Appendix A.
Quality Assurance Project Plan

Intentionally Left Blank

POLYCYCLIC AROMATIC HYDROCARBON (PAH) TRANSPORT STUDY
Quality Assurance Project Plan

Submitted to:
City of San Diego
Transportation and Storm Water Department

Submitted by:
Amec Foster Wheeler
Environment & Infrastructure, Inc.
San Diego, California

June 2016

Amec Foster Wheeler Project No. 5025151122

APPROVAL SIGNATURES

PROJECT ORGANIZATION:

Title:	Name:	Signature:	Date:
City of San Diego Project Manager	Victoria Kalkirtz		10/3/16
Amec Foster Wheeler Project QA Officer	Theodore Von Bitner		9/19/16
Amec Foster Wheeler Project Manager	Kristina Hysler		9/19/16
Laboratory Project Manager (Eurofins)	Brian Whittaker	Brian Whittaker	9/9/16
Laboratory Project Manager (Physis)	Misty Mercier		9/15/16

STATE WATER RESOURCES CONTROL BOARD (SWRCB):

Title:	Name:	Signature:	Date:
Water Resource Control Engineer	Carey Nagoda	Carey Nagoda	9/19/2016

This page intentionally left blank.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ACRONYMS AND ABBREVIATIONS

°	degree(s)
°C	degrees Celsius
µg	micrograms
µg/L	micrograms per liter
µg/mL	micrograms per milliliter
AC	alternating current
Air Toxics	Eurofins Air Toxics Laboratories
Amec Foster Wheeler	Amec Foster Wheeler Environment & Infrastructure, Inc. (previously AMEC Environment & Infrastructure, Inc.)
cfm	cubic feet per minute
CFR	Code of Federal Regulations
City	City of San Diego
CLRP	Comprehensive Load Reduction Plan
COC	chain of custody
CWA	Clean Water Act
DC	direct current
DD	dry deposition
DHS	Department of Health Services
DoD	Department of Defense
DoD-ELAP	Department of Defense - Environmental Laboratory Accreditation Program
DOH	Department of Health
DQO	data quality objective
DRI	Desert Research Institute
EC	European Commission
EDD	electronic data deliverable
EPA	United States Environmental Protection Agency
FB	field blank
FD	field duplicate
FY	fiscal year
GC	gas chromatography

ACRONYMS AND ABBREVIATIONS (continued)

GIS	geographic information system
H&S	Health and Safety
Hg	mercury
HVAS	high-volume air sampler
ID	identification
JHA	Job Hazard Analysis
LCS	laboratory control sample
LD	laboratory duplicate
m^3	cubic meter(s)
m^3/min	cubic meters per minute
MB	method blank
mm	millimeter
mph	mile(s) per hour
MS	mass spectrometry
MSs	matrix spike
MSD	matrix spike duplicate
NADP	National Atmospheric Deposition Program
NELAP	National Environmental Laboratory Accreditation Program
ng	nanogram(s)
ng/L	nanograms per liter
ng/m^3	nanograms per cubic meter
NO_2	nitrogen dioxide
NPS	National Park Service
NWS	National Weather Service
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PFE	pressurized fluid extraction
Physis	Physis Environmental Laboratories, Inc.
Project	PAH Source Tracking Study
Project Watersheds	Downtown Anchorage, B Street/Broadway Piers, Chollas Creek, Switzer Creek and Paleta Creek Watersheds
PUF	polyurethane foam

ACRONYMS AND ABBREVIATIONS (continued)

PUF/XAD-2®	polyurethane foam and XAD-2 resin
QA	quality assurance
QA/QC	quality assurance/quality control
QC	quality control
QAPP	Quality Assurance Project Plan
RH	relative humidity
RL	reporting limit
RPD	relative percent difference
SLA	screening level assessment
SOP	standard operating procedure
SIM	Selected Ion Monitoring
SVOC	semi-volatile organic compound
TAC	Technical Advisory Committee
TMDL	Total Maximum Daily Load
UV	ultraviolet
WD	wet deposition
WNW	west-northwest
WURMP	Watershed Urban Runoff Management Program

This page intentionally left blank.

1.0 DISTRIBUTION LIST

Title:	Name (Affiliation):	Tel. No.:	Email:	QAPP No.:
Contract Manager	Roth Kolb (City of San Diego)	858-541-4328	RKolb@sandiego.gov	
Project Quality Assurance Officer	Ted Von Bitner (Amec Foster Wheeler)	949-363-3232	theodore. vonbitner@amecfw.com	
Project Manager	Kristina Hysler (Amec Foster Wheeler)	619-889-7752	kristina.hysler@amecfw.com	
Field Sampling Manager	Brenda Stevens (Amec Foster Wheeler)	858-514-7729	brenda.stevens@amecfw.com	
Equipment Manager	Kris Green (Amec Foster Wheeler)	619-261-9629	kristopher.green@amecfw.com	
Health and Safety Officer	Jesse Davis (Amec Foster Wheeler)	858-514-6420	jesse.davis@amecfw.com	
Laboratory Project Manager	Kyle Vagadori (Eurofins)	916-985-1000	kylevagadori@eurofinsus.com	
Laboratory Project Manager	Misty Mercier (Physis)	916-605-3339	mistymercier@physislabs.com	
Regional Water Control Board Contact	Cary Nagoda (Monitoring Assessment)	619-521-3003	carey.nagoda @waterboards.ca.gov	
Regional Water Control Board Contact	Melissa Valdovinos (Protection Planning)	619-521-8039	melissa.valdovinos @waterboards.ca.gov	

Laboratory Managers will receive an electronic copy of the Quality Assurance Project Plan (QAPP).

This page intentionally left blank.

2.0 PROJECT/TASK ORGANIZATION

2.1 Involved Parties and Roles

The City of San Diego, consultants, and laboratory staff will have the following roles and responsibilities for this project:

- **Program Manager:** Ruth Kolb is the Storm Water Division Program Manager for the City of San Diego (City) and has responsibility for program oversight.
- **Amec Foster Wheeler Quality Assurance (QA) Officer:** Ted Von Bitner is the Amec Foster Wheeler Project QA Officer. The Amec Foster Wheeler Project QA Officer will be responsible for the project quality assurance and quality control procedures implemented during sampling, laboratory analysis, data management, and data analysis.
- **Amec Foster Wheeler Project Manager:** Kristina Hysler is the Amec Foster Wheeler Project Manager. The Amec Foster Wheeler Project Manager will be responsible for project coordination, overall project development, coordination with the laboratories, scheduling, budget management, and oversight of all project plans and report development.
- **Amec Foster Wheeler Field Sampling Manager:** Brenda Stevens is the Amec Foster Wheeler Sampling Manager and is responsible for development of the monitoring approach, preparation of the field effort and sampling events, and development and maintenance of a database of all project data.
- **Field Coordinators:** Experienced, qualified Amec Foster Wheeler field staff will be in charge of assisting Field Sampling Manager with overseeing field sampling and managing field technicians.
- **Field Technicians:** Qualified Amec Foster Wheeler staff will assist in the collection of samples and report writing.
- **Amec Foster Wheeler Health and Safety (H&S) Officer:** Jesse Davis is the Amec Foster Wheeler Health and Safety Officer and is responsible for implementation of the project Health and Safety Plan and practices.
- **Sampling Equipment:** Kris Green is responsible for field sampling equipment, requisitioning, equipment installation, and sampling activity implementation.
- **Report Writing:** Brenda Stevens is responsible for development of project reports.
- **Eurofins Air Toxics Laboratories QA Officer and Project Manager:** Eurofins Air Toxics Laboratories (Air Toxics), located in Folsom, California, is responsible for the analysis of dry deposition air samples. Sepideh Saeed, the Air Toxics Laboratory Director, ensures that samples are analyzed in accordance with the methods and quality assurance requirements outlined in this QAPP. Kyle Vagadori is the Air Toxics Project Manager who will oversee the day-to-day operations of the project.

- **Physis Environmental Laboratories, Inc. QA Officer and Project Manager:** Physis Environmental Laboratories, Inc. (Physis) will be responsible for the analysis of all water samples. Mark Baker is the Physis Director of Quality Assurance, and he will be responsible for the analysis of samples in accordance with the methods and quality assurance requirements outlined in this QAPP. Misty Mercier is the Physis Project Manager who will oversee the day-to-day operations of the project.

2.2 Project Phases

This project has been designed in five phases that mirror the City's fiscal calendar (July 1 through June 30). Work to be performed within each phase is outlined in Table 2-1. Changes in the project schedule may occur, depending on the findings of a specific phase or on additional project considerations.

Table 2-1. Phase Overview

Phase	Overview	Expected Start Date	Expected Completion Date
Phase I	Develop a project conceptual model and perform a literature review to assess potential sources of polycyclic aromatic hydrocarbons (PAHs) in the Project Watersheds to then recommend next steps.	**Completed**	
Phase II	Develop a monitoring plan to implement the recommendations from Phase I.	**Completed**	
Phase III	Initiate a more intensive sampling period with five dry weather events and four wet weather events.	**Completed**	
Phase IV	Perform final sampling of one dry weather event and two wet weather events. Conduct analysis of the data collected during Phases II, III, and IV. Summarize analytical results in draft and final versions of a report.	October 2016	April 2017
Phase V	Finalize the report by incorporating comments from the project Technical Advisory Committee (TAC) and other interested parties.	Summer 2017	Winter 2017

2.3 Quality Assurance Officer Role

The Amec Project QA Officer position is independent of data generation. The Amec Project QA Officer will ensure that the QA and quality control (QC) procedures described in this document are applied properly throughout the sampling and analysis activities. The Amec Project QA Officer

will coordinate with the project managers and QA officers of participating laboratories to ensure that all QA and QC procedures within this QAPP are understood and followed.

2.4 Persons Responsible for QAPP Update and Maintenance

The Amec Project Manager and Amec Project QA Officer are responsible for maintaining this QAPP. Changes and updates to this QAPP may be made by the Project Manager and Project QA Officer. The Amec Project Manager will be responsible for making the changes and ensuring that these updates are provided to each of the participating agencies listed above. Previous versions should be removed to avoid any confusion regarding the most current version of the QAPP.

2.5 Organizational Chart and Responsibilities

Figure 2-1 presents the organization chart for the Polycyclic Aromatic Hydrocarbon (PAH) Transport Study Monitoring Program.

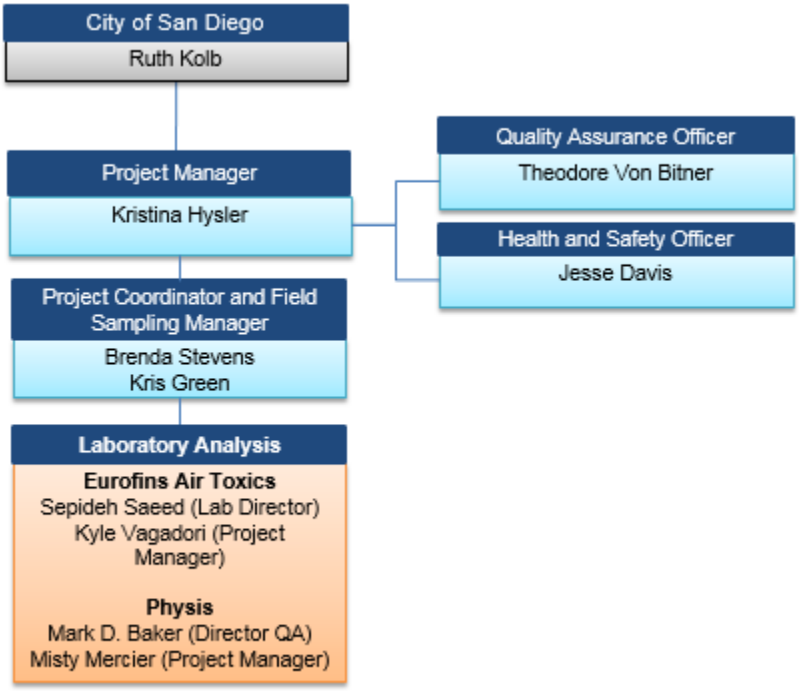


Figure 2-1. Organizational Chart

This page intentionally left blank.

3.0 PROJECT DEFINITION/BACKGROUND

3.1 Problem Definition

Polycyclic aromatic hydrocarbons (PAHs) are an ongoing source of pollution in the environment. PAHs are released from the petroleum products or the incomplete combustion of organic matter from both anthropogenic and natural sources. PAHs are semi-volatile organic compounds (SVOCs) consisting of fused aromatic (i.e., benzene-type) rings. They generally have high melting and boiling points, low vapor pressure, and low water solubility. PAHs may contain from two to seven benzene rings, but those with five or six are most common. Individual PAHs vary in their chemical and physical properties, which dictate their uses, as well as their distribution and fate in the environment. The EPA has designated 16 PAH compounds as priority pollutants. These compounds are often targeted for measurement in environmental samples:

- naphthalene
- acenaphthylene
- acenaphthene
- fluorene
- phenanthrene
- anthracene
- fluoranthene
- pyrene
- benzo(a)anthracene
- chrysene
- benzo(b)fluoranthene
- benzo(k)fluoranthene
- benzo(a)pyrene
- dibenz(a,h)anthracene
- benzo(g,h,i)perylene
- indeno(1,2,3-cd)pyrene.

In urbanized areas, the majority of PAHs are released from anthropogenic sources with either a pyrogenic origin (derived from the incomplete combustion of organic matter, as in gasoline- and diesel-powered engines and the related vehicular exhaust emissions), or a petrogenic origin (via contamination by crude oils, coal, coal tar, asphalt, or various refinery products) (EPA, 2012; Maliszewska-Kordybach, 1999; Tran et al., 1996). PAHs also are released from natural sources via wildfires and volcanic activity.

PAHs are removed from the atmosphere on a continuous basis via wet and dry deposition. Studies suggest that atmospheric deposition represents a significant portion of overall waterbody contaminant loading, relative to other sources, for nutrients, trace metals, and semi-volatile organic contaminants (Sabin et al., 2004). PAHs have been identified on the USEPA 303(d) list as causing toxicity for the Downtown Anchorage, B Street/Broadway Piers, Chollas Creek, Switzer Creek and Paleta Creek watersheds (Project watersheds). Currently, total maximum daily loads (TMDLs) are being developed to address toxicity caused by PAHs. These TMDLs are designed to limit the amount of a specific pollutant that can enter a water body while still meeting Water Quality Standards per the US EPA Clean Water Act. The City of San Diego Transportation and Stormwater Department is conducting a special study to better understand the overall

contribution of atmospherically deposited PAHs to PAH levels in local watersheds, so as to advance the development and implementation of the applicable TMDLs (discussed below).

The PAH Source Tracking Study (Project) is focused on investigating the contribution of aerially deposited PAHs to the Project Watersheds. The study has been designed to answer the following questions:

- What are the sources of PAHs in the Project Watersheds? What are the relative percentages contributed by those sources? Can they be further characterized?
- What are the dry and wet PAH deposition loading rates in the Project Watersheds? How can these data be used to help implement Total Maximum Daily Loads (TMDLs) or guide future management efforts?
- What are the next steps required to characterize sources for TMDL implementation? What type of environmental monitoring is needed and what would be most effective?

3.2 Background

The following San Diego Bay shoreline areas have been listed in the United States Environmental Protection Agency (USEPA) Clean Water Act (CWA) 40 Code of Federal Regulations (CFR) Section 303(d) list of impaired waters:

- Downtown Anchorage
- Vicinity of B Street and Broadway Piers
- Near Chollas Creek
- Near Switzer Creek
- Seventh Street Channel (Paleta Creek)

The majority of these areas have been listed as impaired waters due to sediment toxicity. Currently, investigative orders are being developed to research the sources of these impairments. The water quality impairments and the pending TMDLs in development for each San Diego Bay Shoreline segment are summarized in Table 3-1.

Table 3-1. San Diego Bay Toxicity TMDL Summary

Waterbody	Pollutant Category[1]	Proposed TMDLs in Development
San Diego Bay Shoreline, near Chollas Creek	Benthic Community Effects, Sediment Toxicity	PCBs, PAHs, Chlordane
San Diego Bay Shoreline, near Switzer Creek	Chlordane, PAHs	PCBs, PAHs, Chlordane
San Diego Bay Shoreline, Seventh Street Channel (Paleta Creek)	Benthic Community Effects, Sediment Toxicity	PCBs, PAHs, Chlordane
San Diego Bay Shoreline, Downtown Anchorage	Benthic Community Effects, Sediment Toxicity	PCBs, PAHs, Chlordane
San Diego Bay Shoreline, Vicinity of B Street and Broadway Piers	Benthic Community Effects, Sediment Toxicity, Total Coliform	PCBs, PAHs, Zinc

Notes:
1. Refer to United States Environmental Protection Agency (USEPA) Clean Water Act (CWA) 40 Code of Federal Regulations (CFR) Section 303(d) list of impaired waters
PAH = polycyclic aromatic hydrocarbon; PCB = polychlorinated biphenyl

This page intentionally left blank.

4.0 PROJECT/TASK DESCRIPTION

4.1 Project Phases

The primary goal outlined for the study was to determine if there is significant atmospheric transport of PAHs from emission sources to local waterbodies through the deposition process. The project is broken into five phases as described below.

Phase I (Fiscal Year [FY] 2012) was completed by AMEC Environment & Infrastructure, Inc. (now Amec Foster Wheeler) in FY 2012 and focused on developing a project conceptual model and performing a literature review to assess potential sources of PAHs in the Project Watersheds (AMEC, 2012a). The literature review yielded information on the PAH load contribution by wildfires. A data gap analysis was performed for load contributions from other PAH sources.

The literature sources also provided methods that may be used to link specific PAH compounds to specific sources (also known as "fingerprinting"). Allocation of relative percentages of PAH emissions per source is important when multiple sources of contaminant emissions are present. The relative molar concentration ratios of PAHs, or diagnostic ratios, are considered to be characteristic of a given emission source and, therefore, provide a useful tool to identify pollution emission sources (Tobiszewski and Namieśnik, 2012; Zeng and Vista, 1996). PAH diagnostic ratios have been used to determine emission sources in various environmental matrices such as air, water, sediments, soil, sewage sludge, and tissues (Tobiszewski and Namieśnik, 2012).

Based on the findings of the literature review and data gap analysis, two steps were recommended to estimate the relative percentages contributed by the PAH sources in the Project Watersheds to help implement TMDLs.

1. An air monitoring program should be developed to study wet and dry deposition in the Project Watersheds. Local air monitoring data are not available in these areas. Data on atmospheric concentrations and deposition of SVOCs may be limited in southern California because the current air quality monitoring system is designed to focus on impacts relative to human health rather than on ecological health. This is due to the assumption that the direct impacts of the aerial deposition will have a more immediate impact on human health. However, SVOCs are of great concern in aquatic environments. It was recommended to implement an air monitoring program to evaluate both wet and dry deposition over a minimum one-year time frame. Data from the depositional monitoring may be modeled to estimate deposition velocities from dry deposition.
2. Diagnostic ratios derived from locally available data need further analyses to assess whether the data may help characterize some of the watershed sources. The locally available data were not originally collected with the intention of source characterization.

The City concurred with these recommendations and determined the need for an aerial deposition study in the Pueblo San Diego Watershed to better understand the overall contribution of aerially deposited PAHs to the Project Watersheds. Preliminary monitoring recommendations were to

collect data necessary to estimate PAH loads from dry and wet atmospheric deposition in the Project Watersheds. The primary goal outlined for the study was to determine if the atmosphere is a significant transport mechanism of PAHs to local waterbodies. Preliminary monitoring recommendations were to help collect the data necessary to estimate PAH loads in the Project Watersheds due to dry and wet atmospheric deposition in the Project Watersheds. PAH loading estimates will help guide future management efforts and determine whether the atmosphere is a significant potential transport mechanism of these contaminants to local waterbodies.

Phase II (FY 2013) was completed in by AMEC in FY 2013 and included the development of the Monitoring Plan to implement the recommendations from Phase I regarding development of an atmospheric monitoring program. This Monitoring Plan included:

- In-depth sampling location siting effort
- Final equipment selection
- Analytical laboratory selection

Sampling began during this phase with a pilot study. The pilot study included one month of dry deposition sampling that was conducted during the spring of 2013. The study confirmed that the selected monitoring methodology used was appropriate for the goals of the study.

Phase III (FY 2014) was completed in by AMEC in FY 2014 and included a more intensive sampling period. Sampling included five dry weather events and four wet weather events. Testing from Phase III found generally small concentrations of PAHs in dry deposition (air) and wet weather (water) throughout the study. The most prevalent PAHs in both dry and wet weather aerial deposition samples were naphthalene and phenanthrene. These results are documented in the PAH Source Tracking Study Preliminary Summary Report.

Phase IV (FY 2017) was originally scheduled to commence during FY 2015 but, because of funding issues, will not begin until FY 2017. This phase will include one additional dry depositional monitoring event, and two wet weather events to complete the study. The one remaining dry weather aerial deposition monitoring event will be conducted between the wet weather events to give data temporal context. Analysis of data collected during Phases II through IV will begin, and results will be summarized in a draft report. Further analysis linking specific PAH compounds to specific sources will be conducted, if feasible, on the data collected, and an attempt will be made to allocate relative percentages of PAH emissions per source.

This QAPP has been developed as part of Phase IV to present the methods selected to implement an atmospheric deposition monitoring program in the Project Watersheds now that the project will be funded by the State Water Board.

Phase V (FY 2018) will include the finalization of the project report. This report will incorporate comments from the project team and the City. The decision to publish results in peer-reviewed journals will be made at the end of the FY.

4.2 Mobilization and Staffing

Sampling mobilizations require considerable planning; therefore, it is critical to plan and prepare all possible aspects of the field effort well in advance. A Staffing Plan, which designates personnel and equipment required for each facet of dry deposition or storm sampling, will be completed as soon as a potential event is forecast.

The Staffing Plan will include the following:

- Personnel assigned for each position
- Shift (i.e., start-up and relief) and zone designations
- Equipment mobilization
- Communication channels
- Safety protocols
- General monitoring program protocol

Field teams will not be mobilized during or near certain holidays if the mobilization should continue through that holiday. This includes the following dates:

- Thanksgiving Day and the day after Thanksgiving
- Christmas: December 24 and 25
- New Year: December 31 and January 1

4.2.1 Dry Deposition

For dry deposition field activities, field teams will be composed of two team members. Each team member will be trained in project sampling protocols, clean hand techniques, and equipment operation. Teams will visit every site and will start each sampler.

4.2.2 Wet Deposition

For wet deposition field activities, field teams will be composed of two team members. Each team member will be trained in project sampling protocols, clean hand techniques, and equipment operation. Teams will visit every site and will start each sampler.

This page intentionally left blank.

5.0 QUALITY OBJECTIVES AND CRITERIA

Data Quality Objectives (DQOs) are quantitative and qualitative statements that define project objectives and specify the acceptable ranges of field sampling and laboratory performance. Numeric DQOs for the constituents being analyzed are listed in Table 5-1. DQOs for this project include the following:

- Accuracy
- Precision
- Completeness

Accuracy describes how close the measurement is to its true value. Accuracy is the overall agreement of a measurement to a known value and includes a combination of random error (precision) and systematic error (bias) components of both sampling and analytical operations (EPA, 2008). Assessment of accuracy involves the measurement of a sample of known concentration and comparison of the known value with the measured value. The accuracy of chemical measurements will be checked by performing spike analyses using a standard prior to and/or during sample analysis. A standard is a known concentration of a certain solution. Standards can be purchased from chemical or scientific supply companies. Standards might also be prepared by a professional partner (i.e., a commercial or research laboratory). The concentration of the standards will be unknown to the analyst until after measurements are determined. The concentration of the standards should also be within the mid-range of the equipment standards. Recovery measurements are determined by spiking a replicate sample in the laboratory with a known concentration of the analyte. Accuracy of the project data will be determined by comparing results from matrix spikes (MSs)/matrix spike duplicates (MSDs), field blanks, blank spikes, and method blanks to the accuracy objectives specified in Table 5-1 for samples.

Precision describes how well repeated measurements agree under identical or exceptionally similar conditions. This is the random component of error. Precision is estimated by various statistical techniques typically using some derivation of the standard deviation. The evaluation of precision described here relates to repeated measurements/samples collected in the field (field duplicates) or the laboratory (laboratory replicates and MSs/MSDs). Precision measurements will be determined by comparing results from laboratory replicates and MSDs with the precision objectives specified in Table 5-1. Relative percent differences (RPDs) will be calculated to determine the precision between duplicate samples, using the following equation:

Equation 5-1: $$RPD = \frac{abs[x_1 - x_2]}{0.5 * (x_1 + x_2)} * 100$$

Completeness is the fraction of planned data that must be collected to fulfill the statistical criteria of the project. For this project there are no statistical criteria that require a certain percentage of data. However, it is expected that at least 75 percent of the measurements could be taken when anticipated (EPA, 2008). This accounts for adverse weather conditions and safety concerns. The project team will determine completeness by comparing the number of measurements planned to be collected with the number of measurements actually collected that were also deemed valid. An invalid measurement would be one that does not meet the sampling method requirements and the DQOs. Completeness will be measured as a percentage of the number of samples collected that meet their respective DQOs compared to the anticipated total number of samples. This calculation is shown as:

Equation 5-2: $$Completeness = \frac{Actual\ number\ of\ samples\ collected}{Project\ required\ total\ samples\ to\ be\ collected} * 100$$

Numerical DQOs for constituent accuracy, precision, and completeness for PAH air and water samples are summarized in Table 5-1.

Table 5-1. Data Quality Objectives for PAH Samples

Constituent	RL	Units	Accuracy (% Recovery and Blank Results)	Precision (% RPD)	Completeness	Holding Time [(a)]
Dry Deposition (AIR ANALYSIS)						
Polycyclic Aromatic Hydrocarbons	0.1	µg	LCS: 60-120% FB and MB: <RL	FD, LD, and MSD[(b)]: < 25	75%	7 Days/ 40 Days
Wet Deposition (WATER ANALYSIS)						
Polycyclic Aromatic Hydrocarbons	5	ng/L	MSs[(b)]: 50-150% FB and MB: <RL	FD, LD, and MSD[(b)]: < 25	90%	7 Days/ 40 Days

Notes:
(a) The first time period represents the holding time for preparation, preservation, or extraction required by the method and the second time period represents the holding time for analysis given that the appropriate preparation was conducted.
(b) To process MS/MDSs, three replicates are required from the field since the media cannot be split prior to extraction.
µg = micrograms; % = percent; FB = field blank; FD = field duplicate; LCS = laboratory control sample; LD = laboratory duplicate; MB = method blank; ng/L = nanograms per liter; RL = reporting limit

Data quality objectives of the meteorological parameters are presented in Table 5-2. Meteorological stations measure in-situ meteorological parameters at each station throughout the duration of sample collection. Stations will continuously collect meteorological parameters.

Table 5-2. Data Quality Objectives for Meteorological Measurements

Parameter	Method	Resolution (Accuracy)	Range
Wind Speed	Davis Instruments 6250 Vantage Vue Weather Station (Model No. 6357)	1 mph (±2 mph)	2–150 mph
Wind Direction	Davis Instruments 6250 Vantage Vue Weather Station (Model No. 6357)	1° in numeric display; 16 points [22.5°] on compass rose (±3°)	0–360°
Temperature	Davis Instruments 6250 Vantage Vue Weather Station (Model No. 6357)	0.1°C (±0.5°C)	0–60°C
Relative Humidity (RH)	Davis Instruments 6250 Vantage Vue Weather Station (Model No. 6357)	1% (± 3%)	0–100% RH
Precipitation	Davis Instruments 6250 Vantage Vue Weather Station (Model No. 6357)	0.01" (±4% or 1 tip)	0–199.99 inches
Barometric Pressure	Davis Instruments 6250 Vantage Vue Weather Station (Model No. 6357)	0.01” Hg (±0.03" Hg)	16.00–32.50 inches
Dewpoint	Davis Instruments 6250 Vantage Vue Weather Station (Model No. 6357)	1°C (±1.5°C)	-76° to +54°C

Notes:
° = degrees; % = percent; ± = plus or minus; Hg = mercury; mph = miles per hour

This page intentionally left blank.

6.0 SPECIAL TRAINING AND CERTIFICATION

6.1 Training

All field personnel are required to receive training on sampling standard operating procedures (SOPs) and safety procedures prior to engaging in any field activities. This will include training in the use of the sampling equipment and clean sample handling techniques, along with all appropriate health and safety protocols. Specifically, the following elements will be included in the training of all field personnel:

- Review of Project Job Hazard Analysis (JHA) and Project Screening Level Assessment (SLA) (Appendix A)
- Field equipment training and sampling SOPs

6.2 Training and Certification Documentation

Amec Foster Wheeler will maintain records of training for Sampling SOPs and Health and Safety training. Training is provided by the Amec Health and Safety officer and provided to all Amec staff. Training documents and certifications will be stored in the Amec Foster Wheeler San Diego for Dry and Wet Weather and will be documented if located elsewhere.

6.3 Training Personnel

Field technicians will review the JHA and SLA and consult with the Field Coordinators if they have any questions before mobilization. Field training will be performed by the Field Sampling Manager and will be mandatory for all field coordinators and technicians. The Field Sampling Manager will train the field personnel in sampling protocols and procedures in accordance with this QAPP. The Project Manager or Field Sampling Manager will also communicate any updates or revisions of these protocols in a timely manner. At the end of the field training, all participants must demonstrate proficiency in all the required sampling activities.

This page intentionally left blank.

7.0 DOCUMENTS AND RECORDS

7.1 Documentation

At the time of a site visit, records of the visit must be accurately recorded in a field log. Field data sheets for dry and wet deposition sampling, provided in Appendix B, will be used to record general observations such as weather and any other unusual occurrences.

During dry deposition sampling, the following will be recorded by routinely for each sample at each of the sites:

- Date (DD/MM/YY)
- Start time (00:00)
- Stop time (00:00)
- Counter reading (TE-1000 High-Volume Air Sampler)

  Magnehelic reading (inches of H_20) (TE-1000 High-Volume Air Sampler)
- Maximum, minimum, and actual temperature (degrees Celsius [ºC]) (Davis Instruments Vantage Vue)

The following general information should be entered during each dry and wet deposition site visit:

- Alphanumeric site identification
- Date
- Time
- Monitoring Program
- Weather conditions
- Equipment condition
- Miscellaneous comments
- Field team

Chain of custody (COC) forms are also important field visit documentation. Their purposed and required information are detailed in Section 10.3.

Equipment calibration will also be documented both for field equipment and laboratory equipment. The required information is provided in Section 14.

7.2 Reporting Procedures

Amec Foster Wheeler will complete and submit to the City one data deliverable with the draft report. The data deliverable will contain the following:

- Laboratory results
- Meteorological data
- Field forms

The laboratory results will be submitted in Microsoft Access database format. The field form will include the completed Field Data Log Sheets and the Site Selection Field Sheets in PDF format.

Amec Foster Wheeler will prepare and submit to the City a draft project report. The report will include analysis of data collected during Phase II through Phase IV. The report will provide a review and analysis of the data provided in the electronic data deliverable (EDD) and include a discussion of the potential use of diagnostic ratios to determine PAH sources. The draft report will be submitted to the City prior to the completion of FY 2017 for review and comment. Amec Foster Wheeler will address the City's comments and incorporate any changes into the final version of the project report to be submitted during the next fiscal year in Phase V of the project.

7.3 Laboratory Data Package Deliverables

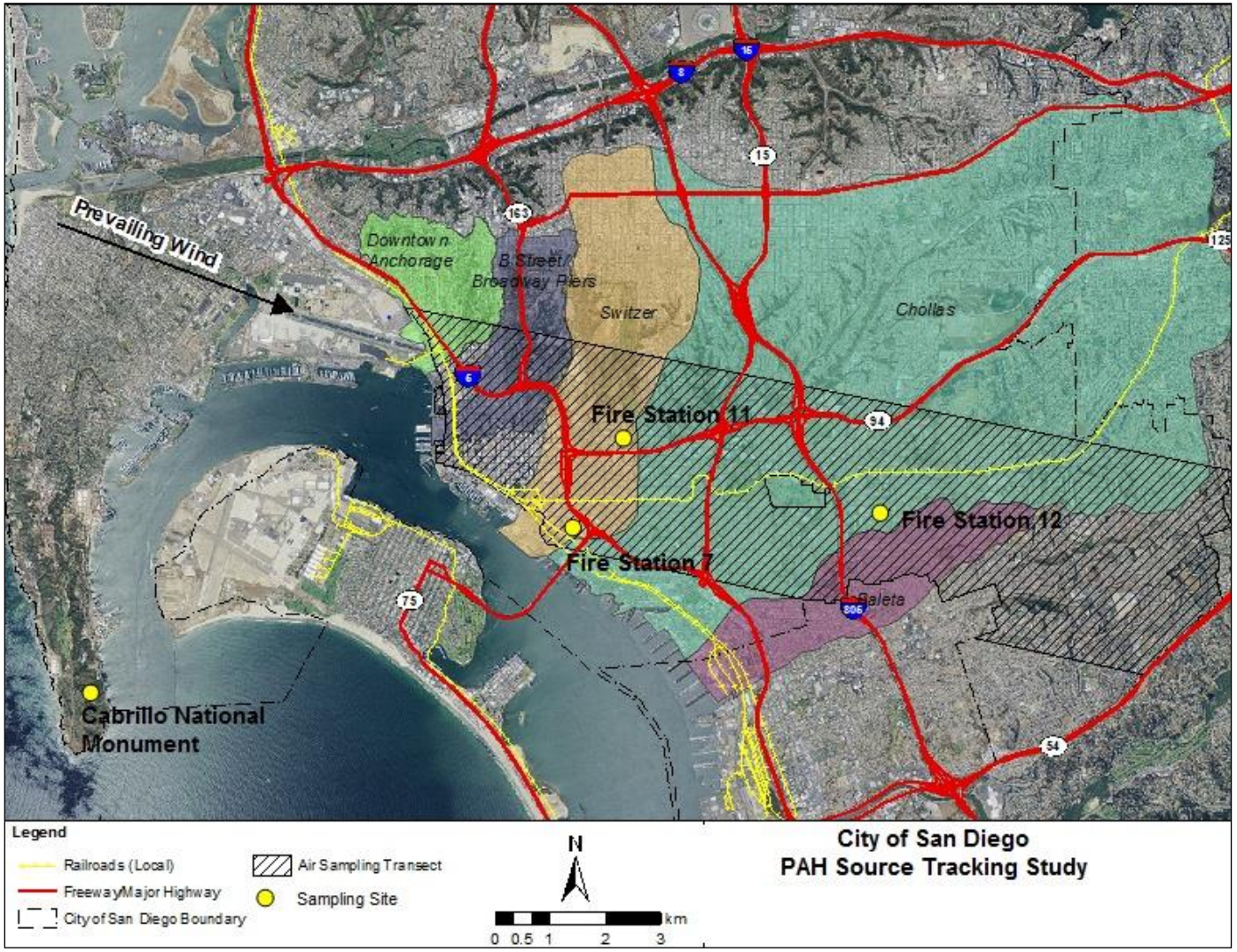
Laboratories are required to provide a three-week turnaround on the deliverable package per event. The deliverable package will include a pdf file of the level 2 report and standard Excel EDD electronic data files emailed. The hard copy will include standard narratives identifying any analytical problems, QA/QC exceedances, and corrective actions. The electronic data files will be submitted in PDF and Microsoft Excel workbook files and will contain all information found in the hard copy reports submitted by the laboratory. Individual data sets may be submitted to Amec Foster Wheeler as either Microsoft Excel workbook files or as Microsoft Access database files.

8.0 SAMPLING PROCESS DESIGN (EXPERIMENTAL DESIGN)

8.1 Monitoring Site Selection

The site selection criteria and site descriptions are presented in this section. A sampling transect following the prevailing wind pattern direction of known and potential PAH emission sources was targeted for this study. The sampling transect runs roughly perpendicular to the San Diego Bay coastline, running inland approximately parallel to the angle of the prevailing winds. Based on hourly data collected over 10 years from 1992–2002, the prevailing winds in San Diego originate from west-northwest (WNW) (Desert Research Institute [DRI], 2012; National Weather Service [NWS], 2012; Wind Direction, 2012). The sampling transect runs approximately 281 degrees (°) to 303° following the prevailing WNW wind pattern direction as shown in Figure 8-1. Figure 8-1 also identifies the Project Watersheds, prevailing wind patterns, targeted transect sampling area selected for this project, and the selected monitoring sites detailed in Section 8.2. A total of three transect sites were selected. Additionally, a reference site was determined to represent conditions with minimum urban influence.

This page intentionally left blank.



Note: Sampling Transect lies within City of San Diego Boundaries Only

Figure 8-1. PAH Sampling Sites Within Project Watersheds

This page intentionally left blank.

Site selection was based on recommendations discussed in the Site Selection Technical Memorandum (AMEC, 2012b), a desktop geographic information system (GIS) analysis, and field verification efforts. The site selection process consisted of multiple steps to ensure that the appropriate monitoring and logistical conditions were met. The general phased approach included:

- A GIS analysis assessed City buildings and/or properties within the desired transect area to create a preliminary site list.
- A preliminary site evaluation was performed by field crews to determine if the sites had any disqualifying characteristics such as obvious access problems or horizontal obstructions to prevailing winds such as tall buildings, trees, wires, etc. Field crews noted approximate distances to major emission sources, approximate distances to horizontal obstructions, available power sources, and rooftop accessibility.
- The appropriate agencies were contacted to determine accessibility to candidate structures or buildings and obtain any additional site characteristic information.
- From the final list of candidate sites, the best representative sites were determined for transect or point source sampling to achieve the project goals. The selection of a representative monitoring site took into account the following factors:
    - Distance from stationary as well as mobile PAH sources. Sites near stationary or mobile PAH sources were undesirable because of the likely resulting skewed PAH analytical results. The PAH Source Tracking Study Development Technical Memorandum includes a summary of sources.
    - Transport characteristics of constituents from mobile and stationary sources along with the influences of meteorology and topography on these characteristics. Disqualifying characteristics would include horizontal obstructions to prevailing winds such as tall buildings, trees, wires, etc.
    - Availability of space and utilities for operating sampling equipment at potential sites (e.g., power source, 24-hour access, etc.). Sites must be accessible year-round to facilitate dry and wet deposition sampling throughout the duration of the project.
- Any required permitting applications were submitted to the appropriate agencies to receive access to sampling sites.

Atmospheric considerations affect the spatial and temporal variability of the pollutants and their transport to the sampling site (EPA, 2008). Effects of buildings, terrain, and heat sources or sinks on the air trajectories can produce local anomalies of excessive pollutant concentrations. Both the transport and the diffusion of air pollutants are altered by topographical features. Major topographical features were avoided in sampling site selection. The size of topographical features may influence surrounding areas. For example, minor features are likely to be have little impact, while major features, including deep river valleys or mountain ranges, may affect a broader region.

Table 8-1 summarizes the influence of topography on air flow.

