauge					
Pressure Gauge					
Flow Rate (Pre)					
Flow Rate (Post)					
Flow Rate (Average)					

MET Station On-site? Y / N

General Comments:

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-15

Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

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January 1999

Method TO-15
Acknowledgements

This Method was prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b), which was prepared under Contract No. 68-C3-0315, WA No. 3-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, and Scott Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development, were responsible for overseeing the preparation of this method. Additional support was provided by other members of the Compendia Workgroup, which include:

- John O. Burckle, EPA, ORD, Cincinnati, OH
- James L. Cheney, Corps of Engineers, Omaha, NB
- Michael Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- Heidi Schultz, ERG, Lexington, MA
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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- Bill Taylor, Graseby, Smyrna, GA
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

Finally, recognition is given to Frances Beyer, Lynn Kaufman, Debbie Bond, Cathy Whitaker, and Kathy Johnson of Midwest Research Institute's Administrative Services staff whose dedication and persistence during the development of this manuscript has enabled it's production.

DISCLAIMER

METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

TABLE OF CONTENTS

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METHOD TO-15

Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/ Mass Spectrometry (GC/MS)

1. Scope

1.1 This method documents sampling and analytical procedures for the measurement of subsets of the 97 volatile organic compounds (VOCs) that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. Table 1 is the list of the target VOCs along with their CAS number, boiling point, vapor pressure and an indication of their membership in both the list of VOCs covered by Compendium Method TO-14A (1) and the list of VOCs in EPA's Contract Laboratory Program (CLP) document entitled: *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites (2)*.

Many of these compounds have been tested for stability in concentration when stored in specially-prepared canisters (see Section 8) under conditions typical of those encountered in routine ambient air analysis. The stability of these compounds under all possible conditions is not known. However, a model to predict compound losses due to physical adsorption of VOCs on canister walls and to dissolution of VOCs in water condensed in the canisters has been developed (3). Losses due to physical adsorption require only the establishment of equilibrium between the condensed and gas phases and are generally considered short term losses, (i.e., losses occurring over minutes to hours). Losses due to chemical reactions of the VOCs with cocollected ozone or other gas phase species also account for some short term losses. Chemical reactions between VOCs and substances inside the canister are generally assumed to cause the gradual decrease of concentration over time (i.e., long term losses over days to weeks). Loss mechanisms such as aqueous hydrolysis and biological degradation (4) also exist. No models are currently known to be available to estimate and characterize all these potential losses, although a number of experimental observations are referenced in Section 8. Some of the VOCs listed in Title III have short atmospheric lifetimes and may not be present except near sources.

1.2 This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume. The VOC concentration range for ambient air in many cases includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.3 This method applies under most conditions encountered in sampling of ambient air into canisters. However, the composition of a gas mixture in a canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example, low humidity conditions in the sample may lead to losses of certain VOCs on the canister walls, losses that would not happen if the humidity were higher. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs can be recovered from canisters near their original concentrations after storage times of up to thirty days (see Section 8).

1.4 Use of the Compendium Method TO-15 for many of the VOCs listed in Table 1 is likely to present two difficulties: (1) what calibration standard to use for establishing a basis for testing and quantitation, and (2) how

to obtain an audit standard. In certain cases a chemical similarity exists between a thoroughly tested compound and others on the Title III list. In this case, what works for one is likely to work for the other in terms of making standards. However, this is not always the case and some compound standards will be troublesome. The reader is referred to the Section 9.2 on standards for guidance. Calibration of compounds such as formaldehyde, diazomethane, and many of the others represents a challenge.

1.5 Compendium Method TO-15 should be considered for use when a subset of the 97 Title III VOCs constitute the target list. Typical situations involve ambient air testing associated with the permitting procedures for emission sources. In this case sampling and analysis of VOCs is performed to determine the impact of dispersing source emissions in the surrounding areas. Other important applications are prevalence and trend monitoring for hazardous VOCs in urban areas and risk assessments downwind of industrialized or source-impacted areas.

1.6 Solid adsorbents can be used in lieu of canisters for sampling of VOCs, provided the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17 which specifically addresses the use of multisorbent packings. The two sample collection techniques are different but become the same upon movement of the sample from the collection medium (canister or multisorbent tubes) onto the sample concentrator. Sample collection directly from the atmosphere by automated gas chromatographs can be used in lieu of collection in canisters or on solid adsorbents.

2. Summary of Method

2.1 The atmosphere is sampled by introduction of air into a specially-prepared stainless steel canister. Both subatmospheric pressure and pressurized sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into the pre-evacuated and passivated canister.

2.2 After the air sample is collected, the canister valve is closed, an identification tag is attached to the canister, and the canister is transported to the laboratory for analysis.

2.3 Upon receipt at the laboratory, the canister tag data is recorded and the canister is stored until analysis. Storage times of up to thirty days have been demonstrated for many of the VOCs (5).

2.4 To analyze the sample, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapor in the sample breaks through the concentrator during sampling, to a degree depending on the multisorbent composition, duration of sampling, and other factors. Water content of the sample can be further reduced by dry purging the concentrator with helium while retaining target compounds. After the concentration and drying steps are completed, the VOCs are thermally desorbed, entrained in a carrier gas stream, and then focused in a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then released by thermal desorption and carried onto a gas chromatographic column for separation.

As a simple alternative to the multisorbent/dry purge water management technique, the amount of water vapor in the sample can be reduced below any threshold for affecting the proper operation of the analytical system by

reducing the sample size. For example, a small sample can be concentrated on a cold trap and released directly to the gas chromatographic column. The reduction in sample volume may require an enhancement of detector sensitivity.

Other water management approaches are also acceptable as long as their use does not compromise the attainment of the performance criteria listed in Section 11. A listing of some commercial water management systems is provided in Appendix A. One of the alternative ways to dry the sample is to separate VOCs from condensate on a low temperature trap by heating and purging the trap.

2.5 The analytical strategy for Compendium Method TO-15 involves using a high resolution gas chromatograph (GC) coupled to a mass spectrometer. If the mass spectrometer is a linear quadrupole system, it is operated either by continuously scanning a wide range of mass to charge ratios (SCAN mode) or by monitoring select ion monitoring mode (SIM) of compounds on the target list. If the mass spectrometer is based on a standard ion trap design, only a scanning mode is used (note however, that the Selected Ion Storage (SIS) mode for the ion trap has features of the SIM mode). Mass spectra for individual peaks in the total ion chromatogram are examined with respect to the fragmentation pattern of ions corresponding to various VOCs including the intensity of primary and secondary ions. The fragmentation pattern is compared with stored spectra taken under similar conditions, in order to identify the compound. For any given compound, the intensity of the primary fragment is compared with the system response to the primary fragment for known amounts of the compound. This establishes the compound concentration that exists in the sample.

Mass spectrometry is considered a more definitive identification technique than single specific detectors such as flame ionization detector (FID), electron capture detector (ECD), photoionization detector (PID), or a multidetector arrangement of these (see discussion in Compendium Method TO-14A). The use of both gas chromatographic retention time and the generally unique mass fragmentation patterns reduce the chances for misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3. Significance

3.1 Compendium Method TO-15 is significant in that it extends the Compendium Method TO-14A description for using canister-based sampling and gas chromatographic analysis in the following ways:

- Compendium Method TO-15 incorporates a multisorbent/dry purge technique or equivalent (see Appendix A) for water management thereby addressing a more extensive set of compounds (the VOCs mentioned in Title III of the CAAA of 1990) than addressed by Compendium Method TO-14A. Compendium Method TO-14A approach to water management alters the structure or reduces the sample stream concentration of some VOCs, especially water-soluble VOCs.
- Compendium Method TO-15 uses the GC/MS technique as the only means to identify and quantitate target compounds. The GC/MS approach provides a more scientifically-defensible detection scheme which is generally more desirable than the use of single or even multiple specific detectors.
- In addition, Compendium Method TO-15 establishes method performance criteria for acceptance of data, allowing the use of alternate but equivalent sampling and analytical equipment. There are several new and viable commercial approaches for water management as noted in Appendix A of this method on which to base a VOC monitoring technique as well as other approaches to sampling (i.e., autoGCs and solid

adsorbents) that are often used. This method lists performance criteria that these alternatives must meet to be acceptable alternatives for monitoring ambient VOCs.
- Finally, Compendium Method TO-15 includes enhanced provisions for inherent quality control. The method uses internal analytical standards and frequent verification of analytical system performance to assure control of the analytical system. This more formal and better documented approach to quality control guarantees a higher percentage of good data.

3.2 With these features, Compendium Method TO-15 is a more general yet better defined method for VOCs than Compendium Method TO-14A. As such, the method can be applied with a higher confidence to reduce the uncertainty in risk assessments in environments where the hazardous volatile gases listed in the Title III of the Clean Air Act Amendments of 1990 are being monitored. An emphasis on risk assessments for human health and effects on the ecology is a current goal for the U.S. EPA.

4. Applicable Documents

4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis*.
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures*.
- **Method E355** *Practice for Gas Chromatography Terms and Relationships*.
- **Method D5466** *Standard Test Method of Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology)*.

4.2 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-14, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.
- *Statement-of-Work (SOW) for the Analysis of Air Toxics from Superfund Sites*, U. S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C., Draft Report, June 1990.
- *Clean Air Act Amendments of 1990*, U. S. Congress, Washington, D.C., November 1990.

5. Definitions

[Note: Definitions used in this document and any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E355. Aside from the definitions given below, all pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Gauge Pressure—pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric (barometric) pressure.

5.2 Absolute Pressure—pressure measured with reference to absolute zero pressure, usually expressed in units of kPa, or psi.

5.3 Cryogen—a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typical cryogens are liquid nitrogen (bp -195.8°C), liquid argon (bp -185.7°C), and liquid CO_2 (bp -79.5°C).

5.4 Dynamic Calibration—calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the sampling or analytical system from a manifold through which the gas standards are flowing.

5.5 Dynamic Dilution—means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

5.6 MS-SCAN—mass spectrometric mode of operation in which the gas chromatograph (GC) is coupled to a mass spectrometer (MS) programmed to SCAN all ions repeatedly over a specified mass range.

5.7 MS-SIM—mass spectrometric mode of operation in which the GC is coupled to a MS that is programmed to scan a selected number of ions repeatedly [i.e., selected ion monitoring (SIM) mode].

5.8 Qualitative Accuracy—the degree of measurement accuracy required to correctly identify compounds with an analytical system.

5.9 Quantitative Accuracy—the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

5.10 Replicate Precision—precision determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage (see Section 11 for performance criteria for replicate precision).

5.11 Duplicate Precision—precision determined from the analysis of two samples taken from the same canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

5.12 Audit Accuracy—the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage (see Section 11 for performance criteria for audit accuracy).

6. Interferences and Contamination

6.1 Very volatile compounds, such as chloromethane and vinyl chloride can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column, mitigates this problem.

6.2 Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters.

6.2.1 Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

6.2.2 Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

6.2.3 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

6.2.4 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

6.2.5 In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation (see Compendium Method TO-17 for more information on artifacts).

7. Apparatus and Reagents

[Note: Compendium Method To-14A list more specific requirements for sampling and analysis apparatus which may be of help in identifying options. The listings below are generic.]

7.1 Sampling Apparatus

[Note: Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been used as part of U.S. Environmental Protection Agency's Toxic Air Monitoring Stations (TAMS), Urban Air Toxic Monitoring Program (UATMP), the non-methane organic compound (NMOC) sampling and analysis program, and the Photochemical Assessment Monitoring Stations (PAMS).]

7.1.1 Subatmospheric Pressure (see Figure 1, without metal bellows type pump).

7.1.1.1 Sampling Inlet Line. Stainless steel tubing to connect the sampler to the sample inlet.

7.1.1.2 Sample Canister. Leak-free stainless steel pressure vessels of desired volume (e.g., 6 L), with valve and specially prepared interior surfaces (see Appendix B for a listing of known manufacturers/resellers of canisters).

7.1.1.3 Stainless Steel Vacuum/Pressure Gauges. Two types are required, one capable of measuring vacuum (–100 to 0 kPa or 0 to - 30 in Hg) and pressure (0–206 kPa or 0–30 psig) in the sampling system and a second type (for checking the vacuum of canisters during cleaning) capable of measuring at 0.05 mm Hg (see Appendix B) within 20%. Gauges should be tested clean and leak tight.

7.1.1.4 Electronic Mass Flow Controller. Capable of maintaining a constant flow rate (± 10%) over a sampling period of up to 24 hours and under conditions of changing temperature (20–40°C) and humidity.

7.1.1.5 Particulate Matter Filter. 2-μm sintered stainless steel in-line filter.

7.1.1.6 Electronic Timer. For unattended sample collection.

7.1.1.7 Solenoid Valve. Electrically-operated, bi-stable solenoid valve with Viton® seat and O-rings. A Skinner Magnelatch valve is used for purposes of illustration in the text (see Figure 2).

7.1.1.8 Chromatographic Grade Stainless Steel Tubing and Fittings. For interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis should be chromatographic grade stainless steel or equivalent.

7.1.1.9 Thermostatically Controlled Heater. To maintain above ambient temperature inside insulated sampler enclosure.

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

7.1.1.13 Maximum-Minimum Thermometer. Records highest and lowest temperatures during sampling period.

7.1.1.14 Stainless Steel Shut-off Valve. Leak free, for vacuum/pressure gauge.

7.1.1.15 Auxiliary Vacuum Pump. Continuously draws air through the inlet manifold at 10 L/min. or higher flow rate. Sample is extracted from the manifold at a lower rate, and excess air is exhausted.

[Note: The use of higher inlet flow rates dilutes any contamination present in the inlet and reduces the possibility of sample contamination as a result of contact with active adsorption sites on inlet walls.]

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

7.1.1.17 Optional Fixed Orifice, Capillary, or Adjustable Micrometering Valve. May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Usually appropriate only in situations where screening samples are taken to assess future sampling activity.

7.1.2 Pressurized (see Figure 1 with metal bellows type pump and Figure 3).

7.1.2.1 Sample Pump. Stainless steel, metal bellows type, capable of 2 atmospheres output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

[Note: An alternative sampling system has been developed by Dr. R. Rasmussen, The Oregon Graduate Institute of Science and Technology, 20000 N.W. Walker Rd., Beaverton, Oregon 97006, 503-690-1077, and is illustrated in Figure 3. This flow system uses, in order, a pump, a mechanical flow regulator, and a mechanical compensation flow restrictive device. In this configuration the pump is purged with a large sample flow, thereby eliminating the need for an auxiliary vacuum pump to flush the sample inlet.]

7.1.2.2 Other Supporting Materials. All other components of the pressurized sampling system are similar to components discussed in Sections 7.1.1.1 through 7.1.1.17.

7.2 Analytical Apparatus

7.2.1 Sampling/Concentrator System (many commercial alternatives are available).

7.2.1.1 Electronic Mass Flow Controllers. Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

7.2.1.2 Vacuum Pump. General purpose laboratory pump, capable of reducing the downstream pressure of the flow controller to provide the pressure differential necessary to maintain controlled flow rates of sample air.

7.2.1.3 Stainless Steel Tubing and Stainless Steel Fittings. Coated with fused silica to minimize active adsorption sites.

7.2.1.4 Stainless Steel Cylinder Pressure Regulators. Standard, two-stage cylinder regulators with pressure gauges.

7.2.1.5 Gas Purifiers. Used to remove organic impurities and moisture from gas streams.

7.2.1.6 Six-port Gas Chromatographic Valve. For routing sample and carrier gas flows.

7.2.1.7 Multisorbent Concentrator. Solid adsorbent packing with various retentive properties for adsorbing trace gases are commercially available from several sources. The packing contains more than one type of adsorbent packed in series.

7.2.1.7.1A pre-packed adsorbent trap (Supelco 2-0321) containing 200 mg Carbopack B (60/80 mesh) and 50 mg Carbosieve S-III (60/80 mesh) has been found to retain VOCs and allow some water vapor to pass through (6). The addition of a dry purging step allows for further water removal from the adsorbent trap. The steps constituting the dry purge technique that are normally used with multisorbent traps are illustrated in Figure 4. The optimum trapping and dry purging procedure for the Supelco trap consists of a sample volume of 320 mL and a dry nitrogen purge of 1300 mL. Sample trapping and drying is carried out at 25°C. The trap is back-flushed with helium and heated to 220°C to transfer material onto the GC column. A trap bake-out at 260°C for 5 minutes is conducted after each run.

7.2.1.7.2 An example of the effectiveness of dry purging is shown in Figure 5. The multisorbent used in this case is Tenax/Ambersorb 340/Charcoal (7). Approximately 20% of the initial water content in the sample remains after sampling 500 mL of air. The detector response to water vapor (hydrogen atoms detected by atomic emission detection) is plotted versus purge gas volume. Additional water reduction by a factor of 8 is indicated at temperatures of 45°C or higher. Still further water reduction is possible using a two-stage concentration/dryer system.

7.2.1.8 Cryogenic Concentrator. Complete units are commercially available from several vendor sources. The characteristics of the latest concentrators include a rapid, "ballistic" heating of the concentrator to release any trapped VOCs into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.2.2 Gas Chromatographic/Mass Spectrometric (GC/MS) System.

7.2.2.1 Gas Chromatograph. The gas chromatographic (GC) system must be capable of temperature programming. The column oven can be cooled to subambient temperature (e.g., -50°C) at the start of the gas chromatographic run to effect a resolution of the very volatile organic compounds. In other designs, the rate of release of compounds from the focusing trap in a two stage system obviates the need for retrapping of compounds on the column. The system must include or be interfaced to a concentrator and have all required accessories including analytical columns and gases. All GC carrier gas lines must be constructed from stainless steel or copper tubing. Non-polytetrafluoroethylene (PTFE) thread sealants or flow controllers with Buna-N rubber components must not be used.

7.2.2.2 Chromatographic Columns. 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25- to 0.53-mm I.D. of varying lengths are recommended for separation of many of the possible subsets of target compounds involving nonpolar compounds. However, considering the diversity of the target list, the choice is left to the operator subject to the performance standards given in Section 11.

7.2.2.3 Mass Spectrometer. Either a linear quadrupole or ion trap mass spectrometer can be used as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the instrument performance acceptance criteria when 50 ng or less of p-bromofluorobenzene (BFB) is analyzed.

7.2.2.3.1Linear Quadrupole Technology. A simplified diagram of the heart of the quadrupole mass spectrometer is shown in Figure 6. The quadrupole consists of a parallel set of four rod electrodes mounted in a square configuration. The field within the analyzer is created by coupling opposite pairs of rods together and applying radiofrequency (RF) and direct current (DC) potentials between the pairs of rods. Ions created in the ion source from the reaction of column eluates with electrons from the electron source are moved through the

parallel array of rods under the influence of the generated field. Ions which are successfully transmitted through the quadrupole are said to possess stable trajectories and are subsequently recorded with the detection system. When the DC potential is zero, a wide band of m/z values is transmitted through the quadrupole. This "RF only" mode is referred to as the "total-ion" mode. In this mode, the quadrupole acts as a strong focusing lens analogous to a high pass filter. The amplitude of the RF determines the low mass cutoff. A mass spectrum is generated by scanning the DC and RF voltages using a fixed DC/RF ratio and a constant drive frequency or by scanning the frequency and holding the DC and RF constant. With the quadrupole system only 0.1 to 0.2 percent of the ions formed in the ion source actually reach the detector.

7.2.2.3.2Ion Trap Technology. An ion-trap mass spectrometer consists of a chamber formed between two metal surfaces in the shape of a hyperboloid of one sheet (ring electrode) and a hyperboloid of two sheets (the two end-cap electrodes). Ions are created within the chamber by electron impact from an electron beam admitted through a small aperture in one of the end caps. Radio frequency (RF) (and sometimes direct current voltage offsets) are applied between the ring electrode and the two end-cap electrodes establishing a quadrupole electric field. This field is uncoupled in three directions so that ion motion can be considered independently in each direction; the force acting upon an ion increases with the displacement of the ion from the center of the field but the direction of the force depends on the instantaneous voltage applied to the ring electrode. A restoring force along one coordinate (such as the distance, r, from the ion-trap's axis of radial symmetry) will exist concurrently with a repelling force along another coordinate (such as the distance, z, along the ion traps axis), and if the field were static the ions would eventually strike an electrode. However, in an RF field the force along each coordinate alternates direction so that a stable trajectory may be possible in which the ions do not strike a surface. In practice, ions of appropriate mass-to-charge ratios may be trapped within the device for periods of milliseconds to hours. A diagram of a typical ion trap is illustrated in Figure 7. Analysis of stored ions is performed by increasing the RF voltage, which makes the ions successively unstable. The effect of the RF voltage on the ring electrode is to "squeeze" the ions in the xy plane so that they move along the z axis. Half the ions are lost to the top cap (held at ground potential); the remaining ions exit the lower end cap to be detected by the electron multiplier. As the energy applied to the ring electrode is increased, the ions are collected in order of increasing mass to produce a conventional mass spectrum. With the ion trap, approximately 50 percent of the generated ions are detected. As a result, a significant increase in sensitivity can be achieved when compared to a full scan linear quadrupole system.

7.2.2.4 GC/MS Interface. Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points for each of the analytes of interest and can be used to achieve all acceptable performance criteria may be used. Gas chromatograph to mass spectrometer interfaces constructed of all-glass, glass-lined, or fused silica-lined materials are recommended. Glass and fused silica should be deactivated.

7.2.2.5 Data System. The computer system that is interfaced to the mass spectrometer must allow the continuous acquisition and storage, on machine readable media, of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as a Selected Ion Current Profile (SICP). Software must also be available that allows integrating the abundance in any SICP between specified time or scan number limits. Also, software must be available that allows for the comparison of sample spectra with reference library spectra. The National Institute of Standards and Technology (NIST) or Wiley Libraries or equivalent are recommended as reference libraries.

7.2.2.6 Off-line Data Storage Device. Device must be capable of rapid recording and retrieval of data and must be suitable for long-term, off-line data storage.

7.3 Calibration System and Manifold Apparatus (see Figure 8)

7.3.1 Calibration Manifold. Stainless steel, glass, or high purity quartz manifold, (e.g.,1.25-cm I.D. x 66-cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heated to ~50°C.

7.3.2 Humidifier. 500-mL impinger flask containing HPLC grade deionized water.

7.3.3 Electronic Mass Flow Controllers. One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders in use for calibration.

7.3.4 Teflon Filter(s). 47-mm Teflon® filter for particulate collection.

7.4 Reagents

7.4.1 Neat Materials or Manufacturer-Certified Solutions/Mixtures. Best source (see Section 9).

7.4.2 Helium and Air. Ultra-high purity grade in gas cylinders. He is used as carrier gas in the GC.

7.4.3 Liquid Nitrogen or Liquid Carbon Dioxide. Used to cool secondary trap.

7.4.4 Deionized Water. High performance liquid chromatography (HPLC) grade, ultra-high purity (for humidifier).

8. Collection of Samples in Canisters

8.1 Introduction

8.1.1 Canister samplers, sampling procedures, and canister cleaning procedures have not changed very much from the description given in the original Compendium Method TO-14. Much of the material in this section is therefore simply a restatement of the material given in Compendium Method TO-14, repeated here in order to have all the relevant information in one place.

8.1.2 Recent notable additions to the canister technology has been in the application of canister-based systems for example, to microenvironmental monitoring (8), the capture of breath samples (9), and sector sampling to identify emission sources of VOCs (10).

8.1.3 EPA has also sponsored the development of a mathematical model to predict the storage stability of arbitrary mixtures of trace gases in humidified air (3), and the investigation of the SilcoSteel™ process of coating the canister interior with a film of fused silica to reduce surface activity (11). A recent summary of storage stability data for VOCs in canisters is given in the open literature (5).

8.2 Sampling System Description

8.2.1 Subatmospheric Pressure Sampling [see Figure 1 (without metal bellows type pump)].

8.2.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.05 mm Hg (see Appendix C for discussion of evacuation pressure). When the canister is opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. This technique may be used to collect grab samples (duration of 10 to 30 seconds) or time-weighted-average (TWA) samples (duration of 1-24 hours) taken through a flow-restrictive inlet (e.g., mass flow controller, critical orifice).

8.2.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate as the pressure approaches atmospheric. However, with a mass flow controller, the subatmospheric sampling system can maintain a constant flow rate from full vacuum to within about 7 kPa (1.0 psi) or less below ambient pressure.

8.2.2 Pressurized Sampling [see Figure 1 (with metal bellows type pump)].

8.2.2.1 Pressurized sampling is used when longer-term integrated samples or higher volume samples are required. The sample is collected in a canister using a pump and flow control arrangement to achieve a typical 101-202 kPa (15-30 psig) final canister pressure. For example, a 6-liter evacuated canister can be filled at 10 mL/min for 24 hours to achieve a final pressure of 144 kPa (21 psig).

8.2.2.2 In pressurized canister sampling, a metal bellows type pump draws in air from the sampling manifold to fill and pressurize the sample canister.

8.2.3 All Samplers.

8.2.3.1 A flow control device is chosen to maintain a constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{P \times V}{T \times 60}$$

where:

F = flow rate, mL/min.
P = final canister pressure, atmospheres absolute. P is approximately equal to

$$\frac{\text{kPa gauge}}{101.2} + 1$$

V = volume of the canister, mL.
T = sample period, hours.

For example, if a 6-L canister is to be filled to 202 kPa (2 atmospheres) absolute pressure in 24 hours, the flow rate can be calculated by:

$$F = \frac{2 \times 6000}{24 \times 60} = 8.3 \text{ mL/min}$$

8.2.3.2 For automatic operation, the timer is designed to start and stop the pump at appropriate times for the desired sample period. The timer must also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

8.2.3.3 The use of the Skinner Magnelatch valve (see Figure 2) avoids any substantial temperature rise that would occur with a conventional, normally closed solenoid valve that would have to be energized during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the Viton® valve seat material. The Skinner Magnelatch valve requires only a brief electrical pulse to open or close at the appropriate start and stop times and therefore experiences no temperature increase. The pulses may be obtained either with an electronic timer that can be programmed for short (5 to 60 seconds) ON periods, or with a conventional mechanical timer and a special pulse circuit. A simple electrical pulse circuit for operating the Skinner Magnelatch solenoid valve with a conventional mechanical timer is illustrated in Figure 2(a). However, with this simple circuit, the valve may operate unreliably during brief power interruptions or if the timer is manually switched on and off too fast. A better circuit incorporating a time-delay relay to provide more reliable valve operation is shown in Figure 2(b).

8.2.3.4 The connecting lines between the sample inlet and the canister should be as short as possible to minimize their volume. The flow rate into the canister should remain relatively constant over the entire sampling period.

8.2.3.5 As an option, a second electronic timer may be used to start the auxiliary pump several hours prior to the sampling period to flush and condition the inlet line.

8.2.3.6 Prior to field use, each sampling system must pass a humid zero air certification (see Section 8.4.3). All plumbing should be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see Section 8.4.1).

8.3 Sampling Procedure

8.3.1 The sample canister should be cleaned and tested according to the procedure in Section 8.4.1.

8.3.2 A sample collection system is assembled as shown in Figures 1 and 3 and must be cleaned according to the procedure outlined in Sections 8.4.2 and 8.4.4.

[Note: The sampling system should be contained in an appropriate enclosure.]

8.3.3 Prior to locating the sampling system, the user may want to perform "screening analyses" using a portable GC system, as outlined in Appendix B of Compendium Method TO-14A, to determine potential volatile organics present and potential "hot spots." The information gathered from the portable GC screening analysis would be used in developing a monitoring protocol, which includes the sampling system location, based upon the "screening analysis" results.

8.3.4 After "screening analysis," the sampling system is located. Temperatures of ambient air and sampler box interior are recorded on the canister sampling field test data sheet (FTDS), as documented in Figure 9.

[Note: The following discussion is related to Figure 1]

8.3.5 To verify correct sample flow, a "practice" (evacuated) canister is used in the sampling system.

[Note: For a subatmospheric sampler, a flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed, as the flow can be measured at the outlet of the system.]

A certified mass flow meter is attached to the inlet line of the manifold, just in front of the filter. The canister is opened. The sampler is turned on and the reading of the certified mass flow meter is compared to the sampler mass flow controller. The values should agree within ±10%. If not, the sampler mass flow meter needs to be recalibrated or there is a leak in the system. This should be investigated and corrected.

[Note: Mass flow meter readings may drift. Check the zero reading carefully and add or subtract the zero reading when reading or adjusting the sampler flow rate to compensate for any zero drift.]

After 2 minutes, the desired canister flow rate is adjusted to the proper value (as indicated by the certified mass flow meter) by the sampler flow control unit controller (e.g., 3.5 mL/min for 24 hr, 7.0 mL/min for 12 hr). Record final flow under "CANISTER FLOW RATE" on the FTDS.

8.3.6 The sampler is turned off and the elapsed time meter is reset to 000.0.

[Note: Whenever the sampler is turned off, wait at least 30 seconds to turn the sampler back on.]

8.3.7 The "practice" canister and certified mass flow meter are disconnected and a clean certified (see Section 8.4.1) canister is attached to the system.

8.3.8 The canister valve and vacuum/pressure gauge valve are opened.

8.3.9 Pressure/vacuum in the canister is recorded on the canister FTDS (see Figure 9) as indicated by the sampler vacuum/pressure gauge.

8.3.10 The vacuum/pressure gauge valve is closed and the maximum-minimum thermometer is reset to current temperature. Time of day and elapsed time meter readings are recorded on the canister FTDS.

8.3.11 The electronic timer is set to start and stop the sampling period at the appropriate times. Sampling starts and stops by the programmed electronic timer.

8.3.12 After the desired sampling period, the maximum, minimum, current interior temperature and current ambient temperature are recorded on the FTDS. The current reading from the flow controller is recorded.

8.3.13 At the end of the sampling period, the vacuum/pressure gauge valve on the sampler is briefly opened and closed and the pressure/vacuum is recorded on the FTDS. Pressure should be close to desired pressure.

[Note: For a subatmospheric sampling system, if the canister is at atmospheric pressure when the field final pressure check is performed, the sampling period may be suspect. This information should be noted on the sampling field data sheet.]

Time of day and elapsed time meter readings are also recorded.

8.3.14 The canister valve is closed. The sampling line is disconnected from the canister and the canister is removed from the system. For a subatmospheric system, a certified mass flow meter is once again connected to the inlet manifold in front of the in-line filter and a "practice" canister is attached to the Magnelatch valve of the sampling system. The final flow rate is recorded on the canister FTDS (see Figure 9).

[Note: For a pressurized system, the final flow may be measured directly.]

The sampler is turned off.

8.3.15 An identification tag is attached to the canister. Canister serial number, sample number, location, and date, as a minimum, are recorded on the tag. The canister is routinely transported back to the analytical laboratory with other canisters in a canister shipping case.

8.4 Cleaning and Certification Program

8.4.1 Canister Cleaning and Certification.

8.4.1.1 All canisters must be clean and free of any contaminants before sample collection.

8.4.1.2 All canisters are leak tested by pressurizing them to approximately 206 kPa (30 psig) with zero air.

[Note: The canister cleaning system in Figure 10 can be used for this task.]

The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period.

8.4.1.3 A canister cleaning system may be assembled as illustrated in Figure 10. Cryogen is added to both the vacuum pump and zero air supply traps. The canister(s) are connected to the manifold. The vent shut-off valve and the canister valve(s) are opened to release any remaining pressure in the canister(s). The vacuum pump is started and the vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) are evacuated to <0.05 mm Hg (see Appendix B) for at least 1 hour.

[Note: On a daily basis or more often if necessary, the cryogenic traps should be purged with zero air to remove any trapped water from previous canister cleaning cycles.]

Air released/evacuated from canisters should be diverted to a fume hood.

8.4.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

8.4.1.5 The zero air shut-off valve is closed and the canister(s) is allowed to vent down to atmospheric pressure through the vent shut-off valve. The vent shut-off valve is closed. Repeat Sections 8.4.1.3 through 8.4.1.5 two additional times for a total of three (3) evacuation/pressurization cycles for each set of canisters.

8.4.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 206 kPa (30 psig) with humid zero air. The canister is then analyzed by a GC/MS analytical system. Any canister that has not tested clean (compared to direct analysis of humidified zero air of less than 0.2 ppbv of targeted VOCs) should not be used. As a "blank" check of the canister(s) and cleanup procedure, the final humid zero air fill of 100% of the canisters is analyzed until the cleanup system and canisters are proven reliable (less than 0.2 ppbv of any target VOCs). The check can then be reduced to a lower percentage of canisters.

8.4.1.7 The canister is reattached to the cleaning manifold and is then reevacuated to <0.05 mm Hg (see Appendix B) and remains in this condition until used. The canister valve is closed. The canister is removed from the cleaning system and the canister connection is capped with a stainless steel fitting. The canister is now ready for collection of an air sample. An identification tag is attached to the inlet of each canister for field notes and chain-of-custody purposes. An alternative to evacuating the canister at this point is to store the canisters and reevacuate them just prior to the next use.

8.4.1.8 As an option to the humid zero air cleaning procedures, the canisters are heated in an isothermal oven not to exceed 100°C during evacuation of the canister to ensure that higher molecular weight compounds are not retained on the walls of the canister.

[Note: For sampling more complex VOC mixtures the canisters should be heated to higher temperatures during the cleaning procedure although a special high temperature valve would be needed].

Once heated, the canisters are evacuated to <0.05 mm Hg (see Appendix B) and maintained there for 1 hour. At the end of the heated/evacuated cycle, the canisters are pressurized with humid zero air and analyzed by a GC/MS system after a minimum of 12 hrs of "aging." Any canister that has not tested clean (less than 0.2 ppbv each of targeted compounds) should not be used. Once tested clean, the canisters are reevacuated to <0.05 mm Hg (see Appendix B) and remain in the evacuated state until used. As noted in Section 8.4.1.7, reevacuation can occur just prior to the next use.

8.4.2 Cleaning Sampling System Components.

8.4.2.1 Sample components are disassembled and cleaned before the sampler is assembled. Nonmetallic parts are rinsed with HPLC grade deionized water and dried in a vacuum oven at 50°C. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

8.4.2.2 The parts are then rinsed with HPLC grade deionized water and dried in a vacuum oven at 100°C for 12 to 24 hours.

8.4.2.3 Once the sampler is assembled, the entire system is purged with humid zero air for 24 hours.

8.4.3 Zero Air Certification.

[Note: In the following sections, "certification" is defined as evaluating the sampling system with humid zero air and humid calibration gases that pass through all active components of the sampling system. The system is "certified" if no significant additions or deletions (less than 0.2 ppbv each of target compounds) have occurred when challenged with the test gas stream.]

8.4.3.1 The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

8.4.3.2 The calibration system and manifold are assembled, as illustrated in Figure 8. The sampler (without an evacuated gas canister) is connected to the manifold and the zero air cylinder is activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Figure 8(b)].

8.4.3.3 The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated canister) to the water management system/VOC preconcentrator of an analytical system.

[Note: The exit of the sampling system (without the canister) replaces the canister in Figure 11.]

After the sample volume (e.g., 500 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed and refocussed on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocussed prior to gas chromatographic separation. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see Section 10) system. The analytical system should not detect greater than 0.2 ppbv of any targeted VOCs in order for the sampling system to pass the humid zero air certification test. Chromatograms (using an FID) of a certified sampler and contaminated sampler are illustrated in Figures 12(a) and 12(b), respectively. If the sampler passes the humid zero air test, it is then tested with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling (e.g., 0.5 to 2 ppbv) as outlined in Section 8.4.4.

8.4.4 Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System

8.4.4.1 Assemble the dynamic calibration system and manifold as illustrated in Figure 8.

8.4.4.2 Verify that the calibration system is clean (less than 0.2 ppbv of any target compounds) by sampling a humidified gas stream, *without* gas calibration standards, with a previously certified clean canister (see Section 8.1).

8.4.4.3 The assembled dynamic calibration system is certified clean if less than 0.2 ppbv of any targeted compounds is found.

8.4.4.4 For generating the humidified calibration standards, the calibration gas cylinder(s) containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs is attached to the calibration system as illustrated in Figure 8. The gas cylinders are opened and the gas mixtures are passed through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

8.4.4.5 After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Figure 8(b).

8.4.4.6 Sample the dynamic calibration gas stream with the sampling system.

8.4.4.7 Concurrent with the sampling system operation, realtime monitoring of the calibration gas stream is accomplished by the on-line GC/MS analytical system [Figure 8(a)] to provide reference concentrations of generated VOCs.

8.4.4.8 At the end of the sampling period (normally the same time period used for experiments), the sampling system canister is analyzed and compared to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

8.4.4.9 A recovery of between 90% and 110% is expected for all targeted VOCs.

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

8.4.5.1 Not all the gases on the Title III list are available/compatible with compressed gas standards. In these cases sampler certification must be approached by different means.

8.4.5.2 Definitive guidance is not currently available in these cases; however, Section 9.2 lists several ways to generate gas standards. In general, Compendium Method TO-14A compounds (see Table 1) are available commercially as compressed gas standards.

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

9.1.1 The analysis of canister samples is accomplished with a GC/MS system. Fused silica capillary columns are used to achieve high temporal resolution of target compounds. Linear quadrupole or ion trap mass spectrometers are employed for compound detection. The heart of the system is composed of the sample inlet concentrating device that is needed to increase sample loading into a detectable range. Two examples of concentrating systems are discussed. Other approaches are acceptable as long as they are compatible with achieving the system performance criteria given in Section 11.

9.1.2 With the first technique, a whole air sample from the canister is passed through a multisorbent packing (including single adsorbent packings) contained within a metal or glass tube maintained at or above the surrounding air temperature. Depending on the water retention properties of the packing, some or most of the water vapor passes completely through the trap during sampling. Additional drying of the sample is accomplished after the sample concentration is completed by forward purging the trap with clean, dry helium or another inert gas (air is not used). The sample is then thermally desorbed from the packing and backflushed from the trap onto a gas chromatographic column. In some systems a "refocusing" trap is placed between the primary trap and the gas chromatographic column. The specific system design downstream of the primary trap depends on technical factors such as the rate of thermal desorption and sampled volume, but the objective in most cases is to enhance chromatographic resolution of the individual sample components before detection on a mass spectrometer.

9.1.3 Sample drying strategies depend on the target list of compounds. For some target compound lists, the multisorbent packing of the concentrator can be selected from hydrophobic adsorbents which allow a high percentage of water vapor in the sample to pass through the concentrator during sampling and without significant loss of the target compounds. However, if very volatile organic compounds are on the target list, the adsorbents required for their retention may also strongly retain water vapor and a more lengthy dry purge is necessary prior to analysis.

9.1.4 With the second technique, a whole air sample is passed through a concentrator where the VOCs are condensed on a reduced temperature surface (cold trap). Subsequently, the condensed gases are thermally desorbed and backflushed from the trap with an inert gas onto a gas chromatographic column. This concentration technique is similar to that discussed in Compendium Method TO-14, although a membrane dryer is not used. The sample size is reduced in volume to limit the amount of water vapor that is also collected (100 mL or less may be necessary). The attendant reduction in sensitivity is offset by enhancing the sensitivity of detection, for example by using an ion trap detector.

9.2 Preparation of Standards

9.2.1 Introduction.

9.2.1.1 When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM). Manufacturer's certificates of analysis must be retained to track the expiration date.

9.2.1.2 The neat standards that are used for making trace gas standards must be of high purity; generally a purity of 98 percent or better is commercially available.

9.2.1.3 Cylinder(s) containing approximately 10 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder. Refer to manufacturer's specifications for guidance on purchasing and mixing VOCs in gas cylinders.

9.2.2 Preparing Working Standards.

9.2.2.1 Instrument Performance Check Standard. Prepare a standard solution of BFB in humidified zero air at a concentration which will allow collection of 50 ng of BFB or less under the optimized concentration parameters.

9.2.2.2 Calibration Standards. Prepare five working calibration standards in humidified zero air at a concentration which will allow collection at the 2, 5, 10, 20, and 50 ppbv level for each component under the optimized concentration parameters.

9.2.2.3 Internal Standard Spiking Mixture. Prepare an internal spiking mixture containing bromochloromethane, chlorobenzene-d_5, and 1,4-difluorobenzene at 10 ppmv each in humidified zero air to be added to the sample or calibration standard. 500 µL of this mixture spiked into 500 mL of sample will result in a concentration of 10 ppbv. The internal standard is introduced into the trap during the collection time for all calibration, blank, and sample analyses using the apparatus shown in Figure 13 or by equivalent means. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

9.2.3 Standard Preparation by Dynamic Dilution Technique.

9.2.3.1 Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

9.2.3.2 Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

$$\text{Manifold Conc.} = \frac{(\text{Original Conc.})\ (\text{Std. Gas Flowrate})}{(\text{Air Flowrate}) + (\text{Std. Gas Flowrate})}$$

9.2.3.3 Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

$$\text{Manifold Conc.} = \frac{(10\ \text{ppm})(1\ \text{mL/min})(1000\ \text{ppb/1 ppm})}{(1000\ \text{mL/min}) + (1\ \text{mL/min})} = 10\ \text{ppb}$$

9.2.4 Standard Preparation by Static Dilution Bottle Technique

[Note: Standards may be prepared in canisters by spiking the canister with a mixture of components prepared in a static dilution bottle (12). This technique is used specifically for liquid standards.]

9.2.4.1 The volume of a clean 2-liter round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in milliliters.

9.2.4.2 The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

9.2.4.3 The flask is placed in a 60°C oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60°C.

9.2.4.4 The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

9.2.4.5 Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

9.2.4.6 Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

9.2.4.7 The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = \frac{(V_a)(d)}{V_f}$$

where: V_a = Volume of liquid neat standard injected into the flask, µL.
d = Density of the liquid neat standard, mg/µL.
V_f = Volume of the flask, L.

9.2.4.8 To obtain concentrations in ppbv, the equation given in Section 9.2.5.7 can be used.

[Note: In the preparation of standards by this technique, the analyst should make sure that the volume of neat standard injected into the flask does not result in an overpressure due to the higher partial pressure produced by the standard compared to the vapor pressure in the flask. Precautions should also be taken to avoid a significant decrease in pressure inside the flask after withdrawal of aliquot(s).]

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

[Note: Standards may be prepared in high pressure cylinders (13). A modified summary of the procedure is provided below.]

9.2.5.1 The standard compounds are obtained as gases or neat liquids (greater than 98 percent purity).

9.2.5.2 An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

9.2.5.3 Predetermined amounts of each neat standard compound are measured using a microliter or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

9.2.5.4 The cylinder is pressurized to 1000 psig with zero nitrogen.

[Note: User should read all SOPs associated with generating standards in high pressure cylinders. Follow all safety requirements to minimize danger from high pressure cylinders.]

9.2.5.5 The contents of the cylinder are allowed to equilibrate (~24 hrs) prior to withdrawal of aliquots into the GC system.

9.2.5.6 If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = \frac{\text{Volume}_{\text{standard}}}{\text{Volume}_{\text{dilution gas}}} \times 10^9$$

[Note: Both values must be expressed in the same units.]

9.2.5.7 If the neat standard is a liquid, the gaseous concentration can be determined using the following equations:

$$V = \frac{nRT}{P}$$

and:

$$n = \frac{(mL)(d)}{MW}$$

where:
- V = Gaseous volume of injected compound at EPA standard temperature (25°C) and pressure (760 mm Hg), L.
- n = Moles.
- R = Gas constant, 0.08206 L-atm/mole °K.
- T = 298°K (standard temperature).
- P = 1 standard pressure, 760 mm Hg (1 atm).
- mL = Volume of liquid injected, mL.
- d = Density of the neat standard, g/mL.
- MW = Molecular weight of the neat standard expressed, g/g-mole.

The gaseous volume of the injected compound is divided by the cylinder volume at STP and then multiplied by 10^9 to obtain the component concentration in ppb units.

9.2.6 Standard Preparation by Water Methods.

[Note: Standards may be prepared by a water purge and trap method (14) and summarized as follows].

9.2.6.1 A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

9.2.6.2 The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

[Note: Extra effort should be made to minimize possible areas of dead volume to maximize transfer of analytes from the water to the canister.]

9.2.6.3 A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

9.2.6.4 This water is transferred into the sparge vessel and purged with nitrogen for 10 mins at 100 mL/min. The sparging vessel is maintained at 40°C.

9.2.6.5 At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (approximately 29 psia).

9.2.6.6 The canister is allowed to equilibrate overnight before use.

9.2.6.7 A schematic of this approach is shown in Figure 14.

9.2.7 Preparation of Standards by Permeation Tubes.

9.2.7.1 Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

9.2.7.2 The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds. Some commercial suppliers of permeation tube equipment are listed in Appendix D.

9.2.8 Storage of Standards.

9.2.8.1 Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

9.2.8.2 It is imperative that a storage logbook be kept to document storage time.

10. GC/MS Operating Conditions

10.1 Preconcentrator

The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents. An example of a system using a solid adsorbent preconcentrator with a cryofocusing trap is discussed in the literature (15). Oven temperature programming starts above ambient.

10.1.1 Sample Collection Conditions

Cryogenic Trap	**Adsorbent Trap**

Set point	-150°C	Set point	27°C
Sample volume	- up to 100 mL	Sample volume	- up to 1,000 mL
Carrier gas purge flow	- none	Carrier gas purge flow	- selectable

[Note: The analyst should optimize the flow rate, duration of sampling, and absolute sample volume to be used. Other preconcentration systems may be used provided performance standards (see Section 11) are realized.]

10.1.2 Desorption Conditions

Cryogenic Trap		**Adsorbent Trap**	
Desorb Temperature	120°C	Desorb Temperature	Variable
Desorb Flow Rate	~ 3 mL/min He	Desorb Flow Rate	~3 mL/min He
Desorb Time	<60 sec	Desorb Time	<60 sec

The adsorbent trap conditions depend on the specific solid adsorbents chosen (see manufacturers' specifications).

10.1.3 Trap Reconditioning Conditions.

Cryogenic Trap		**Adsorbent Trap**	
Initial bakeout	120°C (24 hrs)	Initial bakeout	Variable (24 hrs)
After each run	120°C (5 min)	After each run	Variable (5 min)

10.2 GC/MS System

10.2.1 Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

10.2.2 The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column.

Item	**Condition**	
Carrier Gas:	Helium	
Flow Rate:	Generally 1-3 mL/min as recommended by manufacturer	
Temperature Program:	Initial Temperature:	-50°C
	Initial Hold Time:	2 min
	Ramp Rate:	8° C/min
	Final Temperature:	200°C
	Final Hold Time:	Until all target compounds elute.

10.2.3 The following are the recommended mass spectrometer conditions:

Item	**Condition**

Electron Energy:	70 Volts (nominal)
Mass Range:	35-300 amu [the choice of 35 amu excludes the detection of some target compounds such as methanol and formaldehyde, and the quantitation of others such as ethylene oxide, ethyl carbamate, etc. (see Table 2). Lowering the mass range and using special programming features available on modern gas chromatographs will be necessary in these cases, but are not considered here.
Scan Time:	To give at least 10 scans per peak, not to exceed 1 second per scan].

A schematic for a typical GC/MS analytical system is illustrated in Figure 15.

10.3 Analytical Sequence

10.3.1 Introduction. The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

- Perform instrument performance check using bromofluorobenzene (BFB).
- Initiate multi-point calibration or daily calibration checks.
- Perform a laboratory method blank.
- Complete this sequence for analysis of ≤20 field samples.

10.4 Instrument Performance Check

10.4.1 Summary. It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

10.4.2 Frequency. Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation.

The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

10.4.3 Procedure. The analysis of the instrument performance check standard is performed by trapping 50 ng of BFB under the optimized preconcentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system similar to that shown in Figure 13.

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

10.4.4 Technical Acceptance Criteria. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3.

10.4.5 Corrective Action. If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

10.4.6 Documentation. Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

10.5 Initial Calibration

10.5.1 Summary. Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv.

One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

10.5.2 Frequency. Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met.

If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed.

If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

10.5.3 Procedure. Verify that the GC/MS system meets the instrument performance criteria in Section 10.4.

The GC must be operated using temperature and flow rate parameters equivalent to those in Section 10.2.2. Calibrate the preconcentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques described under Section 9.2 or equivalent.

A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 10.5.1 and 10.5.5.

Quantitation ions for the target compounds are shown in Table 2. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

10.5.4 Calculations.

[Note: In the following calculations, an internal standard approach is used to calculate response factors. The area response used is that of the primary quantitation ion unless otherwise stated.]

10.5.4.1 Relative Response Factor (RRF). Calculate the relative response factors for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

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

where: RRF = Relative response factor.
A_x = Area of the primary ion for the compound to be measured, counts.
A_{is} = Area of the primary ion for the internal standard, counts.
C_{is} = Concentration of internal standard spiking mixture, ppbv.
C_x = Concentration of the compound in the calibration standard, ppbv.

[Note: The equation above is valid under the condition that the volume of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. C_{is} and C_x must be in the same units.]

10.5.4.2 Mean Relative Response Factor. Calculate the mean RRF for each compound by averaging the values obtained at the five concentrations using the following equation:

$$\overline{RRF} = \sum_{i=1}^{n} \frac{x_i}{n}$$

where: $\overline{RRF}$ = Mean relative response factor.
x_i = RRF of the compound at concentration i.
n = Number of concentration values, in this case 5.

10.5.4.3 Percent Relative Standard Deviation (%RSD). Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\overline{RRF}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(RRF_i - \overline{RRF})^2}{N - 1}}$$

where: SD_{RRF} = Standard deviation of initial response factors (per compound).
RRF_i = Relative response factor at a concentration level i.
$\overline{RRF}$ = Mean of initial relative response factors (per compound).

10.5.4.4 Relative Retention Times (RRT). Calculate the RRTs for each target compound over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where: RT_c = Retention time of the target compound, seconds
RT_{is} = Retention time of the internal standard, seconds.

10.5.4.5 Mean of the Relative Retention Times ($\overline{RRT}$). Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT}{n}$$

where: $\overline{RRT}$ = Mean relative retention time for the target compound for each initial calibration standard.

RRT = Relative retention time for the target compound at each calibration level.

10.5.4.6 Tabulate Primary Ion Area Response (Y) for Internal Standard. Tabulate the area response (Y) of the primary ions (see Table 2) and the corresponding concentration for each compound and internal standard.

10.5.4.7 Mean Area Response ($\overline{Y}$) for Internal Standard. Calculate the mean area response ($\overline{Y}$) for each internal standard compound over the initial calibration range using the following equation:

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

where: $\overline{Y}$ = Mean area response.

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

10.5.4.8 Mean Retention Times ($\overline{RT}$). Calculate the mean of the retention times ($\overline{RT}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where: $\overline{RT}$ = Mean retention time, seconds

RT = Retention time for the internal standard for each initial calibration standard, seconds.

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

10.5.5.1 The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

[Note: This exception may not be acceptable for all projects. Many projects may have a specific target list of compounds which would require the lower limit for all compounds.]

10.5.5.2 The RRT for each target compound at each calibration level must be withiin 0.06 RRT units of the mean RRT for the compound.

10.5.5.3 The area response Y of at each calibration level must be within 40% of the mean area response $\overline{Y}$ over the initial calibration range for each internal standard.

10.5.5.4 The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

10.5.6 Corrective Action.

10.5.6.1 Criteria. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

10.5.6.2 Schedule. Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

10.6 Daily Calibration

10.6.1 Summary. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard, which is the nominal 10 ppbv level calibration standard, should contain all the target compounds.

10.6.2 Frequency. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

10.6.3 Procedure. The mid-level calibration standard (10 ppbv) is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 10.5.

10.6.4 Calculations. Perform the following calculations.

[Note: As indicated earlier, the area response of the primary quantitation ion is used unless otherwise stated.]

10.6.4.1 Relative Response Factor (RRF). Calculate a relative response factor (RRF) for each target compound using the equation in Section 10.5.4.1.

10.6.4.2 Percent Difference (%D). Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound using the following equation:

$$\%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where: RRF_c = RRF of the compound in the continuing calibration standard.

$\overline{RRF_i}$ = Mean RRF of the compound in the most recent initial calibration.

10.6.5 Technical Acceptance Criteria. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 10.6 and on a GC/MS system meeting the BFB instrument performance check criteria (see Section 10.4).

The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

10.6.6 Corrective Action. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria.

Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

10.7 Blank Analyses

10.7.1 Summary. To monitor for possible laboratory contamination, laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank

using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

10.7.2 Frequency. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed.

Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects.

10.7.3 Procedure. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25°C). Pressurize the contents to 2 atm.

The blank sample should be analyzed using the same procedure outlined under Section 10.8.

10.7.4 Calculations. The blanks are analyzed similar to a field sample and the equations in Section 10.5.4 apply.

10.7.5 Technical Acceptance Criteria. A blank canister should be analyzed daily.

The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration.

The retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration.

The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL as defined in Section 11.2) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

10.7.6 Corrective Action. If the blanks do not meet the technical acceptance criteria, the analyst should consider the analytical system to be out of control. It is the responsibility of the analyst to ensure that contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measures need to be taken and documented before further sample analysis proceeds.

If an analyte in the blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

10.8 Sample Analysis

10.8.1 Summary. An aliquot of the air sample from a canister (e.g., 500 mL) is preconcentrated and analyzed by GC/MS under conditions stated in Sections 10.1 and 10.2. If using the multisorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

[Note: The analyst should be aware that pressurized samples of high humidity samples will contain condensed water. As a result, the humidity of the sample released from the canister during analysis will vary

in humidity, being lower at the higher canister pressures and increasing in humidity as the canister pressures decreases. Storage integrity of water soluble compounds may also be affected.]

10.8.2 Frequency. If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard.

If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.8.3 Procedure for Instrumental Analysis. Perform the following procedure for analysis.

10.8.3.1 All canister samples should be at temperature equilibrium with the laboratory.

10.8.3.2 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.8.3.3 Connect the sample canister to the inlet of the GC/MS analytical system, as shown in Figure 15 [Figure 16 shows an alternate two stage concentrator using multisorbent traps followed by a trap cooled by a closed cycle cooler (15)]. The desired sample flow is established through the six-port chromatographic valve and the preconcentrator to the downstream flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.8.3.4 Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.8.3.5 Use the arrangement shown in Figure 13, (i.e., a gastight syringe or some alternate method) introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 10 ppbv in the sample. For example, a 0.5 mL volume of a mixture of internal standard compounds, each at 10 ppmv concentration, added to a sample volume of 500 mL, will result in 10 ppbv of each internal standard in the sample.

10.8.3.6 After the sample and internal standards are preconcentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.8.3.7 Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.8.3.8 Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.8.3.9 Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

10.8.4 Calculations. The equation below is used for calculating concentrations.

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

where: C_x = Compound concentration, ppbv.

A_x = Area of the characteristic ion for the compound to be measured, counts.

A_{is} = Area of the characteristic ion for the specific internal standard, counts.

C_{is} = Concentration of the internal standard spiking mixture, ppbv

.

$\overline{RRF}$ = Mean relative response factor from the initial calibration.

DF = Dilution factor calculated as described in section 2. If no dilution is performed, DF = 1.

[Note: The equation above is valid under the condition that the volume (~500 µL) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (~500 mL) of field and QC sample introduced into the trap is the same for each analysis.]

10.8.5 Technical Acceptance Criteria.

[Note: If the most recent valid calibration is an initial calibration, internal standard area responses and RTs in the sample are evaluated against the corresponding internal standard area responses and RTs in the mid level standard (10 ppbv) of the initial calibration.]

10.8.5.1 The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria at the frequency described in Sections 10.4, 10.5 and 10.6.

10.8.5.2 The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

10.8.5.3 All of the target analyte peaks should be within the initial calibration range.

10.8.5.4 The retention time for each internal standard must be within ±0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

10.8.6 Corrective Action. If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.
- The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

[Note: Analysis involving dilution should be reported with a dilution factor and nature of the dilution gas.]

10.8.6.1 Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

10.8.6.2 If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and

corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.8.6.3 If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

11. Requirements for Demonstrating Method Acceptability for VOC Analysis from Canisters

11.1 Introduction

11.1.1 There are three performance criteria which must be met for a system to qualify under Compendium Method TO-15. These criteria are: the method detection limit of ≤0.5 ppbv, replicate precision within 25 percent, and audit accuracy within 30 percent for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

11.1.2 Either SIM or SCAN modes of operation can be used to achieve these criteria, and the choice of mode will depend on the number of target compounds, the decision of whether or not to determine tentatively identified compounds along with other VOCs on the target list, as well as on the analytical system characteristics.

11.1.3 Specific criteria for each Title III compound on the target compound list must be met by the analytical system. These criteria were established by examining summary data from EPA's Toxics Air Monitoring System Network and the Urban Air Toxics Monitoring Program network. Details for the determination of each of the criteria follow.

11.2 Method Detection Limit

11.2.1 The procedure chosen to define the method detection limit is that given in the *Code of Federal Regulations* (40 CFR 136 Appendix B).

11.2.2 The method detection limit is defined for each system by making seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit, computing the standard deviation for the seven replicate concentrations, and multiplying this value by 3.14 (i.e., the Student's t value for 99 percent confidence for seven values). Employing this approach, the detection limits given in Table 4 were obtained for some of the VOCs of interest.

11.3 Replicate Precision

11.3.1 The measure of replicate precision used for this program is the absolute value of the difference between replicate measurements of the sample divided by the average value and expressed as a percentage as follows:

$$\text{percent difference} = \frac{|x_1 - x_2|}{\bar{x}} \times 100$$

where: x_1 = First measurement value.

x_2 = Second measurement value.

$\bar{x}$ = Average of the two values.

11.3.2 There are several factors which may affect the precision of the measurement. The nature of the compound of interest itself such as molecular weight, water solubility, polarizability, etc., each have some effect on the precision, for a given sampling and analytical system. For example, styrene, which is classified as a polar VOC, generally shows slightly poorer precision than the bulk of nonpolar VOCs. A primary influence on precision is the concentration level of the compound of interest in the sample, i.e., the precision degrades as the concentration approaches the detection limit. A conservative measure was obtained from replicate analysis of "real world" canister samples from the TAMS and UATMP networks. These data are summarized in Table 5 and suggest that a replicate precision value of 25 percent can be achieved for each of the target compounds.

11.4 Audit Accuracy

11.4.1 A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value and expressed as a percentage, as illustrated in the following equation:

$$\text{Audit Accuracy, \%} = \frac{\text{Spiked Value} - \text{Observed Value}}{\text{Spiked Value}} \times 100$$

11.4.2 Audit accuracy results for TAMS and UATMP analyses are summarized in Table 6 and were used to form the basis for a selection of 30 percent as the performance criterion for audit accuracy.

12. References

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APPENDIX A.

LISTING OF SOME COMMERCIAL WATER MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

Tekmar Dohrman Company
7143 East Kemper Road
Post Office Box 429576
Cincinnati, Ohio 45242-9576
(513) 247-7000
(513) 247-7050 (Fax)
(800) 543-4461
[Moisture control module]

Entech Laboratory Automation
950 Enchanted Way No. 101
Simi Valley, California 93065
(805) 527-5939
(805) 527-5687 (Fax)
[Microscale Purge and Trap]

Dynatherm Analytical Instruments
Post Office Box 159
Kelton, Pennsylvania 19346
(215) 869-8702
(215) 869-3885 (Fax)
[Thermal Desorption System]

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380
(818) 787-4275 (Fax)
[Multi-adsorbent trap/dry purge]

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(770) 319-9999
(770) 319-0336 (Fax)
(800) 241-6898
[Controlled Desorption Trap]

Varian Chromatography System
2700 Mitchell Drive
Walnut Creek, California 94898
(510) 945-2196
(510) 945-2335 (FAX)
[Variable Temperature Adsorption Trap]

APPENDIX B.

COMMENT ON CANISTER CLEANING PROCEDURES

The canister cleaning procedures given in Section 8.4 require that canister pressure be reduced to <0.05mm Hg before the cleaning process is complete. Depending on the vacuum system design (diameter of connecting tubing, valve restrictions, etc.) and the placement of the vacuum gauge, the achievement of this value may take several hours. In any case, the pressure gauge should be placed near the canisters to determine pressure. The objective of requiring a low pressure evacuation during canister cleaning is to reduce contaminants. If canisters can be routinely certified (<0.2 ppbv for target compounds) while using a higher vacuum, then this criteria can be relaxed. However, the ultimate vacuum achieved during cleaning should always be <0.2mm Hg.

Canister cleaning as described in Section 8.4 and illustrated in Figure 10 requires components with special features. The vacuum gauge shown in Figure 10 must be capable of measuring 0.05mm Hg with less than a 20% error. The vacuum pump used for evacuating the canister must be noncontaminating while being capable of achieving the 0.05 mm Hg vacuum as monitored near the canisters. Thermoelectric vacuum gauges and turbomolecular drag pumps are typically being used for these two components.

An alternate to achieving the canister certification requirement of <0.2 ppbv for all target compounds is the criteria used in Compendium Method TO-12 that the total carbon count be <10ppbC. This check is less expensive and typically more exacting than the current certification requirement and can be used if proven to be equivalent to the original requirement. This equivalency must be established by comparing the total nonmethane organic carbon (TNMOC) expressed in ppbC to the requirement that individual target compounds be <0.2 ppbv for a series of analytical runs.

APPENDIX C.

LISTING OF COMMERCIAL MANUFACTURERS AND RE-SUPPLIERS OF SPECIALLY-PREPARED CANISTERS

BRC/Rasmussen
17010 NW Skyline Blvd.
Portland, Oregon 97321
(503) 621-1435

Meriter
1790 Potrero Drive
San Jose, CA 95124
(408) 265-6482

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823-8812
(814) 353-1300
(800) 356-1688

Scientific Instrumentation Specialists
P.O. Box 8941
815 Courtney Street
Moscow, ID 83843
(208) 882-3860

Graseby
500 Technology Ct.
Smyrna, Georgia 30082
(404) 319-9999
(800) 241-6898

XonTech Inc.
6862 Hayenhurst Avenue
Van Nuys, CA 91406
(818) 787-7380

APPENDIX D.

LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

Kin-Tek
504 Laurel St.
Lamarque, Texas 77568
(409) 938-3627
(800) 326-3627

Vici Metronics, Inc.
2991 Corvin Drive
Santa Clara, CA 95051
(408) 737-0550

Analytical Instrument Development, Inc.
Rt. 41 and Newark Rd.
Avondale, PA 19311
(215) 268-3181

Ecology Board, Inc.
9257 Independence Ave.
Chatsworth, CA 91311
(213) 882-6795

Tracor, Inc.
6500 Tracor Land
Austin, TX
(512) 926-2800

Metronics Associates, Inc.
3201 Porter Drive
Standford Industrial Park
Palo Alto, CA 94304
(415) 493-5632

TABLE 1. VOLATILE ORGANIC COMPOUNDS ON THE TITLE III CLEAN AIR AMENDMENT LIST--MEMBERSHIP IN COMPENDIUM METHOD TO-14A LIST AND THE SOW-CLP LIST OF VOCs

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl chloride (chloromethane); CH3Cl	74-87-3	-23.7	3.8 x 10	50.5	X	X
Carbonyl sulfide; COS	463-58-1	-50.0	3.7 x 10	60.1		
Vinyl chloride (chloroethene); C2H3Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH2N2	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH2O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C4H6	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH3Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl2O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C2H3Br	593-60-2	15.8	l.l x 10	107		
Ethylene oxide; C2H4O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C2H4O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	31.7	500	97	X	X
Propylene oxide; C3H6O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH3I	74-88-4	42.4	400	141.9		
Methylene chloride; CH2Cl2	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C2H3NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS2	75-15-0	46.5	260	76		
Methyl tert-butyl ether; C5H12O	1634-04-4	55.2	249	86		
Propionaldehyde; C2H5CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	57.0	230	99	X	

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C2H5ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C3H4O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	63.0	163	72		
Chloroform; CHCl3	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C2H5N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C2H8N2	57-14-7	63	157.0	60.0		
Hexane; C6H14	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C3H7N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C2H3Cl3	71-55-6	74.1	100	133.4	X	X
Methanol; CH4O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl4	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C4H6O2	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	79.6	77.5	72		X
Benzene; C6H6	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C2H3N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	83.5	61.5	99	X	X
Triethylamine; C6H15N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH6N2	60-34-4	87. 8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C8H18	540-84-l	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C4H8O2	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	104	30.0	115		
Ethyl acrylate; C5H8O2	140-88-5	100	29.3	100		
Methyl methacrylate; C5H8O2	80-62-6	101	28.0	100.1		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmgHg)[1]	MW[1]	TO-14A	CLP-SOW
Methyl methacrylate; C5H8O2	80-62-101	101	28.0	100.1		
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	112	27.8	111	X	X
Toluene; C7H8	108-88-3	111	22.0	92	X	X
Trichloroethylene; C2HCl3	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C2Cl4	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C2H5N3O2	684-93-5	124	10.0	103		
2-Nitropropane; C3H7NO2	79-46-9	120	10.0	89		
Chlorobenzene; C6H5Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C8H10	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C8H10	1330-20-7	142	6.7	106.2	X	X
Styrene; C8H8	100-42-5	145	6.6	104	X	X
p-Xylene; C8H10	106-42-3	138	6.5	106.2	X	X
m-Xylene; C8H10	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr3	75-25-2	149	5.6	252.8		
l,l,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	146	5.0	167.9	X	X
o-Xylene; C8H10	95-47-6	144	5.0	106.2	X	X
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C2H6N2O	62-75-9	152	3.7	74		
Beta-Propiolactone; C3H4O2	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C9Hl2	98-82-8	153	3.2	120		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Cumene (isopropylbenzene); C9H12	98-82-8	153	3.2	120		
Acrylic acid; C3H4O2	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C3H7NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C3H6O3S	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C8H8O	98-86-2	202	1.0	120		
Dimethyl sulfate; C2H6O4S	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	178	0.71	143		
Chloroacetic acid; C2H3ClO2	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C6H7N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C3H7NO2	51-79-6	183	0.54	89		
Acrylamide; C3H5NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C8H11N	121-69-7	192	0.50	121		
Hexachloroethane; C2Cl6	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C4Cl6	87-68-3	215	0.40	260.8	X	X
Isophorone; C9H14O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C4H8N2O2	59-89-2	225	0.32	116.1		
Styrene oxide; C8H8O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C4H10O4S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture);C7H8O	1319-77-3	202	0.26	108		
o-Cresol; C7H8O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)[1]	MW[1]	TO-14A	CLP-SOW
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	240	0.22	110		
Phenol; C6H6O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	213	0.18	181.5	X	X
nitrobenzene; C6H5NO2	98-95-3	211	0.15	123		

[1]Vapor pressure (v.p.), boiling point (BP) and molecularweight (MW) data from:
(a)D. L. Jones and J. bursey, "Simultaneous Control of PM-10 and Hazardous Air Pollutants II: Rationale for Selection of Hazardous Air Pollutants as Potential Particulate Matter," Report EPA-452/R-93/013, U. S. Environmental Protection Agency, Research Triangle Park, NC. October 1992;
(b)R. C. Weber, P. A. Parker, and M. Bowser. Vapor Pressure Distribution of Selected Organic Chemicals, Report EPA-600/2-81-021, U. S. Environmental Protection Agency, Cincinnati, OH, February 1981; and
(c)R. C. Weast, ed., "CRC Handbook of Chemistry and Physics," 59th edition, CRC Press, Boca Raton, 1979.