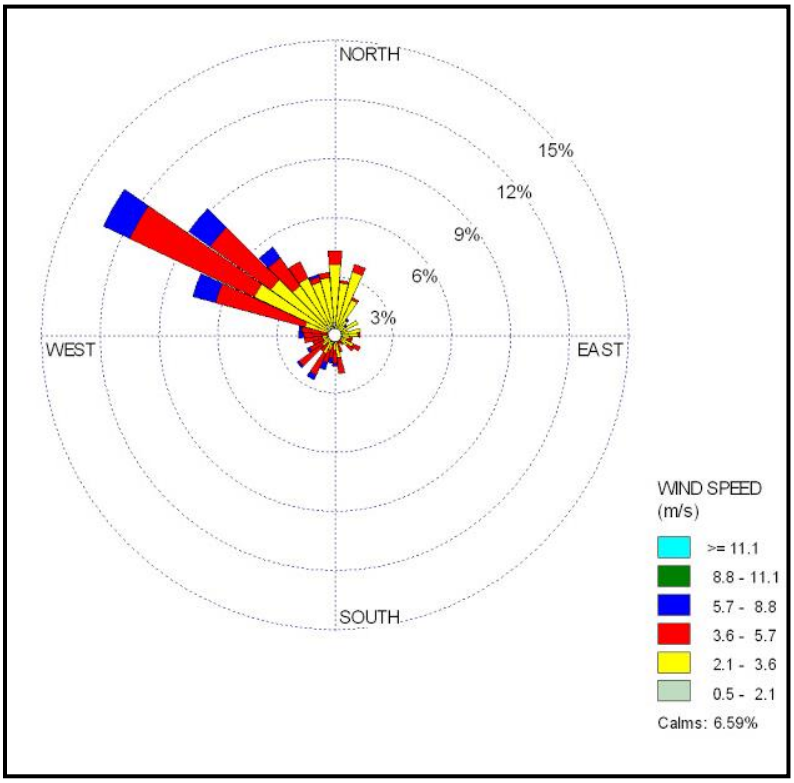
Table 8-1. Relationship of Topography on Air Flow and Sampling Site Selection

Topographical Feature	Influence on Air Flow	Influence on Sampling Site Selection
Slope/Valley	Downward air currents at night and on cold days; up-slope winds on clear days when valley heating occurs. Slope winds and valley-channeled winds; tendency toward down-slope and down-valley winds; tendency toward inversions.	Slopes and valleys are generally only selected as special sites for air monitors because pollutants are well dispersed; concentration levels not representative of other geographic areas; possible placement of monitor to determine concentration levels of a population or industrial center in valley.
Water	Sea or lake breezes inland or parallel to shoreline during the day or in cold weather; land breezes at night.	Monitors on shorelines generally for background reading or obtaining pollution data on water traffic.
Hill	Sharp ridges causing turbulence; air flow around obstructions during stable conditions, but over obstructions during unstable conditions.	Depends on source orientation; upwind source emissions.
Natural or Manmade Obstruction	Eddy effects.	Placement near obstructions not generally representative in readings.

Source: EPA, 2008

Meteorology must be considered in determining not only the geographical location of a sampling site, but also such factors as height, direction, and extension of sampling probes. Atmospheric conditions such as wind speed, wind direction, and humidity can greatly influence the dispersal of pollutants. Topography can also have effects on air flow to sampling sites.

Wind speed can influence the travel time from the pollutant source to the receptor and the dilution of polluted air in the downwind direction. The concentrations of air pollutants are inversely proportional to the wind speed. Wind direction influences the general movements of pollutants in the atmosphere. Wind speed and direction are variable in both horizontal and vertical velocity components. These random motions can be considered atmospheric turbulence, which is either mechanical (caused by structures and changes in terrain) or thermal (caused by heating and cooling of land masses or bodies of water). Turbulent motion can cause the air pollutants to diffuse and spread out. A useful way of displaying wind data is a wind rose diagram constructed to show the distribution of wind speeds and directions. The wind rose diagram shown in Figure 8-2 from the San Diego International Airport at Lindbergh Field represents conditions as they converge on the center from each direction of the compass. The wind rose plot shows that most of the wind comes from the Pacific Ocean to the west of San Diego from the WNW direction.



Source: Chesny Young Meteorology, 2012

Figure 8-2. Wind Rose-San Diego Wind Data

8.2 Sampling Sites

The final sampling sites selected for aerial depositional sampling are presented in Table 8-2. A map showing their locations is presented in Figure 8-1. Based on known sources and the results of the airshed sampling, additional point source sampling stations may be installed to evaluate direct impacts from targeted emission sources. Photographs of each site are provided in Appendix C.

Table 8-2. Sampling Sites and Descriptions

Site Name	Site ID	Latitude	Longitude	Address	Distance from Shoreline (miles)	Elevation (feet)
Cabrillo National Monument (Reference Site)	CNM	32.674396	-117.239777	1800 Cabrillo Memorial Drive San Diego, CA	0.3	365
San Diego Fire Department Station 7	FD07	32.700919	-117.144987	944 Cesar East Chavez Parkway San Diego, CA	0.5	48
San Diego Fire Department Station 11	FD11	32.715621	-117.139975	945 25th Street San Diego, CA	1.4	190
San Diego Fire Department Station 12	FD12	32.704706	-117.087939	4964 Imperial Avenue San Diego, CA	2.8	170

Cabrillo National Monument (Reference Site)
Cabrillo National Monument was selected to represent reference conditions. Per the EPA's Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program (EPA, 2008), shoreline sites serve as good background/reference sampling sites. Cabrillo National Monument is designated as National Park Service (NPS) land and is primarily undeveloped. Cabrillo National Monument is located just west of downtown San Diego in Point Loma. It includes 160 acres of native habitat at the southernmost tip of the peninsula, which is bordered by the Pacific Ocean to the west, San Diego Bay to the east, and urban development to the north (NPS, 2012). Cabrillo National Monument is approximately 0.3 mile east of the Pacific Ocean Shoreline and is at an elevation of 365 feet. The surrounding area is primarily composed of open space/parks, and commercial and undeveloped land.

San Diego Fire Department Station 7
Fire Station 7 serves downtown San Diego and its surrounding areas. It is located in the Pueblo San Diego Watershed. The Fire Station building garages are two stories tall. There are no horizontal obstructions from the WNW direction. This Fire Station is less than 0.1 mile southwest of Interstate 5. The surrounding area primarily consists of commercial, single-family, and multi-family land uses. This site is the closest to the shoreline (0.5 mile from the San Diego Bay) and is at an elevation of 48 feet.

San Diego Fire Department Station 11
Fire Station 11 serves Golden Hill and its surrounding areas. It is located in the Switzer Creek Watershed. The Fire Station building and garages are two stories tall with roof access via the

tower on northwestern corner. There are no horizontal obstructions from the WNW direction. This Fire Station is approximately 0.1 mile north of California State Route 94 and 0.5 mile east of Interstate 5. The surrounding area is primarily composed of road, single-family, and multi-family land uses. This site is approximately 1.4 miles from the San Diego Bay shoreline and is at an elevation of 190 feet.

San Diego Fire Department Station 12

Fire Station 12 serves Lincoln Park/Valencia Park and its surrounding areas. It is located in the Chollas Creek Watershed. The Fire Station building is two stories tall and the garages are one story tall. All surrounding buildings are two stories high and do not obstruct wind flow from the WNW direction to the roofs. This surrounding area primarily consists of single-family, institutional, and road land uses. This site is the furthest away from the shoreline (2.8 miles from San Diego Bay) and is at an elevation of 170 feet.

8.3 Meteorological Parameter Monitoring

San Diego has a Mediterranean-type climate characterized by warm, dry summers and cool, mild winters. A weather station located at Cabrillo National Monument records weather data for the San Diego International Airport at Lindbergh Field, which is directly across San Diego Bay from the monument. The average annual temperature is 64 degrees and the average annual rainfall is 9.5 inches. Rainfall is concentrated in the winter, generally occurring from November to April, but the amount can change year to year, from 3.4 inches to 19.4 inches annually (NPS, 2012).

The impact of meteorological conditions will affect PAH transport rates and compound stability (EPA, 1983). Baseline local meteorological data within the Project Watersheds were obtained from the NWS for siting purposes. During monitoring, meteorological stations will be installed to monitor site-specific conditions during sample collection activities.

Meteorological stations measure *in situ* meteorological parameters at each station throughout the duration of sample collection. The Davis Instruments 6250 Vantage Vue weather station with WeatherLink data logger (Vantage Vue) records the following parameters:

- Wind speed
- Wind direction
- Temperature
- Humidity
- Dew point
- Barometric pressure
- Rainfall

The Vantage Vue weather station has a one-minute data logging interval. Wind speed records include peak and average speeds for the interval. The Vantage Vue sensor provides wind direction to 1-degree resolution and records the average direction. Data can be retrieved using a field computer. Detailed manufacturer specifications for the Vantage Vue weather station are provided in Appendix D.

This page intentionally left blank.

9.0 SAMPLE COLLECTION METHODS

9.1 Dry Deposition Sample Collection

Measuring dry deposition of SVOCs is difficult because dry deposition rates and mechanisms vary between the particle and gaseous phases (Lee and Nicholson, 1994). There is no standard technique for the direct measurement of the dry deposition of SVOCs. Available sampling techniques include collecting dry particles and gases on a depositional surface or measuring the amount of dry particles and gases in the air by using a high-volume air sampler and calculating a deposition rate (ambient air sampling). According to the EPA, ambient air sampling methods are considered to be more accurate (EPA, 2001), and will be the method used for this project.

Phase II served as a pilot study to verify that data were within an acceptable range of variability and that the sampling methods used are comparable to other commonly used aerial deposition measurement methods. The results of the pilot study verified that the sampling methodology used for the project is considered the best choice. These results are documented in the PAH Source Tracking Study- Preliminary Summary Report.

Phase III included five additional months of dry deposition sampling at all four sampling sites. To capture seasonal variability in dry deposition rates, sampling events occurred throughout the year (Table 9-1). The European Commission (EC) found that a 24-hour sampling technique for dry deposition sampling is advisable, for analytical reasons, to avoid sample degradation, interference, and losses. However, to calculate a monthly deposition rate, it is not necessary to collect samples continuously (i.e., every day) or to analyze each sample individually (EC & USEPA, 2005). An acceptable sampling strategy may be based on discontinuous but systematic sampling. A practical way of sampling is to take a 24-hour sample every three to six days.

Table 9-1. Phase III (2013–2014) Dry Deposition Sampling Schedule

Event	Sampling Dates	Sampling Period
Dry Deposition 1	August	Summer
Dry Deposition 2	September	Fall
Dry Deposition 3	January-February	Winter
Dry Deposition 4	April	Spring
Dry Deposition 5	May	Spring

To estimate the annual dry weather deposition rate, monitoring events were expected to consist of four sample collections spaced three to six days apart. Each sample was to be collected over a 24-hour period (referred to as “collection”). Each event was expected to comprise four 24-hour sample collections alternating between weekday (Wednesday–Thursday) and weekend (Saturday–Sunday) sample collections to represent all emission sources. The four collections per event were expected to be analyzed individually and mathematically composited for data analysis

to represent monthly periods. To capture variability in dry deposition rates, sampling events occurred in each season throughout the year.

Samples were planned to alternate between weekday (Wednesday–Thursday) and weekend (Saturday–Sunday) collections. During the first dry weather event, sampling was conducted at CNM1 from Thursday–Friday during collection 1 because a sample cartridge was broken and needed to be replaced. The sampler was started within 24 hours of the start time of the other samplers, so collection days overlapped and samples collected were representative of weekday emissions. Additionally, during collection 4 of the Dry Deposition 1 event, the sampler at FD07 was unplugged by fire station staff. The sampler was started within 24 hours of the start time of the other samplers, consistent with project methodology. Sampling during the winter 2014 event (Dry Deposition 3) was not performed in consecutive weeks because of Santa Ana conditions (i.e., the wind is not in the prevailing direction) from January 15–16 and 25-26, 2014 and was postponed again because of a storm that produced greater than 0.1 inch of rainfall on February 7, 2014. However, since samples were analyzed individually, the sample event is representative of winter deposition rates.

Sample totals for the dry deposition program during Phase III are summarized in Table 9-2.

Table 9-2. Dry Deposition Samples Collected

Sampling Season	Timeline	Matrix	Events	Sites	Total Number of Samples[(1)]	
					Individual 24-hour Sampling	72-hour Composite Sampling
Phase II (FY 2012) – Dry Deposition	April 2013–May 2013	Air	1	1	3	1
Phase III (FY 2013) – Dry Deposition	August 2013–May 2014	Air	5	4	80	NA

(1) Sample counts do not include QAQC samples

Phase IV includes one additional month of dry deposition sampling at all four project sampling sites. These samples will be taken in the fall 2016 and winter 2017 to capture additional samples during those seasons.

9.1.1 High-Volume Air Sampler (HVAS)

The equipment to be used for dry deposition sample collection follows the requirements of EPA Method TO-13A (EPA, 1999). PAH samples will be collected on precleaned and certified high-volume cartridges filled with a combination of polyurethane foam and XAD-2 resin (PUF/XAD-2®). The high volume PUF/XAD-2® sampler, shown in Figures 9-1 and 9-2, consists of a sample head inlet that contains the sampling media (quartz filter and PUF/XAD-2®), a high-volume air blower that allows a large quantity of air to be drawn through the sampling media, and flow controllers and timers to quantify the sampling flow rates (Tisch Environmental, 2012). The

aerosol phase fraction of the PAHs is collected physically on the quartz fiber filter and the vapor phase fraction of the semi-volatile compounds is adsorbed on the PUF/XAD-2® sampling media. Detailed specifications of the high volume air sampler are provided in Appendix E.

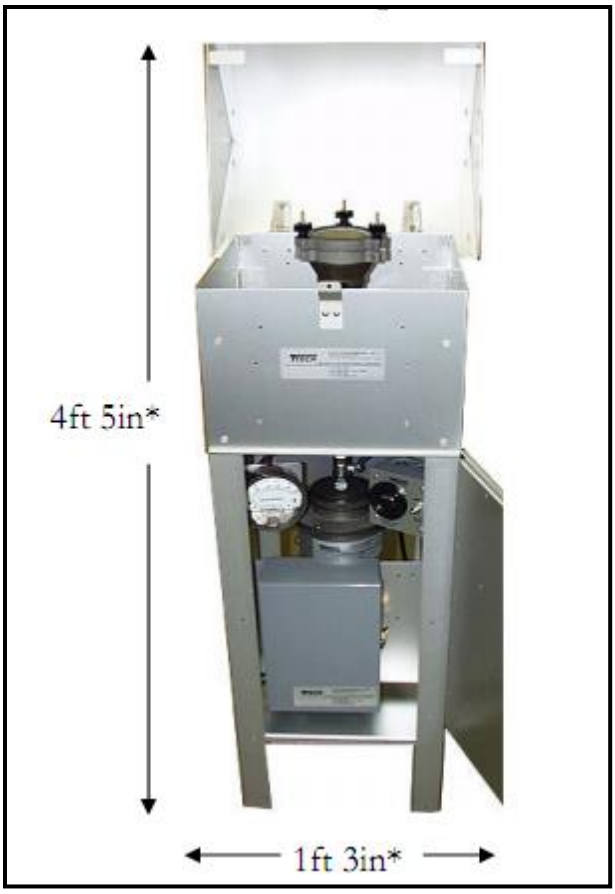


Figure 9-1. PUF/XAD-2® Sampler for Ambient Air

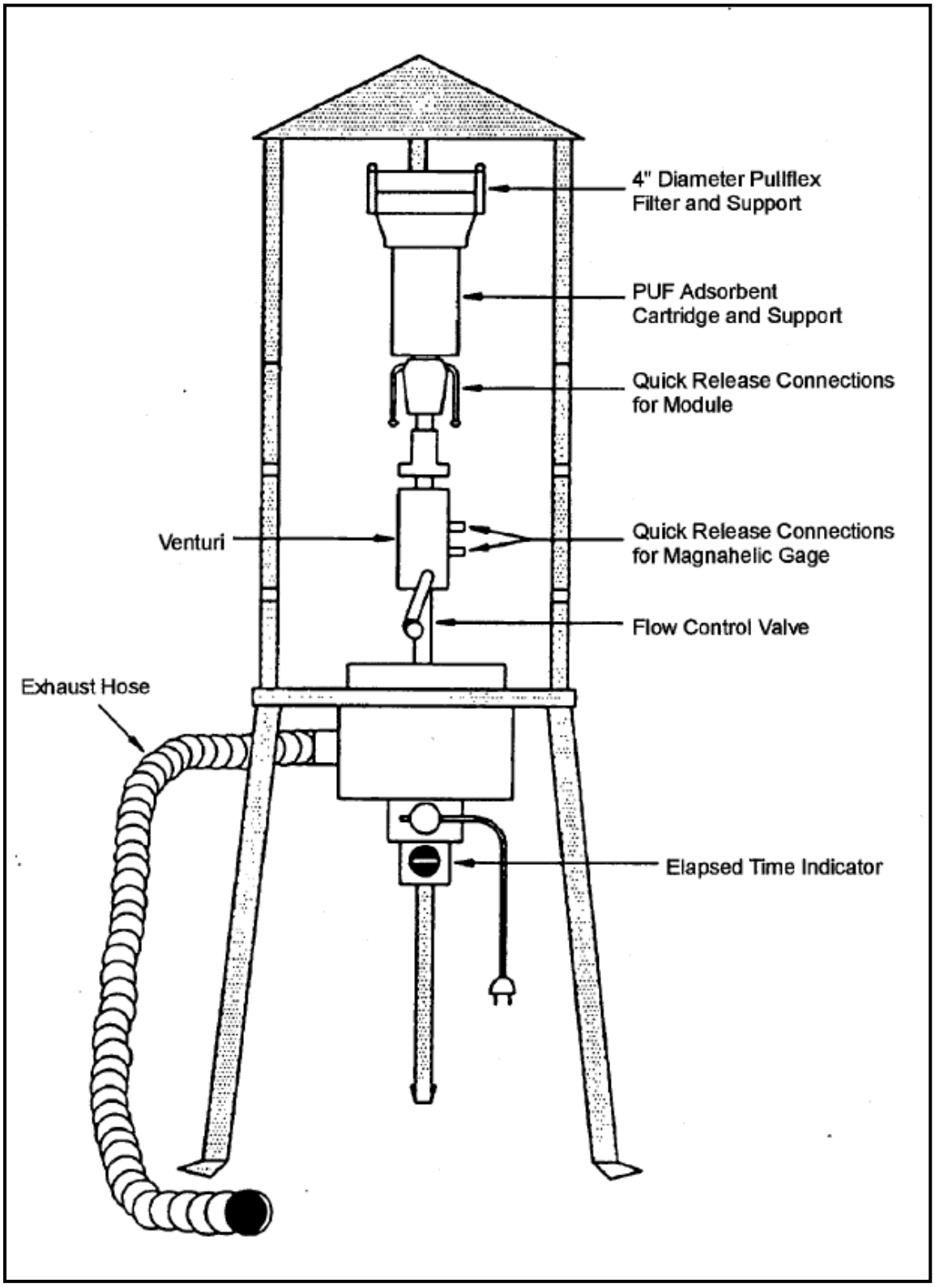


Figure 9-2. Sampler Configuration

This type of high-volume air sampler (HVAS) consists of a filter holder and a cylinder to hold the glass sorbent cartridge, as shown in Figure 9-3. The dual-chamber sampling module allows access to the upper filter media and the lower sorbent media.

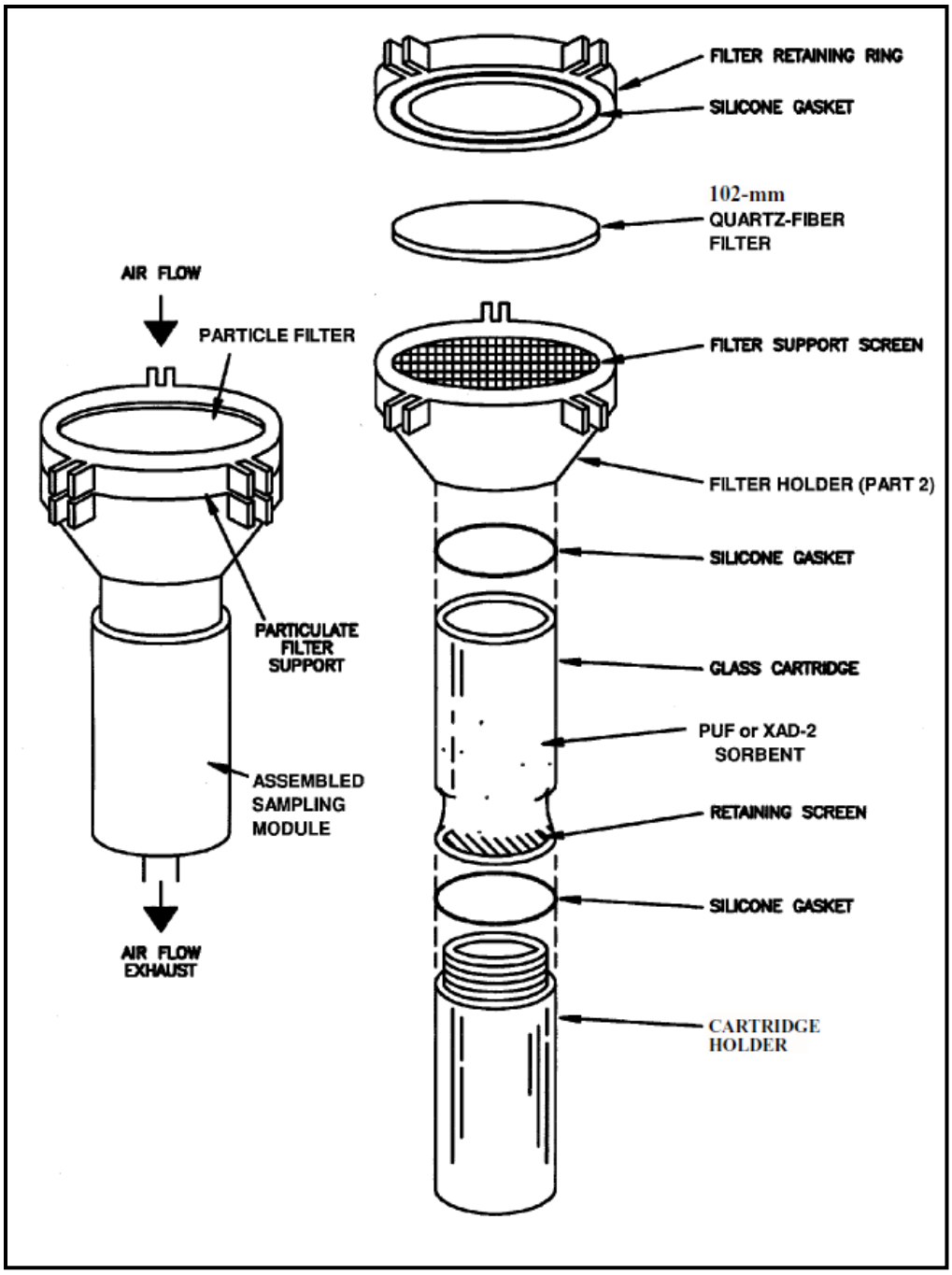


Figure 9-3. Filter and Cartridge Configuration

The sampler will pull ambient air through the filter/sorbent cartridge at a flow rate of approximately 8 standard cubic feet per minute (cfm) [0.225 standard cubic meter per minute (m^3/min)] to obtain a total sample volume of greater than 300 m^3 over a 24-hour period. An adequate volume of the air drawn through the sampling chain is imperative to achieve DQOs. If insufficient sample volume is collected, the sample must be concentrated at the laboratory for analysis. Therefore, sample volume determines the final reporting limits (i.e., increased sample volume lowers the final reporting limit) (Air Toxics, 2012). The equation to determine the minimum flow rate with a set sampling duration is:

Equation 9-1: $$Minimum\ Flow\ Rate\ \left(\frac{L}{min}\right) = \frac{Minimum\ Sample\ Volume\ (L)}{Monitoring\ Duration\ (min)}$$

9.1.2 Quartz Filter and PUF/XAD-2® Adsorbent Cartridge

Naphthalene, acenaphthylene, and acenaphthene possess relatively high vapor pressures and might not be efficiently trapped when using PUF as the sorbent; therefore, a combination PUF/XAD-2® sorbent, shown in Figure 9-4, will be used. In general, XAD-2® resin has higher collection efficiency for both volatile and reactive PAHs (EPA, 1999).

The quartz fiber filters and sorbent cartridges are provided precleaned by the laboratory. All filters and sorbent samples will be submitted for PAH analysis. The cartridges with PUF/XAD-2® sorbent will be prepared for all the sites from the same batches by a rigorous pre-extraction procedure. Cartridges will also be prepared to serve as field and laboratory blanks. The filter and PUFs will be placed in the HVAS using clean stainless-steel tongs. After sample collection, the filters and cartridges will be exposed to the laboratory environment for the minimum amount of time possible to prevent sample degradation.

The samples will be extracted in solvent, and then will be analyzed by gas chromatography (GC)/mass spectrometry (MS) to estimate the mass of each PAH present. The measured result will be presented as a concentration per air volume in micrograms per cubic meter (ug/m^3). The concentration of each PAH will be calculated using the analytical result and the total volume of air that has been drawn through each filter.

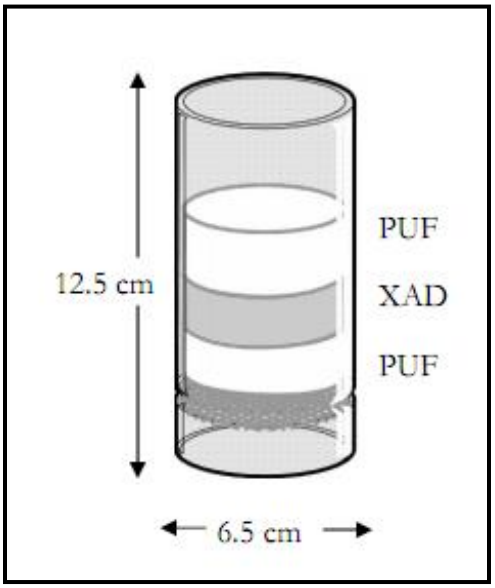


Figure 9-4. PUF/XAD-2® Cartridge

9.1.3 High-Volume Air Sampler Preparation and Maintenance

The sampling equipment will be prepared just prior to a sampling event. Preparation involves disassembling, inspecting, and cleaning all sampler parts. In addition, if the sampler is moved between sites, the modules will be fully disassembled and all parts thoroughly cleaned.

Preventive maintenance will be carried out when necessary. During each visit, the sampler, sampler platform, and auxiliary pieces of equipment will be checked for corrosion or breakages. A number of spare parts are routinely taken to each site and preventive or remedial maintenance carried out when necessary.

9.1.4 Dry Deposition Sampling Preparation and Logistics

Dry depositional sampling will be implemented at the sampling sites presented in Section 8. Sampling will include the following tasks:

- Installation of selected sampling equipment (includes office equipment preparation and infield installation). The sample collectors will be placed in areas away from horizontal obstructions such as buildings, overhanging trees and shrubbery, and away from any obstacle to air flow that may impede sample collection. The National Atmospheric Deposition Program (NADP) Instruction Manual on Site Selection and Installation (NADP, 2011) provides guidelines on sampler placement. These guidelines will be used by field crews when installing sampling equipment.
- Collection of the sample matrices from the samplers and transfer of the samples to the selected laboratory using the appropriate methods.

- Demobilization of the sampling equipment and transfer back to the rental company.
- Coordination with the analytical laboratory to ensure that sample results are received before the Task Order end date.
- Ongoing QA/QC of the analytical data.

EPA Method TO13-A is the applicable sampling procedure for the analysis of PAHs in ambient air (high volume) for a 24-hour sampling period. Because of the expectation of relatively low levels of PAHs in ambient air, this method utilizes a filter and sorbent cartridge to provide the most efficient collection of common PAHs consisting of three or more rings. The dry deposition sampling equipment described in this section was selected to collect air samples in accordance with EPA Method TO-13A. The required equipment includes the following:

- HVAS
- Quartz fiber filter (102 millimeter [mm] binderless quartz microfiber filter)
- Polyurethane foam and XAD-2 resin (PUF/XAD-2®) plug (high volume)
- Glass sample cartridge (for PUF/XAD-2®)
- Airflow calibrator
- Gloves

Prior to sampling, the HVAS will be calibrated utilizing a calibrated orifice transfer standard to achieve the desired flow rate. Airflow rate is measured through a flow venturi utilizing a 0-inch to 100-inch Magnehelic differential pressure gauge that indicates positive, negative, and differential measurements. Periodic calibration is required to maintain flow rate accuracy. Calibration method details are provided in Appendix E. The sampler will be calibrated:

- During the initial installation
- Before and after each sampling event
- Whenever any audit point deviates from the calibration curve by more than 7 percent
- After major repairs or maintenance

Once calibrated, the cartridge will be placed into the sampler. A zero reading of the sampler Magnehelic gauge, all weather parameters, and the elapsed time meter setting on the Field Data Sheet will be recorded. Field crews will attempt to record the Magnehelic reading every 6 hours during the sampling period per EPA Method TO-13A if access allows.

When handling the cartridge, field crews will wear gloves to remove the clean glass sorbent from its shipping container. If shipped with caps, the caps will be removed and stored in the sample container to be reused after the sample has been collected. The cartridge will be inserted into the lower chamber and then the lower chamber will be replaced. After the cartridge has been placed in the sampler, a clean conditioned quartz fiber filter will be placed in the filter holder ring.

At the completion of the sampling period, the sampler will be turned off. The sampling head containing the filter and sorbent cartridge will be removed, and the protective plates will be placed over the filter to protect the cartridge. The PUF cartridge will be removed from the lower module chamber and laid on the aluminum foil in which the sample was originally wrapped. The quartz fiber filter will be removed from the upper chamber using clean Teflon-tipped forceps. The filter will be folded in half twice with the sample side inward and placed in the glass cartridge atop the PUF. The combined samples will be wrapped in the original hexane-rinsed aluminum foil with the caps replaced and shipped to the laboratory in their original aluminum shipping container. Samples will be shipped under blue ice or dry ice and protected from ultraviolet (UV) light to prevent photo-decomposition of the sample. The sample will be stored at 4°C until analysis (if over 24 hours from collection).

The final flow volume that was sampled will be verified using the calibration orifice as described in Method TO-13A, Section 11.3.2 (EPA, 1999). If the measurement indicates that the flow rate may have deviated from the preprogrammed setting at the beginning of the sampling period by more than 10 percent, the sample will be flagged as suspect.

12.1.2 Dry Weather Tracking and Event Selection Criteria

Prior to any dry deposition sampling event, wind patterns will be monitored to ensure that the dominant wind pattern is from the WNW direction. Any changes in the prevailing wind pattern will be noted. Field crews will ensure that sampling equipment is faced in the direction of oncoming winds.

Santa Ana winds will be tracked and sampling schedules will be adjusted accordingly to avoid sampling during these conditions. Santa Ana winds are strong, extremely dry offshore winds that affect southern California during fall and winter. The winds manifest as a dry northeasterly wind and are infamous for exacerbating regional wildfires.

9.2 Wet Deposition Sampling

Collecting and analyzing precipitation samples is the simplest approach for determining PAH concentrations and deriving a bulk deposition flux. Four storm events (with predicted rainfall greater than or equal to 0.1 inch) were monitored throughout the 2013–2014 wet season (October 1 through April 30) during Phase III (Table 9-3). Storms were selected per the requirements listed in Section 9.2.2.1. Two additional storms will be monitored during Phase IV of the project.

Table 9-3. Wet Deposition Sampling Summary per Methodology

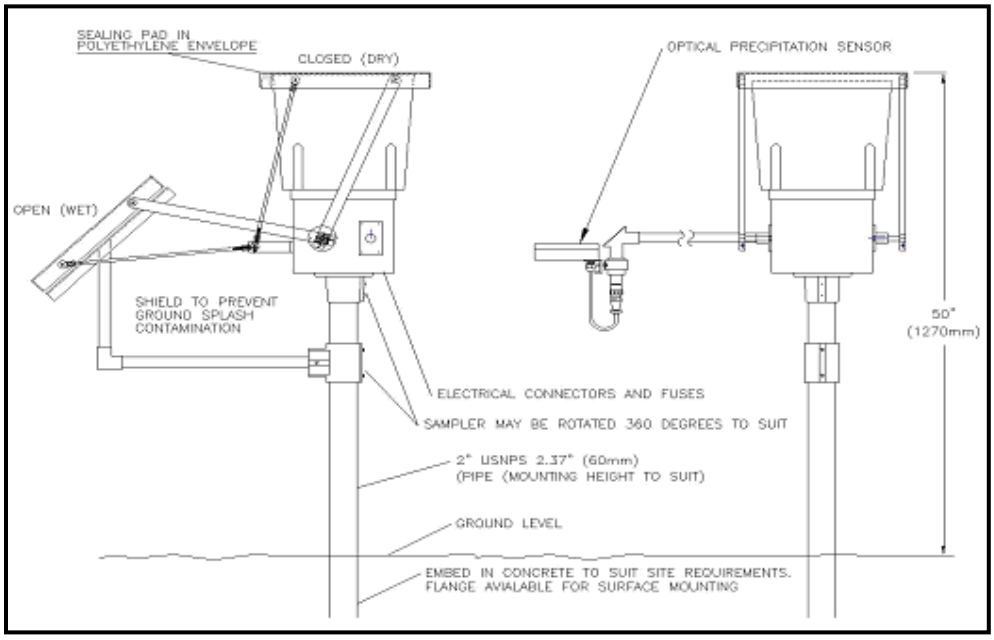
Sampling Season	Timeline	Matrix	Events	Sites	Total Number of Samples(1)
Phase III (FY 2013) – Wet Deposition	October 2013–April 2014	Water	4	4	16

(1) Sample counts do not include QAQC samples

Phase IV (FY 2017) includes two additional wet deposition sampling events at all four project sampling sites.

9.2.1 Wet Deposition Sampler

Wet deposition sampling will be conducted using an N-CON ADS/NTN Atmospheric Deposition Sampler. The sampler has an infrared, optical precipitation sensor that detects the onset of precipitation and uncovers the sample container within five drops. When precipitation ends, the cover returns to the sample container to minimize exposure to dry deposition. The sensor also detects drizzle and heavy fog, which may carry significant amounts of deposition. The compression seal on the underside of the cover prevents leakage of dry deposition into the container and sample evaporation. When the cover is open, the underside is protected from ground splash by a shield that covers, but does not contact, the seal, as shown in Figure 9-5. The ADS/NTN runs on either alternating current (AC) power or direct current (DC) power. The sampler will be installed prior to the beginning of the wet season and demobilized after the end of the season. Detailed manufacturer specifications for the N-CON ADS/NTN Atmospheric Deposition Sampler are provided in Appendix F.



Source: N-Con, 2012 http://www.n-con.com/Products/ads.html

Figure 9-5. Wet Deposition Sampler

Like the dry deposition sampler, the wet deposition sample collector will be placed in an area away from horizontal obstructions that may impede sample collection and according to the NADP Instruction Manual on Site Selection and Installation.

For wet deposition samples, precipitation is collected directly into a sampling container. PAHs are extracted from the aqueous phase and then analyzed by GC/MS. Simple measurements of wet deposition allow the determination of concentrations in precipitation and the derivation of a bulk deposition flux.

9.2.2 Wet Deposition Sampling Preparation and Logistics

Wet deposition sampling will be implemented at the sampling sites presented in Section 8. Each sampling event will last the duration of the storm event. Sampling will include the following tasks:

- Weather tracking
- Preparation of sampling equipment (includes office equipment preparation and infield installation of bottles
- Activation of samplers at each sampling site before precipitation falls
- Monitoring of weather stations and equipment
- Collection and transfer of the samples to the selected laboratory
- Demobilization of the sampling equipment and transfer back to the office
- Coordination with analytical laboratory to ensure that sample results are received before the Task Order end date
- Ongoing QA/QC of the analytical data

The necessary equipment will be loaded into the appropriate vehicles early in the storm preparation sequence. During the sampling season, field crews will utilize the safety equipment, personal rain gear, and other site maintenance equipment. Equipment needed for wet deposition sampling includes:

- N-CON ADS/NTN Atmospheric Deposition Sampler
- Teflon-lined bucket
- Meteorological station
- Safety equipment
- Gloves
- Personal rain gear/storm kits
- Vehicles equipped with mobile communication and highway safety equipment

12.1.2 Wet Weather Tracking and Storm Selection Criteria

Weather will be tracked for sampling purposes from October 1 to April 30. Throughout the storm season, several sources for weather information will be monitored continuously, such as Internet web pages for the NWS and local alert systems.

The following criteria will be used to determine whether mobilization will occur for an impending storm event:

- Storms must be forecast to produce at least 0.1 inch of rainfall.
- The probability of precipitation occurring must be greater than 60 percent.
- Storm events must be preceded by at least 72 hours of dry conditions (less than 0.10 inch of precipitation).

The City of San Diego Program Manager may modify the criteria on a storm-by-storm basis.

10.0 SAMPLE HANDLING AND CUSTODY

10.1 Laboratory Selection

Eurofins Air Toxics, located in Folsom, California, will provide general laboratory services for the dry deposition component of this project, including analytical air testing for all PAHs. Eurofins Air Toxics is an environmental laboratory accredited by the National Environmental Laboratory Accreditation Program (NELAP) and Department of Defense (DoD-ELAP). Eurofins Air Toxics is certified by the following states: Arizona Department of Health (DOH), California Department of Health Services (DHS), Florida DOH, New York DOH, Oregon Department of Environmental Quality, Texas Commission on Environmental Quality, Utah DOH, and Washington Department of Energy. Contact information is provided below:

Eurofins Air Toxics Inc.
180 Blue Ravine Road, Suite B
Folsom, CA 95360
916-985-1000 (office)
916-985-1020 (fax)

Physis Environmental Laboratories, Inc., located in Anaheim, California, will provide laboratory services for the wet deposition component of this project, including analytical testing for PAHs in water samples. Contact information is provided below:

Physis Environmental Laboratories
1904 East Wright Circle
Anaheim, California 92806
Office: (714) 602-5320
Fax: (714) 602-5321

10.2 Sample Containers, Sample Volumes, Preservation Requirements, and Holding Times

All sample containers, preservation methods, and holding times were confirmed by the laboratories and are presented in Table 10-1 and Table 10-2 for dry and wet deposition analyses, respectively. The laboratories will provide appropriate sample containers, including filters and PUF cartridges.

This page intentionally left blank.

Table 10-1. Dry Deposition Air Analysis Holding Times, Sample Volumes, Containers, and Preservation Recommendations

Analyte	Container Type	Minimum Sample Volume	Preservation	Holding Time[(a)]
2-Chloronaphthalene	PUF/XAD-2® Cartridge and Quartz Filter	300 m^3	4°C, keep in dark conditions to limit exposure to light	7 days/40 days[(c)]
2-Methylnaphthalene				
Acenaphthylene				
Acenaphthene				
Anthracene				
Benzo(a)anthracene				
Benzo(a)pyrene				
Benzo(b)fluoranthene				
Benzo(e)pyrene				
Benzo(g,h,i)perylene				
Benzo(k)fluoranthene				
Chrysene				
Coronene[(b)]				
Dibenz(a,h)anthracene				
Fluoranthene				
Fluorene				
Indeno(1,2,3-c,d)pyrene				
Naphthalene				
Perylene[(b)]				
Phenanthrene				
Pyrene				

Notes:
(a) Holding time includes field crew holding times and laboratory staff holding times.
(b) Compounds are not included on laboratory's NELAP accreditation and are not calibrated using 1o-13A SIM.
(c) The first time period represents the holding time for preparation, preservation, or extraction required by the method and the second time period represents the holding time for analysis given that the appropriate preparation was conducted.

Table 10-2. Wet Deposition Water Analysis Holding Times, Sample Volumes, Containers, and Preservation Recommendations

Analyte	Container Type	Minimum Sample Volume	Preservation	Holding Time[(a)]
1-Methylnaphthalene	Amber Glass	2 x 1 liter	4°C, keep in dark conditions to limit exposure to light	7 days/40 days[(b)]
1-Methylphenanthrene				
2,3,5-Trimethylnaphthalene				
2,6-Dimethylnaphthalene				
2-Methylnaphthalene				
Acenaphthene				
Acenaphthylene				
Anthracene				
Benz(a)anthracene				
Benzo(a)pyrene				
Benzo(b)fluoranthene				
Benzo(e)pyrene				
Benzo(g,h,i)perylene				
Benzo(k)fluoranthene				
Biphenyl				
Chrysene				
Dibenz(a,h)anthracene				
Dibenzothiophene				
Fluoranthene				
Fluorene				
Indeno(1,2,3-c,d)pyrene				
Naphthalene				
Perylene				
Phenanthrene				
Pyrene				

Notes:
(a) Holding time includes field crew holding times and laboratory staff holding times.
(b) The first time period represents the holding time for preparation, preservation, or extraction required by the method and the second time period represents the holding time for analysis given that the appropriate preparation was conducted.

10.3 Sample Labeling and Chain of Custody

Sample containers will be prelabeled, to the extent possible, before each sampling event. Prelabeling sample containers simplifies field activities and leaves only date, time, sample identification (ID), and sampling personnel names to be filled out in the field. Each sample collected will be labeled with the following information:

- Project Name
- Event Number
- Date and Time
- Site ID Number
- Sample Type (dry deposition, wet deposition)
- Collected by
- Analysis

Field samples, field blanks, and field duplicate samples (wet deposition only) will be labeled as described below, recorded on the COC form, and then transported to the analytical laboratory.

Each sample collected will receive a unique alphanumeric code (Sample ID Number) for tracking. This code will be standard for all samples and will contain information as it relates to the site, event, and type of sample. The required nomenclature for Sample identification ID Numbers, applicable to all samples, is listed as follows, along with examples in Table 10-3:

- Sample Type
  - DD = Dry deposition sample (air)
  - WD = Wet deposition sample (water)
- Site ID
- Sample Date/Time (at completion of event)
  - YYMMDDHHMM=Date (year/month/day) and Time (hour/minutes [24-hour])
- Sample Type
  - 00 = Primary Sample
  - FB = Field Blank

Table 10-3. Example Sample Identification Numbers

Sample ID	Sample Type	Site ID	Event Type/ Event Number	Sample Type
DW-CNM-1304011200-00	Dry Deposition	CNM	April 1, 2013 12:00	Primary Sample
WW-FD11-1310311500-FB	Wet Deposition	FD11	October 31, 2013 15:00	Field Blank

COC forms will be preprinted along with the sample labels. COC forms will contain the same data as the labels, in some cases with greater detail. COC forms will be completed in the field with dates, times, and sample team names, and will be cross-checked with the sample container labels to ensure they match.

10.3.1 Dry Deposition Samples

After a dry deposition sample has been collected and the sample label is completed, the samples will be immediately packaged for shipment and placed on ice in a cooler for transportation to the laboratory. Samples will be removed from the sampling chambers, and shipped to the laboratory in their original aluminum shipping container. For transport to the laboratory, the following process will be used:

- Samples will be packed with blue ice or dry ice for shipment to ensure a sample temperature of 4°C (± 2°C).
- Exposure to heat, ozone, nitrogen dioxide (NO_2), and UV light will be avoided to prevent sample degradation during transport.
- If the time elapsed between sample collection and receipt at the laboratory exceeds 24 hours, samples will be refrigerated at less than or equal to 4°C.

Transport of the samples will be coordinated by the Field Sampling Manager to make sure that samples are processed and analyzed within the proper holding times. For 24-hour samples, the start of the holding time is considered to be the end of the 24-hour sampling period. COC forms will be reviewed by personnel at the receiving laboratory to verify that all samples are accounted for and received within the holding times. Furthermore, to avoid photodecomposition, where possible, the laboratory will use incandescent or UV-shielded fluorescent lighting during analysis.

10.3.2 Wet Deposition Samples

After a wet deposition sample has been collected, the sample label will be filled out, and the samples will be immediately packaged for shipment and placed on ice in a cooler for transportation to the laboratory. During transport to the laboratory, samples should be packed with blue ice or dry ice for shipment to ensure a sample temperature of 4°C (± 2°C). To prevent sample degradation during transport, exposure to heat, ozone, NO_2, and UV light will be avoided. If the time elapsed between sample collection and receipt at the laboratory exceeds 24 hours, samples will be refrigerated at less than or equal to 4°C to avoid sample degradation.

Transport of the samples will be coordinated by the Field Sampling Manager to make sure samples are processed and analyzed within the proper holding times. The sample time is considered to be the end sampling period when the last sample volume is collected. COC forms will be reviewed by personnel at the receiving laboratory to verify that all samples are accounted for and are received within the holding times. Furthermore, to avoid photodecomposition, where possible, the laboratory will use incandescent or UV-shielded fluorescent lighting during analysis.

This page intentionally left blank.

11.0 ANALYTICAL METHODS

11.1 Chemical Analytes

Separate analytical methods will be used for dry and wet deposition chemical analyses. The EPA's ambient air analysis Method TO-13A will be used for dry deposition analysis, and EPA Method 625 will be used for wet deposition analysis. Both methods include the 16 EPA priority pollutant PAHs. However, EPA Method 625 includes a more extensive list than the constituents included in EPA Method TO-13A. EPA Method TO-13A is the closest match to EPA Method 625 and includes the common list of PAHs that are analyzed in ambient air sampling protocols. Additional information on each analytical method is presented in this section.

11.1.1 Dry Deposition Analysis

Method TO-13A, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Determination of PAHs in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS),* will be used to measure ambient PAH concentrations at the sampling sites presented in Section 8 (EPA, 1999). Method TO-13A is an analysis method used on samples collected on quartz filters and sorbent cartridges. Subsequent analysis of PAHs is done by GC/MS detection. Detailed information on GC/MS analysis under Method TO-13A is included in Appendix G.

The list of dry deposition constituents that will be evaluated and their target reporting limits (RLs) are presented in Table 11-1. Benzo(e)pyrene, coronene, and perylene are special compounds in Method TO-13A. They have been added to the list of constituents because they are analytes included under EPA Method 625. The dry deposition analytical methods from Method TO-13A are modifications of EPA Methods 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*. GC/MS is a highly sensitive and specific method for gas detection and is the preferred analytical method for its sensitivity and selectivity, as well as its ability to analyze complex samples.

Table 11-1. Dry Deposition Constituents and Reporting Limits

Analytes	Method	Units	RL
2-Chloronaphthalene	Method TO-13A GC/MS Selected Ion Monitoring (SIM)	µg	0.1
2-Methylnaphthalene			
Acenaphthylene			
Acenaphthene			
Anthracene			
Benzo(a)anthracene			
Benzo(a)pyrene			
Benzo(b)fluoranthene			
Benzo(e)pyrene			
Benzo(g,h,i)perylene			
Benzo(k)fluoranthene			
Chrysene			
Dibenz(a,h)anthracene			
Fluoranthene			
Fluorene			
Indeno(1,2,3-c,d)pyrene			
Naphthalene			
Phenanthrene			
Pyrene			

Notes:
µg = micrograms; GC/MS = gas chromatography/mass spectrometry; RL = reporting limit

Per EPA Method TO-13A, after sample collection, sample media is extracted in the laboratory using a Soxhlet extraction or Pressurized Fluid Extraction (PFE). The concentrated extracts are analyzed for PAHs using a quadrupole GC/MS in full scan or Selected Ion Monitoring (SIM) mode. Analysis Requirements from Method TO-13A are provided in Table 11-2.

Table 11-2. Analysis Requirements from EPA Method TO-13A

Parameter	EPA Method TO-13A
Extraction	Soxhlet for 18 hours in 10% diethyl ether in hexane. Extraction solvent for XAD extraction solvent is listed as methyl chloride. (PUF extraction solvent is listed is hexane.)
Sample Medium	Whatman Quartz Filter PUF Cartridge, High Volume
Holding Times	Store at 4°C and extract in 7 days. Analyze within 40 days of extraction.

Notes:
PUF = polyurethane foam

Air Toxics performs a modified version of this method. The method modifications, standard target analyte list, limit of quantitation, QC criteria, and QC summary are in Table 11-3.

Table 11-3. Summary of Method Modifications for EPA Method TO-13A

Requirements	EPA Method TO-13A	Air Toxics Modifications
Extraction Solvent	10% diethyl ether in hexane for PUF; methylene chloride for XAD sorbent. Final extract in hexane	Methylene chloride for PUF/XAD-2® cartridge and XAD sorbent. Final extract in methylene chloride.
Glassware Cleaning	Muffle furnace is utilized	Solvent cleaning procedure is used.
Extraction Technique	Soxhlet extraction	Soxhlet extraction or PFE
Reporting List	19 PAHs[(a)]	See Table 11-1[(b)]
Calibration Range	0.1-2.5 µg/mL in hexane	1.0-160 µg/mL in methylene chloride for quad or 0.1-40 µg/mL for SIM
Method Blank	< Method Detection Limit	< Reporting Limit
Matrix Spike Detection	Full scan	SIM
Surrogate Recoveries	60-120 percent	50-150 percent for field surrogates Fluoranthene-d10 and Benzo(a)pyrene-d12

Notes:
(a) Benzo(e)pyrene, coronene, and perylene are nonstandard (also known as special compounds) compounds by EPA Method TO-13A and are not included in the project analyses.
(b) 2-Methylnaphthalene and 2-chloronaphthalene are not included in EPA Method TO-13A but are included in the analyte list
µg/mL = micrograms per milliliter; PFE = pressurized fluid extraction; PUF = polyurethane foam; SIM = selected ion monitoring

11.1.2 Wet Deposition Analysis

PAH concentrations in wet deposition samples will be determined using EPA Method 625, which is also a GC/MS method. EPA Method 625 utilizes a liquid-liquid extraction technique followed by GC/MS analysis. A total of 25 specific PAH compounds are included in the analytical suite. They are listed in Table 11-4 along with their respective target RLs. Detailed information on the analysis under EPA Method 625 is included in Appendix H.

Table 11-4. Wet Deposition Constituents and Reporting Limits

Analytes	Method	Units	RL
1-Methylnaphthalene	EPA Method 625 GC/MS	ng/L	5
1-Methylphenanthrene			
2,3,5-Trimethylnaphthalene			
2,6-Dimethylnaphthalene			
2-Methylnaphthalene			
Acenaphthene			
Acenaphthylene			
Anthracene			
Benz(a)anthracene			
Benzo(a)pyrene			
Benzo(b)fluoranthene			
Benzo(e)pyrene			
Benzo(g,h,i)perylene			
Benzo(k)fluoranthene			
Biphenyl			
Chrysene			
Dibenz(a,h)anthracene			
Dibenzothiophene			
Fluoranthene			
Fluorene			
Indeno(1,2,3-c,d)pyrene			
Naphthalene			
Perylene			
Phenanthrene			
Pyrene			

Notes:
GC/MS = gas chromatography/mass spectrometry; ng/L = nanograms per liter; RL = reporting limit

12.0 QUALITY CONTROL

This section addresses QA/QC activities associated with both field sampling and laboratory analyses. The field QA/QC samples are used to evaluate potential contamination and sampling errors introduced prior to submittal of the samples to the analytical laboratory. Laboratory QA/QC samples provide information to assess potential laboratory contamination, analytical precision, and accuracy. If any QA/QC standards are not met, the appropriate corrective actions will be taken in accordance with Section 15 of this document and the laboratories' QA Manuals. The Project Manager is responsible for making decisions on corrective actions pertaining to laboratory analysis. If issues are identified, the Amec Foster Wheeler Project Manager and the Laboratory Project Manager will be notified immediately, with the issue documented and corrective action made.

12.1 Field Quality Assurance/Quality Control

The main types of field QA/QC samples that will be utilized are field blanks. Field blanks verify that field conditions and field sampling activities are non-contaminating. Field blanks are submitted blind to the laboratory. During wet deposition sampling, the analytical laboratory will be instructed to run a field duplicate for 10 percent of the time. Twice as much of the minimum sample volume must be collected in order to run the field duplicate. The frequency of the Field Quality Assurance/Quality Control samples is presented in Table 12-1.

Table 12-1. Field Quality Control Sample Frequency

QA/QC Sample Type	Minimum Sampling Frequency and DQOs
Field Blank (FB) – Dry Deposition	1 per collection event (6 total)
Field Blank (FB) – Wet Deposition	10% of sample count (2 total)
Field Duplicate (FD) – Wet Deposition	10% of sample count as volume allows

12.1.2 Dry Deposition Field Blanks

For dry deposition, QA/QC samples will be collected in accordance with EPA Method TO-13A. During each sampling episode, at least one field blank will be collected and submitted to the analytical laboratory for analysis in conjunction with primary samples. The field blank is treated exactly as the sample except that air is not drawn through the filter/sorbent cartridge assembly and submitted to the analytical laboratory for analysis.

To determine whether the batch is suitable for field use, at least one cartridge from each batch, or equipment blank, prepared using the method described EPA Method TO-13A must be analyzed and must have detections less than or equal to the detection limit to meet acceptance criteria. Cartridges are certified clean if they meet the general guidelines of:

- **Naphthalene:** < 500 nanograms (ng)/cartridge

- **Other PAHs:** <200 ng total/cartridge

Because of the persistence of naphthalene, cartridges are considered clean if naphthalene is detected at less than five times the concentration of the lowest calibration standard.

12.1.2 Wet Deposition Field Blanks

For wet deposition water sample field blanks, sample bottles will be filled with reagent-grade, analyte-free deionized water in the field during a sampling event. During wet deposition sampling, the analytical laboratory will be instructed to run a field duplicate for 25 percent of the time. Twice as much of the minimum sample volume is needed to run a duplicate; so duplicates are dependent on the volume collected.

12.2 Laboratory Quality Assurance/ Quality Control

Laboratories must demonstrate that data quality meets the method-specific performance criteria through ongoing analysis of standards, spiked samples, blanks and other measures to evaluate and document data quality. Analytical QA for this program includes the following:

- Employment of analytical chemists trained in the procedures to be followed
- Adherence to documented procedures, EPA approved methods, and written SOPs
- Frequent and proper calibration and maintenance of analytical instruments
- Use of QC samples, internal standards, and surrogates
- Complete documentation of sample tracking and analysis

Internal laboratory QC checks include the use of laboratory replicates, method blanks, blank spikes, and MSs/MSDs, as follows:

- **Laboratory Duplicate (LD)** – A sample is split by the laboratory into two portions and each portion is analyzed. Once analyzed, the results are evaluated by calculating the RPD between the two sets of results. This serves as a measure of the reproducibility, or precision, of the sample analysis. Typically, replicate results should fall within an accepted RPD range, depending upon the analysis.
- **Laboratory Method Blanks (MB)** – A method blank is an analysis of a known clean sample matrix that has been subjected to the same complete analytical procedure as the field sample to determine whether potential contamination has been introduced during processing. The laboratory method blank is analyzed along with each batch of less than or equal to 20 samples through the entire extraction, concentration, and analysis process. Blank analysis results are evaluated by checking against the RL for that analyte. Results obtained should be less than the RL for each analyte.
- **Laboratory Control Sample (LCS)** –The laboratory control sample procedure involves spiking known amounts of the analyte of interest into a known, clean, sample matrix to

assess the possible matrix effects on spike recoveries. The recovery of the spike is a measure of the accuracy of the analysis. High or low recoveries of the analytes in the matrix spikes may be caused by interferences in the sample. Laboratory control samples assess these possible matrix effects since the LCS is known to be free from interferences. The spike recoveries are compared against accepted and known method dependent acceptance limits. Results outside these limits are subject to corrective action.

- **MSs/MSDs** – MSs/MSDs involve adding a known amount of the chemical(s) of interest to one of the actual samples being analyzed. One sample is split into three separate portions. One portion is analyzed to determine the concentration of the analyte in question in an unspiked state. The other two portions are spiked with a known concentration of the analytes of interest. The recovery of the spike, after accounting for the concentration of the analyte in the original sample, is a measure of the accuracy of the analysis. An additional precision measure is made by calculating the RPD of the duplicate spike recoveries. Both the RPD values and spike recoveries are compared against accepted and known method dependent acceptance limits. Results outside these limits are subject to corrective action.

The frequency of the Eurofins laboratory QA/QC samples is presented in Table 12-2.

Table 12-2. Laboratory Quality Control Sample Frequency

QA/QC Sample Type	Minimum Sampling Frequency and DQOs
Method Blank (MB)	With each sample batch of up to 20 samples. Less than RL.
Laboratory Control Spike (LCS)	With each sample batch of up to 20 samples. 60–120% recovery.
Laboratory Duplicate (LD)	With each sample batch of up to 20 samples.

This page intentionally left blank.

13.0 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Laboratory instruments are inspected and maintained in accordance with lab SOPs. These SOPs have been reviewed by each respective Laboratory Director or Quality Office and found to be compliant. Each instrument has a technician assigned for testing, inspection, and maintenance. Any glassware, sample containers, and collection equipment sent by a laboratory will be inspected prior to use. A logbook is used to track the maintenance. These SOPs can be provided upon request.

Field instrumentation is calibrated before each field event and calibration logs or notes are maintained in the field notebook. The calibration, and inspections that occur during calibration, serve as the regular testing and maintenance of the equipment.

This page intentionally left blank.

14.0 INSTRUMENT/ EQUIPMENT CALIBRATION AND FREQUENCY

14.1 Laboratory Instrumentation

Laboratory equipment is calibrated on the basis of manufacturer recommendations and accepted laboratory protocols. Laboratories maintain calibration practices as part of their method SOPs maintained by their Laboratory Directors and QA Officers, and these SOPs can be provided upon request.

14.2 Field Instrument/Equipment

Calibration for the HVAS will be conducted according to the manufacturer's specifications (Appendix F) and EPA Method TO-13A (Appendix H) at the following times:

- During the initial installation
- Before and after each sampling event
- After major repairs or maintenance

The high-volume air sampler will be calibrated in the field using a calibrated orifice flow rate transfer standard. Results that deviate more than 7 percent from the known flow rate and do not maintain an adjusted offset will be documented and will require the equipment to be replaced or repaired. Calibration measurements will be recorded and a calibration log will be maintained. Calibration frequencies of field sampling equipment are provided in Table 14-1.

Table 14-1. Calibration of Field Sampling Equipment and Sampling Instruments

Equipment	Calibration Description	Responsible Person	Frequency	SOP Reference
TE-1000 High-Volume Air Sampler	Orifice Flow Rate Transfer Standard	Amec Foster Wheeler Technical Staff	Prior to each event	TE-1000 Manual and EPA Method TO-13A
Davis Instruments Vantage Vue	Maintenance and Troubleshooting*	Amec Foster Wheeler Technical Staff	Annually	Vantage Vue Integrated Sensor Suite Installation Manual

*Refer to Appendix D for further calibration protocol

14.2.1 Wet Deposition Equipment Testing

All wet deposition equipment will be field tested prior to the start of each event to verify proper functionality. All measurement probes will be cleared of debris.

This page intentionally left blank.

15.0 INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

15.1.1 Inspection/Acceptance

The Field Sampling Manager is in charge of ordering sampling containers. The ordered supplies will be examined for damage as they are received, per Table 15-1. The glassware, sample containers, and collection equipment will be inspected prior to use. EPA Method TO-13A describes the procedure for the preparation and cleaning of the filter, sorbent, and filter/sorbent cartridge assembly. Air Toxics will provide sampling filters and sorbents prepared and ready for sampling.

Table 15-1. Inspection/Acceptance Testing Requirements for Consumables and Supplies

Program	Project-Related Supplies/ Consumables	Inspection/ Testing Specifications (Source)	Acceptance Criteria	Frequency (%)	Responsible Individual
Dry Deposition	Pre-Certified PUF/XAD-2® Cartridge	COC form of cartridge certification and visual inspection for tampering during shipment (Air Toxics)	Enclosed and un-tampered with in their shipping containers	100	Amec Foster Wheeler
Dry Deposition	Filter	Visual inspection for pinholes, tears, creases, or other flaws that may affect the collection efficiency of the filter (Air Toxics)	Enclosed and un-tampered with in their shipping containers; no visible damage to filter	100	Amec Foster Wheeler
Wet Deposition	Precleaned Sample Bottles	Closed bottle (Physis)	Lids screwed on bottles	100	Amec Foster Wheeler
Dry and Wet Deposition	Gloves	New box (McMaster Carr)	New box	As needed	Amec Foster Wheeler

Preparation of the cartridge must be performed immediately prior to field deployment. Amec Foster Wheeler will order the prepared sampling media as close to the time of the sampling event as possible. Two days will be allowed for shipment. Although cartridges are considered clean for up to 30 days from the date of certification when sealed in their containers per EPA Method TO-13A, media will be returned to the laboratory if unused within 15 days to be recertified, because using canisters beyond 15 days increases the risk of having unacceptable initial vacuum at the start of sampling. Air Toxics will ship media in their shipping containers with a chain of custody form indicating cartridge number, surrogate concentration, date of cartridge certification, and any other pertinent information.

The filters and PUF/XAD-2® cartridge and caps will be obtained from Air Toxics pre-certified. The Field Sampling Manager will make sure sufficient field supplies are on hand prior to the start of sampling for each monitored storm event. Field supplies will be stored at the Amec Foster Wheeler office. Laboratory supplies will be stored at the laboratories conducting the work. Inspection and testing requirements for laboratory supplies are specified in the laboratory's QA/QC procedures.

15.1.2 Corrective Action

Corrective action is taken when an analysis is deemed suspect for some reason. The reasons include exceedances of the allowable RPD and spike recovery ranges, and blank hits. The corrective action typically involves the following:

- Check of procedure
- Review of documents and calculations to identify any possible error
- Error correction
- Re-analysis of the sample extract, if available, to see whether results can be improved
- Complete reprocessing and re-analysis of additional sample material, if it is available

Failures (e.g., instrument failures) that occur during data collection and laboratory analyses will be the responsibility of the field crew or laboratory conducting the work, respectively. In the case of field instruments, problems will be addressed through instrument cleaning, repair, or replacement of parts or of the entire instrument, as warranted. Field crews will carry basic spare parts and consumables with them, and will have access to spare parts stored at the office. Records of the repairs or replacements of field instruments will be maintained at the Amec Foster Wheeler office. The laboratories have procedures in place to follow when failures occur, will identify individuals responsible for corrective action, and will develop appropriate documentation. Corrective actions taken by laboratories need to be thoroughly documented and scientifically defensible.

16.0 NON-DIRECT MEASUREMENTS

There are no non-direct measurements that will be fundamental to the success of this study.

This page intentionally left blank.

17.0 DATA MANAGEMENT

17.1 Data Management

The Project Manager has responsibility for the laboratory data management. The laboratory will provide data in both hardcopy and electronic formats. Electronic data will be kept indefinitely within the Amec database and hard copy documentation will be kept for a minimum of 5 years and a maximum of 10 years within the Amec library.

The Field Sampling Manager is responsible for tracking the analytical process to ensure that laboratories are meeting the required turnaround times and are providing a complete deliverable package. The Field Sampling Manager will receive the original hardcopy from the laboratory, log the date of receipt, and verify completeness. The hardcopy originals will then be transferred to the Project Manager and filed with the other original project documentation to maintain complete project records.

The electronic submittals will conform to reporting protocols. A relational database will be developed and used for the data. Laboratory data will be maintained and managed with Microsoft Excel and/or Microsoft Access. Data from the meteorological data loggers will also be stored in the same database system and linked to the laboratory database.

17.2 Field Observations

Amec Foster Wheeler will review all Field Data Sheets for completeness, maintain the original hardcopies, and scan electronic copies to portable document format (*.pdf) for storage in the project file. Field data sheets will be transcribed into an electronic spreadsheet. Photographs of the monitoring sites taken by field personnel will be uploaded into the project file within three business days of field visits. Field team members will name the photographs using the site ID and the date the photo was taken. Copies of field data sheets and photographs for each event will be submitted to the Project Manager with the quarterly sampling summary.

17.3 Analytical Data

Laboratories will provide data in *.pdf, hardcopy, and an EDD. The Project Manager will review all lab reports and EDDs for accuracy and completeness. Analytical results will be submitted to the Project Manager within three weeks of submittal of samples.

Within two weeks of receipt, the Project Manager will screen preliminary data deliverables for the following major items:

- A 75-percent check between electronic data provided by the laboratory and the hard copy reports
- Conformity check between the COC forms and laboratory reports
- A check for laboratory data report completeness
- A check for typographical errors on the laboratory reports
- A check for suspect values, data qualifiers, and review of laboratory QC data

This page intentionally left blank.

18.0 ASSESSMENTS AND RESPONSE ACTIONS

The Project Manager will be responsible for the day-to-day oversight of monitoring activities, laboratory analyses, and/or data reporting. Any failures (e.g., instrument failures) that occur during data collection and/or laboratory analyses will be the responsibility of the field crew or laboratory conducting the work, respectively. It is the responsibility of the Project Manager and the Laboratory's QA Officer to report any assessments and proposed corrective actions to the Lead Agency's Project Manager. The Project Manager will relay deviations to the Project's QA Officer. The Project's QA Officer has the authority to stop all sampling and analytical work if the deviations noted are considered detrimental to data quality. The following describes how deviations from the QAPP will be identified.

Three types of assessments will be performed as part of this project to ensure that the sampling and analysis activities are in accordance with the approved QAPP. Assessment activities and results will be documented in writing first by field or laboratory reports, and then in final reporting, as follows:

- **Surveillance of Sample Collection Activities:** The Field Sampling Manager will be responsible for oversight of sampling activities and will review field datasheets to verify that the samples were collected in accordance with QAPP requirements. If the Field Sampling Manager identifies any of the field activities to be in violation of QAPP requirements, the Project Manager will be contacted immediately. The Project Manager has the authority to stop field activities until corrective actions are successfully implemented. Corrective actions may include additional training to improve field team performance and QAPP compliance, or appropriate resampling of sites, as needed. Any corrective actions will be documented. Any actions necessary will be communicated to the Project Manager. Assessment of wet season sample collection will occur by the Field Sampling Manager once per field season; assessment of dry weather sample collection will occur at the beginning and end of dry season collection.
- **Data Quality Assessment:** Each Laboratory Manager will be responsible for providing a summary of QC data to the Project Manager. If it is determined that the precision and accuracy objectives were not met, the Project Manager will notify the Laboratory Manager. Laboratory techniques will be reviewed to minimize errors, and samples will be re-analyzed, if possible.
- **Assessment of Data Entry:** Once the performance criteria are met, the Project Manager will review data files to ensure that errors are detected and corrected and that proper documentation is provided and any action is scientifically defensible. The Project Manager will retain original data files and qualified data will be retained in the City's database.

This page intentionally left blank.

19.0 REPORTS TO MANAGEMENT

Amec Foster Wheeler will provide post-event (dry and wet) sampling summaries to the City Project Manager as a status of monitoring activities.

The project reports are detailed within the Monitoring Plan. Table 19-1 presents the management reports.

Table 19-1. Management Reports

Type of Report	Frequency (daily, weekly, monthly, quarterly, annually, etc.)	Projected Delivery Dates	Person(s) Responsible for Report Preparation	Report Recipients
Dry Weather Sampling Summary	Post-event Summary	Post-event Summary	Project Manager, Amec Foster Wheeler	City of San Diego
Wet Weather Sampling Summary	Post-event Summary	Post-event Summary	Project Manager, Amec Foster Wheeler	City of San Diego

This page intentionally left blank.

20.0 DATA REVIEW, VERIFICATION, AND VALIDATION

All analytical data will be reviewed and compared with the DQOs described in Section 5 of this QAPP, along with the applicable QA/QC practices. If results fail to meet any DQO, the Project Manager will flag them for further review. Batch QC samples will be reviewed to determine the potential cause of failure to meet the DQO. Data will be separated into three categories: data meeting all DQOs (acceptable data), data failing precision or recovery criteria (further investigation warranted), and data failing to meet accuracy criteria (further investigation warranted).

If further investigation is warranted on the basis of data failing precision or recovery criteria, all aspects of the data will be assessed for data quality by the Project Manager. At that point, the data will either be accepted or rejected. If accepted, the data will be flagged with a “J” qualifier per the EPA specifications (EPA, 2002). If data fail to meet accuracy criteria, or the cause of the failure cannot be identified and rectified, the data will be excluded from the results. All rejected data will be retained in the project database, and will be qualified as “rejected.” The ultimate decision of whether to accept or reject a data point will be made by the Project Manager in consultation with the Project QA Officer.

If the analysis for more than 10 percent of data fails to meet the DQO, the Project Manager and Project QA Officer will meet to discuss the appropriateness of the DQO and any potential modifications. All proposed modifications of DQOs will require a reissuance of the QAPP.

This page intentionally left blank.

21.0 VERIFICATION AND VALIDATION METHODS

Data verification is the process of evaluating the completeness, correctness, and conformance of the dataset against the method, procedural, or contractual requirements. The goal of data validation is to evaluate whether the data quality goals established during the planning phase have been achieved. Data quality indicators will be continuously monitored by the analyst producing the data (i.e., field and lab personnel), as well as the Laboratory or Project Manager throughout the project to ensure that corrective actions are taken in a timely manner. Data validation is an analyte-specific and sample-specific process that extends verification to determine the analytical quality of the dataset. Laboratory and field personnel responsible for conducting QC analysis will be responsible for documenting when data do not meet measurement quality objectives as determined by data quality indicators.

21.1 Data Verification and Validation Responsibilities

Data collected in the field will be verified by the Project Manager. The laboratories will maintain COC forms and sample manifests.

Verification and validation of laboratory data are the responsibility of the laboratory section supervisor and Project Manager. Laboratories will maintain analytical reports including QC documentation. The Laboratory QA Officer will perform checks of all of its records.

The Project QA Officer and Project Manager are responsible for oversight of field data and laboratory data obtained from the contracted laboratory and sampling agency. All data records will be checked visually and recorded as checked by initials and dates.

Reconciliation and correction of any data that fail to meet the DQOs will be done by the Project Manager in consultation with the Laboratory QA Officer. Any corrections require a unanimous agreement between Project Manager, Laboratory QA officer, and any other qualified individuals; ensuring that the correction is appropriate.

21.2 Process for Data Verification and Validation

Data verification and validation for sample collection and handling activities will consist of the following tasks:

- Verification that the sampling activities, sampling locations, number of samples collected, and type of analysis performed are in accordance with QAPP requirements
- Documentation of any field changes or discrepancies
- Verification that the field activities and field data (including sample location, sample type, sample date and time, name of field personnel, etc.) were properly documented
- Verification of proper completion of sample labels and COC forms, and secure storage of samples
- Verification that all samples recorded on COC forms were received by the laboratory

Data verification and validation for the sample analysis activities will include all of the following:

- Verification that appropriate methodology has been followed
- Verification that instrument calibrations have been adequately conducted
- Verification that QC samples meet performance criteria
- Verification that analytical results are complete
- Verification that documentation is complete

Verification and validation of data entry includes:

- Sorting data to identify missing or mistyped (too large or too small) values
- Double-checking all typed values
- Verifying that correct data types correspond to database fields (i.e., text for text, integers for integers, number for numbers, dates for dates, times for times, etc.)

22.0 RECONCILIATION WITH USER REQUIREMENTS

The overall goal of this project is to identify sources of PAHs within the Project Watersheds and to help guide future management efforts. Air and water data collected during this project will provide a means of determining the concentrations of aerially deposited PAHs in these locations and if these values are significant. PAH loading estimates will help define whether the atmosphere is a significant potential transport mechanism of these contaminants to local waterbodies. This information will potentially be used to support management decisions regarding PAH sources.

This page intentionally left blank.

23.0 REFERENCES

Air Toxics Ltd. 2012. Sorbent & Solution Sampling Guide. http://www.eurofinsus.com/media/15871/sorbent-guide.pdf.

AMEC Environment and Infrastructure, Inc. (AMEC)[1]. 2012a. PAH Source Tracking Study Development Technical Memorandum. Prepared for the City of San Diego.

AMEC. 2012b. PAH Source Tracking Study-Site Selection Technical Memorandum. Prepared for the City of San Diego.

AMEC. 2015. PAH Source Tracking Study- Preliminary Summary Report. Prepared for the City of San Diego.

Chesny Young Meteorology. 2012. Wind Rose Plots: San Diego http://enb110-mcy-2012.blogspot.com/2012/10/wind-rose-plots-san-diego-ca.html. Visited January 17, 2013.

Desert Research Institute (DRI). 2012. http://www.wrcc.dri.edu/htmlfiles/westwinddir.html# CALIFORNIA

Environment Canada (EC) and United States Environmental Protection Agency (USEPA). 2005. Atmospheric Deposition of Toxic Substances to the Great Lakes: IADN Results through 2005. Air Quality Research Division, Environment Canada and Great Lakes National Program Office, USEPA. Toronto, Ontario and Chicago, Illinois.

Lee, D. and K.W. Nicholson. 1994. *The Measurement of Atmospheric Concentrations and Deposition of Semi-Volatile Organic Compounds*. Environmental Monitoring and Assessment. 32: 59-91.

Maliszewska-Kordybach, B. 1999. Sources, Concentrations, Fate and Effects of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment. Part A: PAHs in Air. Polish Journal of Environmental Studies 8: 131-136.

National Atmospheric Deposition Program (NADP). 2011. Instruction Manual NADP/NTN Site Selection and Installation Revised 2011-05 Version 1.5.

National Park Service (NPS). 2012. Cabrillo National Monument http://www.nps.gov/ cabr/index.htm Visited January 17, 2013.

National Weather Service (NWS). 2012. http://www.wrh.noaa.gov/sgx/media/ media.php?wfo=sgx

[1] AMEC Environment & Infrastructure, Inc. (AMEC) is now known as Amec Foster Wheeler Environment & Infrastructure, Inc. (Amec Foster Wheeler)

Sabin, L.D, Schiff, K.C., Lim, J.H., Stolzenchach, K.D., 2004. Atmospheric concentrations of PAH, pesticides, and other semi-volatile organic compounds in the Los Angeles coastal region. Atmospheric Pesticides. 61-72.

Tisch Environmental. 2012. Products-TE-1000, PUF Polyurethane Foam Sampler in Ambient Air and Pesticide Sampler. http://tisch-env.com/products/15-VOC-Ambient-Monitors-Active-and-Passive/33-TE-1000/

Tobiszewski, M., and J. Namieśnik. 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environmental Pollution 162: 110-119.

Tran, K., C.C. Yu, and E.Y. Zeng. 1996. Petrogenic and Biogenic Sources of N-Alkanes off San Diego, California. Southern California Coastal Water Research Project. Annual Report 1994-1995: 53-62.

United States Environmental Protection Agency (EPA). 1983. Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air. EPA Environmental Monitoring Systems Laboratory. June 1983. EPA-600/4-83-027.

EPA. 1999. Compendium of Methods for the Determination of Toxic Organic Compounds, Second Edition. Compendium Method TO-13A. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS). January 1999. EPA Center for Environmental Research Information. EPA/625/R-96/010b.

EPA. 2001. Frequently Asked Questions About Atmospheric Deposition. A Handbook for Watershed Managers. Office of Wetlands, Oceans, and Watersheds. U.S. Environmental Protection Agency. http://www.epa.gov/oaqps001/gr8water/handbook/airdep_sept.pdf

EPA. 2002. Guidance on Environmental Data Verification and Data Validation. EPA QA/G-8.

EPA. 2008. QA Handbook for Air Pollution Measurement Systems, Volume II, Ambient Air Quality Monitoring Program. EPA-454/B-08-003.

EPA. 2012 PAH Chemical Fact Sheets. http://www.epa.gov/ogwdw/pdfs/factsheets/soc/tech/pahs.pdf

Wind Direction. 2012. http://www.wrcc.dri.edu/htmlfiles/westwinddir.html

Zeng, E.Y., and C.L. Vista. 1996. Compositional Indices of Polycyclic Aromatic Hydrocarbon Sources off San Diego, California. Southern California Coastal Water Research Project. Annual Report 1994-1995: 38-52

APPENDIX A
JOB HAZARD ANLAYSIS (JHA) AND SCREENING LEVEL ASSESSMENT (SLA)

This page intentionally left blank.

AHA - - PAH Source Transport Study
Phase IV

Activity/Work Task:	PAH Source Transport Study-Phase IV		
Project Location:	City of San Diego, CA		
Contract Number:	5025151122		
Date Prepared:	9/22/2015	**Date Accepted:**	
Prepared by (Name/Title):	Paige Samblanet, Technical Professional I		
Reviewed by (Name/Title):	Jesse Davis, HSE		

Notes: (Field Notes, Review Comments, etc.)
Monitoring for this project will occur at 4 sampling locations. One dry deposition sampling event will be conducted, which consists of operating a high volume air sampler to measure polycyclic aromatic hydrocarbons (PAH) concentrations in ambient air. Two wet deposition sampling will be conducted. For wet deposition a sampler with a precipitation sensor which detects the onset of precipitation and uncovers the sampler container will be operated throughout the duration of the storm. This AHA involves the following:

- Establishing site specific measures

This AHA is not an exhaustive summary of all hazards associated with the Site. Refer to the site HASP for additional requirements. Contractor to follow general site safety controls for Slips Trips and Falls, Biological hazards, cuts lacerations and pinch points, and emergency procedures.

Overall Risk Assessment Code (RAC) (Use highest code)	**M**

Risk Assessment Code (RAC) Matrix

Severity	**Probability**				
	Frequent	Likely	Occasional	Seldom	Unlikely
Catastrophic	**E**	**E**	**H**	**H**	**M**
Critical	**E**	**H**	**H**	**M**	**L**
Marginal	**H**	**M**	**M**	**L**	**L**
Negligible	**M**	**L**	**L**	**L**	**L**

Step 1: Review each **"Hazard"** with identified safety **"Controls"** and determine RAC (See above)

"Probability" is the likelihood to cause an incident, near miss, or accident and identified as: Frequent, Likely, Occasional, Seldom or Unlikely.

"Severity" is the outcome/degree if an incident, near miss, or accident did occur and identified as: Catastrophic, Critical, Marginal, or Negligible

Step 2: Identify the RAC (Probability/Severity) as E, H, M, or L for each "Hazard" on AHA. Annotate the overall highest RAC at the top of AHA.

RAC Chart

- **E = Extremely High Risk**
- **H = High Risk**
- **M = Moderate Risk**
- **L = Low Risk**

Job Steps	Hazards	Controls	RAC
1) Prepare sampling equipment.	1a) Back injury and strains when lifting equipment.	1a-i) Use proper lifting technique. Do not twist back, stay balanced and use your legs. When lifting objects weighing 50 lbs or more, two or more employees are required to execute the lift.	**M**
2) Load sampling supplies and equipment into vehicle.	2a) Back injury and strains when lifting equipment.	2a-i) Use proper lifting technique. Do not twist back, stay balanced and use your legs. When lifting objects weighing 50 lbs or more, two or more employees are required to execute the lift.	**M**
	2b) Pinching and/or crushing of hands and fingers.	2b-i) Use proper lifting techniques. Dry off hands before lift to avoid slippage. Use appropriate canvas or leather gloves.	
3) Drive vehicle to/from sampling location.	3a) Traffic accidents.	3a-i) Always wear seat belts. Drive defensively/follow traffic regulations.	**M**
		3a-ii) Perform pre-operation inspection on vehicle. Check tires for proper inflation, and headlights and horn for proper functioning. Always drive with headlights on for increased visibility.	

		3a-iii) Cellular telephones are prohibited from use unless the vehicle is safely parked. This includes Company owned or rented vehicles and personal vehicles being used for Company business.	
	3b) Wet, slippery pavements.	3b-i) Drive vehicle in accordance with company policy, drive in right lane, use 3 second rule or extended distance from vehicle in front of you, drive speed limit or slower depending upon conditions.	
4) Installing Monitoring Equipment	4a) Falling from climbing/descending ladders	4a-i) Inspect ladder before climbing and make sure it is stabilized.	L
		4a-ii) Maintain good footing on ladder and maintain contact with the ladder using both hands to keep a safe grip.	
	4b) Back injury and strains when lifting/hoisting equipment.	4b-i) Use proper lifting technique. Do not twist back, stay balanced and use your legs. When lifting objects weighing 50 lbs or more, two or more employees are required to execute the lift.	
		4b-ii) Use proper lifting techniques. Dry off hands before lift to avoid slippage. Use appropriate canvas or leather gloves.	
	4c) Exposure to solvent (hexane) used to clean equipment	4c-i) Handle bottle with care and use cotton or nylon gloves when cleaning equipment.	
5) Working at site locations.	5a) Trip and fall.	5a-i) Be aware of your surroundings, do not get too close to edge of roof. Use caution when on top of roof.	M
		5a-ii) Wear proper footwear.	
		5a-iii) Remain cautious and aware of surface conditions at all times. Beware of slippery surfaces and check for other hazards that can compromise secure footing/traction.	
	5b) Heat illness.	5b-i) Avoid dehydration. Avoid excessive sun of heat exposure. Wear hat, sunglasses and sunscreen.	
		5b-ii) Ensure there is sufficient amounts of cool water available at all times. Each employee should drink at a minimum one quart of water per hour for the entire shift.	
		5b-iii) Ensure that there is access to an open area with shade that is either open to the air or provided with ventilation or cooling for a period of no less than 5 minutes. **Do not wait until you feel ill to seek out shade.**	
		5b-iv) Know the signs and symptoms of heat illness and how to respond to them.	