TABLE 2. CHARACTERISTIC MASSES (M/Z) USED FOR QUANTIFYING THE TITLE III CLEAN AIR ACT AMENDMENT COMPOUNDS

Compound	CAS No.	Primary Ion	Secondary Ion
Methyl chloride (chloromethane); CH3Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-S8-1	60	62
Vinyl chloride (chloroethene); C2H3Cl	7S-01-4	62	64
Diazomethane; CH2N2	334-88-3	42	41
Formaldehyde; CH2O	50-00-0	29	30
1,3-Butadiene; C4H6	106-99-0	39	54
Methyl bromide (bromomethane); CH3Br	74-83-9	94	96
Phosgene; CCl2O	75-44-5	63	65
Vinyl bromide (bromoethene); C2H3Br	593-60-2	106	108
Ethylene oxide; C2H4O	75-21-8	29	44
Ethyl chloride (chloroethane); C2H5Cl	75-00-3	64	66
Acetaldehyde (ethanal); C2H4O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); C2H2Cl2	75-35-4	61	96
Propylene oxide; C3H6O	75-56-9	58	57
Methyl iodide (iodomethane); CH3I	74-88-4	142	127
Methylene chloride; CH2Cl2	75-09-2	49	84, 86
Methyl isocyanate; C2H3NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C3H5Cl	107-05-1	76	41, 78
Carbon disulfide; CS2	75-15-0	76	44, 78
Methyl tert-butyl ether; C5H12O	1634-04-4	73	41, 53
Propionaldehyde; C2H5CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); C2H4Cl2	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C4H5Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C2H5ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C3H4O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C4H8O	106-88-7	42	41, 72
Chloroform; CHCl3	67-66-3	83	85, 47
Ethyleneimine (aziridine); C2H5N	151-56-4	42	43
1,1-Dimethylhydrazine; C2H8N2	57-14-7	60	45, 59
Hexane; C6H14	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylazindine); C3H7N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C3H3N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); C2H3Cl3	71-55-6	97	99, 61
Methanol; CH4O	67-56-1	31	29
Carbon tetrachloride; CCl4	56-23-5	117	119
Vinyl acetate; C4H6O2	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C4H8O	78-93-3	43	72

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Benzene; C6H6	71-43-2	78	77,50
Acetonitrile (cyanomethane); C2H3N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane); C2H4Cl2	107-06-2	62	64, 27
Triethylamine; C6H15N	121-44-8	86	58, 101
Methylhydrazine; CH6N2	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); C3H6Cl2	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C8H18	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); C4H8O2	123-91-1	88	58
Bis(chloromethyl) ether; C2H4Cl2O	542-88-1	79	49, 81
Ethyl acrylate; C5H8O2	140-88-5	55	73
Methyl methacrylate; C5H8O2	80-62-6	41	69, 100
1,3-Dichloropropene; C3H4Cl2 (cis)	542-75-6	75	39, 77
Toluene; C7H8	108-88-3	91	92
Trichloethylene; C2HCl3	79-01-6	130	132, 95
1,1,2-Trichloroethane; C2H3Cl3	79-00-5	97	83, 61
Tetrachloroethylene; C2Cl4	127-18-4	166	164, 131
Epichlorohydrin (l-chloro-2,3-epoxy propane); C3H5ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); C2H4Br2	106-93-4	107	109
N-Nitrso-N-methylurea; C2H5N3O2	684-93-5	60	44, 103
2-Nitropropane; C3H7NO2	79-46-9	43	41
Chlorobenzene; C6H5Cl	108-90-7	112	77, 114
Ethylbenzene; C8H10	100-41-4	91	106
Xylenes (isomer & mixtures); C8H10	1330-20-7	91	106
Styrene; C8H8	100-42-5	104	78, 103
p-Xylene; C8H10	106-42-3	91	106
m-Xylene; C8H10	108-38-3	91	106
Methyl isobutyl ketone (hexone); C6H12O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr3	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C2H2Cl4	79-34-5	83	85
o-Xylene; C8H10	95-47-6	91	106
Dimethylcarbamyl chloride; C3H6ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C2H6N2O	62-75-9	74	42
Beta-Propiolactone; C3H4O2	57-57-8	42	43
Cumene (isopropylbenzene); C9H12	98-82-8	105	120
Acrylic acid; C3H4O2	79-10-7	72	45, 55
N,N-Dimethylformamide; C3H7NO	68-12-2	73	42, 44
1,3-Propane sultone; C3H6O3S	1120-71-4	58	65, 122

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Acetophenone; C8H8O	98-86-2	105	77,120
Dimethyl sulfate; C2H6O4S	77-78-1	95	66,96
Benzyl chloride (a-chlorotoluene); C7H7Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C3H5Br2Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C4H8Cl2O	111-44-4	93	63, 95
Chloroacetic acid; C2H3ClO2	79-11-8	50	45, 60
Aniline (aminobenzene); C6H7N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C6H4Cl2	106-46-7	146	148, 111
Ethyl carbamate (urethane); C3H7NO2	51-79-6	31	44, 62
Acrylamide; C3H5NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C8H11N	121-69-7	120	77, 121
Hexachloroethane; C2Cl6	67-72-1	201	199, 203
Hexachlorobutadiene; C4Cl6	87-68-3	225	227, 223
Isophorone; C9H14O	78-59-1	82	138
N-Nitrosomorpholine; C4H8N2O2	59-89-2	56	86, 116
Styrene oxide; C8H8O	96-09-3	91	120
Diethyl sulfate; C4H10O4S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture); C7H8O	1319-77-3		
o-Cresol; C7H8O	95-48-7	108	107
Catechol (o-hydroxyphenol); C6H6O2	120-80-9	110	64
Phenol; C6H6O	108-95-2	94	66
1,2,4-Trichlorobenzene; C6H3Cl3	120-82-1	180	182, 184
Nitrobenzene; C6H5NO2	98-95-3	77	51, 123

TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria[1]
50	8.0 to 40.0 Percent of m/e 95
75	30.0 to 66.0 Percent of m/e 95
95	Base Peak, 100 Percent Relative Abundance
96	5.0 to 9.0 Percent of m/e 95 (See note)
173	Less than 2.0 Percent of m/e 174
174	50.0 to 120.0 Percent of m/e 95
175	4.0 to 9.0 Percent of m/e 174
176	93.0 to 101.0 Percent of m/e 174
177	5.0 to 9.0 Percent of m/e 176

[1]All ion abundances must be normalized to m/z 95, the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 percent that of m/z 95.

TABLE 4. METHOD DETECTION LIMITS (MDL)[1]

TO-14A List	Lab #1, SCAN	Lab #2, SIM
Benzene	0.34	0.29
Benzyl Chloride	--	--
Carbon tetrachloride	0.42	0.15
Chlorobenzene	0.34	0.02
Chloroform	0.25	0.07
1,3-Dichlorobenzene	0.36	0.07
1,2-Dibromoethane	--	0.05
1,4-Dichlorobenzene	0.70	0.12
1,2-Dichlorobenzene	0.44	--
1,1-Dichloroethane	0.27	0.05
1,2-Dichloroethane	0.24	--
1,1-Dichloroethene	--	0.22
cis-1,2-Dichloroethene	--	0.06
Methylene chloride	1.38	0.84
1,2-Dichloropropane	0.21	--
cis-1,3-Dichloropropene	0.36	--
trans-1,3-Dichloropropene	0.22	--
Ethylbenzene	0.27	0.05
Chloroethane	0.19	--
Trichlorofluoromethane	--	--
1,1,2-Trichloro-1,2,2-trifluoroethane		--
1,2-Dichloro-1,1,2,2-tetrafluoroethane	--	--
Dichlorodifluoromethane	--	--
Hexachlorobutadiene	--	--
Bromomethane	0.53	--
Chloromethane	0.40	--
Styrene	1.64	0.06
1,1,2,2-Tetrachloroethane	0.28	0.09
Tetrachloroethene	0.75	0.10
Toluene	0.99	0.20
1,2,4-Trichlorobenzene	--	--
1,1,1-Trichloroethane	0.62	0.21
1,1,2-Trichloroethane	0.50	--
Trichloroethene	0.45	0.07
1,2,4-Trimethylbenzene	--	--
1,3,5-Trimethylbenzene	--	--
Vinyl Chloride	0.33	0.48
m,p-Xylene	0.76	0.08
o-Xylene	0.57	0.28

[1]Method Detection Limits (MDLs) are defined as the product of the standard deviation of seven replicate analyses and the student's "t" test value for 99% confidence. For Lab #2, the MDLs represent an average over four studies. MDLs are for MS/SCAN for Lab #1 and for MS/SIM for Lab #2.

TABLE 5. SUMMARY OF EPA DATA ON REPLICATE PRECISION (RP) FROM EPA NETWORK OPERATIONS[1]

Monitoring Compound Identification	EPA's Urban Air Toxics Monitoring Program (UATMP)			EPA's Toxics Air Monitoring Stations (TAMS)		
	%RP	#	ppbv	%RP	#	ppbv
Dichlorodifluoromethane	--		--	13.9	47	0.9
Methylene chloride	16.3	07	4.3	19.4	47	0.6
1,2-Dichloroethane	36.2	31	1.6	--	--	--
1,1,1-Trichloroethane	14.1	44	1.0	10.6	47	2.0
Benzene	12.3	56	1.6	4.4	47	1.5
Trichloroethene	12.8	08	1.3	--	--	--
Toluene	14.7	76	3.1	3.4	47	3.1
Tetrachloroethene	36.2	12	0.8	--	--	--
Chlorobenzene	20.3	21	0.9	--	--	--
Ethylbenzene	14.6	32	0.7	5.4	47	0.5
m-Xylene	14.7	75	4.0	5.3	47	1.5
Styrene	22.8	59[2]	1.1	8.7	47	0.2[2]
o-Xylene	--		--	6.0	47	0.5
p-Xylene	--					
1,3-Dichlorobenzene	49.1	06	0.6	--	--	--
1,4-Dichlorobenzene	14.7	14	6.5	--	--	--

[1]Denotes the number of replicate or duplicate analysis used to generate the statistic. The replicate precision is defined as the mean ratio of absolute difference to the average value.
[2]Styrene and o-xylene coelute from the GC column used in UATMP. For the TAMS entries, both values were below detection limits for 18 of 47 replicates and were not included in the calculation.

TABLE 6. AUDIT ACCURACY (AA) VALUES[1] FOR SELECTED COMPENDIUM METHOD TO-14A COMPOUNDS

Selected Compounds From TO-14A List	FY-88 TAMS AA(%), N=30	FY-88 UATMP AA(%), N=3
Vinyl chloride	4.6	17.9
Bromomethane	--	6.4
Trichlorofluoromethane	6.4	--
Methylene chloride	8.6	31.4
Chloroform	--	4.2
1,2-Dichloroethane	6.8	11.4
1,1,1-Trichloroethane	18.6	11.3
Benzene	10.3	10.1
Carbon tetrachloride	12.4	9.4
1,2-Dichloropropane	--	6.2
Trichloroethene	8.8	5.2
Toluene	8.3	12.5
Tetrachloroethene	6.2	--
Chlorobenzene	10.5	11.7
Ethylbenzene	12.4	12.4
o-Xylene	16.2	21.2

[1]Audit accuracy is defined as the relative difference between the audit measurement result and its nominal value divided by the nominal value. N denotes the number of audits averaged to obtain the audit accuracy value. Information is not available for other TO-14A compounds because they were not present in the audit materials.

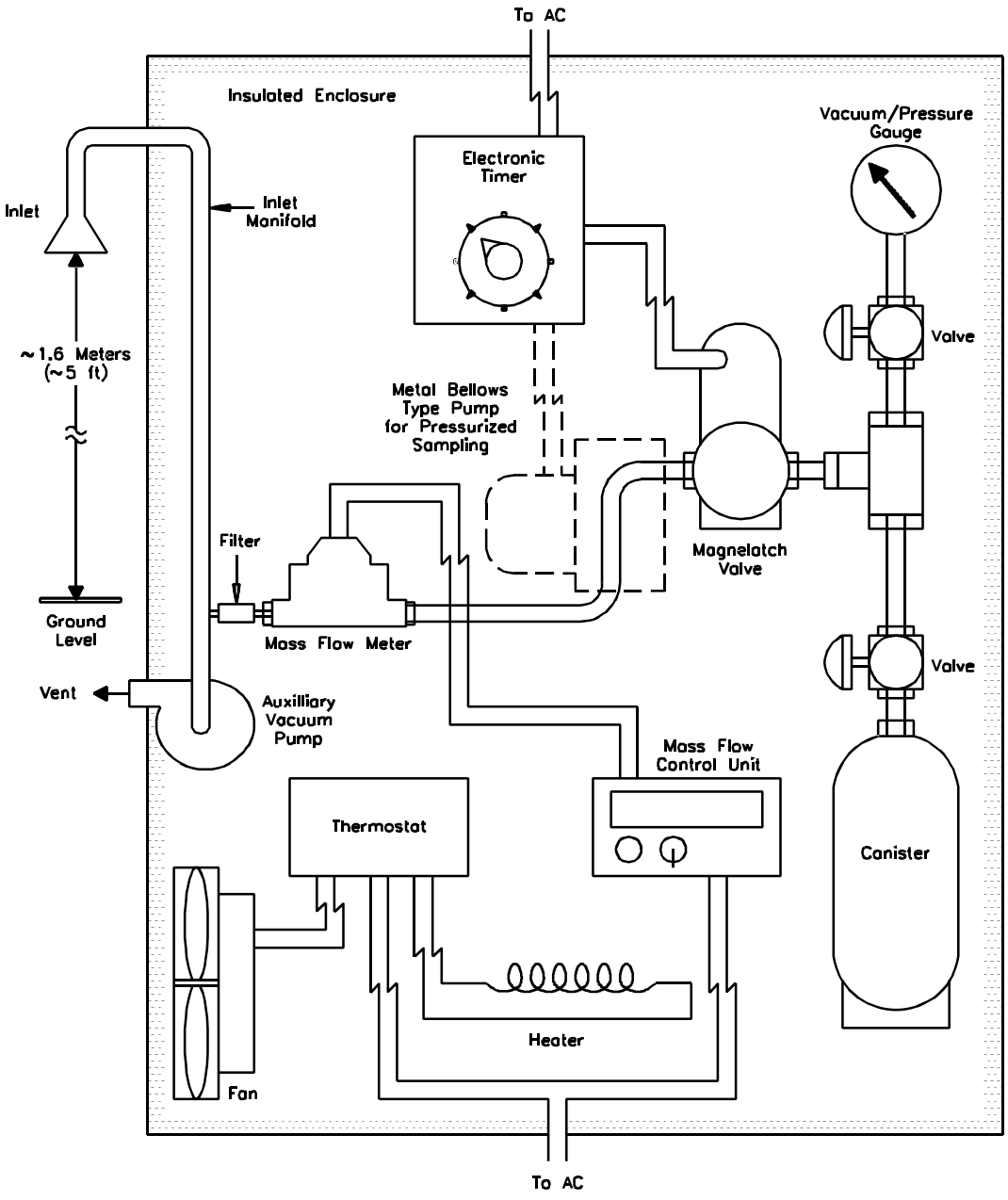
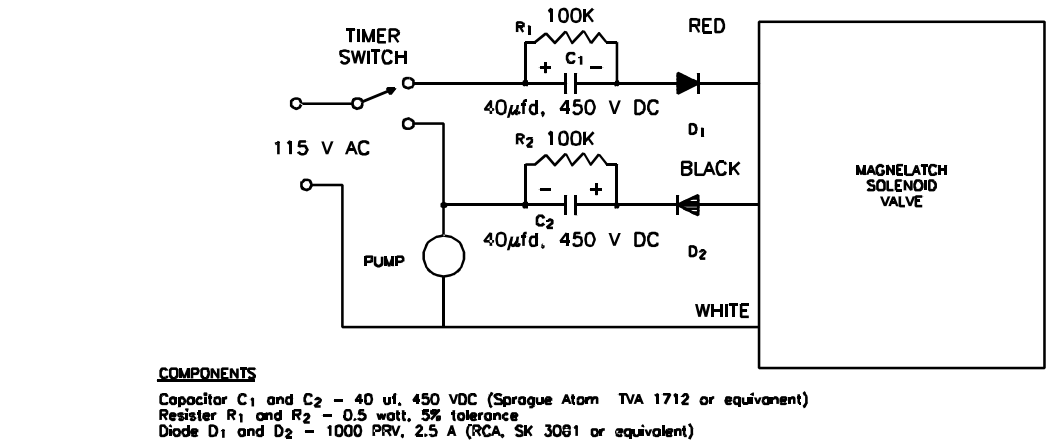
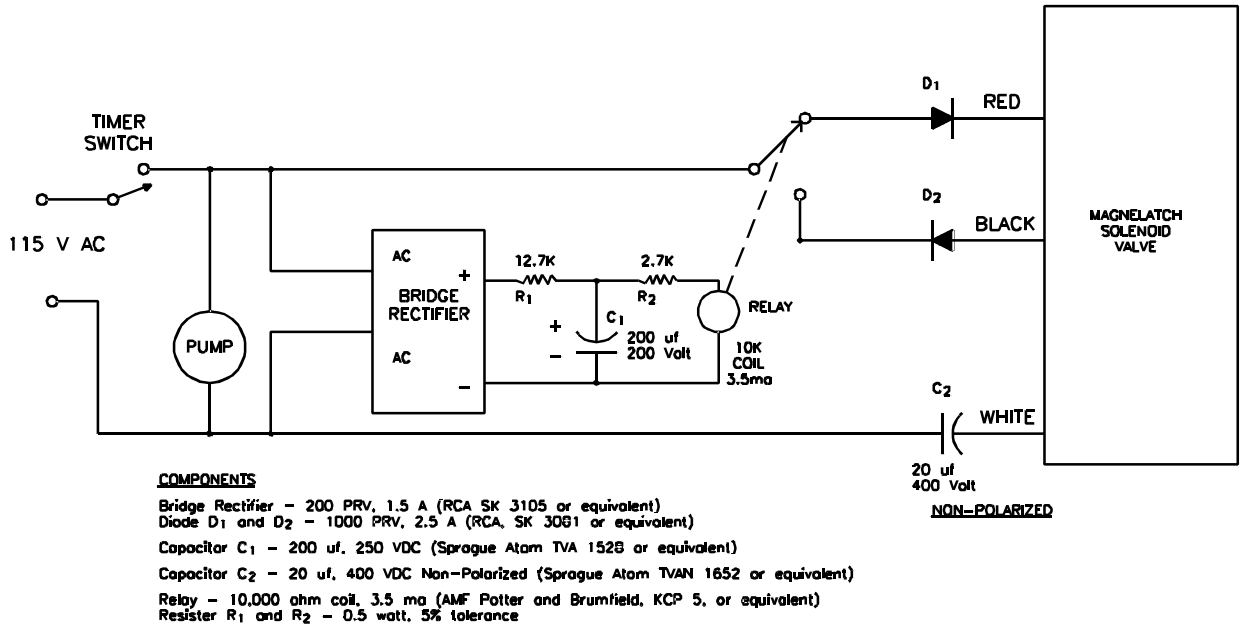


Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.



(a). Simple Circuit for Operating Magnelatch Valve



(b). Improved Circuit Designed to Handle Power Interruptions

Figure 2. Electrical pulse circuits for driving Skinner magnelatch solenoid valve with mechanical timer.

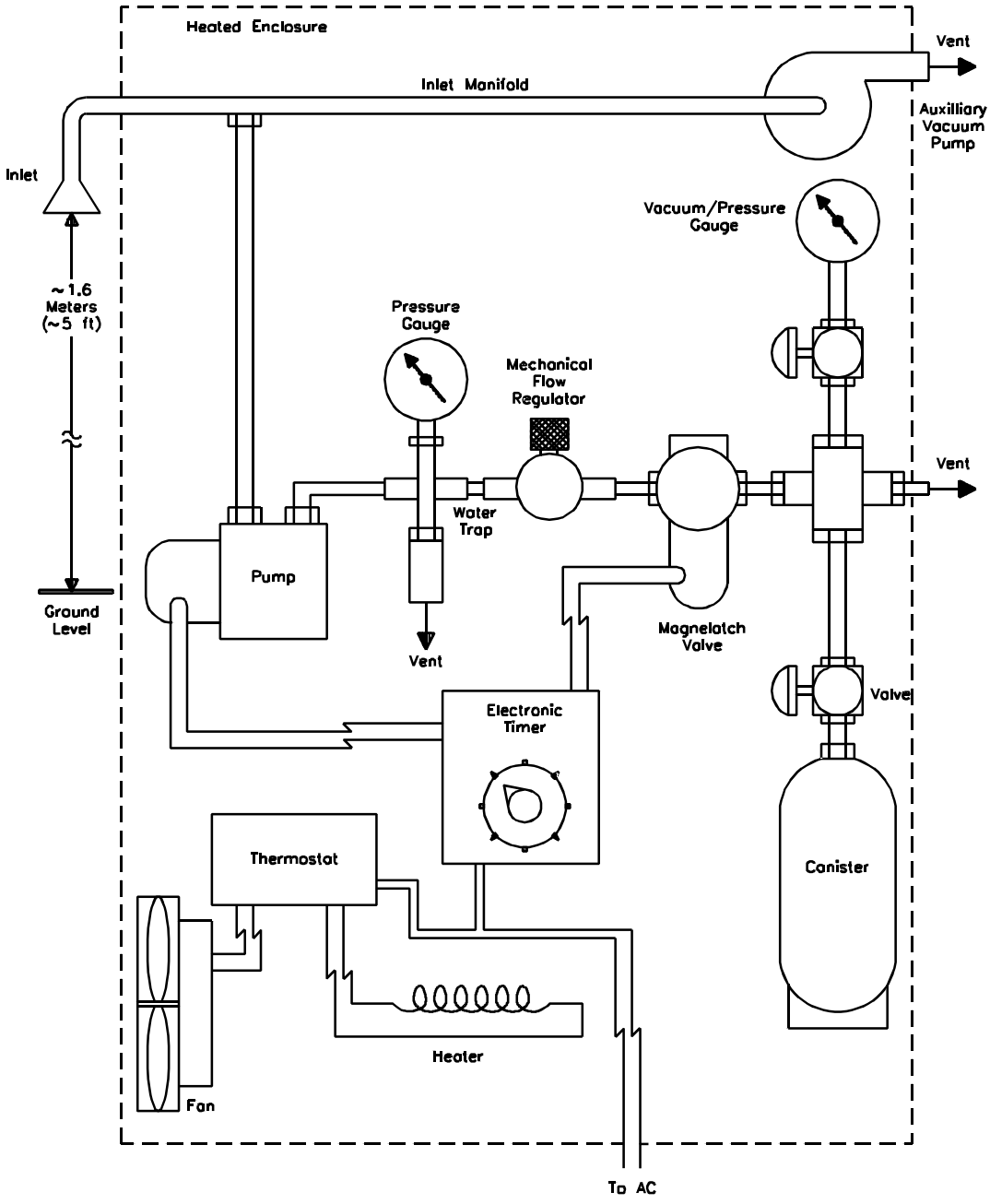


Figure 3. Alternative sampler configuration for pressurized canister sampling.

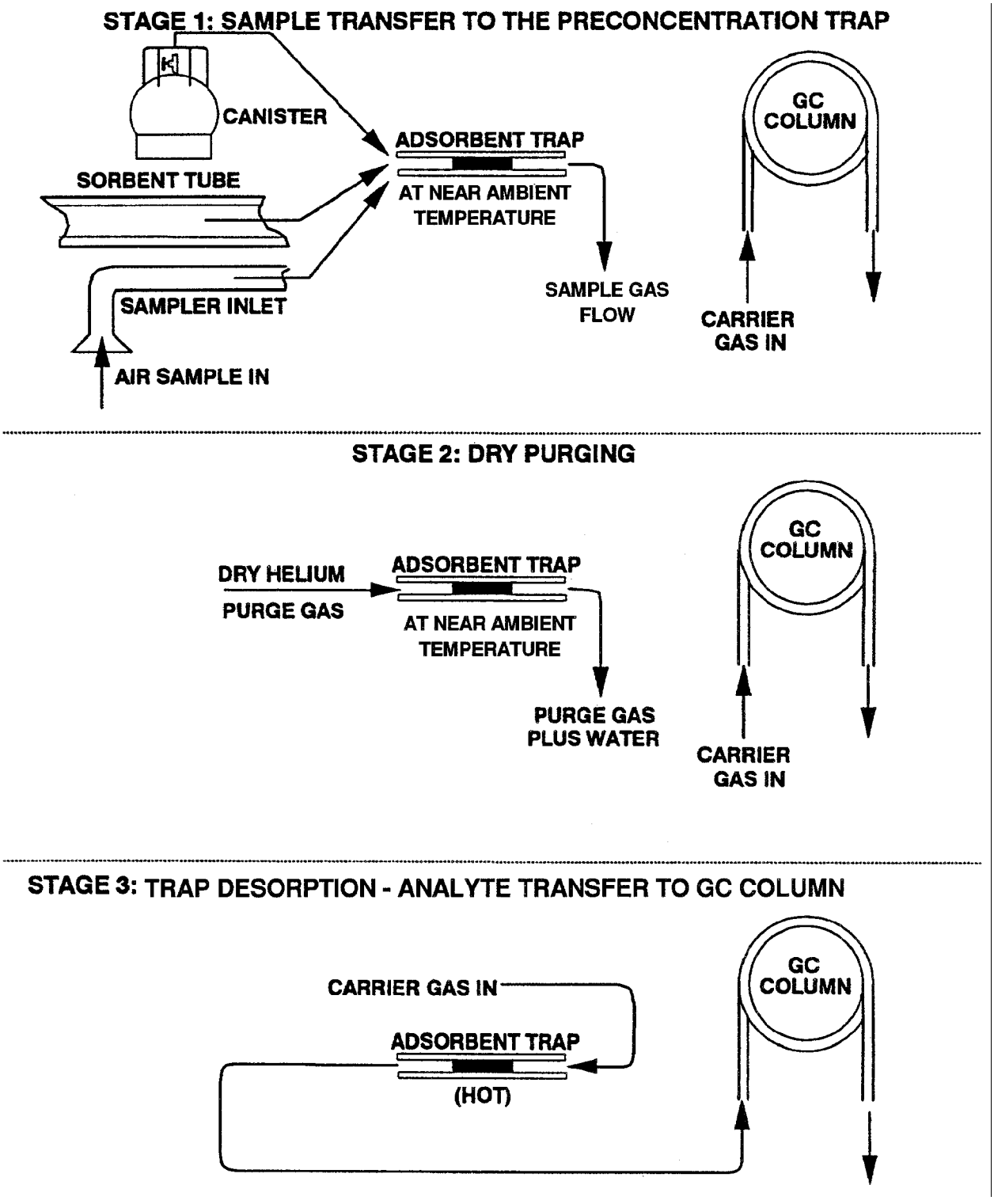


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

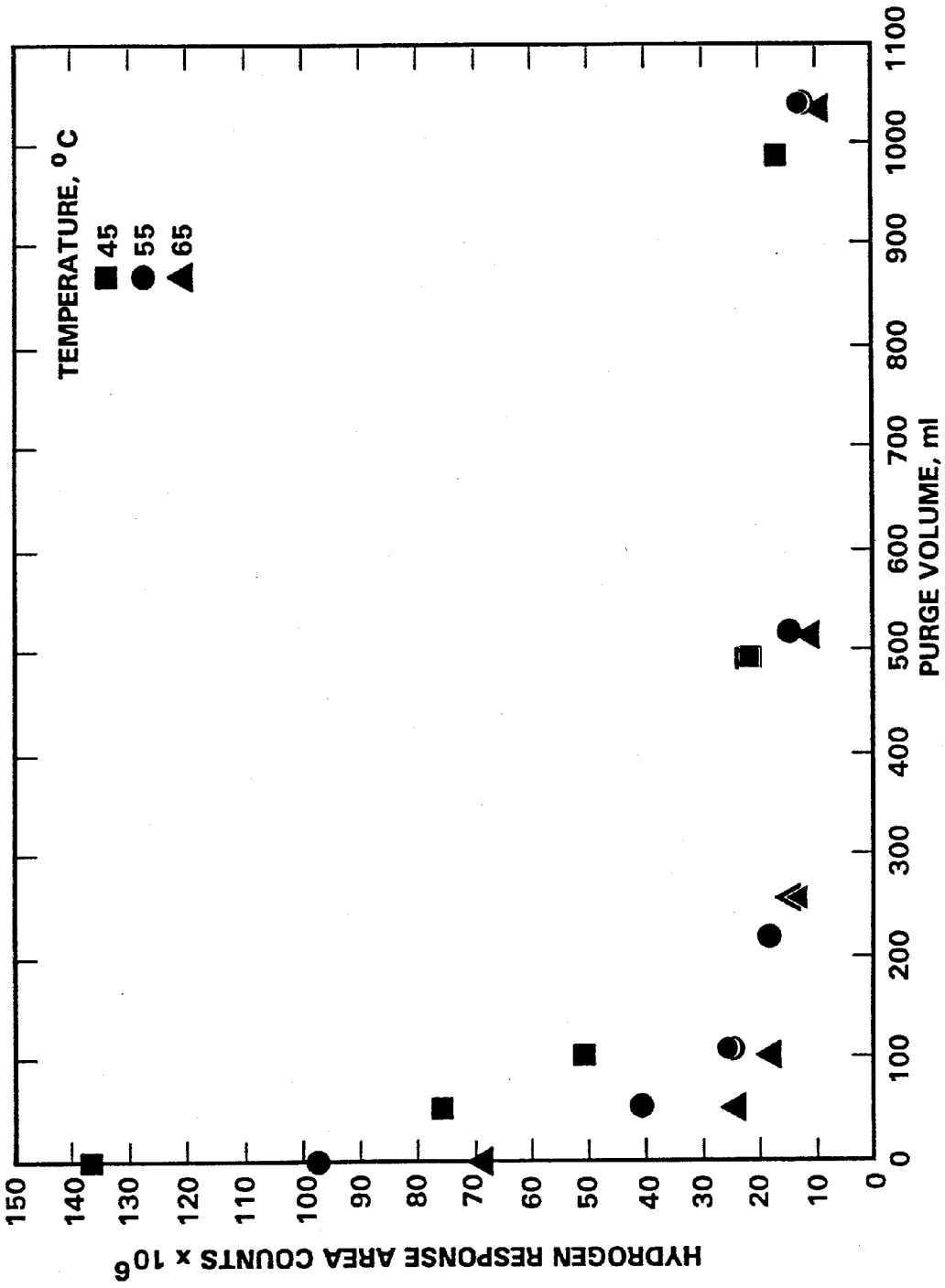


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

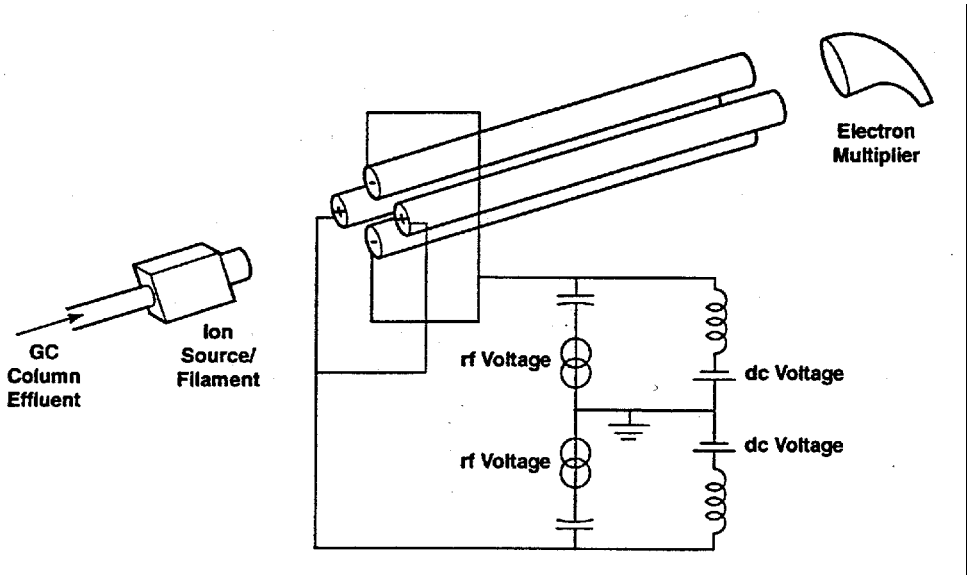


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

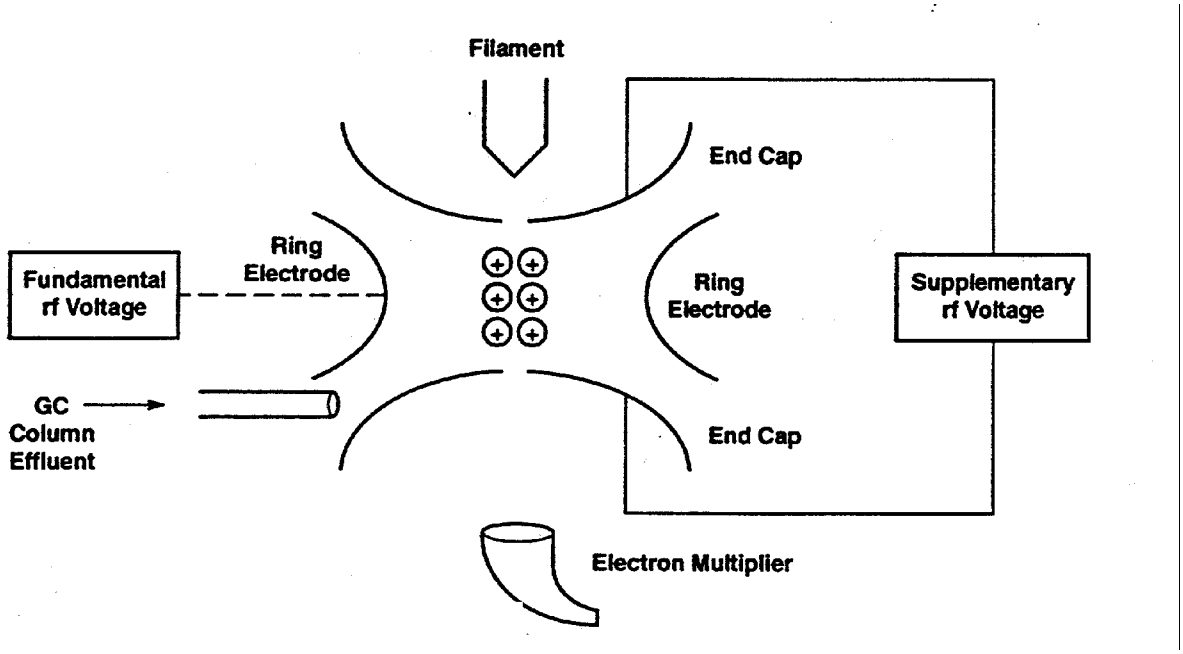


Figure 7. Simplified diagram of an ion trap mass spectrometer.

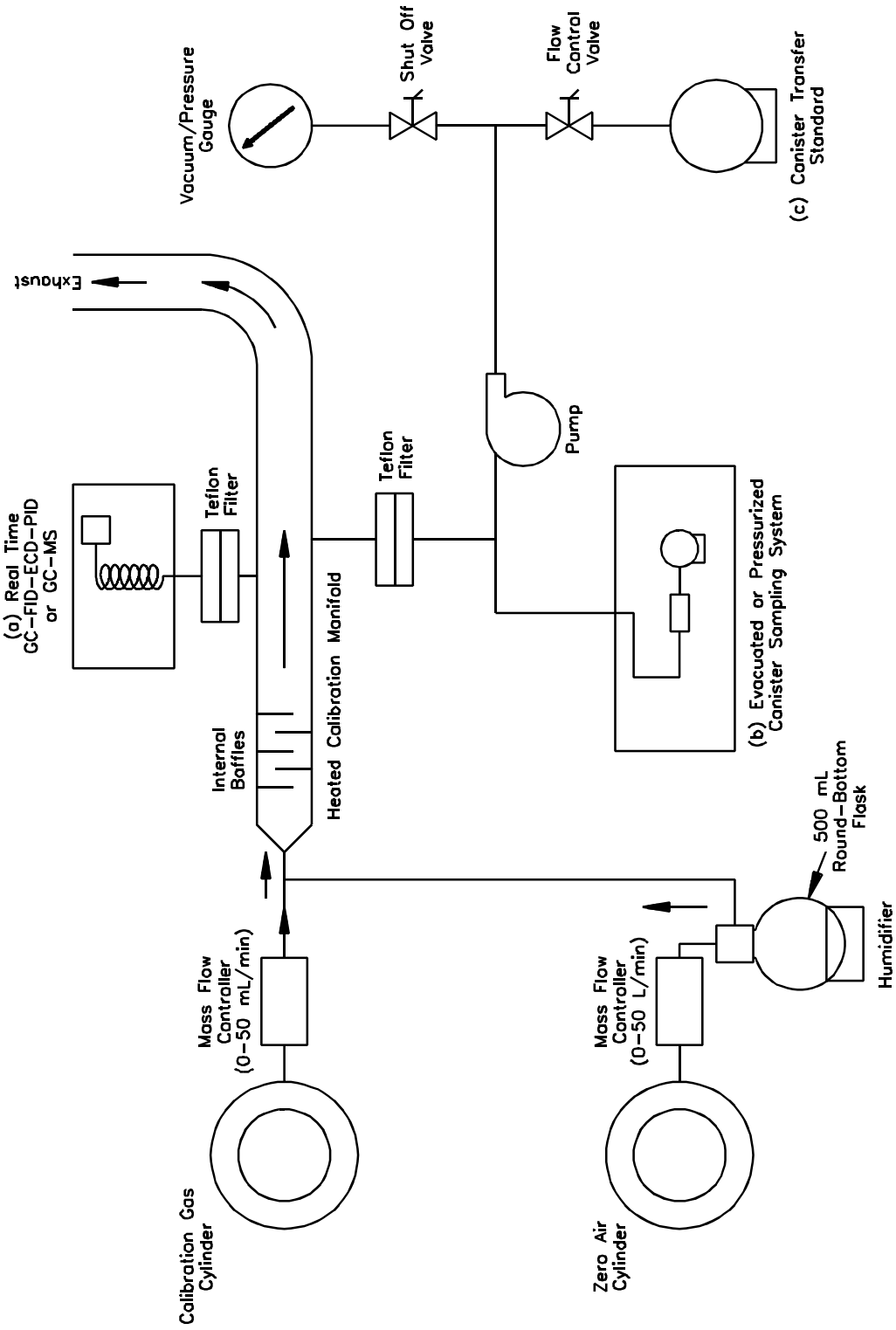


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET

A.GENERAL INFORMATION

SITE LOCATION: _____
SITE ADDRESS: _____
_____
SAMPLING DATE: _____

SHIPPING DATE: _____
CANISTER SERIAL NO.: _____
SAMPLER ID: _____
OPERATOR: _____
CANISTER LEAK
CHECK DATE: _____

B. SAMPLING INFORMATION

	TEMPERATURE				PRESSURE	
	INTERIOR	AMBIENT	MAXIMUM	MINIMUM	CANISTER PRESSURE	
START						
STOP						

	SAMPLING TIMES		FLOW RATES		
	LOCAL TIME	ELAPSED TIME METER READING	MANIFOLD FLOW RATE	CANISTER FLOW RATE	FLOW CONTROLLER READOUT
START					
STOP					

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

DATA RECEIVED: _____
RECEIVED BY: _____
INITIAL PRESSURE: _____
FINAL PRESSURE: _____
DILUTION FACTOR: _____
ANALYSIS
GC-FID-ECD DATE: _____
GC-MSD-SCAN DATE: _____
GC-MSD-SIM DATE: _____
RESULTS*: _____
_____
GC-FID-ECD: _____
GC-MSD-SCAN: _____
GC-MSD-SIM: _____

_____
SIGNATURE/TITLE

Figure 9. Canister sampling field test data sheet (FTDS).

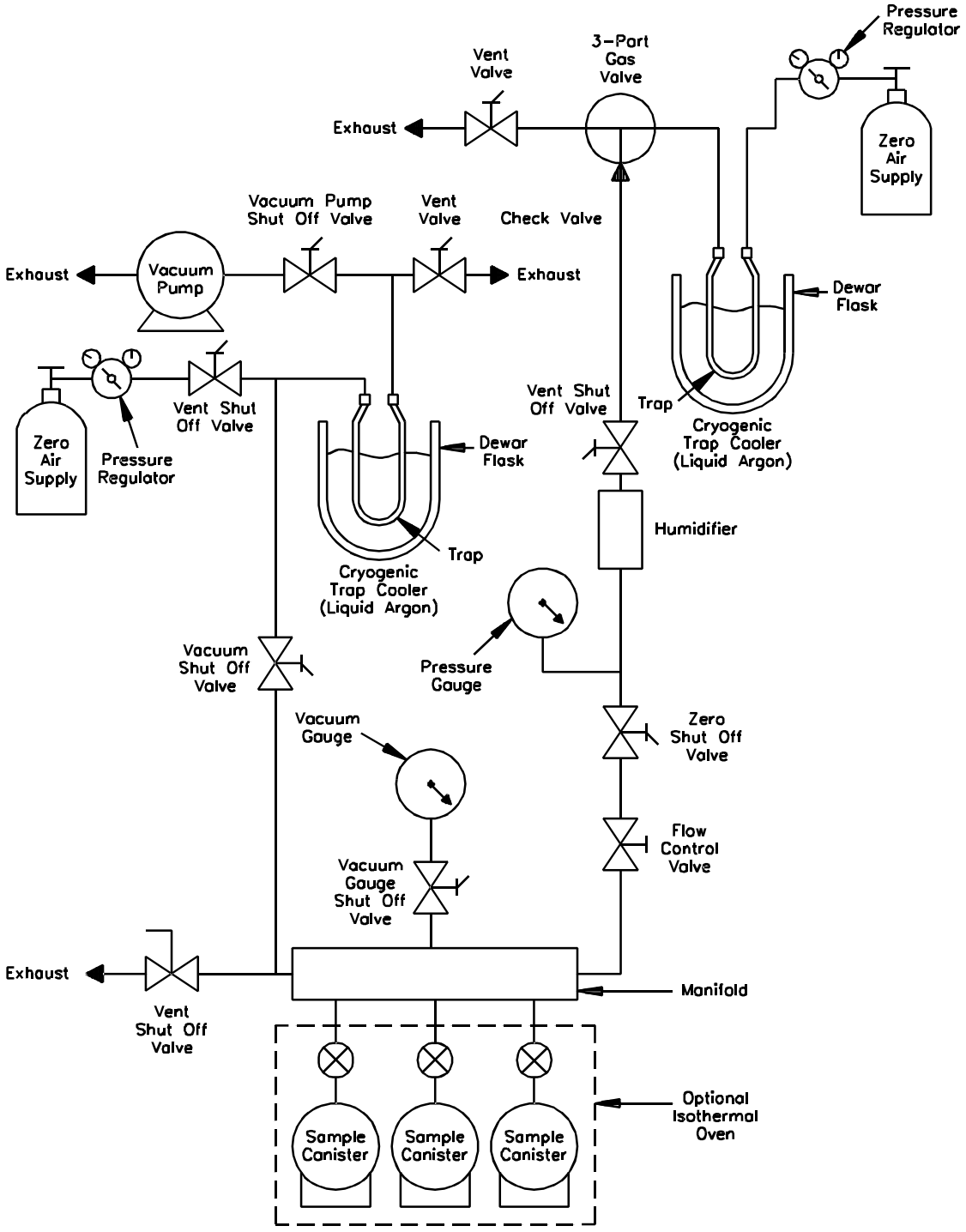


Figure 10. Canister cleaning system.

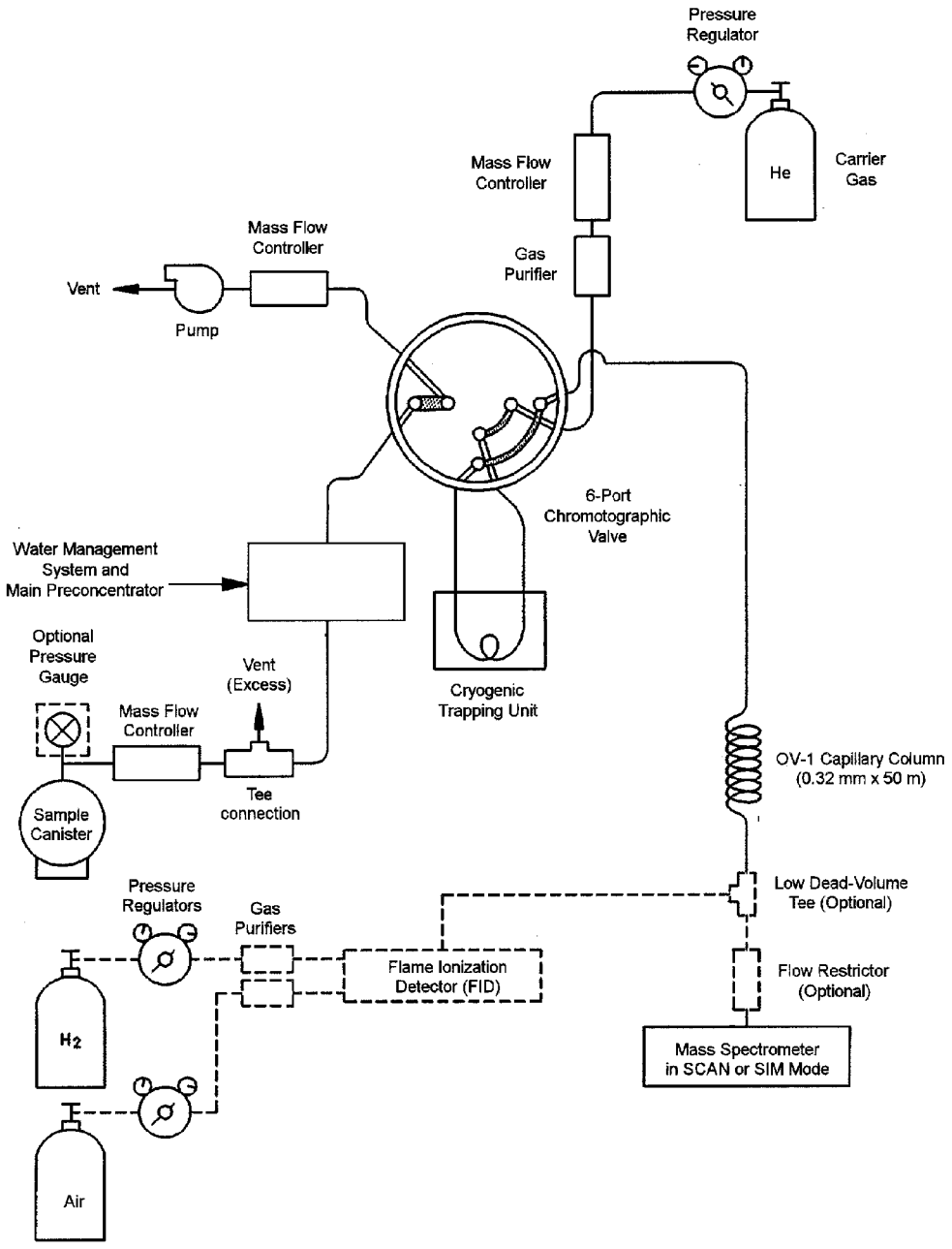
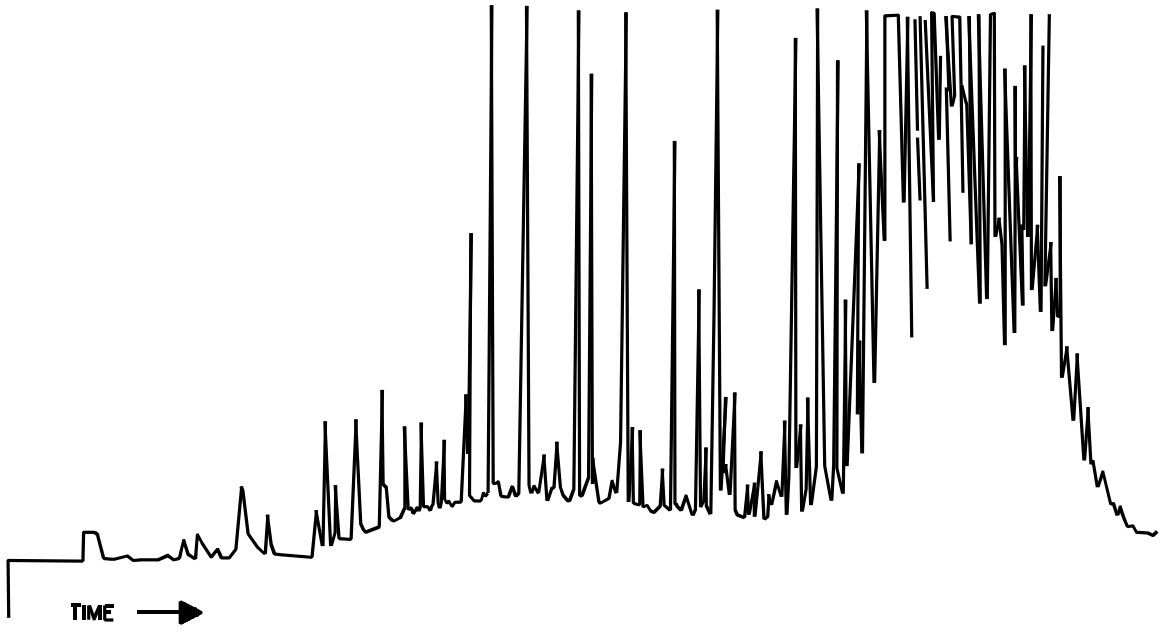


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]

(a). Certified Sampler



(b). Contaminated Sampler

Figure 12. Example of humid zero air test results for a clean sample canister (a) and a contaminated sample canister (b).

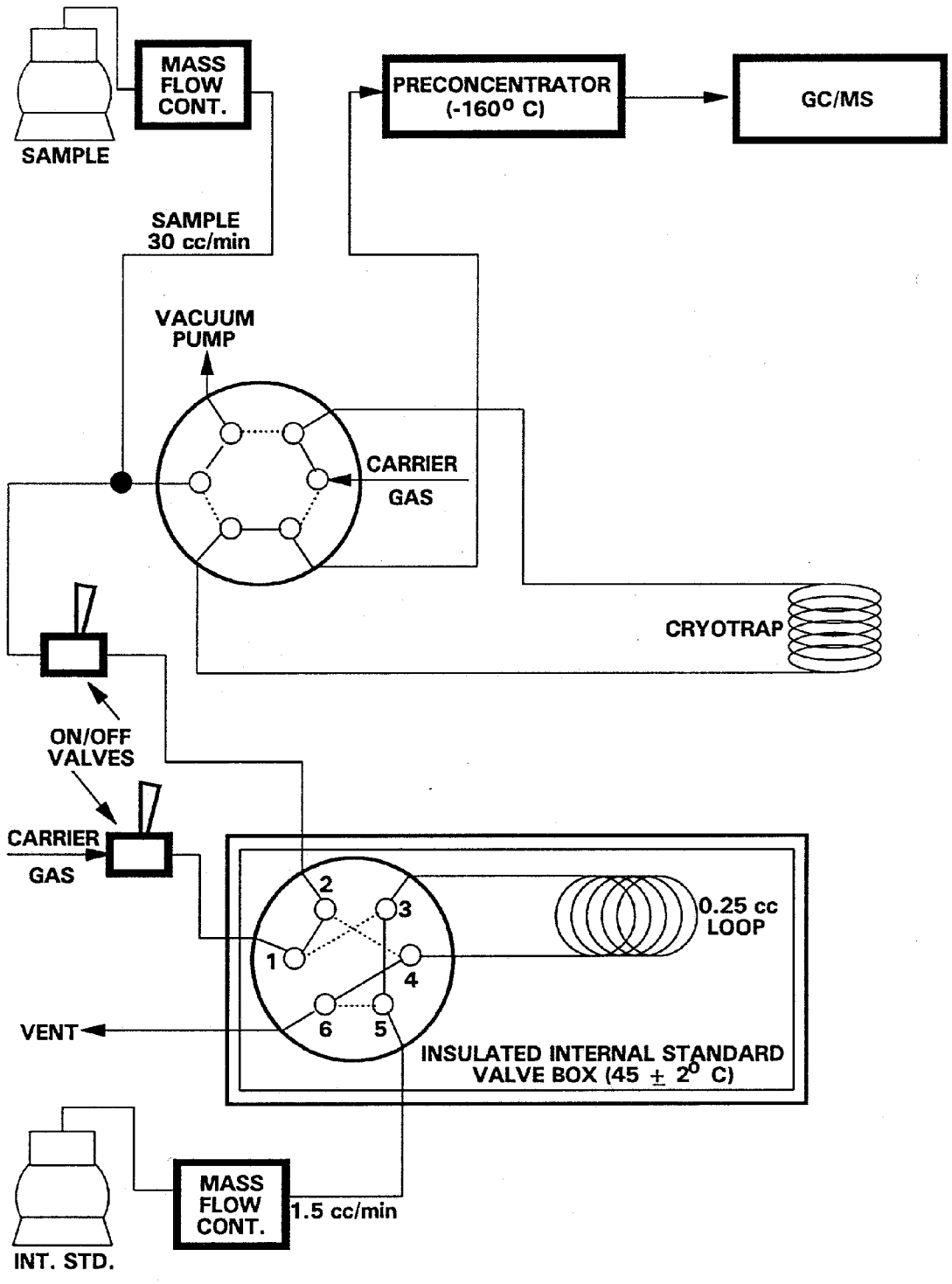


Figure 13. Diagram of design for internal standard addition.

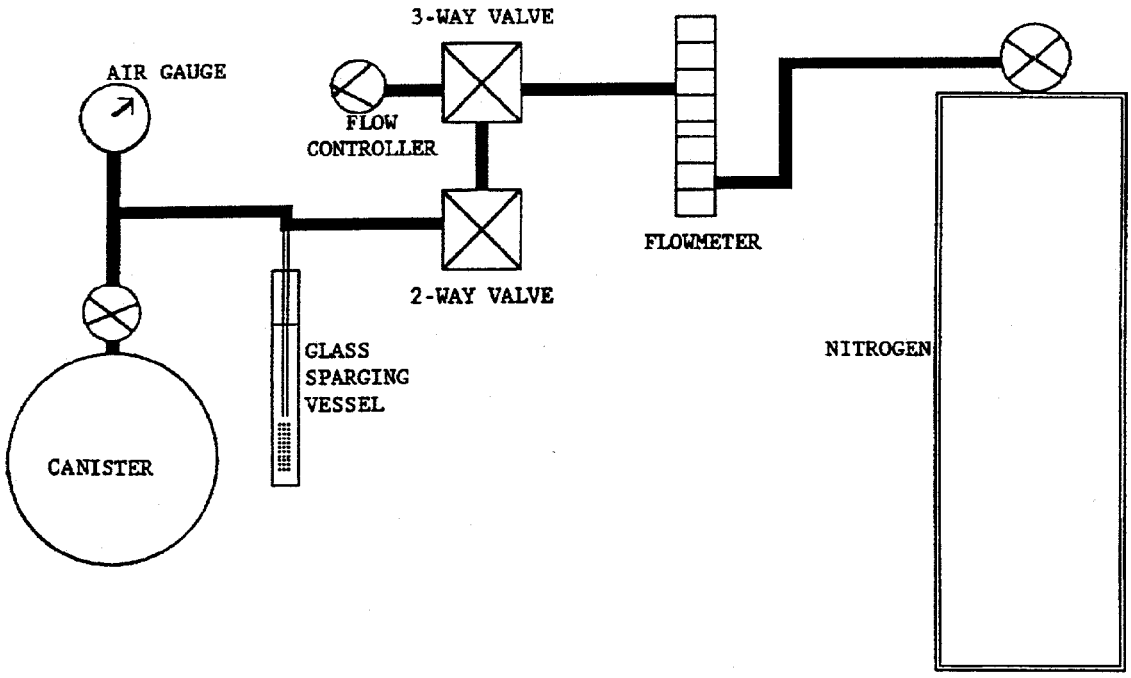


Figure 14. Water method of standard preparation in canisters.

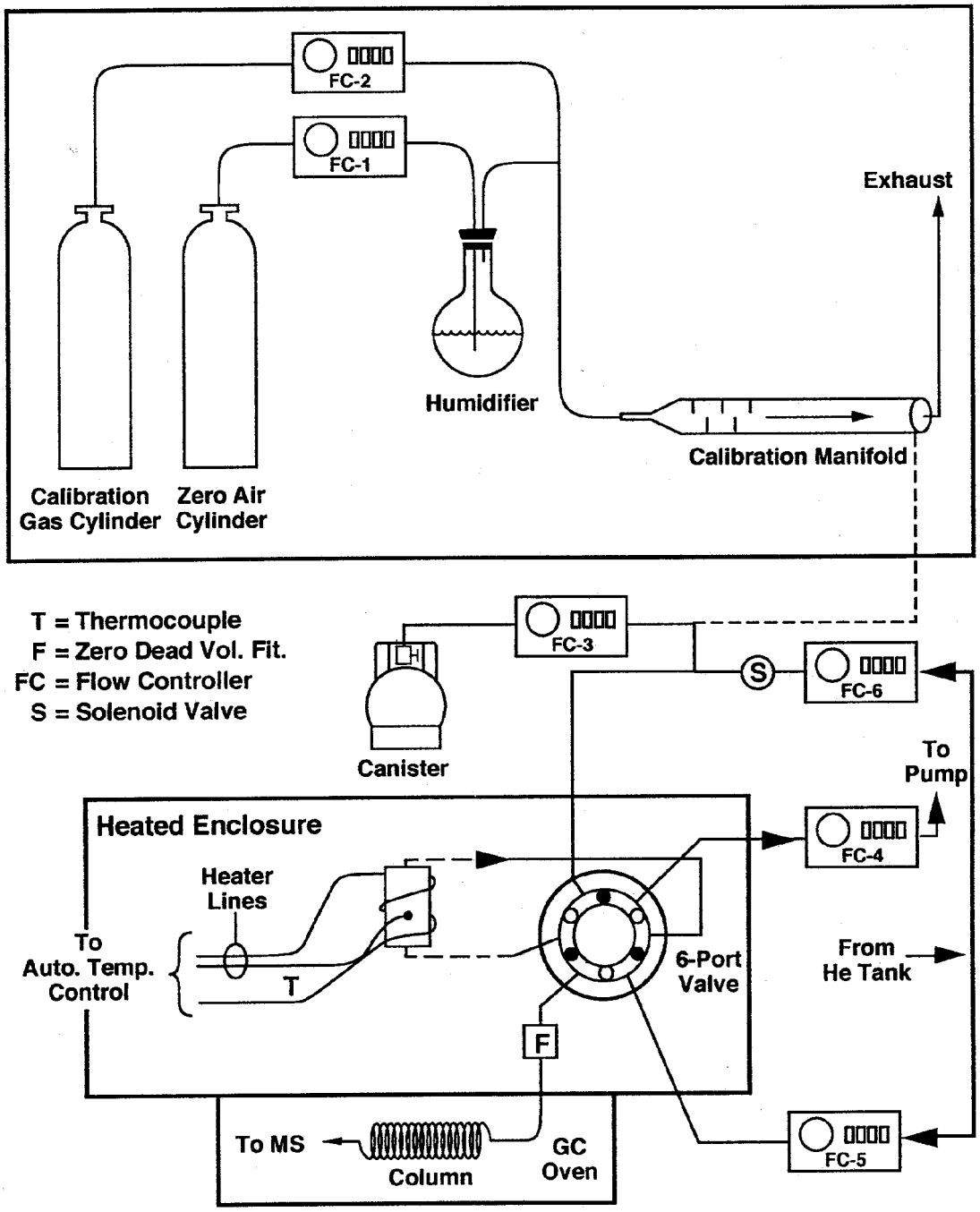


Figure 15. Diagram of the GC/MS analytical system.

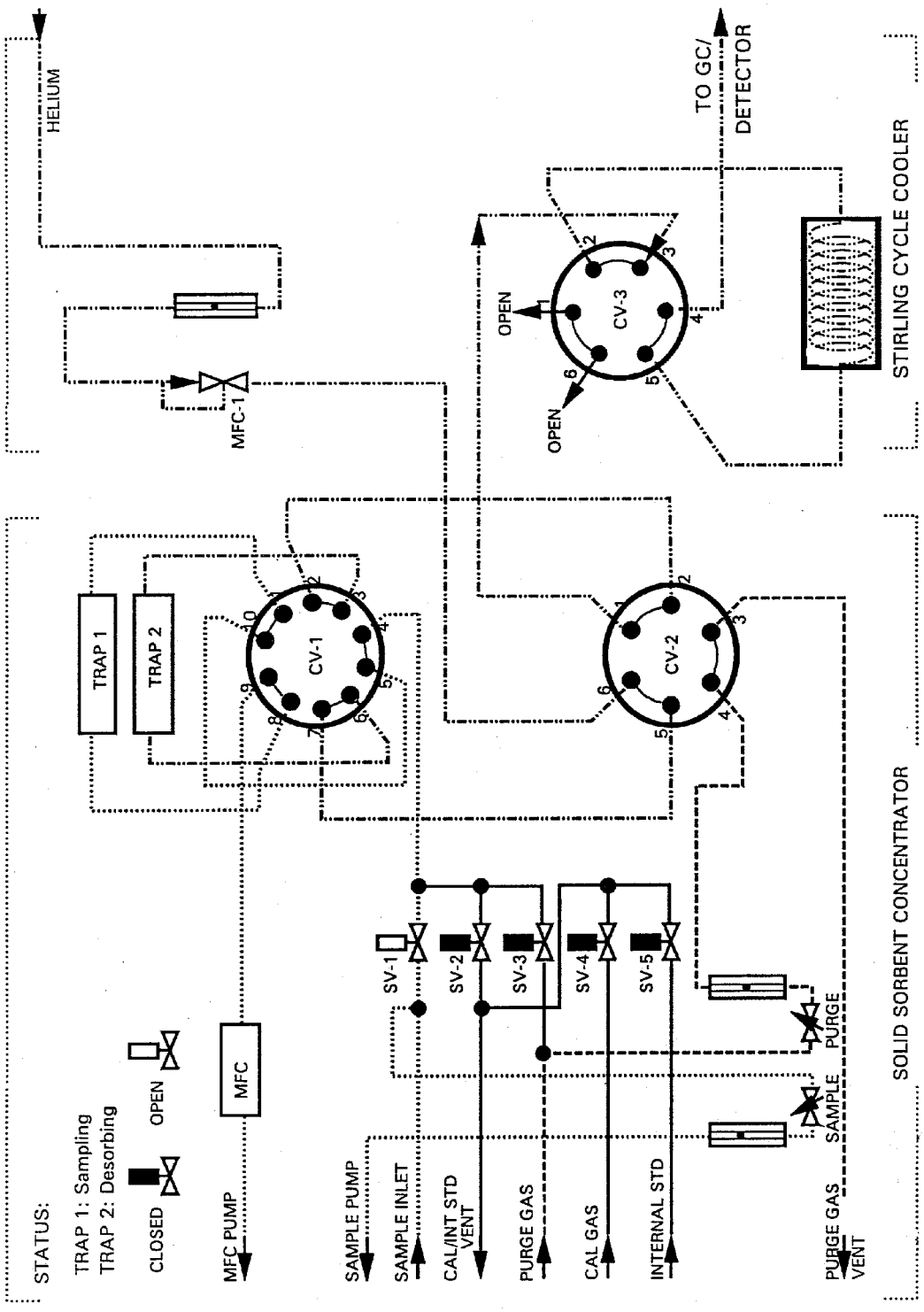


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).

EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-13A

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

Method TO-13A
Acknowledgements

This Method was prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b), under Contract No. 68-C3-0315, WA No. 3-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, and Scott R. Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development (ORD), were responsible for overseeing the preparation of this method. Additional support was provided by other members of the Compendia Workgroup, which include:

- John O. Burckle, U.S. EPA, ORD, Cincinnati, OH
- James L. Cheney, Corps of Engineers, Omaha, NB
- Michael Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- Heidi Schultz, ERG, Lexington, MA
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

Method TO-13 was originally published in March of 1989 as one of a series of peer-reviewed methods in the second supplement to *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-13 has been revised and updated as Method TO-13A in this Compendium to incorporate new or improved sampling and analytical technologies.

This method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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- Jane Chuang, Battelle Laboratories, Cincinnati, OH
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

Finally, recognition is given to Frances Beyer, Lynn Kaufman, Debbie Bond, Cathy Whitaker, and Kathy Johnson of Midwest Research Institute's Administrative Services staff whose dedication and persistence during the development of this manuscript has enabled its production.

DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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METHOD TO-13A

**Determination of Polycyclic Aromatic Hydrocarbons (PAHs)
in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)**

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METHOD TO-13A

Determination of Polycyclic Aromatic Hydrocarbons (PAHs)
in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)

1. Scope

1.1 Polycyclic aromatic hydrocarbons (PAHs) have received increased attention in recent years in air pollution studies because some of these compounds are highly carcinogenic or mutagenic. In particular, benzo[a]pyrene (B[a]P) has been identified as being highly carcinogenic. To understand the extent of human exposure to B[a]P and other PAHs, reliable sampling and analytical methods are necessary. This document describes a sampling and analysis procedure for common PAHs involving the use of a combination of quartz filter and sorbent cartridge with subsequent analysis by gas chromatography with mass spectrometry (GC/MS) detection. The analytical methods are modifications of EPA Test Method 610 and 625, *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, and Methods 8000, 8270, and 8310, *Test Methods for Evaluation of Solid Waste*.

1.2 Fluorescence methods were among the very first methods used for detection of B[a]P and other PAHs as carcinogenic constituents of coal tar (1-7). Fluorescence methods are capable of measuring subnanogram quantities of PAHs, but tend to be fairly non-selective. The normal spectra obtained are often intense and lack resolution. Efforts to overcome this difficulty led to the use of ultraviolet (UV) absorption spectroscopy (8) as the detection method coupled with pre-speciated techniques involving liquid chromatography (LC) and thin layer chromatography (TLC) to isolate specific PAHs, particularly B[a]P. As with fluorescence spectroscopy, the individual spectra for various PAHs are unique, although portions of spectra for different compounds may be the same. As with fluorescence techniques, the possibility of spectral overlap requires complete separation of sample components to ensure accurate measurement of component levels. Hence, the use of UV absorption coupled with pre-speciation involving LC and TLC and fluorescence spectroscopy declined and was replaced with the more sensitive high performance liquid chromatography (HPLC) with UV/fluorescence detection (9) or highly sensitive and specific gas chromatography/mass spectrometry (GC/MS) for detection (10-11).

1.3 The choice of GC/MS as the recommended procedure for analysis of B[a]P and other PAHs was influenced by its sensitivity and selectivity, along with its ability to analyze complex samples.

1.4 The analytical methodology has consequently been defined, but the sampling procedures can reduce the validity of the analytical results. Recent studies (12-17) have indicated that non-volatile PAHs (vapor pressure $<10^{-8}$ mm Hg) may be trapped on the filter, but post-collection volatilization problems may distribute the PAHs downstream of the filter to the back-up sorbent. A wide variety of sorbents such as Tenax®, XAD-2® and polyurethane foam (PUF) have been used to sample common PAHs. All sorbents have demonstrated high collection efficiency for B[a]P in particular. In general, XAD-2® resin has a higher collection efficiency (18-21) for volatile PAHs than PUF, as well as a higher retention efficiency. PUF cartridges, however, are easier to handle in the field and maintain better flow characteristics during sampling. Likewise, PUF has demonstrated (22) its capability in sampling organochlorine pesticides, polychlorinated biphenyls (22), and polychlorinated dibenzo-p-dioxins (23). PUF also has demonstrated a lower recovery efficiency and storage capability for naphthalene than XAD-2®. There have been no significant losses of PAHs up to 30 days of storage at room temperature (23°C) using XAD-2®. It also appears that XAD-2® resin has a higher collection efficiency for volatile PAHs than PUF, as well as a higher retention efficiency for both volatile and reactive PAHs.

Consequently, while the literature cites weaknesses and strengths of using either XAD-2® or PUF, this method includes the utilization of PUF as the primary sorbent.

1.5 This method includes the qualitative and quantitative analysis of the following PAHs (see Figure 1) specifically by utilizing PUF as the sorbent followed by GC/MS analysis:

Acenaphthene (low collection efficiency; see Section 6.1.3)	Coronene
Acenaphthylene (low collection efficiency; see Section 6.1.3)	Dibenz(a,h)anthracene
Anthracene	Fluoranthene
Benz(a)anthracene	Fluorene
Benzo(a)pyrene	Benzo(b)fluoranthene
Benzo(e)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(g,h,i)perylene	Naphthalene (low collection efficiency; see Section 6.1.3)
Benzo(k)fluoranthene	Phenanthrene
Chrysene	Pyrene
	Perylene

The GC/MS method is applicable to the determination of PAHs compounds involving three member rings or higher. Naphthalene, acenaphthylene, and acenaphthene have only ~35 percent recovery when using PUF as the sorbent. Nitro-PAHs have ***not*** been fully evaluated using this procedure; therefore, they are not included in this method.

1.6 With optimization to reagent purity and analytical conditions, the detection limits for the GC/MS method range from 1 ng to 10 pg based on field experience.

2. Summary of Method

2.1 Filters and sorbent cartridges (containing PUF or XAD-2®) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light) before careful installation on the sampler.

2.2 Approximately 300 m^3 of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent.

2.3 The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labeled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.

2.4 The filters and sorbent cartridge are extracted by Soxhlet extraction with appropriate solvent. The extract is concentrated by Kuderna-Danish (K-D) evaporator, followed by silica gel cleanup using column chromatography to remove potential interferences prior to analysis by GC/MS.

2.5 The eluent is further concentrated by K-D evaporation, then analyzed by GC/MS. The analytical system is verified to be operating properly and calibrated with five concentration calibration solutions.

2.6 A preliminary analysis of the sample extract is performed to check the system performance and to ensure that the samples are within the calibration range of the instrument. If the preliminary analysis indicates non-performance, then recalibrate the instrument, adjust the amount of the sample injected, adjust the calibration solution concentration, and adjust the data processing system to reflect observed retention times, etc.

2.7 The samples and the blanks are analyzed and used (along with the amount of air sampled) to calculate the concentration of PAHs in the air sample**.**

3. Significance

3.1 As discussed in Section 1, several documents have been published that describe sampling and analytical approaches for common PAHs. The attractive features of these methods have been combined in this procedure. Although this method has been validated in the laboratory, one must use caution when employing it for specific applications.

3.2 Because of the relatively low levels of common PAHs in the environment, the methodology suggest the use of high volume (0.22 m^3/min) sampling technique to acquire sufficient sample for analysis. However, the volatility of certain PAHs prevents efficient collection on filter media alone. Consequently, this method utilizes both a filter and a backup sorbent cartridge, which provides for efficient collection of most PAHs involving three member rings or higher.

4. Applicable Documents

4.1 ASTM Standards

- **Method D1356** *Definitions of Terms Relating to Atmospheric Sampling and Analysis*.
- **Method 4861-94** *Standard Practice for Sampling and Analysis of Pesticides and Polychlorinated Biphenyl in Air*
- **Method E260** *Recommended Practice for General Gas Chromatography Procedures*.
- **Method E355** *Practice for Gas Chromatography Terms and Relationships*.
- **Method E682** *Practice for Liquid Chromatography Terms and Relationships*.

4.2 EPA Documents

- *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA-600/4-83-027, June 1983.
- *Quality Assurance Handbook for Air Pollution Measurement Systems*, U. S. Environmental Protection Agency, EPA-600/R-94-038b, May 1994.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-13, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/-4-89-018, March 1989.

4.3 Other Documents

- Existing Procedures (24-32).
- Ambient Air Studies (33-50).
- General Metal Works, Inc., "Operating Procedures for Model PS-1 Sampler," Village of Cleves, OH 45002 (800-543-7412).
- Illinois Environmental Protection Agency, Division of Air Quality, "Chicago Air Quality: PCB Air Monitoring Plan (Phase 2)," Chicago, IL, IEAP/APC/86/011, April 1986.
- Thermo Environmental, Inc. (formerly Wedding and Associates), "Operating Procedures for the Thermo Environmental Semi-Volatile Sampler," 8 West Forge Parkway, Franklin, MA 02038 (508-520-0430).
- American Chemical Society (ACS), "Sampling for Organic Chemicals in Air," *ACS Professional Book*, ACS, Washington, D.C., 1996.
- International Organization for Standardization (ISO), "Determination of Gas and Particle-Phase Polynuclear Aromatic Hydrocarbons in Ambient Air - Collected on Sorbent-Backed Filters with Gas Chromatographic/Mass Spectrometric Analysis," ISO/TC 146/SC 3/WG 17N, Case Postale 56, CH-1211, Genève 20, Switzerland.

5. Definitions

[Note: Definitions used in this document and in any user-prepared standard operating procedures (SOPs) should be consistent with ASTM Methods D1356, E260, and E255. All abbreviations and symbols are defined within this document at point of use.]

5.1 Retention time (RT)-time to elute a specific chemical from a chromatographic column. For a specific carrier gas flow rate, RT is measured from the time the chemical is injected into the gas stream until it appears at the detector.