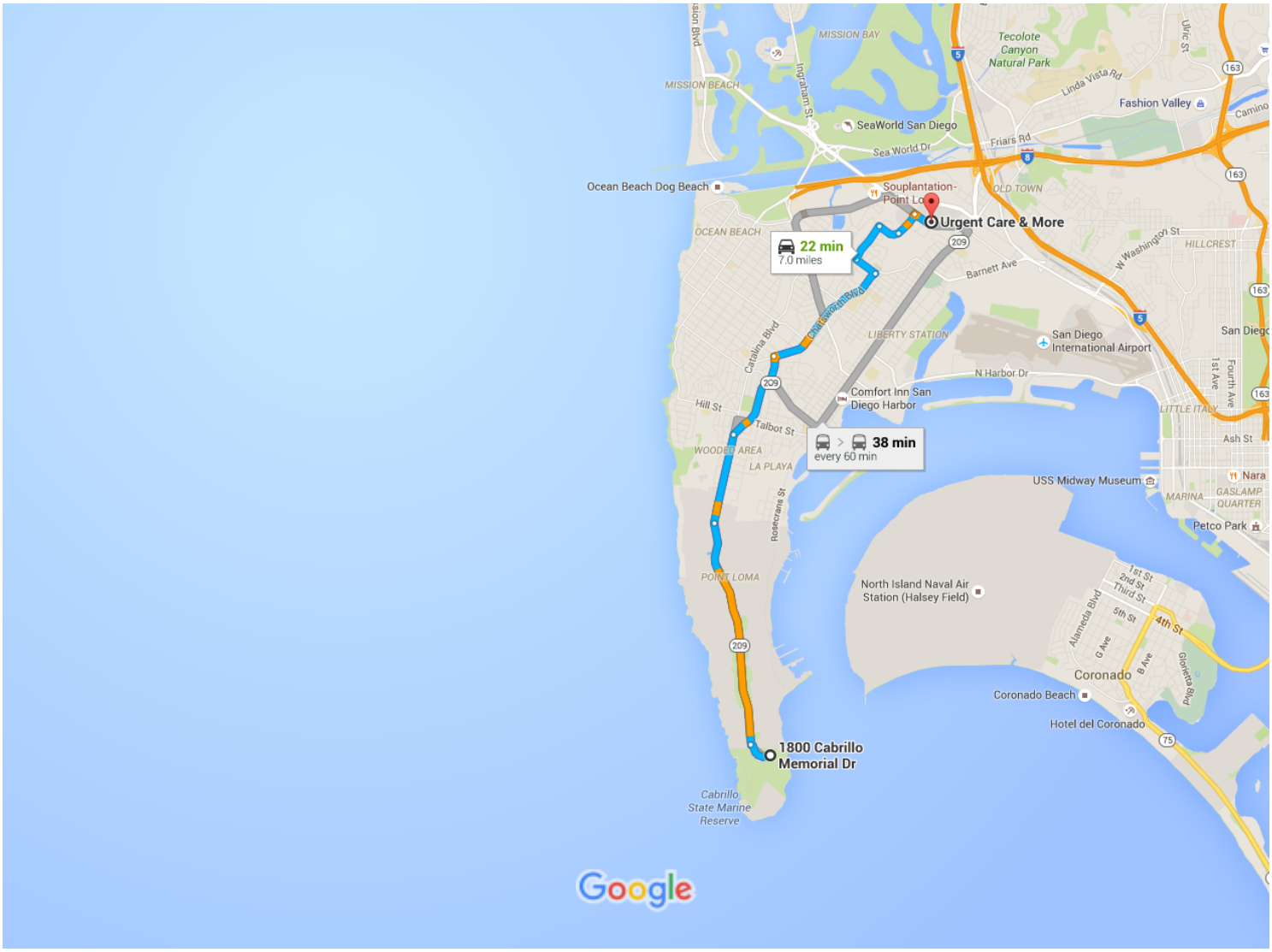
6) Unload samples and equipment back at office and/or laboratory.	6a) Trip and fall.	6a-i) Be aware of your surroundings, go around standing water or slippery inclines.	M
		6a-ii) Wear proper footwear.	
		6a-iii) Remain cautious and aware of surface conditions at all times. Beware of slippery surface particularly mud, wet vegetation, and algae or biological growth on the pavement and curbing. Check for other hazards that can compromise secure footing/traction, such as uneven surfaces, car parts, tools and equipment.	
7) Report writing	7a) Ergonomic injury due to repetitive motion.	7a-i) Do not perform computer works for excessive periods of time. Take micro breaks every 15-20 minutes.	L
		7a-ii) Perform ergonomic stretching exercises on a regular basis.	
		7a-iii) If you have any ergonomic concerns, contact your local H&S representative to request an ergonomic evaluation of your work space.	
	7b) Trips and falls in hallways and passageways due to obstructions	7b-i) All floors shall be free of dangerous projections or obstructions and any tripping hazards, and maintained in good repair, and be dry or slip-resistant. Wipe up spills promptly; never leave file or desk drawers open. Ensure unobstructed walking space between or around: • office or workstation-24” • hallway, walkway or common area-44”	

Google Maps

1800 Cabrillo Memorial Dr, San Diego, CA 92106 to Urgent Care & More

Drive 7.0 miles, 22 min

CNM to Urgent Care



Map data ©2016 Google 1 mi

1800 Cabrillo Memorial Dr

San Diego, CA 92106

Continue to Cabrillo Memorial Dr

2 min (0.3 mi)

1. Head southwest

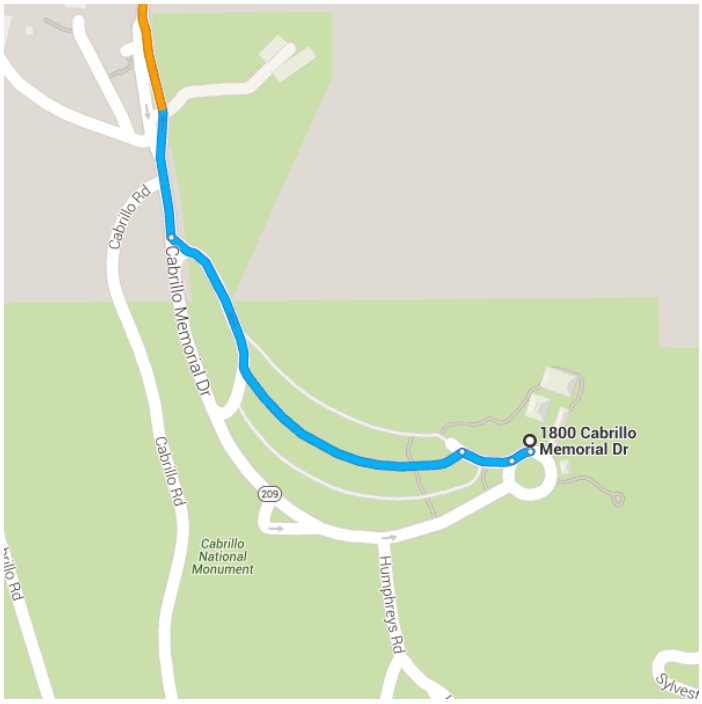
59 ft

2. Use the left lane to turn slightly right toward Cabrillo Memorial Dr

148 ft

3. Turn left toward Cabrillo Memorial Dr

0.2 mi



Continue on Cabrillo Memorial Dr. Take Chatsworth Blvd to Elliott St

13 min (5.5 mi)

4. Continue onto Cabrillo Memorial Dr

2.3 mi

5. Continue onto Catalina Blvd

0.9 mi

6. Slight right onto Cañon St

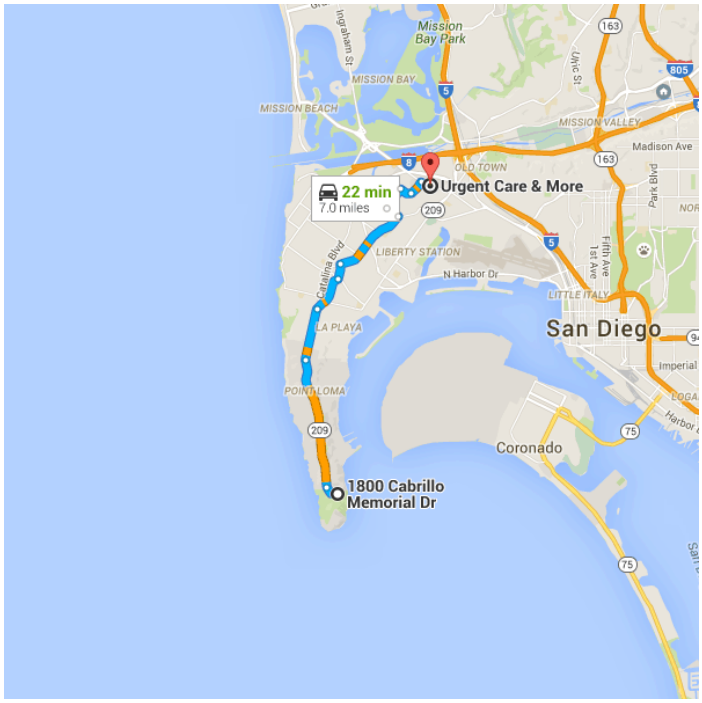
0.7 mi

7. Turn left onto Del Mar Ave

0.3 mi

8. Turn right at the 3rd cross street onto Chatsworth Blvd

1.3 mi



Take Poinsettia Dr to Midway Dr

4 min (1.1 mi)

9. Turn left onto Elliott St

0.2 mi

10. Turn right onto Poinsettia Dr

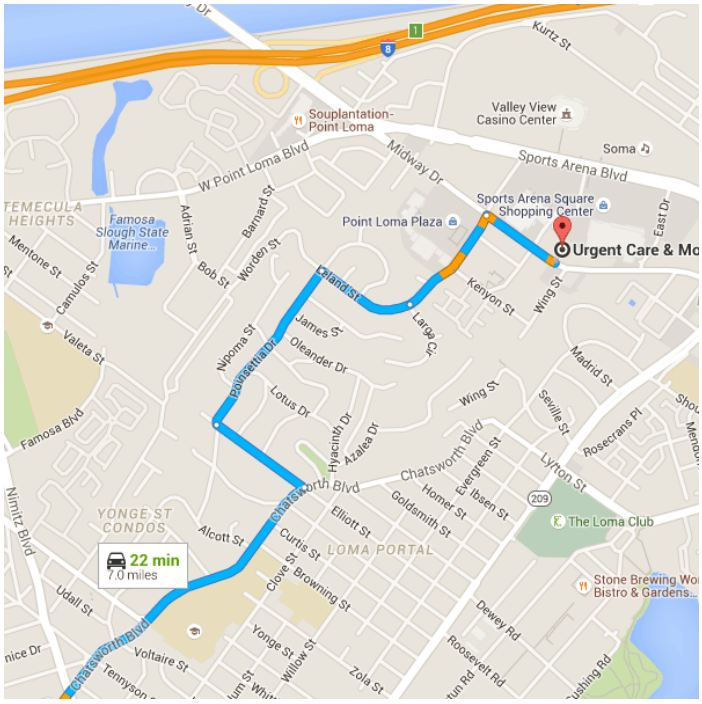
0.4 mi

11. Turn right onto Leland St

0.2 mi

12. Continue onto Kemper St

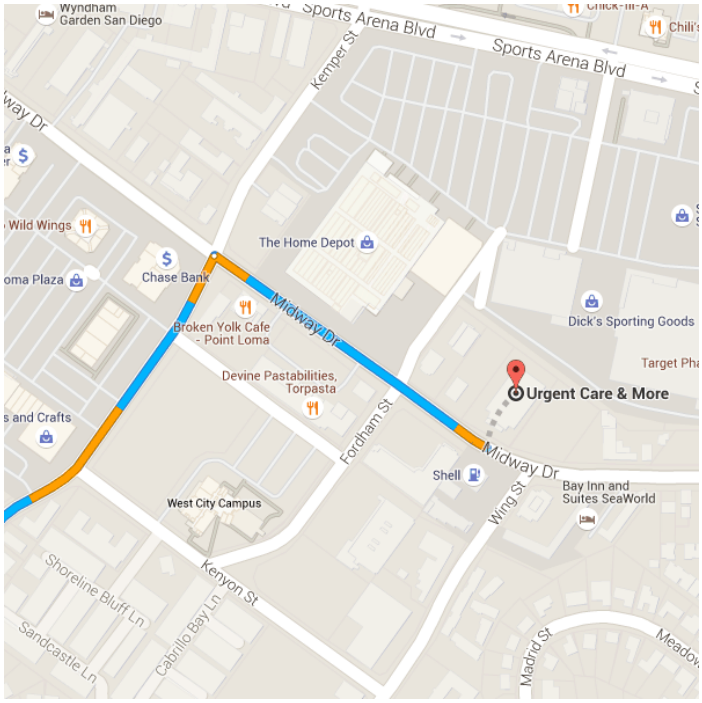
0.3 mi



13. Turn right onto Midway Dr

Destination will be on the left

49 s (0.2 mi)



Urgent Care & More

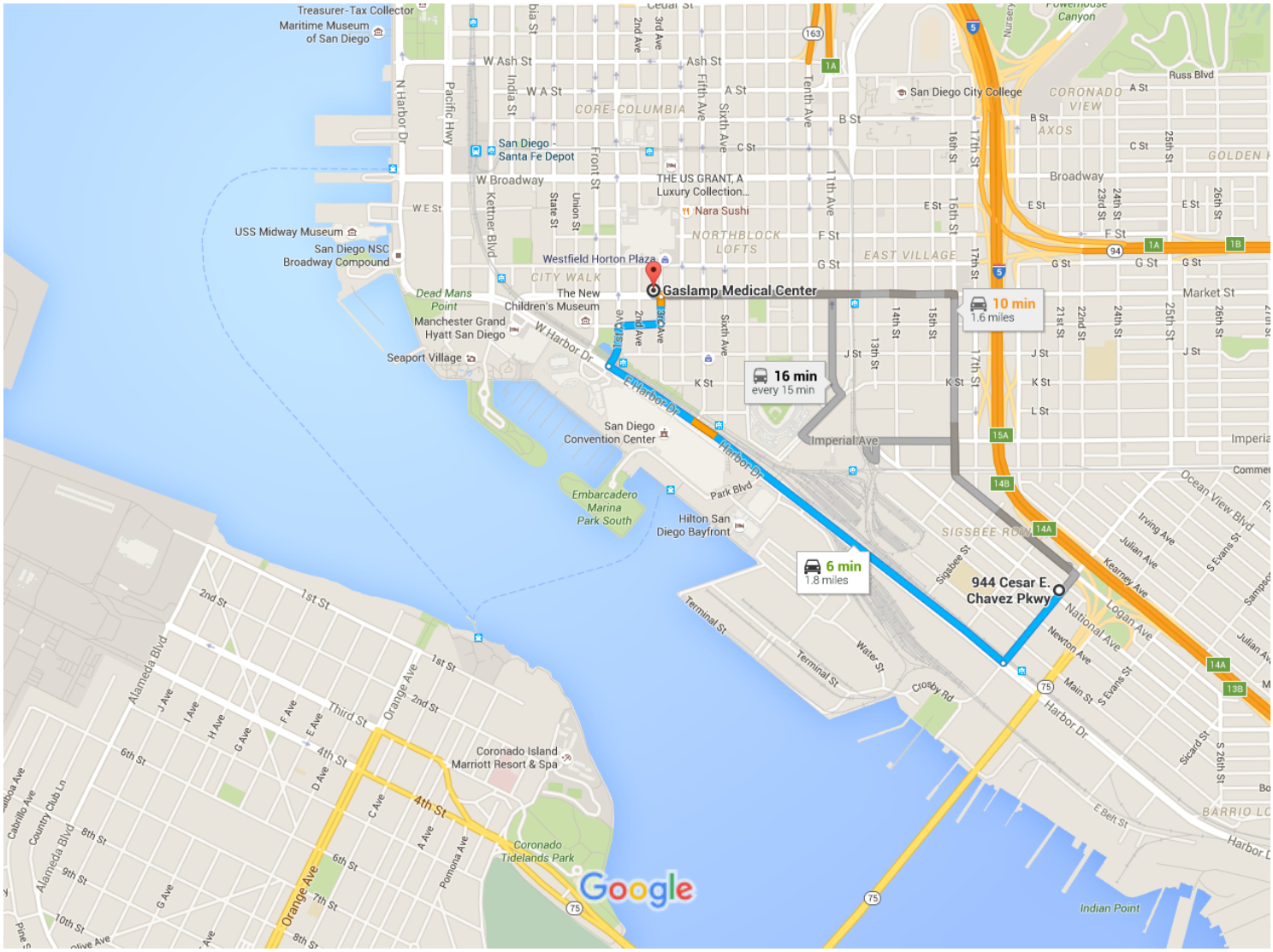
3434 Midway Drive, San Diego, CA 92110

These directions are for planning purposes only. You may find that construction projects, traffic, weather, or other events may cause conditions to differ from the map results, and you should plan your route accordingly. You must obey all signs or notices regarding your route.

Google Maps

944 Cesar E. Chavez Pkwy, San Diego, CA 92113 Drive 1.8 miles, 6 min to Gaslamp Medical Center

FD07 to Gaslamp Medical Center



944 Cesar E. Chavez Pkwy

San Diego, CA 92113

1. Head southwest on Cesar E. Chavez Pkwy toward National Ave — 0.2 mi
2. Turn right onto E Harbor Dr — 1.2 mi
3. Turn right onto 1st Ave — 0.1 mi
4. Turn right onto Island Ave — 0.1 mi

5. Turn left onto 3rd Ave

348 ft

6. Turn left at the 1st cross street onto Market St

Destination will be on the right

135 ft

Gaslamp Medical Center

250 Market Street, San Diego, CA 92101

These directions are for planning purposes only. You may find that construction projects, traffic, weather, or other events may cause conditions to differ from the map results, and you should plan your route accordingly. You must obey all signs or notices regarding your route.

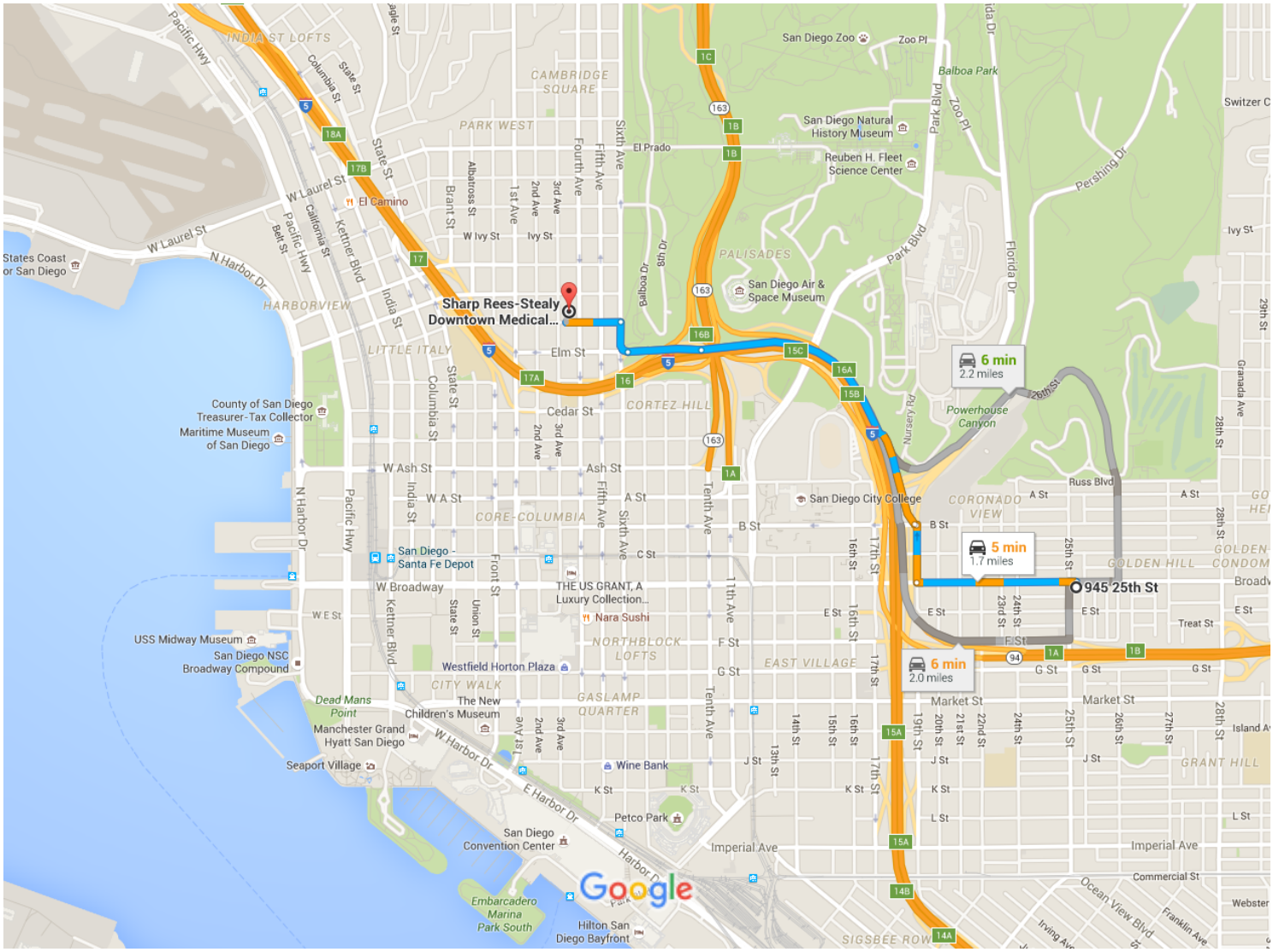
Google Maps

Google Maps

945 25th St, San Diego, CA 92102 to Sharp Rees-Stealy Downtown Medical Center and Urgent Care

Drive 1.7 miles, 5 min

FD11 to Downtown Medical Center



945 25th St

San Diego, CA 92102

Take Broadway and I-5 N to Fir St

4 min (1.6 mi)

1. Head west on Broadway toward 25th St

0.4 mi

2. Turn right onto 19th St

0.1 mi

3. Turn left onto B St

30 ft

4. Turn right to merge onto I-5 N

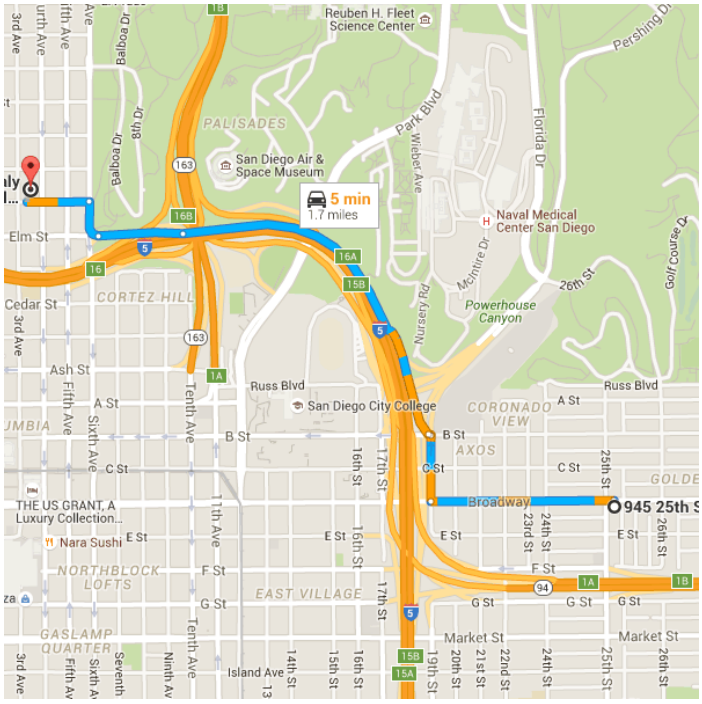
0.8 mi

5. Use the right lane to take exit 16B for 6th Avenue toward Downtown

0.2 mi

6. Turn right onto Sixth Ave

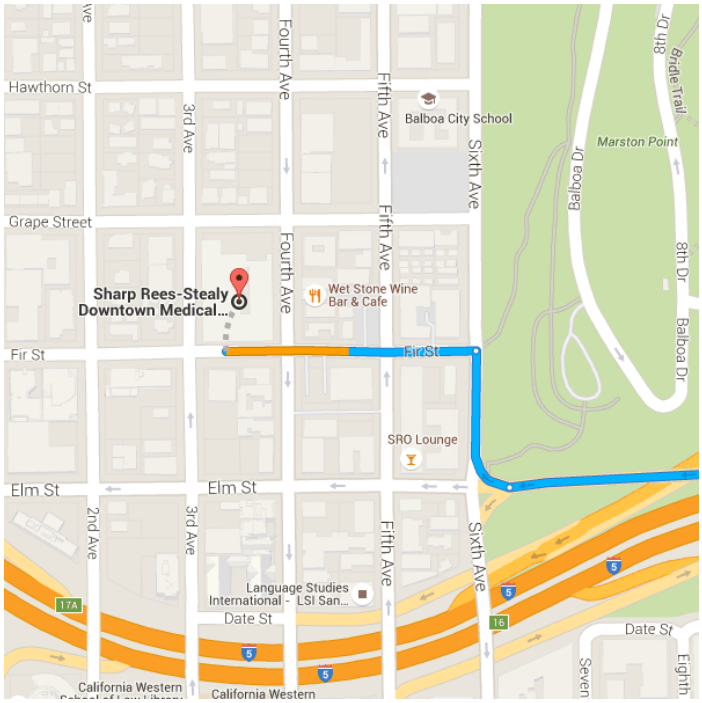
443 ft



7. Turn left onto Fir St

Destination will be on the right

1 min (0.1 mi)



Sharp Rees-Stealy Downtown Medical Center and Urgent Care

300 Fir Street, San Diego, CA 92101

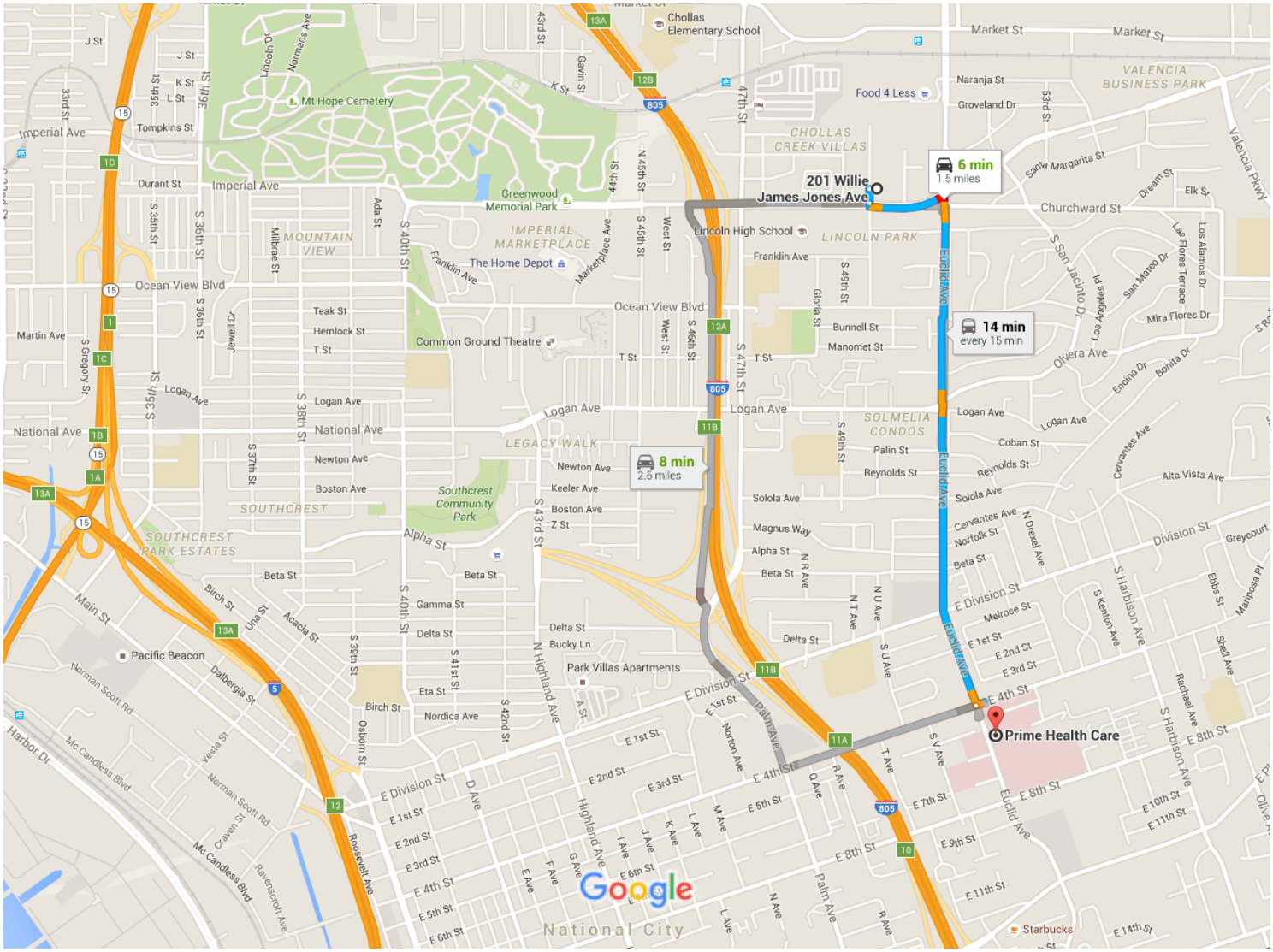
These directions are for planning purposes only. You may find that construction projects, traffic, weather, or other events may cause conditions to differ from the map results, and you should plan your route accordingly. You must obey all signs or notices regarding your route.

Google Maps

201 Willie James Jones Ave, San Diego, CA 92102 to Prime Health Care

Drive 1.5 miles, 6 min

FD12 to Primary Health Care



Map data ©2016 Google 1000 ft

201 Willie James Jones Ave

San Diego, CA 92102

1. Head south on Willie James Jones Ave toward Imperial Ave

190 ft

2. Turn left at the 1st cross street onto Imperial Ave

0.2 mi

3. Turn right onto Euclid Ave

1.3 mi

4. Turn left onto E 4th St

Destination will be on the right

112 ft

AHA - - PAH Source Transport Study
Phase IV

Equipment to be Used	Training Requirements/Competent or Qualified Personnel name(s)	Inspection Requirements
PPE (Hard Hat, safety glasses, gloves, steel toe work boots, high visibility safety vest, hearing protection)	**Competent / Qualified Personnel:** Paige Samblanet/Technical Professional **Training requirements:** List specific certification (as applicable) Site Specific HASP Orientation Toolbox safety meeting Task kick-off meeting	Daily inspection of equipment per manufacturer's instructions. Tag tools that are defective and remove from service. Inspect all PPE prior to use

Reviewers and Approvals

(Signatures)

☒ Project Manager Date

☒ Office LHSR Date

AHA - - PAH Source Transport Study
Phase IV

AHA DAILY RENEWAL

Date:	Weather:	
Changes noted:		
Site Supervisor (Print & Sign):		
Name(s):		
Date:	Weather:	
Changes noted:		
Site Supervisor (Print & Sign):		
Name(s):		
Date:	Weather:	
Changes noted:		
Site Supervisor (Print & Sign):		
Name(s):		

APPENDIX B
FIELD DATA SHEETS

This page intentionally left blank.

City of San Diego
PAH Transport Study Phase II
AMEC Project No. 5025121032

PAH Wet Deposition Field Data Log Sheet

Site ID		**Field Crew**		**Date**	
Site-Specific Event	Wet Weather 1 2 3 4 5			**Time**	

ATMOSPHERIC CONDITIONS

Weather Sunny Partly Cloudy Overcast Fog Raining

Last Rain > 72 Hours < 72 Hours **Rainfall** None < 0.1" > 0.1"

SAMPLE COLLECTION

Sample Type	Date	Time	Sample ID
Chemistry (PAHs)			

Rain Event Start Time: _____

Rain Event End Time: _____

Total Volume Collected	Total Rainfall (in)

NOTES/COMMENTS

City of San Diego
PAH Transport Study Phase II
AMEC Project No. 5025121032

PAH Dry Deposition Field Data Log Sheet

Site ID _____ **Field Crew** _____

Dry Deposition Sampling Event Pilot Dry 1 Dry 2 Dry 3

ATMOSPHERIC CONDITIONS

Sky Sunny Partly Cloudy Overcast Fog Raining

Last Rain > 72 Hours < 72 Hours **Rainfall** None < 0.1" > 0.1"

PUF SAMPLER

Sampler I.D. No.: _____

Lab PUF Sample No.: _____

PUF Cartridge Certification Date: _____

Date/Time PUF Cartridge Installed: _____

Elapsed Timer:

Start: _____

Stop: _____

Diff. _____

Sampling Time

Start: _____

Stop: _____

Diff. _____

Audit flow check within +/- 10 of set point: (YES/NO)

TIME	TEMP (^{o}F)	BAROMETRIC PRESSURE ("Hg)	MAGNEHELIC READING	CALCULATED FLOW RATE (std. m3)	READ BY
Avg.					

NOTES/COMMENTS

APPENDIX C
SITE PHOTOGRAPH LOG

This page intentionally left blank.

Cabrillo National Monument - Reference Site (CNM)

Visitor's Center Sampling Location A,
On Northwest end of the Visitor's Center

Visitor's Center Sampling Location A,
On Northwest end of the Visitor's Center
Northeast from Visitor's Center

Visitor's Center Sampling Location B
On Southwest end of the Visitor's Center

Visitor's Center Sampling Location B
On Southwest end of the Visitor's Center
Northwest from Visitor's Center, no horizontal obstructions

San Diego Fire Department Station 7 (FD7)

View from rooftop, and surrounding commercial and residential areas

Sampler installed on rooftop; view of surrounding commercial and residential areas to the west

Fire Station 7 Building

San Diego Fire Department Station 11 (FD11)

Northwest view from rooftop, surrounding residential area

South view from rooftop, surrounding residential area

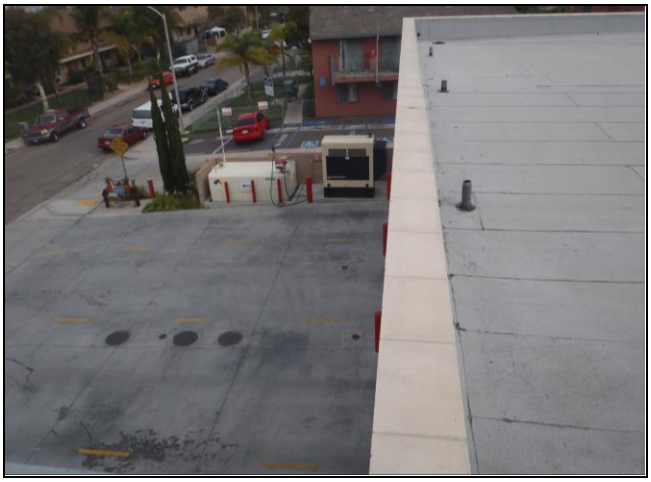
Southeast view from rooftop, surrounding residential area

Fire Station 11 Building

San Diego Fire Department Station 12 (FD12)

Southwest view from rooftop,
institutional/school building

Northeast view from rooftop,
surrounding residential area



North view from rooftop,
FD12 garages and surrounding residential area

Fire Station 12 Building

APPENDIX D
DAVIS VANTAGE VUE INTEGRATED SENSOR SUITE INSTALLATION MANUAL AND SPECIFICATIONS

This page intentionally left blank.

Vantage VUE™

Integrated Sensor Suite Installation Manual

Model #6357

3465 Diablo Ave., Hayward, CA 94545 USA
510.732.9229 • www.davisnet.com

Davis Instruments

Table of Contents

Davis Instruments

3465 Diablo Avenue, Hayward, CA 94545-2778 U.S.A.
510-732-9229 • Fax: 510-732-9188
E-mail: info@davisnet.com • www.davisnet.com

Integrated Sensor Suite Installation Manual.
Rev. A, June 18, 2009
Document Part Number: 07395.262
For Vantage Vue Weather Stations and Systems

Introduction

The Vantage Vue™ wireless Integrated Sensor Suite (ISS) collects outside weather data and sends the data wirelessly to a Vantage Vue console via a low-power radio. The ISS is solar powered and includes a battery back-up.

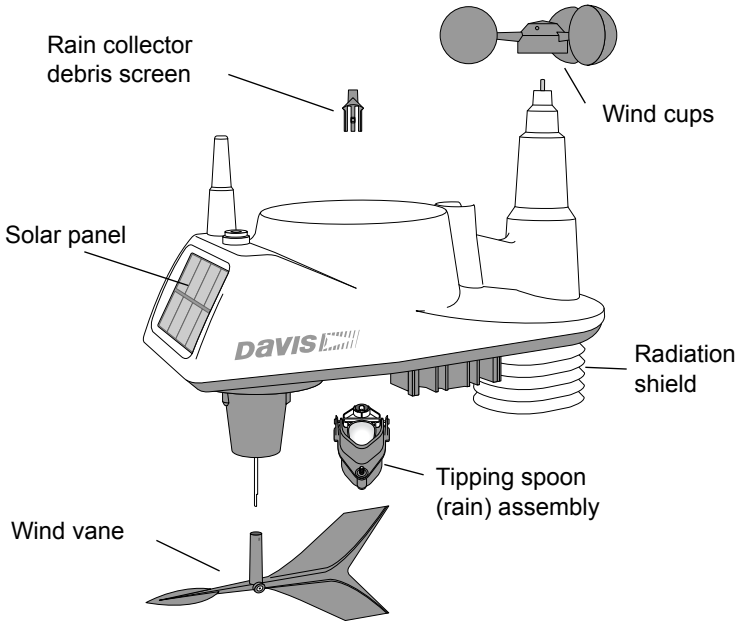
The Vantage Vue ISS contains a rain collector, temperature/humidity sensor, anemometer, and wind vane. The temperature/humidity sensor is mounted in a passive radiation shield to minimize the impact of solar radiation on sensor readings. The anemometer measures wind speed, and the wind vane measures wind direction.

The Sensor Interface Module (SIM) is housed within the ISS and comprises the "brains" of the Vantage Vue system and the radio transmitter. The SIM collects outside weather data from the ISS sensors and transmits that data to your Vantage Vue console.

Note: Your Vantage Vue ISS can transmit to an unlimited number of consoles, so you can purchase additional consoles to use in different rooms. It can also transmit to Davis Vantage Pro2 consoles and Davis Weather Envoys as well as Vantage Vue consoles.

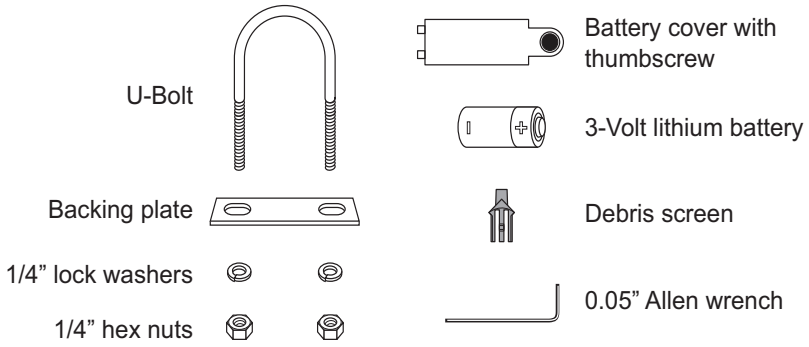
Included Components and Hardware

Vantage Vue ISS Components



Hardware

Hardware included with the Vantage Vue ISS:



Note: If any of the hardware components are missing or not included, contact Customer Service toll free at 1-800-678-3669 about receiving replacement hardware or other components.

Tools Needed

- Adjustable wrench or 7/16″ (11 mm) wrench
- Compass or local area map

Preparing the ISS for Installation

Follow the steps in the order; each builds on tasks completed in previous steps.

Note: Use a clean, well-lit work table or work area to prepare the ISS for installation.

- Attach the wind cups to the anemometer
- Attach the wind vane
- Install the debris screen in the rain collector
- Install the rain collector tipping spoon assembly
- Install the ISS battery to apply power

Note: At this point, we recommend that you set up your console, and then come back to finish the installation of the ISS. See your *Vantage Vue Console Manual*.

Additional steps for advanced set up:

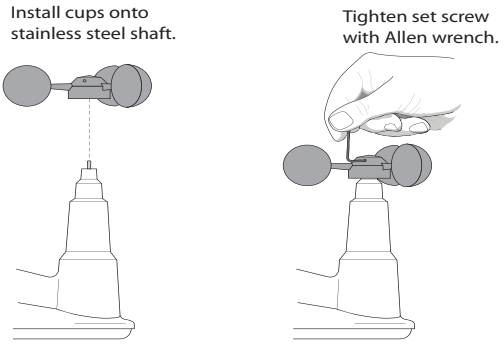
- Verify transmitter ID
- Change the transmitter ID for wireless communication, if necessary

- Verify data from the ISS

Attach the Wind Cups to the Anemometer

The Vantage Vue anemometer measures wind speed. The wind cups are mounted on the anemometer shaft on the top of the ISS assembly.

1. Gently slide the wind cup assembly down onto the anemometer's stainless steel shaft as far as it will go, as shown.
2. Use the Allen wrench provided to tighten the set screw near the top of the "hub" section of the wind cups, as shown. Ensure that the set screw is screwed in fully and is tight.
3. Pull gently on the hub to ensure that the anemometer is securely fastened to the shaft.
4. Spin the wind cups to make sure they spin freely.

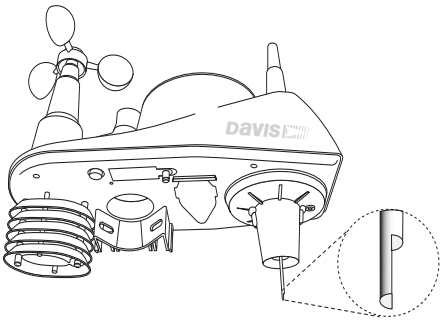


Note: If the wind cups don't spin freely, loosen the set screw, remove them from the shaft, and repeat the wind cup installation process.

Attach the Wind Vane

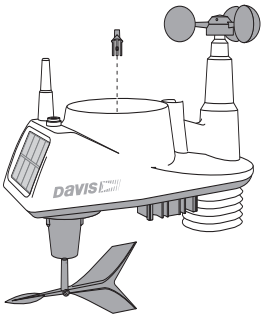
The Vantage Vue wind vane measures wind direction. The wind vane is mounted on a stainless steel shaft on the opposite side of the ISS assembly from the wind cups.

1. Hold the ISS assembly on its side with the anemometer and radiation shields on your left, the wind vane shaft on your right and the wind cups away from you.:
2. When the ISS is held in this manner, the wind vane shaft is horizontal, and will orient itself so that its flat side will be facing *to the right*, as shown.
3. Holding the ISS assembly with your left hand, grasp the wind vane with your right hand so that the "arrowhead" end *is pointed down*.
4. Gently slide the wind vane onto the wind vane shaft, rotating the wind vane slightly left and right if necessary, until the end of the shaft is visible and flush with the bottom surface of the wind vane.
5. Secure the wind vane to the shaft by firmly tightening the wind vane set screw with the Allen wrench provided.



Install the Debris Screen

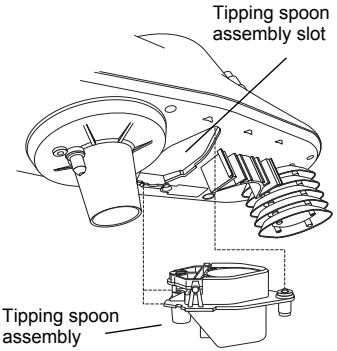
The Vantage Vue ISS rain collector debris screen captures debris that may otherwise clog your rain collector.



1. Locate the small black plastic ISS debris screen in your hardware package.

   The debris screen has four small tabs that hold it in place in the base of the rain collector.
2. Holding the ISS assembly with one hand, and holding the debris screen by the top, press it into the opening at the bottom of the rain collector until the tabs snap into the opening.

Install the Rain Collector Tipping Spoon Assembly

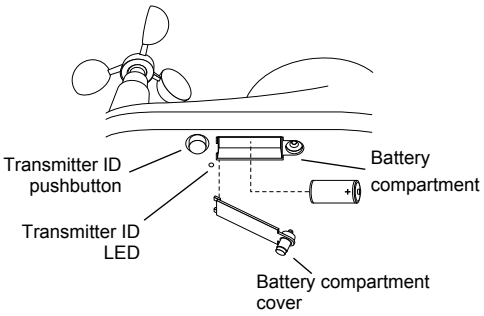


1. Locate the tipping spoon assembly slot on the underside of the ISS Base.
2. Insert the wider end of the tipping spoon assembly into the slot first, sliding it under the raised lip of the slot.
3. Fit the narrow end into the slot and tighten the thumbscrew securely.

Install the Battery

The Vantage Vue ISS SIM board stores energy from the solar panel for power at night. A 3-volt lithium battery provides a backup power source. The battery compartment is located on the underside of the ISS base. The compartment cover is included in the hardware packet.

To install the ISS backup battery.



1. Insert the 3-volt lithium battery into the ISS battery compartment, being sure to match the "+" sign on the battery with the "+" sign embossed on the inside of the battery compartment.
2. Ensure that the battery is properly in place, install the battery compartment cover, and tighten the thumbscrew.

   To verify power, wait 30 seconds then push and release the white transmitter ID pushbutton next to the battery compartment. The green transmitter ID LED next to the battery compartment will illuminate when you press the pushbutton.

Note: Press the pushbutton once and release it. Do not press it multiple times or hold it down.

When you release the pushbutton, the LED will blink once, then begin to flash every 2.5 seconds to show transmission of a data packet. This flashing will stop within a few minutes to conserve battery life.

Note: If you have not already set up and powered your Vantage Vue console, do so before continuing with the ISS installation.

3. Wait 5 minutes for the console to acquire the radio signal and populate data fields.

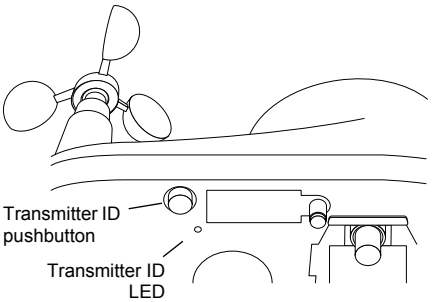
Advanced Installations: Confirm the Transmitter ID of the ISS

Your Vantage Vue console can be used to listen to a Vantage Pro2 ISS instead of a Vantage Vue ISS, and an optional anemometer transmitter kit.

Note: If you are using only the Vantage Vue console and ISS, and there are no other Davis weather stations nearby, you can skip to "Verify Data from the ISS" on page 6.

In order to communicate, the console and ISS must have the same transmitter ID. At the factory, both IDs are set to a default of number 1. To confirm the transmitter ID of your Vantage Vue ISS:

1. Push and release the transmitter ID pushbutton once. It will illuminate and go off when you release it.
2. After a short pause, it will blink one or more (up to 8) times. Note the number of times the transmitter ID LED blinks, indicating its transmitter ID.



Unless you have intentionally changed your transmitter ID, the LED should blink *one time* because the default transmitter ID for the ISS is "1." If you have changed the ID, the LED should blink the number of times equal to the ID you have set (i.e., twice for an ID of '2,' three times for an ID of '3,' etc.).

After blinking the transmitter ID, the light will begin to flash every 2.5 seconds, indicating packet transmission.

Note: The transmitter on the ISS and receiver on the console will communicate with each other only when both are set to the same transmitter ID.

Note: If you hold the pushbutton too long and accidentally enter the "set new transmitter ID" mode when you did not want to, simply release the pushbutton and wait four seconds. As long as you do not press the pushbutton again, the original transmitter ID will remain in effect.

Advanced Installations: Set a New Transmitter ID on the ISS

Note: In most cases, it will not be necessary to change the transmitter ID. If it is necessary to change the transmitter ID, **you must use the same ID for the ISS and console**.

The Vantage Vue ISS transmits weather information to the Vantage Vue console using one of eight selectable transmitter IDs. The default transmitter ID for both the ISS and the Vantage Vue console is 1. Change the transmitter ID if another Davis Instruments

wireless weather station is operating nearby and already uses transmitter ID 1, or if you have an optional Anemometer Transmitter Kit with ID 1.

To set a new transmitter ID:

1. Push and hold the transmitter ID pushbutton until the LED begins flashing quickly. This indicates it is in the setup mode.
2. Release the pushbutton, and the LED will go dark.
3. Push the pushbutton the number of times equal to your desired new transmitter ID. That is, if you want to change the ID to "3," push the pushbutton three times; for a desired ID of "4," push the pushbutton four times.

   After four seconds have elapsed with no further presses, the LED will blink the same number of times as the new transmitter ID. (After blinking the transmitter ID number, the light will begin to flash each time a packet is transmitted, about every 2.5 seconds.)

Verify Data from the ISS

To verify reception of ISS data by the Vantage Vue console, you will need your powered-up console and the ISS.

1. If the console is in Setup Mode, press and hold **DONE** until the Current Weather screen displays. The antenna icon appears under the wind compass rose. Watch this icon to see that "transmission waves" appear, indicating reception of a packet.

   Sensor readings from the ISS should display on the screen within a few minutes.
2. At the top right corner of the screen, look for the outside temperature.
3. Gently spin the wind cups to check wind speed, pressing the **WIND** button on the console to alternate between speed and direction in the windcompass rose.
4. Gently turn the wind vane, and allow 5 seconds for the wind direction display to stabilize before moving it again.

Note: A good way to ensure that your console is listening to your ISS and not another Davis station nearby, is to make sure the wind values displayed match your wind vane's direction in reference to the solar panels, which are assumed to be facing south. For example, if you move the vane to point directly away from the ISS, the console should show a wind direction of south; if you then turn the vane 180° so it is pointed back at the radiation shield, the wind direction on the console should change to north.

   Approximately one minute after acquisition of the signal, the outside relative humidity reading should be displayed on the console, below the outside temperature display.
5. Confirm rain display. On your console screen, select the RAIN DAY display. (See *Vantage Vue Console Manual*.). Carefully hold your ISS over a sink and, while watching the RAIN DAY display on your console, slowly pour one-half cup of water into the Rain Collector. Wait two seconds to see if the display registers a rain reading.

Note: This method confirms that the rain display is functioning. It **cannot** be used to verify accuracy.

6. Current data displayed on the console confirms successful communication.

Note: In some cases it may take as long as five minutes for a reading to register on your console.

If communication problems exist between the wireless ISS and the console, see "Troubleshooting ISS Reception" on page 12 in the Maintenance and Troubleshooting section of this manual.

Installing the ISS

Choosing a Location for the ISS

The ISS assembly includes the rain collector, wind vane, anemometer, temperature and humidity sensors, radiation shield, and SIM housing. You will use the U-bolt and associated nuts and washers that are included with your ISS mounting hardware package to install the ISS on a pole. (See "Hardware" on page 2.)

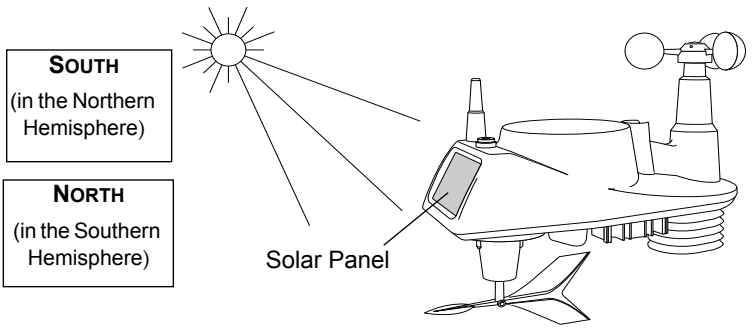
To ensure that the Vantage Vue weather station performs at its best, use these guidelines to select the optimum mounting location for the ISS. Be sure to take into consideration ease of access for maintenance and wireless transmission range when siting the station.

Note: When selecting a location for installing your ISS, especially on a rooftop, make sure it is a location far from power lines. Seek professional help if you are uncertain about the safety of your installation.

ISS Installation Guidelines

Note: These siting guidelines reflect an ideal condition. Rarely is it possible to create the perfect installation. The better the siting, the more accurate your data will be.

- Place the ISS away from sources of heat such as chimneys, heaters, air conditioners and exhaust vents.
- Place the ISS at least 100' (30 m) away from any asphalt or concrete roadway that readily absorbs and radiates heat from the sun. Avoid installations near fences or sides of buildings that receive a lot of sun during the day.
- Install the ISS as level as possible to ensure accurate rain and wind measurements. Use the built in bubble level on the top of the ISS, just above the solar panel, to make sure the ISS is level.
- In the Northern Hemisphere, the solar panel should face south for maximum sun exposure.
- In the Southern Hemisphere, the solar panel should face north for maximum sun exposure.



Note: If you install the ISS with the solar panel pointing in a direction other than south, you will need to use the wind direction calibration function in the Vantage Vue console in order to obtain accurate wind direction readings. See *Vantage Vue Console Manual* for more information.

- Ideally, mount the ISS so that it is between 5′ (1.5 m) and 7′ (2.1 m) above the ground in the middle of a gently sloping or flat, regularly mowed grassy or naturally landscaped area that drains well when it rains. You can also mount the ISS on the roof, between 5′ (1.5 m) and 7′ (2.1 m) above the roof surface. For areas with average maximum yearly snow depths over 3′ (0.9 m), mount the ISS at least 2′ (0.6 m) above this depth.
- Never install the ISS where it will be directly sprayed by a sprinkler system.
- Avoid installations near bodies of water such as swimming pools or ponds.
- Do not locate the ISS under tree canopies or near the sides of buildings that create "rain shadows." For heavily forested areas, site the ISS in a clearing or meadow.
- Site the ISS in a location with good sun exposure throughout the day.
- *For agricultural applications:*
  - Install the ISS so that it is between 5′ (1.5 m) and 7′ (2.1 m) above the ground and in the middle of the farm between similar crop types (ie. two orchards, two vineyards, or two row crops), if possible.
  - Avoid areas exposed to extensive or frequent applications of agricultural chemicals (which can degrade the sensors).
  - Avoid installation over bare soils. The ISS performs best when installed over well-irrigated, regularly mowed grass
  - If the last three guidelines cannot be met, install the ISS at the edge of the primary crop of interest.

Siting guidelines that may affect the anemometer

- For optimal wind data, mount the ISS so that the wind cups are at least 7′ (2.1 m) above obstructions such as trees or buildings that may obstruct wind flow.
- For optimal wind data, you may mount the ISS on a roof, keeping in mind ease of access to the ISS for maintenance and safety considerations. Ideally, mount it so that the wind cups are at least 7′ (2.1 m) above the roof apex.
- The standard for meteorological and aviation applications is to place the anemometer 33′ (10 m) above the ground. Seek professional help for this such installation.
- The standard for *agricultural applications* is to place the wind cups 6′ (2 m) above the ground. This is important for evapotranspiration (ET) calculations.

Note: For roof mounting, and ease of installation, we recommend using the optional tripod (#7716). For other installations, use the Mounting Pole Kit (#7717).

Note: For more detailed siting suggestions, see Application Note #30 on the Davis Support website (http://www.davisnet.com/support/weather).

Mounting the ISS

The Vantage Vue ISS can only be mounted on the top of a pole or rod.

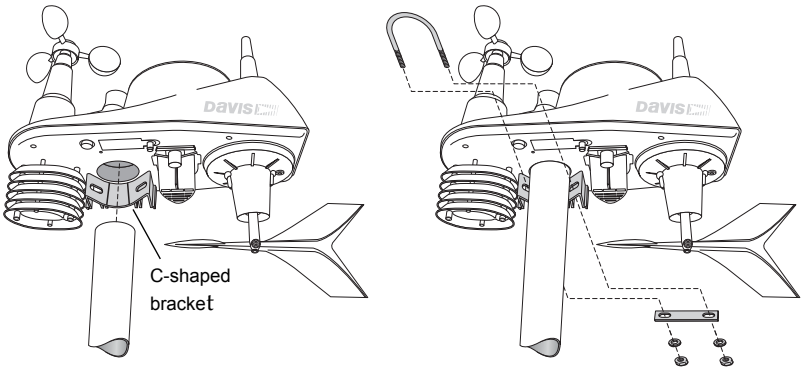
Note: A mounting pole is not included with your Vantage Vue ISS and must be purchased separately, either from Davis Instruments or from your local hardware retailer.

Recommended Accessories for Pole Mounting

- Use the Mounting Tripod (#7716) for easiest mounting.
- Use the Mounting Pole Kit (#7717) to raise the installation height of the ISS by up to 37.5" (0.95 m).

General Guidelines for Installing on a Pole

- With the supplied U-bolt, the ISS can be mounted on a pole or rod having an outside diameter ranging from 1" to 1.75" (25 – 44 mm).
- To mount on a smaller pole, obtain a U-bolt that fits the base openings but that has a longer threaded section. If mounting the ISS on a smaller pole with the included U-bolt, the threaded sections of the U-bolt will be too short to securely mount the ISS.



Installing the ISS on a Pole

1. If you are mounting your ISS on a Davis Mounting Tripod or the pole included with a Davis Mounting Pole Kit, follow the instructions included with those Davis products for proper installation.
   If you are not using one of these Davis products, mount on a galvanized steel pole having an outside diameter ranging from 1" to 1.75" (25 – 44 mm).

Note: It is important that the mounting pole be plumb. You may wish to use a level such as a magnetic "torpedo level" to assure that the ISS, when mounted on top of the pole, will be level.

2. Using the illustration above as a guide, hold the ISS so that the wind cups and radiation shield are on the left and gently place the ISS on top of the pole.
3. While holding the mounting base of the ISS against the pole, place the two ends of the U-bolt around the pole and through the two holes in the C-shaped bracket on the base.
4. Slide the metal backing plate over the bolt ends where they extend out from the far side of the bracket.
5. Secure the backing plate with a lock washer and hex nut on each of the bolt ends, as shown in the illustration.

6. Tighten the hex nuts **with your fingers only** so that the ISS is just secure enough on the pole for you to release your grip.
7. If you are in the Northern Hemisphere, rotate the ISS on the pole so that the solar panel is facing south; if you are in the Southern Hemisphere, rotate the ISS so that the solar panel is facing north. The more precisely the solar panels face due south or north, the more accurate your wind direction readings will be.

Note: Do not rely on a compass unless it is properly calibrated. In North America there can be up to 15° variation between true north and a raw compass reading.

8. When the ISS is properly oriented, tighten the hex nuts with a wrench. Do not exceed 96 inch-pounds (10.8 newton-meters) of torque.

Note: You can refer to the bubble level on the top of the ISS to make sure it is as level as possible.

Finishing the Installation

The wind vane is calibrated at the factory to be accurate when the solar panel is pointing south. If your solar panel does not point south, you must calibrate your console so that it displays accurate wind direction readings. In any case, you can also calibrate your console to fine-tune your station for greatest accuracy. Refer to your *Vantage Vue Console Manual* to calibrate your console.

Note: Calibration **must** be done if you are in the Southern Hemisphere, or if you are in the Northern Hemisphere and cannot install your ISS with the solar panel facing south.

Clearing Data Collected During Testing and Installation

Now that the ISS is mounted outside, any data that was collected and stored in the console during testing and mounting should be cleared.

To clear all the collected data on the console:

1. On the console, press **WIND** so that selection arrow appears adjacent to the wind data on the display. Confirm that wind speed is displayed on the compass rose.
2. Press **2ND**, then press and hold **CLEAR** for at least six seconds and until you see "CLEARING NOW" in the weather center.

Maintenance and Troubleshooting

Maintenance

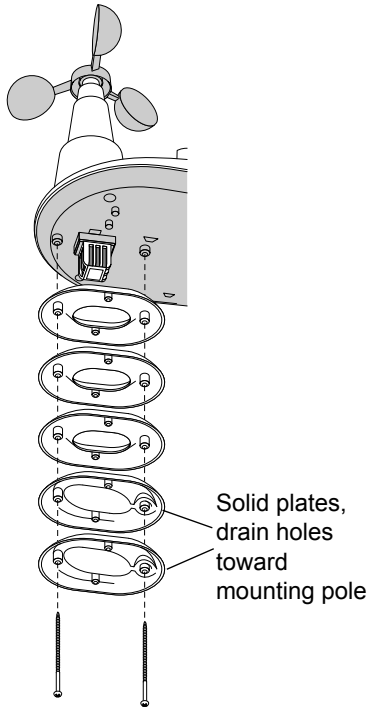
Cleaning the Radiation Shield

The outer surface of the radiation shield should be cleaned when there is excessive dirt and build-up on the plates. Use a damp cloth to clean the outer edge of each ring.

Note: Spraying down or using water excessively to clean the radiation shield can damage the sensitive sensors or alter the data the ISS is transmitting.

Check the radiation shield for debris or insect nests at least once a year and clean when necessary. A buildup of material inside the shield reduces its effectiveness and may cause inaccurate temperature and humidity readings.

1. Using a Phillips head screwdriver, loosen the two #6 x 2 $^1/_2$″ screws holding the five radiation shield plates together, as shown.
2. Taking care to maintain the order in which the five plates are assembled, separate the plates as shown and remove all debris from inside the shield.
3. Reassemble the plates in the same order in which they were disassembled, and fasten them together using a Phillips head screwdriver to tighten the #6 x 2 $^1/_2$″ screws, as shown.



Cleaning the Rain Collector, Debris Screen, and Tipping Spoon Module

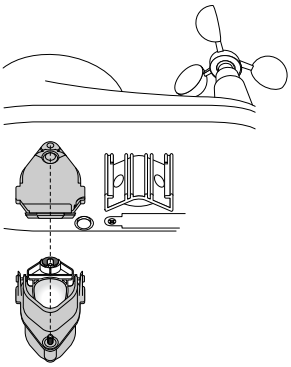
To maintain accuracy, thoroughly clean the rain collector cone and debris screen as needed or at least once a year.

Note: Cleaning the rain collector and tipping spoon may cause false rain readings. See “Clearing Data Collected During Testing and Installation” on page 10.

1. Use a damp, soft cloth to remove any debris from the rain collector and debris screen.
2. Use pipe cleaners to clear any debris remaining in the screen.
3. When all parts are clean, rinse with clear water.

To clean the tipping spoon assembly, it must first be removed from the ISS base.

1. Unscrew the thumbscrew securing the tipping spoon assembly to the ISS base. Slide the assembly down and away from the base.
2. Use a damp, soft cloth to gently remove any debris from the tipping spoon assembly, being careful not to damage any moving parts or scratch the spoon.
3. When all parts are clean, rinse with clear water, and replace the assembly. (See "Install the Rain Collector Tipping Spoon Assembly" on page 4.)



Troubleshooting

Troubleshooting ISS Reception

If the console isn't displaying data from the ISS:

1. Verify that the ISS and console are powered and that the console is not in Setup Mode. (See *Vantage Vue Console Manual*.)
2. Make sure that the ISS battery is properly installed.
3. Walk around the room with the console, standing for a few moments in various locations, to see if you are picking up signals from the ISS. Look on the screen below the wind compass rose for the small graphic of a radio antenna.

Note: If you do not see the antenna icon, press 2ND and SETUP to enter Setup Mode, then press DONE to return to the Current Weather Screen. The icon should appear.

4. Small "transmission waves" display above the antenna icon and toggle on and off when the console receives a transmission.

   If you do not see the antenna's transmission wave graphic slowly blinking, regardless of where you stand with the console, you should call Technical Support.
5. If the Transmitter ID LED does not light after pressing the Transmitter Pushbutton, there is a problem with the ISS transmitter. Call Technical Support.
6. If, after pressing the Transmitter Pushbutton, the Transmitter ID LED flashes every 2.5 seconds (indicating transmission) but your console isn't picking up a signal anywhere in the room, it could be related to one of the following causes:
   - You changed the ISS Transmitter ID at the ISS or console, but not at both.
   - Reception is being disrupted by frequency interference from outside sources, or the distance and barriers are too great.

Note: Interference has to be strong to prevent the console from receiving a signal while in the same room as the ISS.

   - There is a problem with the Vantage Vue console.
7. If a problem with receiving the wireless transmission still exists, please contact Technical Support.

Note: See "Contacting Davis Instruments" on page 13.

Problems Using Two Transmitting Stations

A single Vantage Vue console can receive signals from one ISS, either a Vantage Vue or a Vantage Pro2 ISS, and an optional anemometer transmitter kit. Make sure the transmitter IDs are configured correctly. See your *Vantage Vue Console Manual* for information on configuring transmitter IDs.

Most Common Rain Collector Problem

"My rain data seems too low."

If the rain collector seems to be under-reporting rainfall, clean the debris screen and tipping spoon module to clear out any debris.

Most Common Anemometer Problems

"The wind cups are spinning but my console displays 0 mph."

The wind cups may not be turning the shaft. Remove the cups from the anemometer by loosening the set screw. Put the cups back onto the shaft and make sure to slide them down the shaft as far as possible. Retighten the set screw.

"The wind cups don't spin or don't spin as fast as they should."

The anemometer may be located where wind is blocked by something, or there may be friction interfering with the cups' rotation. Remove the wind cups by loosening the set screw, and clear out any insects or debris which may be interfering with the cup rotation. Turn the shaft the cups rotate on. If it feels gritty or stiff, contact Davis Technical Support.

Note: Do not lubricate the shaft or bearings in any way.

"Readings aren't what I expected them to be."

Comparing data from your ISS to measurements from TV, radio, newspapers, or a neighbor is NOT a valid method of verifying your readings. Readings can vary considerably over short distances. How you site the ISS and anemometer can also make a big difference. If you have questions, contact Davis Technical Support.

Contacting Davis Instruments

If you have questions about the ISS or Vantage Vue system, or encounter problems installing or operating the weather station, please contact Davis Technical Support.

Note: Please do not return items to the factory for repair without prior authorization.

(510) 732-7814 – Technical Support phone, Monday – Friday, 7:00 a.m. – 5:30 p.m. Pacific Time.

(510) 670-0589 – Technical Support Fax.

support@davisnet.com – E-mail to Technical Support.

info@davisnet.com – General e-mail.

www.davisnet.com – Download manuals and specifications from the Support section. Watch for FAQs and other updates. Subscribe to the e-newsletter.

Appendix A: Specifications

See complete specifications for your Vantage Vue station on our website: www.davisnet.com

Integrated Sensor Suite (ISS) Specifications

Operating Temperature	-40° to +150°F (-40° to +65°C)
Non-operating (Storage) Temperature	-40° to +158°F (-40° to +70°C)
Current Draw (ISS SIM only)	0.20 mA (average), 30 mA (peak) at 3.3 VDC
Solar Power Panel (ISS SIM)	0.5 Watts / 0.75 Watts
Battery (ISS SIM)	CR-123 3-Volt Lithium cell
Battery Life (3-Volt Lithium cell)	8 months without sunlight - greater than 2 years depending on solar charging
Connectors, Sensor	Pogo Pins
Cable Type	6-conductor, 28 AWG
Wind Speed Sensor	Wind cups with magnetic switch
Wind Direction Sensor	Wind vane with magnetic encoder
Rain Collector Type	Tipping spoon, 0.01" per tip (0.2 mm with metric rain cartridge, Part No. 7345.319), 17.7 in^2 (114 cm^2) collection area
Temperature Sensor Type	PN Junction Silicon Diode
Relative Humidity Sensor Type	Film capacitor element
Housing Material	UV-resistant ABS & ASA plastic

Update Interval by Sensor		
BAR	Barometric Pressure	1 min.
HUMIDITY	Inside Humidity	1 min.
	Outside Humidity	50 sec.
	Dew Point	10 sec.
RAIN	Rainfall Amount	20 sec.
	Rain Storm Amount	20 sec.
	Rain Rate	20 sec.
TEMPERATURE	Inside Temperature	1 min.
	Outside Temperature	10 sec.
	Heat Index	10 sec.
	Wind Chill	10 sec.
WIND	Wind Speed	2.5 sec.
	Wind Direction	2.5 sec.
	Direction of High Speed	2.5 sec.

Vantage Vue™ Weather Station

6250 6357 6351

VANTAGE VUE™

The VantageVue™ (#6250) wireless weather station includes two components: the Integrated Sensor Suite (ISS) (#6357) which houses and manages the external sensor array, and the console (#6351) which provides the user interface, data display, and calculations. The Vantage Vue ISS and console communicate via an FCC-certified, license-free frequency-hopping transmitter and receiver. Frequency-hopping spread-spectrum (FHSS) technology provides greater communication strength over longer distances and areas of weaker reception. User-selectable transmitter ID codes allow up to eight stations to coexist in the same geographic area. (The Vantage Vue console can also receive and display data from any Vantage Pro2™ or Vantage Pro2 Plus ISS. The Vantage Pro2 Plus includes two additional sensors: the UV sensor and the solar radiation sensor.) The console may be powered by batteries or by the included AC-power adapter. The wireless ISS is solar-powered with a battery backup. Use WeatherLink™ for Vantage Vue to let your weather station interface with a computer, to log weather data, and upload weather information to the internet.

The Vantage Vue station relies on passive shielding to reduce solar-radiation induced temperature errors in the outside temperature sensor readings.

Integrated Sensor Suite (ISS)

Operating Temperature	-40° to +150°F (-40° to +65°C)
Non-operating (Storage) Temperature	-40° to +158°F (-40° to +70°C)
Current Draw	0.20 mA (average), 30 mA (peak) at 3.3 VDC
Solar Power Panel	0.5 Watts
Battery	CR-123 3-Volt Lithium cell
Battery Life (3-Volt Lithium cell)	8 months without sunlight - greater than 2 years depending on solar charging
Wind Speed Sensor	Wind cups with magnetic switch
Wind Direction Sensor	Wind vane with magnetic encoder
Rain Collector Type	Tipping spoon, 0.01" per tip (0.2 mm with metric rain cartridge, Part No. 7345.319), 18.0 in^2 (116 cm^2) collection area
Temperature Sensor Type	PN Junction Silicon Diode
Relative Humidity Sensor Type	Film capacitor element
Housing Material	UV-resistant ABS & ASA plastic
ISS Dimensions	12.95" x 5.75" x 13.40" (329 mm x 146 mm x 340 mm)
Package weight:	5.44 lbs (2.47 kg)

Console Specifications

Console Operating Temperature	+32° to +140°F (0° to +60°C)
Non-Operating (Storage) Temperature	+14° to +158°F (-10° or +70°C)
Console Current Draw	0.9 mA average, 30 mA peak, (add 120 mA for display lamps, add 0.125 mA for each transmitter station received by console) at 4.4 VDC
Power Adapter	5 VDC, 300 mA
Battery Backup	3 C-cells
Battery Life (no AC power)	Up to 9 months (approximately)
Housing Material	UV-resistant ABS plastic
Console Display Type	LCD Transflective
Display Backlight	LEDs
Dimensions:	
Console (with antenna)	7.5" x 5.75" x 4.5" (190 mm x 146 mm x 114 mm)
Console (with antenna) mounted on wall	7.5" x 7.0 " x 3.0" (190 mm x 178 mm x 76 mm)
Display	4.13" x 3.0" (105 mm x 76 mm)
Weight (with batteries)	1.48 lbs. (.67 kg)

DAVIS Davis Instruments 3465 Diablo Ave., Hayward, CA 94545-2778
(510) 732-9229 • FAX (510) 670-0589 • sales@davisnet.com • www.davisnet.com
DS6250, 6357, 6351 (Rev. B, 8/5/09)

Data Displayed on Console

Data display categories are listed with General first, then in alphabetical order.

General

Historical Data	Includes the past 25 values plus the current value listed unless otherwise noted; all can be cleared and all totals reset
Daily Data	Includes the earliest time of occurrence of highs and lows; period begins/ends at 12:00 am
Monthly Data	Period begins/ends at 12:00 am on the first of the month
Yearly Data	Period begins/ends at 12:00 am on the first of January unless otherwise noted
Current Data	Current data appears in the right most column in the console graph and represents the latest value within the last period on the graph; totals can be set or reset
Graph Time Interval	10 min., 1 hour, 1 day, 1 month, 1 year (user-selectable, availability depends upon variable selected) (2.5 seconds for Last 25 Wind Speeds)
Graph Time Span	26 Intervals (Current Interval plus 25 past values included; see Graph Intervals to determine time span)
Graph Variable Span (Vertical Scale)	Automatic (varies depending upon data range); Maximum and Minimum value in range appear in Weather Center
Alarm Indication	Alarms sound for only 2 minutes (except for time) if operating on battery power. Alarm message is displayed in Weather Center as long as threshold is met or exceeded. Alarms can be silenced (but not cleared) by pressing the DONE key.
Transmission Interval	Varies with transmitter ID code from 2.25 seconds (#1=shortest), to 3 seconds (#8=longest)
Update Interval	Varies with sensor - see individual sensor specs

Barometric Pressure

Resolution and Units	0.01" Hg, 0.1 mm Hg, 0.1 hPa/mb (user-selectable)
Range	16.00" to 32.50" Hg, 410 to 820 mm Hg, 540 to 1100.0 hPa/mb
Elevation Range	-999’ to +15,000’ (-600 m to +4660 m). (Note that console screen limits entry of lower elelvation to -999’ when using feet as elevation unit.)
Uncorrected Reading Accuracy	±0.03" Hg (±0.8 mm Hg, ±1.0 hPa/mb) (at room temperature)
Sea-Level Reduction Equations Used	United States Method employed prior to use of current "R Factor" method ("NOAA"), Altimeter Setting
NOAA Equation Source	Smithsonian Meteorological Tables
NOAA Equation Accuracy	±0.01" Hg (±0.3 mm Hg, ±0.3 hPa/mb)
NOAA Elevation Accuracy Required	±10’ (3m) to meet equation accuracy specification
Overall Accuracy	±0.03" Hg (±0.8 mm Hg, ±1.0 hPa/mb)
Trend (change in 3 hours)	Change 0.06" (2 hPa/mb, 1.5 mm Hg) = Rapidly Change 0.02" (.7hPa/mb, .5 mm Hg)= Slowly
Trend Indication	5 position arrow: Rising (rapidly or slowly), Steady, or Falling (rapidly or slowly)
Update Interval	1 minute
Current Data	Instant and Hourly Reading; Daily, Monthly, Yearly High and Low; Barometer change 24-hour
Historical Data	15-min. and Hourly Reading; Daily, Monthly Highs and Lows
Alarms	High Threshold from Current Trend for Storm Clearing (Rising Trend Low Threshold from Current Trend for Storm Warning (Falling Trend)
Range for Rising and Falling Trend Alarms	0.01 to 0.25" Hg (0.1 to 6.4 mm Hg, 0.1 to 8.5 hPa/mb)

Clock

Resolution	1 minute
Units	Time: 12 or 24 hour format (user-selectable)
Date	US or International format (user-selectable)
Accuracy	±8 seconds/month
Adjustments	Time: Automatic Daylight Savings Time (for users in North America and Europe that observe it in AUTO mode, MANUAL setting available for all other areas) Date: Automatic Leap Year
Alarms	Once per day at set time when active

Dewpoint (calculated)

Resolution and Units	1°F or 1°C (user-selectable)
Range	-105° to +130°F (-76° to +54°C)
Accuracy	±3°F (±1.5°C) (typical)
Update Interval	10 to 12 seconds
Source	World Meteorlogical Organization (WMO)
Equation Used	WMO Equation with respect to saturation of moist air over water
Variables Used	Instant Outside Temperature and Instant Outside Relative Humidity
Current Data	Instant Calculation; Daily, Monthly High and Low
Historical Data	Hourly Calculations; Daily, Monthly, Yearly Highs and Lows
Alarms	High and Low Threshold from Instant Calculation

Evapotranspiration (calculated, requires Vantage Pro2 ISS with solar radiation sensor)

Resolution and Units	0.01" or 0.2 mm (user-selectable)
Range	Daily to 32.67" (999.9 mm); Monthly & Yearly to 199.99" (1999.9 mm)
Accuracy	Greater of 0.01" (0.25 mm) or ±5%, Reference: side-by-side comparision against a CIMIS ET weather station
Update Interval	1 hour
Calculation and Source	Modified Penman Equation as implemented by CIMIS (California Irrigation Management Information System) including Net Radiation calculation
Current Data	Latest Hourly Total Calculation, Daily, Monthly, Yearly Total
Historical Data	Hourly, Daily, Monthly, Yearly Totals
Alarm	High Threshold from Latest Daily Total Calculation

Forecast

Variables Used	Barometric Reading & Trend, Wind Speed & Direction, Rainfall, Temperature, Humidity, Latitude & Longitude, Time of Year
Update Interval	1 hour
Display Format	Icons on top center of display; displays weather condtions that may occur for the next 12 hours.
Variables Predicted	Sky Condition, Precipitation

Heat Index (calculated)

Resolution and Units	1°F or 1°C (user-selectable)
Range	-40° to +165°F (-40° to +74°C)
Accuracy	±3°F (±1.5°C) (typical)
Update Interval	10 to 12 seconds
Source	United States National Weather Service(NWS)/NOAA
Formulation Used	Steadman (1979) modified by US NWS/NOAA and Davis Instruments to increase range of use
Variables Used	Instant Outside Temperature and Instant Outside Relative Humidity
Current Data	Instant Calculation; Daily, Monthly High
Historical Data	Hourly Calculations; Daily, Monthly, Yearly Highs
Alarm	High Threshold from Instant Calculation

Humidity

Inside Relative Humidity (sensor located in console)

Resolution and Units	1%
Range	0 to 100% RH
Accuracy	±3% (0 to 90% RH), ±4% (90 to 100% RH)
Update Interval	1 minute
Current Data	Instant (user adjustable) and Hourly Reading; Daily, Monthly High and Low
Historical Data	Hourly Readings; Daily, Monthly, Yearly Highs and Lows
Alarms	High and Low Threshold from Instant Reading

Outside Relative Humidity (sensor located in ISS)

Resolution and Units	1%
Range	0 to 100% RH
Accuracy	±3% (0 to 90% RH), ±4% (90 to 100% RH)
Temperature Coefficient	0.03% per °F (0.05% per °C), reference 68°F (20°C)
Drift	±0.5% per year

Update Interval	50 seconds to 1 minute
Current Data	Instant (user adjustable) and Hourly Reading; Daily, Monthly, Yearly High and Low
Historical Data	Hourly Readings; Daily, Monthly Highs and Lows
Alarms	High and Low Threshold from Instant Reading

Moon Phase

Console Resolution	1/8 (12.5%) of a lunar cycle, 1/4 (25%) of lighted face on console
WeatherLink Resolution	0.09% of a lunar cycle, 0.18% of lighted face maximum (depends on screen resolution)
Range	New Moon, Waxing Cresent, First Quarter, Waxing Gibbous, Full Moon, Wanning Gibbous, Last Quarter, Waning Cresent
Accuracy	±38 minutes