5.2 Sampling efficiency (SE)-ability of the sampler to trap and retain PAHs. The %SE is the percentage of the analyte of interest collected and retained by the sampling medium when it is introduced into the air sampler and the sampler is operated under normal conditions for a period of time equal to or greater than that required for the intended use.

5.3 Dynamic retention efficiency-ability of the sampling medium to retain a given PAH that has been added to the sorbent trap in a spiking solution when air is drawn through the sampler under normal conditions for a period of time equal to or greater than that required for the intended use.

5.4 Polycyclic aromatic hydrocarbons (PAHs)-two or more fused aromatic rings.

5.5 Method detection limit (MDL)-the minimum concentration of a substance that can be measured and reported with confidence and that the value is above zero.

5.6 Kuderna-Danish apparatus-the Kuderna-Danish (K-D) apparatus is a system for concentrating materials dissolved in volatile solvents.

5.7 MS-SCAN-the GC is coupled to a mass spectrometer where the instrument is programmed to acquire all ion data.

5.8 Sublimation-the direct passage of a substance from the solid state to the gaseous state and back into the solid form without at any time appearing in the liquid state. Also applied to the conversion of solid to vapor without the later return to solid state, and to a conversion directly from the vapor phase to the solid state.

5.9 Surrogate standard-a chemically inert compound (not expected to occur in the environmental sample) that is added to each sample, blank, and matrix-spiked sample before extraction and analysis. The recovery of the surrogate standard is used to monitor unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within acceptable limits.

5.10 CAL-calibration standards are defined as five levels of calibration: CAL 1, CAL 2, CAL 3, CAL 4, and CAL 5. CAL 1 is the lowest concentration and CAL 5 is the highest concentration. CAL 3, which is the mid-level standard, is designated as the solution to be used for continuing calibrations.

5.11 Continuing calibration check-a solution of method analytes used to evaluate the mass spectrometer response over a period of time. A continuing calibration check (CCC) is performed once each 12-hour period. The CCC solution (CAL 3) is the standard of the calibration curve.

5.12 GC Response (A_x)-the peak area or height of analyte, x.

5.13 Internal standard (IS)-a compound added to a sample extract in known amounts and used to calibrate concentration measurements of other compounds that are sample components. The internal standard must be a compound that is not a sample component.

6. Limitations and Interferences

6.1 Limitations

6.1.1 PAHs span a broad spectrum of vapor pressures (e.g., from 1.1 x 10^{-2} kPa for naphthalene to 2 x 10^{-13} kPa for coronene at 25°C). PAHs that are frequently found in ambient air are listed in Table 1. Those with vapor pressures above approximately 10^{-8} kPa will be present in the ambient air substantially distributed between the gas and particulate phases. This method will permit the collection of both phases.

6.1.2 Particulate-phase PAHs will tend to be lost from the particle filter during sampling due to volatilization. Therefore, separate analysis of the filter will not reflect the concentrations of the PAHs originally associated with particles, nor will analysis of the sorbent provide an accurate measure of the gas phase. Consequently, this method calls for *extraction of the filter and sorbent together* to permit accurate measurement of total PAH air concentrations.

6.1.3 Naphthalene, acenaphthylene, and acenaphthene possess relatively high vapor pressures and may not be efficiently trapped by this method when using PUF as the sorbent. The sampling efficiency for naphthalene has been determined to be about 35 percent for PUF. The user is encouraged to use XAD-2® as the sorbent if these analytes are part of the target compound list (TCL**).**

6.2 Interferences

6.2.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that result in discrete artifacts and/or elevated baselines in the detector profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

6.2.2 Glassware must be scrupulously cleaned (51). All glassware should be cleaned as soon as possible after use by rinsing with the last solvent used in it and then high-purity acetone and hexane. These rinses should be followed by detergent washing with hot water and rinsing with copious amounts of tap water and several portions of reagent water. The glassware should then be drained dry and heated in a muffle furnace at 400°C for four hours. Volumetric glassware must not be heated in a muffle furnace; rather it should be solvent rinsed with acetone and spectrographic grade hexane. After drying and rinsing, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Glassware should be stored inverted or capped with aluminum foil.

[Note: The glassware may be further cleaned by placing in a muffle furnace at 450°C for 8 hours to remove trace organics.]

6.2.3 The use of high purity water, reagents, and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

6.2.4 Matrix interferences may be caused by contaminants that are coextracted from the sample. Additional clean-up by column chromatography may be required (see Section 12.3).

6.2.5 During sample transport and analysis, heat, ozone, NO_2, and ultraviolet (UV) light may cause sample degradation. Incandescent or UV-shielded fluorescent lighting in the laboratory should be used during analysis.

6.2.6 The extent of interferences that may be encountered using GC/MS techniques has not been fully assessed. Although GC conditions described allow for unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere. The use of column chromatography for sample clean-up prior to GC analysis will eliminate most of these interferences. The analytical system must, however, be routinely demonstrated to be free of internal contaminants such as contaminated solvents, glassware, or other reagents which may lead to method interferences. A laboratory reagent blank should be analyzed for each reagent used to determine if reagents are contaminant-free.

6.2.7 Concern about sample degradation during sample transport and analysis was mentioned above. Heat, ozone, NO_2, and ultraviolet (UV) light also may cause sample degradation. These problems should be addressed as part of the user-prepared standard operating procedure (SOP) manual. Where possible, incandescent or UV-shielded fluorescent lighting should be used during analysis. During transport, field samples should be shipped back to the laboratory chilled (~4°C) using blue ice/dry ice.

7. Safety

7.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and are included in the reference list (52-54).

7.2 B[a]P has been tentatively classified as a known or suspected, human or mammalian carcinogen. Many of the other PAHs have been classified as carcinogens. Care must be exercised when working with these substances. This method does not purport to address all of the safety problems associated with its use. It is the responsibility of whomever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. The user should be thoroughly familiar with the chemical and physical properties of targeted substances (see Table 1 and Figure 1).

7.3 All PAHs should be treated as carcinogens. Neat compounds should be weighed in a glove box. Spent samples and unused standards are toxic waste and should be disposed according to regulations. Counter tops and equipment should be regularly checked with "black light" for fluorescence as an indicator of contamination.

7.4 The sampling configuration (filter and backup sorbent) and collection efficiency for target PAHs has been demonstrated to be greater than 95 percent (except for naphthalene, acenaphthylene and acenaphthene). Therefore, no field recovery evaluation will be required as part of this procedure.

[Note: Naphthalene, acenaphthylene and acenaphthene have demonstrated significant breakthrough using PUF cartridges, especially at summer ambient temperatures. If naphthalene, acenaphthylene and acenaphthene are target PAHs, the user may want to consider replacing the PUF with XAD-2® in order to minimize breakthrough during sampling.]

8. Apparatus

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in the use of this equipment during various field-monitoring programs over the last several years. Other manufacturers' equipment should work as well; however, modifications to these procedures may be necessary if another commercially available sampler is selected.]

8.1 Sampling

8.1.1 High-volume sampler (see Figure 2). Capable of pulling ambient air through the filter/sorbent cartridge at a flow rate of approximately 8 standard cubic feet per minute (scfm) (0.225 std m^3/min) to obtain a total sample volume of greater than 300 m^3 over a 24-hour period. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

Recent EPA studies have concluded that sample volumes *less than* 300 m^3 still collect enough PAHs on the filter/PUF for quantitation. The user is encouraged to investigate appropriate sample volume needed to meet project specific data quality objectives.

8.1.2 Sampling module (see Figure 3). Metal filter holder (Part 2) capable of holding a 102-mm circular particle filter supported by a 16-mesh stainless-steel screen and attaching to a metal cylinder (Part 1) capable of holding a 65-mm O.D. (60-mm I.D.) x 125-mm borosilicate glass sorbent cartridge containing PUF or XAD-2®. The filter holder is equipped with inert sealing gaskets (e.g., polytetrafluorethylene) placed on either side of the

filter. Likewise, inert, pliable gaskets (e.g., silicone rubber) are used to provide an air-tight seal at each end of the glass sorbent cartridge. The glass sorbent cartridge is indented 20 mm from the lower end to provide a support for a 16-mesh stainless-steel screen that holds the sorbent. The glass sorbent cartridge fits into Part 1, which is screwed onto Part 2 until the sorbent cartridge is sealed between the silicone gaskets. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.1.3 High-volume sampler calibrator. Capable of providing multipoint resistance for the high-volume sampler. Major manufacturers are**:**

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.1.4 Ice chest. To hold samples at 4°C or below during shipment to the laboratory after collection.

8.1.5 Data sheets. Used for each sample to record the location and sample time, duration of sample, starting time, and volume of air sampled.

8.2 Sample Clean-Up and Concentration (see Figure 4).

8.2.1 Soxhlet apparatus extractor (see Figure 4a). Capable of extracting filter and sorbent cartridges (5.75-cm x 12.5-cm length), 1,000 mL flask, and condenser, best source.

8.2.2 Pyrex glass tube furnace system. For activating silica gel at 180°C under purified nitrogen gas purge for an hour, with capability of raising temperature gradually, best source.

8.2.3 Glass vial. 40 mL, best source.

8.2.4 Erlenmeyer flask. 50 mL, best source.

[Note: Reuse of glassware should be minimized to avoid the risk of cross contamination. All glassware that is used must be scrupulously cleaned as soon as possible after use. Rinse glassware with the last solvent used in it and then with high-purity acetone and hexane. Wash with hot water containing detergent. Rinse with copious amounts of tap water and several portions of distilled water. Drain, dry, and heat in a muffle furnace at 400°C for 4 hours. Volumetric glassware must not be heated in a muffle furnace; rather, it should be rinsed with high-purity acetone and hexane. After the glassware is dry and cool, rinse it with hexane, and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.]

8.2.5 White cotton gloves. For handling cartridges and filters, best source.

8.2.6 Minivials. 2 mL, borosilicate glass, with conical reservoir and screw caps lined with Teflon®-faced silicone disks, and a vial holder, best source.

8.2.7 Teflon®-coated stainless steel spatulas and spoons. Best source.

8.2.8 Kuderna-Danish (K-D) apparatus (see Figure 4b). 500 mL evaporation flask (Kontes K-570001-500 or equivalent), 10 mL graduated concentrator tubes (Kontes K570050-1025 or equivalent) with ground-glass stoppers, 1 mL calibrated K-D concentration tubes, and 3-ball macro Snyder Column (Kontes K-570010500, K-50300-0121, and K-569001-219, or equivalent), best source.

8.2.9 Adsorption column for column chromatography (see Figure 4c). 1-cm x 10-cm with stands.

8.2.10 Glove box. For working with extremely toxic standards and reagents with explosion-proof hood for venting fumes from solvents, reagents, etc.

8.2.11 Vacuum oven. Vacuum drying oven system capable of maintaining a vacuum at 240 torr (flushed with nitrogen) overnight.

8.2.12 Concentrator tubes and a nitrogen evaporation apparatus with variable flow rate. Best source.

8.2.13 Laboratory refrigerator. Best source.

8.2.14 Boiling chips. Solvent extracted, 10/40 mesh silicon carbide or equivalent, best source**.**

8.2.15 Water bath. Heated, with concentric ring cover, capable of ±5°C temperature control, best source.

8.2.16 Nitrogen evaporation apparatus. Best source.

8.2.17 Glass wool. High grade, best source**.**

8.3 Sample Analysis

8.3.1 Gas Chromatography with Mass Spectrometry Detection Coupled with Data Processing System (GC/MS/DS). The gas chromatograph must be equipped for temperature programming, and all required accessories must be available, including syringes, gases, and a capillary column. The gas chromatograph injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used, but they may severely reduce column lifetime for nonchemically bonded columns. In this protocol, a 2 µL injection volume is used consistently to maximize auto sampler reproducibility. With some gas chromatograph injection ports, however, 1 µL injections may produce some improvement in precision and chromatographic separation. A 1 µL injection volume may be used if adequate sensitivity and precision can be achieved.

[Note: If 1 µL is used as the injection volume, the injection volumes for all extracts, blanks, calibration solutions and performance check samples must be 1 µL.]

All GC carrier gas lines must be constructed from stainless steel or copper tubing. Poly-tetrafluoroethylene (PTFE) thread sealants or flow controllers should only be used.

8.3.2 Gas chromatograph-mass spectrometer interface. The GC is usually coupled directly to the MS source. The interface may include a diverter valve for shunting the column effluent and isolating the mass spectrometer source. All components of the interface should be glass or glass-lined stainless steel. Glass can be deactivated by silanizing with dichorodimethylsilane. The interface components should be compatible with 320°C temperatures. Cold spots and/or active surfaces (adsorption sites) in the GC/MS interface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the MS source. Graphite ferrules should be avoided in the gas chromatograph injection area since they may adsorb PAHs. Vespel® or equivalent ferrules are recommended.

8.3.3 Mass spectrometer. The MS should be operated in the full range data acquisition (SCAN) mode with a total cycle time (including voltage reset time) of one second or less (see Section 13.3.2). Operation of the MS in the SCAN mode allows monitoring of all ions, thus assisting with the identification of other PAHs beyond Compendium Method TO-13A target analyte list. In addition, operating in the SCAN mode assists the analyst with identification of possible interferences from non-target analytes due to accessibility of the complete mass spectrum in the investigative process. The MS must be capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact (EI) ionization mode. The mass spectrometer must be capable of producing a mass spectrum for a 50 ng injection of decafluorotriphyenyl phosphine (DFTPP) which meets all of the response criteria (see Section 13.3.3). To ensure sufficient precision of mass spectral data, the MS scan rate must allow acquisition of at least five scans while a sample compound elutes from the GC. The

GC/MS system must be in a room with atmosphere demonstrated to be free of all potential contaminants which will interfere with the analysis. The instrument must be vented outside the facility or to a trapping system which prevents the release of contaminants into the instrument room.

8.3.4 Data system. A dedicated computer data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and multi-ion detector (MID) traces (displays of intensities of each m/z being monitored as a function of time) must be acquired during the analyses. Quantifications may be reported based upon computer generated peak areas or upon measured peak heights (chart recording). The detector zero setting must allow peak-to-peak measurement of the noise on the baseline. The computer should have software that allows searching the GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as Selected Ion Current Profile (SICP). The software used must allow integrating the abundance in any SICP between specified time or scan number limits. The data system should be capable of flagging all data files that have been edited manually by laboratory personnel.

8.3.5 Gas chromatograph column. A fused silica DB-5 column (30 m x 0.32 mm I.D.) crosslinked 5 percent phenyl methylsilicone, 1.0 µm film thickness is utilized to separate individual PAHs. Other columns may be used for determination of PAHs. Minimum acceptance criteria must be determined as per Section 13.3. At the beginning of each 12-hour period (after mass resolution has been demonstrated) during which sample extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples.

8.3.6 Balance. Mettler balance or equivalent.

8.3.7 All required syringes, gases, and other pertinent supplies. To operate the GC/MS system.

8.3.8 Pipettes, micropipettes, syringes, burets, etc. Used to make calibration and spiking solutions, dilute samples if necessary, etc., including syringes for accurately measuring volumes such as 25 µL and 100 µL.

9. Equipment and Materials

9.1 Materials for Sample Collection (see Figure 3)

9.1.1 Quartz fiber filter. 102 millimeter binderless quartz microfiber filter, Whatman Inc., 6 Just Road, Fairfield, NJ 07004, Filter Type QMA-4.

9.1.2 Polyurethane foam (PUF) plugs (see Figure 5a). 3-inch thick sheet stock polyurethane type (density .022 g/cm^3). The PUF should be of the polyether type used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH; University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; Supelco, Supelco Park, Bellefonte, PA; and SKC Inc., 334 Valley View Road, Eighty Four, PA.

9.1.3 XAD-2® resin (optional). Supelco, Supelco Park, Bellefonte, PA.

9.1.4 Teflon® end caps (see Figure 5a). For sample cartridge; sources of equipment are Tisch Environmental, Village of Cleves, OH; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC.

9.1.5 Sample cartridge aluminum shipping containers (see Figure 5b). For sample cartridge shipping; sources of equipment are Tisch Environmental, Village of Cleves, OH; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC.

9.1.6 Glass sample cartridge (see Figure 5a). For sample collection; sources of equipment are Tisch Environmental, Village of Cleves, OH; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC.

9.1.7 Aluminum foil. Best source.

9.1.8 Hexane, reagent grade. Best source.

9.2 Sample Clean-up and Concentration

9.2.1 Methylene chloride (extraction solvent for XAD-2®; optional). Chromatographic grade, glass-distilled, best source.

9.2.2 Sodium sulfate-anhydrous (ACS). Granular (purified by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray).

9.2.3 Boiling chips. Solvent extracted or heated in a muffle furnace at 450°C for 2 hours, approximately 10/40 mesh (silicon carbide or equivalent).

9.2.4 Nitrogen. High purity grade, best source.

9.2.5 Hexane. Chromatographic grade, glass-distilled, best source (extraction solvent for PUF).

9.2.6 Glass wool. Silanized, extracted with methylene chloride and hexane, and dried.

9.2.7 Diethyl ether. High purity, glass distilled (extraction solvent for PUF).

9.2.8 Pentane. High purity, glass distilled.

9.2.9 Silica gel. High purity, type 60, 70-230 mesh.

9.3 GC/MS Sample Analysis

9.3.1 Gas cylinder of helium. Ultra high purity, best source.

9.3.2 Chromatographic-grade stainless steel tubing and stainless steel fitting. For interconnections, Alltech Applied Science, 2051 Waukegan Road, Deerfield, IL 60015, 312-948-8600, or equivalent.

[Note: All such materials in contact with the sample, analyte, or support gases prior to analysis should be stainless steel or other inert metal. Do not use plastic or Teflon® tubing or fittings.]

9.3.3 Native and isotopically labeled PAH isomers for calibration and spiking standards. Cambridge Isotopes, 20 Commerce Way, Woburn, MA 01801 (617-547-1818). Suggested isotopically labeled PAH isomers are: D_{10}-fluoranthene, D_{12}-benzo(a)pyrene, D_{10}-fluorene, D_{10}-pyrene, D_{12}-perylene, D_{10}-acenaphthene, D_{12}-chrysene, D_8-naphthalene and D_{10}-phenanthrene.

9.3.4 Decafluorotriphenylphosphine (DFTPP). Used for tuning GC/MS, best source.

9.3.5 Native stock pure standard PAH analytes. For developing calibration curve for GC/MS analysis, best source.

10. Preparation of PUF Sampling Cartridge

[Note: This method was developed using the PS-1 sample cartridge provider by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring program over the last several years. Other manufacturers' equipment should work as well; however, modifications to these procedures may be necessary if another commercially available sampler is selected.]

10.1 Summary of Method

10.1.1 This part of the procedure discusses pertinent information regarding the preparation and cleaning of the filter, sorbent, and filter/sorbent cartridge assembly. The separate batches of filters and sorbents are extracted with the appropriate solvent.

10.1.2 At least one PUF cartridge assembly and one filter from each batch, or 10 percent of the batch, whichever is greater, should be tested and certified before the batch is considered for field use.

10.1.3 Prior to sampling, the cartridges are spiked with field surrogate compounds.

10.2 Preparation of Sampling Cartridge

10.2.1 Bake the Whatman QMA-4 quartz filters at 400°C for 5 hours before use.

10.2.2 Set aside the filters in a clean container for shipment to the field or prior to combining with the PUF glass cartridge assembly for certification prior to field deployment.

10.2.3 The PUF plugs are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 5a). During cutting, rotate the die at high speed (e.g., in a drill press) and continuously lubricate with deionized or distilled water. Pre-cleaned PUF plugs can be obtained from commercial sources (see Section 9.1.2)**.**

10.2.4 For initial cleanup, place the PUF plugs in a Soxhlet apparatus and extract with acetone for 16 hours at approximately 4 cycles per hour. When cartridges are reused, use diethyl ether/hexane (5 to 10 percent volume/volume [v/v]) as the cleanup solvent.

[Note: A modified PUF cleanup procedure can be used to remove unknown interference components of the PUF blank. This method consists of rinsing 50 times with toluene, acetone, and diethyl ether/hexane (5 to 10 percent v/v), followed by Soxhlet extraction. The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2 to 4 hours (until no solvent odor is detected). The extract from the Soxhlet extraction procedure from each batch may be analyzed to determine initial cleanliness prior to certification.]

10.2.5 If using XAD-2® in the cartridge, initial cleanup of the resin is performed by placing approximately 50-60 grams in a Soxhlet apparatus and extracting with methylene chloride for 16 hours at approximately 4 cycles per hour. At the end of the initial Soxhlet extraction, the spent methylene chloride is discarded and replaced with a fresh reagent. The XAD-2® resin is once again extracted for 16 hours at approximately 4 cycles per hour. The XAD-2® resin is removed from the Soxhlet apparatus, placed in a vacuum oven connected to an ultra-pure nitrogen gas stream, and dried at room temperature for approximately 2-4 hours (until no solvent odor is detected).

10.2.6 Fit a nickel or stainless steel screen (mesh size 200/200) to the bottom of a hexane-rinsed glass sampling cartridge to retain the PUF or XAD-2® sorbents, as illustrated in Figure 5a. If using XAD-2® alone, then place a small diameter (~1/4") PUF plug on top of the nickel or stainless steel screen to retain the XAD-2® in the glass cartridge. Place the Soxhlet-extracted, vacuum-dried PUF (2.5-cm thick by 6.5-cm diameter) on top of the screen in the glass sampling cartridge using polyester gloves. Place ~200 g of the clean XAD-2® inside the glass sampling cartridge on top of the small diameter PUF plug.

10.2.7 Wrap the sampling cartridge with hexane-rinsed aluminum foil, cap with the Teflon® end caps (optional), place in a cleaned labeled aluminum shipping container, and seal with Teflon® tape. Analyze at least 1 cartridge from each batch of cartridges prepared using the procedure described in Section 10.3, before the batch is considered acceptable for field use.

The acceptance level of the cartridge is for each target PAH analyte to be less than or equal to the detection limit requirements to meet the project data quality objectives. It is generally not possible to eliminate the presence of naphthalene, but the amount detected on the cleaned PUF cartridge should be less than five times the concentration of the lowest calibration standard (~500 ng). This amount is insignificant compared to the amount collected from a typical air sample.

In general, the following guidelines are provided in determining whether a cartridge is clean for field use:

- Naphthalene <500 ng/cartridge
- Other PAHs <200 ng total/cartridge

10.3 Procedure for Certification of PUF Cartridge Assembly

[Note: The following procedure outlines the certification of a filter and PUF cartridge assembly. If using XAD-2® as the sorbent, the procedure remains the same, except the solvent is methylene chloride rather than 10 percent diethyl ether/hexane.]

10.3.1 Extract one filter and PUF sorbent cartridge by Soxhlet extraction and concentrate using a K-D evaporator for each lot of filters and cartridges sent to the field.

10.3.2 Assemble the Soxhlet apparatus. Charge the Soxhlet apparatus (see Figure 4a) with 700 mL of the extraction solvent (10 percent v/v diethyl ether/hexane) and reflux for 2 hours. Let the apparatus cool, disassemble it, and discard the used extraction solvent. Transfer the filter and PUF glass cartridge to the Soxhlet apparatus (the use of an extraction thimble is optional).

[Note: The filter and sorbent assembly are tested together in order to reach detection limits, to minimize cost and to prevent misinterpretation of the data. Separate analyses of the filter and PUF would not yield useful information about the physical state of most of the PAHs at the time of sampling due to evaporative losses from the filter during sampling.]

10.3.3 Add between 300 and 350 mL of diethyl ether/hexane (10 percent v/v) to the Soxhlet apparatus. Reflux the sample for 18 hours at a rate of at least 3 cycles per hour. Allow to cool, then disassemble the apparatus.

10.3.4 Assemble a K-D concentrator (see Figure 4b) by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

10.3.5 Transfer the extract by pouring it through a drying column containing about 10 cm of anhydrous granular sodium sulfate (see Figure 4c) and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of 10 percent diethyl ether/hexane to complete the quantitative transfer.

10.3.6 Add one or two clean boiling chips and attach a 3-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL of the extraction solvent to the top of the column. Place the K-D apparatus on a hot water bath (~50°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 1 hour. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches approximately 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 5 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of cyclohexane. A 1-mL syringe is recommended for this operation.

10.3.7 Concentrate the extract to 5 mL and analyze using GC/MS.

10.3.8 The acceptance level of the cartridge is for each target PAH analyte to be less than or equal to the detection limit requirements to meet the project data qulity objectives. It is generally not possible to eliminate the presence of naphthalene, but the amount detected on the cleaned PUF cartridge should be less than five times the concentration of the lowest calibration standard (~500 ng). This amount is insignificant compared to the amount collected from a typical air sample.

In general, the following guidelines are provided in determining whether a cartridge is clean for field use:

- Naphthalene <500 ng/cartridge
- Other PAHs <200 ng total/cartridge

Cartridges are considered clean for up to 30 days from date of certification when sealed in their containers.

10.4 Deployment of Cartridges for Field Sampling

10.4.1 Immediately prior to field deployment, add surrogate compounds (i.e., chemically inert compounds not expected to occur in an environmental sample) to the center of the PUF cartridge, using a microsyringe. Spike 20 μL of a 50 μg/mL solution of the surrogates onto the center bed of the PUF trap to yield a final concentration of 1 μg. The surrogate compounds must be added to each cartridge assembly. The following field surrogate compounds should be added to each PUF cartridge prior to field deployment to monitor matrix effects, breakthrough, etc.

Field Surrogate Compound	Total Spiked Amount (µg)
D_{10}-Fluoranthene	1
D_{12}-Benzo(a)pyrene	1

Fill out a "chain-of-custody" indicating cartridge number, surrogate concentration, date of cartridge certification, etc. The chain-of-custody must accompany the cartridge to the field and return to the laboratory.

10.4.2 Use the recoveries of the surrogate compounds to monitor for unusual matrix effects and gross sample processing errors. Evaluate surrogate recovery for acceptance by determining whether the measured concentration falls within the acceptance limits of 60-120 percent.

10.4.3 Cartridges are placed in their shipping containers and shipped to the field. Blank cartridges do not need to be chilled when shipping to the field until after exposure to ambient air.

11. Assembly, Calibration, and Collection Using Sampling System

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in the use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well; however, modifications to these procedures may be necessary if another commercially available sampler is selected.]

11.1 Sampling Apparatus

The entire sampling system is diagrammed in Figure 2. This apparatus was developed to operate at a rate of 4 to 10 scfm (0.114 to 0.285 std m^3/min) and is used by EPA for high-volume sampling of ambient air. The method write-up presents the use of this device.

The sampling module (see Figure 3) consists of a filter and a glass sampling cartridge containing the PUF utilized to concentrate PAHs from the air. A field portable unit has been developed by EPA (see Figure 6).

11.2 Calibration of Sampling System

Each sampler should be calibrated (1) when new, (2) after major repairs or maintenance, (3) whenever any audit point deviates from the calibration curve by more than 7 percent, (4) before/after each sampling event, and (5) when a different sample collection medium, other than that which the sampler was originally calibrated to, will be used for sampling.

11.2.1 Calibration of Orifice Transfer Standard. Calibrate the modified high volume air sampler in the field using a calibrated orifice flow rate transfer standard. Certify the orifice transfer standard in the laboratory against a positive displacement rootsmeter (see Figure 7). Once certified, the recertification is performed rather infrequently if the orifice is protected from damage. Recertify the orifice transfer standard performed once per year utilizing a set of five multi-hole resistance plates.

[Note: The set of five multihole resistance plates is used to change the flow through the orifice so that several points can be obtained for the orifice calibration curve. The following procedure outlines the steps to calibrate the orifice transfer standard in the laboratory.]

11.2.1.1 Record the room temperature (T_1 in °C) and barometric pressure (P_b in mm Hg) on the Orifice Calibration Data Sheet (see Figure 8). Calculate the room temperature in K (absolute temperature) and record on Orifice Calibration Data Sheet.

$$T_1 \text{ in K} = 273° + T_1 \text{ in °C}$$

11.2.1.2 Set up laboratory orifice calibration equipment as illustrated in Figure 7. Check the oil level of the rootsmeter prior to starting. There are three oil level indicators, one at the clear plastic end, and two sight glasses, one at each end of the measuring chamber.

11.2.1.3 Check for leaks by clamping both manometer lines, blocking the orifice with cellophane tape, turning on the high-volume motor, and noting any change in the rootsmeter's reading. If the rootsmeter's reading changes, there is a leak in the system. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the hi-vol motor, remove the cellophane tape, and unclamp both manometer lines.

11.2.1.4 Install the 5-hole resistance plate between the orifice and the filter adapter.

11.2.1.5 Turn manometer tubing connectors one turn counter-clockwise. Make sure all connectors are open.

11.2.1.6 Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required for the water manometer, remove tubing connector and add clean water.)

11.2.1.7 Turn on the high-volume motor and let it run for 5 minutes to set the motor brushes. Turn the motor off. Ensure manometers are set to zero. Turn the high-volume motor on.

11.2.1.8 Record the time in minutes required to pass a known volume of air (approximately 5.6 to 8.4 m^3 of air for each resistance plate) through the rootsmeter by using the rootsmeter's digital volume dial and a stopwatch.

11.2.1.9 Record both manometer readings [orifice water manometer ($\triangle$H) and rootsmeter mercury manometer ($\triangle$P)] on Orifice Calibration Data Sheet (see Figure 8).

[Note: $\triangle H$ is the sum of the difference from zero (0) of the two column heights.]

11.2.1.10 Turn off the high-volume motor.

11.2.1.11 Replace the 5-hole resistance plate with the 7-hole resistance plate.

11.2.1.12 Repeat Sections 11.2.1.3 through 11.2.1.11.

11.2.1.13 Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 8). Only a minute is needed for warm-up of the motor. Be sure to tighten the orifice enough to eliminate any leaks. Also check the gaskets for cracks.

[Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.]

11.2.1.14 Correct the measured volumes on the Orifice Calibration Data Sheet:

$$V_{std} = V_m \left(\frac{P_a - \triangle P}{P_{std}}\right)\left(\frac{T_{std}}{T_a}\right)$$

where:

V_{std} = standard volume, std m^3

V_m = actual volume measured by the rootsmeter, m^3

P_a = barometric pressure during calibration, mm Hg

$\triangle P$ = differential pressure at inlet to volume meter, mm Hg

P_{std} = 760 mm Hg

T_{std} = 298 K

T_a = ambient temperature during calibration, K.

11.2.1.15 Record standard volume on Orifice Calibration Data Sheet.

11.2.1.16 The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q_{std} = \frac{V_{std}}{\theta}$$

where:

Q_{std} = standard volumetric flow rate, std m^3/min

θ = elapsed time, min

11.2.1.17 Record the standard flow rates to the nearest 0.01 std m^3/min.

11.2.1.18 Calculate and record $\sqrt{\triangle H\ (P_1/P_{std})(298/T_1)}$ value for each standard flow rate.

11.2.1.19 Plot each $\sqrt{\triangle H\ (P_1/P_{std})(298/T_1)}$ value (y-axis) versus its associated standard flow rate (x-axis) on arithmetic graph paper and draw a line of best fit between the individual plotted points.

[Note: This graph will be used in the field to determine standard flow rate.]

11.2.2 Calibration of the High-Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

For this calibration procedure, the following conditions are assumed in the field:

- The sampler is equipped with an valve to control sample flow rate.
- The sample flow rate is determined by measuring the orifice pressure differential using a Magnehelic gauge.
- The sampler is designed to operate at a standardized volumetric flow rate of 8 ft^3/min (0.225 m^3/min), with an acceptable flow rate range within 10 percent of this value.
- The transfer standard for the flow rate calibration is an orifice device. The flow rate through the orifice is determined by the pressure drop caused by the orifice and is measured using a "U" tube water manometer or equivalent.
- The sampler and the orifice transfer standard are calibrated to standard volumetric flow rate units (scfm or scmm).
- An orifice transfer standard with calibration traceable to NIST is used.
- A "U" tube water manometer or equivalent, with a 0- to 16-inch range and a maximum scale division of 0.1 inch, will be used to measure the pressure in the orifice transfer standard.
- A Magnehelic gauge or equivalent with a 9- to 100-inch range and a minimum scale division of 2 inches for measurements of the differential pressure across the sampler's orifice is used.
- A thermometer capable of measuring temperature over the range of 32° to 122°F (0° to 50°C) to ±2°F (±1°C) and referenced annually to a calibrated mercury thermometer is used.
- A portable aneroid barometer (or equivalent) capable of measuring ambient barometric pressure between 500 and 800 mm Hg (19.5 and 31.5 in. Hg) to the nearest mm Hg and referenced annually to a barometer of known accuracy is used.
- Miscellaneous handtools, calibration data sheets or station log book, and wide duct tape are available.

11.2.2.1 Set up the calibration system as illustrated in Figure 9. Monitor the airflow through the sampling system with a venturi/Magnehelic assembly, as illustrated in Figure 9. Audit the field sampling system once per quarter using a flow rate transfer standard, as described in the EPA *High-Volume Sampling Method, 40 CVR 50, Appendix B.* Perform a single-point calibration before and after each sample collection, using the procedures described in Section 11.2.3.

11.2.2.2 Prior to initial multi-point calibration, place an empty glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.20 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 min and then adjust the flow control valve to achieve the desire flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Calibration Data Sheet (see Figure 10).

11.2.2.3 Place the orifice transfer standard on the sampling head and attach a manometer to the tap on the transfer standard, as illustrated in Figure 9. Properly align the retaining rings with the filter holder and secure by tightening the three screw clamps. Connect the orifice transfer standard by way of the pressure tap to a

manometer using a length of tubing. Set the zero level of the manometer or Magnehelic. Attach the Magnehelic gauge to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on face of the gauge.

11.2.2.4 To leak test, block the orifice with a rubber stopper, wide duct tape, or other suitable means. Seal the pressure port with a rubber cap or similar device. Turn on the sampler.

Caution: *Avoid running the sampler for too long a time with the orifice blocked. This precaution will reduce the chance that the motor will be overheated due to the lack of cooling air. Such overheating can shorten the life of the motor*.

11.2.2.5 Gently rock the orifice transfer standard and listen for a whistling sound that would indicate a leak in the system. A leak-free system will not produce an upscale response on the sampler's magnehelic. Leaks are usually caused either by damaged or missing gaskets, by cross-threading, and/or not screwing sample cartridge together tightly. All leaks must be eliminated before proceeding with the calibration. When the sample is determined to be leak-free, turn off the sampler and unblock the orifice. Now remove the rubber stopper or plug from the calibrator orifice.

11.2.2.6 Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a Magnehelic reading of approximately 70 in. is obtained. Allow the Magnehelic and manometer readings to stabilize and record these values on the orifice transfer Field Calibration Data Sheet (see Figure 10).

11.2.2.7 Record the manometer reading under Y1 and the Magnehelic reading under Y2 on the Field Calibration Data Sheet. For the first reading, the Magnehelic should still be at 70 inches as set above.

11.2.2.8 Set the Magnehelic to 60 inches by using the sampler's flow control valve. Record the manometer (Y1) and Magnehelic (Y2) readings on the Field Calibration Data Sheet (see Figure 10).

11.2.2.9 Repeat the above steps using Magnehelic settings of 50, 40, 30, 20, and 10 inches.

11.2.2.10 Turn the voltage variator to maximum power, open the flow control valve, and confirm that the Magnehelic reads at least 100 inches. Turn off the sampler and confirm that the Magnehelic reads zero.

11.2.2.11 Read and record the following parameters on the Field Calibration Data Sheet. Record the following on the calibration data sheet:

- Data, job number, and operator's signature.
- Sampler serial number.
- Ambient barometric pressure.
- Ambient temperature.

11.2.2.12 Remove the "dummy" cartridge and replace with a sample cartridge.

11.2.2.13 Obtain the manufacturer high volume orifice calibration certificate.

11.2.2.14 If not performed by the manufacturer, calculate values for each calibrator orifice static pressure (Column 6, inches of water) on the manufacturer's calibration certificate using the following equation:

$$\sqrt{\triangle H(P_a/760)[298/(T_a + 273)]}$$

where:

P_a = the barometric pressure (mm Hg) at time of manufacturer calibration, mm Hg
T_a = temperature at time of calibration, °C

11.2.2.15 Perform a linear regression analysis using the values in Column 7 of the manufacturer's High Volume Orifice Calibration Certificate for flow rate (Q_{std}) as the "X" values and the calculated values as the Y

values. From this relationship, determine the correlation (CC1), intercept (B1), and slope (M1) for the Orifice Transfer Standard.

11.2.2.16 Record these values on the Field Calibration Data Sheet (see Figure 10).

11.2.2.17 Using the Field Calibration Data Sheet values (see Figure 10), calculate the Orifice Manometer Calculated Values (Y3) for each orifice manometer reading using the following equation:

Y3 Calculation

$$Y3 = \{Y1(P_a/760)[298/(T_a + 273)]\}^{½}$$

11.2.2.18 Record the values obtained in Column Y3 on the Field Calibration Data Sheet (see Figure 10).

11.2.2.19 Calculate the Sampler Magnehelic Calculated Value (Y4) using the following equation:

Y4 Calculation

$$Y4 = \{Y2(P_a/760)[298/(T_a + 273)]\}^{½}$$

11.2.2.20 Record the value obtained in Column Y4 on the Field Calibration Data Sheet (see Figure 10).

11.2.2.21 Calculate the Orifice Flow Rate (X1) in scm using the following equation:

X1 Calculation

$$X1 = \frac{Y3 - B1}{M1}$$

11.2.2.22 Record the values obtained in Column X1 on the Field Calibration Data Sheet (see Figure 10).

11.2.2.23 Perform a linear regression of the values in Column X1 (as X) and the values in Column Y4 (as Y). Record the relationship for correlation (CC2), intercept (B2), and slope (M2) on the Field Calibration Data Sheet. The correlation coefficient must be 0.990 or greater.

11.2.2.24 Using the following equation, calculate a set point (SP) for the manometer to represent a desired flow rate:

Set Point

$$\text{Set point (SP)} = [(\text{Expected } P_a)/(\text{Expected } T_a)(T_{std}/P_{std})][M2\ (\text{Desired flow rate}) + B2]^2$$

where:

P_a = Expected atmospheric pressure (P_a), mm Hg
T_a = Expected atmospheric temperature (T_a), 273 + °C
M2 = Slope of developed relationship
B2 = Intercept of developed relationship
T_{std} = Temperature standard, 273 + 25°C
P_{std} = Pressure standard, 760 mm Hg

11.2.2.25 During monitoring, calculate a flow rate from the observed Magnehelic reading using the following equations:

Flow Rate

$$Y5 = [\text{Average Magnehelic Reading } (\triangle H)\ (P_a/T_a)(T_{std}/P_{std})]^{½}$$

$$X2 = \frac{Y5 - B2}{M2}$$

where:

Y5 = Corrected average magnehelic reading
X2 = Instant calculated flow rate, scm

11.2.2.26 The relationship in calibration of a sampling system between Orifice Transfer Standard and flow rate through the sampler is illustrated in Figure 11.

11.2.3 Single-Point Audit of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

Single point calibration checks are required as follows:

- Prior to the start of each 24-hour test period.
- After each 24-hour test period. The post-test calibration check may serve as the pre-test calibration check for the next sampling period if the sampler is not moved.
- Prior to sampling after a sample is moved.

For samplers, perform a calibration check for the operational flow rate before each 24-hour sampling event and when required as outlined in the user quality assurance program. The purpose of this check is to track the sampler's calibration stability. Maintain a control chart presenting the percentage difference between a sampler's indicated and measured flow rates. This chart provides a quick reference of sampler flow-rate drift problems and is useful for tracking the performance of the sampler. Either the sampler log book or a data sheet will be used to document flow-check information. This information includes, but is not limited to, sampler and orifice transfer standard serial number, ambient temperature, pressure conditions, and collected flow-check data.

In this subsection, the following is assumed:

- The flow rate through a sampler is indicated by the orifice differential pressure;
- Samplers are designed to operate at an actual flow rate of 8 scfm, with a maximum acceptable flow-rate fluctuation range of ±10 percent of this value;
- The transfer standard will be an orifice device equipped with a pressure tap. The pressure is measured using a manometer; and
- The orifice transfer standard's calibration relationship is in terms of standard volumetric flow rate (Q_{std}).

11.2.3.1 Perform a single point flow audit check before and after each sampling period utilizing the Calibrated Orifice Transfer Standard (see Section 11.2.1).

11.2.3.2 Prior to single point audit, place a "dummy" glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.19 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desired flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Test Data Sheet (see Figure 12).

11.2.3.3 Place the flow rate transfer standard on the sampling head.

11.2.3.4 Properly align the retaining rings with the filter holder and secure by tightening the three screw clamps. Connect the flow rate transfer standard to the manometer using a length of tubing.

11.2.3.5 Using tubing, attach one manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.

11.2.3.6 Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)

11.2.3.7 Turn on the high-volume motor and let run for 5 minutes.

11.2.3.8 Record the pressure differential indicated, $\triangle H$, in inches of water, on the Field Test Data Sheet. Be sure a stable $\triangle H$ has been established.

11.2.3.9 Record the observed Magnehelic gauge reading in inches of water on the Field Test Data Sheet. Be sure stable $\triangle M$ has been established.

11.2.3.10 Using previous established Orifice Transfer Standard curve, calculate Q_{xs} (see Section 11.2.2.23).

11.2.3.11 This flow should be within ±10 percent of the sampler set point, normally, 0.224 m^3. If not, perform a new multipoint calibration of the sampler.

11.2.3.12 Remove flow rate transfer standard and dummy sorbent cartridge.

11.3 Sample Collection

11.3.1 General Requirements

11.3.1.1 The sampler should be located in an unobstructed area, at least 2 meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.

11.3.1.2 All cleaning and sample module loading and unloading should be conducted in a controlled environment, to minimize any chance of potential contamination.

11.3.1.3 When new or when using the sampler at a different location, all sample contact areas need to be cleaned. Use triple rinses of reagent grade hexane or methylene chloride contained in Teflon® rinse bottles. Allow the solvents to evaporate before loading the PUF modules.

11.3.2 Preparing Cartridge for Sampling

11.3.2.1 Detach the lower chamber of the cleaned sample head. While wearing disposable, clean, lint-free nylon, or cotton gloves, remove a clean glass sorbent module from its shipping container. Remove the Teflon® end caps (if applicable). Replace the end caps in the sample container to be reused after the sample has been collected.

11.3.2.2 Insert the glass module into the lower chamber and tightly reattach the lower chambers to the module.

11.3.2.3 Using clean rinsed (with hexane) Teflon®-tipped forceps, carefully place a clean conditioned fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter. Place the

aluminum protective cover on top of the cartridge head. Tighten the 3 screw clamps. Ensure that all module connections are tightly assembled. Place a small piece of aluminum foil on the ball-joint of the sample cartridge to protect from back-diffusion of semi-volatiles into the cartridge during transporting to the site.

[Note: Failure to do so could expose the cartridge to contamination during transport.]

11.3.2.4 Place the cartridge in a carrying bag to take to the sampler.

11.3.3 Collection

11.3.3.1 After the sampling system has been assembled, perform a single point flow check as described in Sections 11.2.3.

11.3.3.2 With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon® squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.

11.3.3.3 With the sample cartridge removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warm-up for approximately 5 minutes.

11.3.3.4 Attach a "dummy" sampling cartridge loaded with the exact same type of filter and PUF media to be used for sample collection.

11.3.3.5 Turn the sampler on and adjust the flow control valve to the desired flow as indicated by the Magnehelic gauge reading determined in Section 11.2.2.24. Once the flow is properly adjusted, take extreme care not to inadvertently alter its setting.

11.3.3.6 Turn the sampler off and remove the "dummy" module. The sampler is now ready for field use.

11.3.3.7 Check the zero reading of the sampler Magnehelic. Record the ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUF cartridge number on the Field Test Data Sheet (see Figure 12). Attach the loaded sampler cartridge assembly to the sampler.

11.3.3.8 Place the voltage variator and flow control valve at the settings used in Section 11.3.2, and the power switch. Activate the elapsed time meter and record the start time. Adjust the flow (Magnehelic setting), if necessary, using the flow control valve.

11.3.3.9 Record the Magnehelic reading every 6 hours during the sampling period. Use the calibration factors (see Section 11.2.2.24) to calculate the desired flow rate. Record the ambient temperature, barometric pressure, and Magnehelic reading at the beginning and during sampling period.

11.3.4 Sample Recovery

11.3.4.1 At the end of the desired sampling period, turn the power off. Carefully remove the sampling head containing the filter and sorbent cartridge. Place the protective "plate" over the filter to protect the cartridge during transport to a clean recovery area. Also, place a piece of aluminum foil around the bottom of the sampler cartridge assembly.

11.3.4.2 Perform a final calculated sampler flow check using the calibration orifice, assembly, as described in Section 11.3.2. If calibration deviates by more than 10 percent from initial reading, mark the flow data for that sample as suspect and inspect and/or remove from service, record results on Field Test Data Sheet, Figure 12.

11.3.4.3 Transport the sampler cartridge assembly to a clean recovery area.

11.3.4.4 While wearing white cotton gloves, remove the PUF glass cartridge from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally wrapped.

11.3.4.5 Carefully remove the quartz fiber filter from the upper chamber using clean Teflon®-tipped forceps.

11.3.4.6 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the PUF.

11.3.4.7 Wrap the combined samples in the original hexane-rinsed aluminum foil, attach Teflon® end caps (if applicable) and place them in their *original* aluminum shipping container. Complete a sample label and affix it to the aluminum shipping container.

11.3.4.8 Chain-of-custody should be maintained for all samples. Store the containers under blue ice or dry ice and protect from UV light to prevent possibly photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, refrigerate sample at 4°C.

11.3.4.9 Return at least one field blank filter/PUF cartridge to the laboratory with each group of samples. Treat a field blank exactly as the sample except that air is not drawn through the filter/sorbent cartridge assembly.

11.3.4.10 Ship and store field samples chilled (<4°C) using blue ice until receipt at the analytical laboratory, after which samples should be refrigerated at less than or equal to 4°C for up to 7 days prior to extraction; extracts should be analyzed within 40 days of extraction.

12. Sample Extraction, Concentration, and Cleanup

[Note: The following sample extraction, concentration, solvent exchange and analysis procedures are outlined for user convenience in Figure 13.]

12.1 Sample Identification

12.1.1 The chilled (<4°C) samples are returned in the aluminum shipping container (containing the filter and sorbents) to the laboratory for analysis. The "chain-of-custody" should be completed.

12.1.2 The samples are logged in the laboratory logbook according to sample location, filter and sorbent cartridge number identification, and total air volume sampled (uncorrected).

12.1.3 If the time span between sample registration and analysis is greater than 24-hours, then the sample must be kept refrigerated at <4°C. Minimize exposure of samples to fluorescent light. All samples should be extracted within one week (7 days) after sampling.

12.2 Soxhlet Extraction and Concentration

[Note: If PUF is the sorbent, the extraction solvent is 10 percent diethyl ether in hexane. If XAD-2® resin is the sorbent, the extraction solvent is methylene chloride.]

12.2.1 Assemble the Soxhlet apparatus (see Figure 4a). Immediately before use, charge the Soxhlet apparatus with 700 to 750 mL of 10 percent diethyl ether in hexane and reflux for 2 hours. Let the apparatus cool, disassemble it, transfer the diethyl ether in hexane to a clean glass container, and retain it as a blank for later analysis, if required. Place the sorbent and filter together in the Soxhlet apparatus (the use of an extraction thimble is optional).

[Note: The filter and sorbent are analyzed together in order to reach detection limits, avoid questionable interpretation of the data, and minimize cost.]

12.2.1.1 Prior to extraction, add appropriate laboratory surrogate standards to the Soxhlet solvent. A surrogate standard (i.e., a chemically compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the laboratory surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measure concentration falls within the acceptance limits. Spike 20 μL of a 50 μg/mL solution of the surrogates onto the PUF cartridge, prior to Soxhlet extraction, to yield a final concentration of 1 μg. The following laboratory surrogate standards have been

successfully utilized in determining Soxhlet extraction effects, sample process errors, etc., for GC/MS/DS analysis.

Laboratory Surrogate Standard	Total Spiked Amount (µg)
D_{10}-Fluorene	1
D_{10}-Pyrene	1

Section 13.2 outlines preparation of the laboratory surrogates. Add the laboratory surrogate compounds to the PUF cartridge. Add 700 mL of 10 percent diethyl ether in hexane to the apparatus and reflux for 18 hours at a rate of at least 3 cycles per hour. Allow to cool, then disassemble the apparatus.

12.2.1.2 Dry the extract from the Soxhlet extraction by passing it though a drying column containing about 10 grams of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator assembly. Wash the extractor flask and sodium sulfate column with 100-125 mL of 10 percent diethyl ether/hexane to complete the quantitative transfer.

12.2.2 Assemble a K-D concentrator (see Figure 4b) by attaching a 10 mL concentrator tube to a 500 mL evaporative flask.

[Note: Other concentration devices (vortex evaporator) or techniques may be used in place of the K-D as long as qualitative and quantitative recovery can be demonstrated.]

12.2.2.1 Add two boiling chips, attach a three-ball macro-Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65°C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in one hour. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an approximate volume of 5 mL, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 minutes while cooling.

12.2.2.2 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of cyclohexane. A 5 mL syringe is recommended for this operation. The extract is now ready for further concentration to 1.0 mL by nitrogen blowdown.

12.2.2.3 Place the 1 mL calibrated K-D concentrator tube with an open micro-Snyder attachment in a warm water bath (30 to 3 5°C) and evaporate the solvent volume to just below 1 mL by blowing a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon) above the extract.

12.2.2.4 The internal wall of the concentrator tube must be rinsed down several times with hexane during the operation.

12.2.2.5 During evaporation, the tube solvent level must be kept below the water level of the bath. the extract must never be allowed to become dry.

12.2.2.6 Bring the final volume back to 1.0 mL with hexane. Transfer the extract to a Teflon®-sealed screw-cap amber vial, label the vial, and store at 4°C (±2°C).

[Note: It is not necessary to bring the volume to exactly 1.0 mL if the extract will be cleaned up by solid phase extraction cleanup methods. Final volume is brought to 1.0 mL after cleanup.]

12.3 Sample Cleanup

12.3.1 If the extract is cloudy, impurities may be removed from the extract by solid phase extraction using activated silica gel. Clean-up procedures may not be needed for relatively clean matrix samples.

12.3.2 Approximately 10 grams of silica gel, type 60 (70-230 mesh), are extracted in a Soxhlet extractor with 10 percent diethyl ether for 6 hours (minimum rate, 3 cycles/hr) and then activated by heating in a foil-covered glass container for 16 hours at 150°C.

12.3.3 Using a disposable Pasteur pipette (7.5-mm x 14.6-cm), place a small piece of glass wool in the neck of the pipette. Prepare a slurry of activated silica gel in 10 percent diethyl ether. Place 10 grams of the activated silica gel slurry into the column using additional 10 percent diethyl ether. Finally, 1 gram of anhydrous sodium sulfate is added to the top of the silica gel. Prior to use, the column is rinsed with 10 percent diethyl ether at 1 mL/min for 1 hour to remove any trace of contaminants. It is then pre-eluted with 40 mL of pentane and the eluate discarded.

12.3.4 While the pentane pre-elutant covers the top of the column, 1 mL of the sample extract is transferred to the column, and washed on with 2 mL of *n*-hexane to complete the transfer. Allow to elute through the column. Immediately prior to exposure of the sodium sulfate layer the air, add 25 mL of pentane and continue the elution process. The pentane eluate is discarded.

12.3.5 The column is finally eluted at 2 mL/min with 25 mL of 10 percent diethyl ether in pentane (4:6 v/v) and collected in a 50 mL K-D flask equipped with a 5 mL concentrator tube for concentration to less than 5 mL. The concentrate is further concentrated to 1.0 mL under a gentle stream of nitrogen as previously described.

12.3.6 The extract is now ready for GC/MS analysis. Spike the extract with internal standards (ISs) before analysis. The following internal standards (ISs) have been successfully used in PAH analysis by GC/MS.

Internal Standard (IS)	**Total Spiked Amount (µg)**
D_8-Naphthalene	0.5
D_{10}-Acenaphthene	0.5
D_{10}-Phenanthrene	0.5
D_{12}-Chrysene	0.5
D_{12}-Perylene	0.5

Section 13.2 outlines preparation of the ISs.

13. Gas Chromatography with Mass Spectrometry Detection

13.1 General

13.1.1 The analysis of the extracted sample for benzo[a]pyrene and other PAHs is accomplished by an electron ionization gas chromatograph/mass spectrometer (EI GC/MS) in the mode with a total cycle time (including voltage reset time) of 1 second or less. The GC is equipped with an DB-5 fused silica capillary column (30-m x 0.32-mm I.D.) with the helium carrier gas for analyte separation. The GC column is temperature controlled and interfaced directly to the MS ion source.

13.1.2 The laboratory must document that the EI GC/MS system is properly maintained through periodic calibration checks. The GC/MS system should be operated in accordance with specifications outlined in Table 2.

13.1.3 The GC/MS is tuned using a 50 ng/µL solution of decafluorotriphenylphosphine (DFTPP). The DFTPP permits the user to tune the mass spectrometer on a daily basis. If properly tuned, the DFTPP key ions and ion abundance criteria should be met as outlined in Table 3.

13.1.4 The GC/MS operating conditions are outlined in Table 2. The GC/MS system should be calibrated using the internal standard technique. Figure 14 outlines the following sequence involving the GC/MS calibration.

13.2 Calibration of GC/MS/DS

13.2.1 Standard Preparation

Stock PAH Standards Including Surrogate Compounds

13.2.1.1 Prepare stock standards of B[a]P and other PAHs. The stock standard solution of B[a]P (2.0 µg/µL) and other PAHs can be user prepared from pure standard materials or can be purchased commercially.

13.2.1.2 Place 0.2000 grams of native B[a]P and other PAHs on a tared aluminum weighing disk and weigh on a Mettler balance.

13.2.1.3 Quantitatively transfer the material to a 100 mL volumetric flask. Rinse the weighing disk with several small portions of 10 percent diethyl ether/hexane. Ensure all material has been transferred.

13.2.1.4 Dilute to mark with 10 percent diethyl ether/hexane.

13.2.1.5 The concentration of the stock standard solution of B[a]P or other PAHs in the flask is 2.0 µg/µL.

[Note: Commercially prepared stock PAH standards may be used at any concentration if they are certified by the manufacturer or by an independent source.]

13.2.1.6 Transfer the stock standard solutions into Teflon®-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

13.2.1.7 Stock PAH standard solutions must be replaced after 1 year or sooner if comparison with quality control check samples indicates a problem.

Mix Internal Standard (IS) Solution

13.2.1.8 For PAH analysis, deuterated internal standards are selected that are similar in analytical behavior to the compound of interest. The following internal standards are suggested for PAH analysis:

D_{12}-Perylene
Benzo(e)pyrene
Benzo(a)pyrene
Benzo(k)fluoranthene

D_{10}-Acenaphthene
Acenaphthene (if using XAD-2® as the sorbent)
Acenaphthylene (if using XAD-2® as the sorbent)
Fluorene
Benzo(g,h,i)perylene
Dibenz(a,h)anthracene
Indeno(1,2,3-cd)pyrene
Perylene
Benzo(b)fluoranthene
Coronene

D_{12}-Chrysene
Benz(a)anthracene
Chrysene
Pyrene

D_8-Naphthalene
Naphthalene (if using XAD-2® as the sorbent)

D_{10}-Phenanthrene
Anthracene
Fluoranthene
Phenanthrene

13.2.1.9 Purchase a mix IS solution containing specific IS needed for quantitation at a concentration of 2,000 ng/µL.

Mixed Stock PAH Standard Including Surrogate Compounds

13.2.1.10 Prepare a mixed stock PAH standard by taking 125 µL of the stock PAH standard(s) and diluting to mark with hexane in a 10-mL volumetric flask. The concentration of the mixed stock PAH standard(s) is 25 ng/µL.

Calibration PAH Standards Including Surrogate Compounds

13.2.1.11 Calibration PAH standards can be generated from the stock PAH standard using serial dilution utilizing the following equation:

$$C_1V_1 = C_2V_2$$

where:

C_1 = Concentration of stock PAH standards, ng/µL
V_1 = Volume of stock PAH standard solution taken to make calibration PAH standards, µL
V_2 = Final volume diluted to generate calibration PAH standards, µL
C_2 = Final concentration of calibration PAH standards, ng/µL

13.2.1.12 Using the above equation, prepare a series of calibration PAH standards which include the surrogate compounds (i.e., 2.50 ng/µL, 1.25 ng/µL, 0.50 ng/µL, 0.25 ng/µL, and 0.10 ng/µL) according to the scheme illustrated in Table 4 and described below.

- For CAL 5, transfer 1.00 mL of the mixed PAH stock standard in a 10-mL volumetric flask and dilute to 10.0 mL with hexane. The resulting concentration is 2.5 ng/µL for the PAH analytes.
- To prepare CAL 4, transfer 500 µL of the mixed PAH stock standard solution to a 10-mL volumetric flask and dilute to 10.0 mL with hexane. The resulting concentration is 1.25 ng/µL for PAH analytes.
- To prepare CAL 3, transfer 200 µL of the mixed PAH stock solution to a 10-mL volumetric flask and dilute to 10-mL with hexane. The resulting concentration is 0.50 ng/µL for PAH analytes.
- To prepare CAL 2, transfer 100 μL of the mixed PAH stock solution to a 10-mL volumetric flask and dilute to 10-mL with hexane. The resulting concentration is 0.25 ng/μL for PAH analytes.
- To prepare CAL 1, transfer 40 µL of the mixed PAH stock solution to a 10-mL volumetric flask and dilute to 10-mL with hexane. The resulting concentration is 0.10 ng/µL for PAH analytes.

13.2.2 Internal Standard Spiking

13.2.2.1 Prior to GC/MS analysis, each 1 mL aliquot of the five calibration standards is spiked with internal standard to a final concentration of 0.5 ng/µL. To do this, first prepare a 1:40 dilution of the 2,000 ng/µL mixed internal standard solution by diluting 250 µL to a volume of 10 mL to yield a concentration of 50 ng/µL.

13.2.2.2 Each 1.0-mL portion of calibration standard and sample extract is then spiked with 10 µL of the internal standard solution prior to analysis by GC/MS/DS operated in the SCAN mode.

13.2.3 Storage, Handling, and Retention of Standards

13.2.3.1 Store the stock and mixed standard solutions at 4°C (±2°C) in Teflon®-lined screw-cap amber bottles. Store the working standard solutions at 4°C (±2°C) in Teflon®-lined screw-cap amber bottles.

13.2.3.2 Protect all standards from light. Samples, sample extracts, and standards must be stored separately.

13.2.3.3 Stock standard solutions must be replaced every 12 months, or sooner, if comparison with quality control check samples indicates a problem. Diluted working standards are usable for 6 months. Analysis difficulties, which warrant investigation, may require preparation of new standards. All standards are securely stored at ~4°C (±2°C) but above freezing. The concentration, preparation and expiration date, and solvent are identified on standard vial labels. Each standard is uniquely identified with its laboratory notebook number and a prefix. This procedure helps provide traceability to standard preparation.

13.2.3.4 Take care to maintain the integrity of each standard. The solvent, hexane, is volatile and can easily evaporate. Make sure each vial is sealed after use, and mark the solvent level on the side of the vial. When retrieving a vial for use, if the solvent level does not match the mark, dispose of the standard and obtain a new one.

13.3 GC/MS Instrument Operating Conditions

13.3.1 Gas Chromatograph (GC). The following are the recommended GC analytical conditions, as also outlined in Table 3, to optimize conditions for compound separation and sensitivity.

Carrier Gas:	Helium
Linear Velocity:	28-29 cm^3/sec
Injector Temperature:	250-300°C
Injector:	Grob-type, splitless, 2 µL
Temperature Program:	Initial Temperature: 70°C
Initial Hold Time:	4.0 ± 0.1 min.
Ramp Rate:	10°C/min to 300°C, hold for 10 min
Final Temperature:	300°C
Final Hold Time:	10 min (or until all compounds of interest have eluted).
Analytical Time:	Approximately 50 min.

13.3.2 Mass Spectrometer. Following are the required mass spectrometer conditions for scan data acquisition:

Transfer Line Temperature:	290°C
Source Temperature:	According to manufacturer's specifications
Electron Energy:	70 volts (nominal)
Ionization Mode:	EI
Mass Range:	35 to 500 amu, SCAN data acquisition
Scan Time:	At least 5 scans per peak, not to exceed 1 second per scan

13.3.3 Instrument Performance Check for GC/MS.

13.3.3.1 Summary. It is necessary to establish that the GC/MS meet tuning and standard mass spectral abundance criteria prior to initiating any on-going data collection, as illustrated in Figure 14. This is accomplished through the analysis of decafluorotriphenylphosphine (DFTPP).

13.3.3.2 Frequency. The instrument performance check solution of DFTPP will be analyzed initially and once per 12-hour time period of operation. Also, whenever the laboratory takes corrective action which may change or affect the mass spectral criteria (e.g., ion source cleaning or repair, column replacement, etc.), the instrument performance check must be verified irrespective of the 12-hour laboratory requirement. The 12-hour

time period for GC/MS analysis begins at the injection of the DFTPP, which the laboratory submits as documentation of a compliance tune. The time period ends after 12 hours have elapsed. To meet instrument performance check requirements, samples, blanks, and standards must be injected within 12 hours of the DFTPP injection.

13.3.3.3 Procedure. Inject 50 ng of DFTPP into the GC/MS system. DFTPP may be analyzed separately or as part of the calibration standard.

13.3.3.4 Technical Acceptance Criteria. The following criteria have been established in order to generate accurate data:

- Prior to the analysis of any samples, blanks, or calibration standards, the laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check solution containing DFTPP.
- The GC/MS system must be tuned to meet the manufacturer's specifications, using a suitable calibrant. The mass calibration and resolution of the GC/MS system are verified by the analysis of the instrument performance check solution.
- The abundance criteria listed in Table 3 must be met for a 50 ng injection of DFTPP. The mass spectrum of DFTPP must be acquired by averaging three scans (the peak apex scan and the scans immediately preceding and following the apex). Background subtraction is required, and must be accomplished using a single scan prior to the elution of DFTPP.

[Note: All ion abundance MUST be normalized to m/z 198, the nominal base peak, even though the ion abundances of m/z 442 may be up to 110 percent of m/z 198.]

- The above criteria are based on adherence to the acquisition specifications identified in Table 4 and were developed for the specific target compound list associated with this document. The criteria are based on performance characteristics of instruments currently utilized in routine support of ambient air program activities. These specifications, in conjunction with relative response factor criteria for target analytes, are designed to control and monitor instrument performance associated with the requirements if this document. As they are performance-based criteria for these specific analytical requirements, they may not be optimal for additional target compounds.
- If the mass spectrometer has the ability for autotuning, then the user may utilize this function following manufacturer's specifications. Autotune automatically adjusts ion source parameters within the detector using FC-43 (Heptacos). Mass peaks at m/z 69, 219, and 502 are used for tuning. After the tuning is completed, the FC-43 abundances at m/z 50, 69, 131, 219, 414, 502, and 614 are further adjusted such that their relative intensities match the selected masses of DFTPP.

13.3.3.5 Corrective Action. If the DFTPP acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other actions to achieve the acceptance criteria. DFTPP acceptance criteria MUST be met before any standards, or required blanks, are analyzed. Any standards, field samples, or required blanks analyzed when tuning criteria have not been met will require reanalysis.

13.3.4 Initial Calibration for GC/MS.

13.3.4.1 Summary. Prior to the analysis of samples and required blanks, and after tuning criteria (instrument performance check) have been met, each GC/MS system will be initially calibrated at a minimum of five concentrations to determine instrument sensitivity and the linearity of GC/MS response for the analyte compounds and the surrogates.

13.3.4.2 Frequency. Each GC/MS system must be initially calibrated whenever the laboratory takes corrective action, which may change or affect the initial calibration criteria (e.g., ion source cleaning or repair,

column replacement, etc.), or if the continuing calibration acceptance criteria have not been met. If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within the 12-hour time period if the initial calibration standard (CAL 3) is the same concentration as the continuing calibration standard and both meet the continuing calibration technical acceptance criteria. Quantify all sample results using the mean of the relative response factors ($\overline{\text{RRFs}}$) from the initial calibration.

13.3.4.3 Procedure. Perform the following activities to generate quantitative data:

- Set up the GC/MS system.
- Warm all standard/spiking solutions, sample extracts, and blanks to ambient temperature (~1 hour) before analysis.
- Tune the GC/MS system to meet the technical acceptance criteria (see Section 13.3.3).
- Prepare five calibration standards containing the target compounds, internal standards, and surrogate compounds at the concentrations outlined in Table 4.
- Calibrate the GC/MS by injecting 2.0 µL of each standard. If a compound saturates when the CAL 5 standard is injected, and the system is calibrated to achieve a detection sensitivity of no less than the MDL for each compound, the laboratory must document it and attach a quantitation report and chromatogram. In this instance, the laboratory must calculate the results based on a four-point initial calibration for the *specific compound* that saturates. Secondary ion quantitation is only allowed when there are sample interferences with the primary quantitation ion. If secondary ion quantitation is used, calculate a relative response factor using the area response from the most intense secondary ion which is free of interferences and document the reasons for the use of the secondary ion.
- Record a mass spectrum of each target compound. Figure 15(a) through 15(q) documents the mass spectrum for each of the 16 target PAHs discussed in Compendium Method TO-13A. Judge the acceptability of recorded spectra by comparing them to spectra in libraries. If an acceptable spectrum of a calibration standard component is not acquired, take necessary actions to correct GC/MS performance. If performance cannot be corrected, report sample extract data for the particular compound(s), but document the affected compound(s) and the nature of the problem.

13.3.4.4 Calculations. Perform the following calculations to generate quantitative data:

[Note: In the following calculations, the area response is that of the primary quantitation ion unless otherwise stated.]

- **Relative Response Factors (RRFs)**. Calculate RRFs for each analyte target compound and surrogate using the following equation with the appropriate internal standard. Table 5 outlines characteristic ions for the surrogate compounds and internal standards. Table 6 outlines primary quantitation ions for each PAH. Use the following equation for RRF calculation.

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

where:

A_x = area of the primary quantitation ion for the compound to be measured, counts
A_{is} = area of the primary quantitation ion for the internal standard, counts
C_{is} = concentration or amount of the internal standard, ng/µL

C_x = concentration or amount of the compound to be measured, ng/µL

- **Percent Relative Standard Deviation (%RSD)**. Using the RRFs from the initial calibration, calculate the %RSD for all target compounds and surrogates using the following equations:

$$\%RSD = \frac{SD_{RRF}}{\bar{x}} \times 100$$

and

$$SD_{RRF} = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N - 1}}$$

where:

SD_{RRF} = standard deviation of initial response factors (per compound)
x = mean of initial relative response factors (per compound)
X_i = ith RRF
N = number of determinations

- **Relative Retention Times (RRT)**. Calculate the RRTs for each target compound and surrogate over the initial calibration range using the following equation:

$$RRT = \frac{RT_c}{RT_{is}}$$

where:

RT_c = retention time of the target compound, minutes
RT_{is} = retention time of the internal standard, minutes

- **Mean of the Relative Retention Times ($\overline{RRT}$)**. Calculate the mean of the relative retention times ($\overline{RRT}$) for each analyte target compound and surrogate over the initial calibration range using the following equation:

$$\overline{RRT} = \sum_{i=1}^{n} \frac{RRT_i}{n}$$

where:

$\overline{RRT}$ = mean relative retention time for the target compound or surrogate for each initial calibration standard, minutes
RRT = relative retention time for the target compound or surrogate for each initial calibration standard, minutes

- **Mean Area Response ($\overline{Y}$) for Internal Standard**. Calculate the area response (Y) mean for primary quantitation ion each internal standard compound over the initial calibration range using the following equation:

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

where:

$\overline{Y}$ = mean area response, counts
Y_i = area response for the primary quantitation ion for the internal standard for each calibration standard, counts

- **Mean of the Retention Time ($\overline{RT}$) For Internal Standard**. Calculate the mean of the retention times ($\overline{RT}$) for each internal standard over the initial calibration range using the following equation:

$$\overline{RT} = \sum_{i=1}^{n} \frac{RT_i}{n}$$

where:
$\overline{RT}$ = mean retention time, minutes
RT = retention time for the internal standard for each initial calibration standard, minutes

13.3.4.5 Technical Acceptance Criteria. All initial calibration standards must be analyzed at the concentration levels at the frequency described in Section 13.3.3 on a GC/MS system meeting the DFTPP instrument performance check criteria.

- The relative response factor (RRF) at each calibration concentration for each target compound and surrogate that has a required minimum response factor value must be greater than or equal to the minimum acceptable relative response factor (see Table 7) of the compound.
- The percent relative standard deviation (%RSD) over the initial calibration range for each target compound and surrogate that has a required maximum %RSD must be less than or equal to the required maximum value (see Table 7). For all the other target compounds, the value for %RSD must be less than or equal to 30 percent. When the value for %RSD exceeds 30 percent, analyze additional aliquots of appropriate CALs to obtain an acceptable %RSD of RRFs over the entire concentration range, or take action to improve GC/MS performance.
- The relative retention time for each of the target compounds and surrogates at each calibration level must be within ±0.06 relative retention time units of the mean relative retention time for the compound.
- The retention time shift for each of the internal standards at each calibration level must be within ±20.0 seconds compared to the mean retention time ($\overline{RT}$) over the initial calibration range for each internal standard.
- The compounds must meet the minimum RRF and maximum %RSD criteria for the initial calibration.

13.3.4.6 Corrective Action. If the technical acceptance criteria for initial calibration are not met, the system should be inspected for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the acceptance criteria. Initial calibration technical acceptance criteria MUST

be met before any samples or required blanks are analyzed in a 12-hour time period for an initial calibration analytical sequence.

13.3.5 Continuing Calibration.

13.3.5.1 Summary. Prior to the analysis of samples and required blanks and after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a continuing calibration standard (see Table 4, CAL 3) to ensure that the instrument continues to meet the instrument sensitivity and linearity requirements of the method. The continuing calibration standard (CAL 3) shall contain the appropriate target compounds, surrogates, and internal standards.