Rainfall

Resolution and Units	0.01" or 0.2 mm (user-selectable) (1 mm at totals ≥ 2000 mm)
Range	0 to 199.99" (0 to 6553 mm)
Rain Rate	0 to 40"/hr (0 to 1016 mm)
Accuracy	Greater of 4% or 1 tip
Storm Determination Method	0.02" (0.5 mm) begins a storm event, 24 hours without further accumlulation ends a storm event
Current Data	Totals for Past 15-min, Past 24-hour, Daily, Monthly, Yearly (start date user-selectable) and Storm (with begin date); Umbrella is displayed when 15 minute total exceeds zero
Historical Data	Totals for 15-min, Daily, Monthly, Yearly (start date user-selectable) and Storm (with begin and end dates)
Alarms	High Threshold from Latest Flash Flood (15-min. total, default is 0.50", 12.7 mm), 24-hour Total, Storm Total,
Range for Rain Alarms	0 to 99.99" (0 to 999.7 mm)

Rain Rate

Resolution and Units	0.01" or 0.2 mm (user-selectable) at typical rates (see Fig. 3 and 4)
Range	0, 0.04"/hr (1 mm/hr) to 40"/hr (0 to 1016 mm/hr)
Accuracy	±5% when rate is under 5"/hr (127mm/hr)
Update Interval	20 to 24 seconds
Calculation Method	Measures time between successive tips of rain collector. Elapsed time greater than 15 minutes or only one tip of the rain collector constitutes a rain rate of zero.
Current Data	Instant and Hourly, Daily, Monthly and Yearly High
Historical Data	Hourly, Daily, Monthly and Yearly Highs
Alarm	High Threshold from Instant Reading

Solar Radiation (requires Vantage Pro2 ISS with solar radiation sensor)

Resolution and Units	1 W/m^2
Range	0 to 1800 W/m^2
Accuracy	±5% of full scale (Reference: Eppley PSP at 1000 W/m^2)
Drift	up to ±2% per year
Cosine Reponse	±3% for angle of incidence from 0° to 75°
Temperature Coefficient	-0.067% per °F (-0.12% per °C); reference temperature = 77°F (25 °C)
Update Interval	50 seconds to 1 minute (5 minutes when dark)
Current Data	Instant Reading and Hourly Average; Daily, Monthly High

Sunrise and Sunset

Resolution	1 minute
Accuracy	±1 minute
Reference	United States Naval Observatory

Temperature

Inside Temperature (sensor located in console)

Resolution and Units	Current Data: 0.1°F or 1°F or 0.1°C or 1°C (user-selectable) Historical Data and Alarms: 1°F or 1°C (user-selectable)

Range	+32° to +140°F (0° to +60°C)
Sensor Accuracy	±1°F (±0.5°C)
Update Interval	1 minute
Current Data	Instant Reading (user adjustable); Daily, Monthly, Yearly High and Low
Historical Data	Hourly Readings; Daily and Monthly Highs and Lows; Highs and Lows for Last 25 Days; Temp change per hour, Temp chamge for last 24 hours.
Alarms	High and Low Thresholds from Instant Reading

Outside Temperature (sensor located in ISS)

Resolution and Units	Current Data: 0.1°F or 1°F or 0.1°C or 1°C (user-selectable) nominal (see Fig. 1) Historical Data and Alarms: 1°F or 1°C (user-selectable)
Range	-40° to +150°F (-40° to +65°C)
Sensor Accuracy	±1°F (±0.5°C) above +20°F (-7°C); ±2°F (±1°C)under +20°F (-7°C) (see Fig. 2)
Radiation Induced Error (Passive Shield)	+4°F (2°C) at solar noon (insolation = 1040 W/m^2, avg. wind speed ≤ 2 mph (1 m/s)) (reference: RM Young Model 43408 Fan-Aspirated Radiation Shield)
Update Interval	10 to 12 seconds
Current Data	Instant Reading (user adjustable); Daily, Monthly, Yearly High and Low
Historical Data	Hourly Readings; Daily, Monthly, Yearly Highs and Lows
Alarms	High and Low Thresholds from Instant Reading

Ultra Violet (UV) Radiation Index (requires Vantage Pro2 ISS with UV sensor)

Resolution and Units	0.1 Index
Range	0 to 16 Index
Accuracy	±5% of full scale (Reference: Yankee UVB-1 at UV index of 10 (Extremely High))
Cosine Reponse	±4% (0° to 65° incident angle); 9% (65° to 85° incident angle)
Update Interval	50 seconds to 1 minute (5 minutes when dark)
Current Data	Instant Reading

Wind

Wind Chill (Calculated)

Resolution and Units	1°F or 1°C (user-selectable)
Range	-110° to +135°F (-79° to +57°C)
Accuracy	±2°F (±1°C) (typical)
Update Interval	10 to 12 seconds
Source	United States National Weather Service (NWS)/NOAA
Equation Used	Osczevski (1995) (adopted by US NWS in 2001)
Variables Used	Instant Outside Temperature and 10-min. Avg. Wind Speed
Current Data	Instant Calculation; Hourly, Daily, Monthly, Yearly Low
Historical Data	Hourly, Daily and Monthly Lows
Alarm	Low Threshold from Instant Calculation

Wind Direction

Display Resolution	16 points (22.5°) on compass rose, 1° in numeric display
Range	0-360°
Accuracy	±3°
Update Interval	2.5 to 3 seconds
Current Data	Instant Reading (user adjustable); 10-min. Dominant; Hourly, Daily, Monthly Dominant
Historical Data	Past 6 10-min. Dominants on compass rose only; Hourly, Daily, Monthly Dominants

Wind Speed

Resolution and Units	1 mph, 1 km/h, 0.5 m/s, or 1 knot (user-selectable)
Range	2 to 150 mph, 2 to 130 knots, 1 to 67 m/s, 3 to 241 km/h
Update Interval	Instant Reading: 2.5 to 3 seconds, 10-minute Average: 1 minute
Accuracy	±2 mph (2 kts, 3 km/h, 1 m/s) or ±5%, whichever is greater
Current Data	Instant Reading; 10-minute and Hourly Average; 10-minute High Gust with Direction of Gust; 2-minute Average; Hourly High; Daily, Monthly and Yearly High with Direction of High; Beaufort Scale
Historical Data	2.5 sec., 10 min. and Hourly Averages; Hourly Highs; Daily, Monthly and Yearly Highs with Direction of Highs
Alarms	High Thresholds from Instant Reading and 10-minute Average

Wireless Communication Specifications

Transmit/Receive Frequency..... US Models: 902 - 928 MHz FHSS
Overseas Models: 868.0 -868.6 MHz FHSS

ID Codes Available 8

Output Power..... 902 - 928 MHz FHSS: FCC-certified low power, less than 8 mW, no license required
868.0 -868.6 MHz FHSS: CE-compliant, less than 8 mW, no license required

Range:

Line of Sight ..... up to 1000 feet (300 m)

Through Walls..... 200 to 400 feet (60 to 120 m)

Sensor Charts

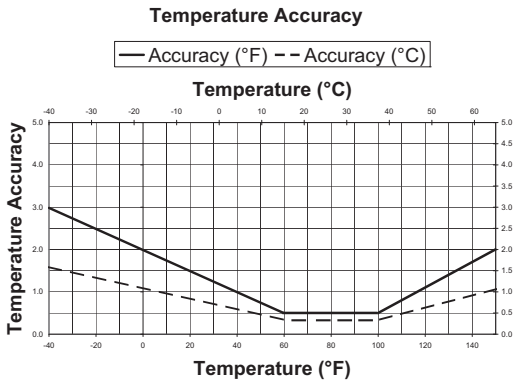


Figure 2. Temperature Accuracy

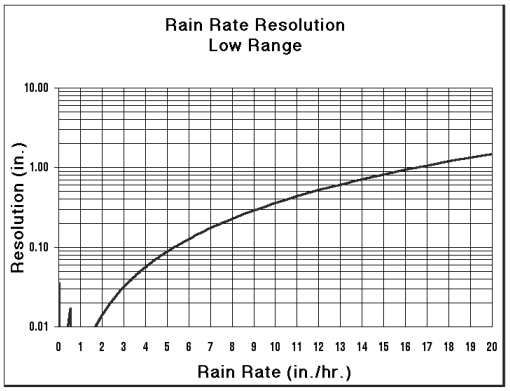


Figure 3. Low Range Rain Rate Resolution

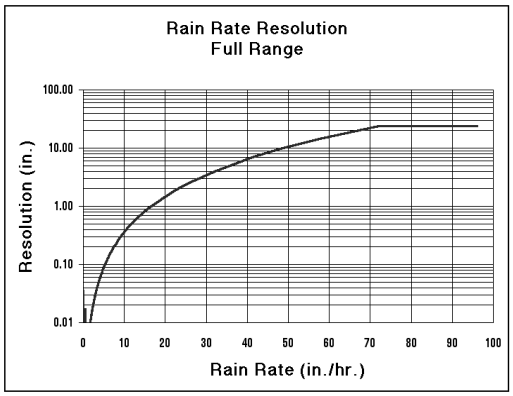


Figure 4. Full Range Rain Rate Resolution

Package Dimensions

Product #	Package Dimensions (Length x Width x Height)	Package Weight	UPC Codes
6250 Complete Station	18.25" x 7.25" x 15.25" (46.4 cm x 18.4 cm x 18.7 cm)	6.88 lbs (3.12 kg)	0 11698 00912 1
6351 Console	8.0" x 8.0" x 4.0" (20.3 cm x 20.3 cm x 10.1 cm)	1.76 lbs .80 kg	0 11698 00913 8
6357 ISS	18.25" x 7.25" x 15.25" (46.4 cm x 18.4 cm x 38.7 cm)	5.44 lbs (2.47 kg)	0 11698 00914 5

APPENDIX E
TISCH ENVIRONMENTAL TE-PUF OPERATIONS MANUAL

This page intentionally left blank.

Tisch Environmental, Inc.

OPERATIONS MANUAL

TE-PUF Poly-Urethane Foam
High Volume Air Sampler

145 South Miami Avenue
Village of Cleves, Ohio 45002

Toll Free: TSP AND - PM10
(877) 263 - 7610
Direct: (513) 467-9000
FAX: (513) 467-9009
Web Site: Tisch-Env.com
Email: sales@tisch-env.com

PREFACE

Tisch Environmental, Inc. is a third generation family owned business. The owners Wilbur J. Tisch and James P. Tisch have been involved in the High Volume Air Pollution field for the last 20 years. Started in March of 1998, they would like to welcome you to their company.

The intent of this manual is to instruct the user with unpacking, assembly, operating and calibration techniques. For information on air sampling principles, procedures and requirements please contact the local Environmental Protection Agency Office serving your area.

CONTENTS

INTRODUCTION

TE-PUF Poly-Urethane Foam sampler is a complete system designed to simultaneously collect suspended airborne particulates as well as trap airborne pesticide vapors at flow rates up to 280 liters per minute. The TE-PUF features the latest in technological advances for accurately measuring airborne particulates and vapors.

1. Samples semivolatile organic compounds.

2. Especially designed for sampling airbourne particulates and vapor contamination from pesticide compounds.

3. Successfully demonstrated to efficiently collect a number of organochlorine and organophosphate pesticides.

4. By-pass blower motor design permits continuous sampling for extended periods at rates to 280 liters per minute.

5. Proven sampler components housed in an anodized aluminum shelter for outdoor service.

6. Samples in accordance with U.S. EPA Method TO-4, " Method for the Determination of Organochlorine Pesticides and Polychlorinated Biphenyls in Ambient Air ".

A dual chambered aluminum sampling module contains both filtering systems. The upper chamber supports the airborne particulate filter media in a circular filter holder. The lower chamber encapsulates a glass cartridge which contains the PolyUrethane Foam for vapor entrapment.

A wide variety of sorbents can be used in a manner that permits their continual use. Poly urethane foam or wet/dry granular solid media can be used individually or in combination.The dual chambered sampling module is designed for easy access to both upper and lower media. The threaded lower canister is removed with the cartridge intact for immediate exchange. Filter support screens and module components are equipped with gaskets providing a leak proof seal during the sampling process. Air flow rates are infinitely variable up to 280 liters per minute. The voltage variator adjusting screw alters the blower motor speed to achieve the flow rate desired. Air flow rate is measured through the flow venturi utilizing a 0-100" Magnehelic Gage. Periodic calibration is necessary to maintain on-site sampling accuracy. A Seven Day Mechanical Timer (TE-5007) is included as standard equipment and permits weekly scheduling with individual settings for each day and 14 trippers to turn the sampler On and Off as desired. Any day or days may be omitted. Day and night periods are distinctly marked. Other timers and programmers are available optionally to suit any sampling requirement.

UNPACKING

1. Shelter Box - 46" x 20" x 22" 70 lbs

TE-1001	PUF Anodized Aluminum Shelter
TE-5007	7-Day Mechanical Timer
TE-1003	Flow Venturi & Calibration Valve
TE-5010	Motor Voltage Control
TE-1004	PUF Blower Motor Assembly
TE-1002	Dual Sampling Module
TE-1023	Exhaust Hose
TE-1005	Magnehelic Gauge

2. Lid Box - 19" x 14" x 14" 9 lbs

TE-5001-10	Gabled Roof

***** Save the shipping containers and packing material for future use.**

ASSEMBLY:

a. Open shelter box and remove Anodized Aluminum Shelter.

b. Inside of shelter is the exhaust hose. Unwrap and insert end with speed clamp on end of blower motor discharge. Tighten with a flat edge screwdriver and put end of hose down wind of sampler.

c. Enclosed in the 13" x 10" x 7" box on bottom of shelter is the TE-1002 Dual Sampling Module. Remove from box.

d. Take out rubber plug that is in quick disconnect on shelter. Insert Dual Sampling Module and lock in place by pushing rings down for a tight seal.

e. Take off cover that is on top of 4" filter holder. Turning motor on with cover in place will damage motor.

f. Open lid box and remove 5001-10 Roof.

Gabled Roof ASSEMBLY

Lid parts bag contents (taped inside of lid):

5 pcs 10-24 x 1/2 pan head screws
5 pcs 10-24 stop nuts
1 pc 6-32 x 3/8 pan head screw
1 pc 6-32 hex nut
1 pc 20" chain with “S” hook
1 pc TE-5001-10-9 roof back catch
1 pc TE-5001-10-10 front catch
1 pc TE-5001-10-11 rear lid hasp

1. Secure TE-5001-10-10 front catch to the shelter using 2 10-24 pan head screws with stop nuts.

2. Secure TE-5001-10-9 roof back catch to the back of shelter using 10-24 pan head screw with stop nut.

3. Secure TE-5001-10-11 rear lid hasp inside the lid with the slotted end angled up using 2 - 10-24 pan head screws with stop nuts.

   Note: These three items may need adjustment after the shelter lid is installed.

4. Remove 4 - 10-24 x 1/2 pan head screws from the nutserts in back of shelter.

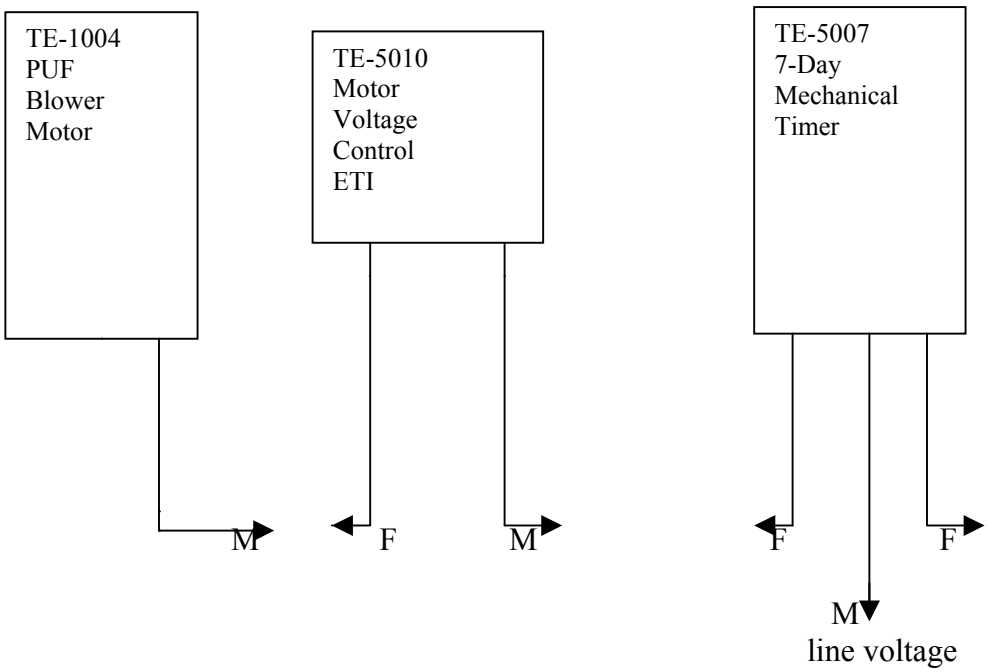
5. Attach the lid to the shelter by placing the lid hinge plates on the **"OUTSIDE"** of the shelter top and tighten the 4 - 10-24 x 1/2 pan head screws into the nutserts.

6. Adjust the front catch to be sure that the lid slot lowers over it when closing the lid. The rear lid hasp should align with the roof back catch when the lid is open.

7. Attach the chain and **"S"** hook assembly to the side of the shelter with a 6-32 pan head screw and nut.

8. The lid can now be secured in an open or closed position with the **"S"** hook.

ELECTRICAL HOOK-UP



The TE-1004 PUF Blower Motor male cord set plugs into the TE-5010 Motor Voltage Control Female cord set.

The male cord set of the Motor Voltage Control plugs into the TE-5007 7-Day Mechanical Timer timed female cord set which is on the left side of timer.

The other female cord set on timer (on the right) is hot all the time and is an extra plug.

The male cord set of timer plugs into the line voltage.

CALIBRATION REQUIREMENTS for TE-PUF Sampler

The TE-PUF Sampler should be calibrated:

1. Upon installation
2. After motor maintenance
3. At least once every three months
4. After 360 sampling hours

CALIBRATION PROCEDURE

Step 1: Calibration of the PUF Sampler is performed without a foam plug (TE-1010) or filter paper in the sampling module. However the empty glass cartridge must remain in the module to insure a good seal through the module.

Step 2: Install the TE-5040A Calibrator (orifice) on top of the 4" Filter Holder. Tighten and make sure of no leaks.

Step 3: Open both ports on top of manometer and connect tubing from manometer port to the pressure tap on the TE-5040A Calibrator. Leave the opposite side of manometer port open to the atmosphere.

Step 4: Open ball valve fully (handle should be straight up), this is located inside of shelter directly above the blower motor.

Step 5: Turn the system on by tripping the manual switch on the timer. Allow a few minutes for motor to warm-up.

Step 6: Adjust and tighten the voltage control screw (variac) on the TE-5010 to obtain a reading of 70 inches on the dial of the Magnehelic Gage (or 80 whatever is desired). Do not change until completion of calibration.

Step 7: With 70 inches on the gage as your first calibration point, record this figure and the orifice manometer reading on your data sheet. To read a manometer one side goes up and one goes down, add both sides together, this is your inches of water.

Step 8: Close the ball valve slightly to readjust the dial gage down to 60 inches. Record this figure and the orifice manometer reading on your data sheet.

Step 9: Using the above procedure, adjust the ball valve for readings at 50, 40, and 30 inches and record on data sheet. You should have 5 sets of numbers 10 numbers in all.

Step 10: Manually turn sampler off.

An example of a TE-PUF Sampler Calibration Data Sheet has been attached with data filled in from a typical calibration. This includes the transfer standard orifice calibration relationship which was taken from the Orifice Calibration Worksheet that accompanies the calibrator orifice. Since this calibration is for a PUF sampler, the slope and intercept for this orifice uses **standard** flows rather than actual flows.

The five orifice manometer readings taken during the calibration have been recorded in the column on the data worksheet titled H_2O (in). The five Magnehelic Gage readings taken during the calibration have been recorded under the column titled FLOW (magn).

The orifice manometer readings need to be converted to the standard air flows they represent using the following equation:

$$\mathbf{Qstd = 1/m[Sqrt((H_20)(Pa/760)(298/Ta))-b]}$$

where: Qstd = actual flow rate as indicated by the calibrator orifice, m^3/min
H_20 = orifice manometer reading during calibration, in. H_20
Ta = ambient temperature during calibration, K (K = 273 + °C)
298 = standard temperature, a constant that never changes, K
Pa = ambient barometric pressure during calibration, mm Hg
760 = standard barometric pressure, a constant that never changes, mm Hg
m = *Qstandard slope of orifice* calibration relationship
b = *Qstandard intercept of orifice* calibration relationship.

Once these standard flow rates have been determined for each of the five run points, they are recorded in the column titled Qstd, and are represented in cubic meters per minute.

The Magnehelic Gage readings taken during the calibration need to be corrected to the current meteorological conditions using the following equation:

$$\text{FLOW (corrected)} = \mathbf{Sqrt((magn)(Pa/760)(298/Ta))}$$

where: FLOW (corrected) = Magnehelic Gage readings corrected to current Ta and Pa
magn = Magnehelic Gage readings during calibration
Pa = ambient barometric pressure during calibration, mm Hg
760 = standard barometric pressure, a constant, mm Hg
Ta = ambient temperature during calibration, K (K = 273 + °C)
298 = standard temperature, a constant, K

After each of the Magnehelic Gage readings have been corrected, they are recorded in the column titled FLOW (corrected).

Using Qstd and FLOW (corrected) as the x and y axis respectively, a slope, intercept, and correlation coefficient can be calculated using the least squares regression method. The correlation coefficient should never be less than 0.990 after a five point calibration. A coefficient below .990 indicates a calibration that is not linear and the calibration should be performed again. If this occurs, it is most likely the result of an air leak during the calibration.

The equations for determining the slope (m) and intercept (b) are as follows:

$$m = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}} \quad ; \quad b = \bar{y} - m\bar{x}$$

where: n = number of observations
$\bar{y} = \Sigma y/n$; $\bar{x} = \Sigma x/n$
Σ = sum of.

The equation for the coefficient of correlation (r) is as follows:

$$r = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sqrt{\left[\sum x^2 - \frac{(\sum x)^2}{n}\right]\left[\sum y^2 - \frac{(\sum y)^2}{n}\right]}}$$

where: n = number of observations
Σ = sum of

If you wanted to set this sampler at .242 m^3/min (8.5 CFM or 242 LPM) (Make sure the ball valve is open fully, a 4" filter is in place, and the module is loaded) you would turn the voltage control screw or variac until the Magnehelic Gage read 60 inches. By making sure that the sampler is operating at a Magnehelic Gage reading that is within the acceptable range, it can be assumed that valid PUF data is being collected.

Example Problems

The following example problems use data from the attached calibration worksheet.

After all the sampling site information, calibrator information, and meteorological information have been recorded on the worksheet, standard air flows need to be determined from the orifice manometer readings taken during the calibration using the following equation:

1. **$Qstd = 1/m[Sqrt((H_20)(Pa/760)(298/Ta))-b]$**

where: Qstd = actual flow rate as indicated by the calibrator orifice, m^3/min
H_20 = orifice manometer reading during calibration, in. H_20
Ta = ambient temperature during calibration, K (K = 273 + °C)
298 = standard temperature, a constant that never changes, K
Pa = ambient barometric pressure during calibration, mm Hg
760 = standard barometric pressure, a constant that never changes, mm Hg
m = *Qstandard slope of orifice* calibration relationship
b = *Qstandard intercept of orifice* calibration relationship.

Note that the ambient temperature is needed in degrees Kelvin to satisfy the Qstd equation. Also, the barometric pressure needs to be reported in millimeters of mercury. In our case the two following conversions may be needed:

2. **degrees Kelvin = [5/9 (degrees Fahrenheit - 32)] + 273**

3. **millimeters of mercury = 25.4(inches of H_2O/13.6)**

Inserting the numbers from the calibration worksheet run point number one we get:

4. Qstd = 1/10.19[Sqrt((8.2)(635/760)(298/295)) - (-.03523)]

5. Qstd = .098[Sqrt((8.2)(.836)(1.01)) + .03523]

6. Qstd = .098[Sqrt(6.924) + .03523]

7. Qstd = .098[2.631 + .03523]

8. Qstd = .098[2.666]

9. Qstd = .261

Throughout these example problems you may find that your answers vary some from those arrived at here. This is probably due to different calculators carrying numbers to different decimal points. The variations are usually slight and should not be a point of concern.

With the Qstd determined, the corrected Magnehelic Gage reading FLOW (corrected) for this run point needs to be calculated using the following equation:

10. **FLOW (corrected) = Sqrt((magn)(Pa/760)(298/Ta))**

where: FLOW (corrected) = Magnehelic Gage readings corrected to standard
magn = Magnehelic Gage readings during calibration
Pa = ambient barometric pressure during calibration, mm Hg.
760 = standard barometric pressure, mm Hg
Ta = ambient temperature during calibration, K (K = 273 + °C)
298 = standard temperature, K.

Inserting the data from run point one on the calibration worksheet we get:

11. FLOW (corrected) = Sqrt((70)(635/760)(298/295))

12. FLOW (corrected) = Sqrt((70)(.836)(1.01))

13. FLOW (corrected) = Sqrt(59.105)

14. FLOW (corrected) = 7.69

This procedure should be completed for all five run points.

Using Qstd as our x-axis, and FLOW (corrected) as our y-axis, a slope, intercept, and correlation coefficient can be determined using the least squares regression method.

The equations for determining the slope (m) and intercept (b) are as follows:

15. $$m = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sum x^2 - \frac{(\sum x)^2}{n}} \quad ; \quad b = \bar{y} - m\bar{x}$$

where: n = number of observations
$\bar{y} = \Sigma y/n$; $\bar{x} = \Sigma x/n$
Σ = sum of.

The equation for the coefficient of correlation (r) is as follows:

16. $$r = \frac{\sum xy - \frac{(\sum x)(\sum y)}{n}}{\sqrt{\left[\sum x^2 - \frac{\left(\sum x\right)^2}{n}\right]\left[\sum y^2 - \frac{\left(\sum y\right)^2}{n}\right]}}$$

where: n = number of observations
Σ = sum of

Before these can be determined, some preliminary algebra is necessary. Σx, Σy, Σx^2, Σxy, $(\Sigma x)^2$, $(\Sigma y)^2$, n, $\bar{y}$, and $\bar{x}$ need to be determined.

17. $\Sigma x = .262 + .242 + .223 + .198 + .175 = 1.1$
18. $\Sigma y = 7.69 + 7.12 + 6.50 + 5.81 + 5.03 = 32.15$
19. $\Sigma x^2 = (.262)^2 + (.242)^2 + (.223)^2 + (.198)^2 + (.175)^2 = .246766$
20. $\Sigma y^2 = (7.69)^2 + (7.12)^2 + (6.50)^2 + (5.81)^2 + (5.03)^2 = 211.1375$
21. $\Sigma xy = (.262)(7.69) + (.242)(7.12) + (.223)(6.5) + (.198)(5.81) + (.175)(5.03) = 7.21795$
22. $n = 5$
23. $\bar{x} = \Sigma x/n = .22$
24. $\bar{y} = \Sigma y/n = 6.43$
25. $(\Sigma x)^2 = (1.1)^2 = 1.21$
26. $(\Sigma y)^2 = (32.15)^2 = 1033.6225$

Inserting the numbers:

27. $$\text{slope} = \frac{7.21795 - \frac{(1.1)(32.15)}{5}}{.246766 - \frac{1.21}{5}}$$

28. $$\text{slope} = \frac{7.21795 - \frac{(35.365)}{5}}{46766 - \frac{1.21}{5}}$$

29. $$\text{slope} = \frac{7.21795 - 7.073}{.246766 - .242}$$

30. $$\text{slope} = \frac{.14495}{.004766}$$

31. $\text{slope} = 30.41$

32. intercept = 6.43 - (30.41)(.22)

33. intercept = 6.43 - 6.69

34. intercept = -0.26

35. correlation coeff. =
$$\frac{7.21795 - \frac{(1.1)(32.15)}{5}}{\sqrt{\left[.246766 - \frac{(1.1)^2}{5}\right]\left[211.1375 - \frac{(32.15)^2}{5}\right]}}$$

36. correlation coeff. =
$$\frac{7.21795 - \frac{(35.365)}{5}}{\sqrt{[(.246766 - .242)]\ [(211.1375 - 206.7245)]}}$$

37. correlation coeff. =
$$\frac{(7.21795 - 7.073)}{\sqrt{[(.246766 - .242)][(211.1375 - 206.7245)]}}$$

38. correlation coeff. =
$$\frac{.14495}{\sqrt{(.004766)(4.413)}}$$

39. correlation coeff. =
$$\frac{.14495}{\sqrt{.0210323}}$$

40. correlation coeff. =
$$\frac{.14495}{.1450251}$$

41. correlation coeff. = .999

A calibration that has a correlation coefficient of less than .990 is not considered linear and should be re-calibrated. Since the correlation coeff. is > .990 , we have a good calibration.

Tisch Environmental Inc.
PUF SAMPLER CALIBRATION

SITE

Location-> Cleves, Ohio
Sampler-> TE-PUF
Date-> 7/98
Tech-> Jim Tisch

CONDITIONS

Sampler Elevation (feet)	5,000		
Sea Level Pressure (in Hg)	30.00	Corrected Pressure (mm Hg)	635
Temperature (deg F)	71	Temperature (deg K)	295
Seasonal SL Press. (in Hg)	30.00	Corrected Seasonal (mm Hg)	635
Seasonal Temp. (deg F)	71	Seasonal Temp. (deg K)	295

CALIBRATION ORIFICE

Make-> Tisch
Model-> TE-5040A
Serial#-> 4
Qstd Slope-> 10.19000
Qstd Intercept-> -0.03523
Date Certified-> 7-98

Plate or Test #	H2O (in)	CALIBRATION Qstd (m3/min)	FLOW (magn)	FLOW (corrected)	LINEAR REGRESSION
1	8.20	0.262	70.0	7.69	Slope = 30.3016
2	7.00	0.242	60.0	7.12	Intercept = -0.2288
3	5.90	0.223	50.0	6.50	Corr. coeff.= 0.9996
4	4.65	0.198	40.0	5.81	
5	3.60	0.175	30.0	5.03	

Calculations

$Qstd = 1/m[Sqrt(H2O(Pa/Pstd)(Tstd/Ta))-b]$
$Flow\ (corrected) = Sqrt((magn)(Pa/Pstd)(Tstd/Ta))$

Qstd = standard flow rate
Flow (magn)= reading off of magnehelic gauge
Flow (corrected)= corrected flow rate
m = calibrator Qstd slope
b = calibrator Qstd intercept
Ta = actual temperature during calibration (deg K)
Pa = actual pressure during calibration (mm Hg)
Tstd = 298 deg K
Pstd = 760 mm Hg
For subsequent calculation of sampler flow:
$1/m([Sqrt(magn)(Pav/760)(298/Tav)]-b)$

m = sampler slope
b = sampler intercept
(magn)= magnehelic reading
Tav = daily average temperature
Pav = daily average pressure

Tisch Environmental Inc.
PUF SAMPLER CALIBRATION

SITE

Location->
Sampler-> TE-PUF
Date->
Tech->

CONDITIONS

Sampler Elevation (feet)
Sea Level Pressure (in Hg)
Temperature (deg F)
Seasonal SL Press. (in Hg)
Seasonal Temp. (deg F)

Corrected Pressure (mm Hg)
Temperature (deg K)
Corrected Seasonal (mm Hg)
Seasonal Temp. (deg K)

CALIBRATION ORIFICE

Make-> Tisch
Model-> TE-5040A
Serial#->

Qstd Slope->
Qstd Intercept->
Date Certified->

Plate or Test #	H2O (in)	CALIBRATION Qstd (m3/min)	FLOW (magn)	FLOW (corrected)	LINEAR REGRESSION
1					
2					Slope =
3					Intercept =
4					Corr. coeff.=
5					

Calculations

Qstd = 1/m[Sqrt(H2O(Pa/Pstd)(Tstd/Ta))-b]
Flow (corrected)=Sqrt((magn)(Pa/Pstd)(Tstd/Ta))

Qstd = standard flow rate
Flow (magn)= reading off of magnehelic gauge
Flow (corrected)= corrected flow rate
m = calibrator Qstd slope
b = calibrator Qstd intercept
Ta = actual temperature during calibration (deg K)
Pa = actual pressure during calibration (mm Hg)
Tstd = 298 deg K
Pstd = 760 mm Hg
For subsequent calculation of sampler flow:
1/m([Sqrt(magn)(Pav/760)(298/Tav)]-b)

m = sampler slope
b = sampler intercept
(magn)= magnehelic reading
Tav = daily average temperature
Pav = daily average pressure

UNIT OPERATION

1. The PUF Sampler may be operated at ground level or on roof tops. In urban or congested areas, it is recommended that the sampler be placed on the roof of a single story building. The sampler should be located in an unobstructed area, at least two meters from any obstacle to air flow. The exhaust hose should be stretched out in a down wind direction if possible.

2. The sampler should be operated for 24 hours in order to obtain average daily levels of airborne pesticides.

3. On and off times and weather conditions during sampling periods should be recorded. Air concentrations may fluctuate with time of day, temperature, humidity, wind direction and velocity and other climatological conditions.

4. Magnehelic Gage readings should be taken at the beginning and end of each sampling period to obtain an average magnehelic gage reading.

5. Blower motor brushes should be inspected frequently and replaced before expending. An electrical source of 110 volts, 15 amps is required.

SAMPLING MODULE

1. Release the three (3) swing bolts on the 4" filter holder (FH-2104) and remove the triangle cover (cover must be off when sampler is **"ON"**) and hold down ring.

2. Install a clean 102mm dia. glass fiber filter on the support screen in between the teflon gaskets and secure it with the hold down ring and swing bolts.

3. Unscrew together the 4" filter holder and the sampling module cap leaving the module tube in place with the glass cartridge exposed.

4. Load the glass cartridge with foam and or foam/granular solids and replace in the module tube. Fasten the glass cartridge with the module cap and 4" filter holder assembly while making sure that the module assembly, 4" filter holder and all fittings are snug.

5. The glass cartridge and glass fiber filter should be removed from the sampler with forceps and clean gloved hands and immediately placed in a sealed container for transport to the laboratory. Similar care should be taken to prevent contamination of the filter paper and vapor trap (foam) when loading the sampler.

6. It is recommended to have two (2) sampling modules for each sampling system so that filter and foam exchange can take place in the laboratory.

DESCRIPTIONS OF SAMPLING MEDIA (SORBENTS)

1. Two types of sampling media are recommended for use with the PUF Sampler: polyurethane foams and granular solid sorbents. Foams may be used separately or in combination with granular solids. The sorbent may be extracted and reused (after drying) without unloading the cartridge.

2. Polyurethane Foam (PUF):

   Part number TE-1010 three inch plug is recommended. Also available are two inch (TE-1011) and one inch (TE-1012). This type of foam is white and yellows on exposure to light. Color does not effect the collection efficiency of the material.

3. Granular Solids:

   a. Porous (macroreticular) chromatography sorbents recommended. Pore sizes and mesh sizes must be selected to permit air flow rates of at least 200 liters/minute. Approximately 25 cm^3 of sorbent is recommended. The granular solids may be sandwiched between two layers of foam to prevent loss during sampling and extraction.

DETERMINATION OF FLOW RATE

To figure out the total volume of air that flowed through the PUF sampler during your sampling run take a set-up magnehelic gage reading (when you set the sampler up manually turn it on and take a magnehelic gage reading; in our example it should be 60 inches) and a pick-up reading (after the sample has been taken again manually turn sampler on and take a magnehelic gage reading; for our example let's say it read 54 inches). Take 60 + 54 = 114 114/2 = 57 so the magnehelic gage reading you would use is 57 inches. Put that into the formula (on bottom of worksheet):

1/m([Sqrt(magn)(Pav/760)(298/Tav)]- b)

m = sampler slope
b = sampler intercept
magn = average magnehelic gage reading
Tav = daily average temperature
Pav = daily average pressure
Sqrt = square root

Example:

m^3/min = 1/30.278([Sqrt(57)(727/760)(298/295)]-(-.2293))
m^3/min = .033 ([Sqrt(57)(.957)(1.01)] + .2293)
m^3/min = .033 ([Sqrt(55.094)] + .2293)
m^3/min = .033 ([(7.423)] + .2293)
m^3/min = .033 (7.423 + .2293)
m^3/min = .033 (7.652)
m^3/min = .253
lpm = 253

Total liters of air = lpm x 60 x hours that sampler ran

Let's say our sampler ran 23.3 hours
(end ETI reading - start ETI reading)

** Make sure ETI is in hours otherwise convert to hours **

Total liters of air = 253 x 60 x 23.3 = 353,694 liters of air

MAINTENANCE

A regular maintenance schedule will allow a monitoring network to operate for longer periods of time without system failure. Our customers may find the adjustments in routine maintenance frequencies are necessary due to the operational demands on their sampler(s). We recommend that the following cleaning and maintenance activities be observed until a stable operating history of the sampler has been established.

TE-PUF Sampler

The TE-PUF sampler should be routinely inspected and maintained as follows:

1. Power cords should be checked for crimps, cracks or exposed junctions each sample day. Do not allow power cords or outlets to be immersed in water; if necessary raise the cords above the ground by taping them to the shelter legs.

2. Inspect the TE-1002 Dual Sampling Module.

   a. Make sure all gaskets are sealing properly; replace if necessary.
   b. Clean any dirt that is built up around the module and filter holder.
   c. Make sure quick disconnect is working correctly by making a good seal.

TE-1004 Blower Motor Assembly

1. The motor assembly is durable and has a long life if maintained properly.
The routine maintenance required is:

   a. Inspecting and replacing the motor flange gasket and motor cushion routinely.

   b. Replacing the motor **TE-33384** carbon brushes every 400 to 500 hours of operation. It is imperative that the brushes be replaced before the brush shunt touches the motor commutator.

Totally expended brushes greatly reduce motor life!!

MOTOR BRUSH REPLACEMENT Model TE-PUF Sampler–Brush part #TE-33384 (220volt Brush part #TE-33378)

CAUTION: Ensure that all electrical power to the TE-PUF Sampler is disconnected prior to opening the motor housing. Unplug the motor power cord.

1. Remove the Motor Mounting Cover by removing the four bolts. This will expose the flange gasket and the motor. Turn motor over.

2. Remove ground wires from backplate and carefully lift the metal housing from the motor.

3. With a screwdriver carefully remove the plastic fan cover by prying in between brush and cover until both sides pop loose.

4. With a screwdriver carefully pry the brass quick disconnect tabs away from the expended brushes.

5. With a screwdriver remove brush holder and release **TE-33384** brushes.

6. With new **TE-33384** brushes, carefully slide quick disconnect tabs firmly into tab slot until seated.

7. Push brush carbon against commutator until plastic brush housing falls into place on commutator end bracket.

8. Replace brush holder clamps onto brushes.

9. Assemble motor after brush replacement: snap plastic fan cover back into place, feed ground wires back through backplate, put housing back on to motor, pull cord set back to normal postion, **** Make sure wires do not get smashed between metal ring and housing! **** fasten ground wires to backplate, turn motor over, tighten flange on top of housing and gasket.

****WARNING** Change Brushes Before Brush Shunt Touches Commutator !!**

MOTOR BRUSH SEATING PROCEDURE

CAUTION: Direct application of full voltage after changing brushes will cause arcing, commutator pitting, and reduce overall life.

To achieve best performance from new **TE-33384** brushes they must be seated on the commutator before full voltage is applied. After brush change apply 50% voltage for fifteen to twenty minutes to accomplish this seating. Use of **TE-5010** Flow Selector on system provides the reduced voltage for brush seating.

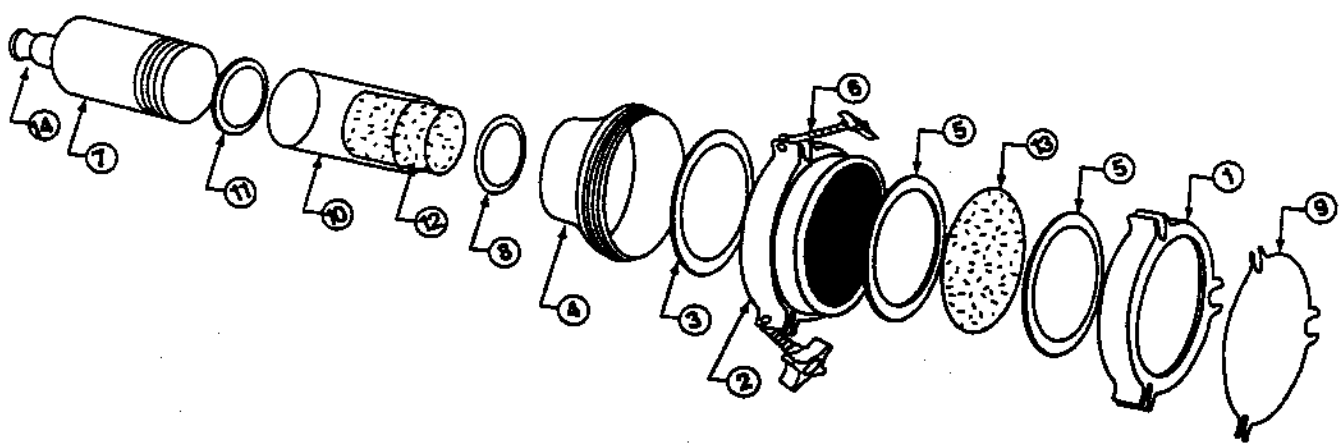
POLY URETHANE FOAM SAMPLER

TE-1000PUF **Poly-Urethane Foam Sampler For Pesticide Particulate/Vapor includes: anodized aluminum shelter, 4" particulate/vapor sampling module, flow venturi, blower motor assembly, magnehelic pressure gage, motor speed control/elapsed time indicator and 7-day mechanical timer Complete System**

	TE-1001	PUF Anodized Aluminum Shelter with Gabled Roof
	TE-1002	Particulate/Vapor Sampling Module Less Glass Cartridge
1)	TE-1008-1	4" Hold Down Frame
2)	TE-1008-2	4" Filter Holder Body w/ stainless steel screens
3)	TE-1008-8	Filter Holder Gasket (Silicone 4 1/2" OD)
4)	TE-1002-2	Module Reducer
5)	TE-1008-5	Teflon Gasket each (2 - Required)
6)	TE-1002-14	Plastic Thumb Nut, Brass Bolt, Washer and S/S Bolt Each (3 Required)
7)	TE-1002-3	Module Body
8)	TE-1002-6	Upper Module Gasket (Silicone 2 7/8")
9)	TE-1008-9	Aluminum Cover for 4" Filter Holder
10)	TE-1009	Glass Cartridge w/ stainless steel screens
11)	TE-1002-8	Lower Module Gasket (Silicone 2 9/16")
12)	TE-1010	3" Long Polyurethane Vapor Collection Substrate (unwashed) package of 10
	TE-1011	2" Long Polyurethane Vapor Collection Substrate (unwashed) package of 10
	TE-1012	1" Long Polyurethane Vapor Collection Substrate (unwashed) package of 10
13)	TE-QMA4	Micro-Quartz Filter Media 4" Round (100 per box)
14)	TE-1002-4	Module Plug Coupler
	TE-1008	4" Round Filter Holder Complete
	TE-1003	Flow Venturi & Calibration Value System
	TE-1003-1	Quick-Disconnect (Between Floor Flange & Module)
	TE-1003-1-1	Gasket for Quick Disconnect
	TE-1003-4	Flow Venturi
	TE-1003-6	Calibration Value
	TE-1005	Magnehelic Pressure Gage (0-100") of water
	TE-5010	Motor speed Voltage Control / Elapsed Time Indicator
	TE-5007	7-Day Mechanical Timer
	TE-1023	Exhaust Hose, 10 Ft. Length with Hose Clamp
	TE-5040	PUF Calibration Kit with calibration orifice, slack tube manometer, NIST traceable calibration certificate and carrying case.
	TE-5040A	PUF Calibration Orifice only with NIST traceable Calibration Certificate and tubing
	TE-P-RECAL	**Re-calibration of calibration orifice for PUF System (Required Annually)**

FLOW RECORDER FOR PUF SAMPLER

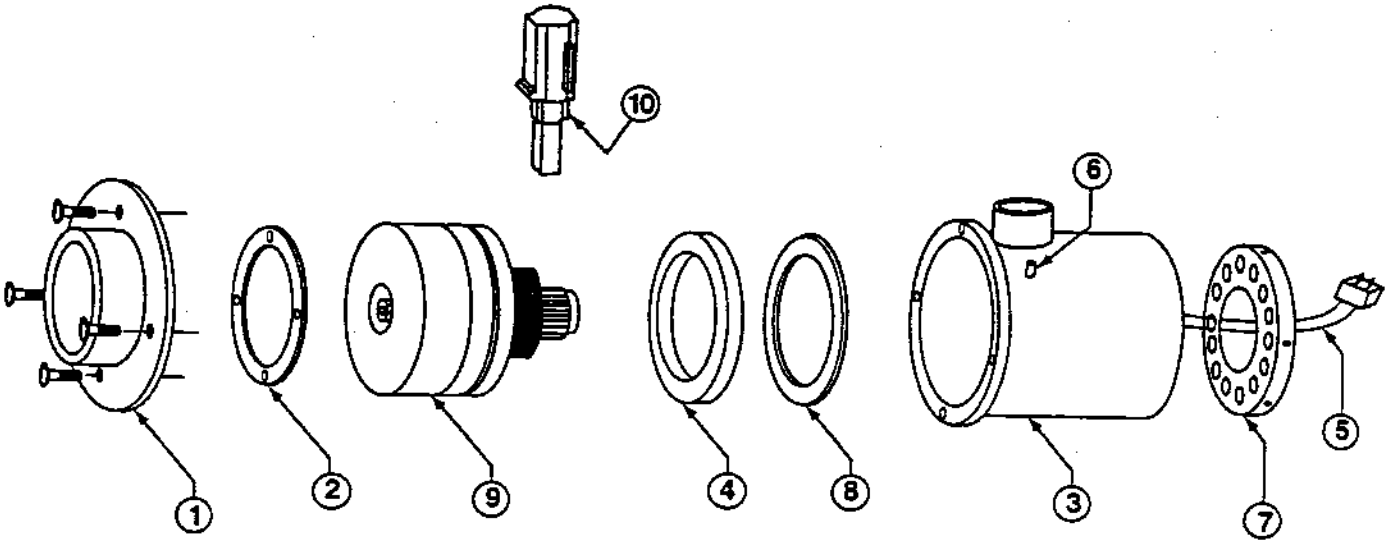
TE-33	Flow Recorder with 60 8" Charts
TE-10771	Recorder Charts 8" box of 60
TE-160	Recorder Pen Point



Tisch Environmental, Inc., Tel: 513-467-9000, Fax: 513-467-9009, E-Mail: sales@tisch-env.com, www.tisch-env.com

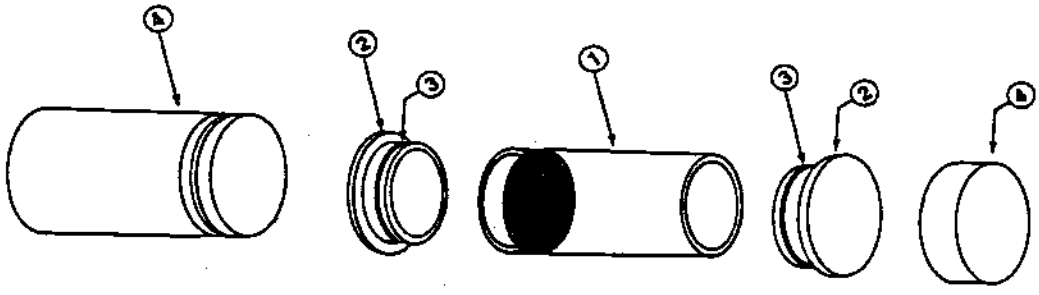
PUF BLOWER MOTOR ASSEMBLY

	TE-1004	PUF Blower Motor Assembly
1)	TE-1004-1	Blower Motor Flange
2)	TE-1004-2	Flange Gasket
3)	TE-1004-3	Blower Motor Housing with Integral side Exhaust
4)	TE-5005-4	Motor Cushion
5)	TE-5010-4	Power Cord
6)	TE-5005-8	Pressure Tap
7)	TE-1004-7	Back Plate
8)	TE-1004-8	Motor Spacer Ring
9)	TE-116336	Replacement Motor for 110V PUF Blower
	TE-116125	Replacement Motor for 220V PUF Blower
10)	TE-33384	Replacement Motor Brushes for 110V Motor TE-116336
	TE-33378	Replacement Motor Brushes for 220V Motor TE-116125



GLASS CARTRIDGE AND TEFLON END CAPS

1)	TE-1009	Glass Cartridge
2)	TE-1026	Teflon End Cap with Silicone "O" Ring each (2 - Required)
3)	TE-1026-1	Silicone End Cap "O" Ring each (2 - Required)
4)	TE-1027	Aluminum Screw top shipping Container



FLOW CONTROLLED PUF SAMPLING SYSTEM

TE-PNY1123	**Mass Flow Controlled PUF** PolyUrethane Foam Sampler including: 8"x10" stainless steel filter holder, 6" long spool piece with endcaps, motor assembly, 8" well type manometer, 7-day mechanical timer, filter media holder filter paper cartridge, elapsed time indicator, mass flow controller with 20 to 30 SCFM air flow probe and anodized aluminum shelter.
TE-1123-1	6" Long Spool Piece (To Hold Foam)
TE-1123-2	Female End Cap (For Spool Piece)
TE-1123-3	Male End Cap (For Spool Piece)
TE-1123-4	Foam 3" Long by 3 3/8" Diameter (Package of 10)

APPENDIX F
N-CON SYSTEMS COMPANY PRODUCT OVERVIEW

This page intentionally left blank.

Product Overview

ADS/NTN

Atmospheric Deposition Sampler

Wet only deposition collector Model 00-120-2

N-CON Systems Co., Inc.

Reliable and Valid Sample Collection: NADP approved for NTN Sites

Closed cover sealing sample collection container

Open cover resting on splash shield

- **Compact to minimize splash area**
- **Prompt opening and closing of sample container**
- **Does not "hunt" under marginal precipitation conditions**
- **Reliable, heavy duty cover drive motor**
- **Easy mounting**
- **Operates on 110VAC/220VAC or 12VDC**
- **Simple maintenance**
- **Plug & Play replacement parts**
- **Responsive to light snow, drizzle or heavy fog**

How the ADS/NTN works:

The infrared, optical precipitation sensor detects the onset of precipitation and uncovers the sample container within five (5) drops. Within two minutes, after precipitation stops, cover returns to sample container to minimize exposure to dry deposition. Sensor also detects drizzle, heavy fog or light snow, which may carry significant amounts of deposition.

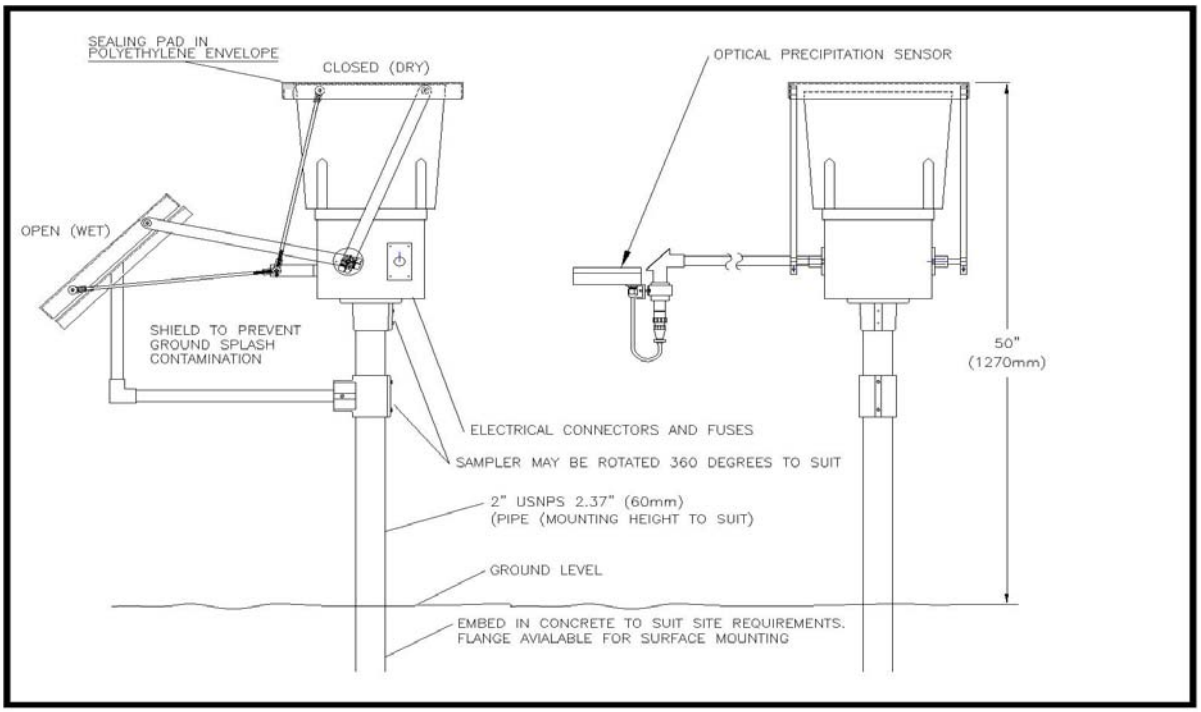
Collection of uncontaminated wet deposition samples is essential to precipitation chemistry validity. Compact design minimizes splash from exterior surfaces. In areas with high wind, the sampler may be fitted with an optional Alter Screen. The compression seal on the underside of the cover prevents leakage of dry deposition in to the container and retards sample evaporation. When the cover System is opened the underside is protected from ground splash by a shield that covers, but does not contact the seal.

Reliability is essential to the collection of valid samples. The ADS/NTN runs interchangeably on either line power (110VAC or 220VAC) or (12VDC) with an optional external power converter. Cover drive is rated for 20 years of typical service. All parts are easy to replace without special tools.

The ADS/NTN is mounted on a 2" NPS pipe by a socket secured with 2 set screws, so that it may be easily rotated.

The sampler also provides a 4 conductor cable to connect to an unpowered auxiliary contact that closes during precipitation events. This contact can operate a user furnished data logger and/or event recorder pen in a Belfort Universal Raingage. System will also interface with a variety of electronic, weighing rain gages.

A normally open contact is also provided for monitoring power continuity.



.Technical Specifications

SAMPLE CONTAINER:
NADP Type
Capacity: 3.5 US Gallons
Material: Rigid Polyethylene, with carrying handle
Cover: Snap-on lid with "O" ring seal
Furnished: 1 each

PRECIPITATION SENSOR:
Type: Infra-red transmitter and receiver
Opening: Within 5 drops of onset of precipitation
Closing: Within 2 minutes of end of precipitation

OUTPUT FOR DATA LOGGER OR EVENT RECORDER:
Two unpowered, normally open contacts
1 Contact is closed for the duration of sampling event
1 contact is closed to indicate power to system is on

DIMENSIONS:
16" (41cm) Wide
15" (38cm) Deep (less sensor)
24" (61cm) High

WEIGHT:
Net: 36 Pounds (16 Kg)
Shipping: 55 Pounds (25Kg.)

MOUNTING:
Direct mounting on 2" NPS pipe
(2.375 Dia. 68mm Dia.)
With mounting collar and set screws

MATERIALS OF CONSTRUCTION:
Control Housing:
Aluminum (5052H32) .125"
White polyester powder coat
Sample Container Cover:
Aluminum (5052H32) .090"
White polyester powder coat

OPTIONAL EXTRAS:
See Price List

N-CON Systems Company, Inc.
180 North Street ■ P.O. Box 809
Crawford, GA 30630 USA
(706) 743-8110 ■ (800) 932-6266 ■ Fax: (706) 743-8114
e-mail: nconsys@n-con.com website: www.n-con.com

Made in the United States by an American owned company

APPENDIX G
EPA METHOD TO-13A

This page intentionally left blank.

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.

Author(s)

- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC
- Greg Jungclaus, Midwest Research Institute, Kansas City, MO

Peer Reviewers

- Nancy Wilson, U.S. EPA, NERL, RTP, NC
- Joan Bursey, ERG, Morrisville, NC
- Irene D. DeGraff, Supelco, Bellefonte, PA
- 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.

This page intentionally left blank

METHOD TO-13A

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

TABLE OF CONTENTS

TABLE OF CONTENTS, CONTINUED

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

1. Dubois, L., Zdrojgwski, A., Baker, C., and Monknao, J.L., "Some Improvement in the Determination of Benzo[a]Pyrene in Air Samples," *J. Air Pollut. Contr. Assoc.*, 17:818-821, 1967.

2. Intersociety Committee, "Tentative Method of Analysis for Polynuclear Aromatic Hydrocarbon of Atmospheric Particulate Matter," *Health Laboratory Science*, 7(1):31-40, 1970.

3. Cautreels, W., and Van Cauwenberghe, K., "Experiments on the Distribution of Organic Pollutants Between Airborne Particulate Matter and Corresponding Gas Phase," *Atmos. Environ.*, 12:1133-1141, 1978.

4. "Tentative Method of Microanalysis for Benzo[a]Pyrene in Airborne Particles and Source Effluents," American Public Health Association, *Health Laboratory Science*, 7(1):56-59, 1970.

5. "Tentative Method of Chromatographic Analysis for Benzo[a]Pyrene and Benzo[k]Fluoranthene in Atmospheric Particulate Matter," American Public Health Association, *Health Laboratory Science*, 7(1):60-67, 1970.

6. "Tentative Method of Spectrophotometric Analysis for Benzo[a]Pyrene in Atmospheric Particulate Matter," American Public Health Association, *Health Laboratory Science*, 7(1):68-71, 1970.

7. Jones, P.W., Wilkinson, J.E., and Strup, P.E., *Measurement of Polycyclic Organic Materials and Other Hazardous Organic Compounds in Stack Gases: State-of-the-Art*, U. S. Environmental Protection Agency, Research Triangle Park, NC, U.S. EPA-600/2-77-202, 1977.

8. Walling, J.F., *Standard Operating Procedure for Ultrasonic Extraction and Analysis of Residual Benzo[a]Pyrene from Hi-Vol Filters via Thin-Layer Chromatography*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Methods Development and Analysis Division, Research Triangle Park, NC, EMSL/RTP-SOP-MDAD-015, December, 1986.

9. Rasor, S., *Standard Operating Procedure for Polynuclear Aromatic Hydrocarbon Analysis by High Performance Liquid Chromatography Methods*, Acurex Corporation, Research Triangle Park, NC, 1978.

10. Rapport, S. W., Wang, Y. Y., Wei, E. T., Sawyer, R., Watkins, B. E., and Rapport, H., "Isolation and Identification of a Direct-Acting Mutagen in Diesel Exhaust Particulates," *Envir. Sci. Technol.*, 14:1505-1509, 1980.

11. Konlg, J., Balfanz, E., Funcke, W., and Romanowski, T., "Determination of Oxygenated Polycyclic Aromatic Hydrocarbons in Airborne Particulate Matter by Capillary Gas Chromatography and Gas Chromatography/Mass Spectrometry," *Anal. Chem.*, 55:599-603, 1983.

12. Chuang, J. C., Bresler, W. E., and Hannan, S. W., *Evaluation of Polyurethane Foam Cartridges for Measurement of Polynuclear Aromatic Hydrocarbons in Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Methods Development and Analysis Division, Research Triangle Park, NC, EPA-600/4-85-055, September 1985.

13. Chuang, J. C., Hannan, S. W., and Koetz, J. R., *Stability of Polynuclear Aromatic Compounds Collected from Air on Quartz Fiber Filters and XAD-2 Resin*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Methods Development and Analysis Division, Research Triangle Park, NC, EPA-600/4-86-029, September 1986.

14. Feng, Y., and Bidleman, T. F., "Influence of Volatility on the Collection of Polynuclear Aromatic Hydrocarbon Vapors with Polyurethane Foam," *Envir. Sci. Technol.*, 18:330-333, 1984.

15. Yamasaki, H., Kuwata, K., and Miyamoto, H., "Effects of Ambient Temperature on Aspects of Airborne Polycyclic Aromatic Hydrocarbons," *Envir. Sci. Technol.*, 16:89-194, 1982.

16. Galasyn, J. F., Hornig, J. F., and Soderberg, R. H., "The Loss of PAH from Quartz Fiber High Volume Filters," *J. Air Pollut. Contr. Assoc.*, 34:57-59, 1984.

17. You, F., and Bidleman, T. F., "Influence of Volatility on the Collection of Polynuclear Aromatic Hydrocarbon Vapors with Polyurethane Foam," *Envir. Sci. Technol.*, 18:330-333, 1984.

18. Chuang, J. C., Hannan, S. W., and Koetz, J. R., *Comparison of Polyurethane Foam and XAD-2 Resin as Collection Media for Polynuclear Aromatic Hydrocarbons in Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Methods Development and Analysis Division, Research Triangle Park, NC, EPA-600/4-86-034, December 1986.

19. Chuang, J. C., Mack, G. A., Mondron, P. J., and Peterson, B. A., *Evaluation of Sampling and Analytical Methodology for Polynuclear Aromatic Compounds in Indoor Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Methods Development and Analysis Division, Research Triangle Park, NC, EPA-600/4-85-065, January 1986.

20. Lewis, R. G., Brown, A. R., and Jackson, M. D., "Evaluation of Polyurethane Foam for High-Volume Air Sampling of Ambient Levels of Airborne Pesticides, Polychlorinated Biphenyls, and Polychlorinated Naphthalenes," *Anal. Chem.*, 49:1668-1672, 1977.

21. Lewis, R. G., and Jackson, M. D., "Modification and Evaluation of a High-Volume Air Sampler for Pesticides and Other Semi-volatile Industrial Organic Chemicals," *Anal. Chem.*, 54:592-594, 1982.

22. Winberry, W. T., and Murphy, N. T., *Supplement to Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, NC, EPA-600/4-87-006, September 1986.

23. Winberry, W. T., and Murphy, N. T., *Second Supplement to Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, NC, EPA 600/4-89-018, June 1989.

24. *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, EPA-600/4-82-057, July 1982.

25. *ASTM Annual Book of Standards*, Part 31, D 3694, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.

26. Burke, J. A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48:1037, 1965.

27. Cole, T., Riggin, R., and Glaser, J., *Evaluation of Method Detection Limits: Analytical Curve for EPA Method 610 - PNAs*, 5th International Symposium on Polynuclear Aromatic Hydrocarbons, Battelle, Columbus, OH, 1980.

28. *Handbook of Analytical Quality Control in Water and Wastewater Laboratories*, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH, EPA-600/4-79-019, March 1979.

29. *ASTM Annual Book of Standards*, Part 31, D 3370, "Standard Practice for Sampling Water," American Society for Testing and Materials, Philadelphia, PA, p. 76, 1980.

30. *Protocol for the Collection and Analysis of Volatile POHC's (Principal Organic Hazardous Constituents) Using VOST (Volatile Organic Sampling Train)*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/8-84-007, March 1984.

31. *Sampling and Analysis Methods for Hazardous Waste Combustion - Methods 3500, 3540, 3610, 3630, 8100, 8270, and 8310; Test Methods for Evaluating Solid Waste* (SW-846), U.S. Environmental Protection Agency, Office of Solid Waste, Washington, D.C.

32. Riggin, R. M., *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, NC, EPA-600/4-84-041, April 1984.

33. Chuang, C. C., and Peterson, B. A., *Review of Sampling and Analysis Methodology for Polynuclear Aromatic Compounds in Air from Mobile Sources, Final Report*, U. S. Environmental Protection Agency, Research Triangle Park, NC, EPA-600/S4-85-045, August 1985.

34. *Measurement of Polycyclic Organic Matter for Environmental Assessment*, U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Research Triangle Park, NC, EPA-600/7-79-191, August 1979.

35. Hudson, J. L., *Standard Operating Procedure No. FA 113C: Monitoring for Particulate and Vapor Phase Pollutants Using the Portable Particulate/Vapor Air Sampler*, U.S. Environmental Protection Agency, Region VII, Environmental Monitoring and Compliance Branch, Environmental Services Division, Kansas City, KS, March 1987.

36. Trane, K. E., and Mikalsen, A., "High-Volume Sampling of Airborne Polycyclic Aromatic Hydrocarbons Using Glass Fibre Filters and Polyurethane Foam," *Atmos. Environ.*, 15:909-918, 1981.

37. Keller, C. D., and Bidleman, T. F., "Collection of Airborne Polycyclic Hydrocarbons and Other Organics with a Glass Fiber Filter - Polyurethane Foam System," *Atmos. Environ.*, 18:837-845, 1984.

38. Hunt, G. T., and Pangaro, N., "Ambient Monitoring of Polynuclear Aromatic Hydrocarbons (PAHs) Employing High Volume Polyurethane Foam (PUF) Samplers," In *Polynuclear Aromatic Hydrocarbons*, Cooke, M., Dennis, and A. J., Eds, Battelle Press, Columbus, OH, pp. 583-608, 1985.

39. Alfeim, I., and Lindskog, A., "A Comparison Between Different High Volume Sampling Systems for Collecting Ambient Airborne Particles for Mutagenicity Testing and for Analysis of Organic Compounds," *Sci. Total Environ.*, 34:203-222, 1984.

40. Umlauf, G., and Kaupp, H., "A Sampling Device for Semivolatile Organic Compounds in Ambient Air," *Chemosphere*, 27:1293-1296, 1993.

41. Hippelein, M., Kaupp, H., Dorr, G., and McLachlan, M. S., "Testing of a Sampling System and Analytical Method for Determination of Semivolatile Organic Chemicals in Air," *Chemosphere*, 26:2255-2263, 1993.

42. Ligocki, M. P., and Ponkow, J. F., "Assessment of Adsorption/Solvent Extraction with Polyurethane Foam and Adsorption/Thermal Desorption with Tenax-GC for Collection and Analysis of Ambient Organic Vapors," *Anal. Chem.*, 57:1138-1144, 1985.

43. Yamasaki, H., Kuwata, K., and Miyamoto, H., "Effects of Ambient Temperature on Aspects of Airborne Polycyclic Aromatic Hydrocarbons," *Envir. Sci. Technol.*, 16:189-194, 1982.

44. Hart, K. M., and Pankow, J. F., "High-Volume Air Sampler for Particle and Gas Sampling: Use of Backup Filters to Correct for the Adsorption of Gas-Phase Polycyclic Aromatic Hydrocarbons to the Front Filter," *Envir. Sci. Technol.*, 28:655-661, 1994.

45. Kaupp, H., and Umlauf, G., "Atmospheric Gas-Particle Partitioning of Organic Compounds: Comparison of Sampling Methods," *Atmos. Environ.*, 13:2259-2267, 1992.

46. Coutant, R. W., Brown, L., Chuang, J. C., Riggin, R. M., and Lewis, R. G., "Phase Distribution and Artifact Formation in Ambient Air Sampling for Polynuclear Aromatic Hydrocarbons," *Atmos. Environ.*, 22:403-409, 1988.

47. Coutant, R. W., Callahan, P. J., Kuhlman, M. R., and Lewis, R. G., "Design and Performance of a High-Volume Compound Annular Denuder," *Atmos. Environ.*, 23:2205-2211.

48. Lewis, R. G., Kelly, T. J., Chuang, J. C., Callahan, P. J., and Coutant, R. W., "Phase Distributions of Airborne Polycyclic Aromatic Hydrocarbons in Two U.S. Cities," In *Proceedings of the 9th World Clean Air Congress & Exhibition*, Montreal, Ontario, Canada, 1991, Vol., Paper IU-11E.02.

49. Kaupp, H., and Umlauf, G., "Atmospheric Gas-Particle Partitioning of Organic Compounds: Comparison of Sampling Methods," *Atmos. Environ.*, 26A:2259-2267, 1992.

50. Riggin, R. M., *Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air*, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Quality Assurance Division, Research Triangle Park, NC, EPA-600/4-83-027, June 1983.

51. *ASTM Annual Book of Standards*, Part 31, D 3694, "Standard Practice for Preparation of Sample Containers and for Preservation," American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.

52. *Carcinogens - Working with Carcinogens*, Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

53. *OSHA Safety and Health Standards, General Industry,* (29CFR1910), Occupational Safety and Health Administration, OSHA, 2206, Revised, January 1976.

54. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

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

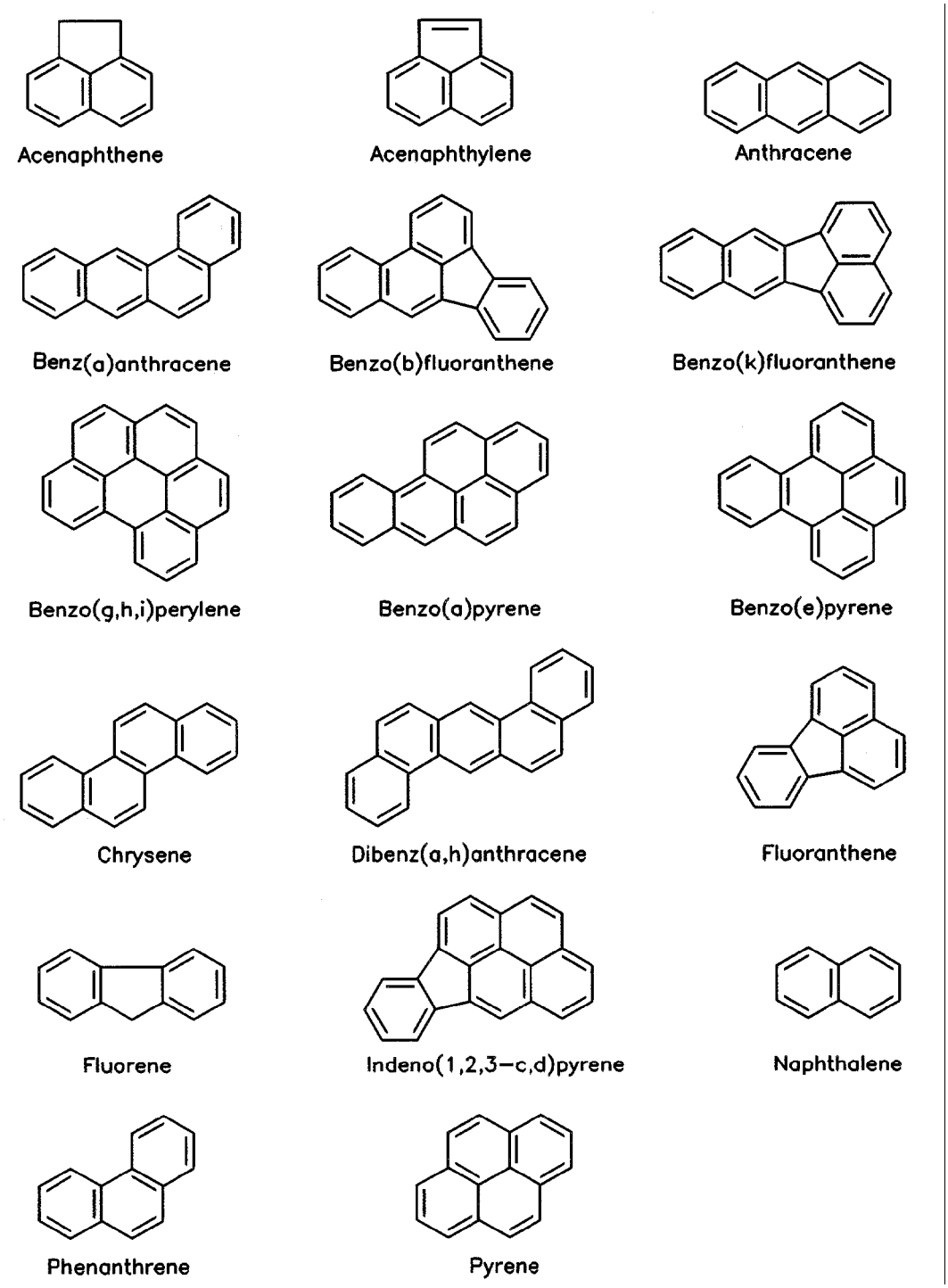


Figure 1. Ring structure of common PAHs.

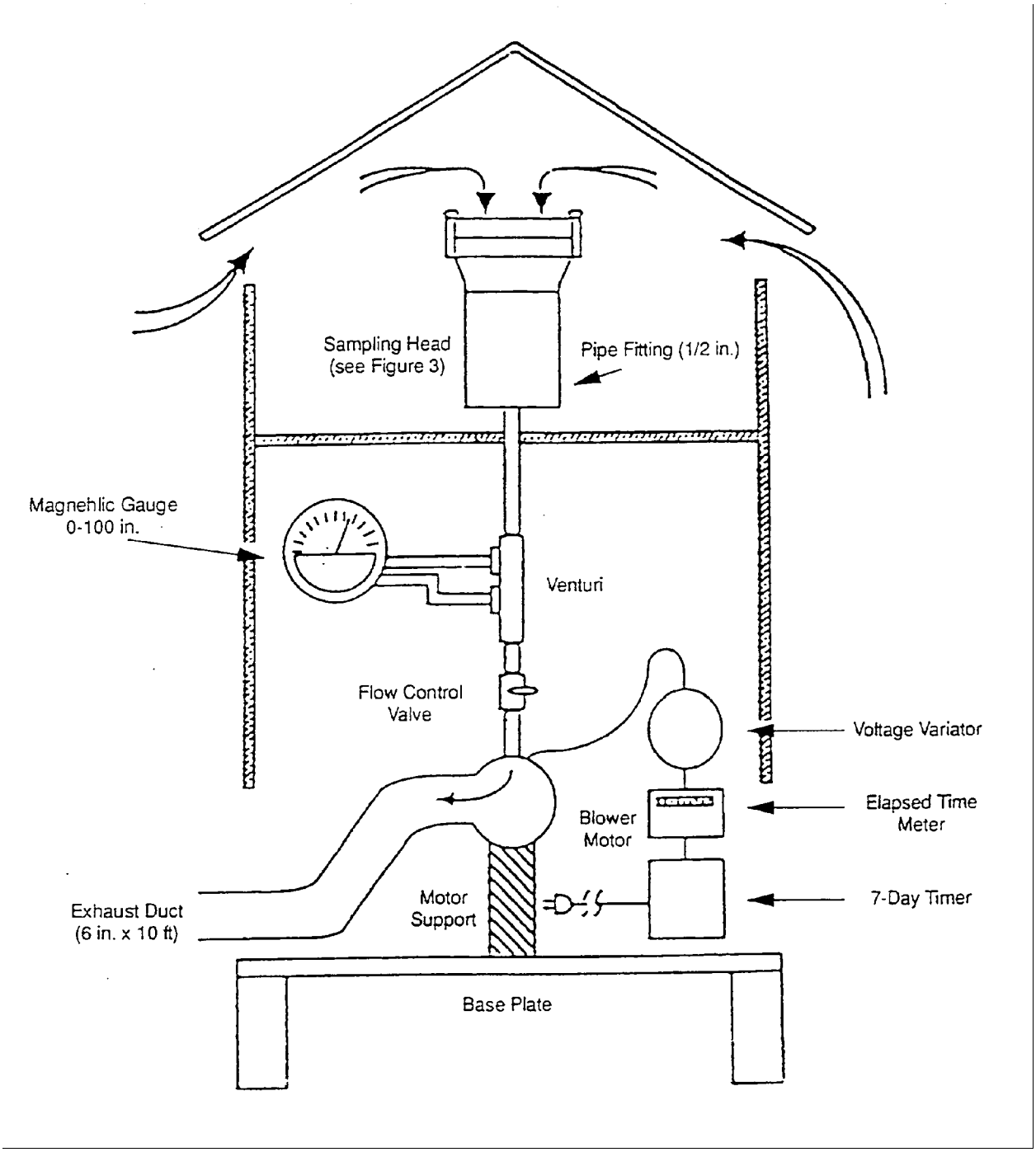


Figure 2. Typical high volume air sampler for PAHs.

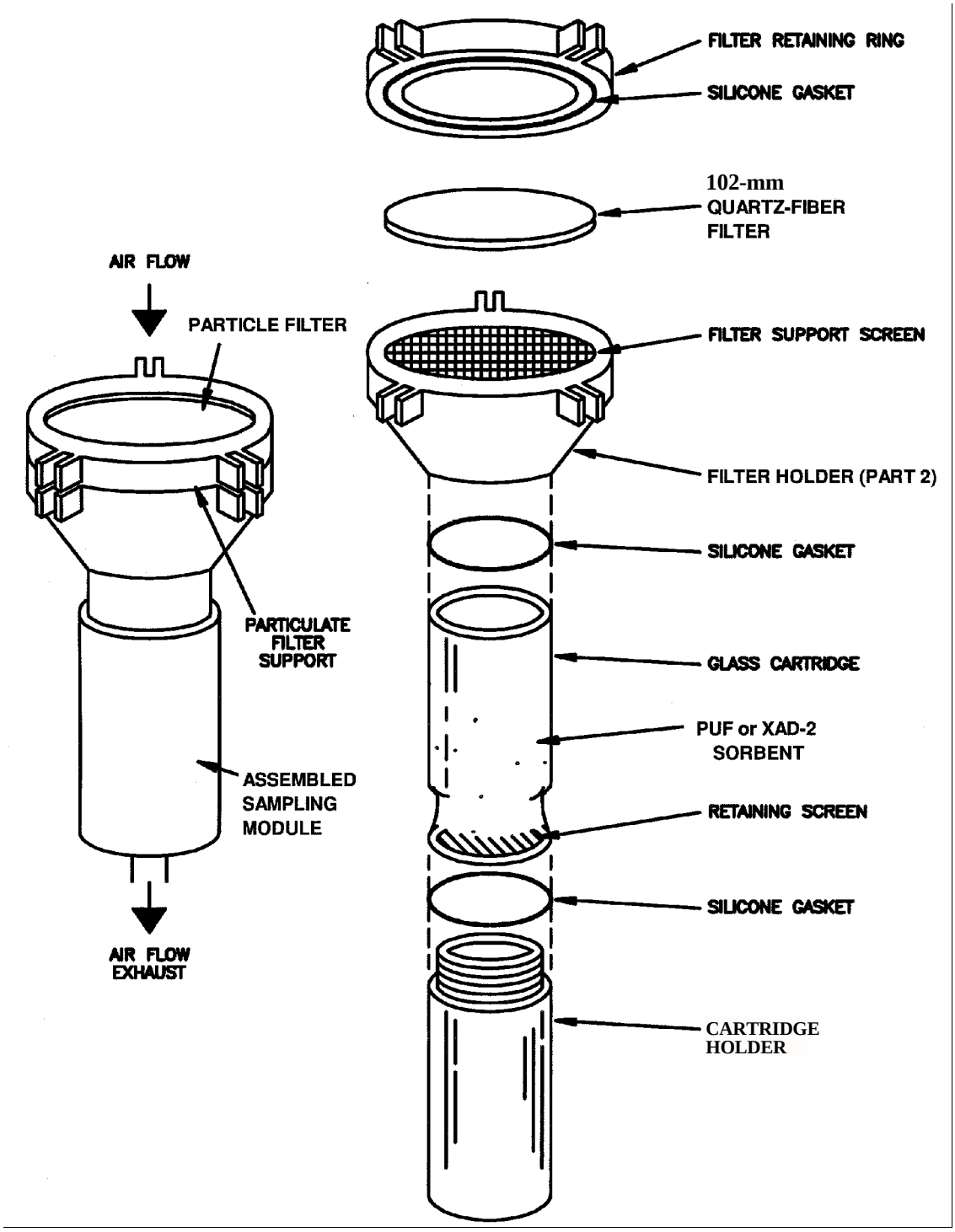


Figure 3. Typical absorbent cartridge assembly for sampling PAHs.