13.3.5.2 Frequency. Each GC/MS used for analysis must be calibrated once every time period of operation. The 12-hour time period begins with injection of DFTPP. If time still remains in the 12-hour time period after meeting the technical acceptance criteria for the initial calibration, samples may be analyzed. It is not necessary to analyze a continuing calibration standard within this 12-hour time period, if the initial calibration standard that is the same concentration as the continuing calibration standard meets the continuing calibration technical acceptance criteria.

13.3.5.3 Procedure. The following activities should be performed for continuing calibration:

- Set up the GC/MS system as specified by the manufacturer.
- Tune the GC/MS system to meet the technical acceptance criteria (see Section 13.3.3).
- Analyze the CAL 3 standard solution containing all the target analytes, surrogate compounds, and internal standards using the procedure listed for the initial calibration.
- Allow all standard/spiking solutions and blanks to warm to ambient temperature (approximately 1 hour) before preparation or analysis.
- Start the analysis of the continuing calibration by injecting 2.0 µL of the CAL 3 standard solution.

13.3.5.4 Calculations. The following calculations should be performed:

- **Relative Response Factor (RRF)**. Calculate a relative response factor (RRF) for each target compound and surrogate.
- **Percent Difference (%D)**. Calculate the percent difference between the mean relative response factor ($\overline{RRF}$) from the most recent initial calibration and the continuing calibration RRF for each analyte target compound and surrogate using the following equation:

$$\%D_{RRF} = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where:

$\%D_{RRF}$ = percent difference between relative response factors

$\overline{RRF_i}$ = average relative response factor from the most recent initial calibration

RRF_c = relative response factor from the continuing calibration standard

13.3.5.5 Technical Acceptance Criteria. The continuing calibration standard must be analyzed for the compounds listed in concentration levels at the frequency described and on a GC/MS system meeting the DFTPP instrument performance check and the initial calibration technical acceptance criteria. The relative response factor for each target analyte and surrogate that has a required minimum relative response factor value must be greater than or equal to the compound's minimum acceptable relative response factor. For an acceptable

continuing calibration, the %D between the measured RRF for each target/surrogate compound of the CAL 3 standard and the mean value calculated during initial calibration must be within ±30 percent. If the criteria for %D are not met for the target or surrogate compounds, remedial action must be taken and recalibration may be necessary.

13.3.5.6 Corrective Action. If the continuing calibration technical acceptance criteria are not met, recalibrate the GC/MS instrument. It may be necessary to clean the ion source, change the column, or take other corrective actions to achieve the acceptance criteria. Continuing calibration technical acceptance criteria ***MUST*** be met before any samples or required blanks are analyzed in a 12-hour continuing calibration analytical sequence. Any samples or required blanks analyzed when continuing calibration criteria were not met will require reanalysis. Remedial actions, which include but are not limited to the following, must be taken if criteria are not met:

- Check and adjust GC and/or MS operating conditions.
- Clean or replace injector liner.
- Flush column with solvent according to manufacturers instructions.
- Break off a short portion (approximately 0.33 cm) of the column.
- Replace the GC column (performance of all initial calibration procedures are then required).
- Adjust MS for greater or lesser resolution.
- Calibrate MS mass scale.
- Prepare and analyze new continuing calibration.
- Prepare a new initial calibration curve.

13.3.6 Laboratory Method Blank (LMB).

13.3.6.1 Summary. The purpose of the LMB is to monitor for possible laboratory contamination. Perform all steps in the analytical procedure using all reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. An LMB is an unused, certified filter/cartridge assembly which is carried though the same extraction procedure as a field sample. The LMB extract must contain the same amount of surrogate compounds and internal standards that is added to each sample. All field samples must be extracted and analyzed with an associated LMB.

13.3.6.2 Frequency. Analyze an LMB along with each batch of ≤20 samples through the entire extraction, concentration, and analysis process. The laboratory may also analyze a laboratory reagent blanks which is the same as an LMB except that no surrogate compounds or internal standards are added. This demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions for those compounds.

13.3.6.3 Procedure. Extract and analyze a clean, unused filter and glass cartridge assembly.

13.3.6.4 Technical Acceptance Criteria. Following are the technical criteria for the LMB:

- All blanks must be analyzed on a GC/MS system meeting the DFTPP instrument performance check and initial calibration or continuing calibration technical acceptance criteria.
- The percent recovery for each of the surrogates in the blank must be within the acceptance windows.
- The area response change for each of the internal standards for the blank must be within -50 percent and +100 percent compared to the internal standards in the most recent continuing calibration analysis.
- The retention time for each of the internal standards must be within ±20.0 seconds between the blank and the most recent CAL 3 analysis.
- The LMB must not contain any target analyte at a concentration greater than the MDL and must not contain additional compounds with elution characteristics and mass spectral features that would interfere

with identification and measurement of a method analyte at its MDL. If the LMB that was extracted along with a batch of samples is contaminated, the entire batch of samples must be flagged.

13.3.6.5 Corrective Action. Perform the following if the LCBs exceed criteria:

- If the blanks do not meet the technical acceptance criteria, the analyst must consider the analytical system to be out of control. It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measure *MUST* be taken and documented before further sample analysis proceeds.
- All samples processed with a method blank that is out of control (i.e., contaminated) will require data qualifiers to be attached to the analytical results.

13.3.7 Laboratory Control Spike (LCS).

13.3.7.1 Summary. The purpose of the LCS is to monitor the extraction efficiency of Compendium Method TO-13A target analytes from a clean, uncontaminated PUF cartridge. An LCS is an unused, certified PUF that is spiked with the target analytes (1 μg) and carried through the same extraction procedures as the field samples. The LCS must contain the same amount of surrogate compounds and internal standards that is added to each sample. All field samples must be extracted and analyzed with an associated LCS. All steps in the analytical procedure must use the same reagents, standards, surrogate compounds, equipment, apparatus, glassware, and solvents that would be used for a sample analysis.

13.3.7.2 Frequency. Analyze an LCS along with each of $\leq$20 samples through the entire extraction, concentration, and analysis. (The laboratory may also analyze a laboratory reagent blank which is the same as an LMB except that no surrogate compounds or internal standards are added. This demonstrates that reagents contain no impurities producing an ion current above the level of background noise for quantitation ions of those compounds.)

13.3.7.3 Procedure. Extract and analyze a clean, unused certified PUF cartridge assembly.

13.3.7.4 Technical Acceptance Criteria. Technical criteria for the LCS are:

- All LCSs must be analyzed on a GC/MS system meeting the DFTPP instrument performance check and initial calibration or continuing calibration technical acceptance criteria.
- The percent recovery for each of the surrogates in the LCS must be within the acceptance windows.
- The area response change for each of the internal standards for the LCS must be within -50 percent and +100 percent compared to the internal standards in the most recent continuing calibration analysis.
- The retention time for each of the internal standards must be within ±20.0 seconds between the LCS and the most recent CAL 3 analysis.
- All target analytes spiked on the certified PUF cartridge must meet a percent recovery between 60-120 to be acceptable.

13.3.7.5 Corrective Action. Perform the following if the LCS exceed criteria:

- If the LCS do not meet the technical acceptance criteria, the analyst must consider the analytical system to be out of control. It is the analyst's responsibility to ensure that method interferences caused by contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms be eliminated. If contamination is a problem, the source of the contamination must be investigated and appropriate corrective measure *MUST* be taken and documented before further sample analysis proceeds.

- All samples processed with a LCS that is out of control (i.e., contaminated) will require re-analysis or data qualifiers to be attached to the analytical results.

13.4 Sample Analysis by GC/MS

13.4.1 Summary. The sample extract is analyzed by GC/MS and quantitated by the internal standard method.

13.4.2 Frequency. Before samples can be analyzed, the instrument must meet the GC/MS tuning and initial calibration or continuing calibration technical acceptance criteria. If there is time remaining in the 12-hour time period with a valid initial calibration or continuing calibration, samples may be analyzed in the GC/MS system that meet the instrument performance check criteria.

13.4.3 Procedure. For sample analysis, perform the following:

- Set up the GC/MS system.
- All sample extracts must be allowed to warm to ambient temperature (~1 hour) before analysis. All sample extracts must be analyzed under the same instrumental conditions as the calibration standards.
- Add the internal standard spiking solution to the 1.0 mL extract. For sample dilutions, add an appropriate amount of the internal standard spiking solution to maintain the concentration of the internal standards at 2 ng/µL in the diluted extract.
- Inject 2.0 µL of sample extract into the GC/MS, and start data acquisition.
- When all semi-volatile target compounds have eluted from the GC, terminate the MS data acquisition and store data files on the data system storage device. Use appropriate data output software to display full range mass spectra and SICPs. The sample analysis using the GC/MS is based on a combination of retention times and relative abundances of selected ions (see Table 6). These qualifiers should be stored on the hard disk of the GC/MS data computer and are applied for identification of each chromatographic peak. The retention time qualifier is determined to be +0.10 minute of the library retention time of the compound. The acceptance level for relative abundance is determined to be ±15% of the expected abundance. Three ions are measured for most of the PAH compounds. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (e.g., with an *). The data should be manually examined by the analyst to determine the reason for the flag and whether the compound should be reported as found. Although this step adds some subjective judgment to the analysis, computer-generated identification problems can be clarified by an experienced operator. Manual inspection of the quantitative results should also be performed to verify concentrations outside the expected range.

13.4.4 Dilutions. The following section provides guidance when an analyte exceeds the calibration curve.

- When a sample extract is analyzed that has an analyte target compound concentration greater than the upper limit of the initial calibration range or saturated ions from a compound excluding the compound peaks in the solvent front), the extract must be diluted and reanalyzed. Secondary ion quantitation is *only* allowed when there are sample interferences with the primary quantitation ion. If secondary ion quantitation is used, calculate a relative response factor using the area response for the most intense secondary ion which is free of sample interferences, and document the reasons for the use of the secondary ion.
- Calculate the sample dilution necessary to keep the semi-volatile target compounds that required dilution within the upper half of the initial calibration range so that no compound has saturated ions (excluding the compound peaks in the solvent front). Dilute the sample in hexane in a volumetric flask. Analyze the sample dilution.

- The dilution factor chosen should keep the response of the largest peak for a *target compound* in the upper half of the initial calibration range of the instrument.
- If the on-column concentration of any target compound in any sample exceeds the initial calibration range, that sample must be diluted, the internal standard concentration readjusted, and the sample extract reanalyzed.
- Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

13.4.5 Quantitation. This section provides guidance for quantitating PAH analytes.

- Target components identified shall be quantified by the internal standard method. The internal standards used for the target compounds are the ones nearest the retention time of a given analyte.
- The relative response factor (RRF) from the daily continuing calibration standard analysis (or RRF of CAL 3) if the sample is analyzed in the same 12-hour sequence as the initial calibration) is used to calculate the concentration in the sample. Secondary ion quantitation is allowed *only* when there are sample interferences with the primary ion. If secondary ion quantitation is performed, document the reasons. The area of a secondary ion cannot be substituted for the area of a primary ion unless a relative response factor is calculated using the secondary ion.
- A retention time window is calculated for each single component analyte and surrogate. Windows are established as ±0.01 RRT units of the retention time for the analyte in CAL 3 of the initial calibration or the continuing calibration.

13.4.6 Calculations. Perform the following calculations:

13.4.6.1 Calculation of Concentration. Calculate target compound concentrations using the following equation:

$$\text{Concentration, (ng/std m}^3\text{)} = \frac{A_x I_s V_t D_f}{A_{is} V_i \overline{RRF}}$$

where:

A_x = area response for the compound to be measured, counts
A_{is} = area response for the internal standard, counts
I_s = amount of internal standard, ng/µL
$\overline{RRF}$ = the mean RRF from the most recent initial calibration, dimensionless
V_i = volume of air sampled, std m^3
V_t = volume of final extract, µL
D_f = dilution factor for the extract. If there was no dilution, D_f equals 1. If the sample was diluted, the D_f is greater than 1.

The concentrations calculated can be converted to ppb_v for general reference. The analyte concentration can be converted to ppb_v using the following equation:

$$C_A(ppb_v) = C_A(ng/m^3) \times 24.4/MW_A$$

where:

C_A = concentration of analyte calculated, ng/std. m^3
MW_A = molecular weight of analyte, g/g-mole
24.4 = molar volume occupied by ideal gas at standard temperature and pressure (25°C and 760 mm Hg), L/mole.

13.4.6.2 Estimated Concentration. The equation in Section 13.4.6.1 is also used for calculating the concentrations of the non-target compounds. Total area counts (or peak heights) from the total ion chromatogram generated by the mass spectrometer for Compendium Method TO-13A PAHs (see Figure 16) are to be used for both the non-target compound to be measured (A_x) and the internal standard (A_{is}). Associate the nearest internal standard free of interferences with the non-target compound to be measured. A relative response factor (RRF) of one (1) is to be assumed. The value from this quantitation shall be qualified as estimated ("J") (estimated, due to lack of a compound-specific response factor) and "N" (presumptive evidence of presence), indicating the quantitative and qualitative uncertainties associated with this non-target component. An estimated concentration should be calculated for all tentatively identified compounds (TICs) as well as those identified as unknowns.

13.4.6.3 Surrogate Percent Recovery (%R). Calculate the surrogate percent recovery using the following equation:

$$\%R = \frac{Q_d}{Q_a} \times 100$$

where:
Q_d = Quantity determined by analysis, ng
Q_a = Quantity added to sample/blank, ng

The surrogate percent recovery must fall between 60-120% to be acceptable.

13.4.6.4 Percent Area Response Change (%ARC). Calculate the percent area response change (%ARC) for the sample/blank analysis compared to the most recent CAL 3 analysis for each of the internal standard compounds using the following equation:

$$\%ARC = \frac{A_s - A_x}{A_x} \times 100$$

where:
%ARC = percent area response change, %
A_s = area response of the internal standard in the sample/blank analysis, counts
A_x = area response of the internal standard in the most recent CAL 3 analysis, counts

The area change for the internal standard must not exceed -50 to +100 percent.

13.4.6.5 Internal Standard Retention Time Shift (RTS). Calculate the retention time shift (RTS) between the sample/blank analysis and the most recent CAL 3 analysis for each of the internal standards using the following equation:

$$RTS = RT_s - RT_x$$

where:

RT_s = retention time of the IS in the sample
RT_x = retention time of the IS in the most recent CAL 3 analysis.

13.4.7 Technical Acceptance Criteria. The following guideline is provided as technical acceptance criteria.

13.4.7.1 All target compound concentrations must not exceed the upper limit of the initial calibration range and no compound ion (excluding the compound peaks in the solvent front) may saturate the detector.

13.4.7.2 Internal standard responses and retention times in all samples must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 seconds from the latest continuing calibration standard or CAL 3 if samples are analyzed in the same 12-hour sequence as the initial calibration, the chromatographic system must be inspected for malfunctions, and corrections made as required. The SICP of the internal standards must be monitored and evaluated for each field and QC sample. If the SICP area for any internal standard changes by more than a factor of -50 to +100 percent, the mass spectrometric system must be inspected for malfunction and corrections made as appropriate. If the analysis of a subsequent sample or standard indicates that the system is functioning properly, then corrections may not be required.

13.4.7.3 When target compounds are below the low standard, but the spectrum meets the identification criteria, report the concentration/amount with a "J." For example, if the low standard corresponds to 0.1μg and an amount of 0.05 μg is calculated, report as "0.05J."

13.4.8 Corrective Action. The following section provides guidance if analyte exceeds the technical criteria.

- If the sample technical acceptance criteria for the surrogates and internal standards are not met, check calculations, surrogate and internal standard solutions, and instrument performance. It may be necessary to recalibrate the instrument or take other corrective action procedures to meet the surrogate and internal standard technical acceptance criteria.
- Sample analysis technical acceptance criteria *must* be met before data are reported. Samples contaminated from laboratory sources, or associated with a contaminated method blank, or any samples analyzed that are not meet the technical acceptance criteria will require reanalysis.
- The samples or standards with SICP areas outside the limits must be reanalyzed. If corrections are made, then the laboratory must demonstrate that the mass spectrometric system is functioning properly. This must be accomplished by the analysis of a standard or sample that meets the SICP criteria. After corrections are made, the reanalysis of samples analyzed while the system was malfunctioning is required.
- If after reanalysis, the SICP areas for all internal standards are inside the technical acceptance limits (-50 to +100 percent), then the problem with the first analysis is considered to have been within the control of the laboratory. Therefore, submit *only* data from the analysis with SICPs within the technical acceptance limits. This is considered the *initial* analysis and must be reported as such on all data deliverables.
- If the reanalysis of the sample does not solve the problem (i.e., the SICP areas are outside the technical acceptance limits for both analyses) then the laboratory must submit the SICP data and sample data from both analyses. Distinguish between the initial analysis and the reanalysis on all data deliverables, using the sample suffixes specified.
- Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window.
- If sample peaks are not detected, or all are less than full-scale deflection, the undiluted extract is acceptable for GC/MS analysis. If any sample ions are greater than the 120 percent of the initial calibration curve range, calculate the dilution necessary to reduce the major ion to between half- and full-range response.

14. Quality Assurance/Quality Control (QA/QC)

14.1 General System QA/QC

14.1.1 Each laboratory that uses Compendium Method TO-13A must operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate a typical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation**.**

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

14.1.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike, and deuterated/surrogate samples must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

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

14.2 Process, Field, and Solvent Blanks

14.2.1 One PUF cartridge and filter from each batch of approximately 20 should be analyzed without shipment to the field for the compounds of interest to serve as a process blank. A blank level specified in Section 10.2 for each cartridge/filter assembly is considered to be acceptable.

14.2.2 During each sampling episode, at least one cartridge and filter should be shipped to the field and returned, without drawing air through the sampler, to serve as a field blank.

14.2.3 During the analysis of each batch of samples at least one solvent process blank (all steps conducted but no cartridge or filter included) should be carried through the procedure and analyzed. Blank levels should be those specified in Section 10.2 for single components to be acceptable.

14.2.4 Because the sampling configuration (filter and backup sorbent) has been tested for targeted PAHs in the laboratory in relationship to collection efficiency and has been demonstrated to be greater than 95 percent for targeted PAHs (except naphthalene, acenaphthylene, and acenaphthene), no field recovery evaluation is required as part of the QA/QC program outlined in this section.

15. References

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TABLE 1. FORMULAE AND PHYSICAL PROPERTIES OF SELECTED PAHs

Compound	Formula	Molecular Weight	Melting Point, °C	Boiling Point, °C	Vapor Pressure, kPa	CAS RN #
Naphthalene	$C_{10}H_8$	128.18	80,2	218	1.1x10	91-20-3
Acenaphthylene	$C_{12}H_8$	152.20	92-93	265-280	3.9x10	208-96-8
Acenaphthene	$C_{12}H_{10}$	154.20	90-96	278-279	2.1x10	83-32-9
Fluorene	$C_{13}H_{10}$	166.23	116-118	293-295	8.7x10	86-73-7
Anthracene	$C_{14}H_{10}$	178.24	216-219	340	36x10	120-12-7
Phenanthrene	$C_{14}H_{10}$	178.24	96-101	339-340	2.3x10	85-01-8
Fluoranthene	$C_{16}H_{10}$	202.26	107-111	375-393	6.5x10	206-44-0
Pyrene	$C_{16}H_{10}$	202.26	150-156	360-404	3.1x10	129-00-0
Benz(a)anthracene	$C_{18}H_{12}$	228.30	157-167	435	1.5x10	56-55-3
Chrysene	$C_{18}H_{12}$	228.30	252-256	441-448	5.7x10	218-01-9
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	167-168	481	6.7x10	205-99-2
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	198-217	480-471	2.1x10	207-08-9
Perylene	$C_{20}H_{12}$	252.32	273-278	500-503	7.0x10	198-55-8
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	177-179	493-496	7.3x10	50-32-8
Benzo(e)pyrene	$C_{20}H_{12}$	252.32	178-179	493	7.4x10	192-92-2
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.34	275-278	525	1.3x10	191-24-2
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	162-163	--	ca.10	193-39-5
Dibenz(a,h)anthracene	$C_{22}H_{14}$	278.35	266-270	524	1.3x10	53-70-3
Coronene	$C_{24}H_{12}$	300.36	438-440	525	2.0x10	191-07-1

Many of these compounds sublime.

TABLE 2. GC-MS OPERATING CONDITIONS

Activity	Conditions
Gas Chromatography	
Column	J&W Scientific, DB-5 crosslinked 5% phenylmethyl silicone (30 m x 0.32 mm, 1.0 µm film thickness) or equivalent
Carrier Gas	Helium, velocity between 28-30 cm^3/sec at 250°C
Injection Volume	2 µL, Grob-type, splitless
Injector Temperature	290°C
Temperature Program	
Initial Column Temperature	70°C
Initial Hold Time	4 ± 0.1 min.
Program	10°C/min to 300°C and hold 10 min.
Final Temperature	300°C
Final Hold Time	10 min. or until all compounds of interest have eluted
Mass Spectrometer	
Transfer Line Temperature	290°C or According to Manufacturer's Specification
Source Temperature	According to Manufacturer's Specifications
Electron Energy	70 volts (nominal)
Ionization Mode	EI
Mass Range	35 to 500 amu, full range data acquisition (SCAN) mode
Scan Time	At least 5 scans per peak, not to exceed 1 second per scan.

TABLE 3. DFTPP KEY IONS & ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30 to 60% of mass 198
68 70	Less than 2% of mass 69 Less than 2% of mass 69
127	40 to 60% of mass 198
197 198 199	Less than 2% of mass 198 Base peak, 100% relative abundance 5 to 9% of mass 198
275	10 to 30% of mass 198
365	Greater than 1.0% of mass 198
441 442 443	Present but less than mass 443 40% of mass 198 17 to 23% of mass 442

TABLE 4. COMPOSITION AND APPROXIMATE CONCENTRATION OF CALIBRATION SOLUTIONS

Target Compound	Concentration, ng/µL				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
PAHs	0.10	0.25	0.50	1.25	2.50
Acenaphthene	0.10	0.25	0.50	1.25	2.50
Acenaphthylene	0.10	0.25	0.50	1.25	2.50
Anthracene	0.10	0.25	0.50	1.25	2.50
Benz(a)anthracene	0.10	0.25	0.50	1.25	2.50
Benzo(a)pyrene	0.10	0.25	0.50	1.25	2.50
Benzo(b)fluoranthene	0.10	0.25	0.50	1.25	2.50
Benzo(e)pyrene	0.10	0.25	0.50	1.25	2.50
Benzo(g,h,i)perylene	0.10	0.25	0.50	1.25	2.50
Benzo(k)fluoranthene	0.10	0.25	0.50	1.25	2.50
Chrysene	0.10	0.25	0.50	1.25	2.50
Perylene	0.10	0.25	0.50	1.25	2.50
Dibenz(a,h)anthracene	0.10	0.25	0.50	1.25	2.50
Fluoranthene	0.10	0.25	0.50	1.25	2.50
Fluorene	0.10	0.25	0.50	1.25	2.50
Indeno(1,2,3-c,d)pyrene	0.10	0.25	0.50	1.25	2.50
Naphthalene	0.10	0.25	0.50	1.25	2.50
Coronene	0.10	0.25	0.50	1.25	2.50
Phenanthrene	0.10	0.25	0.50	1.25	2.50
Pyrene	0.10	0.25	0.50	1.25	2.50

TABLE 4. (Continued)

Target Compound	Concentration, ng/µL				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
SUGGESTED INTERNAL STANDARDS					
D_8-Naphthalene	0.5	0.5	0.5	0.5	0.5
D_{10}-Acenaphthene	0.5	0.5	0.5	0.5	0.5
D_{10}-Phenanthrene	0.5	0.5	0.5	0.5	0.5
D_{12}-Chrysene	0.5	0.5	0.5	0.5	0.5
D_{12}-Perylene	0.5	0.5	0.5	0.5	0.5
SUGGESTED SURROGATE COMPOUNDS					
D_{10}-Fluoranthene (field)	0.10	0.25	0.50	1.25	2.50
D_{12}-Benzo[a]pyrene (field)	0.10	0.25	0.50	1.25	2.50
D_{10}-Fluorene (lab)	0.10	0.25	0.50	1.25	2.50
D_{10}-Pyrene (lab)	0.10	0.25	0.50	1.25	2.50

TABLE 5. CHARACTERISTIC IONS FOR SURROGATE SUGGESTED STANDARDS

Classification	Primary Ion	Secondary Ion
Internal Standards		
D_8-Naphthalene	136	68,137
D_{10}-Acenaphthene	164	162,165
D_{10}-Phenanthrene	188	94,189
D_{12}-Chrysene	240	120,241
D_{12}-Perylene	264	260,265
Laboratory Surrogates		
D_{10}-Fluorene	176	88,177
D_{10}-Pyrene	212	106,213
Field Surrogates		
D_{10}-Fluoranthene	212	106,213
D_{12}-Benzo(a)pyrene	264	132,265

TABLE 6. EXAMPLE OF CHARACTERISTIC IONS FOR COMMON PAHs

Analyte	Primary Ion	Secondary Ion(s)
Pyrene	202	101,203
Benz(a)anthracene	228	229,226
Chrysene	228	226,229
Benzo(a)pyrene	252	253,126
Benzo(b)fluoranthene	252	253,126
Benzo(k)fluoranthene	252	253,126
Benzo(g,h,i)perylene	276	138,277
Dibenz(a,h)anthracene	278	139,279
Anthracene	178	179,176
Phenanthrene	178	179,176
Acenaphthene	154	153,152
Acenaphthylene	152	151,153
Benzo(e)pyrene	252	253,126
Fluoranthene	202	101,203
Fluorene	166	165,167
Ideno(1,2,3-cd)pyrene	276	138,227
Naphthalene	128	129,127
Perylene	252	253,126
Coronene	300	150,301

TABLE 7. EXAMPLE OF RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF COMMON SEMI-VOLATILE COMPOUNDS

Semi-volatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Difference
Naphthalene	0.700	30	30
Acenaphthylene	1.300	30	30
Acenaphthene	0.800	30	30
Fluorene	0.900	30	30
Phenanthrene	0.700	30	30
Anthracene	0.700	30	30
Fluoranthene	0.600	30	30
Pyrene	0.600	30	30
Benz(a)anthracene	0.800	30	30
Chrysene	0.700	30	30
Benzo(b)fluoranthene	0.700	30	30
Benzo(k)fluoranthene	0.700	30	30
Benzo(a)pyrene	0.700	30	30
Indeno(1,2,3-cd)pyrene	0.500	30	30
Dibenz(a,h)anthracene	0.400	30	30
Benzo(g,h,i)perylene	0.500	30	30
Perylene	0.500	30	30
Coronene	0.700	30	30

TABLE 8. MINIMUM SAMPLING EQUIPMENT CALIBRATION AND ACCURACY REQUIREMENTS

Equipment	Acceptance limits	Frequency and method of measurement	Action if require-ments are not met
Sampler	Indicated flow rate = true flow rate, ±10%.	Calibrate with certified transfer standard on receipt, after maintenance on sampler, and any time audits or flow checks deviate more than ±10% from the indicated flow rate or ±10% from the design flow rate.	Recalibrate
Associated equipment			
Sampler on/off timer	±30 min/24 hour	Check at purchase and routinely on sample-recovery days	Adjust or replace
Elapsed-time meter	±30 min/24 hour	Compare with a standard time-piece of known accuracy at receipt and at 6-month intervals	Adjust or replace
Flowrate transfer standard (orifice device)	Check at receipt for visual damage	Recalibrate annually against positive displacement standard volume meter	Adopt new calibration curve

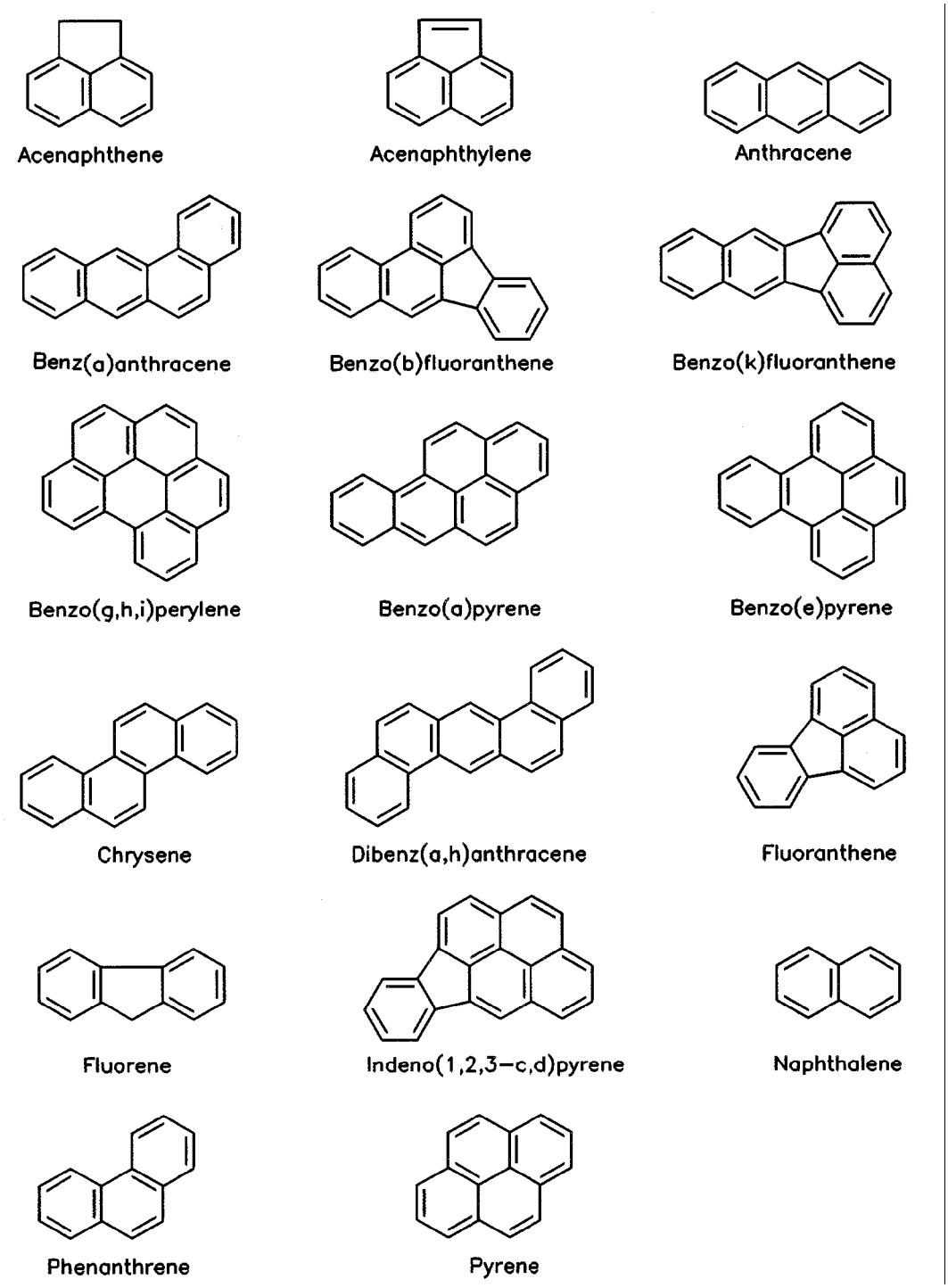


Figure 1. Ring structure of common PAHs.

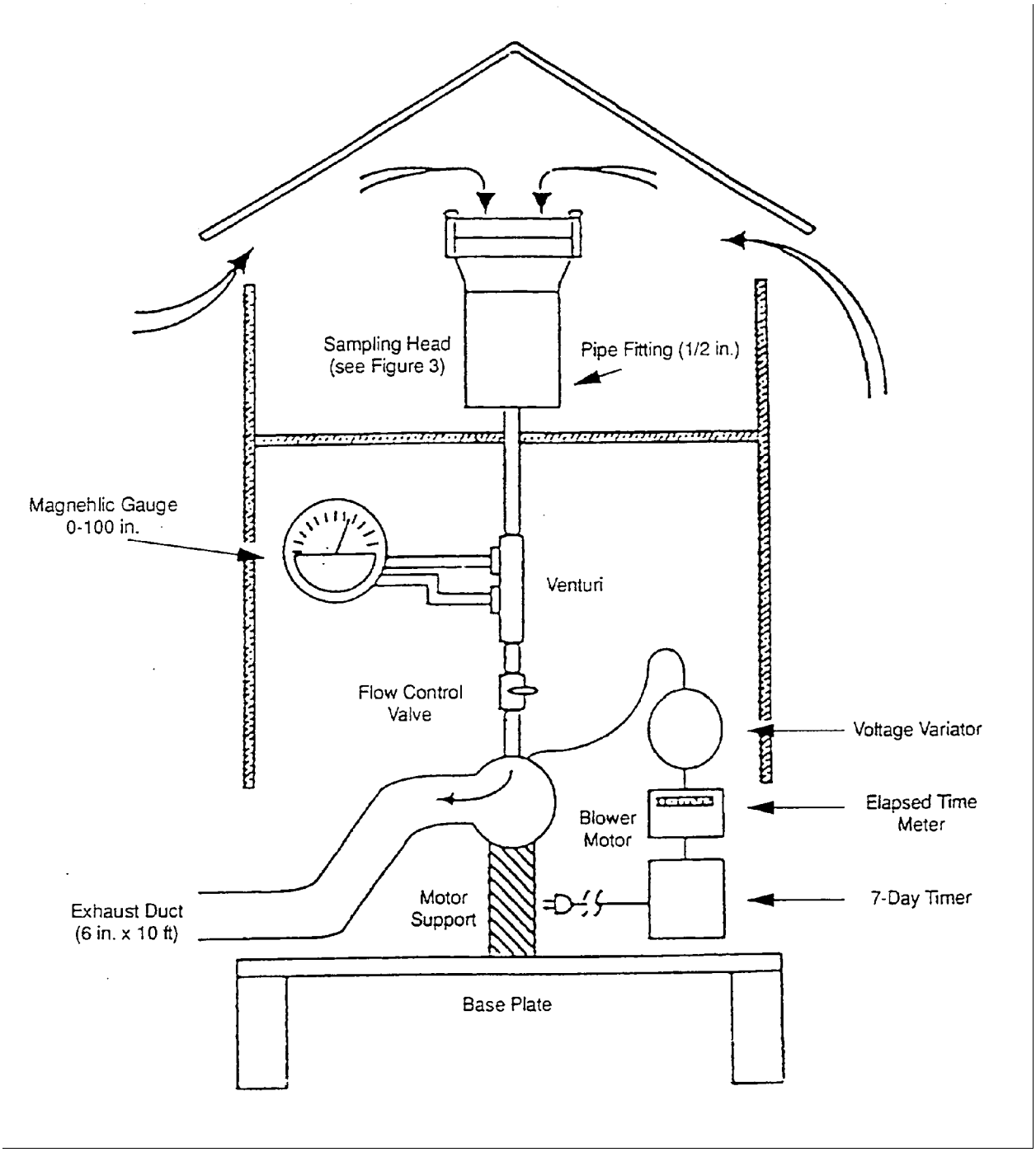


Figure 2. Typical high volume air sampler for PAHs.

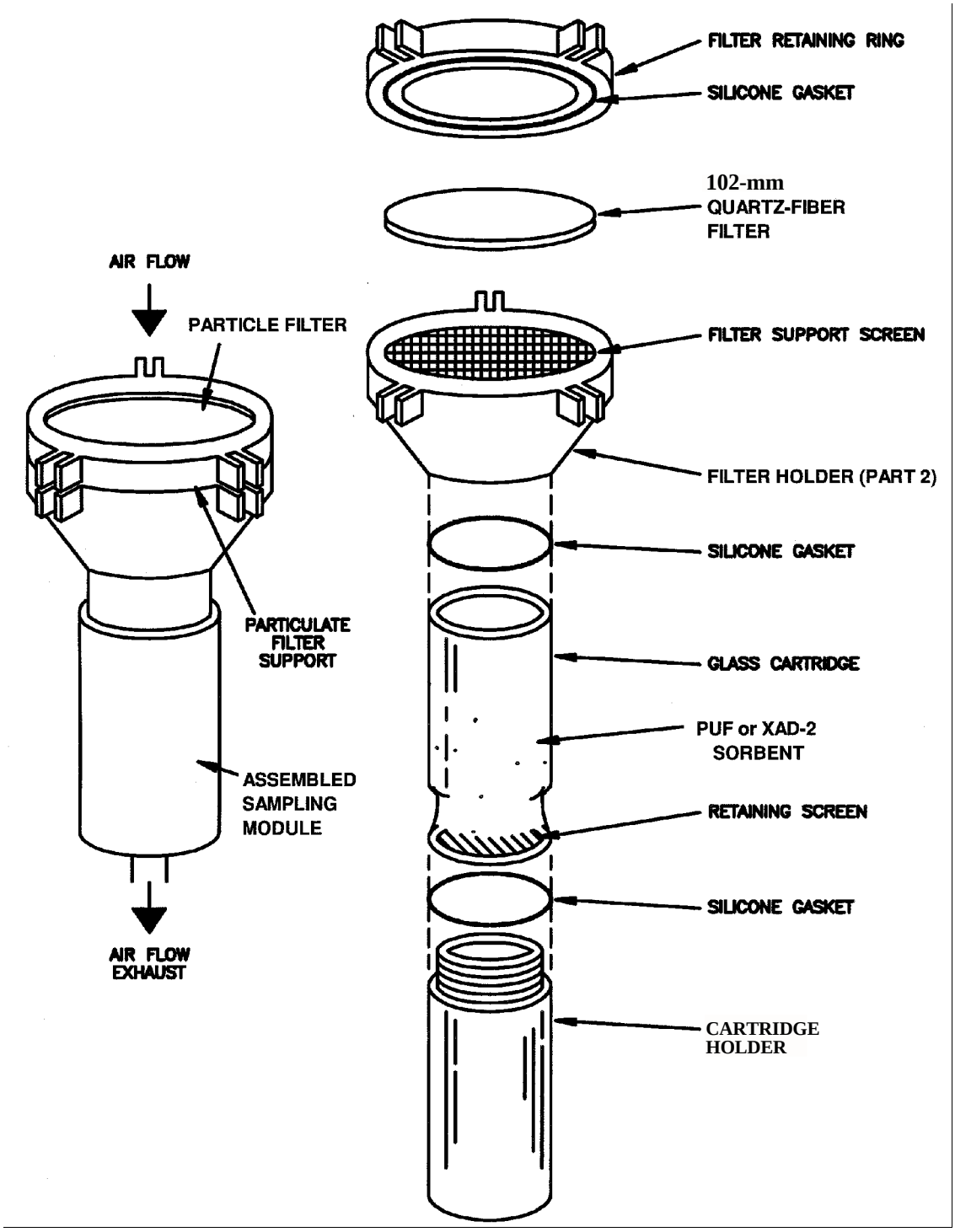


Figure 3. Typical absorbent cartridge assembly for sampling PAHs.

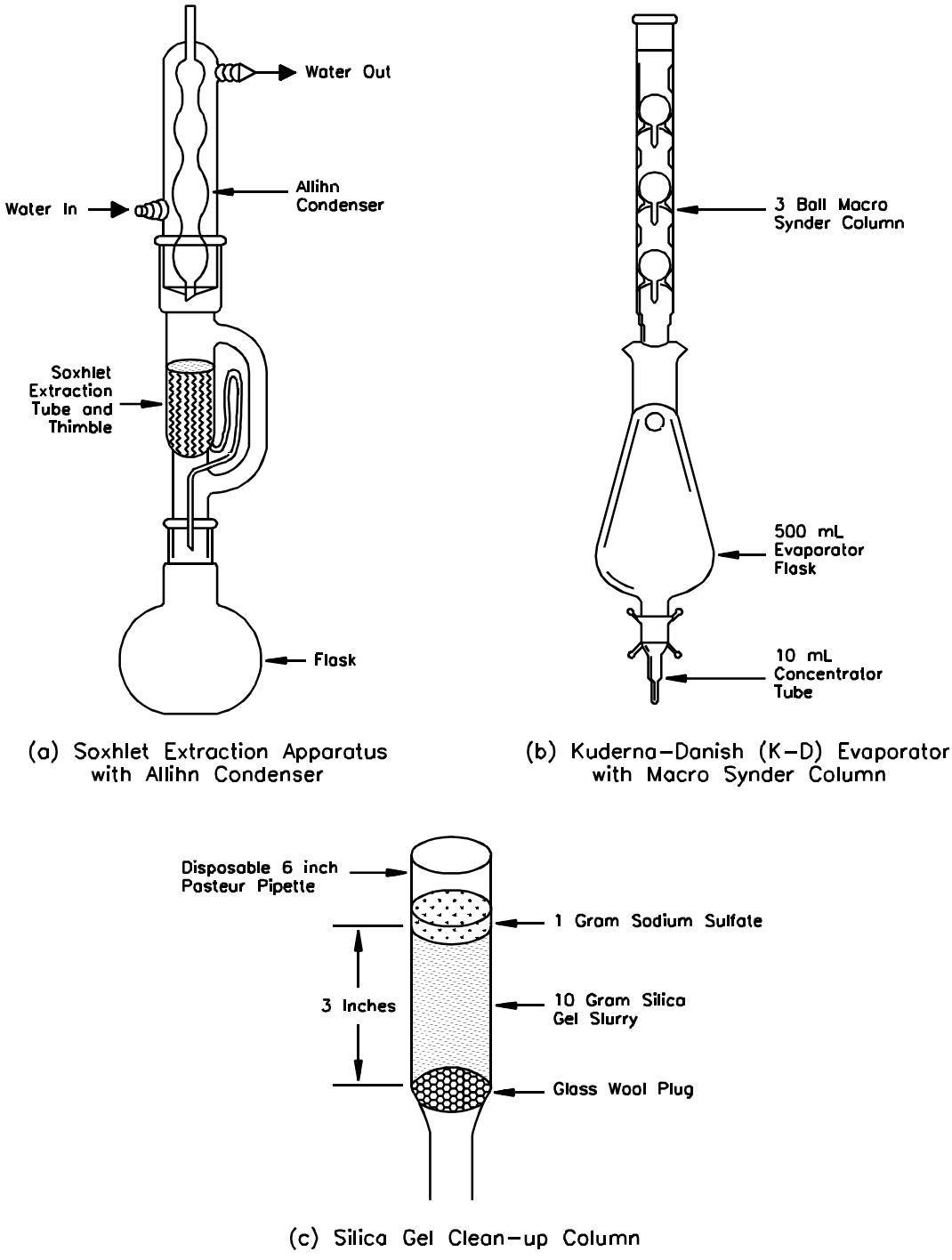
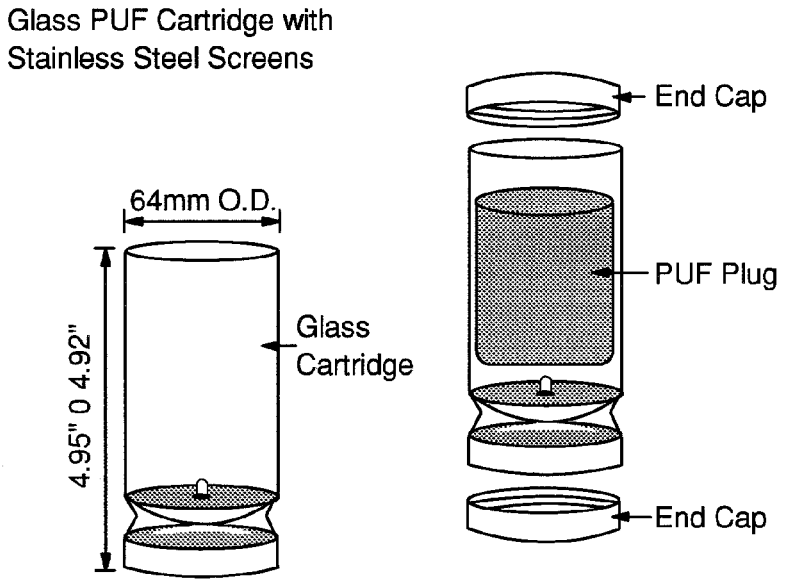
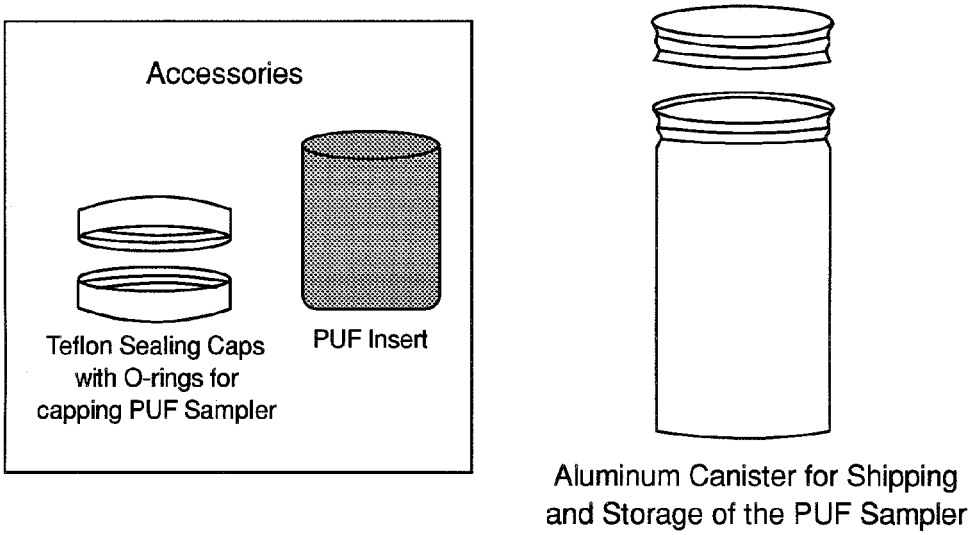


Figure 4. Apparatus used for sample clean-up and extraction.



5a. Glass PUF cartridge, plug, and end caps.



5b. PUF shipping container.

Figure 5. Glass PUF cartridge (5a) and shipping container (5b) for use with Compendium Method TO-13A.

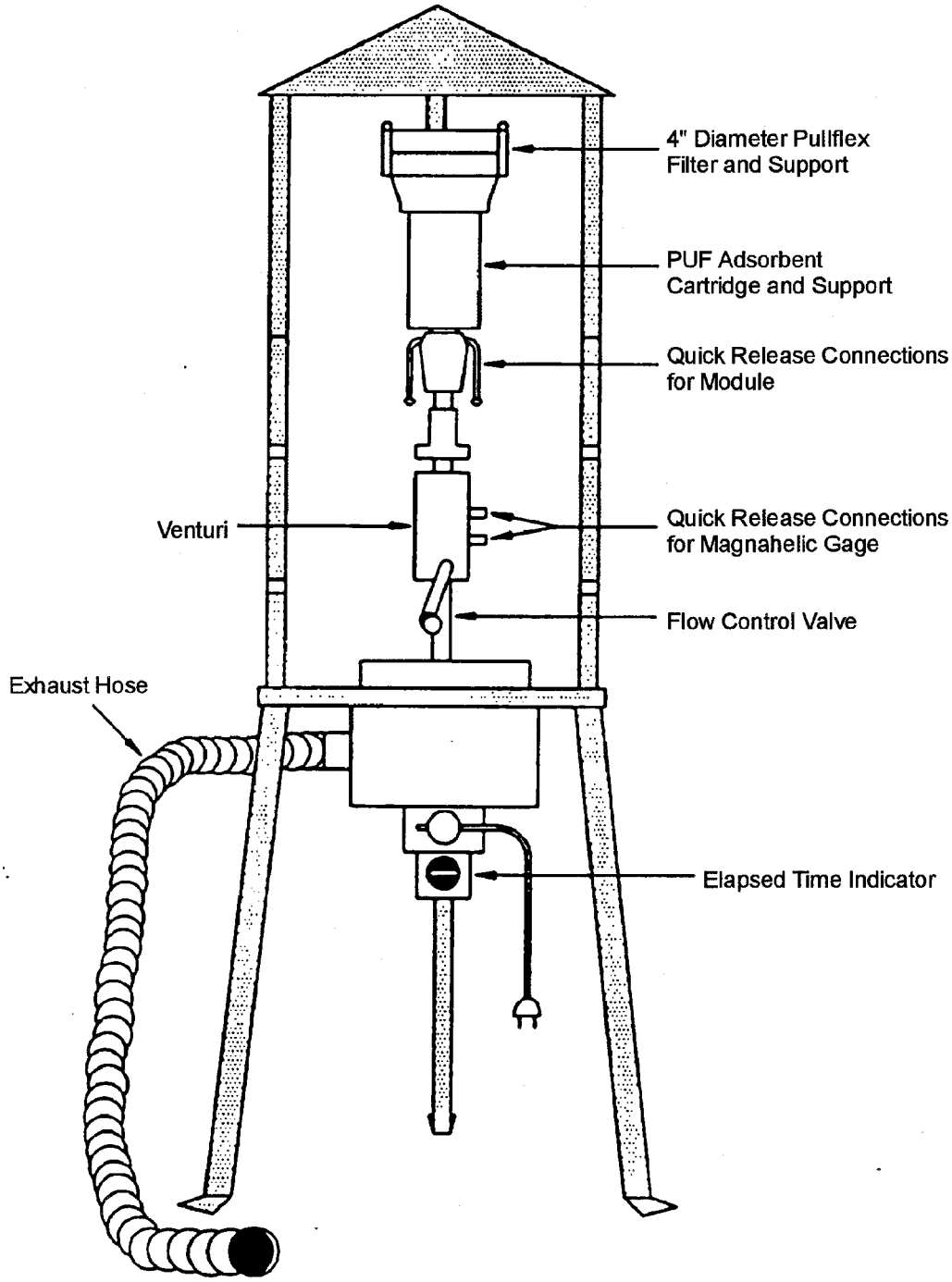


Figure 6. Example of a field portable high volume air sampler for sampling PAHs developed by EPA.

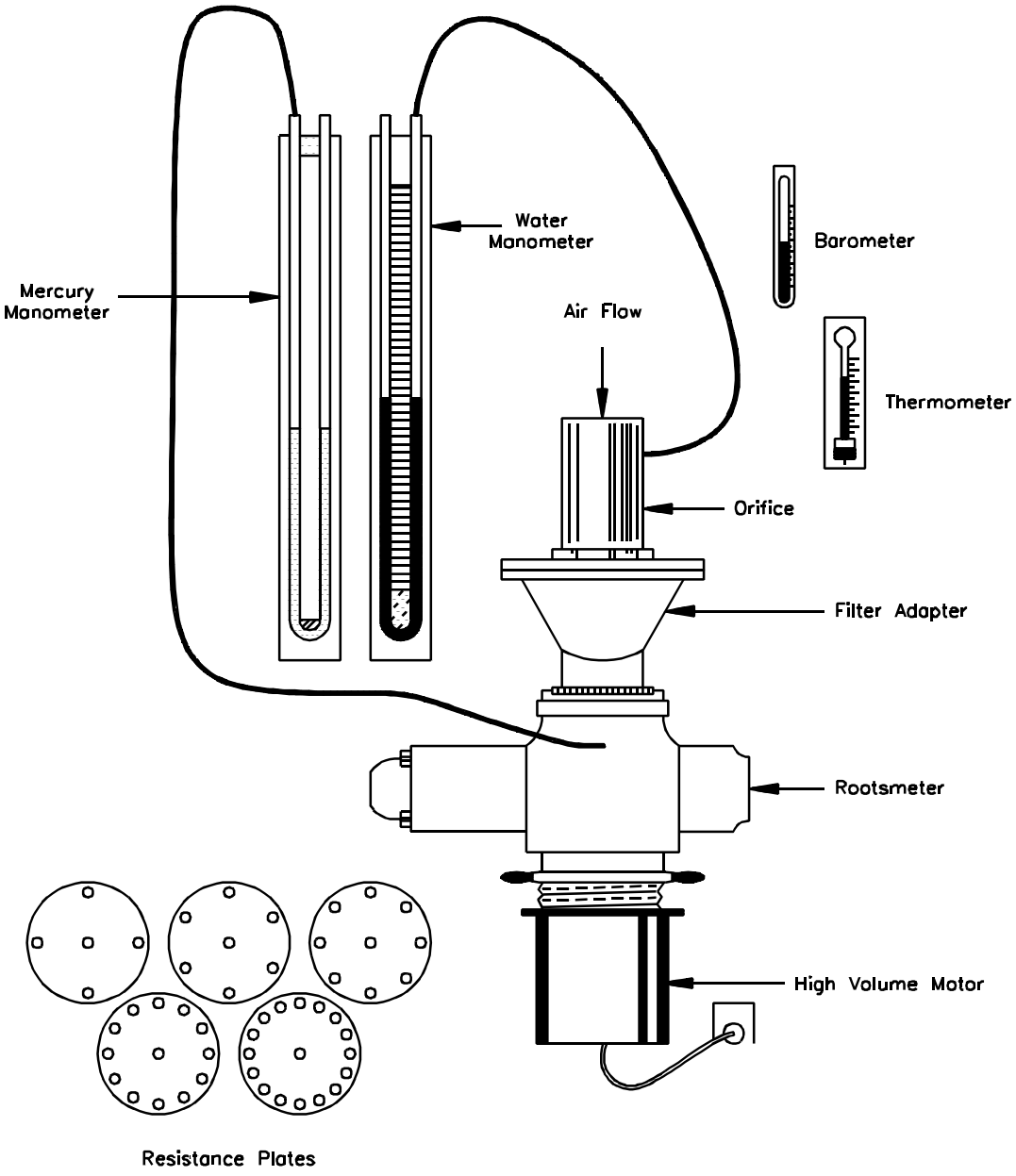


Figure 7. Positive displacement rootsmeter used to calibrate orifice transfer standard used in Compendium Method TO-13A.

COMPENDIUM METHOD TO-13A
ORIFICE CALIBRATION DATA SHEET

T_1 _____ Name _____

P_1 _____ mmHg Date _____

Orifice No. _____

Rootsmeter No. _____

Resistance Plants (No. of holes)	Air Volume Measured by Rootsmeter V_m		Standard Volume, V_{std} (std m^3)	Time for Air Volume to Pass Through Rootsmeter, θ (min)	Rootsmeter Pressure Differential, ΔP (mm Hg)	Pressure Drop Across Orifice, ΔH (in. H_2O)	x-Axis Standard Flowrate, Q_{std} (std m^3/min)	
	(R^3)	(m^3)						
5	200	5.66						
7	200	5.66						
10	300	8.50						
13	300	8.50						
18	300	8.50						

Factors: $(R^3)(0.02832\ \frac{m^3}{R^3}) = m^3$ and (in. Hg) $25.4\ (\frac{mm\ Hg}{in.\ Hg}) = mm\ Hg$

Calculation Equations:

1. $V_{std} = V_m\ (\frac{P_1 - \Delta P}{P_{std}})(\frac{T_{std}}{T_1})$

where:

$T_{std} = 296°K$

$P_{std} = 760.0$ mm Hg

2. $Q_{std} = \frac{V_{std}}{\theta}$

Figure 8. Example of a high-volume orifice calibration data sheet for Compendium Method TO-13A.

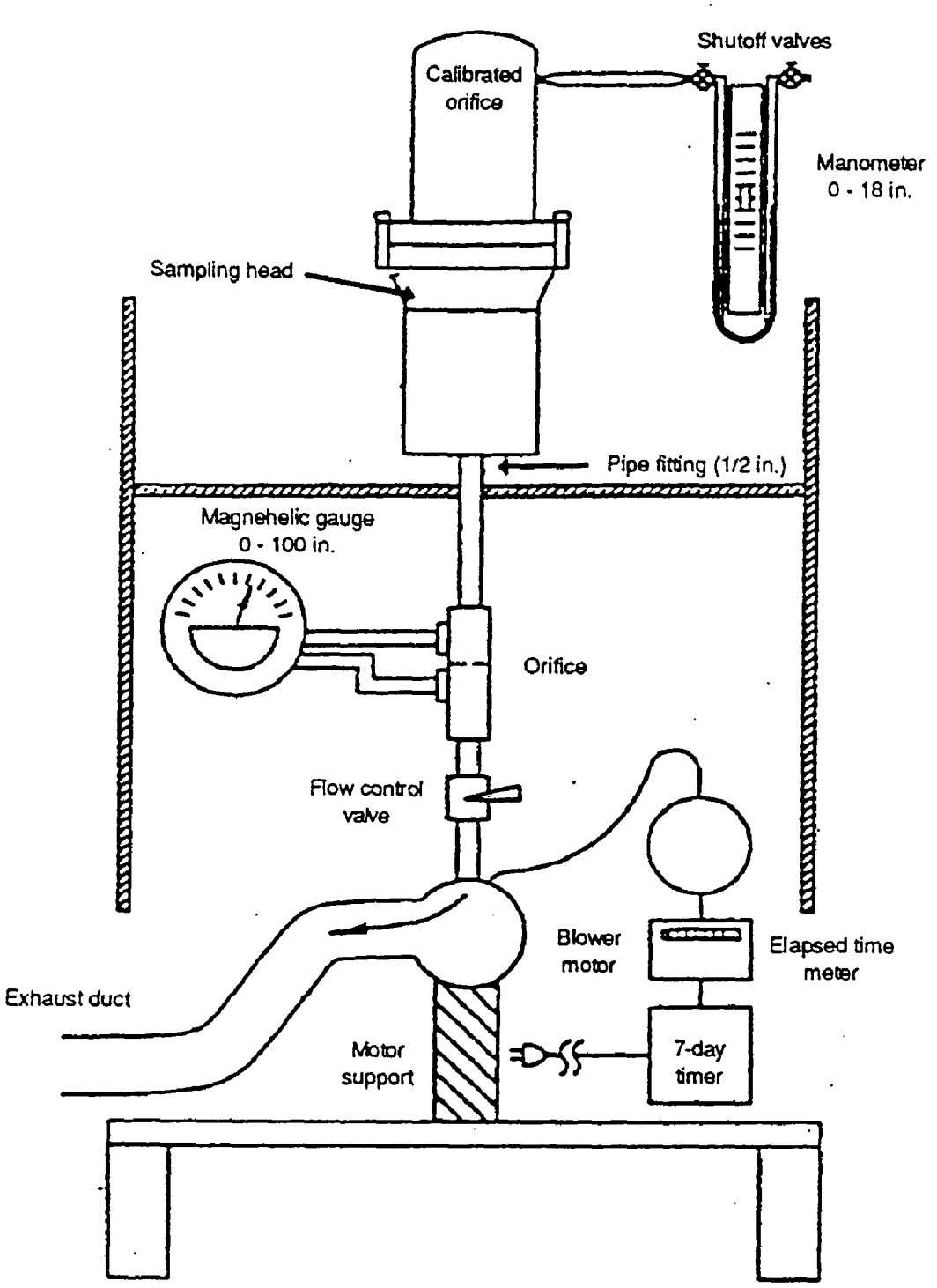


Figure 9. Typical field calibration configuration for Compendium Method TO-13A sampler.

FIELD CALIBRATION DATA SHEET FOR COMPENDIUM METHOD TO-13A PAH
SAMPLER CALIBRATION

Sampler ID: _____

Sampler Location: _____

Calibration Orifice ID: _____

Job No.: _____

High Volume Transfer Orifice Data:

Correlation Coefficient (CC1): _____ Slope (M1): _____

(CC2): _____ (M2): _____

Intercept (B1): _____

(B2): _____

Calibration Date: ___ Time: _____

Calibration Ambient Temperature: ___°F ___°C CALIBRATOR'S SIGNATURE

Calibration Ambient Barometric Pressure: ___ "Hg ___ mm Hg _____

Calibration set point (SP): _____

SAMPLER CALIBRATION

Actual values from calibration		Calibrated values		
Orifice manometer, inches (Y1)	Monitor magnehelic, inches (Y2)	Orifice manometer (Y3)	Monitor magnehelic (Y4)	Calculated value orifice flow, scm (X1)
	70			
	60			
	50			
	40			
	30			
	20			
	10			

Definitions

Y1 = Calibration orifice reading, in. H_2O

Y2 = Monitor magnehelic reading, in. H_2O

P_a = Barometric pressure actual, mm Hg

B1 = Manufacturer's Calibration orifice Intercept

M1 = Manufacturer's Calibration orifice manometer slope

Y3 = Calculated value for orifice manometer
= $\{Y1(Pa/760)[298/(Ta + 273)]\}^{½}$

Y4 = Calculated value for magnehelic
= $\{Y2(Pa/760)[298/(Ta + 273)]\}^{½}$

X1 = Calculated value orifice flow, scm
= (Y3 - B1)/M1

P_{std} = Barometric pressure standard, 760 mm Hg

T_a = Temperature actual, °C

T_{std} = Temperature standard, 25°C

Figure 10. Typical orifice transfer field calibration data sheet for Compendium Method TO-13A.

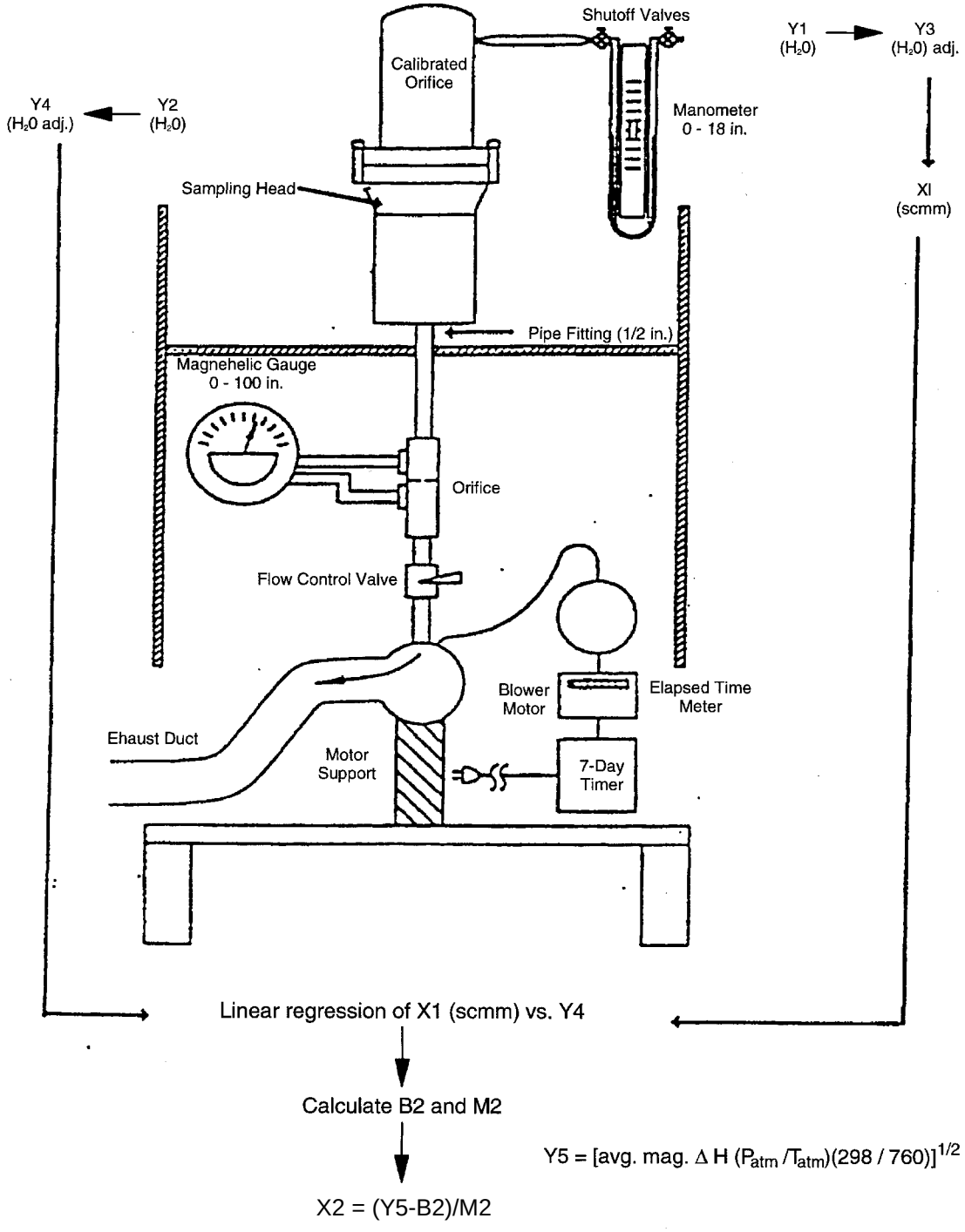


Figure 11. Example of relationship between orifice transfer standard and flow rate through Compendium Method TO-13A sampler.

COMPENDIUM METHOD TO-13A
FIELD TEST DATA SHEET
GENERAL INFORMATION

- **Sampler I.D. No.:** _____
- **Lab PUF Sample No.:** _____
- **Sample location:** _____
  _____
  _____
- **Operator:** _____
- **Other:** _____
  _____
  _____

- **PUF Cartridge Certification Date:** _____
- **Date/Time PUF Cartridge Installed:** _____
- **Elapsed Timer:** _____
  Start _____
  Stop _____
  Diff. _____
- **Sampling**

  M1 _____ **B1** _____
  M2 _____ **B2** _____

	Start	Stop
• Barometric pressure ("Hg)	_____	_____
• Ambient Temperature (°F)	_____	_____
• Rain	Yes _____ No _____	Yes _____ No _____

- **Sampling time**
  Start _____
  Stop _____
  Diff. _____

- **Audit flow check within ±10 of set point**
  _____ **Yes**
  _____ **No**

TIME	TEMP	BAROMETRIC PRESSURE	MAGNEHELIC READING	CALCULATED FLOW RATE (std. m^3)	READ BY
Avg.					

- Comments

_____
_____
_____

Figure 12. Example of typical Compendium Method TO-13A field test data sheet (FTDS).

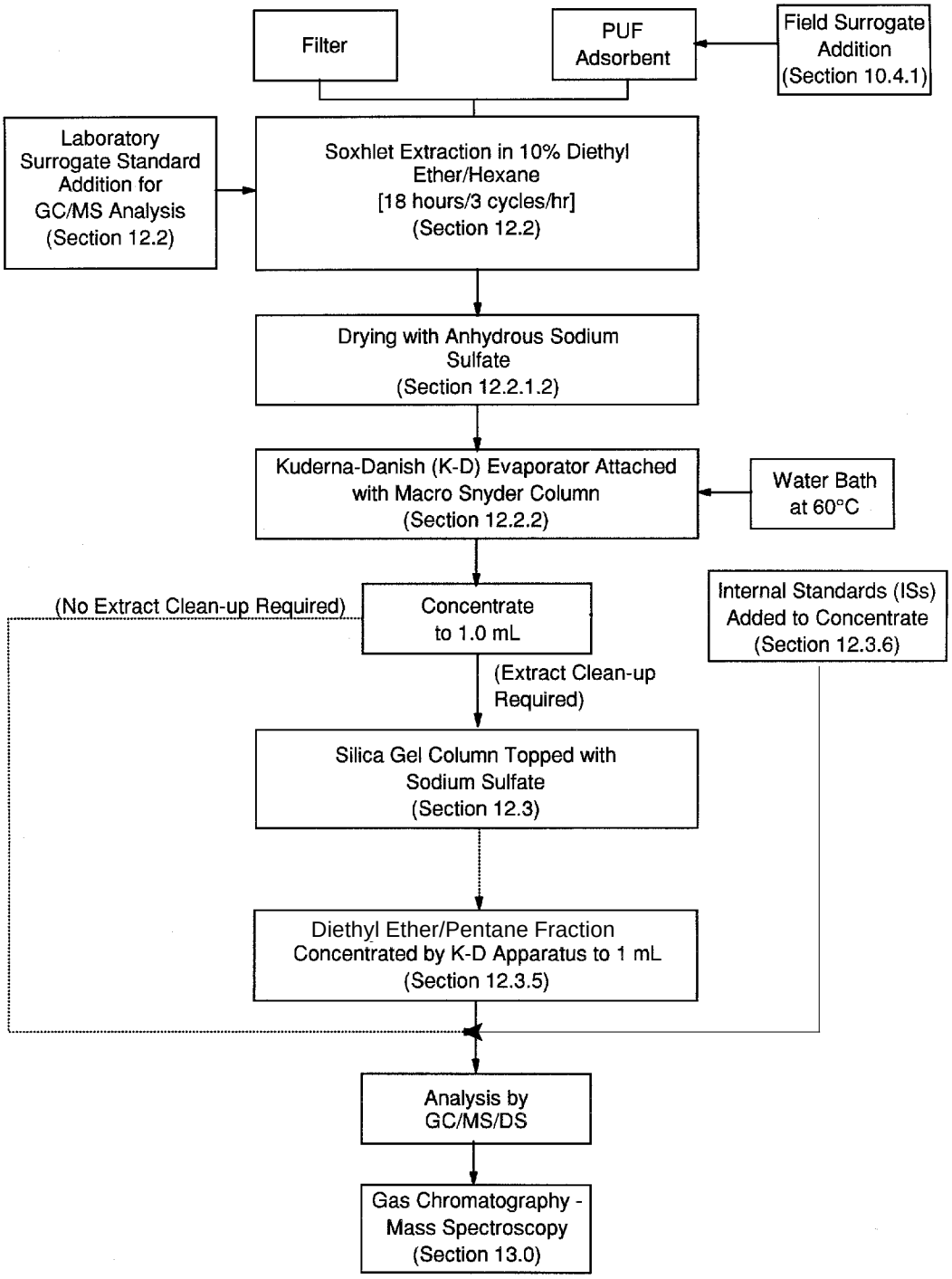


Figure 13. Sample clean-up, concentration, separation and analysis sequence for common PAHs.
[Note: XAD-2 sequence is similar to PUF except methylene chloride is the solvent.]

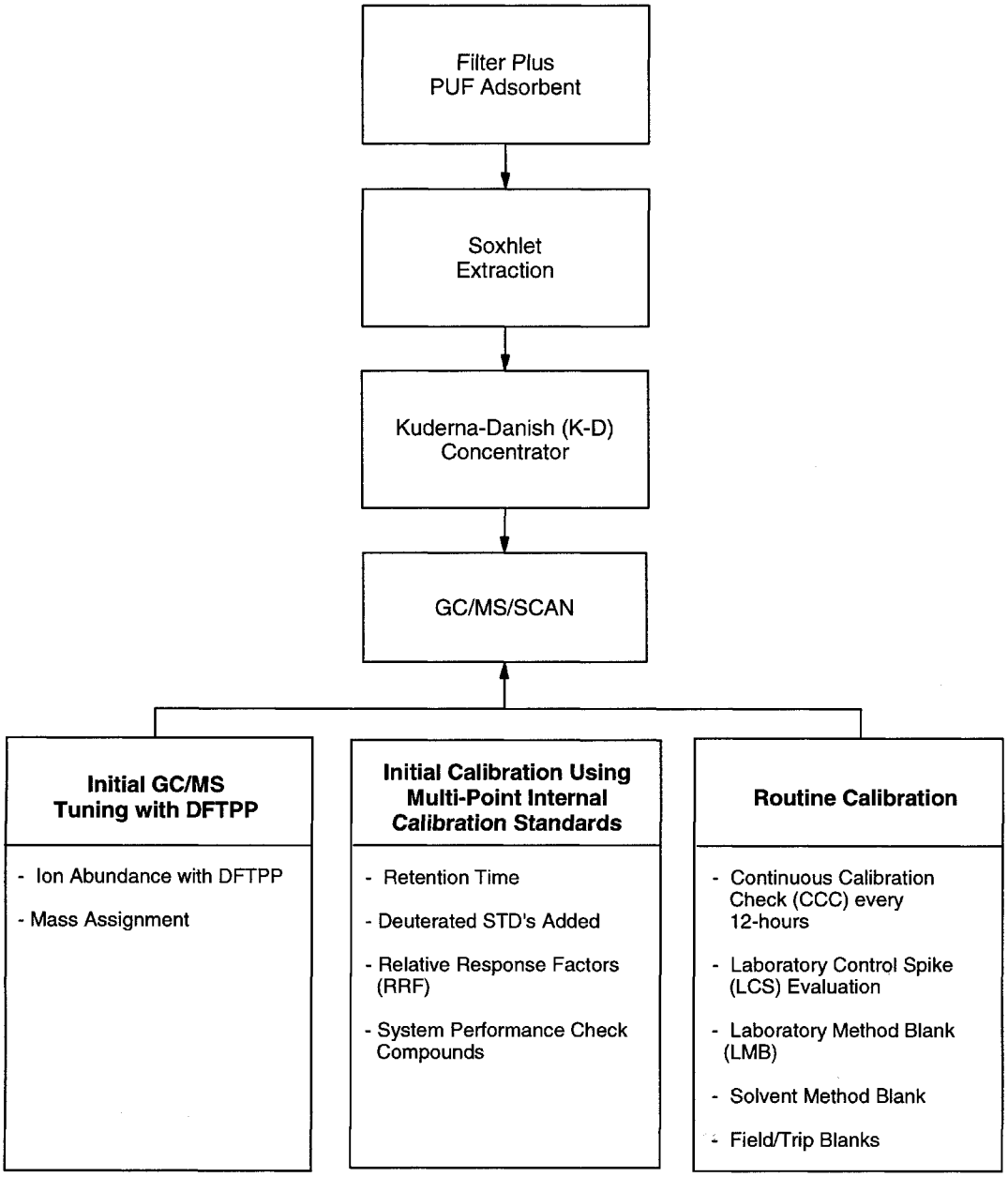


Figure 14. Typical quality assurance specifications for GC/MS/DS operation.

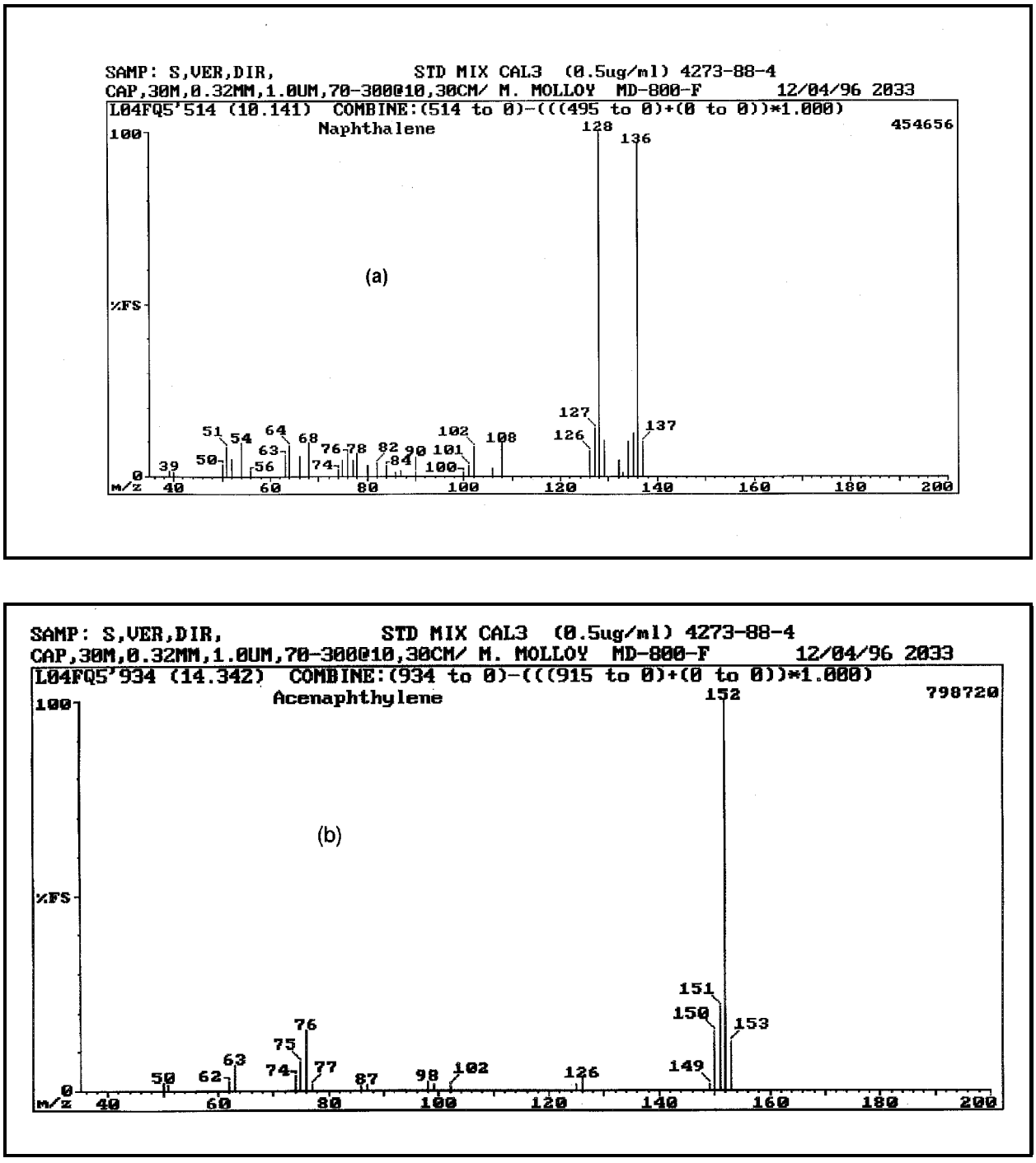
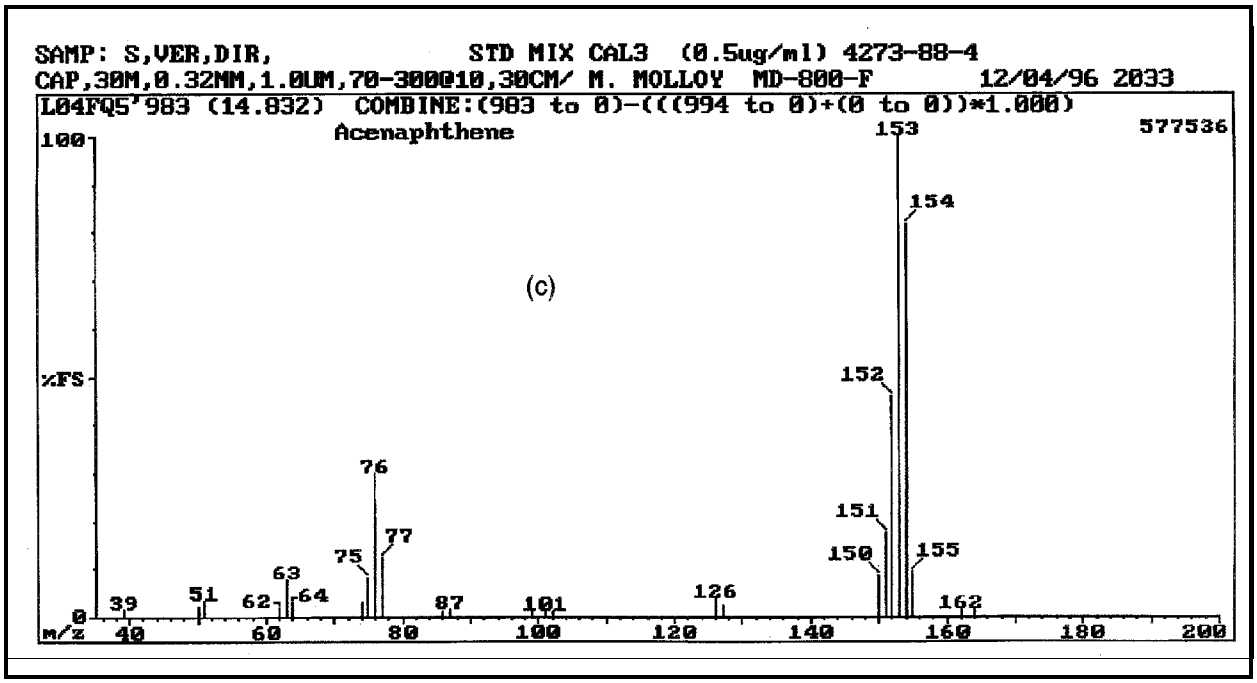


Figure 15. Mass spectra of Compendium Method TO-13A compounds for (a) naphthalene and (b) acenaphthylene.



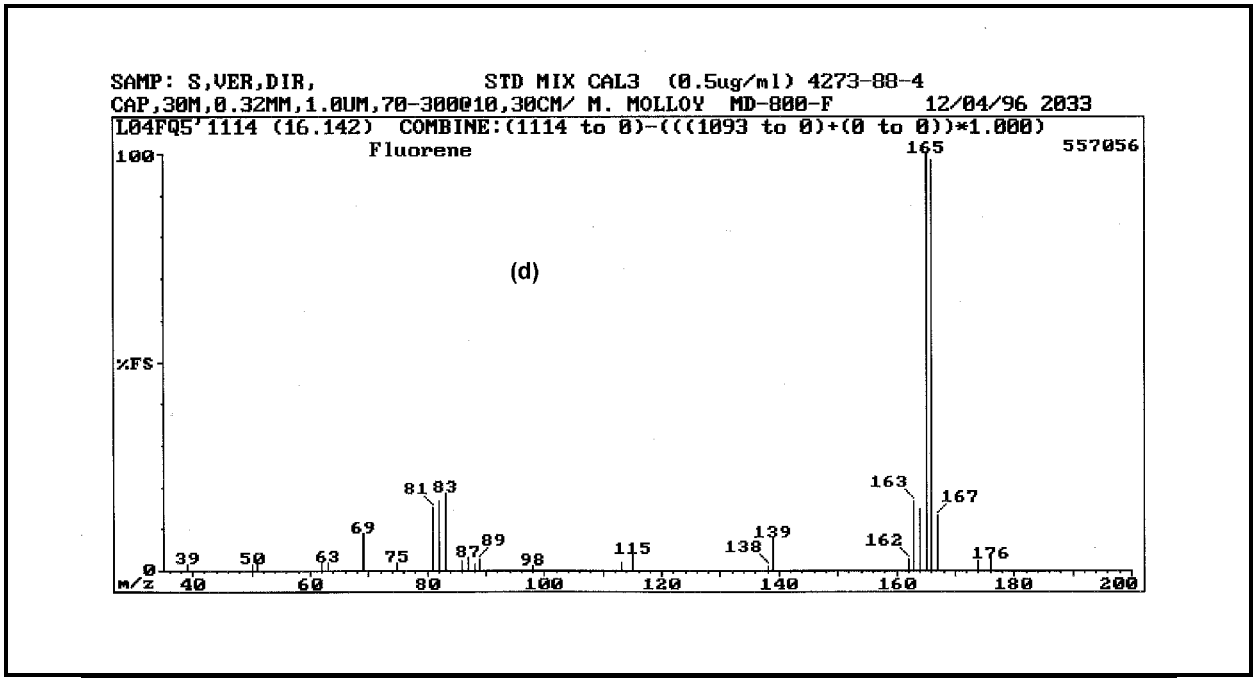
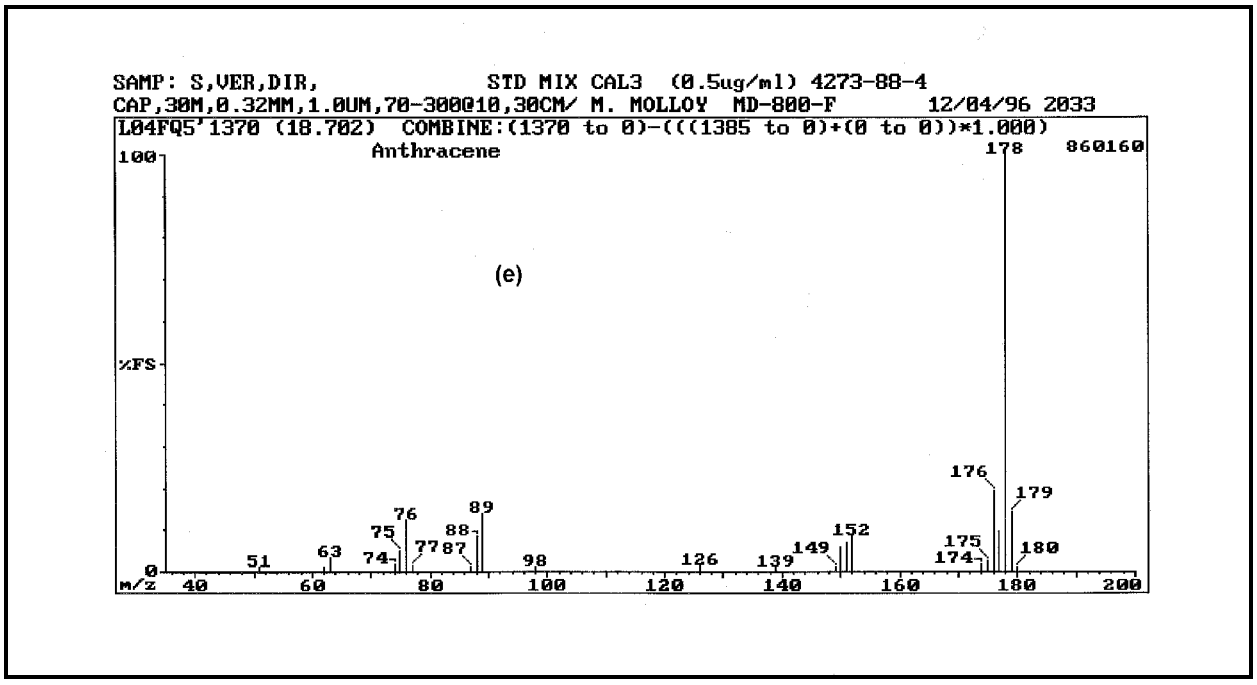


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (c) acenaphthene and (d) fluorene.



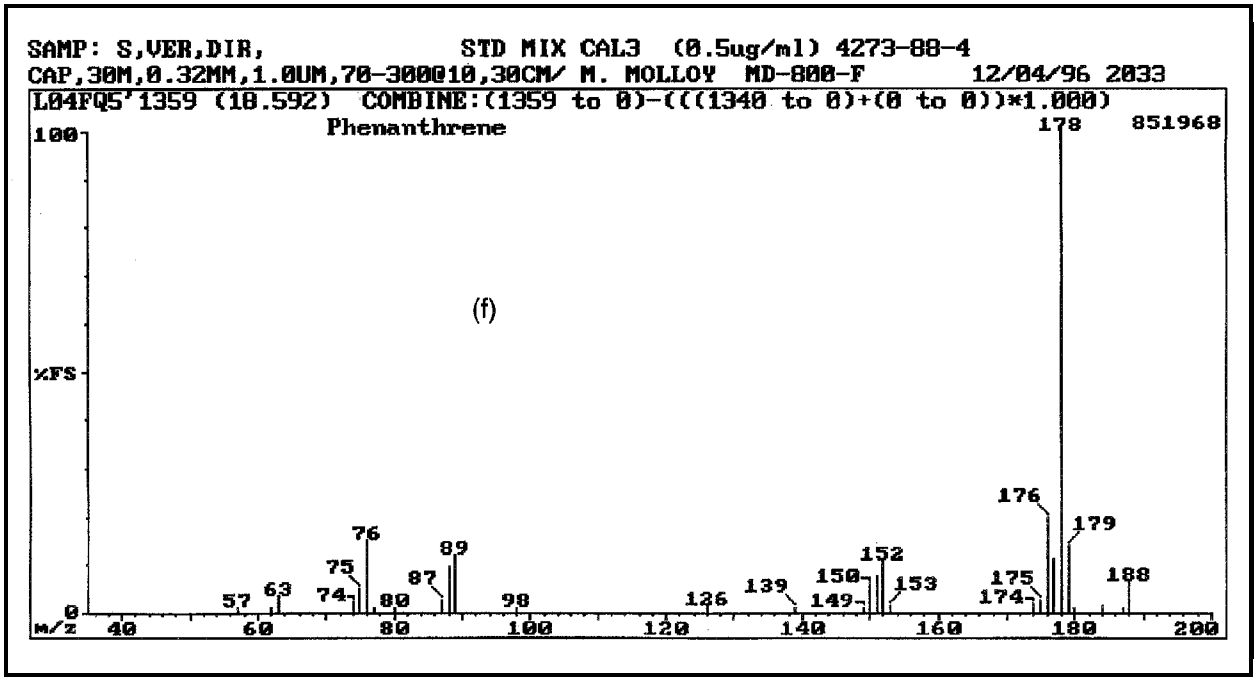
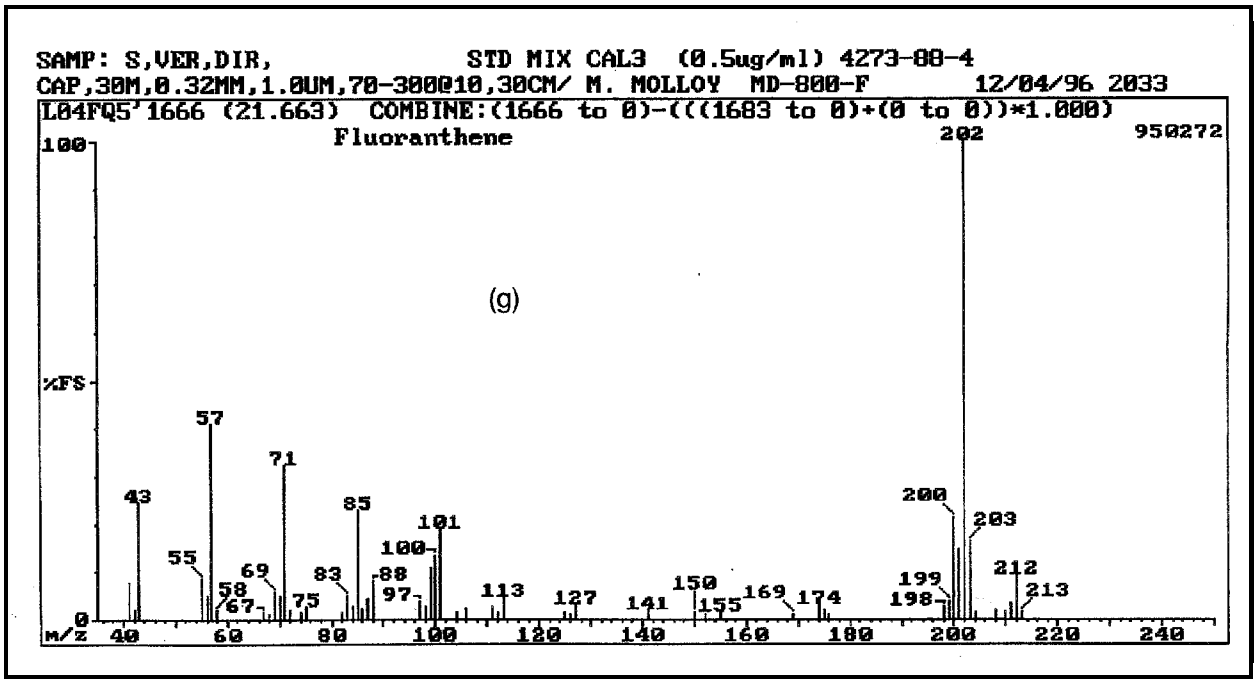


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (e) anthracene and (f) phenanthrene.



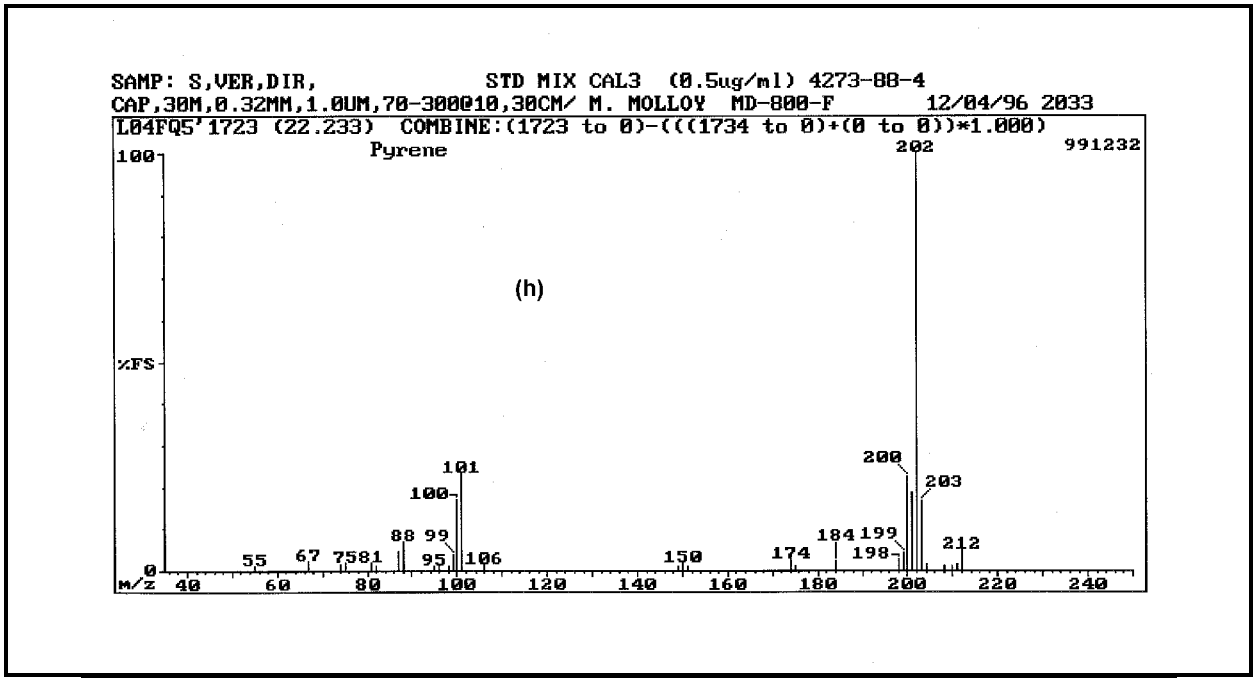


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (g) fluoranthene and (h) pyrene.

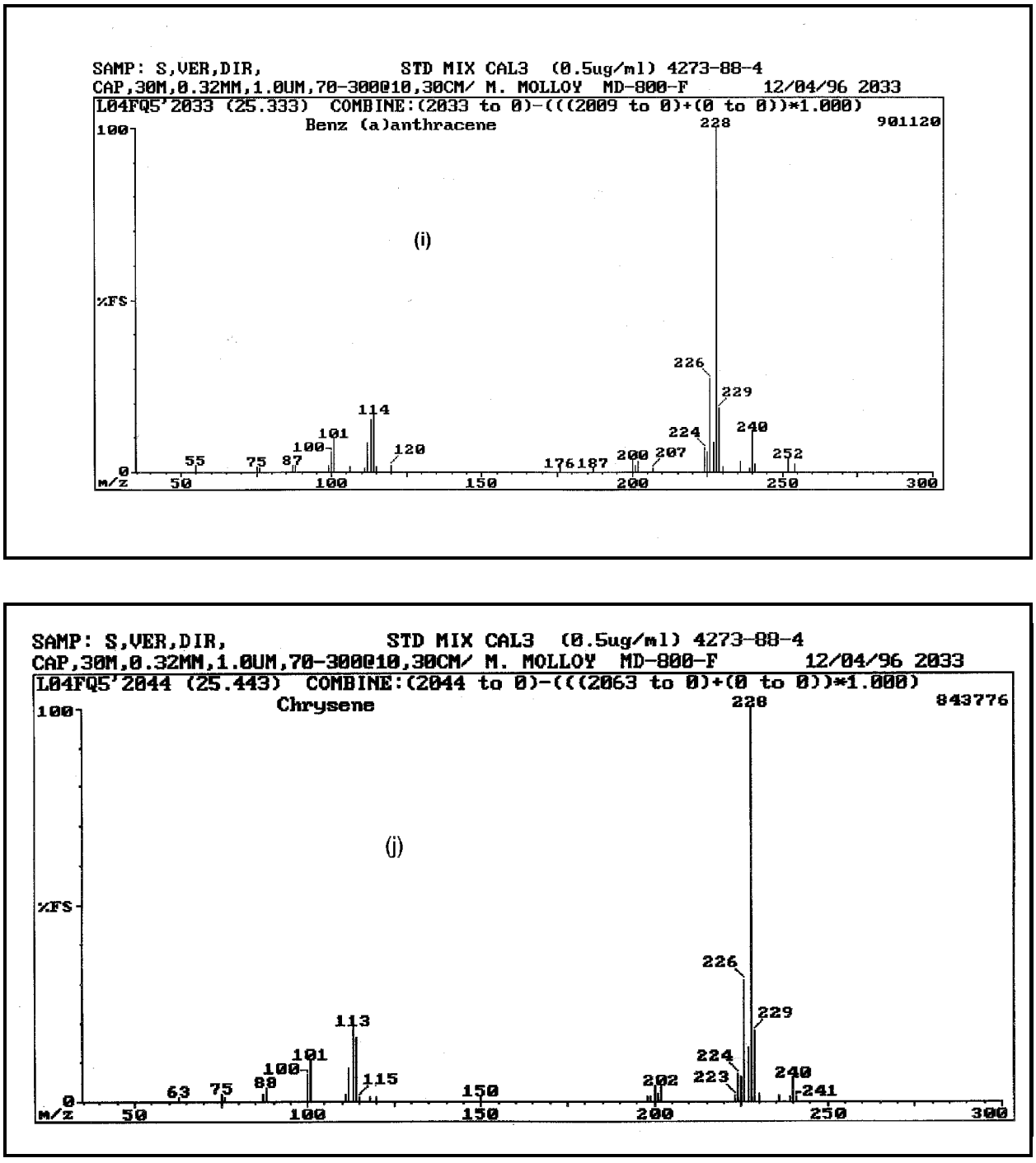
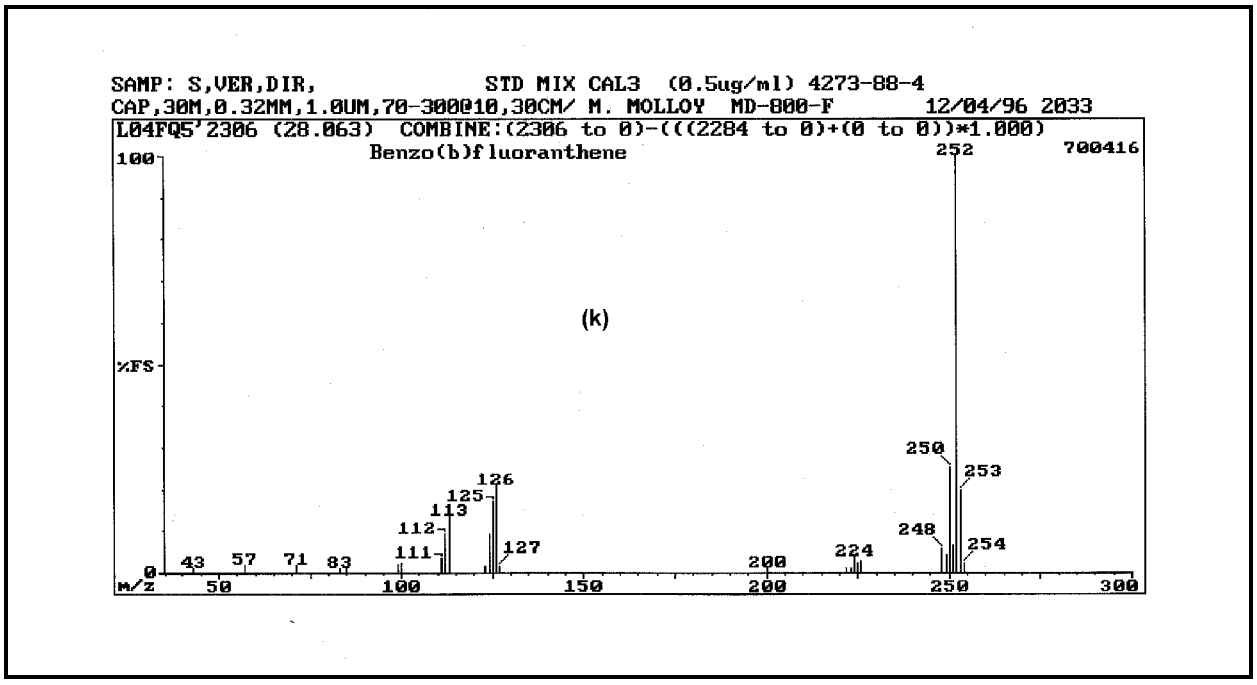


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (i) benz(a)anthracene and (j) chrysene.



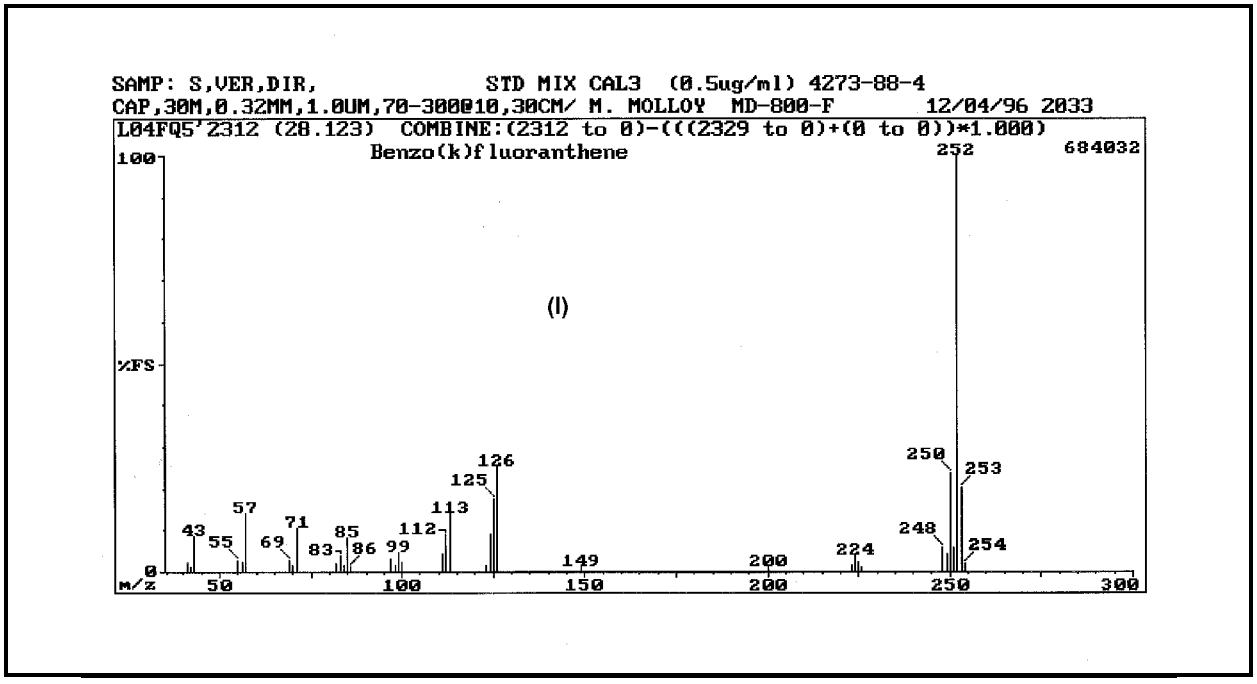
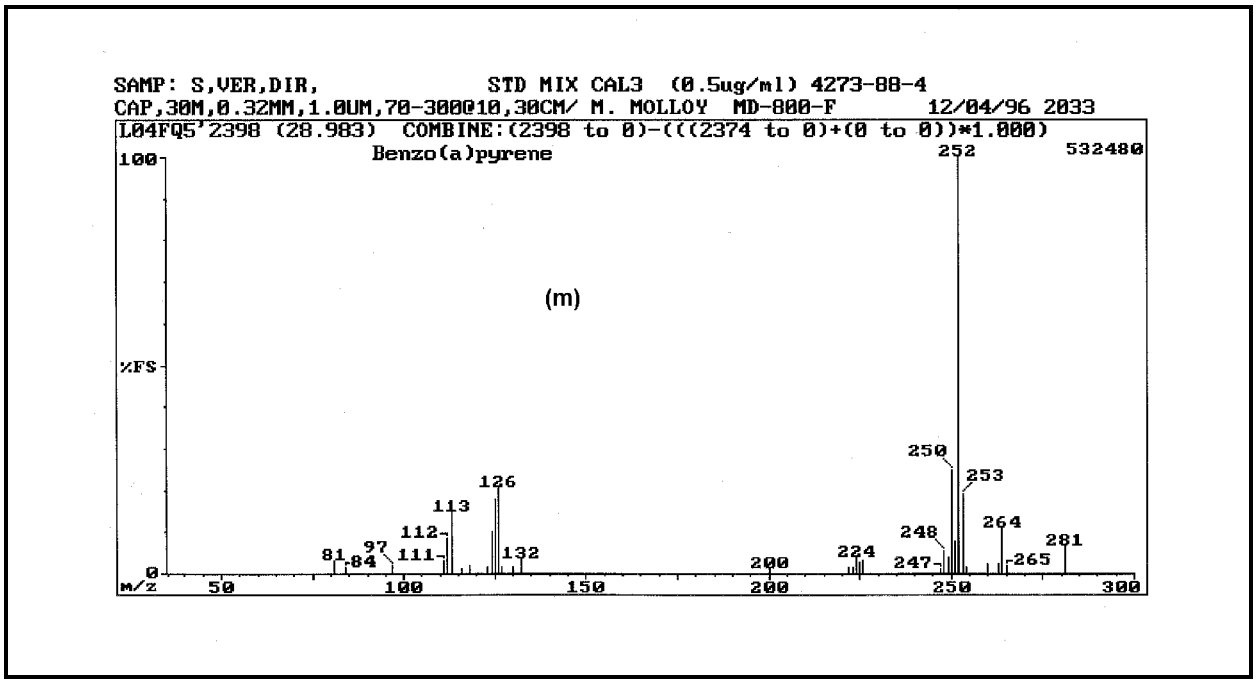


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (k) benzo(b)fluoranthene and (l) benzo(k)fluoranthene.



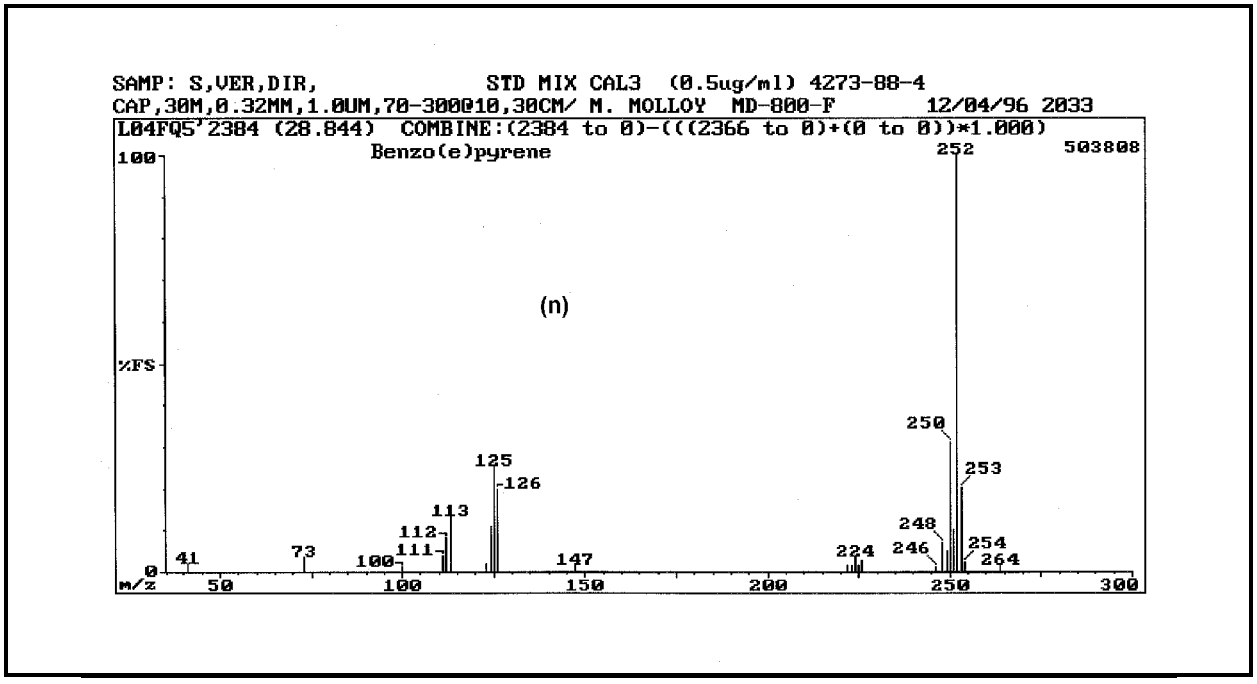
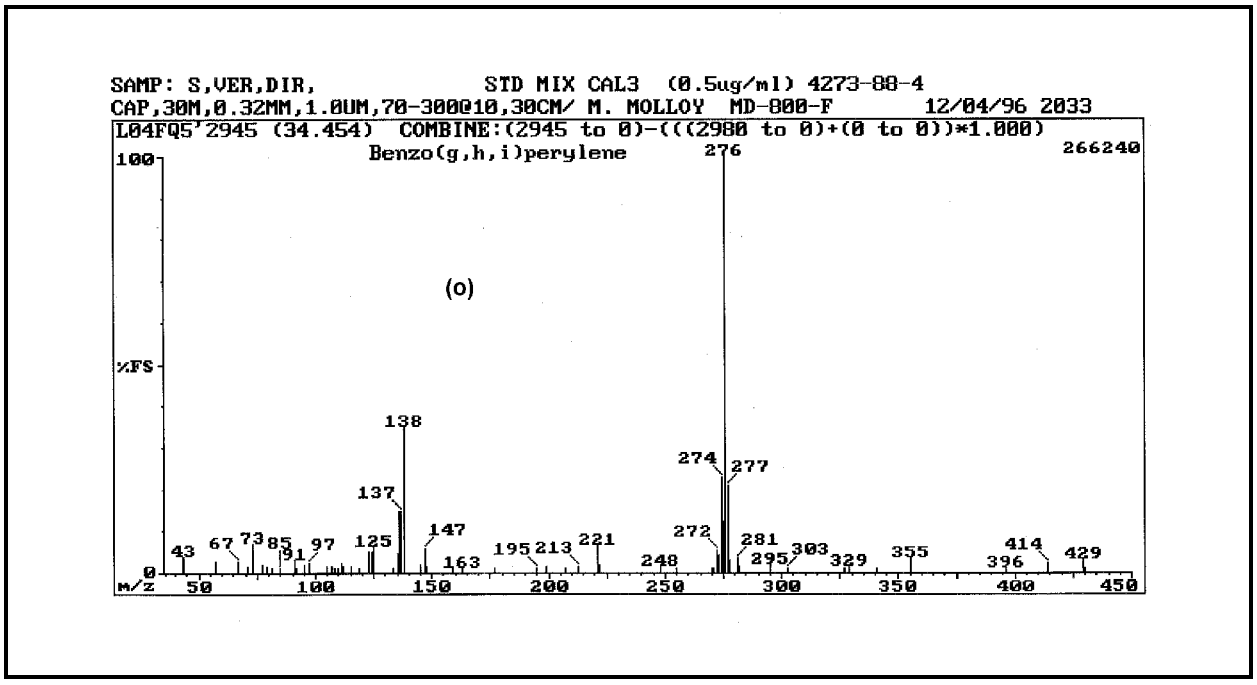


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (m) benzo(a)pyrene and (n) benzo(e)pyrene.



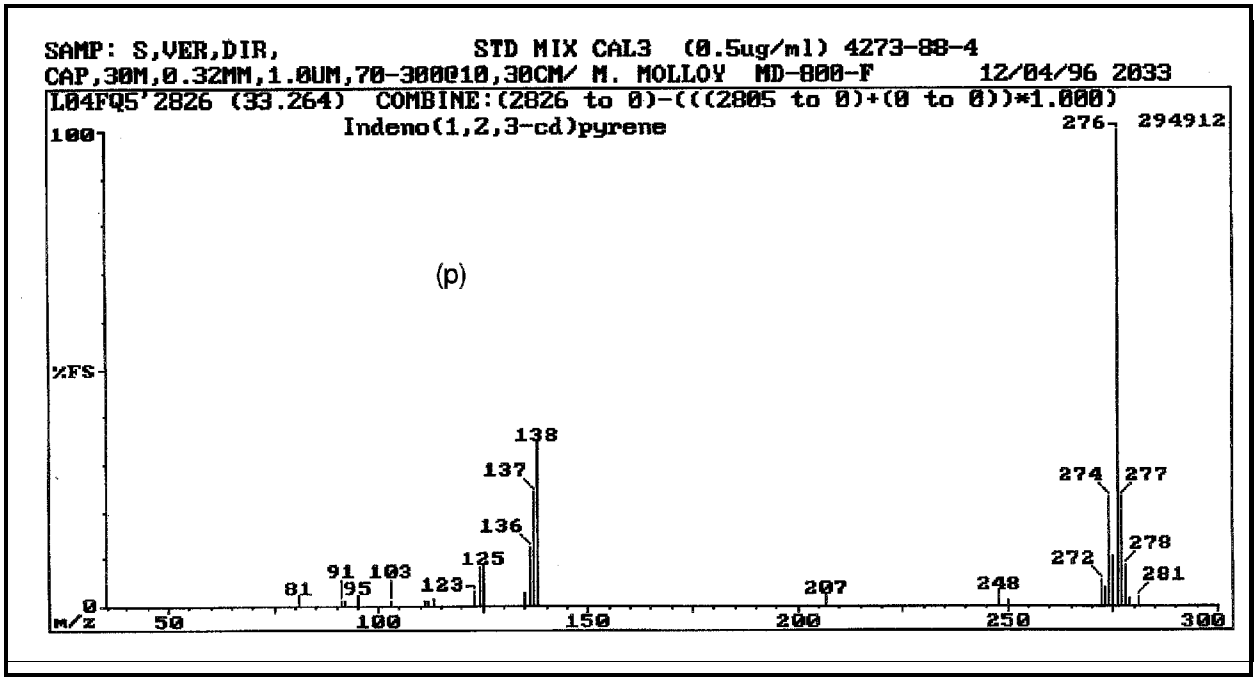


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (o) benzo(g,h,i)perylene and (p) indeno(1,2,3-cd)pyrene.

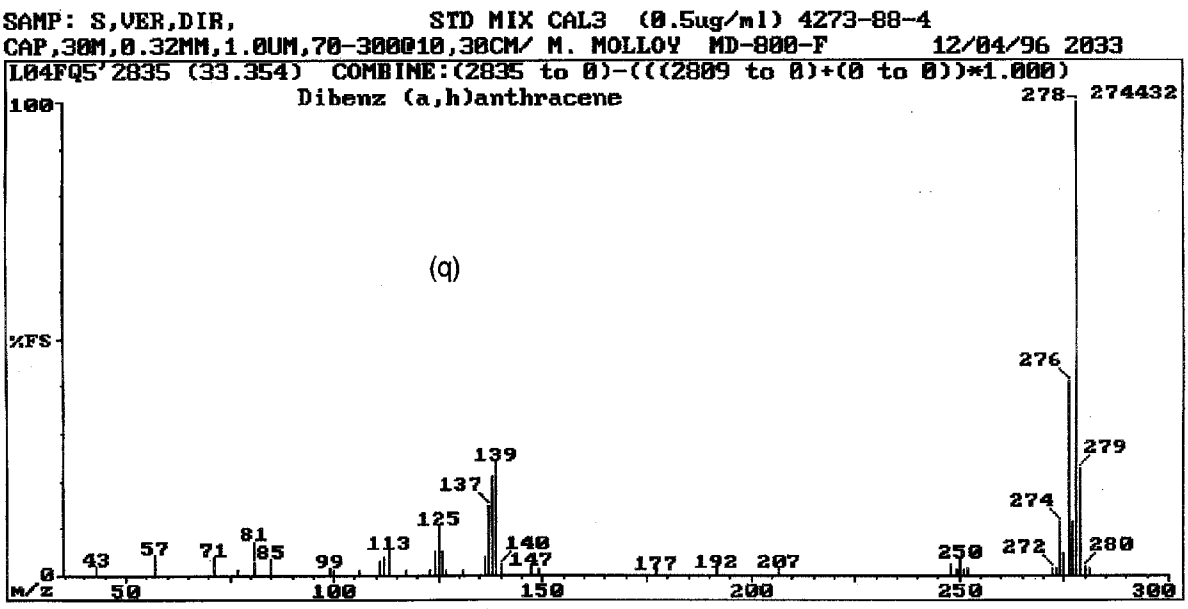


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (q) dibenz(a,h)anthracene.

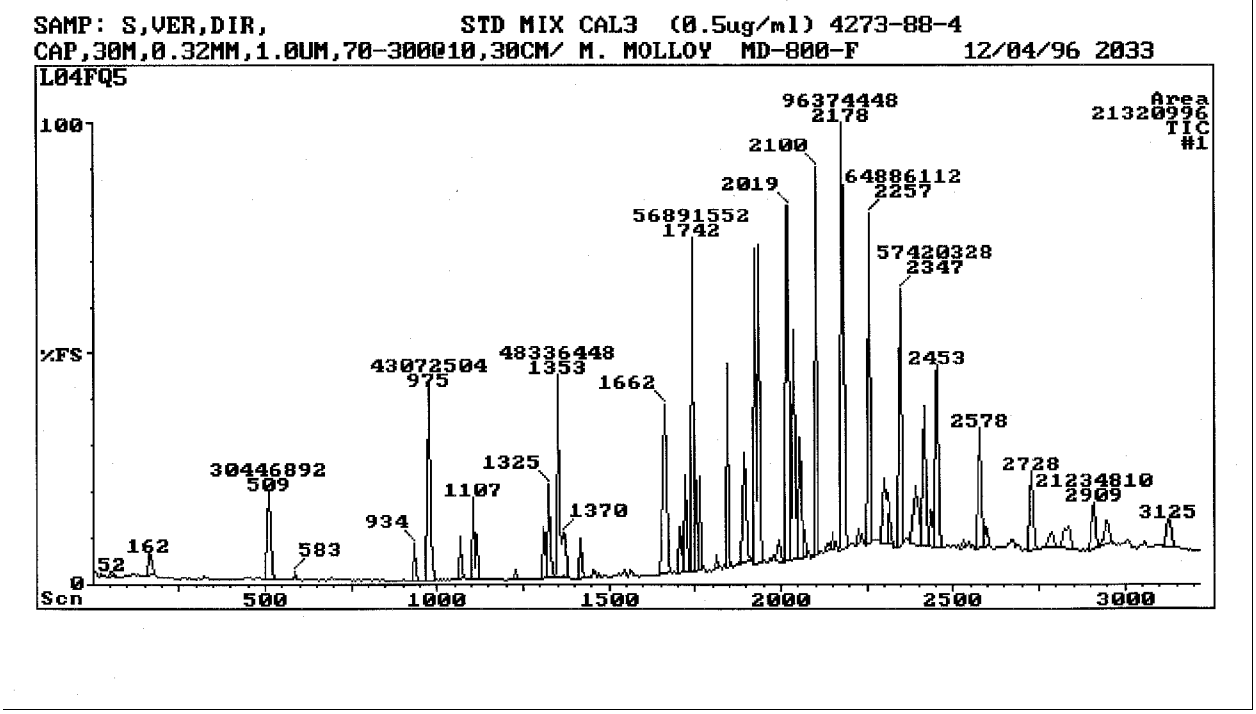


Figure 16. Total ion chromatogram (TIC) of Compendium Method TO-13A target PAHs.

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EPA/625/R-96/010b

Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air

Second Edition

Compendium Method TO-9A

Determination Of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins And Dibenzofurans In Ambient Air

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

January 1999

Method TO-9A
Acknowledgements

This Method was prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition* (EPA/625/R-96/010b), which was prepared under Contract No. 68-C3-0315, WA No. 3-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John Burckle, and Scott Hedges, Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA Office of Research and Development, were responsible for overseeing the preparation of this method. Additional support was provided by other members of the Compendia Workgroup, which include:

- John O. Burckle, U.S. EPA, ORD, Cincinnati, OH
- James L. Cheney, Corps of Engineers, Omaha, NB
- Michael Davis, U.S. EPA, Region 7, KC, KS
- Joseph B. Elkins Jr., U.S. EPA, OAQPS, RTP, NC
- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Justice A. Manning, U.S. EPA, ORD, Cincinnati, OH
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- Heidi Schultz, ERG, Lexington, MA
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Method TO-9 was originally published in March of 1989 as one of a series of peer reviewed methods in the second supplement to *"Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air,"* EPA 600/4-89-018. In an effort to keep these methods consistent with current technology, Method TO-9 has been revised and updated as Method TO-9A in this Compendium to incorporate new or improved sampling and analytical technologies.

This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

Finally, recognition is given to Frances Beyer, Lynn Kaufman, Debbie Bond, Cathy Whitaker, and Kathy Johnson of Midwest Research Institute's Administrative Services staff whose dedication and persistence during the development of this manuscript has enabled it's production.

DISCLAIMER

This Compendium has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Method TO-9A

Determination Of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins And Dibenzofurans In Ambient Air

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TABLE OF CONTENTS (continued)

METHOD TO-9A

Determination Of Polychlorinated, Polybrominated And Brominated/Chlorinated Dibenzo-p-Dioxins And Dibenzofurans In Ambient Air

1. Scope

1.1 This document describes a sampling and analysis method for the quantitative determination of polyhalogenated dibenzo-p-dioxins and dibenzofurans (PHDDs/PHDFs) in ambient air, which include the polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs/PCDFs), polybrominated dibenzo-p-dioxins and dibenzofurans (PBDDs/PBDFs), and bromo/chloro dibenzo-p-dioxins and dibenzofurans (BCDDs/BCDFs). The method uses a high volume air sampler equipped with a quartz-fiber filter and polyurethane foam (PUF) adsorbent for sampling 325 to 400 m^3 ambient air in a 24-hour sampling period. Analytical procedures based on high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS) are used for analysis of the sample.

1.2 The sampling and analysis method was evaluated using mixtures of PHDDs and PHDFs, including the 2,3,7,8-substituted congeners (1,2). It has been used extensively in the U.S. Environmental Protection Agency (EPA) ambient air monitoring studies (3,4) for determination of PCDDs and PCDFs.

1.3 The method provides accurate quantitative data for tetra- through octa-PCDDs/PCDFs (total concentrations for each isomeric series).

1.4 Specificity is attained for quantitative determination of the seventeen 2,3,7,8-substituted PCDDs/PCDFs and specific 2,3,7,8-substituted PBDD/PBDF and BCDD/BCDF congeners.

1.5 Minimum detection limits (MDLs) in the range of 0.01 to 0.2 picograms/$meter^3$ (pg/m^3) can be achieved for these compounds in ambient air.

1.6 Concentrations as low as 0.2 pg/m^3 can be accurately quantified.

1.7 The method incorporates quality assurance/quality control (QA/QC) measures in sampling, analysis, and evaluation of data.

1.8 The analytical procedures also have been used for the quantitative determination of these types of compounds in sample matrices such as stack gas emissions, fly ash, soil, sediments, water, and fish and human tissue (5-9).

1.9 The method is similar to methods used by other EPA, industry, commercial, and academic laboratories for determining PCDDs and PCDFs in various sample matrices (10-25). This method is an update of the original EPA Compendium Method TO-9, originally published in 1989 (26).

1.10 The method does not separately quantify gaseous PHDDs and PHDFs and particulate-associated PHDDs and PHDFs because some of the compounds volatilize from the filter and are collected by the PUF adsorbent. For example, most of the OCDD is collected by the filter and most of the TCDDs are collected by the PUF during sampling. PCDDs/PCDFs may be distributed between the gaseous and particle-adsorbed phases in ambient air. Therefore, the filter and PUF are combined for extraction in this method.

1.11 The sampling and analysis method is very versatile and can be used to determine other brominated and brominated/chlorinated dioxins and furans in the future when more analytical standards become available for use in the method. A recent modification of the sample preparation procedure provides the capability required to determine PCDDs, PCDFs, PCBs, and PAHs in the same sample (27).

2. Summary of Method

2.1 Quartz-fiber filters and glass adsorbent cartridges are pre-cleaned with appropriate solvents and dried in a clean atmosphere. The PUF adsorbent plugs are subjected to 4-hour Soxhlet extraction using an oversized extractor to prevent distortion of the PUF plug. The PUF plugs are then air dried in a clean atmosphere and installed in the glass cartridges. A 50 microliter (μL) aliquot of a 16 picogram/microliter (pg/μL) solution of $^{37}Cl_4$-2,3,7,8-TCDD is spiked to the PUF in the laboratory prior to field deployment. (Different amounts and additional $^{13}C_{12}$-labeled standards such as $^{13}C_{12}$-1,2,3,6,7,8-HxCDF may also be used if desired.) The cartridges are then wrapped in aluminum foil to protect from light, capped with Teflon® end caps, placed in a cleaned labeled shipping container, and tightly sealed with Teflon® tap until needed.

2.2 For sampling, the quartz-fiber filter and glass cartridge containing the PUF are installed in the high-volume air sampler.

2.3 The high-volume sampler is then immediately put into operation, usually for 24 hours, to sample 325 to 400 m^3 ambient air.

[Note: Significant losses were not detected when duplicate samplers were operated 7 days and sampled 2660 m^3 ambient air (1-4).]

2.4 The amount of ambient air sampled is recorded at the end of the sampling session. Sample recovery involves placing the filter on top of the PUF. The glass cartridge is then wrapped with the original aluminum foil, capped with Teflon® end caps, placed back into the original shipping container, identified, and shipped to the analytical laboratory for sample processing.

2.5 Sample preparation typically is performed on a "set" of 12 samples, which consists of 9 test samples, a field blank, a method blank, and a matrix spike.

2.6 The filter and PUF are combined for sample preparation, spiked with 9 $^{13}C_{12}$-labeled PCDD/PCDF and 4 PBDD/PBDF internal standards (28), and Soxhlet extracted for 16 hours. The extract is subjected to an acid/base clean-up procedure followed by clean-up on micro columns of silica gel, alumina, and carbon. The extract is then spiked with 0.5 ng $^{13}C_{12}$-1,2,3,4-TCDD (to determine extraction efficiencies achieved for the $^{13}C_{12}$-labeled internal standards) and then concentrated to 10 μL for HRGC-HRMS analysis in a 1 mL conical reactivial.

2.7 The set of sample extracts is subjected to HRGC-HRMS selected ion monitoring (SIM) analysis using a 60-m DB-5 or 60-m SP-2331 fused silica capillary column to determine the sampler efficiency, extraction efficiency, and the concentrations or the MDLs achieved for the PHDDs/PHDFs (28). Defined identification criteria and QA/QC criteria and requirements are used in evaluating the analytical data. The analytical results along with the volume of air sampled are used to calculate the concentrations of the respective tetra- through octa-isomers, the concentrations of the 2,3,7,8-chlorine or -bromine substituted isomers, or the MDLs. The concentrations and/or

MDLs are reported in pg/m^3. The EPA toxicity equivalence factors (TEFs) can be used to calculate the 2,3,7,8-TCDD toxicity equivalents (TEQs) concentrations, if desired (18).

3. Significance

3.1 The PHDDs and PHDFs may enter the environment by two routes: (1) manufacture, use and disposal of specific chemical products and by-products and (2) the emissions from combustion and incineration processes. Atmospheric transport is considered to be a major route for widespread dispersal of these compounds in stack gas emissions throughout the environment. The PCDDs/PCDFs are found as complex mixtures of all isomers in emissions from combustion sources. The isomer profiles of PCDDs/PCDFs found in ambient air are similar to those found in combustion sources. Isomer profiles of PCDDs/PCDFs related to chemical products and by-products are quite different in that only a few specific and characteristic isomers are detectable, which clearly indicate they are not from a combustion source.

3.2 The 2,3,7,8-substituted PCDDs/PCDFs are considered to be the most toxic isomers. Fortunately, they account for the smallest percentage of the total PCDD/PCDF concentrations found in stack gas emissions from combustion sources and in ambient air. The 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), 1 of 22 TCDD isomers and the most toxic member of PCDDs/PCDFs, is usually found as a very minor component in stack gas emissions (0.5 to 10 percent of total TCDD concentration) and is seldom found in ambient air samples. All of the 2,3,7,8-substituted PCDDs/PCDFs are retained in tissue of life-forms such as humans, fish, and wildlife, and the non 2,3,7,8-substituted PCDDs/PCDFs are rapidly metabolized and/or excreted.

3.3 Attention has been focused on determining PHDDs/PHDFs in ambient air only in recent years. The analyses are time-consuming, complex, difficult, and expensive. Extremely sensitive, specific, and efficient analytical procedures are required because the analysis must be performed for very low concentrations in the pg/m^3 and sub pg/m^3 range. The MDLs, likewise, must be in the range of 0.01 to 0.2 pg/m^3 for the results to have significant meaning for ambient air monitoring purposes. The background level of total PCDDs/PCDFs detected in ambient air is usually in the range of 0.5 to 3 pg/m^3, and the PBDFs is in the range of 0.1 to 0.2 pg/m^3 (2,3,14). Because PCDDs/PCDFs, PBDDs/PBDFs, and BCDDs/BCDFs can be formed by thermal reactions, there has been an increasing interest in ambient air monitoring, especially in the vicinities of combustion and incineration processes such as municipal waste combustors and resource recovery facilities (19,20). PBDDs/PBDFs can be created thermally (22,23), and they may also be formed in certain chemical processes (21). BCDDs/BCDFs have been detected in ash from combustion/incineration processes (9). The sampling and analysis method described here can be used in monitoring studies to accurately determine the presence or absence of pg/m^3 and sub pg/m^3 levels of these compounds in ambient air (26,27).

4. Safety

4.1 The 2,3,7,8-TCDD and other 2,3,7,8-chlorine or bromine substituted isomers are toxic and can pose health hazards if handled improperly. Techniques for handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD and the other PHDDs and PHDFs. Only highly trained individuals who are thoroughly versed in appropriate laboratory procedures and familiar with the hazards of 2,3,7,8-TCDD should handle these substances. A good laboratory practice involves routine physical examinations and blood checks of employees working with 2,3,7,8-TCDD. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed.

4.2 The toxicity or carcinogenicity of the other penta-, hexa-, hepta-, and octa-PHDDs/PHDFs with chlorine or bromine atoms in positions 2,3,7,8 are known to have similar, but lower, toxicities. However, each compound should be treated as a potential health hazard and exposure to these compounds must be minimized.

4.3 While the procedure specifies benzene as the extraction solution, many laboratories have substituted toluene for benzene (28). This is due to the carcinogenic nature of benzene. The EPA is presently studying the replacement of benzene with toluene.

4.4 A laboratory should develop a strict safety program for working with these compounds, which would include safety and health protocols; work performed in well ventilated and controlled access laboratory; maintenance of current awareness file of OSHA regulations regarding the safe handling of chemicals specified in the method; protective equipment; safety training; isolated work area; waste handling and disposal procedures; decontamination procedures; and laboratory wipe tests. Other safety practices as described in EPA Method 613, Section 4, July 1982 version, EPA Method 1613 Revision A, April 1990, Office of Water and elsewhere (29,30).

5. Applicable Documents

5.1 ASTM Standards

- Method D1365 *Definitions of Terms Relating to Atmospheric Sampling and Analysis.*
- Method E260 *Recommended Practice for General Gas Chromatography Procedures.*
- Method E355 *Practice for Gas Chromatography Terms and Relationships.*

5.2 EPA Documents

• *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II*, U. S. Environmental Protection Agency, EPA 600/R-94-038b, May 1994.
• *Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin by High Resolution Gas Chromatography-High Resolution Mass Spectrometry*, U. S. Environmental Protection Agency, EPA 600/40-86-004, January 1986.
• "Evaluation of an EPA High Volume Air Sampler for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans," undated report by Battelle under Contract No. 68-02-4127, Project Officers Robert G. Lewis and Nancy K. Wilson, U. S. Environmental Protection Agency, Research Triangle Park, North Carolina.
• *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-9, Second Supplement*, U. S. Environmental Protection Agency, EPA 600/4-89-018, March 1989.
• *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U. S. Environmental Protection Agency, EPA 600/4-83-027, June 1983.
• "Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by High Resolution Gas Chromatography - Low Resolution Mass Spectrometry," U. S. Environmental Protection Agency/OSW, SW-846, RCRA 8280 HRGC-LRMS, January 1987.
• "Analytical Procedures and Quality Assurance for Multimedia Analysis of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans by High Resolution Gas Chromatography - High Resolution Mass Spectrometry," U. S. Environmental Protection Agency/OSW, SW-846, RCRA 8290 HRGC-HRMS, June 1987.

• Harless, R., "Analytical Procedures and Quality Assurance Plan for the Determination of PCDDs and PCDFs Ambient Air near the Rutland, Vermont Municipal Incinerator," Final Report, U. S. Environmental Protection Agency, AREAL, RTP, NC, 1988.
• *Feasibility of Environmental Monitoring and Exposure Assessment for a Municipal Waste Combustor: Rutland, Vermont Pilot Study*, U. S. Environmental Protection Agency, EPA 600/8-91/007, March 1991.
• "Method 23, Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Dibenzofurans (PCDFs) from Stationary Sources." *Federal Register*, Vol. 56, No. 30, February 13, 1991.
• *Method 1613 Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC-HRMS*, U. S. Environmental Protection Agency, Office of Solid Waste, Washington, DC, April 1990.

5.3 Other Documents

• "Operating Procedures for Model PS-1 Sampler," Graseby/General Metal Works, Inc., Village of Cleves, OH 45002 (800-543-7412).
• "Chicago Air Quality: PCB Air Monitoring Plan, Phase 2," IEAP/APC/86-011, Illinois Environmental Protection Agency, Division of Air Pollution Control, April 1986.
• "Operating Procedures for the Thermo Environmental Semi-volatile Sampler," Thermo Environmental Instruments, Inc. (formerly Wedding and Associates), 8 West Forge Parkway, Franklin, MA 02038 (508-520-0430).

6. Definitions

[Note: Definitions used in this document and any user-prepared Standard Operating Procedures (SOPs) should be consistent with those used in ASTM D1356. All abbreviations and symbols are defined within this document at the point of first use.]

6.1 Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)—compounds that contain from 1 to 8 chlorine atoms, resulting in a total of 75 PCDDs and 135 PCDFs. The structures are shown in Figure 1. The numbers of isomers at different chlorination levels are shown in Table 1. The seventeen 2,3,7,8-substituted PCDDs/PCDFs are shown in Table 2.

6.2 Polybrominated dibenzo-p-dioxins (PBDDs) and polybrominated dibenzofurans (PBDFs)—compounds that have the same structure and contain from 1 to 8 bromine atoms, resulting in a total of 75 PBDDs and 135 PBDFs. The structures and isomers are the same as those of the PCDDs/PCDFs shown in Figure 1 and Tables 1 and 2.

6.3 Brominated/chlorinated dibenzo-p-dioxins (BCDDs) and brominated/chlorinated dibenzofurans (BCDFs)—compounds with the same structures and may contain from 1 to 8 chlorine and bromine atoms, resulting in 1550 BCDD congeners and 3050 BCDF congeners.

6.4 Polyhalogenated dibenzo-p-dioxins (PHDDs) and polyhalogenated dibenzofurans (PHDFs)—dibenzo-p-dioxins and dibenzofurans substituted with 1 or more halogen atoms.

6.5 Isomer—compounds having the sample number and type of halogen atoms, but substituted in different positions. For example, 2,3,7,8-TCDD and 1,2,3,4-TCDD are isomers. Additionally, there are 22 isomers that constitute the homologues of TCDDs.

6.6 Isomeric group—a group of dibenzo-p-dioxins or dibenzofurans having the same number of halogen atoms. For example, the tetra-chlorinated dibenzo-p-dioxins.

6.7 Internal Standard—is an isotopically-labeled analog that is added to all samples, including method blanks (process and field) and quality control samples, before extraction. They are used along with response factors to measure the concentration of the analytes. Nine PCDD/PCDF and 4 PBDD/PBDF internal standards are used in this method. There is one for each of the chlorinated dioxin and furan isomeric groups with a degree of halogenation ranging from four to eight, with the exception of OCDF.

6.8 High-Resolution Calibration Solutions (see Table 3)—solutions in tridecane containing known amounts of 17 selected PCDDs and PCDFs, 9 internal standards ($^{13}C_{12}$-labeled PCDDs/PCDFs), 2 field standards, 4 surrogate standards, and 1 recovery standard. The set of 5 solutions is used to determine the instrument response of the unlabeled analytes relative to the $^{13}C_{12}$-labeled internal standards and of the $^{13}C_{12}$-labeled internal standards relative to the surrogate, field and recovery standards. Different concentrations and other standards may be used, if desired. Criteria for acceptable calibration as outlined in Section 13.5 should be met in order to use the analyte relative response factors.

6.9 Sample Fortification Solutions (see Table 4)—solutions (in isooctane) containing the $^{13}C_{12}$-labeled internal standards that are used to spike all samples, field blanks, and process blanks before extraction. Brominated standards used only when desired.

6.10 Recovery Standard Solution (see Table 5)—Recovery Standard Solution (see Table 5)—an isooctane solution containing the $^{13}C_{12}$-1,2,3,4-TCDD ($^{13}C_{12}$-2,3,7,8,9-HxDD optional) recovery standards that are added to the extract before final concentration for HRGC-HRMS analysis to determine the recovery efficiencies achieved for the $^{13}C_{12}$-labeled internal standards.

6.11 Air Sampler Field Fortification Solution (see Table 6)—an isooctane solution containing the $^{37}Cl_4$-2,3,7,8-TCDD standard that is spiked to the PUF plugs prior to shipping them to the field for air sampling.

6.12 Surrogate Standard Solution (see Table 7)—an isooctane solution containing 4 $^{13}C_{12}$-labeled standards that may be spiked to the filter or PUF prior to air sampling, to the sample prior to extraction, or to the sample extract before cleanup or before HRGC-HRMS analysis to determine sampler efficiency method efficiency or for identification purposes (28). Other standards and different concentrations may be used, if desired.

6.13 Matrix Spike and Method Spike Solutions (see Table 8)—isooctane solutions of native (non-labeled) PCDDs and PCDFs and PBDDs and PBDFs that are spiked to a clean PUF prior to extraction.

6.14 Sample Set—consists of nine test samples, field blank, method blank, and matrix spiked with native PHDDs/PHDFs. Sample preparation, HRGC-HRMS analysis, and evaluation of data is performed on a sample set.

6.15 Lab Control Spike—standard that is prepared during sample preparation and that contains exactly the same amounts of all of the labeled and unlabeled standards that were used in extraction and cleanup of the sample set for HRGC-HRMS analysis.

6.16 Field Blank—consists of a sample cartridge containing PUF and filter that is spiked with the filed fortification solution, shipped to the field, installed on the sampler, and passively exposed at the sampling area (the sampler is not operated). It is then sealed and returned to the laboratory for extraction, cleanup, and HRGC-HRMS analysis. It is treated in exactly the same manner as a test sample. A field blank is processed with each sampling episode. The field blank represents the background contributions from passive exposure to ambient air, PUF, quartz fiber filter, glassware, and solvents.

6.17 Laboratory Method Blank—represents the background contributions from glassware, extraction and cleanup solvents. A Soxhlet extractor is spiked with a solution of $^{13}C_{12}$-labeled internal standards, extracted, cleaned up, and analyzed by HRGC-HRMS in exactly the same manner as the test samples.

6.18 Solvent Blank—an aliquot of solvent (the amount used in the method) that is spiked with the $^{13}C_{12}$-labeled internal standards and concentrated to 60 μL for HRGC-HRMS analysis. The analysis provides the background contributions from the specific solvent.

6.19 GC Column Performance Evaluation Solution (see Table 9)—a solution containing a mixture of selected PCDD/PCDF isomers, including the first and last chromatographic eluters for each isomeric group. Used to demonstrate continued acceptable performance of the capillary column and to define the PCDD/PCDF retention time windows. Also includes a mixture of tetradioxin isomers that elute closest to 2,3,7,8-TCDD.

6.20 QA/QC Audit Samples—samples of PUF that contain known amounts of unlabeled PCDDS and PCDFs. These samples are submitted as "blind" test samples to the analytical laboratory. The analytical results can then be used to determine and validate the laboratory's accuracy, precision and overall analytical capabilities for determination of PCDDs/PCDFs.

6.21 Relative Response Factor—response of the mass spectrometer to a known amount of an analyte relative to a known amount of a labeled internal standard.

6.22 Method Blank Contamination—the method blank should be free of interferences that affect the identification and quantification of PHDDs and PHDFs. A valid method blank is an analysis in which all internal standard signals are characterized by S/N ratio greater than 10:1 and the MDLs are adequate for the study. The set of samples must be extracted and analyzed again if a valid method blank cannot be achieved.

6.23 Sample Rerun—additional cleanup of the extract and reanalysis of the extract.

6.24 Extract Reanalysis—analysis by HRGC-HRMS of another aliquot of the final extract.

6.25 Mass Resolution Check—a standard method used to demonstrate a static HRMS resolving power of 10,000 or greater (10 percent valley definition).

6.26 Method Calibration Limits (MCLs)—for a given sample size, a final extract volume, and the lowest and highest calibration solutions, the lower and upper MCLs delineate the region of quantitation for which the HRGC-HRMS system was calibrated with standard solutions.

6.27 HRGC-HRMS Solvent Blank—a 1 or 2 μL aliquot of solvent that is analyzed for tetra- through octa-PCDDs and PCDFs following the analysis of a sample that contains high concentrations of these compounds.

An acceptable solvent blank analysis (free of PHDDs/PHDFs) should be achieved before continuing with analysis of the test samples.

6.28 Sampler Spike (SS)—a sampler that is spiked with known amounts of the air sampler field fortification solution (see Table 6) and the matrix spike solutions (see Table 8) prior to operating the sampler for 24 hours to sample 325-400 std m^3 ambient air. The results achieved for this sample can be used to determine the efficiency, accuracy and overall capabilities of the sampling device and analytical method.

6.29 Collocated Samplers (CS)—two samplers installed close together at the same site that can be spiked with known amounts of the air sampler field fortification solution (see Table 6) prior to operating the samplers for 24 hours to sample 325-400 std m^3 ambient air. The analytical results for these two samples can be used to determine and evaluate efficiency, accuracy, precision, and overall capabilities of the sampling device and analytical method.

6.30 Congener—a term which refers to any one particular member of the same chemical family. As an example, there are 75 congeners of chlorinated dibenzo-p-dioxins. A specific congener is denoted by unique chemical notations. For example, 2,4,8,9-tetrachlorodibenzofuran is referred to as 2,4,8,9-TCDF.

6.31 Homologue—a term which refers to a group of structurally related chemicals that have the same degree of chlorination. For example, there are eight homologues of CDDs, monochlorinated through octochlorinated. Notation for homologous classes is as follows:

Class	Acronym	
Dibenzo-p-dioxin	D	
Dibenzofuran	F	
No. of halogens	**Acronym**	**Example**
1	M	
2	D	2,4-DCDD
3	Tr	
4	T	1,4,7,8-TCDD
5	Pe	
6	Hx	
7	Hp	
8	O	
1 through 8	CDDs and CDFs	

7. Interferences And Contamination

7.1 Any compound having a similar mass and mass/charge (m/z) ratio eluting from the HRGC column within ± 2 seconds of the PHDD/PHDF of interest is a potential interference. Also, any compound eluting from the HRGC column in a very high concentration will decrease sensitivity in the retention time frame. Some commonly encountered interferences are compounds that are extracted along with the PCDDs and PCDFs or other PHDDs/PHDFs, e.g., polychlorinated biphenyls (PCBs), methoxybiphenyls, polychlorinated diphenylethers, polychlorinated naphthalenes, DDE, DDT, etc. The cleanup procedures are designed to eliminate the majority of these substances. The capillary column resolution and mass spectrometer resolving power are extremely helpful in segregating any remaining interferences from PCDDs and PCDFs. The severity of an interference

problem is usually dependent on the concentrations and the mass spectrometer and chromatographic resolutions. However, polychlorinated diphenylethers are extremely difficult to resolve from PCDFs because they elute in retention time windows of PCDFs, and their fragment ion resulting from the loss of 2 chlorine atoms is identical to that of the respective PCDF. For example, the molecular ions of hexachlorodiphenylethers must be monitored to confirm their presence or absence in the analysis for TCDFs. This requirement also applies to the other PCDFs and PBDFs.

7.2 Since very low levels of PCDDs and PCDFs must be determined, the elimination of interferences is essential. High purity reagents and solvents must be used, and all equipment must be scrupulously cleaned. All materials, such as PUF, filter solvents, etc., used in the procedures are monitored and analyzed frequently to ensure the absence of contamination. Cleanup procedures must be optimized and performed carefully to minimize the loss of analyte compounds during attempts to increase their concentrations relative to other sample components. The analytical results achieved for the field blank, method blank, and method spike in a "set" of samples is extremely important in evaluating and validating the analytical data achieved for the test samples.

8. Apparatus

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

8.1 High-Volume Sampler (see Figure 2). Capable of pulling ambient air through the filter/adsorbent cartridge at a flow rate of approximately 8 standard cubic feet per minute (scfm) (0.225 std m^3\min) to obtain a total sample volume of greater than 325 scm over a 24-hour period. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.2 High-Volume Sampler Calibrator. Capable of providing multipoint resistance for the high-volume sampler. Major manufacturers are:

- Tisch Environmental, Village of Cleves, OH
- Andersen Instruments Inc., 500 Technology Ct., Smyrna, GA
- Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA

8.3 High Resolution Gas Chromatograph-High Resolution Mass Spectrometer-Data System (HRGC-HRMS-DS)

8.3.1 The GC should be equipped for temperature programming and all of the required accessories, such as gases and syringes, should be available. The GC injection port should be designed for capillary columns. Splitless injection technique, on-column injections, or moving needle injectors may be used. It is important to use the same technique and injection volume at all times.

8.3.2 The HRGC-HRMS interface, if used, should be constructed of fused silica tubing or all glass or glass lined stainless steel and should be able to withstand temperatures up to 340°C. The interface should not degrade the separation of PHDD/PHDF isomers achieved by the capillary column. Active sites or cold spots in the interface can cause peak broadening and peak tailing. The capillary column should be fitted directly into the HRMS ion source to avoid these types of problems. Graphite ferrules can adsorb PHDDs/PHDFs and cause problems. Therefore, Vespel® or equivalent ferrules are recommended.

8.3.3 The HRMS system should be operated in the electron impact ionization mode. The static resolving power of the instrument should be maintained at 10,000 or greater (10% valley definition). The HRMS should be operated in the selected ion monitoring (SIM) mode with a total cycle time of one second or less. At a minimum, the ions listed in Tables 10, 11, and 12 for each of the select ion monitoring (SIM) descriptors should be monitored. It is important to use the same set of ions for both calibration and sample analysis.

8.3.4 The data system should provide for control of mass spectrometer, data acquisition, and data processing. The data system should have the capability to control and switch to different sets of ions (descriptors/mass menus shown in Tables 10, 11, and 12) at different times during the HRGC-HRMS SIM analysis. The SIM traces/displays of ion signals being monitored can be displayed on the terminal in real time and sorted for processing. Quantifications are reported based on computer generated peak areas. The data system should be able to provide hard copies of individual ion chromatograms for selected SIM time intervals, and it should have the capability to allow measurement of noise on the baseline. It should also have the capability to acquire mass-spectral peak profiles and provide hard copies of the peak profiles to demonstrate the required mass resolution.

8.3.5 HRGC columns, such as the DB-5 (28) and SP-2331 fused silica capillary columns, and the operating parameters known to produce acceptable results are shown in Tables 13 and 14. Other types of capillary columns may also be used as long as the performance requirements can be successfully demonstrated.

9. Equipment And Materials

9.1 Materials for Sample Collection (see Figure 3a)

9.1.1 Quartz fiber filter. 102 millimeter bindless quartz microfiber filter, Whatman International Ltd, QMA-4.

9.1.2 Polyurethane foam (PUF) plugs. 3-inch thick sheet stock polyurethane type (density 0.022 g/cm^3). The PUF should be of the polyether type used for furniture upholstery, pillows, and mattresses. The PUF cylinders (plugs) should be slightly larger in diameter than the internal diameter of the cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH; University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC; Thermo Environmental Instruments, Inc., 8 West Forge Parkway, Franklin, MA; Supelco, Supelco Park, Bellefonte, PA; and SKC Inc., 334 Valley View Road, Eighty Four, PA (see Figure 3b).

9.1.3 Teflon® end caps. For sample cartridge. Sources of equipment are Tisch Environmental, Village of Cleves, OH; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC (see Figure 3b).

9.1.4 Sample cartridge aluminum shipping containers. For sample cartridge shipping. Sources of equipment are Tisch Environmental, Village of Cleves, OH; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC (see Figure 3b).

9.1.5 Glass sample cartridge. For sample collection. Sources of equipment are Tisch Environmental, Village of Cleves, OH; Thermo Environmental Instruments, Inc., 8 West Forge, Parkway, Franklin, MA; and University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC (see Figure 3b).

9.2 Laboratory Equipment

9.2.1 Laboratory hoods.
9.2.2 Drying oven.
9.2.3 Rotary evaporator. With temperature-controlled water bath.
9.2.4 Balances.
9.2.5 Nitrogen evaporation apparatus.
9.2.6 Pipettes. Disposal Pasteur, 150-mm long x 5-mm i.d.
9.2.7 Soxhlet apparatus. 500-mL.
9.2.8 Glass funnels.
9.2.9 Desiccator.
9.2.10 Solvent reservoir. 125-mL, Kontes, 12.35-cm diameter.
9.2.11 Stainless steel spoons and spatulas.
9.2.12 Glass wool. Extracted with methylene chloride, stored in clean jar.
9.2.13 Laboratory refrigerator.
9.2.14 Chromatographic columns.
9.2.15 Perfluorokerosenes.

9.3 Reagents and Other Materials

9.3.1 Sulfuric acid. Ultrapure, ACS grade, specific gravity 1.84, acid silica.
9.3.2 Sodium hydroxide. Potassium hydroxide, reagent grade, base silica.
9.3.3 Sodium sulfate.
9.3.4 Anhydrous, reagent grade.
9.3.5 Glass wool. Silanized, extracted with methylene chloride and hexane, and dried.
9.3.6 Diethyl ether. High purity, glass distilled.
9.3.7 Isooctane. Burdick and Jackson, glass-distilled.
9.3.8 Hexane. Burdick and Jackson, glass-distilled.
9.3.9 Toluene. Burdick and Jackson, glass-distilled, or equivalent.
9.3.10 Methylene chloride. Burdock and Jackson, chromatographic grade, glass distilled.
9.3.11 Acetone. Burdick and Jackson, high purity, glass distilled.
9.3.12 Tridecane. Aldrich, high purity, glass distilled.
9.3.13 Isooctane. Burdick and Jackson, high purity, glass distilled.
9.3.14 Alumina. Acid, pre-extracted (16-21 hours) and activated.
9.3.15 Silica gel. High purity grade, type 60, 70-230 mesh; extracted in a Soxhlet apparatus with methylene chloride (see Section 8.18) for 16-24 hours (minimum of 3 cycles per hour) and activated by heating in a foil-covered glass container for 8 hours at 130°C.
9.3.16 18 percent Carbopack C/Celite 545.
9.3.17 Methanol. Burdick and Jackson, high purity, glass distilled.
9.3.18 Nonane. Aldrich, high purity, glass distilled.
9.3.19 Benzene. High purity, glass distilled.

9.4 Calibration Solutions and Solutions of Standards Used in the Method

9.4.1 HRGC-HRMS Calibration Solutions (see Table 3). Solutions containing $^{13}C_{12}$-labeled and unlabeled PCDDs and PCDFs at known concentrations are used to calibrate the instrument. These standards can be obtained from various commercial sources such as Cambridge Isotope Laboratories, 50 Frontage Road, Andover, MA 01810, 508-749-8000.

9.4.2 Sample Fortification Solutions (see Table 4). An isooctane solution (or nonane solution) containing the $^{13}C_{12}$-labeled PCDD/PCDF and PBDD/PBDF internal standards at the listed concentrations. The internal standards are spiked to all samples prior to extraction and are used to measure the concentration of the unlabeled native analytes and to determine MDLs.

9.4.3 Recovery Standard Spiking Solution (see Table 5). An isooctane solution containing $^{13}C_{12}$-1,2,3,4-TCDD at a concentration of 10 pg/μL. Additional recovery standards may be used if desired.

9.4.4 Sampler Field Fortification Solution (see Table 6). An isooctane solution containing 10 pg/μL $^{37}Cl_4$-2,3,7,8-TCDD.

9.4.5 Surrogate Standards Solution (see Table 7). An isooctane solution containing the four $^{13}C_{12}$-labeled standards at a concentration of 100 pg/μL.

9.4.6 Matrix/Method Spike Solution (see Table 8). An isooctane solution containing the unlabeled PCDDs/PCDFs and PBDDs/PBDFs at the concentrations listed.

[Note: All PHDD/PHDF solutions listed above should be stored in a refrigerator at less than or equal to 4°C in the dark. Exposure of the solutions to light should be minimized.]

9.4.7 Column Performance Evaluation Solutions (see Table 9). Isooctane solutions of first and last chromatographic eluting isomers for each isomeric group of tetra- through octa-CDDs/CDFs. Also includes a mixture of tetradioxin isomers that elute closest to 2,3,7,8-TCDD.

10. Preparation Of PUF Sampling Cartridge

10.1 Summary of Method

10.1.1 This part of the procedure discusses pertinent information regarding the preparation and cleaning of the filter, adsorbents, and filter/adsorbent cartridge assembly. The separate batches of filters and adsorbents are extracted with the appropriate solvent.

10.1.2 At least one PUF cartridge assembly and one filter from each batch, or 10 percent of the batch, whichever is greater, should be tested and certified before the batch is considered for field use.

10.1.3 Prior to sampling, the cartridges are spiked with surrogate compounds.

10.2 Preparation of Sampling Cartridge

10.2.1 Bake the quartz filters at 400°C for 5 hours before use.

10.2.2 Set aside the filters in a clean container for shipment to the field or prior to combining with the PUF glass cartridge assembly for certification prior to field deployment.

10.2.3 The PUF plugs are 6.0-cm diameter cylindrical plugs cut from 3-inch sheet stock and should fit, with slight compression, in the glass cartridge, supported by the wire screen (see Figure 2). During cutting, rotate the die at high speed (e.g., in a drill press) and continuously lubricate with deionized or distilled water. Pre-cleaned PUF plugs can be obtained from commercial sources (see Section 9.1.2).

10.2.4 For initial cleanup, place the PUF plugs in a Soxhlet apparatus and extract with acetone for 16 hours at approximately 4 cycles per hour. When cartridges are reused, use diethyl ether/hexane (5 to 10 percent volume/volume [v/v]) as the cleanup solvent.

[Note: A modified PUF cleanup procedure can be used to remove unknown interference components of the PUF blank. This method consists of rinsing 50 times with toluene, acetone, and diethyl ether/hexane (5 to 10 percent v/v), followed by Soxhlet extraction. The extracted PUF is placed in a vacuum oven connected to a water aspirator and dried at room temperature for approximately 2 to 4 hours (until no solvent odor is detected). The extract from the Soxhlet extraction procedure from each batch may be analyzed to determine initial cleanliness prior to certification.]

10.2.5 Fit a nickel or stainless steel screen (mesh size 200/200) to the bottom of a hexane-rinsed glass sampling cartridge to retain the PUF adsorbents, as illustrated in Figure 2. Place the Soxhlet-extracted, vacuum-dried PUF (2.5-cm thick by 6.5-cm diameter) on top of the screen in the glass sampling cartridge using polyester gloves.

10.2.6 Wrap the sampling cartridge with hexane-rinsed aluminum foil, cap with the Teflon® end caps, place in a cleaned labeled aluminum shipping container, and seal with Teflon® tape. Analyze at least 1 PUF plug from each batch of PUF plugs using the procedures described in Section 10.3, before the batch is considered acceptable for field use. A level of 2 to 20 pg for tetra-,penta-, and hexa- and 40 to 150 pg for hepta- and octa-CDDs similar to that occasionally detected in the method blank (background contamination) is considered to be acceptable. Background levels can be reduced further, if necessary. Cartridges are considered clean for up to 30 days from date of certification when stored in their sealed containers.

10.3 Procedure for Certification of PUF Cartridge Assembly

10.3.1 Extract 1 filter and PUF adsorbent cartridge by Soxhlet extraction and concentrate using a Kuderna-Danish (K-D) evaporator for each lot of filters and cartridges sent to the field.

10.3.2 Assemble the Soxhlet apparatus. Charge the Soxhlet apparatus with 300 mL of the extraction solvent (10 percent v/v diethyl ether/hexane) and reflux for 2 hours. Let the apparatus cool, disassemble it, and discard the used extraction solvent. Transfer the filter and PUF glass cartridge to the Soxhlet apparatus (the use of an extraction thimble is optional).

[Note: The filter and adsorbent assembly are tested together in order to reach detection limits, to minimize cost and to prevent misinterpretation of the data. Separate analyses of the filter and PUF would not yield useful information about the physical state of most of the PHDDs and PHDFs at the time of sampling due to evaporative losses from the filter during sampling.]

10.3.3 Add 300 mL of diethyl ether/hexane (10 percent v/v) to the Soxhlet apparatus. Reflux the sample for 18 hours at a rate of at least 3 cycles per hour. Allow to cool; then disassemble the apparatus.

10.3.4 Assemble a K-D concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

10.3.5 Transfer the extract by pouring it through a drying column containing about 10 cm of anhydrous granular sodium sulfate and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of 10 percent diethylether/hexane to complete the quantitative transfer.

10.3.6 Add 1 or 2 clean boiling chips and attach a 3-ball Snyder column to the evaporative flask. Pre-wet the Snyder column by adding about 1 mL of the extraction solvent to the top of the column. Place the K-D apparatus on a hot water bath (50°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus

and the water temperature as required to complete the concentration in one hour. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches approximately 5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 5 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 5 mL of hexane. A 5-mL syringe is recommended for this operation.

10.3.7 Concentrate the extract to 1 mL, cleanup the extract (see Section 12.2.2), and analyze the final extract using HRGC-HRMS.

10.3.8 The level of target compounds must be less than or equal to 2 to 20 pg for tetra-, penta-, and hexa- and 40 to 150 pg for hepta- and octa-CDDs for each pair of filter and adsorbent assembly analyzed is considered to be acceptable.

10.4 Deployment of Cartridges for Field Sampling

10.4.1 Prior to field deployment, add surrogate compounds (i.e., chemically inert compounds not expected to occur in an environmental sample) to the center bed of the PUF cartridge, using a microsyringe. The surrogate compounds (see Table 3) must be added to each cartridge assembly.

10.4.2 Use the recoveries of the surrogate compounds to monitor for unusual matrix effects and gross sampling processing errors. Evaluate surrogate recovery for acceptance by determining whether the measured concentration falls within the acceptance limits.

11. Assembly, Calibration And Collection Using Sampling System

[Note: This method was developed using the PS-1 semi-volatile sampler provided by General Metal Works, Village of Cleves, OH as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

11.1 Description of Sampling Apparatus

The entire sampling system is diagrammed in Figure 1. This apparatus was developed to operate at a rate of 4 to 10 scfm (0.114 to 0.285 std m^3/min) and is used by EPA for high-volume sampling of ambient air. The method write-up presents the use of this device.

The sampling module (see Figure 2) consists of a filter and a glass sampling cartridge containing the PUF utilized to concentrate dioxins/furans from the air. A field portable unit has been developed by EPA (see Figure 4).

11.2 Calibration of Sampling System

Each sampler should be calibrated (1) when new, (2) after major repairs or maintenance, (3) whenever any audit point deviates from the calibration curve by more than 7 percent, (4) before/after each sampling event, and (5) when a different sample collection media, other than that which the sampler was originally calibrated to, will be used for sampling.

11.2.1 Calibration of Orifice Transfer Standard. Calibrate the modified high volume air sampler in the field using a calibrated orifice flow rate transfer standard. Certify the orifice transfer standard in the laboratory against a positive displacement rootsmeter (see Figure 5). Once certified, the recertification is performed rather

infrequently if the orifice is protected from damage. Recertify the orifice transfer standard performed once per year utilizing a set of five multiple resistance plates.

[Note: The set of five multihole resistance plates are used to change the flow through the orifice so that several points can be obtained for the orifice calibration curve. The following procedure outlines the steps to calibrate the orifice transfer standard in the laboratory.]

11.2.1.1 Record the room temperature (T_1 in °C) and barometric pressure (P_b in mm Hg) on the Orifice Calibration Data Sheet (see Figure 6). Calculate the room temperature in K (absolute temperature) and record on Orifice Calibration Data Sheet.

$$T_1 \text{ in K} = 273° + T_1 \text{ in °C}$$

11.2.1.2 Set up laboratory orifice calibration equipment as illustrated in Figure 5. Check the oil level of the rootsmeter prior to starting. There are 3 oil level indicators, 1 at the clear plastic end and 2 site glasses, 1 at each end of the measuring chamber.

11.2.1.3 Check for leaks by clamping both manometer lines, blocking the orifice with cellophane tape, turning on the high volume motor, and noting any change in the rootsmeter's reading. If the rootsmeter's reading changes, there is a leak in the system. Eliminate the leak before proceeding. If the rootsmeter's reading remains constant, turn off the hi-vol motor, remove the cellophane tape, and unclamp both manometer lines.

11.2.1.4 Install the 5-hole resistance plate between the orifice and the filter adapter.

11.2.1.5 Turn manometer tubing connectors 1 turn counter-clockwise. Make sure all connectors are open.

11.2.1.6 Adjust both manometer midpoints by sliding their movable scales until the zero point corresponds with the meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required for the water manometer, remove tubing connector and add clean water.)

11.2.1.7 Turn on the high volume motor and let it run for 5 minutes to set the motor brushes. Turn the motor off. Insure manometers are set to zero. Turn the high volume motor on.

11.2.1.8 Record the time, in minutes, required to pass a known volume of air (approximately 200 to 300 ft^3 of air for each resistance plate) through the rootsmeter by using the rootsmeter's digital volume dial and a stopwatch.

11.2.1.9 Record both manometer readings-orifice water manometer ($\triangle H$) and rootsmeter mercury manometer ($\triangle P$) on Orifice Calibration Data Sheet (see Figure 6).

[Note: $\triangle H$ is the sum of the difference from zero (0) of the two column heights.]

11.2.1.10 Turn off the high volume motor.

11.2.1.11 Replace the 5-hole resistance plate with the 7-hole resistance plate.

11.2.1.12 Repeat Sections 11.2.1.3 through 11.2.1.11.

11.2.1.13 Repeat for each resistance plate. Note results on Orifice Calibration Data Sheet (see Figure 6). Only a minute is needed for warm-up of the motor. Be sure to tighten the orifice enough to eliminate any leaks. Also check the gaskets for cracks.

[Note: The placement of the orifice prior to the rootsmeter causes the pressure at the inlet of the rootsmeter to be reduced below atmospheric conditions, thus causing the measured volume to be incorrect. The volume measured by the rootsmeter must be corrected.]

11.2.1.14 Correct the measured volumes on the Orifice Calibration Data Sheet:

$$V_{std} = V_m \left(\frac{P_a - \triangle P}{P_{std}}\right)\left(\frac{T_{std}}{T_a}\right)$$

where:

V_{std} = standard volume, std m^3
V_m = actual volume measured by the rootsmeter, m^3
P_a = barometric pressure during calibration, mm Hg
$\triangle P$ = differential pressure at inlet to volume meter, mm Hg
P_{std} = 760 mm Hg
T_a = ambient temperature during calibration, K.

11.2.1.15 Record standard volume on Orifice Calibration Data Sheet.

11.2.1.16 The standard flow rate as measured by the rootsmeter can now be calculated using the following formula:

$$Q_{std} = \frac{V_{std}}{\theta}$$

where:

Q_{std} = standard volumetric flow rate, std m^3/min
θ = elapsed time, min

11.2.1.17 Record the standard flow rates to the nearest 0.01 std m^3/min.

11.2.1.18 Calculate and record $\sqrt{\triangle H\ (P_1/P_{std})(298/T_1)}$ value for each standard flow rate.

11.2.1.19 Plot each $\sqrt{\triangle H\ (P_1/P_{std})(298/T_1)}$ value (y-axis) versus its associated standard flow rate (x-axis) on arithmetic graph paper and draw a line of best fit between the individual plotted points.

[Note: This graph will be used in the field to determine standard flow rate.]

11.2.2 Calibration of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

For this calibration procedure, the following conditions are assumed in the field:

- The sampler is equipped with an valve to control sample flow rate.
- The sample flow rate is determined by measuring the orifice pressure differential, using a magnehelic gauge.
- The sampler is designed to operate at a standardized volumetric flow rate of 8 ft^3/min (0.225 m^3/min), with an acceptable flow rate range within 10 percent of this value.
- The transfer standard for the flow rate calibration is an orifice device. The flow rate through the orifice is determined by the pressure drop caused by the orifice and is measured using a "U" tube water manometer or equivalent.
- The sampler and the orifice transfer standard are calibrated to standard volumetric flow rate units (scfm or scmm).

- An orifice transfer standard with calibration traceable to NIST is used.
- A "U" tube water manometer or equivalent, with a 0- to 16-inch range and a maximum scale division of 0.1 inch, will be used to measure the pressure in the orifice transfer standard.
- A magnehelic gauge or equivalent, with a 9- to 100-inch range and a minimum scale division of 2 inches for measurements of the differential pressure across the sampler's orifice is used.
- A thermometer capable of measuring temperature over the range of 32° to 122°F (0° to 50°C) to ±2°F (±1°C) and referenced annually to a calibrated mercury thermometer is used.
- A portable aneroid barometer (or equivalent) capable of measuring ambient barometric pressure between 500 and 800 mm Hg (19.5 and 31.5 in. Hg) to the nearest mm Hg and referenced annually to a barometer of known accuracy is used.
- Miscellaneous handtools, calibration data sheets or station log book, and wide duct tape are available.

11.2.2.1 Monitor the airflow through the sampling system with a venturi/Magnehelic assembly, as illustrated in Figure 7. Set up the calibration system as illustrated in Figure 7. Audit the field sampling system once per quarter using a flow rate transfer standard, as described in the EPA *High Volume-Sampling Method, 40 CVR 50, Appendix B.* Perform a single-point calibration before and after each sample collection, using the procedures described in Section 11.2.3.

11.2.2.2 Prior to initial multi-point calibration, place an empty glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.20 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desire flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on the Field Calibration Data Sheet (see Figure 8).

11.2.2.3 Place the orifice transfer standard on the sampling head and attach a manometer to the tap on the transfer standard, as illustrated in Figure 7. Properly align the retaining rings with the filter holder and secure by tightening the three screw clamps. Connect the orifice transfer standard by way of the pressure tap to a manometer using a length of tubing. Set the zero level of the manometer or magnehelic. Attach the magnehelic gauge to the sampler venturi quick release connections. Adjust the zero (if needed) using the zero adjust screw on face of the gauge.

11.2.2.4 To leak test, block the orifice with a rubber stopper, wide duct tape, or other suitable means. Seal the pressure port with a rubber cap or similar device. Turn on the sampler.

Caution: *Avoid running the sampler from too long a time with the orifice blocked. This precaution will reduce the chance that the motor will be overheated due to the lack of cooling air. Such overheating can shorten the life of the motor*.

11.2.2.5 Gently rock the orifice transfer standard and listen for a whistling sound that would indicate a leak in the system. A leak-free system will not produce an upscale response on the sampler's magnehelic. Leaks are usually caused either by damaged or missing gaskets by cross-threading and/or not screwing sample cartridge together tightly. All leaks must be eliminated before proceeding with the calibration. When the sample is determined to be leak-free, turn off the sampler and unblock the orifice. Now remove the rubber stopper or plug from the calibrator orifice.

11.2.2.6 Turn the flow control valve to the fully open position and turn the sampler on. Adjust the flow control valve until a Magnehelic reading of approximately 70 in. is obtained. Allow the Magnehelic and manometer readings to stabilize and record these values on the Field Calibration Data Sheet (see Figure 8).

11.2.2.7 Record the manometer reading under Y1 and the Magnehelic reading under Y2 on the Field Calibration Data Sheet. For the first reading, the Magnehelic should still be at 70 inches as set above.

11.2.2.8 Set the magnehelic to 60 inches by using the sampler's flow control valve. Record the manometer (Y1) and Magnehelic (Y2) readings on the Field Calibration Data Sheet.

11.2.2.9 Repeat the above steps using Magnehelic settings of 50, 40, 30, 20, and 10 inches.

11.2.2.10 Turn the voltage variator to maximum power, open the flow control valve, and confirm that the Magnehelic reads at least 100 inches. Turn off the sampler and confirm that the magnehelic reads zero.

11.2.2.11 Read and record the following parameters on the Field Calibration Data Sheet. Record the following on the calibration data sheet:

Data, job number, and operator's signature;

- Sampler serial number;
- Ambient barometric pressure; and
- Ambient temperature.

11.2.2.12 Remove the "dummy" cartridge and replace with a sample cartridge.

11.2.2.13 Obtain the Manufacturer High Volume Orifice Calibration Certificate.

11.2.2.14 If not performed by the manufacturer, calculate values for each calibrator orifice static pressure (Column 6, inches of water) on the manufacturer's calibration certificate using the following equation:

$$\sqrt{\triangle H(P_a/760)(298/[T_a + 273])}$$

where:

P_a = the barometric pressure (mm Hg) at time of manufacturer calibration, mm Hg
T_a = temperature at time of calibration, °C

11.2.2.15 Perform a linear regression analysis using the values in Column 7 of the manufacturer High Volume Orifice Calibration Certificate for flow rate (Q_{STD}) as the "X" values and the calculated values as the Y values. From this relationship, determine the correlation (CC1), intercept (B1), and slope (M1) for the Orifice Transfer Standard.

11.2.2.16 Record these values on the Field Calibration Data Sheet (see Figure 8).

11.2.2.17 Using the Field Calibration Data Sheet values (see Figure 8), calculate the Orifice Manometer Calculated Values (Y3) for each orifice manometer reading using the following equation:

Y3 Calculation

$$Y3 = [Y1(P_a/760)(298/\{T_a + 273\})]^{½}$$

11.2.2.18 Record the values obtained in Column Y3 on the Field Calibration Data Sheet (see Figure 8).

11.2.2.19 Calculate the Sampler Magnehelic Calculate Values (Y4) using the following equation:

Y4 Calculation

$$Y4 = [Y2(P_a/760)(298/\{T_a + 273\})]^{½}$$

11.2.2.20 Record the value obtained in Column Y4 on the Field Calibration Data Sheet (see Figure 8).

11.2.2.21 Calculate the Orifice Flow Rate (X1) in scm, using the following equation:

X1 Calculation

$$X1 = \frac{Y3 - B1}{M1}$$

11.2.2.22 Record the values obtained in Column X1, on the Field Calibration Data Sheet (see Figure 8).

11.2.2.23 Perform a linear regression of the values in Column X1 (as X) and the values in Column Y4 (as Y). Record the relationship for correlation (CC2), intercept (B2), and slope (M2) on the Field Calibration Data Sheet.

11.2.2.24 Using the following equation, calculate a set point (SP) for the manometer to represent a desired flow rate:

$$\text{Set point (SP)} = [(\text{Expected } P_a)/(\text{Expected } T_a)(T_{std}/P_{std})][M2\ (\text{Desired flow rate}) + B2]^2$$

where:

P_a = Expected atmospheric pressure (P_a), mm Hg
T_a = Expected atmospheric temperature (T_a), °C
M2 = Slope of developed relationship
B2 = Intercept of developed relationship
T_{std} = Temperature standard, 25°C
P_{std} = Pressure standard, 760 mm Hg

11.2.2.25 During monitoring, calculate a flow rate from the observed Magnehelic reading using the following equations:

$$Y5 = [\text{Average Magnehelic Reading } (\triangle H)\ (P_a/T_a)(T_{std}/P_{std})]^{1/2}$$

$$X2 = \frac{Y5 - B2}{M2}$$

where:

Y5 = Corrected Magnehelic reading
X2 = Instant calculated flow rate, scm

11.2.2.26 The relationship in calibration of a sampling system between Orifice Transfer Standard and flow rate through the sampler is illustrated in Figure 9.

11.2.3 Single-Point Audit of the High Volume Sampling System Utilizing Calibrated Orifice Transfer Standard

Single point calibration checks are required as follows:

- Prior to the start of each 24-hour test period.
- After each 24-hour test period. The post-test calibration check may serve as the pre-test calibration check for the next sampling period if the sampler is not moved.
- Prior to sampling after a sample is moved.

For samplers, perform a calibration check for the operational flow rate before each 24-hour sampling event and when required as outlined in the user quality assurance program. The purpose of this check is to track the sampler's calibration stability. Maintain a control chart presenting the percentage difference between a sampler's indicated and measured flow rates. This chart provides a quick reference of sampler flow-rate drift problems and is useful for tracking the performance of the sampler. Either the sampler log book or a data sheet will be used

to document flowcheck information. This information includes, but is not limited to, sampler and orifice transfer standard serial number, ambient temperature, pressure conditions, and collected flow-check data.

In this subsection, the following is assumed:

- The flow rate through a sampler is indicated by the orifice differential pressure;
- Samplers are designed to operate at an actual flow rate of 8 scfm, with a maximum acceptable flow-rate fluctuation range of ±10 percent of this value;
- The transfer standard will be an orifice device equipped with a pressure tap. The pressure is measured using a manometer; and
- The orifice transfer standard's calibration relationship is in terms of standard volumetric flow rate (Q_{std}).

11.2.3.1 Perform a single point flow audit check before and after each sampling period utilizing the Calibrated Orifice Transfer Standard (see Section 11.2.1).

11.2.3.2 Prior to single point audit, place a "dummy" glass cartridge in the sampling head and activate the sampling motor. Fully open the flow control valve and adjust the voltage variator so that a sample flow rate corresponding to 110 percent of the desired flow rate (typically 0.19 to 0.28 m^3/min) is indicated on the Magnehelic gauge (based on the previously obtained multipoint calibration curve). Allow the motor to warm up for 10 minutes and then adjust the flow control valve to achieve the desired flow rate. Turn off the sampler. Record the ambient temperature and barometric pressure on a Field Test Data Sheet (see Figure 10).

11.2.3.3 Place the flow rate transfer standard on the sampling head.

11.2.3.4 Properly align the retaining rings with the filter holder and secure by tightening the 3 screw clamps. Connect the flow rate transfer standard to the manometer using a length of tubing.

11.2.3.5 Using tubing, attach 1 manometer connector to the pressure tap of the transfer standard. Leave the other connector open to the atmosphere.

11.2.3.6 Adjust the manometer midpoint by sliding the movable scale until the zero point corresponds with the water meniscus. Gently shake or tap to remove any air bubbles and/or liquid remaining on tubing connectors. (If additional liquid is required, remove tubing connector and add clean water.)

11.2.3.7 Turn on high-volume motor and let run for 5 minutes.

11.2.3.8 Record the pressure differential indicated, $\triangle H$, in inches of water, on the Field Test Data Sheet. Be sure stable $\triangle H$ has been established.

11.2.3.9 Record the observed Magnahelic gauge reading, in inches of water, on the Field Test Data Sheet. Be sure stable $\triangle M$ has been established.

11.2.3.10 Using previous established Orifice Transfer Standard curve, calculate Q_{xs} (see Section 11.2.2.23).

11.2.3.11 This flow should be within ±10 percent of the sampler set point, normally, 8 ft^3. If not, perform a new multipoint calibration of the sampler.

11.2.3.12 Remove Flow Rate Transfer Standard and dummy adsorbent cartridge.

11.3 Sample Collection

11.3.1 General Requirements

11.3.1.1 The sampler should be located in an unobstructed area, at least 2 meters from any obstacle to air flow. The exhaust hose should be stretched out in the downwind direction to prevent recycling of air into the sample head.

11.3.1.2 All cleaning and sample module loading and unloading should be conducted in a controlled environment, to minimize any chance of potential contamination.

11.3.1.3 When new or when using the sampler at a different location, all sample contact areas need to be cleared. Use triple rinses of reagent grade hexane or methylene chloride contained in Teflon® rinse bottles. Allow the solvents to evaporate before loading the PUF modules.

11.3.2 Preparing Cartridge for Sampling

11.3.2.1 Detach the lower chamber of the cleaned sample head. While wearing disposable, clean, lint-free nylon, or powder-free surgical gloves, remove a clean glass adsorbent module from its shipping container. Remove the Teflon® end caps. Replace the end caps in the sample container to be reused after the sample has been collected.

11.3.2.2 Insert the glass module into the lower chamber and tightly reattach the lower chambers to the module.

11.3.2.3 Using clean rinsed (with hexane) Teflon-tipped forceps, carefully place a clean conditioned fiber filter atop the filter holder and secure in place by clamping the filter holder ring over the filter. Place the aluminum protective cover on top of the cartridge head. Tighten the 3 screw clamps. Ensure that all module connections are tightly assembled. Place a small piece of aluminum foil on the ball-joint of the sample cartridge to protect from back-diffusion of semi-volatile into the cartridge during transporting to the site.

[Note: Failure to do so could result in air flow leaks at poorly sealed locations which could affect sample representativeness.]

11.3.2.4 Place in a carrying bag to take to the sampler.

11.3.3 Collection

11.3.3.1 After the sampling system has been assembled, perform a single point flow check as described in Sections 11.2.3.

11.3.3.2 With the empty sample module removed from the sampler, rinse all sample contact areas using reagent grade hexane in a Teflon® squeeze bottle. Allow the hexane to evaporate from the module before loading the samples.

11.3.3.3 With the sample cartridge removed from the sampler and the flow control valve fully open, turn the pump on and allow it to warm-up for approximately 5 minutes.

11.3.3.4 Attach a "dummy" sampling cartridge loaded with the exact same type of filter and PUF media to be used for sample collection.

11.3.3.5 Turn the sampler on and adjust the flow control valve to the desired flow as indicated by the Magnehelic gauge reading determined in Section 11.2.2.24. Once the flow is properly adjusted, take extreme care not to inadvertently alter its setting.

11.3.3.6 Turn the sampler off and remove both the "dummy" module. The sampler is now ready for field use.

11.3.3.7 Check the zero reading of the sampler Magnehelic. Record the ambient temperature, barometric pressure, elapsed time meter setting, sampler serial number, filter number, and PUF cartridge number on the Field Test Data Sheet (see Figure 10). Attach the loaded sampler cartridge to the sampler.

11.3.3.8 Place the voltage variator and flow control valve at the settings used in Section 11.3.2, and the power switch. Activate the elapsed time meter and record the start time. Adjust the flow (Magnehelic setting), if necessary, using the flow control valve.

11.3.3.9 Record the Magnehelic reading every 6 hours during the sampling period. Use the calibration factors (see Section 11.2.2.23) to calculate the desired flow rate. Record the ambient temperature, barometric pressure, and Magnehelic reading at the beginning and during sampling period.

11.3.4 Sample Recovery

11.3.4.1 At the end of the desired sampling period, turn the power off. Carefully remove the sampling head containing the filter and adsorbent cartridge to a clean area.

11.3.4.2 While wearing disposable lint free nylon or surgical gloves, remove the PUF cartridge from the lower module chamber and lay it on the retained aluminum foil in which the sample was originally wrapped.

11.3.4.3 Carefully remove the glass fiber filter from the upper chamber using clean Teflon®-tipped forceps.

11.3.4.4 Fold the filter in half twice (sample side inward) and place it in the glass cartridge atop the PUF.

11.3.4.5 Wrap the combined samples in the original hexane rinsed aluminum foil, attached Teflon® end caps and place them in their original aluminum sample container. Complete a sample label and affix it to the aluminum shipping container.

11.3.4.6 Chain-of-custody should be maintained for all samples. Store the containers at <4°C and protect from light to prevent possibly photo-decomposition of collected analytes. If the time span between sample collection and laboratory analysis is to exceed 24 hours, refrigerate sample.

11.3.4.7 Perform a final calculated sample flow check using the calibration orifice, as described in Section 11.3.2. If calibration deviates by more than 10 percent from the initial reading, mark the flow data for that sample as suspect and inspect and/or remove from service.

11.3.4.8 Return at least 1 field filter/PUF blank to the laboratory with each group of samples. Treat a field blank exactly as the sample except that no air is drawn through the filter/adsorbent cartridge assembly.

11.3.4.9 Ship and store samples under ice (<4°C) until receipt at the analytical laboratory, after which it should be refrigerated at less than or equal to 4°C. Extraction must be performed within seven days of sampling and analysis within 40 days after extraction.

12. Sample Preparation

12.1 Extraction Procedure for Quartz Fiber Filters and PUF Plugs

12.1.1 Take the glass sample cartridge containing the PUF plug and quartz fiber filter out of the shipping container and place it in a 43-mm x 123-mm Soxhlet extractor. Add 10 μL of $^{13}C_{12}$-labeled sample fortification solution (see Table 4) to the sample. Put the thimble into a 50 mm Soxhlet extractor fitted with a 500 mL boiling flask containing 275 mL of benzene.

[Note: While the procedure specifies benzene as the extraction solution, many laboratories have substituted toluene for benzene because of the carcinogenic nature of benzene (28). The EPA is presently studying the replacement of benzene with toluene.]

12.1.2 Place a small funnel in the top of the Soxhlet extractor, making sure that the top of the funnel is inside the thimble. Rinse the inside of the corresponding glass cylinder into the thimble using approximately 25 mL of benzene. Place the extractor on a heating mantel. Adjust the heat until the benzene drips at a rate of 2 drops per second and allow to flow for 16 hours. Allow the apparatus to cool.

12.1.3 Remove the extractor and place a 3-bulb Snyder column onto the flask containing the benzene extract. Place on a heating mantel and concentrate the benzene to 25 mL (do not let go to dryness). Add 100 ml of hexane and again concentrate to 25 mL. Add a second 100 mL portion of hexane and again concentrate to 25 mL.

12.1.4 Let cool and add 25 mL hexane. The extract is ready for acid/base cleanup at this point.

12.2 Cleanup Procedures

12.2.1 Acid/Base Cleanup. Transfer the hexane extract to a 250 mL separatory funnel with two 25-mL portions of hexane. Wash the combined hexane with 30 ml of 2 N potassium hydroxide. Allow layers to separate and discard the aqueous layer. Repeat until no color is visible in the aqueous layer, up to a maximum of 4 washes. Partition the extract against 50 ml of 5% sodium chloride solution. Discard the aqueous layer. Carefully add 50 mL of concentrated sulfuric acid. Shake vigorously for 1 minute, allow layers to separate, and discard the acid layer. Repeat the acid wash until no color is visible in the aqueous layer, up to a maximum of 4 washes. Partition the extract against 50 ml of 5% sodium chloride solution. Discard the aqueous layer. Transfer the hexane through a 42-mm x 160-mm filter funnel containing a plug of glass wool and 3-cm of sodium sulfate into a 250-mL Kuderna-Danish (KD) concentrator fitter with a 15-mL catch tube. Rinse the filter funnel with two 25 mL portions of hexane. Place a 3-bulb Snyder column on the KD concentrator and concentrate on a steam bath to 1-2 mL. The extract is ready for the alumina column cleanup at this point, but it can be sealed and stored in the dark, if necessary. An extract that contains obvious contamination, such as yellow or brown color, is subjected to the silica column cleanup prior to the alumina cleanup.

12.2.2 Silica Column Preparation. Gently tamp a plug of glass wool into the bottom of a 5.75-inch (14.6 cm) disposable Pasteur pipette. Pour prewashed 100-200 mesh Bio-Sil®A (silica gel) into the pipette until a height of 3.0 cm of silica gel is packed into the column. Top the silica gel with 0.5 cm of anhydrous granular sodium sulfate. Place columns in an oven set at 220°C. Store columns in the oven until ready for use, at least overnight. Remove only the columns needed and place them in a desiccator until they have equilibrated to room temperature. Use immediately.

12.2.3 Silica Column Cleanup. Position the silica column over the alumina column so the eluent will drip onto the alumina column. Transfer the 2 mL hexane extract from the Acid/Base Cleanup onto the silica column with two separate 0.5-mL portions of hexane. Elute the silica column with an additional 4.0 mL of hexane. Discard the silica column and proceed with the alumina column cleanup at the point where the column is washed with 6.0 mL of carbon tetrachloride.

12.2.4 Alumina Column Preparation. Gently tamp a plug of glass wool into the bottom of a 5.75-inch (14.6 cm) disposable Pasteur pipette. Pour WOELM neutral alumina into the pipette while tapping the column with a pencil or wooden dowel until a height of 4.5 cm of alumina is packed into the column. Top the alumina with a 0.5 cm of anhydrous granular sodium sulfate. Prewash the column with 3 mL dichloromethane. Allow the dichloromethane to drain from the column; then force the remaining dichloromethane from the column with a stream of dry nitrogen. Place prepared columns in an oven set at 225°C. Store columns in the oven until ready for use, at least overnight. Remove only columns needed and place them in a desiccator over anhydrous calcium sulfate until they have equilibrated to room temperature. Use immediately.

12.2.5 Alumina Column Cleanup. Prewet the alumina column with 1 mL of hexane. Transfer the 2 mL hexane extract from acid/base cleanup into the column. Elute the column with 6.0 mL of carbon tetrachloride and archive. Elute the column with 4.0 mL of dichloromethane and catch the eluate in a 12- mL distillation receiver. Add 3 μL tetradecane, place a micro-Snyder column on the receiver and evaporate the dichloromethane just to dryness by means of a hot water bath. Add 2 mL of hexane to the receiver and evaporate just to dryness. Add another 2-mL portion of hexane and evaporate to 0.5 mL. The extract is ready for the carbon column cleanup at this point.

12.2.6 Carbon Column Preparation. Weigh 9.5 g of Bio-Sil®A (100-200 mesh) silica gel, which has been previously heated to 225°C for 24 hours, into a 50-mL screw cap container. Weigh 0.50 g of Amoco PX-21 carbon onto the silica gel cap and shake vigorously for 1 hour. Just before use, rotate the container by hand for at least 1 minute. Break a glass graduated 2.0-mL disposal pipette at the 1.8 mL mark and fire polish the end. Place a small plug of glass wool in the pipette and pack it at the 0.0 mL mark using two small solid glass rods. Add 0.1 mL of Bio-Sil®A 100-200 mesh silica gel. If more than 1 column is to be made at a time, it is best to

add the silica gel to all the columns and then add the carbon-silica gel mixture to all columns. Add 0.40 mL of the carbon silica gel mixture to the column; the top of the mixture will be at the 0.55-mL mark on the pipette. Top the column with a small plug of glass wool.

12.2.7 Carbon Column Cleanup. Place the column in a suitable clamp with the silica gel plug up. Add approximately 0.5 mL of 50 percent benzene-methylene chloride (v/v) to the top of the column. Fit a 10 mL disposable pipette on the top of the carbon column with a short piece of extruded teflon tubing. Add an additional 9.5 mL of the 50 percent benzene-methylene chloride. When approximately 0.5 mL of this solvent remains, add 10 mL of toluene. After all the toluene has gone into the column, remove the 10-mL reservoir and add at least 2.0 mL of hexane to the column. When approximately 0.1 mL of the hexane is left on the top of the column, transfer the sample extract onto the column with a Pasteur pipette. Rinse the distillation receiver column that contained the extract with two separate 0.2 mL portions of hexane and transfer each rinse onto the column. Allow the top of each transfer layer to enter the glass wool before adding the next one. When the last of the transfer solvent enters the glass wool, add 0.5 mL of methylene chloride, replace the 10-mL reservoir, and add 4.5 mL of methylene chloride to it. When approximately 0.5 mL of this solvent remains, add 10 mL of 50 percent benzene-methylene chloride. When all this solvent has gone onto the column, remove the reservoir, take the column out of the holder and rinse each end with toluene, turn the column over, and put it back in the holder. All previous elution solvents are archived. Place a suitable receiver tube under the column and add 0.5 mL of toluene to the top of the column. Fit the 10 mL reservoir on the column and add 9.5 mL of toluene to it. When all toluene has eluted through the column and has been collected in the receiving tube, add 5 mL of tetradecane and concentrate to 0.5 mL using a stream of nitrogen and water bath maintained at 60°C. Transfer the toluene extract to a 2.0 mL graduated Chromoflex® tube with two 0.5-mL portions of benzene. Add 0.5 ng of $^{13}C_{12}$-1,2,3,4-TCDD and store the extracts in the dark at room temperature. Concentrate the extract to 30 μL using a stream of nitrogen at room temperature just prior to analysis or shipping. Transfer the extracts that are to be shipped to a 2 mm i.d. x 75 mm glass tube that has been fire sealed on one end with enough benzene to bring the total volume of the extract to 100 μL. Then fire seal other end of the tube.

12.3 Glassware Cleanup Procedures

In this procedure, take each piece of glassware through the cleaning separately except in the oven baking process. Wash the 100-mL round bottom flasks, the 250 mL separatory funnels, the KD concentrators, etc., that were used in the extraction procedures three times with hot tap water, two times with acetone and two times with hexane. Then bake this glassware in a forced air oven that is vented to the outside for 16 hours at 450°C. Clean the PFTE stopcocks as above except for the oven baking step. Rinse all glassware with acetone and hexane immediately before use.

13. HRGC-HRMS System Performance

13.1 Operation of HRGC-HRMS

Operate the HRMS in the electron impact (EI) ionization mode using the selected ion monitoring (SIM) detection technique. Achieve a static mass resolution of 10,000 (10% valley) before analysis of a set of samples is begun. Check the mass resolution at the beginning and at the end of each day. (Corrective actions should be implemented whenever the resolving power does not meet the requirement.) Chromatography time required for PCDDs and PCDFs may exceed the long-term stability of the mass spectrometer because the instrument is operated in the high-resolution mode and the mass drifts of a few ppm (e.g., 5 ppm in mass) can have adverse effects on the analytical results. Therefore, a mass-drift correction may be required. Use a lock-mass ion for the reference

compound perfluorokerosene (PFK) to tune the mass spectrometer. The selection of the SIM lock-mass ions of PFK shown in the descriptors (see Tables 10, 11 and 12) is dependent on the masses of the ions monitored within each descriptor. An acceptable lock-mass ion at any mass between the lightest and heaviest ion in each descriptor can be used to monitor and correct mass drifts. Adjust the level of the reference compound (PFK) metered inside the ion chamber during HRGC-HRMS analyses so that the amplitude of the most intense selected lock-mass ion signal is kept to a minimum. Under those conditions, sensitivity changes can be more effectively monitored. Excessive use of PFK or any reference substance will cause high background signals and contamination of the ion source, which will result in an increase in "downtime" required for instrument maintenance.

Tune the instrument to a mass resolution of 10,000 (10% valley) at m/z 292.9825 (PFK). By using the peak matching unit (manual or computer simulated) and the PFK reference peak, verify that the exact m/z 392.9761 (PFK) is within 3 parts per million (ppm) of the required value.

Document the instrument resolving power by recording the peak profile of the high mass reference signal (m/z 392.9761) obtained during the above peak matching calibration experiment by using the low mass PFK ion at m/z 292.9825 as a reference. The minimum resolving power of 10,000 should be demonstrated on the high mass ion while it is transmitted at a lower accelerating voltage than the low mass reference ion, which is transmitted at full voltage and full sensitivity. There will be little, if any, loss in sensitivity on the high mass ion if the source parameters are properly tuned and optimized. The format of the peak profile representation should allow for computer calculated and manual determination of the resolution, i.e., the horizontal axis should be a calibrated mass scale (amu or ppm per division). Detailed descriptions for mass resolution adjustments are usually found in the instrument operators manual or instructions.

13.2 Column Performance

After the HRMS parameters are optimized, analyze an aliquot of a column performance solution containing the first and last eluting compounds (see Table 9), or a solution containing all congeners, to determine and confirm SIM parameters, retention time windows, and HRGC resolution of the compounds. Adjustments can be made at this point, if necessary. Some PeCDFs elute in the TCDD retention time window when using the 60 m DB-5 column. The PeCDF masses can be included with the TCDD/TCDF masses in Descriptor 1. Include the PeCDD/PeCDF masses with the TCDD/TCDF masses when using the 60 m SP-2331 polar column. The HRGC-HRMS SIM parameters and retention time windows can be rapidly and efficiently determined and optimized by analysis of a window defining solution of PCDDs/PCDFs using one mass for each isomer for the complete analysis of tetra- through octa- compounds, as illustrated in Figure 11.

13.3 SIM Cycle Time

The total time for each SIM cycle should be 1 second or less for data acquisition, which includes the sum of the mass ion dwell times and ESA voltage reset times.

13.4 Peak Separation

Chromatographic peak separation between 2,3,7,8-TCDD and the co-eluting isomers should be resolved with a valley of 25% or more (see Figure 12).

13.5 Initial Calibration

After the HRGC-HRMS SIM operating conditions are optimized, perform an initial calibration using the 5 calibration solutions shown in Table 3. The quantification relationships of labeled and unlabeled standards are illustrated in Tables 15, 16, 17, and 18. Figures 13 through 22 represent the extracted ion current profiles (EICP) for specific masses for 2,3,7,8-TCDF, 2,3,7,8-TCDD and other 2,3,7,8-substituted PCDF/PCDD (along with their labeled standards) through OCDF and OCDD respectively.

[Note: Other solutions containing fewer or different congeners and at different concentrations may also be used for calibration purposes.]

Referring to Tables 10, 11, or 12, calculate (1) the relative response factors (RRFs) for each unlabeled PCDD/PCDF and PBDD/PBDF [RRF (I)] relative to their corresponding $^{13}C_{12}$-labeled internal standard and (2) the RRFs for the $^{13}C_{12}$-labeled PCDD/PCDF and PBDD/PBDF internal standards [RRF (II)] relative to $^{37}Cl_4$-2,3,7,8-TCDD recovery standard using the following formulae:

$$RRF(I) = \frac{(A_x \times Q_{is})}{(Q_x \times A_{is})}$$

$$RRF(II) = \frac{(A_{is} \times Q_{rs})}{(Q_{is} \times A_{rs})}$$

where:

A_x = the sum of the integrated ion abundances of the quantitation ions (see Tables 10, 11 or 12) for unlabeled PCDDs/PCDFs, and PBDDs/PBDFs and BCDDs/BCDFs.

A_{is} = the sum of the integrated ion abundances of the quantitation ions for the $^{13}C_{12}$-labeled internal standards (see Table 10, 11 or 12).

[Note: Other $^{13}C_{12}$-labeled analytes may also be used as the recovery standard(s)]

A_{rs} = the integrated ion abundance for the quantitation ion of the $^{37}Cl_4$-2,3,7,8-TCDD recovery standard.

Q_{is} = the quantity of the $^{13}C_{12}$-labeled internal standard injected, pg.

Q_x = the quantity of the unlabeled PCDD/PCDF analyte injected, pg.

Q_{rs} = the quantity of the $^{37}Cl_4$-2,3,7,8-TCDD injected, pg.

RRF(I) and RRF(II) = dimensionless quantities. The units used to express Q_{is} and Q_x must be the same.

[Note: $^{13}C_{12}$-1,2,3,7,8-PeBDF is used to determine the response factor for the unlabeled 2,3,7,8-substituted, PeBDD, HxBDF and HxBDD.]

Calculate the average RRFs for the 5 concentration levels of unlabeled and $^{13}C_{12}$-labeled PCDDs/PCDFs and PBDDs/PBDFs for the initial calibration using the following equation:

$$\overline{RRF} = \frac{RRF1 + RRF2 + RRF3 + RRF4 + RRF5}{5}$$

13.6 Criteria Required for Initial Calibration

The analytical data must satisfy certain criteria for acceptable calibration. The isotopic ratios must be within the acceptable range (see Tables 19 and 20). The percent relative standard deviation for the response factors should be less than the values presented in Table 21. The signal-to-noise ratio for the $^{13}C_{12}$-labeled standards must be 10:1 or more and 5:1 or more for the unlabeled standards.

13.7 Continuing Calibration

Conduct an analysis at the beginning of each day to check and confirm the calibration using an aliquot of the calibration solution. This analysis should meet the isotopic ratios and signal to noise ratios of the criteria stated in Section 13.6 (see Table 21 for daily calibration percent difference criteria). It is good practice to confirm the calibration at the end of the day also. Calculate the daily calibration percent difference using the following equation.

$$\%RRF = \frac{RRF_{cc} - \overline{RRF}}{\overline{RRF}} \times 100$$

RRF_{cc} = the relative response factor for a specific analyte in the continuing calibration standard.

14. HRGC-HRMS Analysis And Operating Parameters

14.1 Sample Analysis

Sample Analysis. An aliquot of the sample extract is analyzed with the HRGC-HRMS system using the instrument parameters illustrated in Tables 13 and 14 and the SIM descriptors and masses shown in Tables 10, 11, and 12. A 30-m SE-54 fused silica capillary column is used to determine the concentrations of total tetra-, penta-, hexa-, hepta- and octa-CDDs/CDFs and/or to determine the minimum limits of detections (MLDs) for the compounds. If the tetra-, penta-, and hexa-CDDs/CDFs were detected in a sample and isomer specific analyses are required, then an aliquot of the sample extract is analyzed using the 60 m SP-2331 fused silica capillary column to provide a concentration for each 2,3,7,8-substituted PCDD/PCDF and concentrations for total PCDDs and PCDFs also.

[Note: Other capillary columns such as the DB-5, SE-30, and DB-225 may be used if the performance satisfies the specifications for resolution of PCDDs/PCDFs. The SE-54 column resolves the four HpCDF isomers, two HpCDD isomers, OCDF and OCDD for isomer specific analysis. It does not resolve the tetra-, penta-, and hexa-2,3,7,8-substituted isomers. The SE-54 column is used for the analysis of PBDDs and PBDFs.]

Isomer specificity for all 2,3,7,8-substituted PCDDs/PCDFs cannot be achieved on a single HRGC capillary column at this time. However, many types of HRGC capillary columns are available and can be used for these analyses after their resolution capabilities are confirmed to be adequate using appropriate standards.

Two HRGC columns shown in Table 13 have been used successfully since 1984 (27, 28). The 60-m DB-5 provides an efficient analysis for total concentrations of PCDDs/PCDFs, specific isomers (total tetra-, penta-, hexa-CDDs/CDFs, four HpCDF isomers, two HpCDD isomers, OCDD and OCDF), PBDDs/PBDFs, and/or determination of MDLs. The 60 m SP-2331 column provides demonstrated and confirmed resolution of 2,3,7,8-substituted tetra-, penta-, and hexa-PCDDs/PCDFs (14). The descriptors and masses shown in Tables 10, 11 and 12 must be modified to take into account the elution of some of the PeCDDs and PeCDFs in the tetra retention time window using the SP-2331column.

14.2 Identication Criteria

Criteria used for identification of PCDDs and PCDFs in samples are as follows:

- The integrated ion abundance ratio M/(M+2) or (M+2)/(M+4) shall be within 15 percent of the theoretical value. The acceptable ion abundance ranges are shown in Tables 19 and 20.
- The ions monitored for a given analyte, shown in Tables 10, 11, and 12, shall reach their maximum within 2 seconds of each other.
- The retention time for the 2,3,7,8-substituted analytes must be within 3 seconds of the corresponding $^{13}C_{12}$-labeled internal standard, surrogate, or alternate standard.
- The identification of 2,3,7,8-substituted isomers that do not have corresponding $^{13}C_{12}$-labeled standards is done by comparison to the analysis of a standard that contains the specific congeners. Comparison of the relative retention time (RRT) of the analyte to the nearest internal standard with reference (i.e., within 0.005 RRT time units to the comparable RRTs found in the continuing calibration or literature).
- The signal-to-noise ratio for the monitored ions must be greater than 2.5.
- The analysis shall show the absence of polychlorinated diphenyl- ethers (PCDPEs). Any PCDPEs that co-elute (± 2 seconds) with peaks in the PCDF channels indicates a positive interference, especially if the intensity of the PCDPE peak is 10 percent or more of the PCDF.

Use the identification criteria in Section 14.2 to identify and quantify the PCDDs and PCDFs in the sample. Figure 23 illustrates a reconstructed EICP for an environmental sample, identifying the presence of 2,3,7,8-TCDF as referenced to the labeled standard.

14.3 Quantification

The peak areas of ions monitored for $^{13}C_{12}$-labeled PCDDs/PCDFs and $^{37}Cl_4$-2,3,7,8-TCDD, unlabeled PCDDs/PCDFs, and respective relative response factors are used for quantification. The $^{37}Cl_4$-2,3,7,8-TCDD, spiked to extract prior to final concentration, and respective response factors are used to determine the sample extraction efficiencies achieved for the nine $^{13}C_{12}$-labeled internal standards, which are spiked to the sample prior to extraction (% recovery). The $^{13}C_{12}$-labeled PCDD/PCDF internal standards and response factors are used for quantification of unlabeled PCDDs/PCDFs and for determination of the minimum limits of detection with but one exception: $^{13}C_{12}$-OCDD is used for OCDF. Each $^{13}C_{12}$-labeled internal standard is used to quantify all of the PCDDs/PCDFs in its isomeric group. For example, $^{13}C_{12}$-2,3,7,8-TCDD and the 2,3,7,8-TCDD response factor are used to quantify all of the 22 tetra-chlorinated isomers. The quantification relationships of these standards are shown in Tables 15, 16, 17, and 18. The $^{37}Cl_4$-2,3,7,8-TCDD spiked to the filter of the sampler

prior to sample collection is used to determine the sampler retention efficiency, which also indicates the collection efficiency for the sampling period.

14.4 Calculations

14.4.1 Extraction Efficiency. Calculate the extraction efficiencies (percent recovery) of the 9 $^{13}C_{12}$-labeled PCDD/PCDF or the 3 $^{13}C_{12}$-labeled PBDD/PBDF internal standards measured in the extract using the formula:

$$\%R_{is} = \frac{[A_{is} \times Q_{rs} \times 100]}{[Q_{is} \times A_{rs} \times RRF(II)]}$$

where:

$\%R_{is}$ = percent recovery (extraction efficiency).

A_{is} = the sum of the integrated ion abundances of the quantitation ions (see Tables 10, 11 or 12) for the $^{13}C_{12}$-labeled internal standard.

A_{rs} = the sum of the integrated ion abundances of the quantitation ions (see Table 10, 11 or 12) for the $^{37}Cl_4$- or $^{13}C_{12}$-labeled recovery standard; the selection of the recovery standard(s) depends on the type of homologues.

Q_{is} = quantity of the $^{13}C_{12}$-labeled internal standard added to the sample before extraction, pg.

Q_{rs} = quantity of the $^{37}Cl_4$- or $^{13}C_{12}$-labeled recovery standard added to the sample extract before HRGC-HRMS analysis, pg.

RRF(II) = calculated mean relative response factor for the labeled internal standard relative to the appropriate labeled recovery standard.

14.4.2 Calculation of Concentration. Calculate the concentration of each 2,3,7,8-substituted PCDD/PCDF, other isomers or PBDD/PBDF that have met the criteria described in Sections 14.2 using the following formula:

$$C_x = \frac{[A_x \times Q_{is}]}{[A_{is} \times V_{std} \times RRF(I)]}$$

where:

C_x = concentration of unlabeled PCDD/PCDF, PBDD/PBDF or BCDD/BCDF congener(s), pg/m^3.

A_x = the sum of the integrated ion abundances of the quantitation ions (see Table 11, 12 or 13) for the unlabeled PCDDs/PCDFs, or PBDDs/PBDFs or BCDFs.

A_{is} = the sum of the integrated ion abundances of the quantitation ions (see Table 11, 12 or 13) for the respective $^{13}C_{12}$-labeled internal standard.

Q_{is} = quantity of the $^{13}C_{12}$-labeled internal standard added to the sample before extraction, pg.

V_{std} = standard volume of air, std m^3.

RRF(I) = calculated mean relative response factor for an unlabeled 2,3,7,8-substituted PCDD/PCDF obtained in Section 13.4.

14.5 Method Detection Limits (MDLs)

The ambient background levels of total PCDDs/PCDFs are usually found in the range of 0.3 to 2.9 pg/m^3. Therefore, the MDLs required to generate meaningful data for ambient air should be in the range of 0.02 to 0.15 pg/m^3 for tetra-, penta-, and hexa-CDDs/CDFs. Trace levels, 0.05 to 0.25 pg/m^3, of HpCDDs and OCDD are usually detected in the method blank (background contamination).

An MDL is defined as the amount of an analyte required to produce a signal with a peak area at least 2.5 x the area of the background signal level measured at the retention time of interest. MDLs are calculated for total PHDDs/PHDFs and for each 2,3,7,8-substituted congener. The calculation method used is dependent upon the type of signal responses present in the analysis. For example:

- Absence of response signals of one or both quantitation ion signals at the retention time of the 2,3,7,8-substituted isomer or at the retention time of non 2,3,7,8-substituted isomers. The instrument noise level is measured at the analyte's expected retention time and multiplied by 2.5, inserted into the formula below and calculated and reported as not detected (ND) at the specific MDL.
- Response signals at the same retention time as the 2,3,7,8-substituted isomers or the other isomers that have a S/N ratio in excess of 2.5:1 but that do not satisfy the identification criteria described in 14.2 are calculated and reported as ND at the elevated MDL and discussed in the narrative that accompanies the analytical results. Calculate the MDLs using the following formula:

$$MDL = \frac{[2.5 \times A_x \times Q_{is}]}{[A_{is} \times V_{std} \times \overline{RRF}]}$$

where:

MDL = concentration of unlabeled PHDD/PHDF, pg/m^3.

A_x = sum of integrated ion abundances of the quantitation ions (see Table 10, 11 or 12) for the unlabeled PHDDs/PHDFs which do not meet the identification criteria or 2.5 x area of noise level at the analyte's retention time.

A_{is} = sum of the integrated ion abundances of the quantitation ions (see Table 10, 11, or 12) for the $^{13}C_{12}$-labeled internal standards.

Q_{is} = quantity of the $^{13}C_{12}$-labeled internal standard spiked to the sample prior to extraction, pg.

V_{std} = standard volume of ambient air sampled, std m^3.

$\overline{RRF}$ = mean relative response factor for the unlabeled PHDD/PHDF.

14.6 2,3,7,8-TCDD Toxic Equivalents

Calculate the 2,3,7,8-TCDD toxic equivalents of PCDDs and PCDFs present in a sample according to the method recommended by EPA and the Center for Disease Control (18). This method assigns a 2,3,7,8-TCDD toxicity equivalency factor (TEF) for each of the seventeen 2,3,7,8-substituted PCDDs/PCDFs (see Table 22). The 2,3,7,8-TCDD equivalent of the PCDDs and PCDFs present in the sample is calculated by the respective TEF factors times their concentration for each of the compounds listed in Table 22. The exclusion of the other isomeric groupings (mono-, di-, and tri-chlorinated dibenzodioxins and dibenzofurans) does not mean that they are non-toxic. Their toxicity, as known at this time, is much less than the toxicity of the compounds listed in Table 22. The above procedure for calculating the 2,3,7,8-TCDD toxic equivalents is not claimed to be based on a

thoroughly established scientific foundation. The procedure, rather, represents a "consensus recommendation on science policy." Similar methods are used throughout the world.

15. Quality Assurance/Quality Control (QA/QC)

15.1 Certified analytical standards were obtained from Cambridge Isotope Laboratories, 50 Frontage Road, Andover, MA 01810, 508-749-8000.

15.2 Criteria used for HRGC-HRMS initial and continuing calibration are defined in Sections 13.5 and 13.6.

15.3 Analytical criteria used for identification purposes are defined in Section 14.2.

15.4 All test samples, method blanks, field blanks, and laboratory control samples are spiked with $13C_{12}$-labeled internal standards prior to extraction.

15.5 Sample preparation and analysis and evaluation of data are performed on a set of 12 samples, which may consist of 9 test samples, field blank, method blank, fortified method blank, or a laboratory control sample.

15.6 Method evaluation studies were performed to determine and evaluate the overall method capabilities (1, 2).

15.7 The $^{13}C_{12}$-1,2,3,4-TCDD solution is spiked to filters of all samplers, including field blanks, immediately prior to operation or is spiked to all PUF plugs prior to shipping them to the field for sampling to determine and document the sampling efficiency.

15.8 Minimum equipment calibration and accuracy requirements achieved are illustrated in Table 23.

15.9 QA/QC requirements for data:

Criteria	Requirements
The data shall satisfy all indicated identification criteria	Discussed in Section 14.2
Method efficiency achieved for $^{13}C_{12}$-labeled tetra-, penta-, hexa-CDDs/CDFs and PBDDs/PBDFs	50 to 120%
Method efficiency achieved for $^{13}C_{12}$-labeled HpCDD and OCDD	40 to 120%
Accuracy achieved for PHDDs and PHDFs in method spike at 0.25 to 2.0 pg/m^3 concentration range	70 to 130%
Precision achieved for duplicate method spikes or QA samples	± 30%
Sampler efficiency achieved for $^{13}C_{12}$-1,2,3,4-TCDD	50 to 120%
Method blank contamination	Free of contamination that would interfere with test sample results.
Method detection limit range for method blank and field blank (individual isomers)	0.02 to 0.25 pg/m^3

16. Report Format

The analytical results achieved for a set of 12 samples should be presented in a table such as the one shown in Table 24. The analytical results, analysis, QA/QC criteria, and requirements used to evaluate data are discussed in an accompanying analytical report. The validity of the data in regard to the data quality requirements and any qualification that may apply is explained in a clear and concise manner for the user's information.

17. References

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TABLE 1. NUMBER OF POLYCHLORINATED DIBENZO-P-DIOXIN AND DIBENZOFURAN (PCDD/PCDF) CONGENERS

No. of Chlorine Atoms	No. of PCDD Isomers	No. of PCDF Isomers
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1
Total	75	135

[Note: This also applies for the polybrominated dibenzo-p-dioxins and dibenzofurans (PBDDs/PBDFs).]

TABLE 2. LIST OF 2,3,7,8-CHLORINE SUBSTITUTED PCDD/PCDF CONGENERS

PCDDs	PCDFs
2,3,7,8-TCDD	2,3,7,8-TCDF
1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDF
	2,3,4,7,8-PeCDF
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxCDF
	2,3,4,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDF
	1,2,3,4,7,8,9-HpCDF
1,2,3,4,6,7,8,9-OCDD	1,2,3,4,6,7,8,9-OCDF

TABLE 3. COMPOSITIONS OF THE INITIAL CALIBRATION SOLUTIONS OF LABELED AND UNLABELED PCDDS AND PCDFS

	Concentrations (pg/μL)				
Compound Solution No.	1	2	3	4	5
Unlabeled Analytes					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD	2.5	5	25	250	500
1,2,3,7,8-PeCDF	2.5	5	25	250	500
2,3,4,7,8-PeCDF	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5.0	10	50	500	1000
OCDF	5.0	10	50	500	1000
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100

TABLE 3. (continued)

Compound Solution No.	Concentrations (pg/μL)				
	1	2	3	4	5
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate Standards					
$^{13}C_{12}$-2,3,4,7,8-PeCDF	60	80	100	120	140
$^{13}C_{12}$-1,2,3,4,7,8-HxCD	60	80	100	120	140
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	60	80	100	120	140
$^{13}C_{12}$-1,2,3,6,7,8,9-HpCD	60	80	100	120	140
Field Standards					
$^{37}Cl_4$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100
Recovery Standard					
$^{13}C_{12}$-1,2,3,4-TCDD	50	50	50	50	50

[Note: Standards specified in EPA Method 1613 can also be used in this method.]

TABLE 4. COMPOSITION OF THE SAMPLE FORTIFICATION SOLUTIONS

Analyte	Concentration (pg/μL)
Chlorinated Internal Standards	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Brominated Internal Standards	
$^{13}Cl_{12}$-2,3,7,8-TBDD	0.86
$^{13}C_{12}$-2,3,7,8-TBDF	0.86
$^{13}C_{12}$-1,2,3,7,8-PeBDF	0.86

TABLE 5. COMPOSITION OF RECOVERY STANDARD SOLUTION

Analyte	Concentration (pg/μL)
Recovery Standard	
$^{13}C_{12}$-1,2,3,4-TCDD	10

TABLE 6. COMPOSITION OF AIR SAMPLER FIELD FORTIFICATION STANDARD SOLUTION

Analyte	Concentration (pg/μL)
Field Fortification Standard	
$^{37}Cl_4$-2,3,7,8-TCDD	10

TABLE 7. COMPOSITION OF SURROGATE STANDARD SOLUTION

Analyte	Concentration (pg/μL)
Surrogate Standards	
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100

TABLE 8. COMPOSITION OF MATRIX AND METHOD SPIKE AND METHOD SPIKE SOLUTIONS OF PCDDS/PCDFS AND PBDDS/PBDFS[a]

Analyte	Concentration (pg/μL)	Analyte	Concentration (pg/μL)
Native PCDDs and PCDFs		**Native PBDDs and PBDFs**	
2,3,7,8-TCDD	1	2,3,7,8-TBDD	1
2,3,7,8-TCDF	1	2,3,7,8-TBDF	1
1,2,3,7,8-PeCDD	5	1,2,3,7,8-PeBDD	5
1,2,3,7,8-PeCDF	5	1,2,3,7,8-PeBDF	5
2,3,4,7,8-PeCDF	5	1,2,3,4,7,8-HxBDD	5
1,2,3,4,7,8-HxCDD	5	1,2,3,4,7,8-HxBDF	5
1,2,3,6,7,8-HxCDD	5		
1,2,3,7,8,9-HxCDD	5		
1,2,3,4,7,8-HxCDF	5		
1,2,3,6,7,8-HxCDF	5		
1,2,3,7,8,9-HxCDF	5		
2,3,4,6,7,8-HxCDF	5		
1,2,3,4,6,7,8-HpCDD	5		
1,2,3,4,6,7,8-HpCDF	5		
1,2,3,4,7,8,9-HpCDF	5		
OCDD	10		
OCDF	10		

[a]Solutions at different concentrations and those containing different congeners may also be used.

TABLE 9. HRGC-HRMS COLUMN PERFORMANCE EVALUATION SOLUTIONS

Congener	First Eluted	Last Eluted
SE-54 Column GC Retention Time Window Defining Standard[a]		
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-
OCDF	OCDF	
OCDD	OCDD	
SE-54 TCDD Isomer Specificity Test Standard[b]		
	1,2,3,4-TCDD	
	1,4,7,8-TCDD	2,3,7,8-TCDD
SP-2331 Column TCDF Isomer Specificity Test Standard[c]		
	2,3,4,7-TCDF	
	2,3,7,8-TCDF	
	1,2,3,9-TCDF	

[a]A solution containing these congeners and the seventeen 2,3,7,8-substituted congeners may also be used for these purposes.
[b]A solution containing the 1,2,3,4,-TCDD and 2,3,7,8-TCDD may also be used for this purpose.
[c]Solution containing all tetra- through octa-congeners may also be used for these purposes.

TABLE 10. DESCRIPTORS, MASSES, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE PCDDS AND PCDFS

Descriptor Number	Accurate Mass	m/z Type	Elemental Composition	Compound[2]	Primary m/z
1	292.9825	Lock	$C_7 F_{11}$	PFK	
	303.9016	M	$C_{12} H_4 {}^{35}Cl_4 O$	TCDF	Yes
	305.8987	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF	
	315.9419	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O$	TCDF[3]	Yes
	317.9389	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O$	TCDF[3]	
	319.8965	M	$C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD	Yes
	321.8936	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD	
	327.8847	M	$C_{12} H_4 {}^{37}Cl_4 O_2$	TCDD[4]	
	330.9792	QC	$C_7 F_{13}$	PFK	
	331.9368	M	$^{13}C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD[3]	Yes
	333.9339	M+2	$^{13}C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD[3]	
	375.8364	M+2	$C_{12} H_4 {}^{35}Cl_5 {}^{37}Cl O$	HxCDPE	
2	339.8597	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF	Yes
	341.8567	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF	
	351.9000	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O$	PeCDF[3]	Yes
	353.8970	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O$	PeCDF[3]	
	354.9792	Lock	$C_9 F_{13}$	PFK	
	355.8546	M+2	$C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD	Yes
	357.8516	M+4	$C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD	
	367.8949	M+2	$^{13}C_{12} H_3 {}^{35}Cl_4 {}^{37}Cl O_2$	PeCDD[4]	Yes
	369.8919	M+4	$^{13}C_{12} H_3 {}^{35}Cl_3 {}^{37}Cl_2 O_2$	PeCDD[4]	
	409.7974	M+2	$C_{12} H_3 {}^{35}Cl_6 {}^{37}Cl O$	HpCDPE	

TABLE 10. (continued)

Descriptor Number	Accurate Mass	m/z Type	Elemental Composition	Compound[2]	Primary m/z
3	373.8208	M+2	$C_{12}\ H_2\ ^{35}Cl_5\ ^{37}Cl\ O$	HxCDF	Yes
	375.8178	M+4	$C_{12}\ H_2\ ^{35}Cl_4\ ^{37}Cl_2\ O$	HxCDF	
	383.8639	M	$^{13}C_{12}\ H_2\ ^{35}Cl_6\ O$	HxCDF[3]	Yes
	385.8610	M+2	$^{13}C_{12}\ H_2\ ^{35}Cl_5\ ^{37}Cl\ O$	HxCDF[3]	
	389.8157	M+2	$C_{12}\ H_2\ ^{35}Cl_5\ ^{37}Cl\ O_2$	HxCDD	Yes
	391.8127	M+4	$C_{12}\ H_2\ ^{35}Cl_4\ ^{37}Cl_2\ O_2$	HxCDD	
	392.9760	Lock	$C_9\ F_{15}$	PFK	
	401.8559	M+2	$^{13}C_{12}\ H_2\ ^{35}Cl_5\ ^{37}Cl\ O_2$	HxCDD[3]	Yes
	403.8529	M+4	$^{13}C_{12}\ H_2\ ^{35}Cl_4\ ^{37}Cl_2\ O_2$	HxCDD[3]	
	430.9729	QC	$C_9\ F_{13}$	PFK	
	445.7555	M+4	$C_{12}\ H_2\ ^{35}Cl_6\ ^{37}Cl_2\ O$	OCDPE	
4	407.7818	M+2	$C_{12}H^{35}Cl_6\ ^{37}Cl\ O$	H_pCDF	Yes
	409.7789	M+4	$C_{12}\ H\ ^{35}Cl_5\ ^{37}Cl_2\ O$	HpCDF	
	417.8253	M	$^{13}C_{12}\ H\ ^{35}Cl_7\ O$	HpCDF[3]	Yes
	419.8220	M+2	$^{13}C_{12}\ H\ ^{35}Cl_6\ ^{37}Cl\ O$	HpCDF[3]	
	423.7766	M+2	$C_{12}\ H\ ^{35}Cl_6\ ^{37}Cl\ O_2$	HpCDD	Yes
	425.7737	M+4	$C_{12}\ H\ ^{35}Cl_5\ ^{37}Cl_2\ O_2$	HpCDD	
	430.9729	Lock	$C_9\ F_{17}$	PFK	
	435.8169	M+2	$^{13}C_{12}\ H\ ^{35}Cl_6\ ^{37}Cl\ O_2$	HpCDD[3]	Yes
	437.8140	M+4	$^{13}C_{12}\ H\ ^{35}Cl_5\ ^{37}Cl_2\ O_2$	HpCDD[3]	
	479.7165	M+4	$C_{12}\ H\ ^{35}Cl_7\ ^{37}Cl_2\ O$	NCDPE	

TABLE 10. (continued)

Descriptor Number	Accurate Mass	m/z Type	Elemental Composition	Compound[2]	Primary m/z
5	441.7428	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ O$	OCDF	Yes
	442.9728	Lock	$C_{10}\ F_{17}$	PFK	
	443.7399	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ O$	OCDF	
	457.7377	M+2	$C_{12}\ ^{35}Cl_7\ ^{37}Cl\ O_2$	OCDD	Yes
	459.7348	M+4	$C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ O_2$	OCDD	
	469.7779	M+2	$^{13}C_{12}\ ^{35}Cl_7\ ^{37}Cl\ O_2$	OCDD[3]	Yes
	471.7750	M+4	$^{13}C_{12}\ ^{35}Cl_6\ ^{37}Cl_2\ O_2$	OCDD[3]	
	513.6775	M+4	$C_{12}\ ^{35}Cl_8\ ^{37}Cl_2\ O$	DCDPE	

[1]Nuclidic masses used:
H = 1.007825 C = 12.00000 ^{13}C = 13.003355 F = 18.9984
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903

[2]Compound abbreviations:

Polychlorinated dibenzo-p-dioxins
TCDD = Tetrachlorodibenzo-p-dioxin
PeCDD = Pentachlorodibenzo-p-dioxin
HxCDD = Hexachlorodibenzo-p-dioxin
HpCDD = Heptachlorodibenzo-p-dioxin
OCDD = Octachlorodibenzo-p-dioxin

Polychlorinated dibenzofurans
TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran

Polychlorinated diphenyl ethers
HxCDPE = Hexachlorodiphenyl ether
HpCDPE = Heptachlorodiphenyl ether
OCDPE = Octachlorodiphenyl ether
NCDPE = Nonachlorodiphenyl ether
DCDPE = Decachlorodiphenyl ether

Lock mass and QC compound
PFK = Perfluorokerosene

[3]Labeled compound

[4]There is only one m/z for $^{37}Cl_4$-2,3,7,8-TCDD (recovery standard).

TABLE 11. DESCRIPTORS, M/Z TYPES, EXACT MASSES AND ELEMENTAL COMPOSITIONS OF THE PBDDS AND PBDFS

Descriptor Number	Accurate Mass[1]	Ion Type	Elemental Composition	Compound[2]
1	327.8847	M	$C_{12} H_4 {}^{37}Cl_4 O_2$	TCDD[4]
	330.9792	QC	$C_7 F_{13}$	PFK
	331.9368	M	$C_{12} H_4 {}^{35}Cl_4 O_2$	TCDD[3]
	333.9339	M+2	$C_{12} H_4 {}^{35}Cl_3 {}^{37}Cl O_2$	TCDD[3]
2	417.825	M	$^{13}C_{12} H {}^{35}Cl_7 O$	HpCDF[3]
	419.822	M+2	$^{13}C_{12} H {}^{35}Cl_6 {}^{37}Cl O$	HpCDF[3]
	466.973	QC		PFK
	481.698	M+2	$C_{12} H_4 {}^{79}Br_3 {}^{81}BrO$	TBDF
	483.696	M+4	$C_{12} H_4 {}^{79}Br_2 {}^{81}Br_2 O$	TBDF
	485.694	M+6	$C_{12} H_4 {}^{79}Br {}^{81}Br_3 O$	TBDF
	492.970	LOCK MASS		PFK
	493.738	M+2	$^{13}C_{12} H_4 {}^{79}Br_3 {}^{81}Br O$	TBDF[3]
	495.736	M+4	$^{13}C_{12} H_4 {}^{79}Br_2 {}^{81}Br_2 O$	TBDD[3]
	497.692	M+2	$C_{12} H_4 {}^{79}Br_3 {}^{81}Br O_2$	TBDD
	499.690	M+4	$C_{12} H_4 {}^{79}Br_2 {}^{81}Br_2 O_2$	TBDD
	501.689	M+6	$C_{12} H_4 {}^{79}Br {}^{81}Br_3 O$	TBDD
	509.733	M+2	$^{13}C_{12} H_4 {}^{79}Br_3 {}^{81}BrO_2$	TBDD[3]
	511.731	M+4	$^{13}C_{12} H_4 {}^{79}Br_2 {}^{81}Br_2 O_2$	TBDD[3]
	565.620	M+6	$C_{12} H_5 {}^{79}Br_2 {}^{81}Br_3 O$	PeBDPO
	643.530	M+6	$C_{12} H_4 {}^{79}Br_3 {}^{81}Br_3 O$	HxBDPO

TABLE 11. (continued)

Descriptor Number	Accurate Mass[1]	Ion Type	Elemental Composition	Compound[2]
3	469.778	M+2	$^{13}C_{12}\ ^{35}Cl_7\ ^{37}Cl\ O_2$	OCDD[3]
	471.775	M+4	$^{13}C_{12}\ ^{35}Cl_6\ ^{37}Cl\ O_2$	OCDD[3]
	559.608	M+2	$C_{12}\ H_3\ ^{79}Br_4\ ^{81}Br\ O$	PeBDF
	561.606	M+4	$C_{12}\ H_3\ ^{79}Br_3\ ^{81}Br_2\ O$	PeBDF
	563.604	M+6	$C_{12}\ H_3\ ^{79}Br_2\ ^{81}Br_3\ O$	PeBDF
	566.966	LOCK MASS		PFK
	573.646	M+4	$^{13}C_{12}\ H_3\ ^{79}Br_3\ ^{81}Br_2\ O$	PeBDF[3]
	575.644	M+6	$^{13}C_{12}\ H_3\ ^{79}Br_2\ ^{81}Br_3\ O$	PeBDF[3]
	575.603	M+2	$C_{12}\ H_3\ ^{79}Br_4\ ^{81}Br\ O_2$	PeBDD
	577.601	M+4	$C_{12}\ H_3\ ^{79}Br_3\ ^{37}Br_2\ O_2$	PeBDD
	579.599	M+6	$C_{12}\ H_3\ ^{79}Br_2\ ^{81}Br_3\ O_2$	PeBDD
	589.641	M+4	$^{13}C_{12}\ H_3\ ^{79}Br_3\ ^{37}Br_2\ O_2$	PeBDD[3]
	591.639	M+6	$^{13}C_{12}\ H_3\ ^{79}Br_3\ ^{81}Br_2\ O_2$	PeBDD[3]
	616.963	QC		PFK

TABLE 11. (continued)

Descriptor Number	Accurate Mass[1]	Ion Type	Elemental Composition	Compound[2]
4	643.530	M+6	$C_{12} H_4 {}^{79}Br_3 {}^{81}Br_3 O$	HxBDPO
	721.441	M+6	$C_{12} H_3 {}^{79}Br_4 {}^{81}Br_3 O$	HpBDPO
	616.963	QC		PFK
	639.517	M+4	$C_{12} H_2 {}^{79}Br_4 {}^{81}Br_2 O$	HxBDF
	641.514	M+6	$C_{12} H_2 {}^{79}Br_3 {}^{81}Br_3 O$	HxBDF
	643.512	M+8	$C_{12} H_2 {}^{79}Br_2 {}^{81}Br_4 O$	HxBDF
	655.511	M+4	$C_{12} H_2 {}^{79}Br_4 {}^{81}Br_2 O_2$	HxBDD
	657.509	M+6	$C_{12} H_2 {}^{79}Br_3 {}^{81}Br_3 O_2$	HxBDD
	659.507	M+8	$C_{12} H_2 {}^{79}Br_2 {}^{81}Br_4 O_2$	HxBDD
	666.960	LOCK MASS		PFK
	721.441	M+6	$C_{12} H_3 {}^{79}Br_4 {}^{81}Br_3 O$	HpBDPO
	801.349	M+8	$C_{12} H_2 {}^{79}Br_4 {}^{81}Br_4 O$	OBDPO

TABLE 11. (continued)

Descriptor Number	Accurate Mass[1]	Ion Type	Elemental Composition	Compound[2]
5	717.427	M+4	$C_{12}H\ ^{79}Br_5\ ^{81}Br_2\ O$	HpBDF
	719.425	M+6	$C_{12}H\ ^{79}Br_4\ ^{81}Br_3\ O$	HpBDF
	721.423	M+8	$C_{12}H\ ^{79}Br_3\ ^{81}Br_4\ O$	HpBDF
	733.422	M+4	$C_{12}H\ ^{79}Br_5\ ^{81}Br_2\ O_2$	HpBDD
	735.420	M+6	$C_{12}H\ ^{79}Br_4\ ^{81}Br_3\ O_2$	HpBDD
	737.418	M+4	$C_{12}H\ ^{79}Br_3\ ^{81}Br_4\ O_2$	HpBDD
	754.954	QC		PFK
	770.960	LOCK MASS ALTERNATE		HpTriazine
	801.349	M+8	$C_{12}H_2\ ^{79}Br_4\ ^{81}Br_4\ O$	OBDPO
	816.951	LOCK MASS		PFK
	879.260	M+8	$C_{12}H\ ^{79}Br_5\ ^{81}Br_4\ O$	NBDPO
	865.958	QC ALTERNATE		HpTriazine

[1]Nuclidic masses used: H = 1.007825 C = 12.000000 ^{13}C = 13.003355
O = 15.994915 ^{79}Br = 78.91834 ^{81}Br = 80.91629
^{19}F = 18.9984

[2]Compound abbreviations:

Polybromoinated dibenzo-p-dioxins
TBDD = Tetrabromodibenzo-p-dioxin
PeBDD = Pentabromodibenzo-p-dioxin
HxBDD = Hexabromodibenzo-p-dioxin
HpBDD = Heptabromodibenzo-p-dioxin
OBDD = Octabromodibenzo-p-dioxin

Polybromoinated dibenzofurans
TBDF = Tetrabromodibenzofuran
PeBDF = Pentabromodibenzofuran
HxBDF = Hexabromodibenzofuran
HpBDF = Heptabromodibenzofuran
OBDF = Octabromodibenzofuran

Polybromoinated diphenyl ethers
HxBDPE = Hexabromodiphenyl ether
HpBDPE = Heptabromodiphenyl ether
OBDPE = Octabromodiphenyl ether
NBDPE = Nonabromodiphenyl ether
DBDPE = Decabromodiphenyl ether
PFK = Perfluorokerosene
HpTriazine = Tris-(perfluoroheptyl)-s-Triazine

[3]Labeled Compound

[4]There is only one m/z for $^{37}Cl_4$-2378-TCDD (recovery standard).

TABLE 12. DESCRIPTORS, MASSES, M/Z TYPES, AND ELEMENTAL COMPOSITIONS OF THE BCDDS AND BCDFS

Descriptor Number	Accurate mass[1]	m/z Type	Elemental Composition	Compound[2]	Primary m/z
1	315.942	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF[4]	
	317.939	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF[4]	Yes
	327.885	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD[3]	Yes
	330.979	Lock	C_7F_{13}	PFK	
	331.937	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD[4]	
	333.934	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD[4]	Yes
	347.851	M	$C_{12}H_4{}^{35}Cl_3{}^{79}Br0$	Br Cl_3 DF	
	349.849	M+2	$C_{12}H_4{}^{35}Cl_2{}^{37}Cl{}^{79}BrO$	Br Cl_3 DF	Yes
	363.846	M	$C_{12}H_4{}^{35}Cl_3{}^{79}BrO_2$	Br Cl_3 DD	
	365.844	M+2	$C_{12}H_4{}^{35}Cl_2{}^{37}Cl{}^{79}BrO_2$	Br Cl_3 DD	Yes

TABLE 12. (continued)

Descriptor Number	Accurate mass[1]	m/z Type	Elemental Composition	Compound[2]	Primary m/z
2	351.900	M+2	$^{13}C_{12}$ H_3 $^{35}Cl_5$ O	$PeCDF_4$	
	353.897	M+4	$^{13}C_{12}$ H_3 $^{35}Cl_4$ ^{37}Cl 0	PeCDF[4]	
	354.979	Lock	C_9 F_3	PFK	
	367.895	M+2	$^{13}C_{12}$ H_3 $^{35}Cl_5$ O_2	PeCDD[4]	Yes
	369.892	M+4	$^{13}C_{12}$ H_3 $^{35}Cl_4$ ^{37}Cl O_2	PeCDD[4]	
	381.812	M	C_{12} H_3 $^{35}Cl_4$ ^{79}Br O	Br Cl_4 DF	
	383.809	M+2	C_{12} H_3 $^{35}Cl_3$ ^{37}Cl ^{79}Br O	Br Cl_4 DF	Yes
	397.807	M	C_{12} H_3 $^{35}Cl_4$ ^{79}Br O_2	Br Cl_4 DD	
	399.804	M+2	C_{12} H_3 $^{35}Cl_3$ ^{37}Cl ^{79}Br O_2	Br Cl_4 DD	Yes

[1]Nuclidic masses used:

H = 1.007825 C = 12.00000 ^{13}C = 13.003355
O = 15.994915 ^{35}Cl = 34.968853 ^{37}Cl = 36.965903
F = 18.9984 ^{79}Br = 78.91834 ^{81}Br = 80.91629

[2]Compound abbreviations:

Polychlorinated dibenzo-p-dioxins
TCDD = Tetrachlorodibenzo-p-dioxin
PeCDD = Pentachlorodibenzo-p-dioxin
HxCDD = Hexachlorodibenzo-p-dioxin
HpCDD = Heptachlorodibenzo-p-dioxin
OCDD = Octachlorodibenzo-p-dioxin

Polychlorinated dibenzofurans
TCDF = Tetrachlorodibenzofuran
PeCDF = Pentachlorodibenzofuran
HxCDF = Hexachlorodibenzofuran
HpCDF = Heptachlorodibenzofuran

Brominated/Chlorinated dibenzo-p-dioxins and dibenzofurans
$BrCl_3$DD = Bromotrichloro dibenzo-p-dioxin
$BrCl_4$DD = Bromotetrachloro dibenzo-p-dioxin
$BrCl_3$DF = Bromotrichloro dibenzofuran
$BrCl_4$DF = Bromotetrachloro dibenzofuran

Lock mass and QC compound
PFK = Perfluorokerosene

[3]There is only one m/z for $^{37}Cl_4$-2,3,7,8-TCDD (recovery standard).

[4]Labeled compound

TABLE 13. HRGC OPERATING CONDITIONS

Column Type	DB-5	SE-54	SP-2331
Length (m)	60	30	60
i.d. (mm)	0.25	0.25	0.25
Film Thickness (μm)	0.25	0.25	0.20
Carrier Gas	Helium	Helium	Helium
Carrier Gas Flow (mL/min)	1-2	1-2	1-2
Injector temperature (°C)	290	308	308
Injection Mode	Splitless	<--- Moving needle --->	
Initial Temperature (°C)	200	170.0	150.0
Initial Time (min)	2	7.0	7.0
Rate 1 (°C/min)	5	8.0	10.0
Temperature (°C)	220		
Hold Time (min)	16		
Rate 2 (deg. C/min)	5		
Temperature (°C)	235		
Hold Time (min)	7		
Rate 2 (deg. C/min)	5		
Final Temperature (°C)	330	300.0	250.0
Hold Time (min)	5		

TABLE 14. HRMS OPERATING CONDITIONS

Electron impact ionization	25-70 eV
Mass resolution	>10,000 (10% Valley Definition)
Analysis	Selected ion monitoring (SIM)
Exact masses monitored	Masses shown in Tables 10, 11, 12

TABLE 15. UNLABELED AND LABELED ANALYTE QUANTIFICATION RELATIONSHIPS

Analyte	Internal Standard Used During Quantification
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
Other TCDDs	$^{13}C_{12}$-2,3,7,8-TCDD
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
Other PeCDDs	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
Other HxCDDs	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
Other HpCDDs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
OCDD	$^{13}C_{12}$-OCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
Other TCDFs	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Other PeCDFs	$^{13}C_{12}$-1,2,3,7,8-PeCDF
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
Other HxCDFs	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
Other HpCDFs	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDF	$^{13}C_{12}$-OCDD

TABLE 16. INTERNAL STANDARDS QUANTIFICATION RELATIONSHIPS

Internal Standard	Standard Used During Percent Recovery Determination[a]
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

[a]Surrogate standards shown in Table 7 may also be used.

TABLE 17. SURROGATE/ALTERNATE STANDARDS QUANTIFICATION RELATIONSHIPS

Surrogate Standard	Standard Used During Percent Recovery Determination
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF

[Note: Other surrogate standards may be used instead]

TABLE 18. QUANTIFICATION RELATIONSHIPS OF THE CARBON-LABELED STANDARDS AND THE ANALYTES

Analytes	Quantification Standard
2,3,7,8-TBDD	$^{13}C_{12}$-2,3,7,8-TBDD
2,3,7,8-TBDF	$^{13}C_{12}$-2,3,7,8-TBDF
1,2,3,7,8-PeBDD	$^{13}C_{12}$-1,2,3,7,8-PeBDD
1,2,3,7,8-PeBDF	$^{13}C_{12}$-1,2,3,7,8-PeBDF
2,3,4,7,8-PeBDF	$^{13}C_{12}$-1,2,3,7,8-PeBDF
1,2,3,4,7,8-HxBDD	$^{13}C_{12}$-1,2,3,7,8-PeBDD

[Note: O.5 ng $^{37}Cl_4$-2,3,7,8-TCDD spiked to the extract prior to final concentration to 60 μL was used to determine the method efficiency (% recovery of the $^{13}C_{12}$-labeled PBDDs/PBDFs).

- *Additional 2,3,7,8-substituted PBDDs/PBDFs are now commercially available.*
- *Retention Index for the PBDDs/PBDFs were published by Sovocool, etal., Chemosphere 16, 221-114, 1987; and Donnelly, et al., Biomedical Environmental Mass Spectrometry, 14, pp. 465-472, 1987.]*

TABLE 19. THEORETICAL ION ABUNDANCE RATIOS AND CONTROL LIMITS FOR PCDDS AND PCDFS

No. of Chlorine Atoms	m/z's Forming Ratio	Theoretical Ratio	Control Limits[1]	
			Lower	Upper
4[2]	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[3]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.04	0.88	1.20
7[4]	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

[1]Represent ± 15% windows around the theoretical ion abundance ratios.
[2]Does not apply to $^{37}Cl_4$-2,3,7,8-TCDD (cleanup standard).
[3]Used for $^{13}C_{12}$-HxCDF only.
[4]Used for $^{13}C_{12}$-HpCDF only.

TABLE 20. THEORETICAL ION ABUNDANCE RATIOS AND CONTROL LIMITS FOR PBDDS AND PBDFS

Number of Bromine Atoms	Ion Type	Theoretical Ratio	Control Limits	
			Lower	Upper
4	M+2/M+4	0.68	0.54	0.82
4	M+4/M+6	1.52	1.22	1.82
5	M+2/M+4	0.51	0.41	0.61
5	M+4/M+6	1.02	0.82	1.22
6	M+4/M+6	0.77	0.62	0.92
6	M+6/M+8	1.36	1.09	1.63
7	M+4/M+6	0.61	0.49	0.73
7	M+6/M+8	1.02	0.82	1.22

TABLE 21. MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative Response Factors	
	Initial Calibration RSD	Daily Calibration % Difference
Unlabeled Analytes		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards		
$_{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30

TABLE 21. (continued)

Compound	Relative Response Factors	
	Initial Calibration RSD	Daily Calibration % Difference
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25

TABLE 22. 2,3,7,8-TCDD EQUIVALENT FACTORS (TEFS)[1]
FOR THE POLYCHLORINATED DIBENZODIOXINS
AND POLYCHLORINATED DIBENZOFURANS

Number	Compound	TEF
1	2,3,7,8-TCDD	1.00
2	1,2,3,7,8-PeCDD	0.50
3	1,2,3,4,7,8-HxCDD	0.1
4	1,2,3,6,7,8-HxCDD	0.1
5	1,2,3,7,8,9-HxCDD	0.1
6	1,2,3,4,6,7,8-HpCDD	0.01
7	OCDD	0.001
8	2,3,4,7,8-TCDF	0.10
9	1,2,3,7,8-PeCDF	0.05
10	2,3,4,7,8-PeCDF	0.5
11	1,2,3,4,7,8-HxCDF	0.1
12	1,2,3,6,7,8-HxCDF	0.1
13	1,2,3,7,8,9-HxCDF	0.1
14	2,3,4,6,7,8-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	OCDF	0.001

[1]Interim procedures for Estimating Risks associated with Exposures to mixtures of Chlorinated Dibenzo-p-Dioxins and Dibenzofurans (CDDs/CDFs), WPA-625/3-89-016, March 1989.

[Note: The same TEFs are assigned to the PBDDs/PBDFs and BCDDs/BCDFs.]

TABLE 23. MINIMUM SAMPLING EQUIPMENT CALIBRATION AND ACCURACY REQUIREMENTS

Equipment	Acceptance limits	Frequency and method of measurement	Action if require-ments are not met
Sampler	Indicated flow rate = true flow rate ±10%.	Calibrate with certified transfer standard on receipt, after maintenance on sampler, and any time audits or flow checks deviate more than ±10% from the indicated flow rate or ±10% from the design flow rate.	Recalibrate
Associated equipment			
Sampler on/off timer	±30 min/24 hour	Check at purchase and routinely on sample-recovery days	Adjust or replace
Elapsed-time meter	±30 min/24 hour	Compare with a standard time-piece of known accuracy at receipt and at 6-month intervals	Adjust or replace
Flowrate transfer standard (orifice device)	Check at receipt for visual damage	Recalibrate annually against positive displacement standard volume meter	Adopt new calibration curve

TABLE 24. FORMAT FOR TABLE OF ANALYTICAL RESULTS

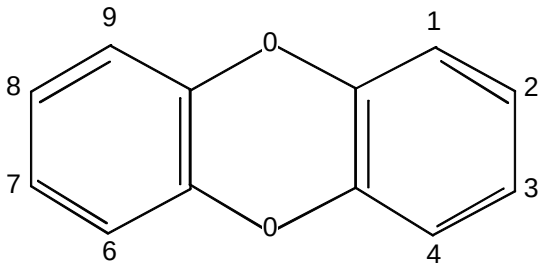
IDENTIFICATION					
AIR SAMPLER EFFICIENCY (% RECOVERY)					
$^{13}C_{12}$-1,2,3,4,-TCDD					
METHOD EFFICIENCY (% RECOVERY)					
$^{13}C_{12}$-2,3,7,8-TCDF					
$^{13}C_{12}$-2,3,7,8-TCDD					
$^{13}C_{12}$-1,2,3,7,8-PeCDF					
$^{13}C_{12}$-1,2,3,7,8-PeCDD					
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF					
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD					
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD					
$^{13}C_{12}$-OCDD					
CONCENTRATIONS DETECTED or MDL (pg/m^3)					
TCDDs (TOTAL)[1]					
2,3,7,8-TCDD					
PeCDDs (TOTAL)					
1,2,3,7,8-PeCDD					
HxCDDs (TOTAL)					
1,2,3,4,7,8-HxCDD					
1,2,3,6,7,8-HxCDD					
1,2,3,7,8,9-HxCDD					
HpCDDs (TOTAL)					
1,2,3,4,6,7,8-HpCDD					

TABLE 24. (continued)

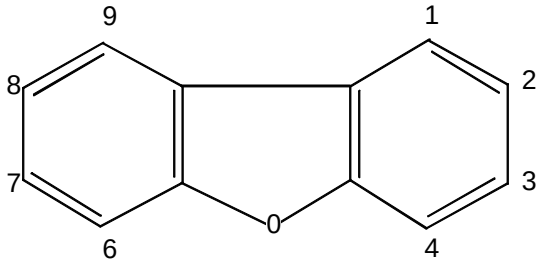
IDENTIFICATION					
OCDD					
TCDFs (TOTAL)					
2,3,7,8-TCDF					
PeCDFs (TOTAL)					
1,2,3,7,8-PeCDF					
2,3,4,7,8-PeCDF					
HxCDFs (TOTAL)					
1,2,3,4,7,8-HxCDF					
1,2,3,6,7,8-HxCDF					
1,2,3,7,8,9-HxCDF					
2,3,4,6,7,8-HxCDF					
HpCDFs (TOTAL)					
1,2,3,4,6,7,8-HpCDF					
1,2,3,4,7,8,9-HpCDF					
OCDF					

[1](TOTAL) = All congeners, including the 2,3,7,8-substituted congeners.
ND = Not detected at specified minimum detection limit (MDL).

[Note: Please refer to text for discussion and qualification that must accompany the results.]



Dibenzo-p-Dioxin



Dibenzofuran

Figure 1. Dibenzo-p-dioxin and dibenzofuran structures.

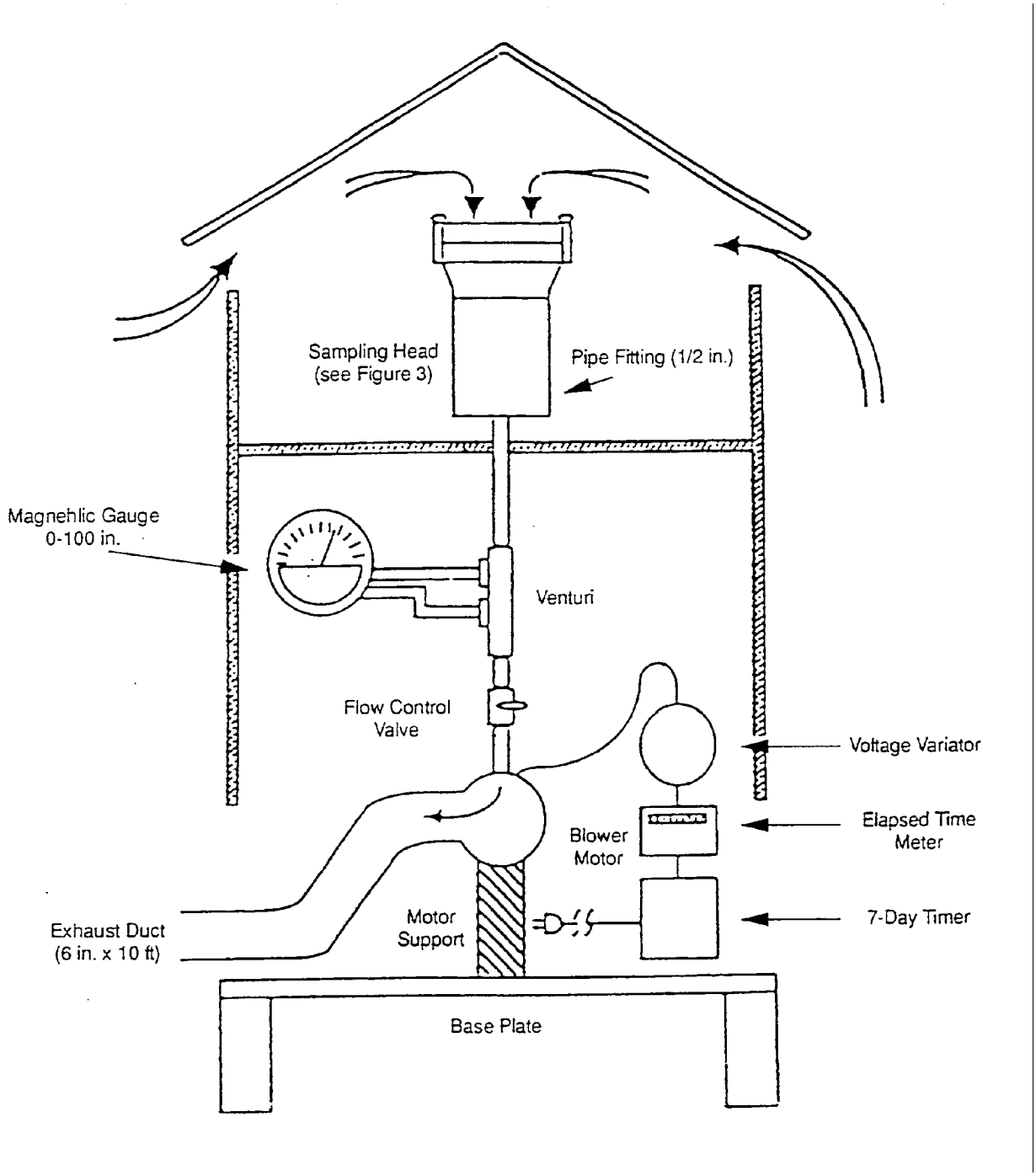


Figure 2. Typical dioxins/furan high volume air sampler.

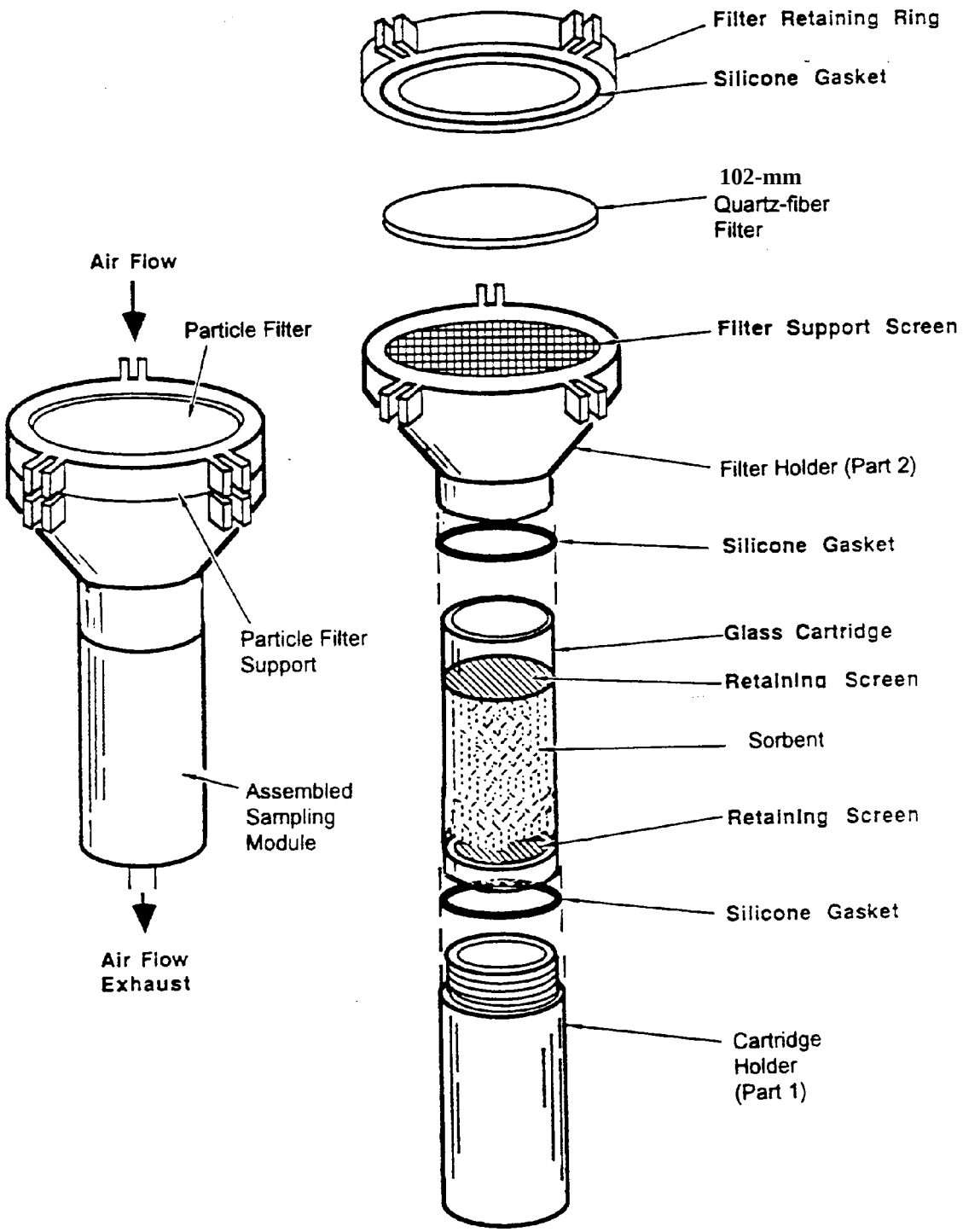
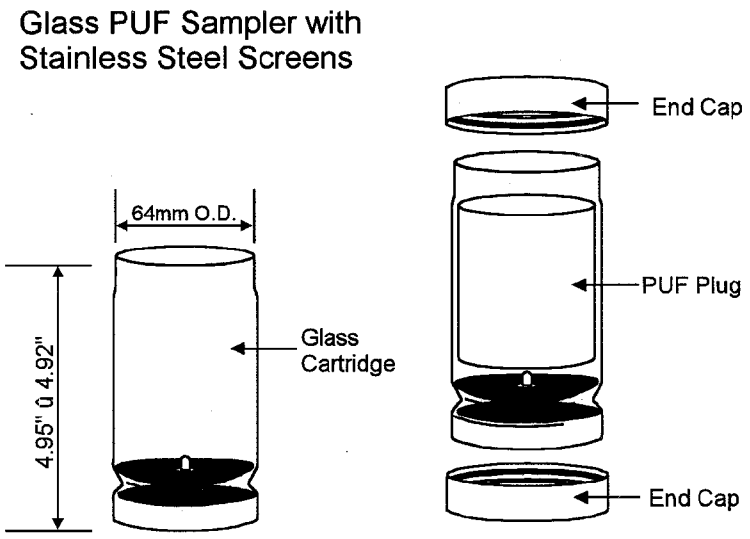
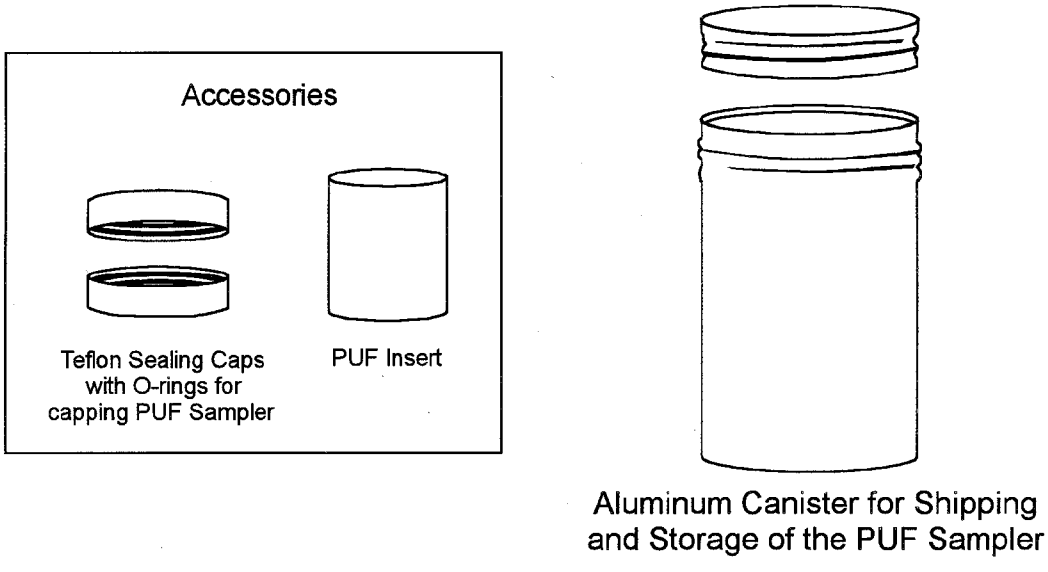


Figure 3a. Typical absorbent cartridge assembly for sampling dioxin/furans.



(1) Glass PUF cartridge, plug, and end caps.



(2) PUF shipping container.

Figure 3b. Typical glass PUF cartridge (1) and shipping container (2) for use with hi-vol sampling systems.

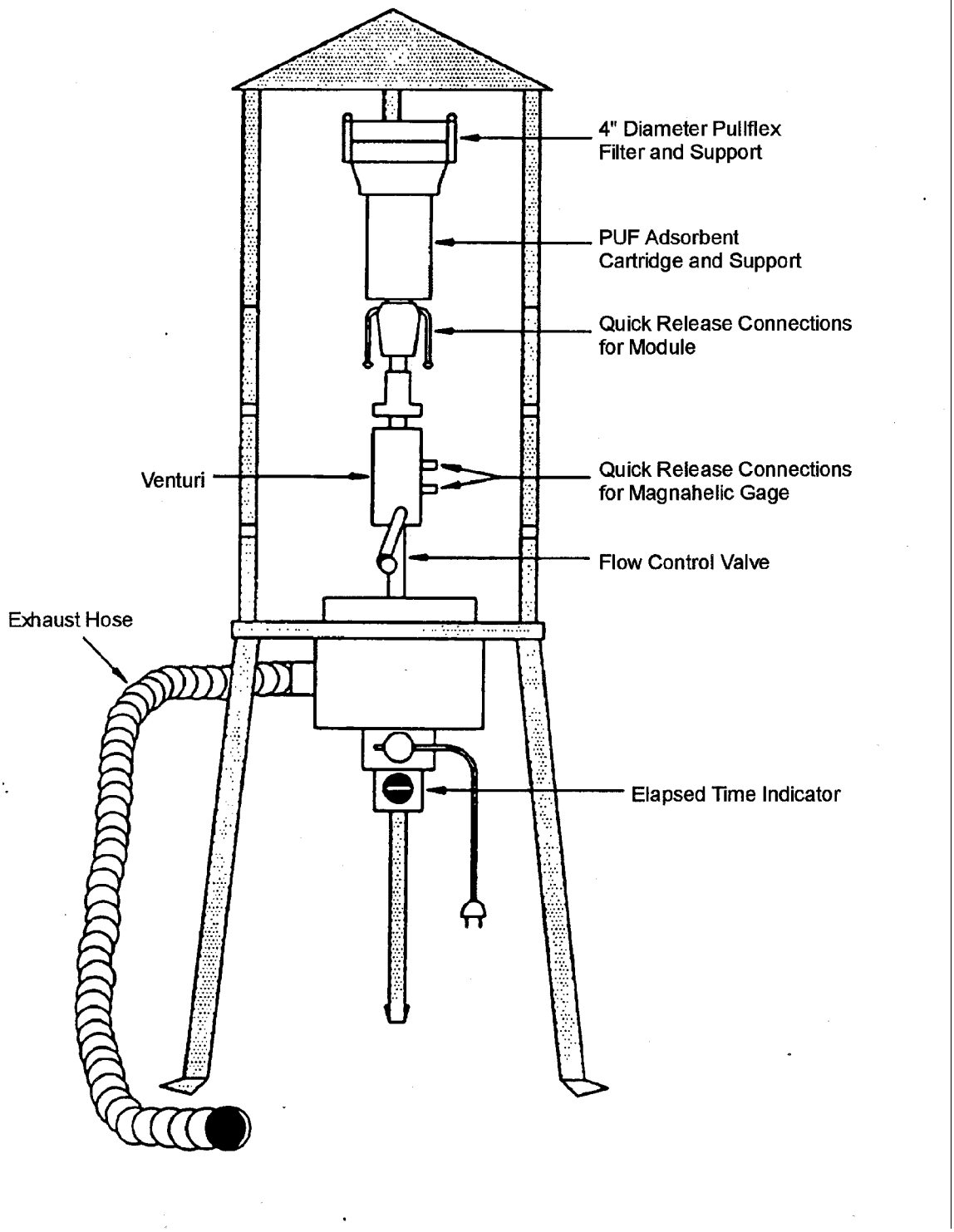


Figure 4. Portable high volume air sampler developed by EPA.

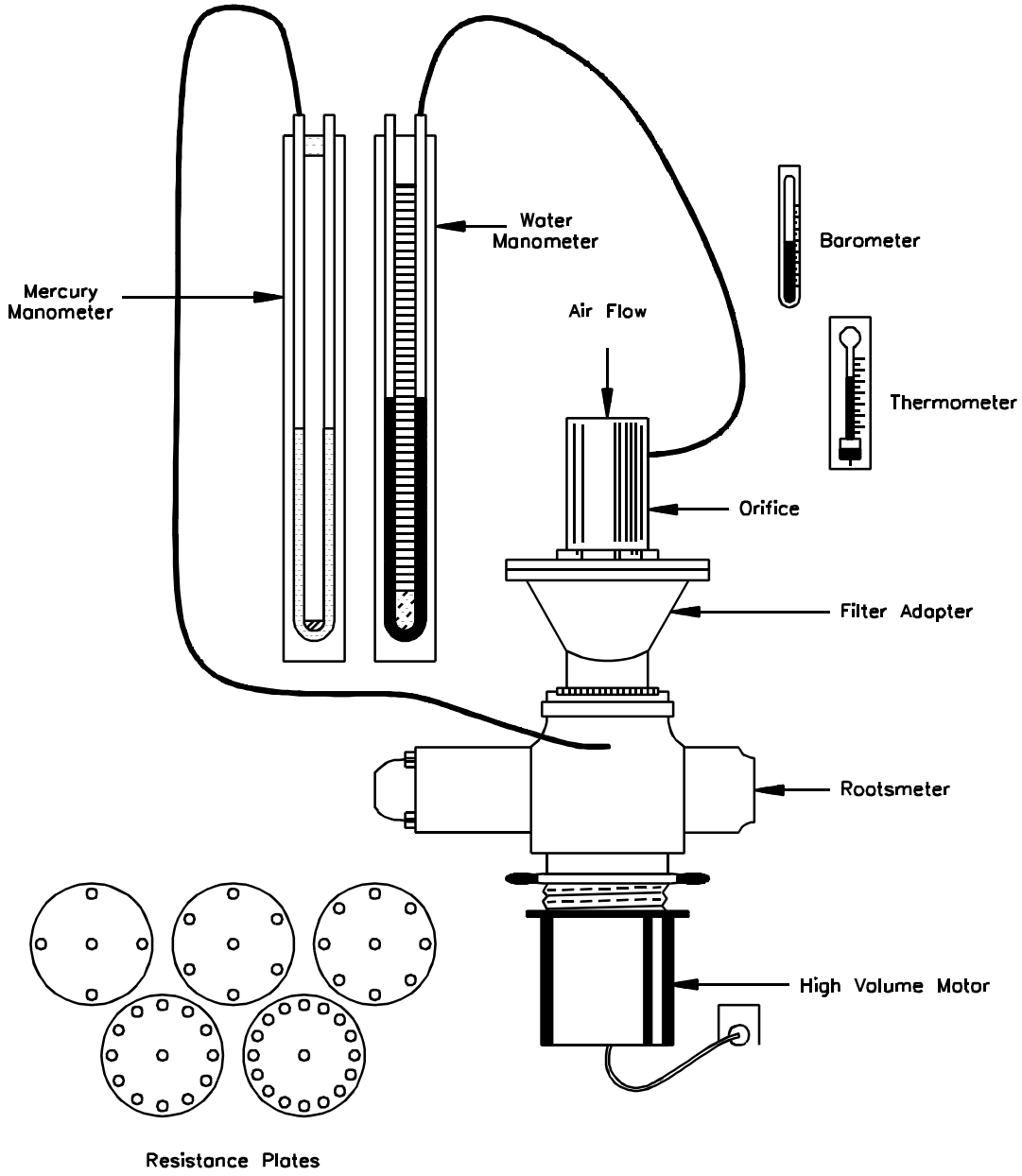


Figure 5. Positive displacement rootsmeter used to calibrate orifice transfer standard.

COMPENDIUM METHOD TO-9A
ORIFICE CALIBRATION DATA SHEET

T_1 _____ Name _____

P_1 _____ mmHg Date _____

Orifice No. _____

Rootsmeter No. _____

Resistance Plants (No. of holes)	Air Volume Measured by Rootsmeter V_m (R^3)	(m^3)	Standard Volume, V_{std} (std m^3)	Time for Air Volume to Pass Through Rootsmeter, θ (min)	Rootsmeter Pressure Differential, ΔP (mm Hg)	Pressure Drop Across Orifice, ΔH (in. H_2O)	x-Axis Standard Flowrate, Q_{std} (std m^3/min)	Y – axis $\sqrt{\Delta H(P_1/P_{std})(298/T_1)}$ value
5	200	5.66						
7	200	5.66						
10	300	8.50						
13	300	8.50						
18	300	8.50						

Factors: $(R^3)(0.02832\ \frac{m^3}{R^3}) = m^3$ and (in. Hg) $25.4\ (\frac{mm\ Hg}{in.\ Hg}) = mm\ Hg$

Calculation Equations:

1. $V_{std} = V_m\ (\frac{P_1 - \Delta P}{P_{std}})(\frac{T_{std}}{T_1})$

where:

$T_{std} = 296°K$
$P_{std} = 760.0$ mm Hg

2. $Q_{std} = \frac{V_{std}}{\theta}$

Figure 6. Orifice calibration data sheet.

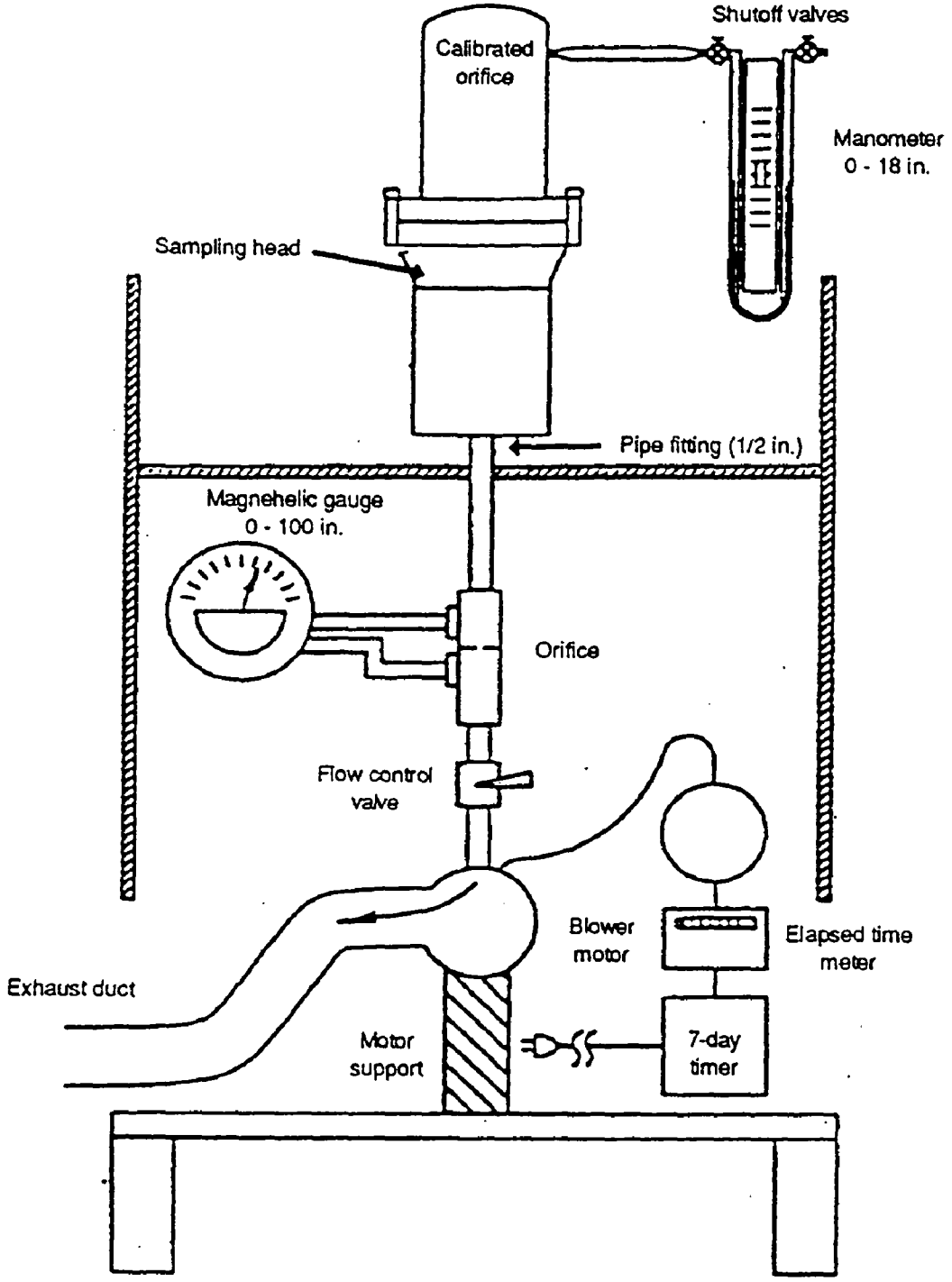


Figure 7. Field calibration configuration of the dioxin/furan sampler.

COMPENDIUM METHOD TO-9A
FIELD CALIBRATION DATA SHEET DIOXIN/FURAN SAMPLER CALIBRATION

Sampler ID: Calibration Orifice ID:

Sampler Location: Job No.:

High Volume Transfer Orifice Data:

Correlation Coefficient (CC1): Slope (M1):
(CC2): (M2):

Intercept (B1):
(B2):

Calibration Date: ___ Time:
Calibration Ambient Temperature: ___°F ___°C CALIBRATOR'S SIGNATURE
Calibration Ambient Barometric Pressure: ___ "Hg ___ mm Hg
Calibration set point (SP): _____

SAMPLER CALIBRATION

Actual values from calibration		Calibrated values		
Orifice manometer, inches (Y1)	Monitor magnehelic, inches (Y2)	Orifice manometer (Y3)	Monitor magnehelic (Y4)	Calculated value orifice flow, scm (X1)
	70			
	60			
	50			
	40			
	30			
	20			
	10			

Definitions

Y1 = Calibration orifice reading, in. H_2O

Y2 = Monitor magnehelic reading, in. H_2O

P_a = Barometric pressure actual, mm Hg

B1 = Manfacturer's Calibration orifice Intercept

M1 = Manufacturer's Calibration orifice manometer slope

Y3 = Calculated value for orifice manometer
= $[Y1(Pa/760)(298/\{Ta + 273\})]^{½}$

Y4 = Calculated value for magnehelic
= $[Y2(Pa/760)(298/\{Ta + 273\})]^{½}$

X1 = Calculated value orifice flow, scm
= $\frac{Y3 - B1}{M1}$

P_{std} = Barometric pressure standard, 760 mm Hg

T_a = Temperature actual, °C

T_{std} = Temperature standard, 25°C

Figure 8. Orifice transfer field calibration data sheet.

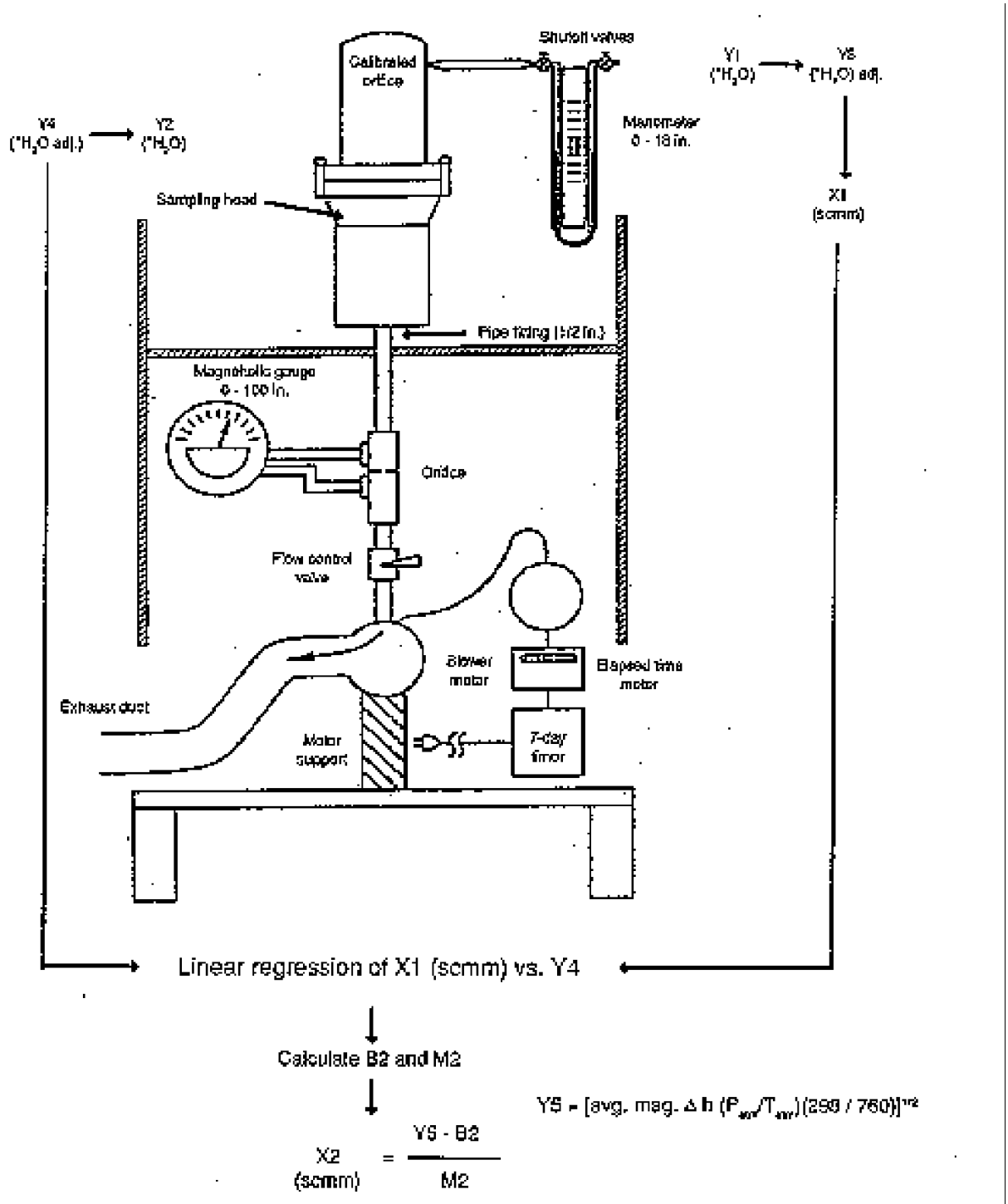


Figure 9. Relationship between orifice transfer standard and flow rate through sampler.

COMPENDIUM METHOD TO-9A
FIELD TEST DATA SHEET
GENERAL INFORMATION

- **Sampler I.D. No.:** _____
- **Lab PUF Sample No.:** _____
- **Sample location:** _____
  _____
  _____
- **Operator:** _____
- **Other:** _____
  _____
  _____

- **PUF Cartridge Certification Date:** _____
- **Date/Time PUF Cartridge Installed:** _____
- **Elapsed Timer:** _____
  Start _____
  Stop _____
  Diff. _____
- **Sampling**

  M1 _____ **B1** _____
  M2 _____ **B2** _____

	Start	Stop
• Barometric pressure ("Hg)	_____	_____
• Ambient Temperature (°F)	_____	_____
• Rain	Yes _____ No _____	Yes _____ No _____

- **Sampling time**
  Start _____
  Stop _____
  Diff. _____

- **Audit flow check within ±10 of set point**
  _____ **Yes**
  _____ **No**

TIME	TEMP	BAROMETRIC PRESSURE	MAGNEHELIC READING	CALCULATED FLOW RATE (scmm)	READ BY
Avg.					

- Comments

_____
_____
_____

Figure 10. Field test data sheet.

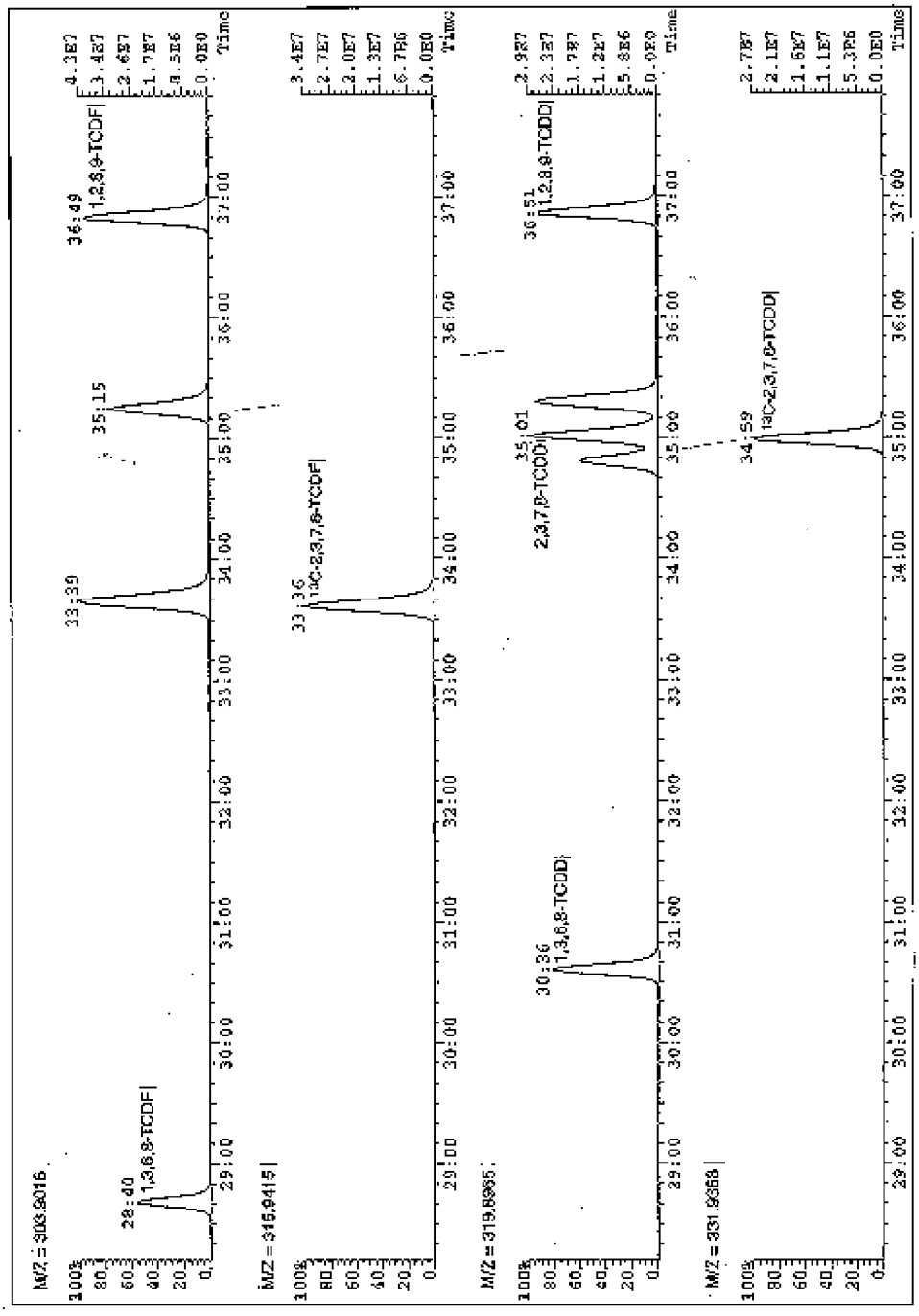


Figure 11. Chromatograms showing the window defining mix. First and last eluting PCDF and PCDD isomer in each group are shown above the respective internal quantification standard (IQS).

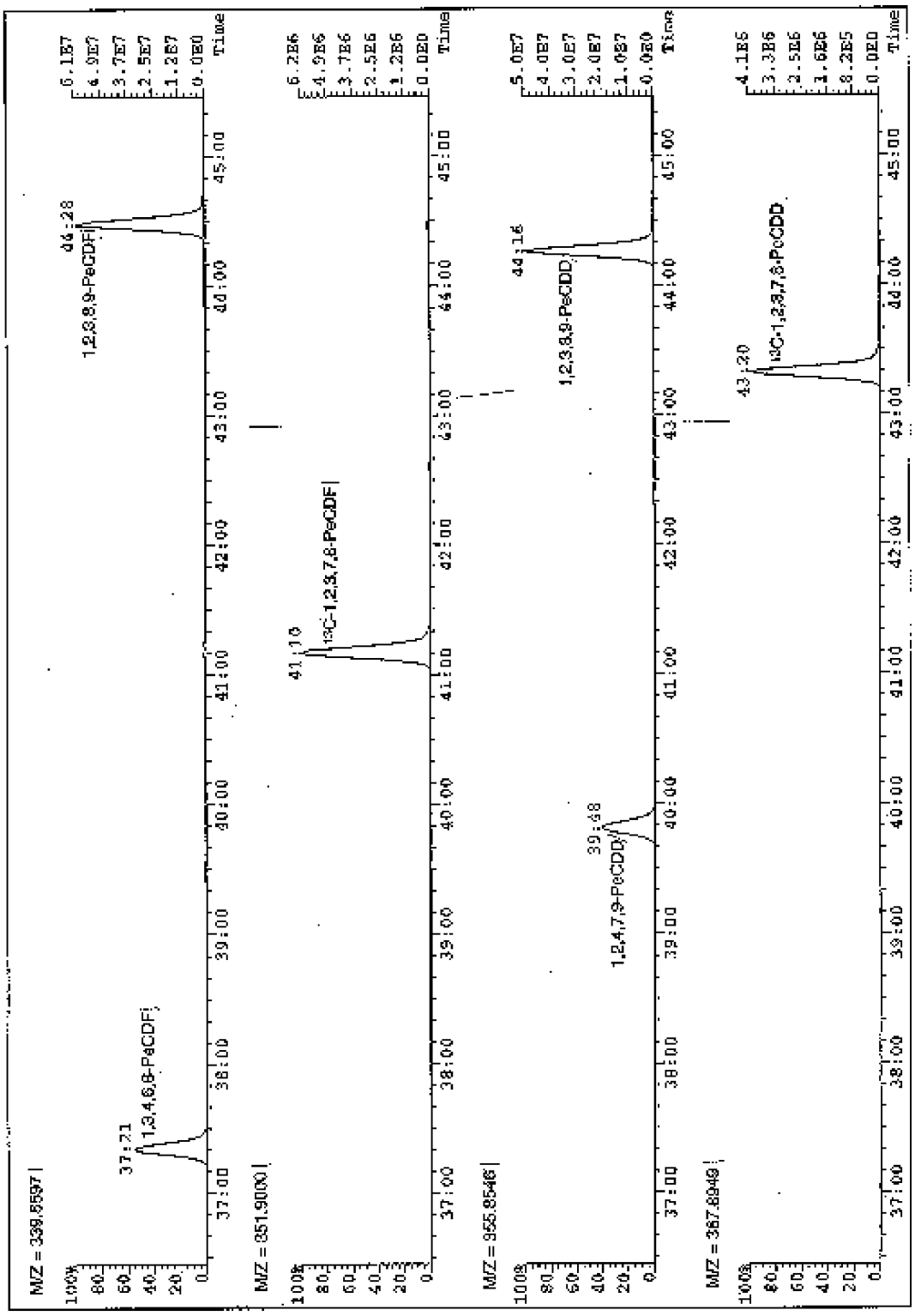


Figure 11. (continued)

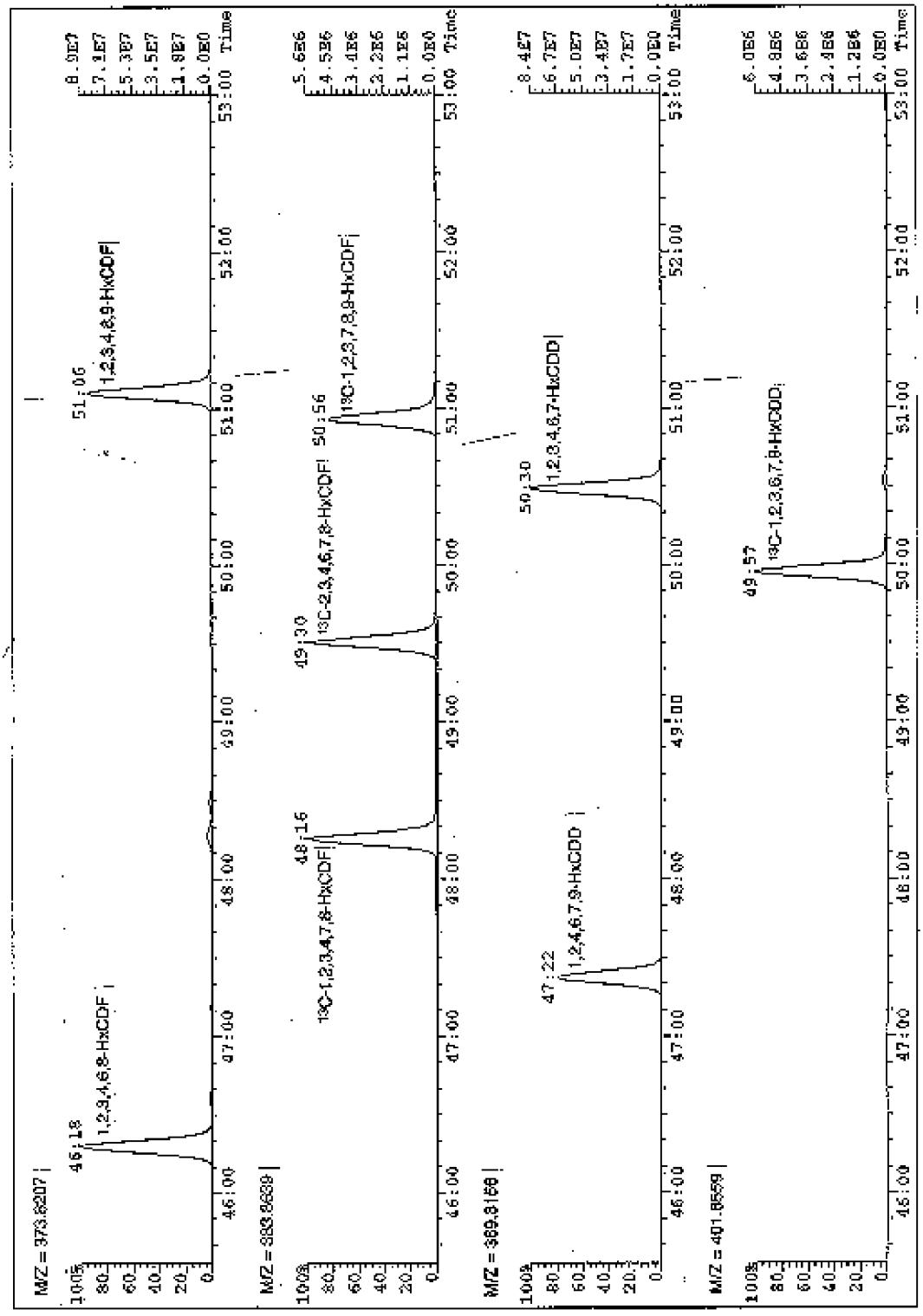


Figure 11. (continued)

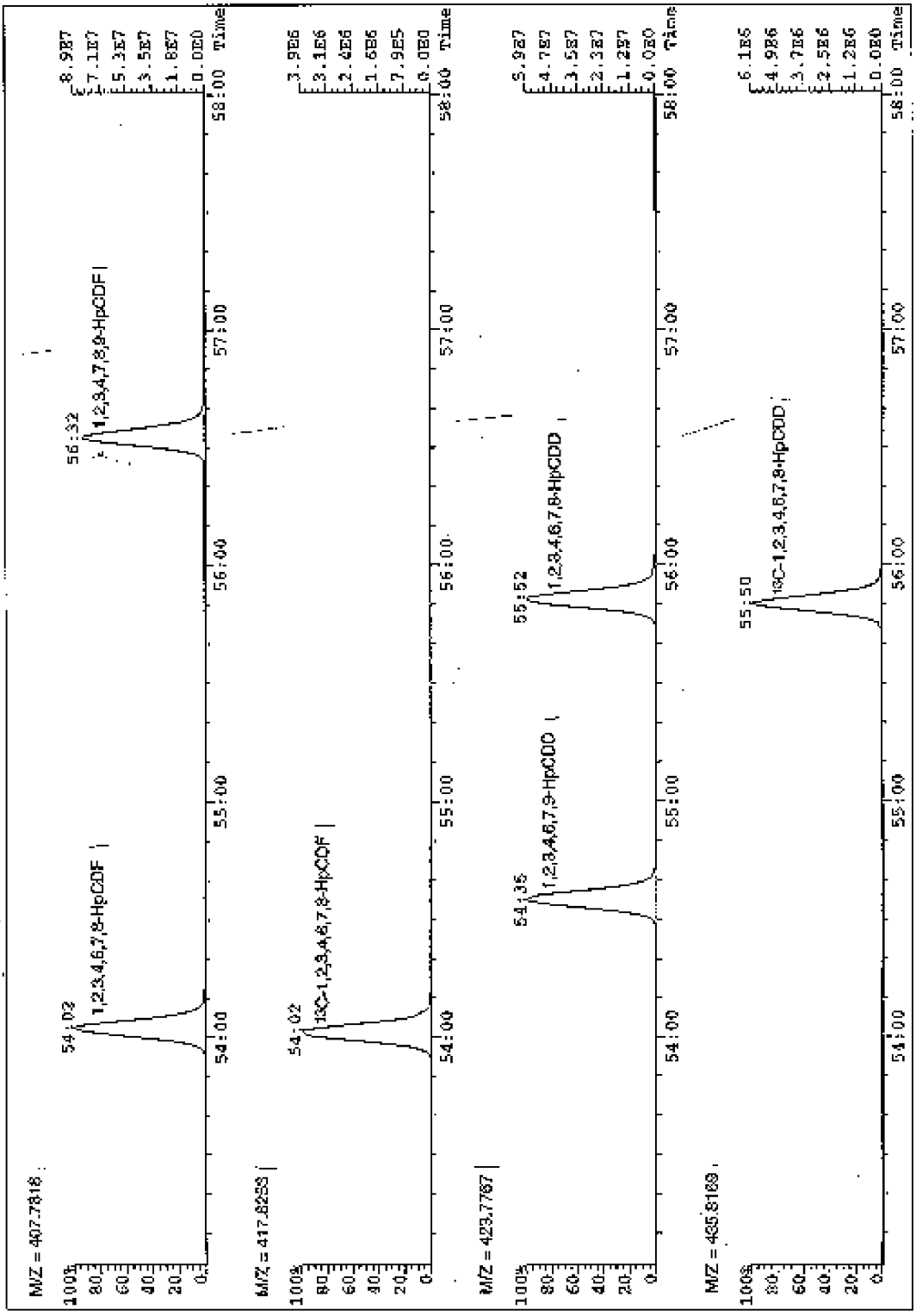


Figure 11. (continued)

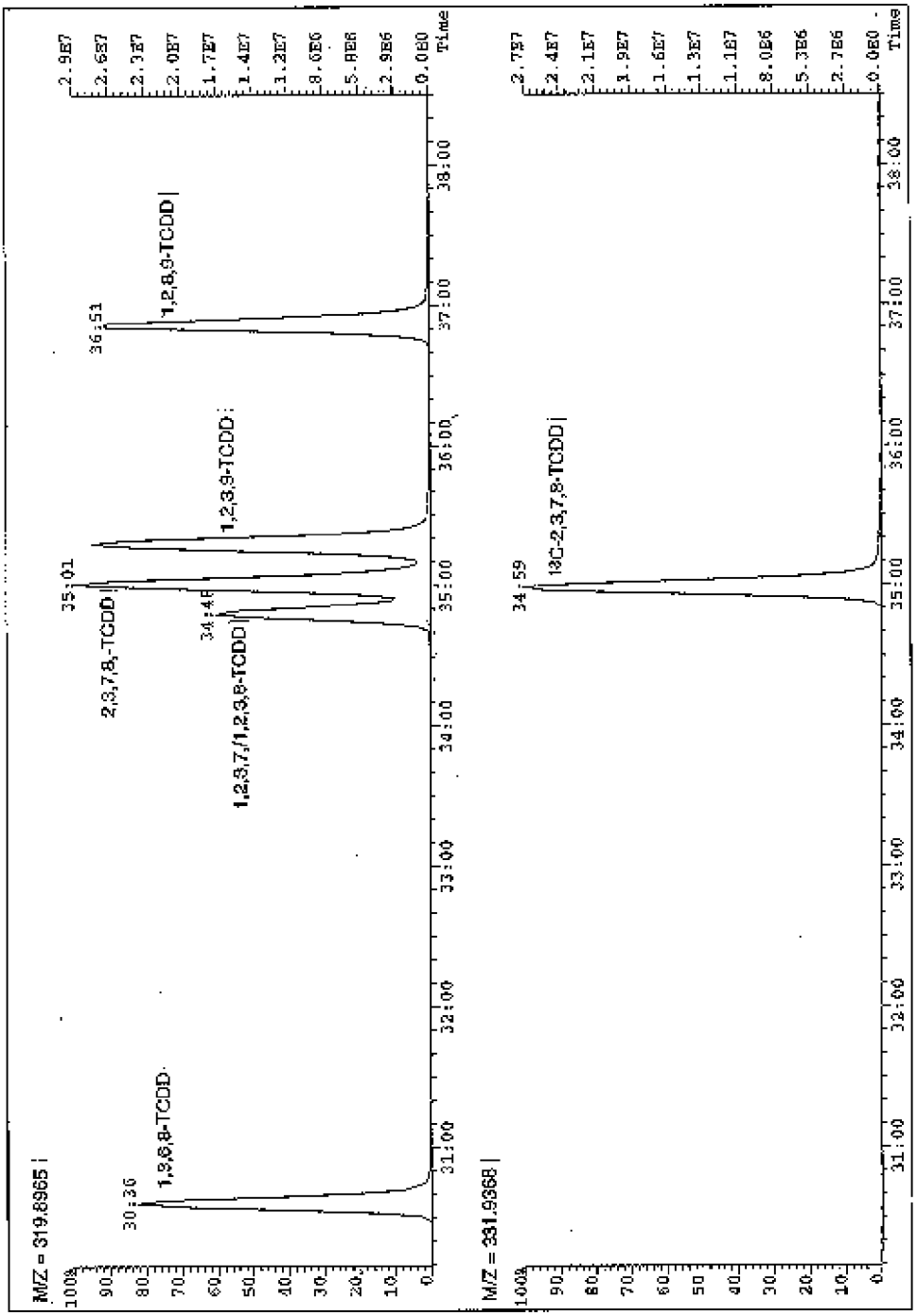


Figure 12. HRGC-HRMS column performance mix showing acceptable separation of 2,3,7,8-TCDD from the adjacent isomers.

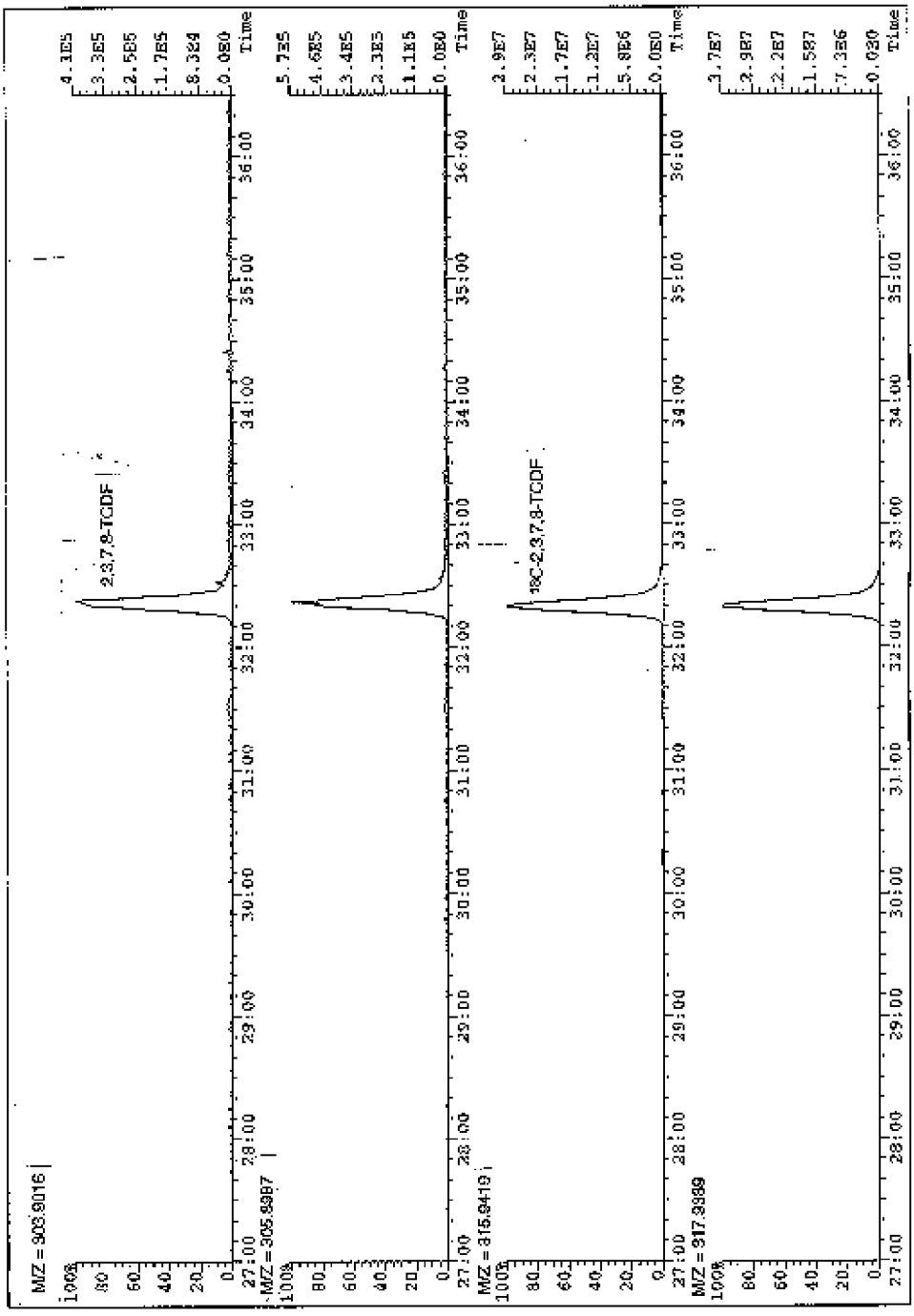


Figure 13. Extracted ion current profiles (EICP) for 2,3,7,8-TCDF and labeled standard.

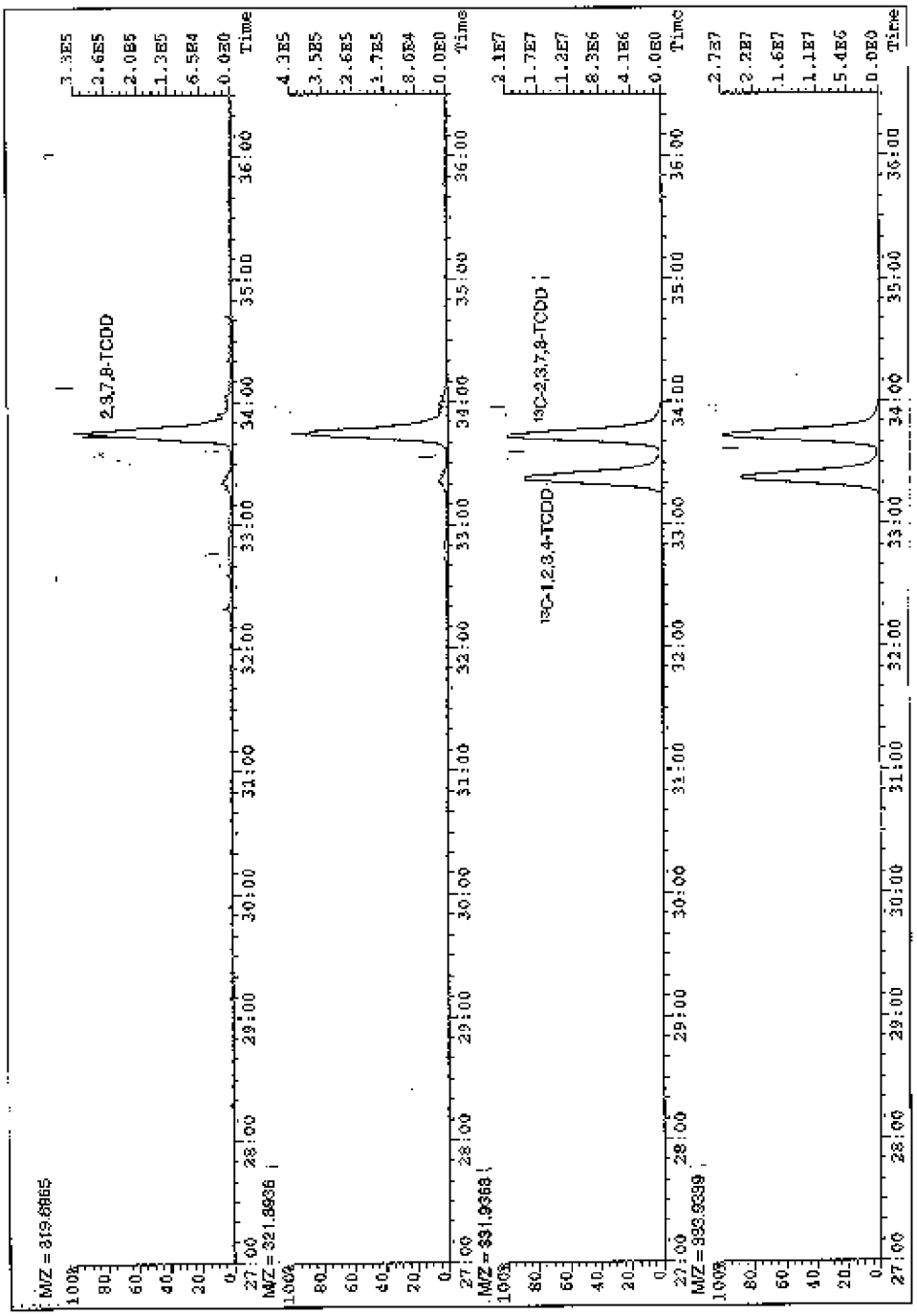


Figure 14. Extracted ion current profiles (HLCP) for 2,3,7,8-TCDD and labeled standard.

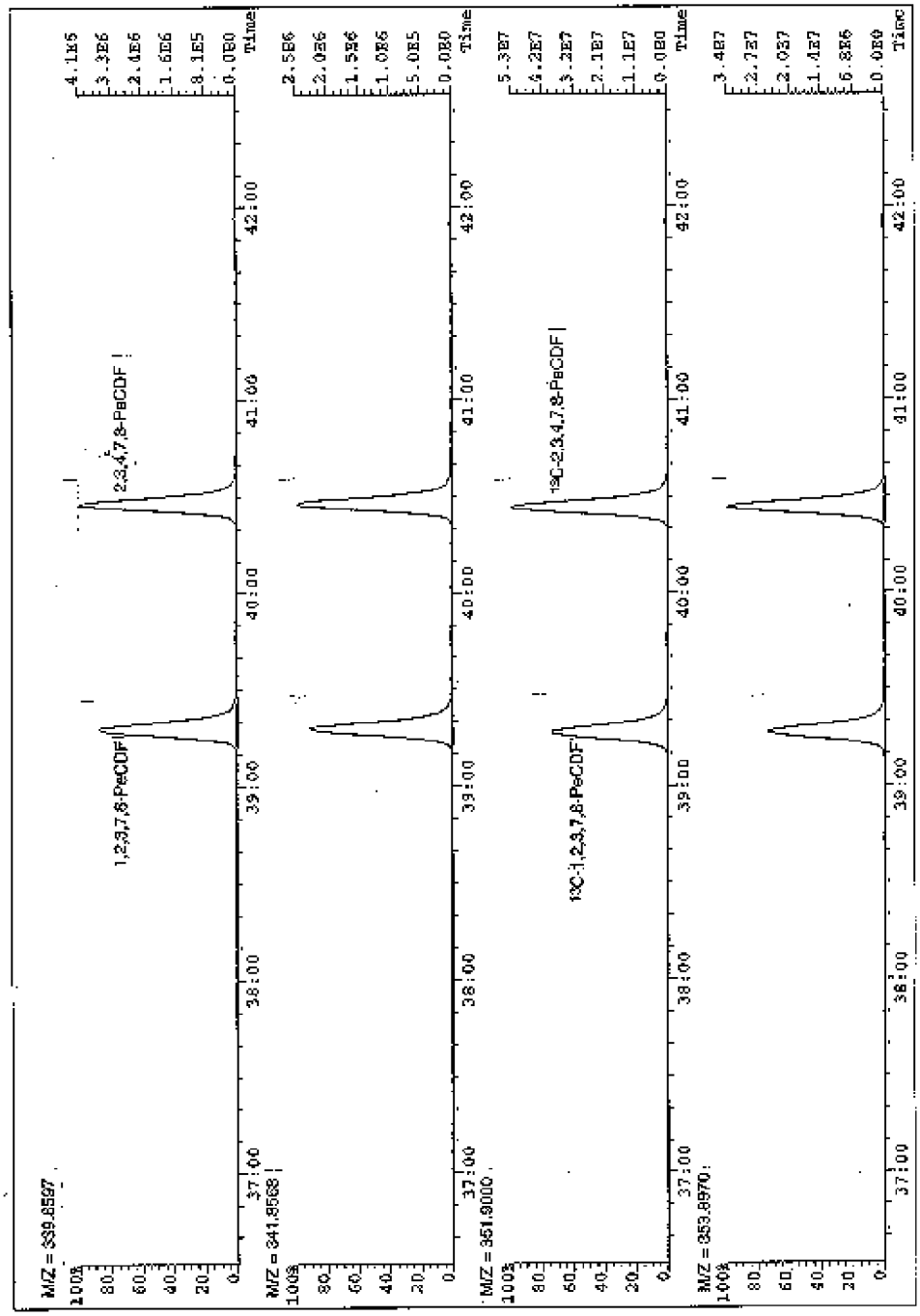


Figure 15. Extracted ion current profiles (ELCP) for 2,3,7,8-substituted PeCDF and labeled standard.

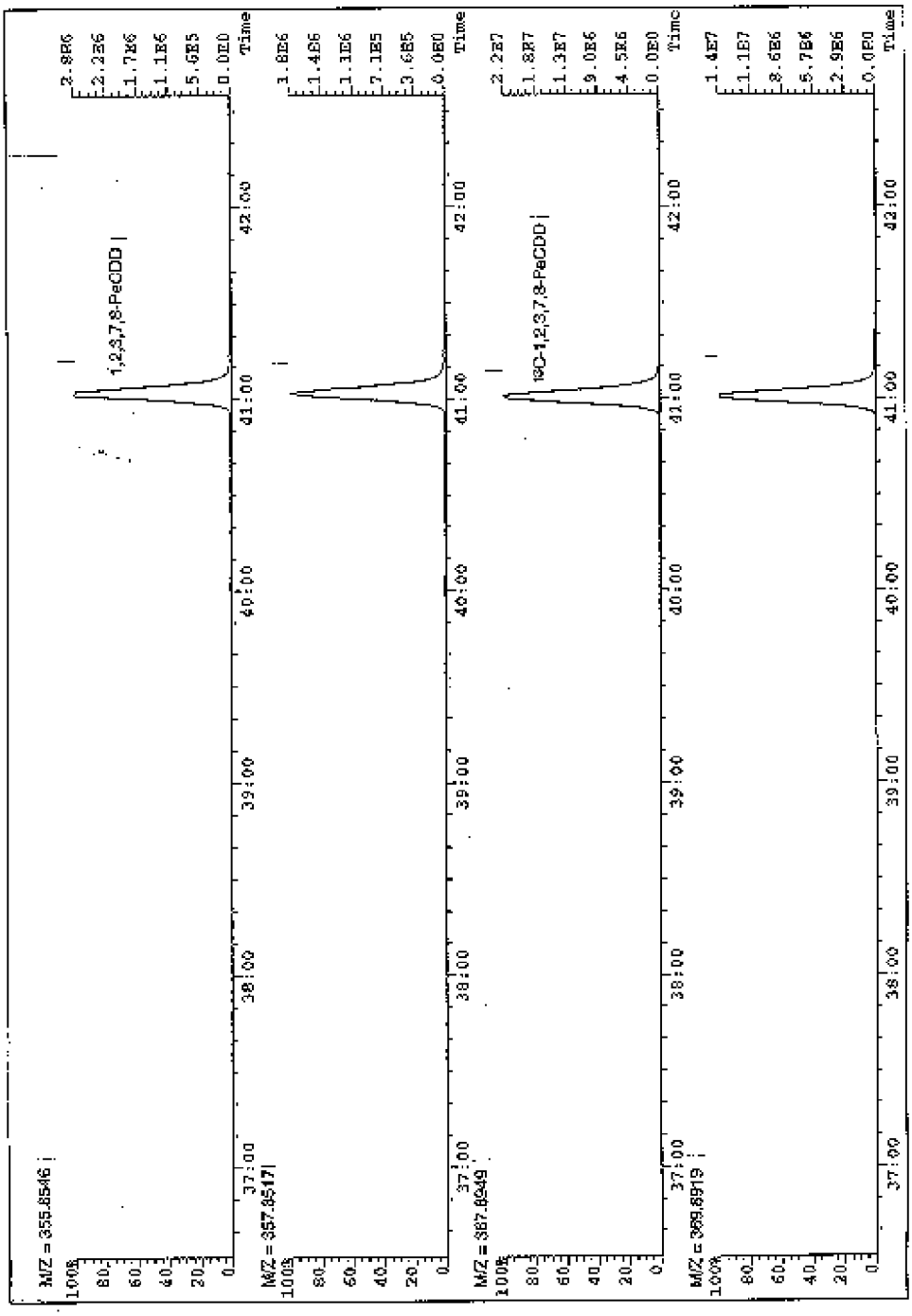


Figure 16. Extracted ion current profiles (EICP) for 2,3,7,8-substituted PeCDD and labeled standard.

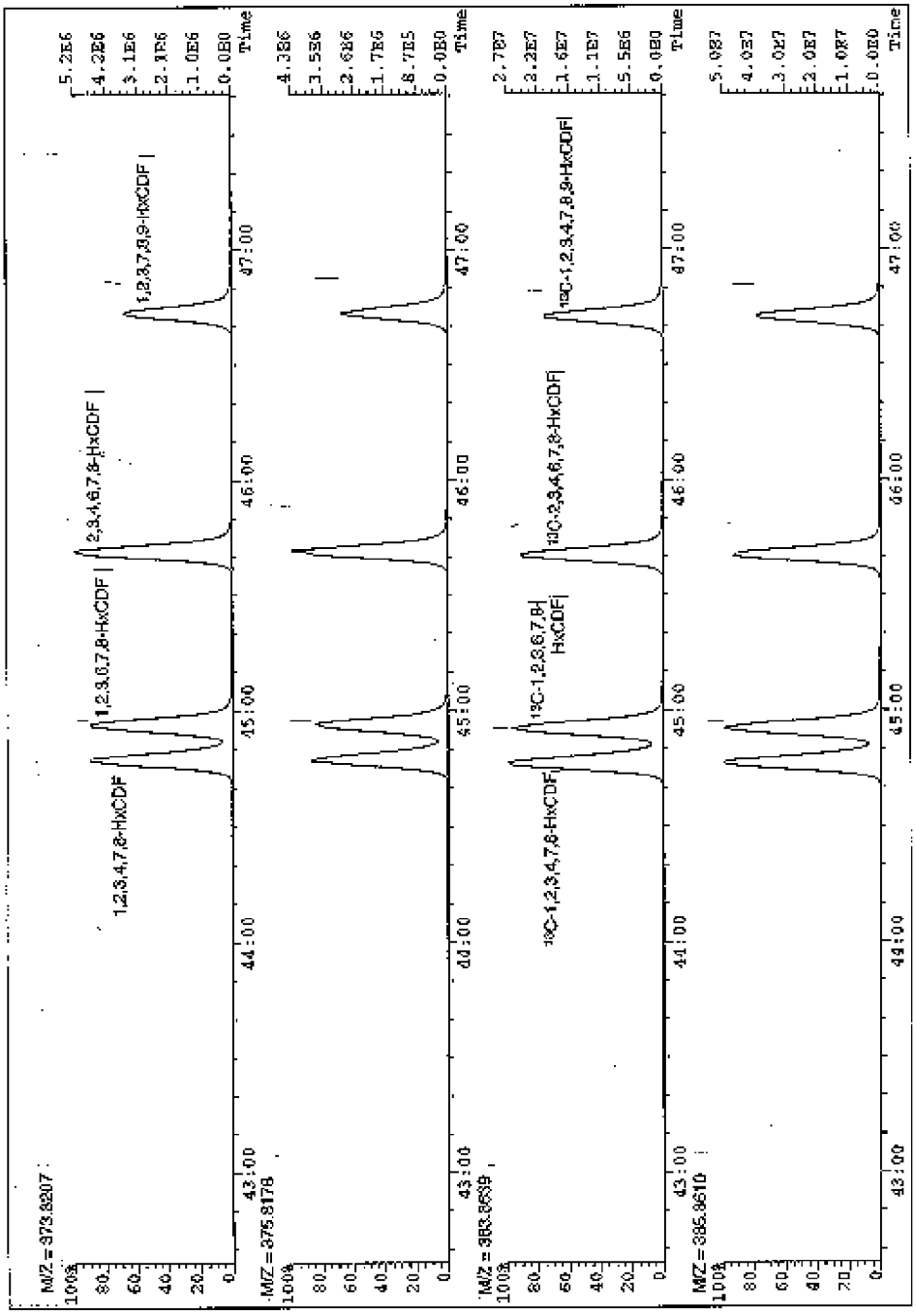


Figure 17. Extracted ion current profiles (EICP) for 2,3,7,8-substituted HxCDF and labeled standard.

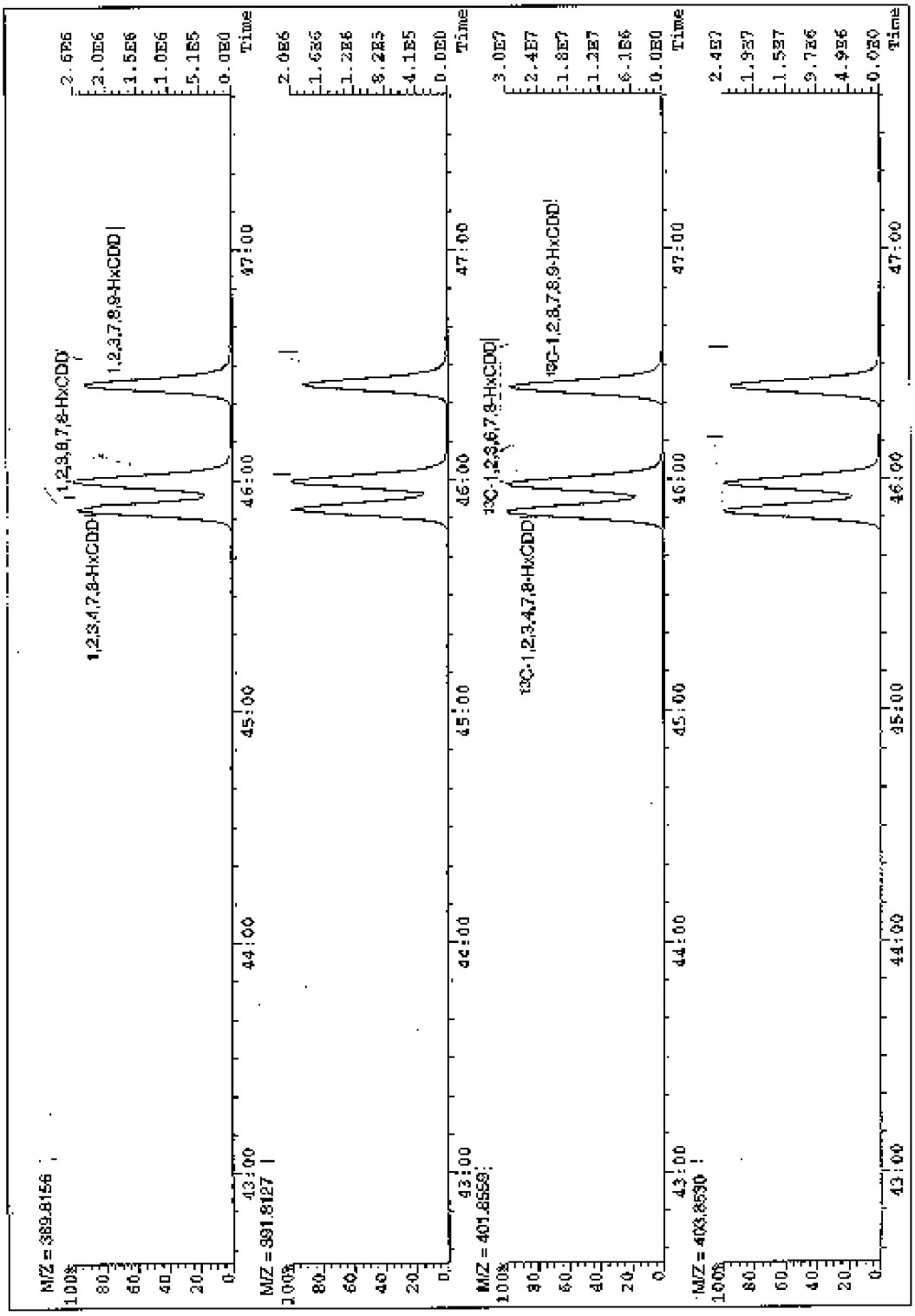


Figure 18. Extracted ion current profiles (EICP) for 2,3,7,8-substituded HxCDD and labeled standard.

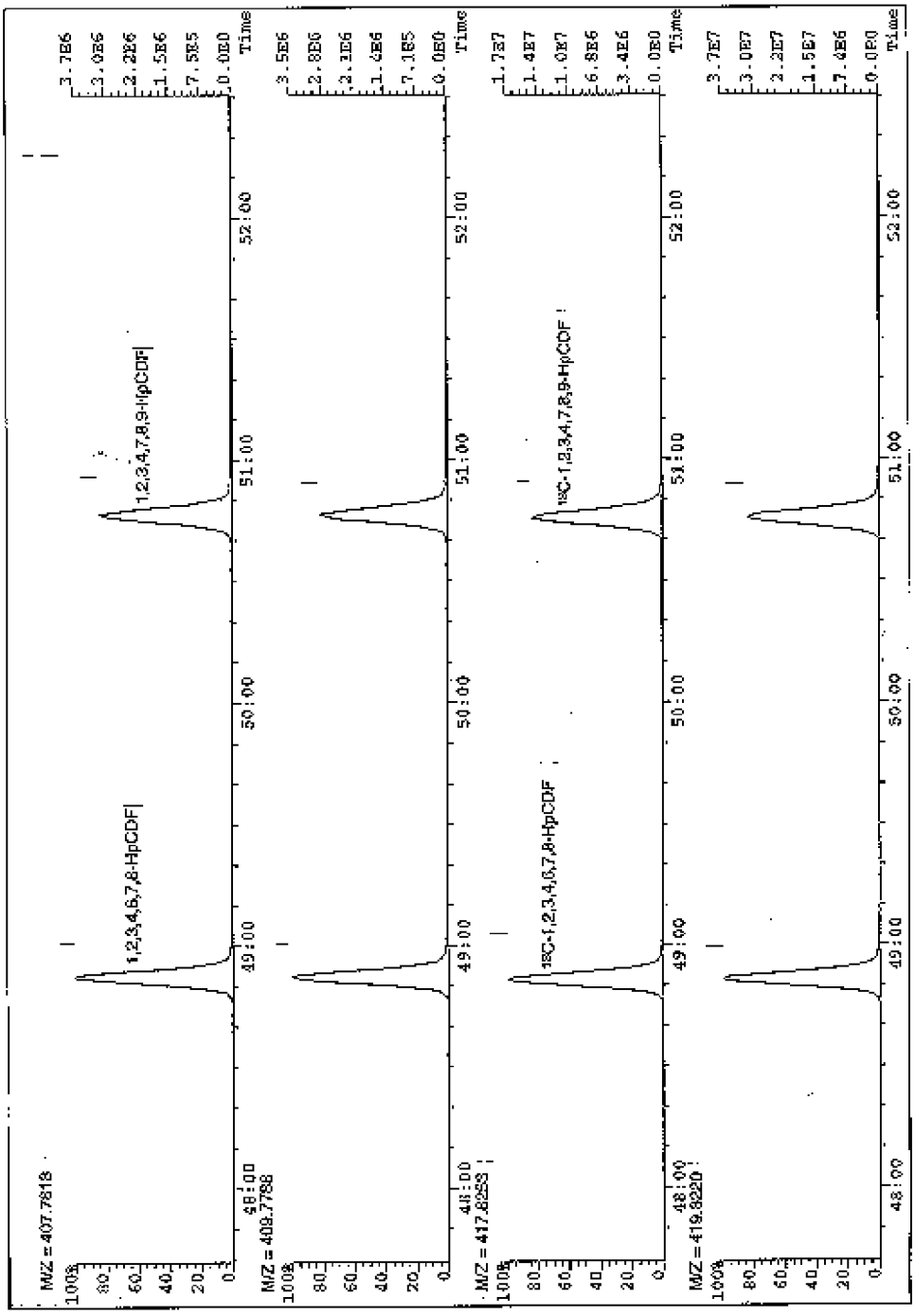


Figure 19. Extracted ion current profiles (EICP) for 2,3,7,8-substituted HpCDF and labeled standard.

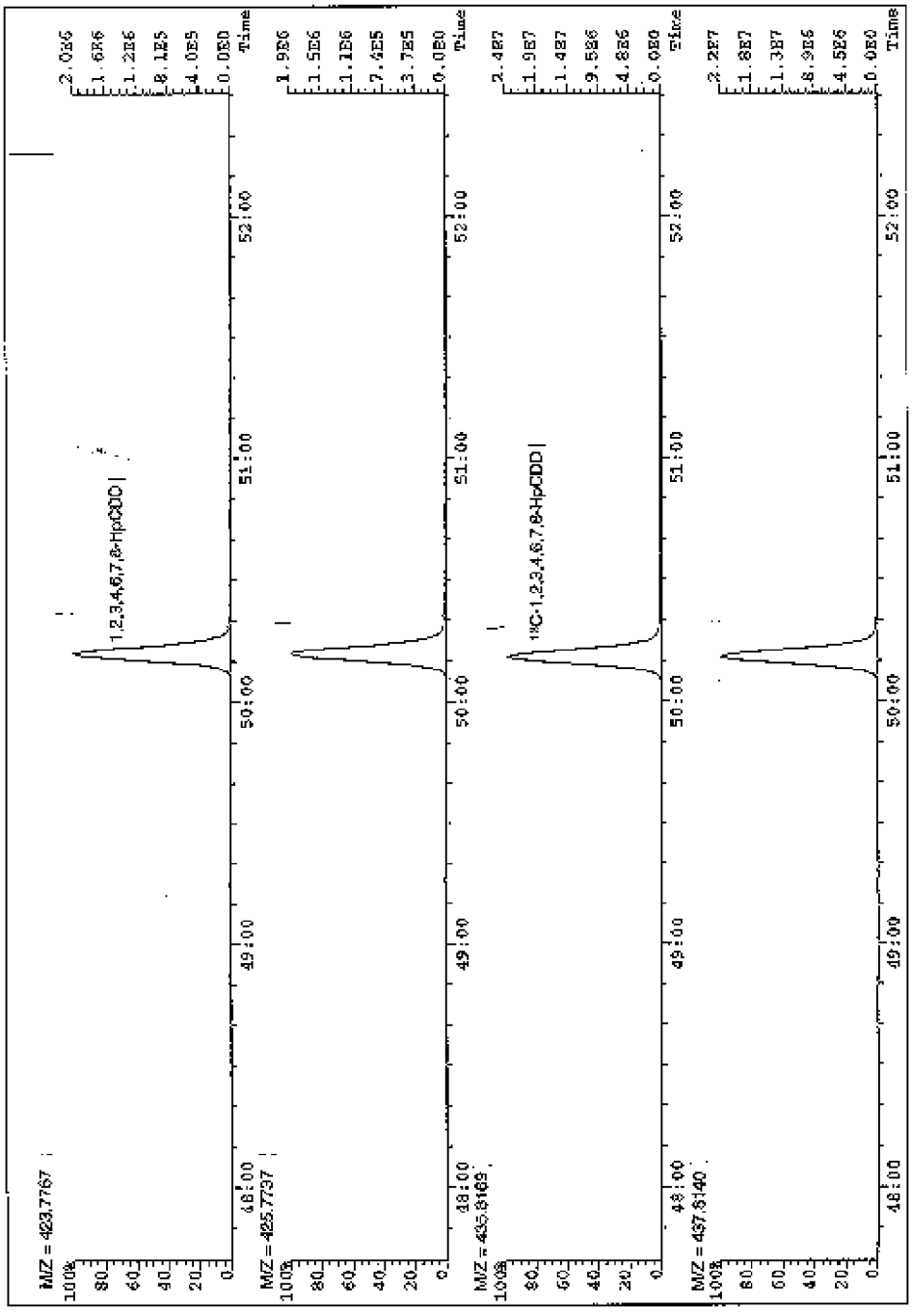


Figure 20. Extracted ion current profiles (EICP) for 2,3,7,8-substituted HpCDD and labeled standard.

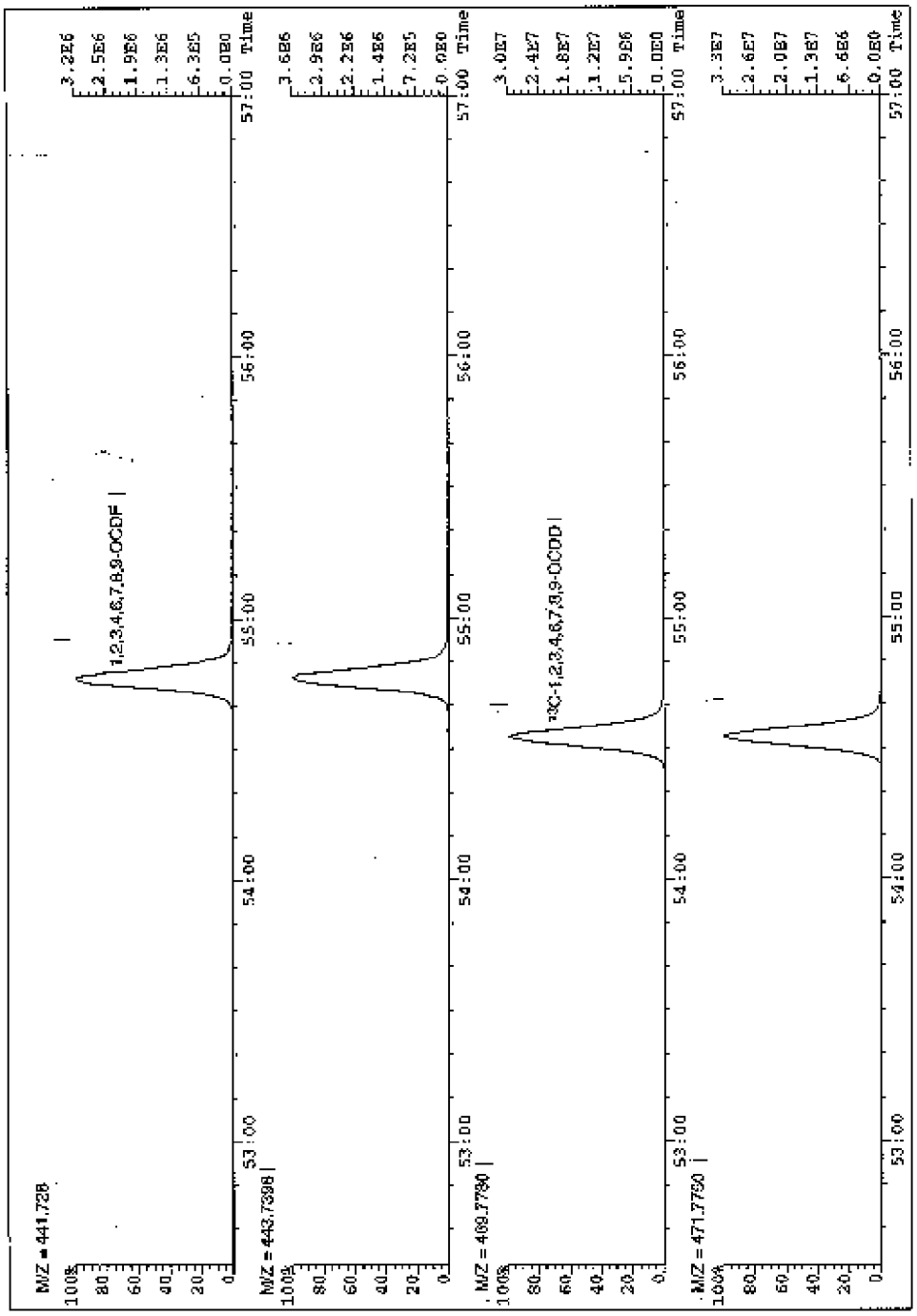


Figure 21. Extracted ion current profiles (EICP) for OCDF and labeled standard.

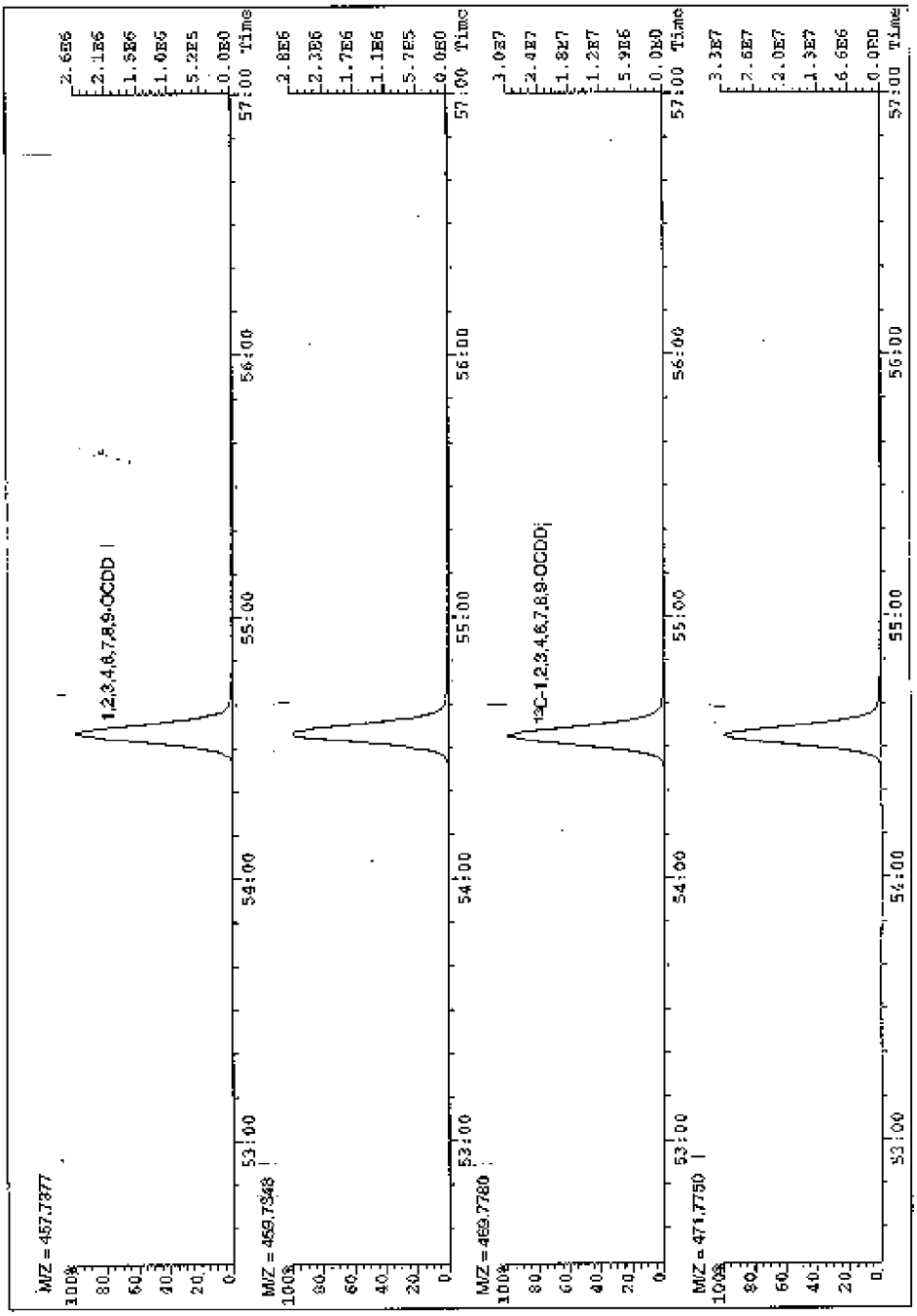


Figure 22. Extracted ion current profiles (EICP) for OCDD and labeled standard.

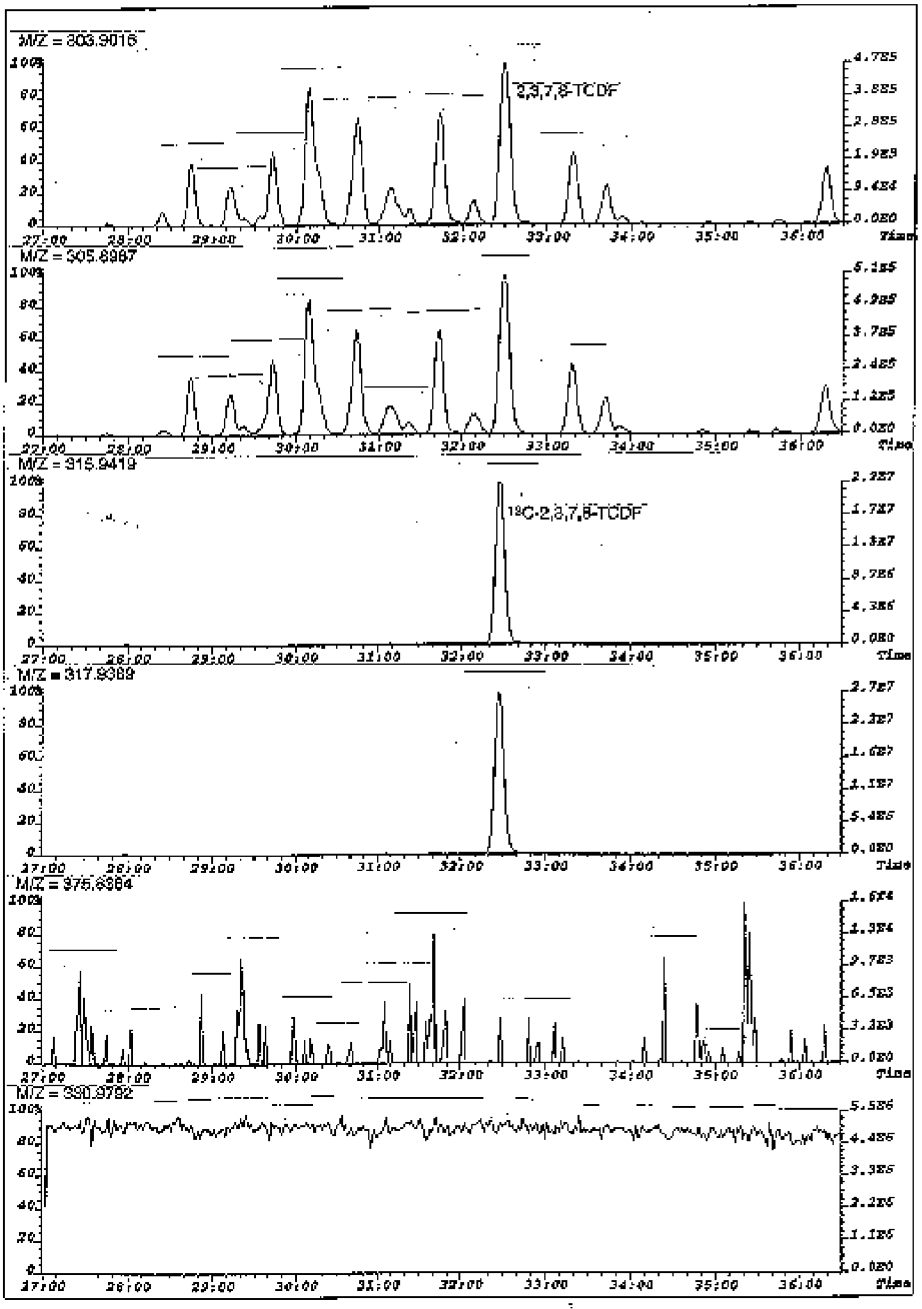


Figure 23. Extracted ion current profiles (EICP) for 2,3,7,8-TCDF and labeled standard in a complex environmental sample showing presence of other TCDF isomers.

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U. S. EPA ENVIRONMENTAL RESPONSE TEAM

STANDARD OPERATING PROCEDURES

SOIL SAMPLING

CONTENTS

SUPERCEDES: SOP #2012; Revision 0.0; 11/16/94; U.S. EPA Contract 68-C4-0022.

1.0 SCOPE AND APPLICATION

The purpose of this standard operating procedure (SOP) is to describe the procedures for the collection of representative soil samples. Sampling depths are assumed to be those that can be reached without the use of a drill rig, direct-push, or other mechanized equipment (except for a back-hoe). Analysis of soil samples may determine whether concentrations of specific pollutants exceed established action levels, or if the concentrations of pollutants present a risk to public health, welfare, or the environment.

These are standard (i.e., typically applicable) operating procedures which may be varied or changed as required, dependent upon site conditions, equipment limitations or limitations imposed by the procedure. In all instances, the actual procedures used should be documented and described in an appropriate site report.

Mention of trade names or commercial products does not constitute U.S. Environmental Protection Agency (EPA) endorsement or recommendation for use.

2.0 METHOD SUMMARY

Soil samples may be collected using a variety of methods and equipment depending on the depth of the desired sample, the type of sample required (disturbed vs. undisturbed), and the soil type. Near-surface soils may be easily sampled using a spade, trowel, and scoop. Sampling at greater depths may be performed using a hand auger, continuous flight auger, a trier, a split-spoon, or, if required, a backhoe.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING, AND STORAGE

Chemical preservation of solids is not generally recommended. Samples should, however, be cooled and protected from sunlight to minimize any potential reaction. The amount of sample to be collected and proper sample container type are discussed in ERT/REAC SOP #2003 Rev. 0.0 08/11/94, *Sample Storage, Preservation and Handling*.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

There are two primary potential problems associated with soil sampling - cross contamination of samples and improper sample collection. Cross contamination problems can be eliminated or minimized through the use of dedicated sampling equipment. If this is not possible or practical, then decontamination of sampling equipment is necessary. Improper sample collection can involve using contaminated equipment, disturbance of the matrix resulting in compaction of the sample, or inadequate homogenization of the samples where required, resulting in variable, non-representative results.

5.0 EQUIPMENT

Soil sampling equipment includes the following:

- Maps/plot plan
- Safety equipment, as specified in the site-specific Health and Safety Plan
- Survey equipment or global positioning system (GPS) to locate sampling points
- Tape measure
- Survey stakes or flags
- Camera and film
- Stainless steel, plastic, or other appropriate homogenization bucket, bowl or pan
- Appropriate size sample containers
- Ziplock plastic bags
- Logbook
- Labels
- Chain of Custody records and custody seals
- Field data sheets and sample labels
- Cooler(s)
- Ice
- Vermiculite
- Decontamination supplies/equipment
- Canvas or plastic sheet
- Spade or shovel
- Spatula
- Scoop
- Plastic or stainless steel spoons
- Trowel(s)
- Continuous flight (screw) auger
- Bucket auger
- Post hole auger
- Extension rods
- T-handle
- Sampling trier
- Thin wall tube sampler
- Split spoons
- Vehimeyer soil sampler outfit
  - Tubes
  - Points
  - Drive head
  - Drop hammer
  - Puller jack and grip
- Backhoe

6.0 REAGENTS

Reagents are not used for the preservation of soil samples. Decontamination solutions are specified in ERT/REAC SOP #2006 Rev. 0.0 08/11/94, *Sampling Equipment Decontamination*, and the site specific work plan.

7.0 PROCEDURES

7.1 Preparation

1. Determine the extent of the sampling effort, the sampling methods to be employed, and the types and amounts of equipment and supplies required.

2. Obtain necessary sampling and monitoring equipment.

3. Decontaminate or pre-clean equipment, and ensure that it is in working order.

4. Prepare schedules and coordinate with staff, client, and regulatory agencies, if appropriate.

5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.

6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors, including extent and nature of contaminant, should be considered when selecting sample location. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions. All staked locations should be utility-cleared by the property owner or the On-Scene-Coordinator (OSC) prior to soil sampling; and utility clearance should always be confirmed before beginning work.

7.2 Sample Collection

7.2.1 Surface Soil Samples

Collection of samples from near-surface soil can be accomplished with tools such as spades, shovels, trowels, and scoops. Surface material is removed to the required depth and a stainless steel or plastic scoop is then used to collect the sample.

This method can be used in most soil types but is limited to sampling at or near the ground surface. Accurate, representative samples can be collected with this procedure depending on the care and precision demonstrated by the sample team member. A flat, pointed mason trowel to cut a block of the desired soil is helpful when undisturbed profiles are required. Tools plated with chrome or other materials should not be used. Plating is particularly common with garden implements such as potting trowels.

The following procedure is used to collect surface soil samples:

1. Carefully remove the top layer of soil or debris to the desired sample depth with a pre-cleaned spade.

2. Using a pre-cleaned, stainless steel scoop, plastic spoon, or trowel, remove and discard a thin layer of soil from the area which came in contact with the spade.

3. If volatile organic analysis is to be performed, transfer the sample directly into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval or location into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.2 Sampling at Depth with Augers and Thin Wall Tube Samplers

This system consists of an auger, or a thin-wall tube sampler, a series of extensions, and a "T" handle (Figure 1, Appendix A). The auger is used to bore a hole to a desired sampling depth, and is then withdrawn. The sample may be collected directly from the auger. If a core sample is to be collected, the auger tip is then replaced with a thin wall tube sampler. The system is then lowered down the borehole, and driven into the soil to the completion depth. The system is withdrawn and the core is collected from the thin wall tube sampler.

Several types of augers are available; these include: bucket type, continuous flight (screw), and post-hole augers. Bucket type augers are better for direct sample recovery because they provide a large volume of sample in a short time. When continuous flight augers are used, the sample can be collected directly from the flights. The continuous flight augers are satisfactory when a composite of the complete soil column is desired. Post-hole augers have limited utility for sample collection as they are designed to cut through fibrous, rooted, swampy soil and cannot be used below a depth of approximately three feet.

The following procedure is used for collecting soil samples with the auger:

1. Attach the auger bit to a drill rod extension, and attach the "T" handle to the drill rod.

2. Clear the area to be sampled of any surface debris (e.g., twigs, rocks, litter). It may be advisable to remove the first three to six inches of surface soil for an area approximately six inches in radius around the drilling location.

3. Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole. This prevents accidental brushing of loose material back down the borehole when removing the auger or adding drill rods. It also facilitates refilling the hole, and avoids possible contamination of the surrounding area.

4. After reaching the desired depth, slowly and carefully remove the auger from the hole. When sampling directly from the auger, collect the sample after the auger is removed from the hole and proceed to Step 10.

5. Remove auger tip from the extension rods and replace with a pre-cleaned thin wall tube sampler. Install the proper cutting tip.

6. Carefully lower the tube sampler down the borehole. Gradually force the tube sampler into the soil. Do not scrape the borehole sides. Avoid hammering the rods as the vibrations may cause the boring walls to collapse.

7. Remove the tube sampler, and unscrew the drill rods.

8. Remove the cutting tip and the core from the device.

9. Discard the top of the core (approximately 1 inch), as this possibly represents material collected before penetration of the layer of concern. Place the remaining core into the appropriate labeled sample container. Sample homogenization is not required.

10. If volatile organic analysis is to be performed, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly.

    When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

11. If another sample is to be collected in the same hole, but at a greater depth, reattach the auger bit to the drill and assembly, and follow steps 3 through 11, making sure to decontaminate the auger and tube sampler between samples.

12. Abandon the hole according to applicable state regulations. Generally, shallow holes can simply be backfilled with the removed soil material.

7.2.3 Sampling with a Trier

The system consists of a trier, and a "T" handle. The auger is driven into the soil to be sampled and used to extract a core sample from the appropriate depth.

The following procedure is used to collect soil samples with a sampling trier:

1. Insert the trier (Figure 2, Appendix A) into the material to be sampled at a 0^{o} to 45^{o} angle from horizontal. This orientation minimizes the spillage of sample.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7.2.4 Sampling at Depth with a Split Spoon (Barrel) Sampler

Split spoon sampling is generally used to collect undisturbed soil cores of 18 or 24 inches in length. A series of consecutive cores may be extracted with a split spoon sampler to give a complete soil column profile, or an auger may be used to drill down to the desired depth for sampling. The split spoon is then driven to its sampling depth through the bottom of the augured hole and the core extracted.

When split spoon sampling is performed to gain geologic information, all work should

be performed in accordance with ASTM D1586-98, "Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils".

The following procedures are used for collecting soil samples with a split spoon:

1. Assemble the sampler by aligning both sides of barrel and then screwing the drive shoe on the bottom and the head piece on top.

2. Place the sampler in a perpendicular position on the sample material.

3. Using a well ring, drive the tube. Do not drive past the bottom of the head piece or compression of the sample will result.

4. Record in the site logbook or on field data sheets the length of the tube used to penetrate the material being sampled, and the number of blows required to obtain this depth.

5. Withdraw the sampler, and open by unscrewing the bit and head and splitting the barrel. The amount of recovery and soil type should be recorded on the boring log. If a split sample is desired, a cleaned, stainless steel knife should be used to divide the tube contents in half, longitudinally. This sampler is typically available in 2 and 3 1/2 inch diameters. A larger barrel may be necessary to obtain the required sample volume.

6. Without disturbing the core, transfer it to appropriate labeled sample container(s) and seal tightly.

7.2.5 Test Pit/Trench Excavation

A backhoe can be used to remove sections of soil, when detailed examination of soil characteristics are required. This is probably the most expensive sampling method because of the relatively high cost of backhoe operation.

The following procedures are used for collecting soil samples from test pits or trenches:

1. Prior to any excavation with a backhoe, it is important to ensure that all sampling locations are clear of overhead and buried utilities.

2. Review the site specific Health & Safety plan and ensure that all safety precautions including appropriate monitoring equipment are installed as required.

3. Using the backhoe, excavate a trench approximately three feet wide and approximately one foot deep below the cleared sampling location. Place excavated soils on plastic sheets. Trenches greater than five feet deep must be sloped or protected by a shoring system, as required by OSHA regulations.

4. A shovel is used to remove a one to two inch layer of soil from the vertical face of the pit where sampling is to be done.

5. Samples are taken using a trowel, scoop, or coring device at the desired intervals. Be sure to scrape the vertical face at the point of sampling to remove any soil that may have fallen from above, and to expose fresh soil for sampling. In many instances, samples can be collected directly from the backhoe bucket.

6. If volatile organic analyses are required, transfer the sample into an appropriate, labeled sample container with a stainless steel lab spoon, or equivalent and secure the cap tightly. Place the remainder of the sample into a stainless steel, plastic, or other appropriate homogenization container, and mix thoroughly to obtain a homogenous sample representative of the entire sampling interval. Then, either place the sample into appropriate, labeled containers and secure the caps tightly; or, if composite samples are to be collected, place a sample from another sampling interval into the homogenization container and mix thoroughly. When compositing is complete, place the sample into appropriate, labeled containers and secure the caps tightly.

7. Abandon the pit or excavation according to applicable state regulations. Generally, shallow excavations can simply be backfilled with the removed soil material.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration

activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA, OHSA and corporate health and safety procedures, in addition to the procedures specified in the site specific Health & Safety Plan..

12.0 REFERENCES

Mason, B.J. 1983. Preparation of Soil Sampling Protocol: Technique and Strategies. EPA-600/4-83-020.

Barth, D.S. and B.J. Mason. 1984. Soil Sampling Quality Assurance User's Guide. EPA-600/4-84-043.

U.S. Environmental Protection Agency. 1984 Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA-600/4-84-076.

de Vera, E.R., B.P. Simmons, R.D. Stephen, and D.L. Storm. 1980. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018.

ASTM D 1586-98, ASTM Committee on Standards, Philadelphia, PA.

APPENDIX A
Figures
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FIGURE 1. Sampling Augers

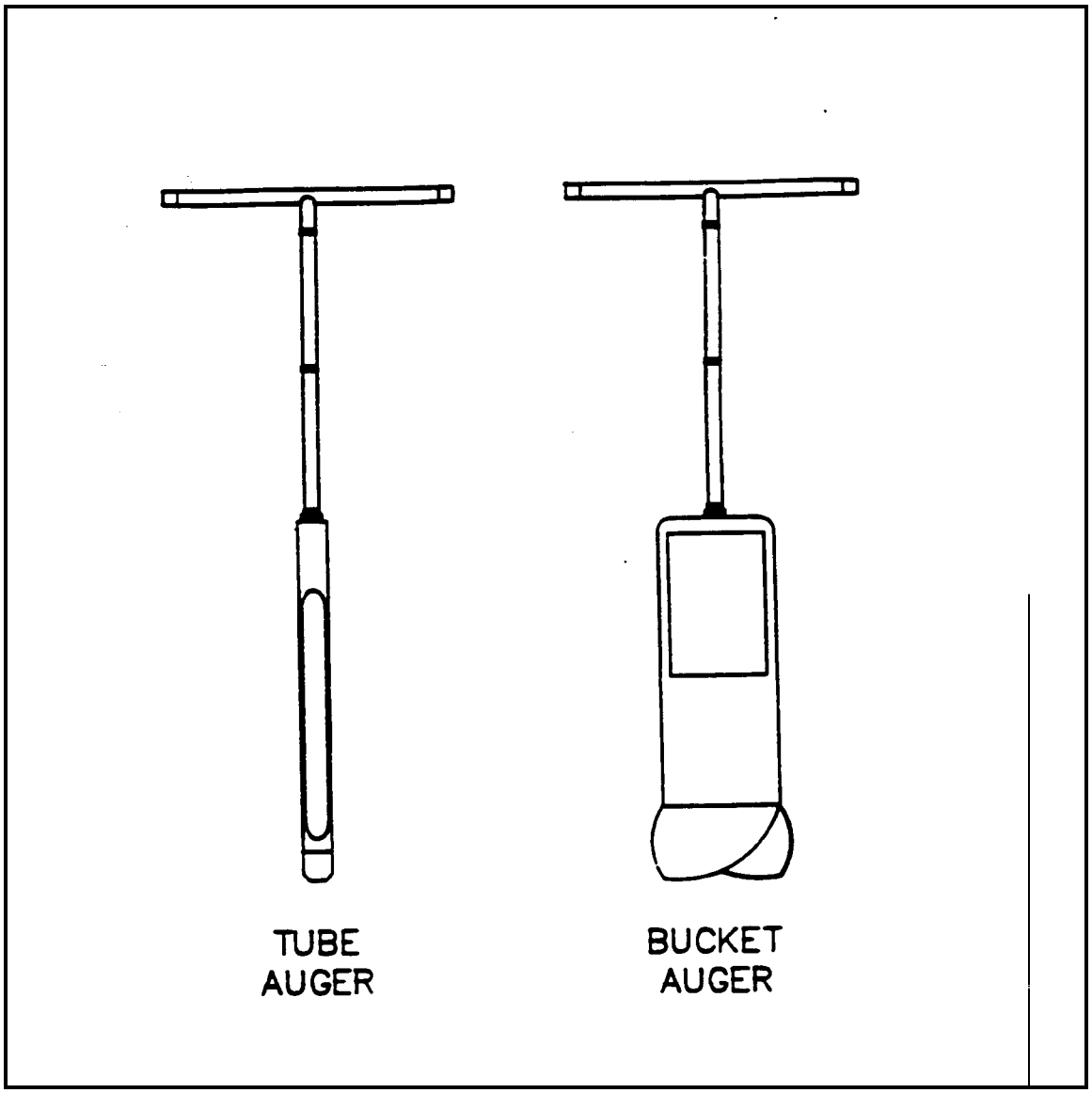

FIGURE 2. Sampling Trier