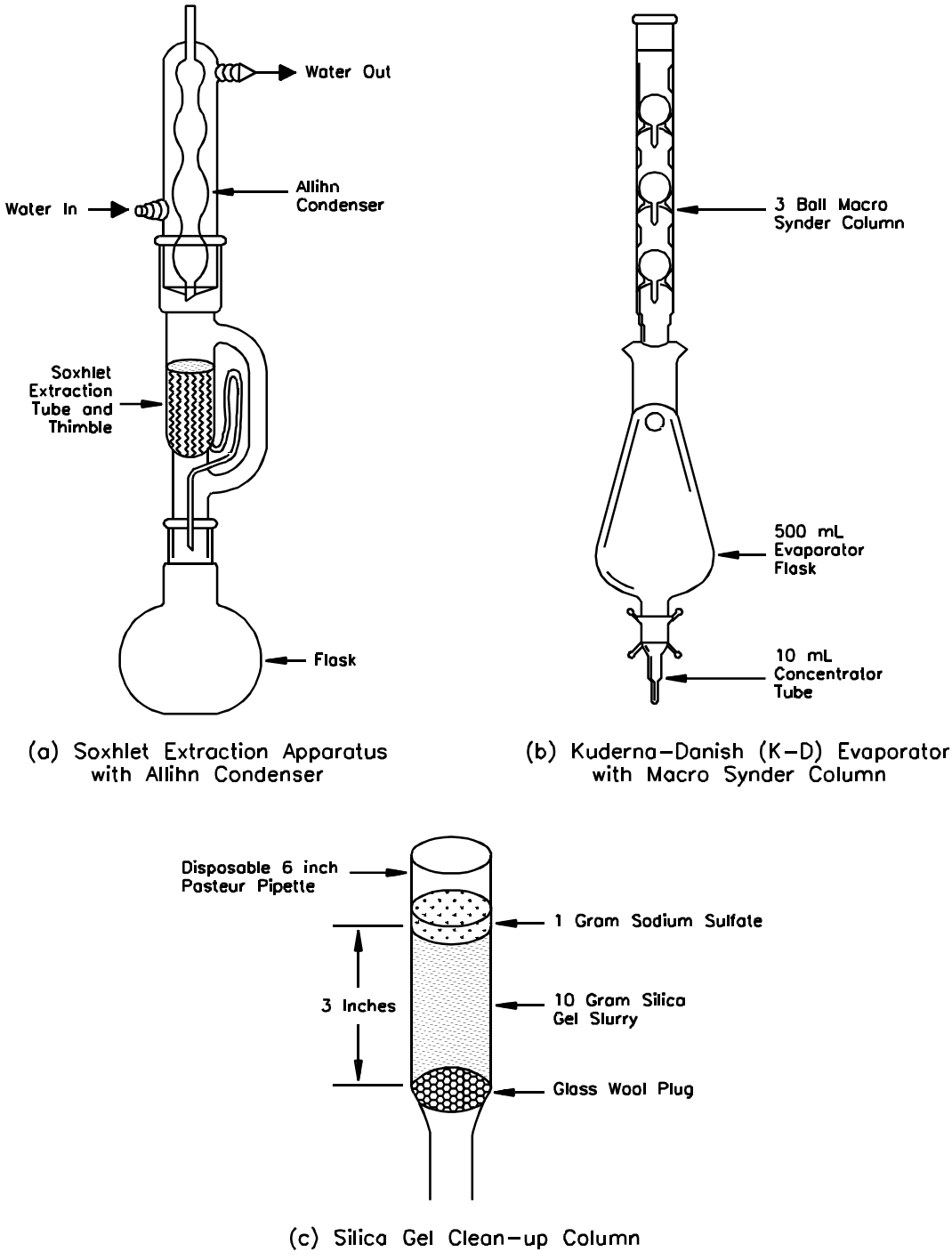
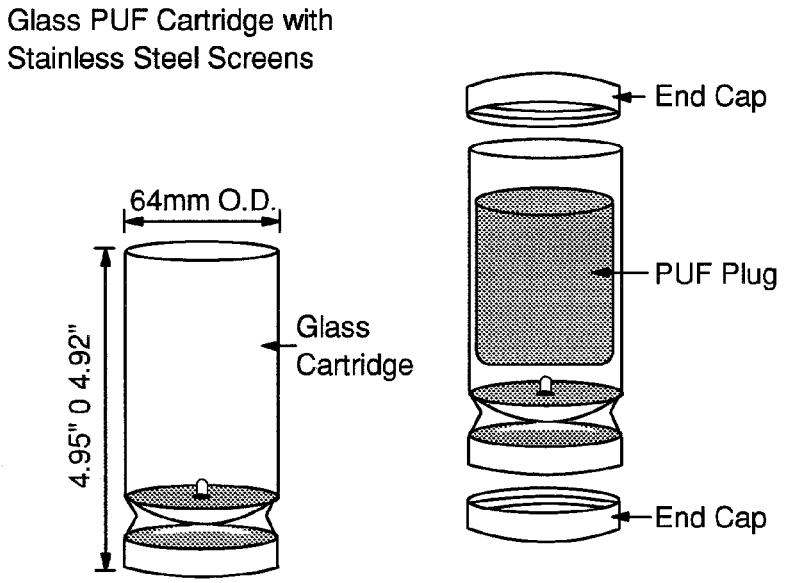
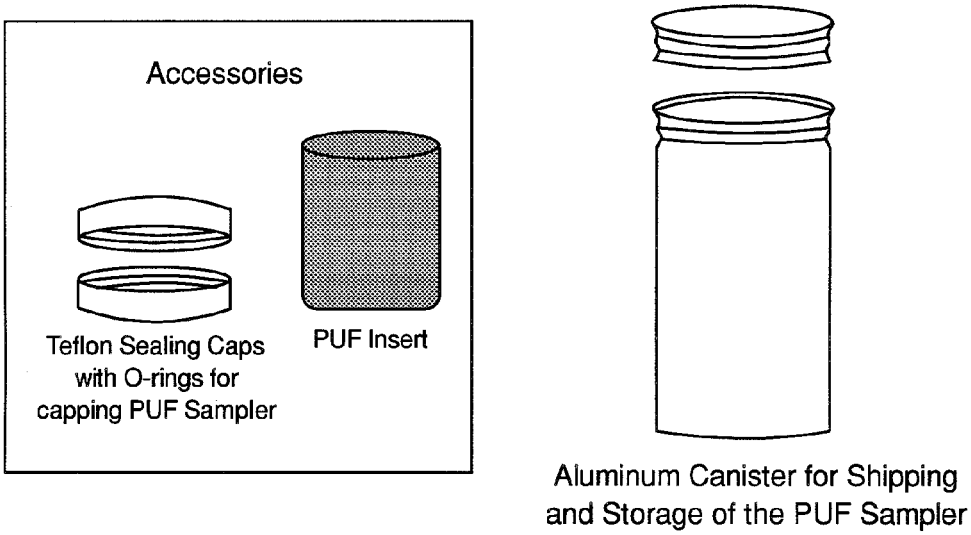


Figure 4. Apparatus used for sample clean-up and extraction.



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.

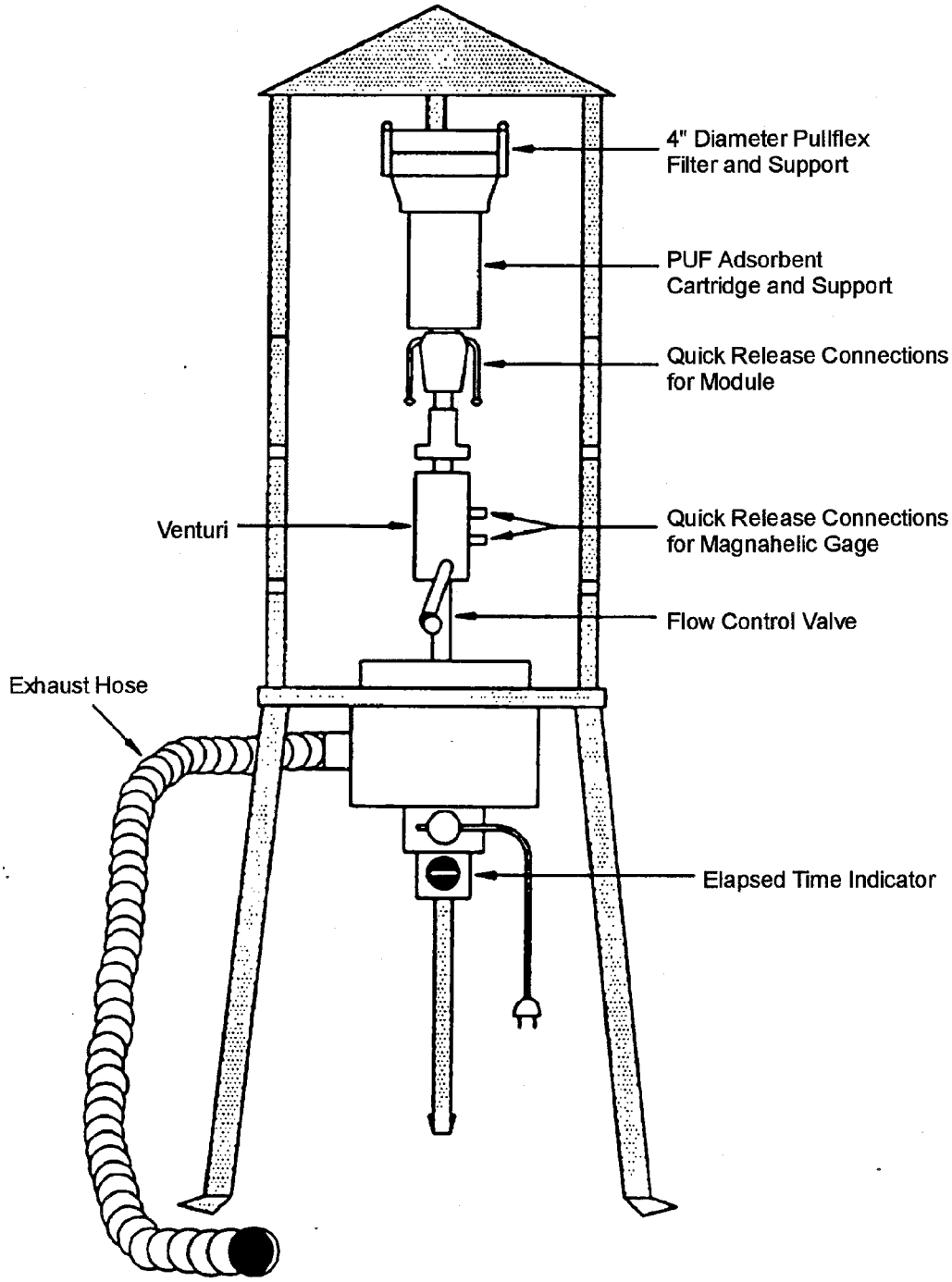


Figure 6. Example of a field portable high volume air sampler for sampling PAHs developed by EPA.

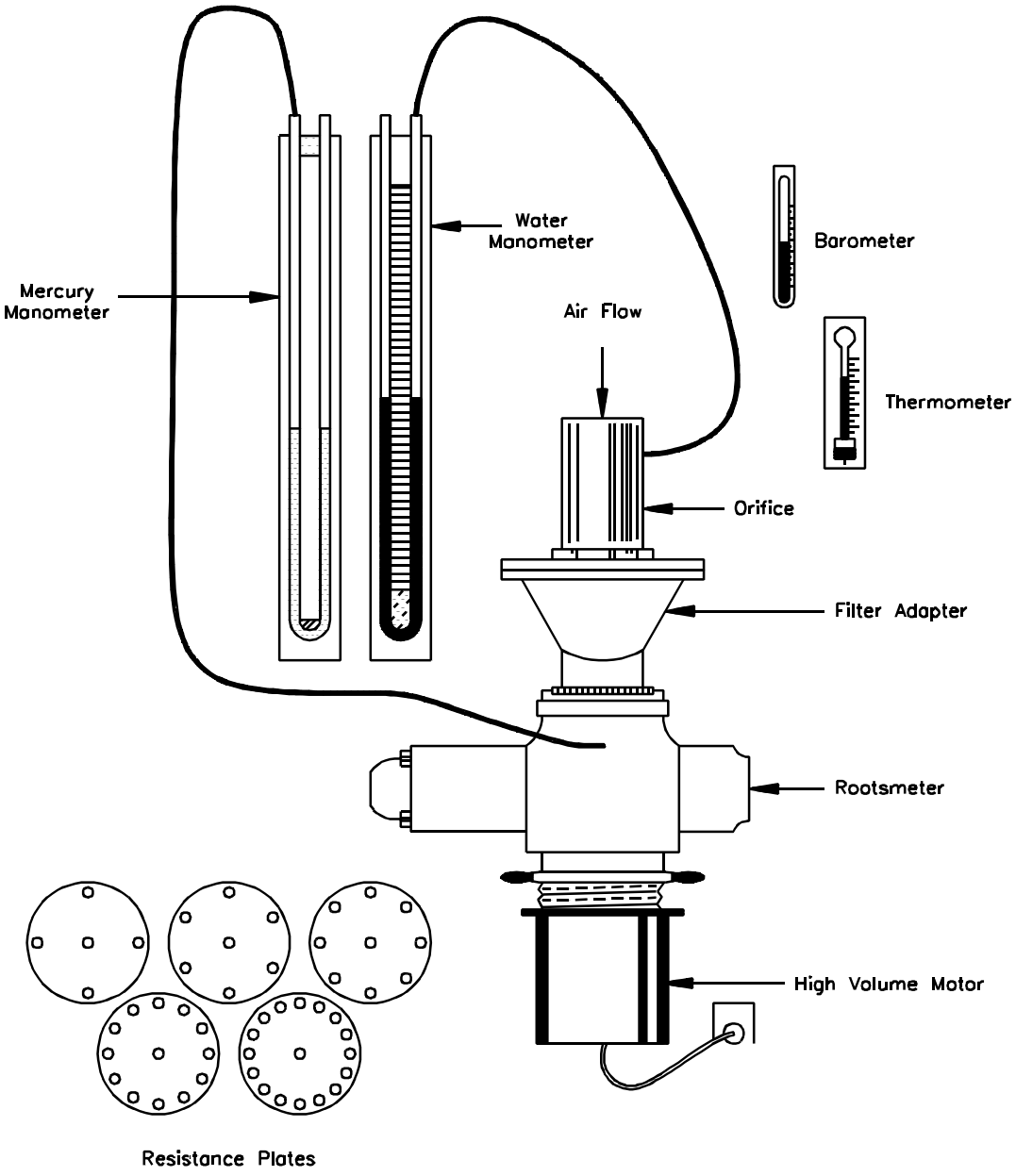


Figure 7. Positive displacement rootsmeter used to calibrate orifice transfer standard used in Compendium Method TO-13A.

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.

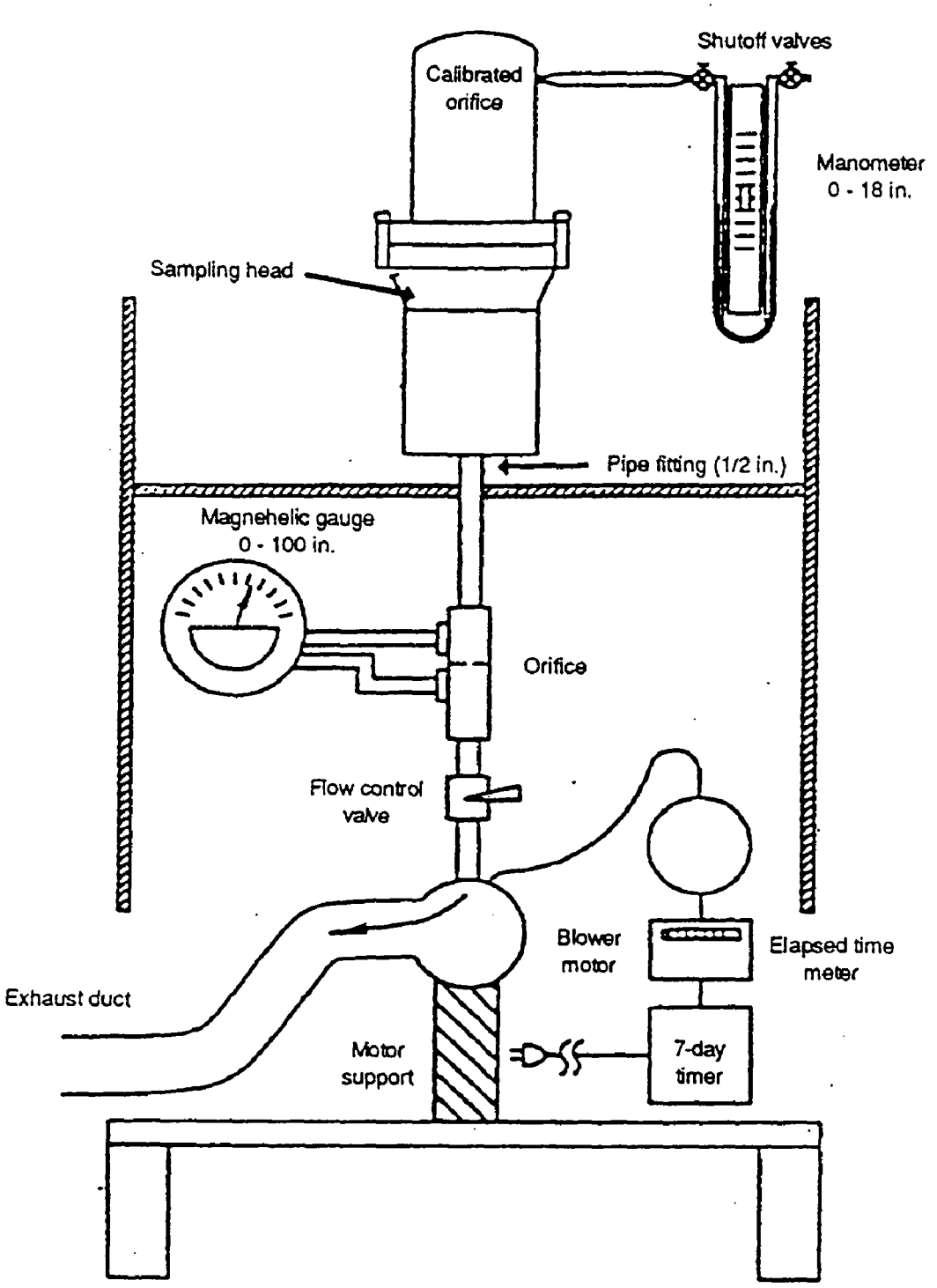


Figure 9. Typical field calibration configuration for Compendium Method TO-13A sampler.

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.

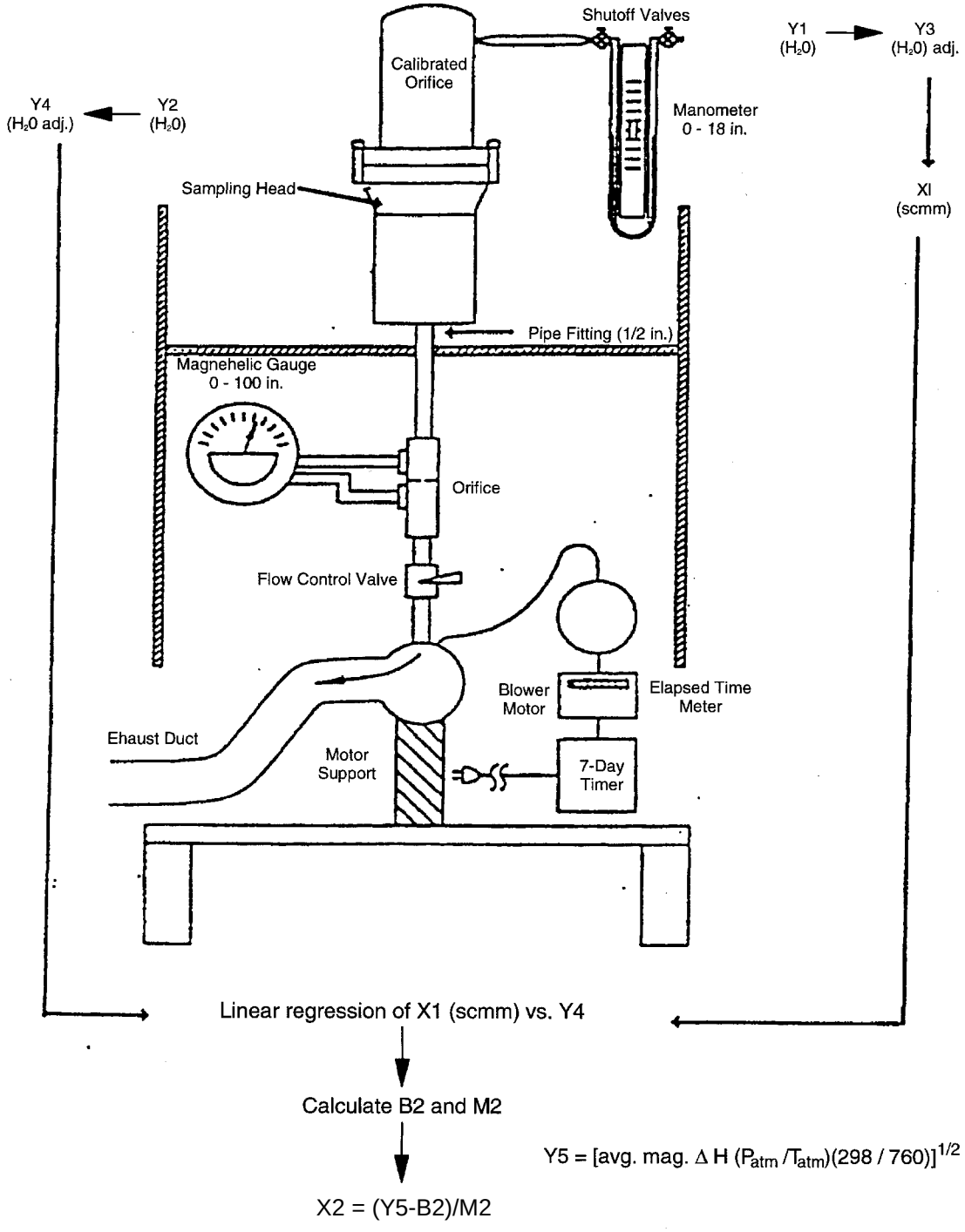


Figure 11. Example of relationship between orifice transfer standard and flow rate through Compendium Method TO-13A sampler.

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** _____	**Yes** _____
	No _____	**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).

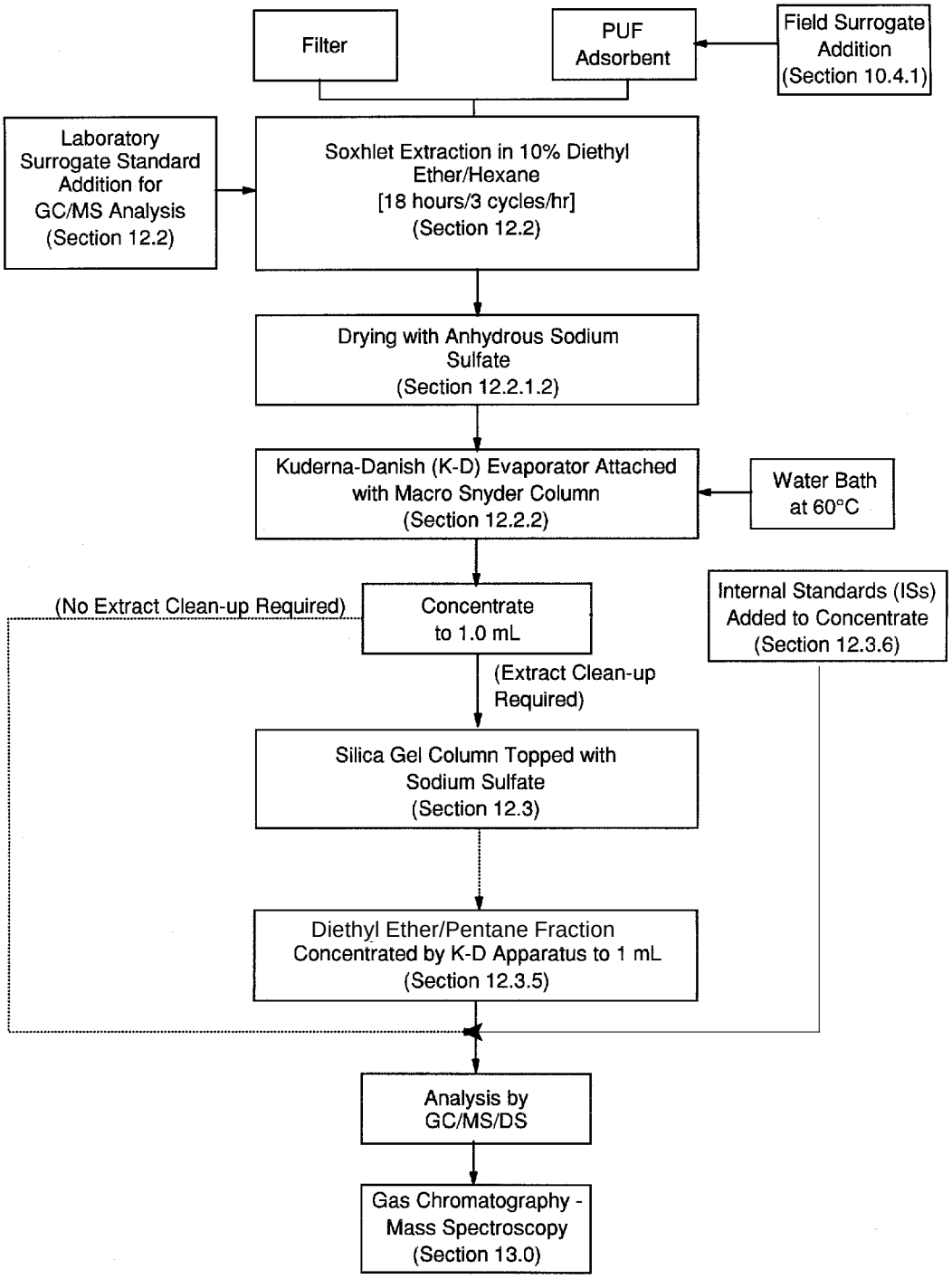


Figure 13. Sample clean-up, concentration, separation and analysis sequence for common PAHs.
[Note: XAD-2 sequence is similar to PUF except methylene chloride is the solvent.]

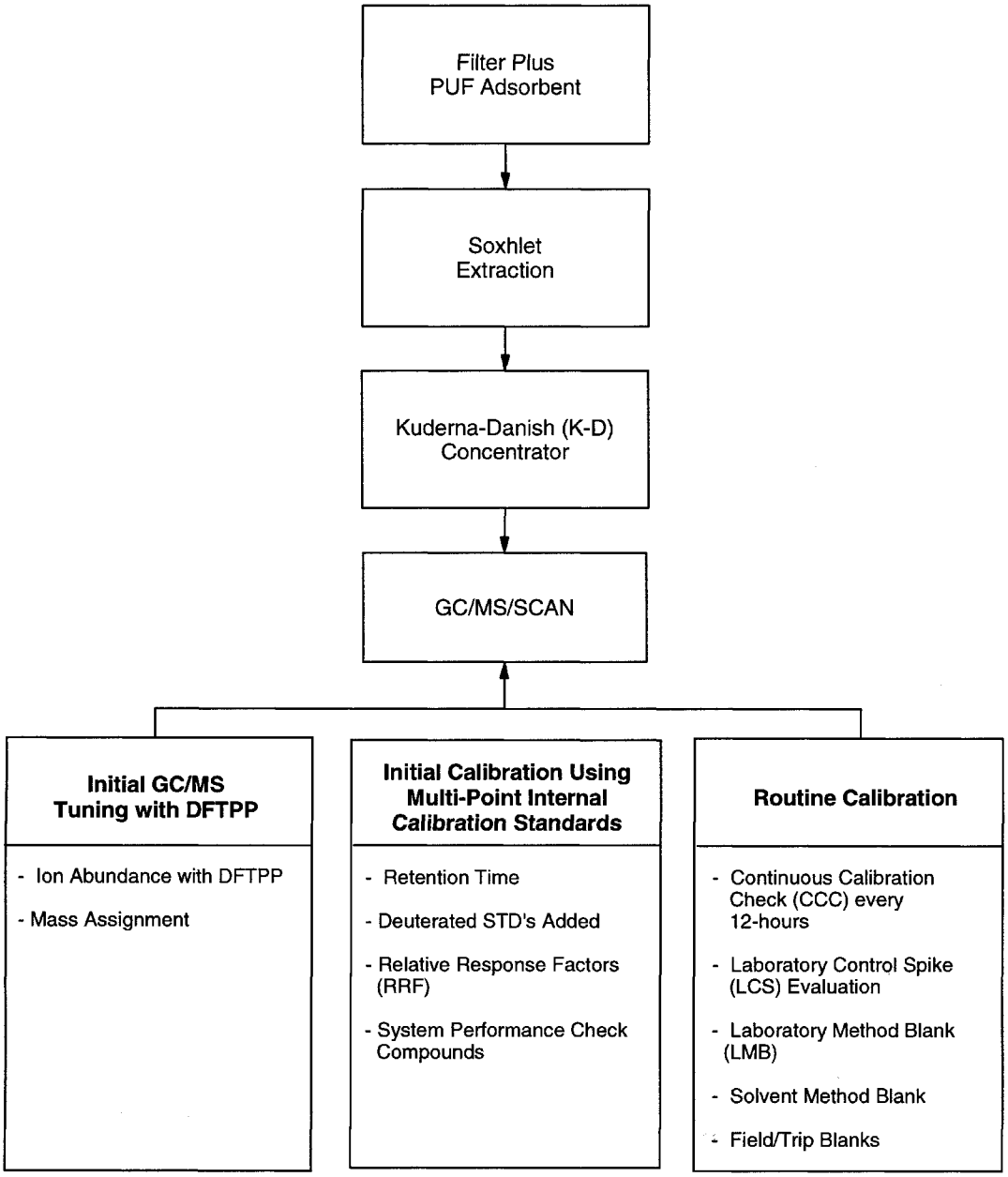


Figure 14. Typical quality assurance specifications for GC/MS/DS operation.

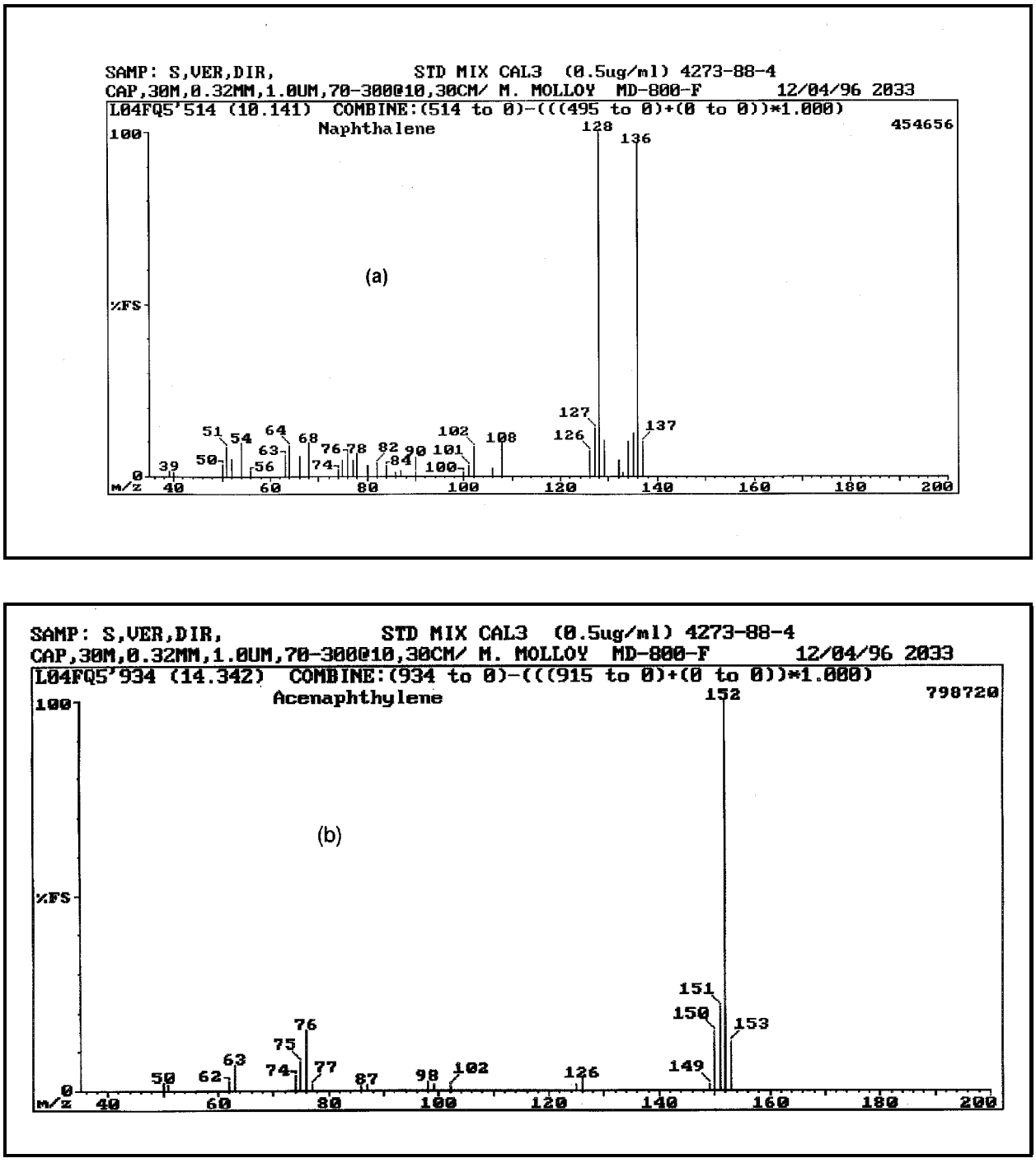
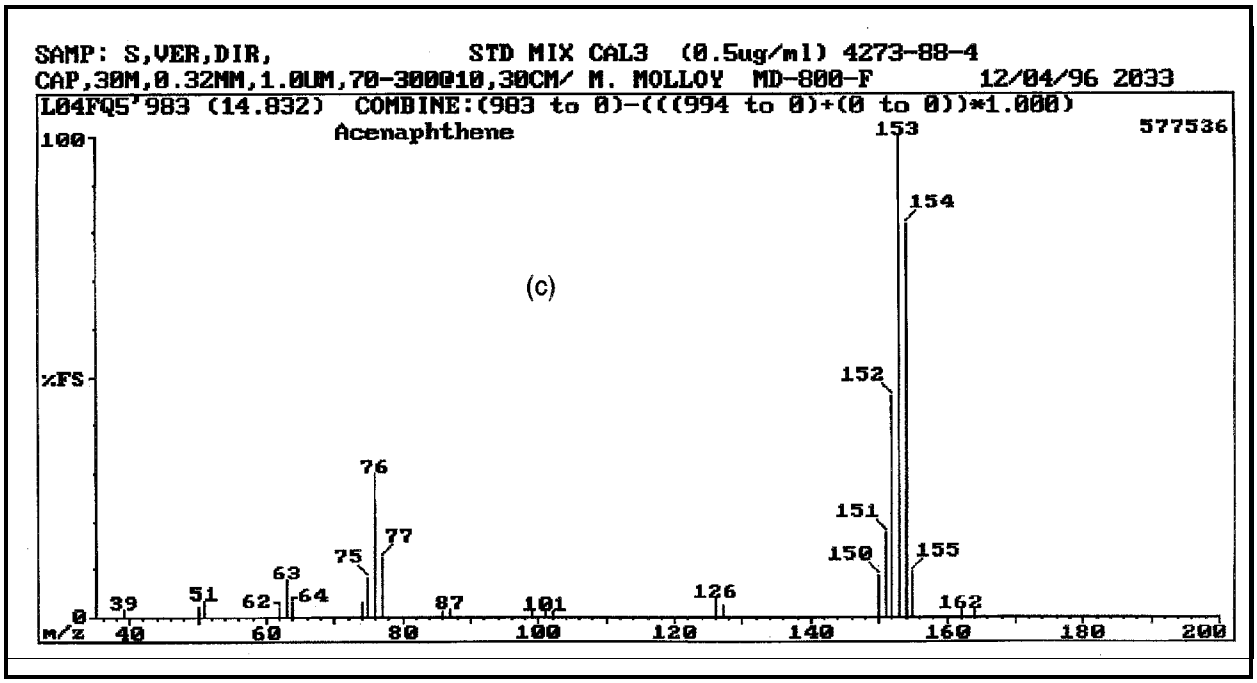


Figure 15. Mass spectra of Compendium Method TO-13A compounds for (a) naphthalene and (b) acenaphthylene.



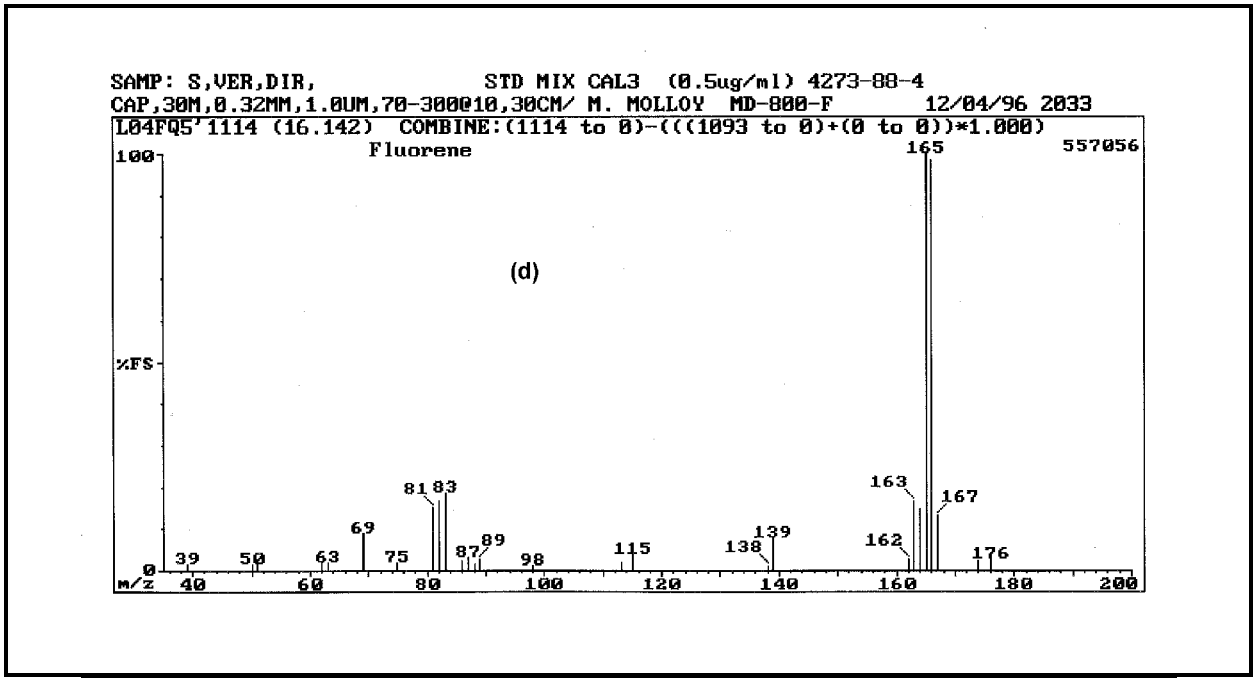
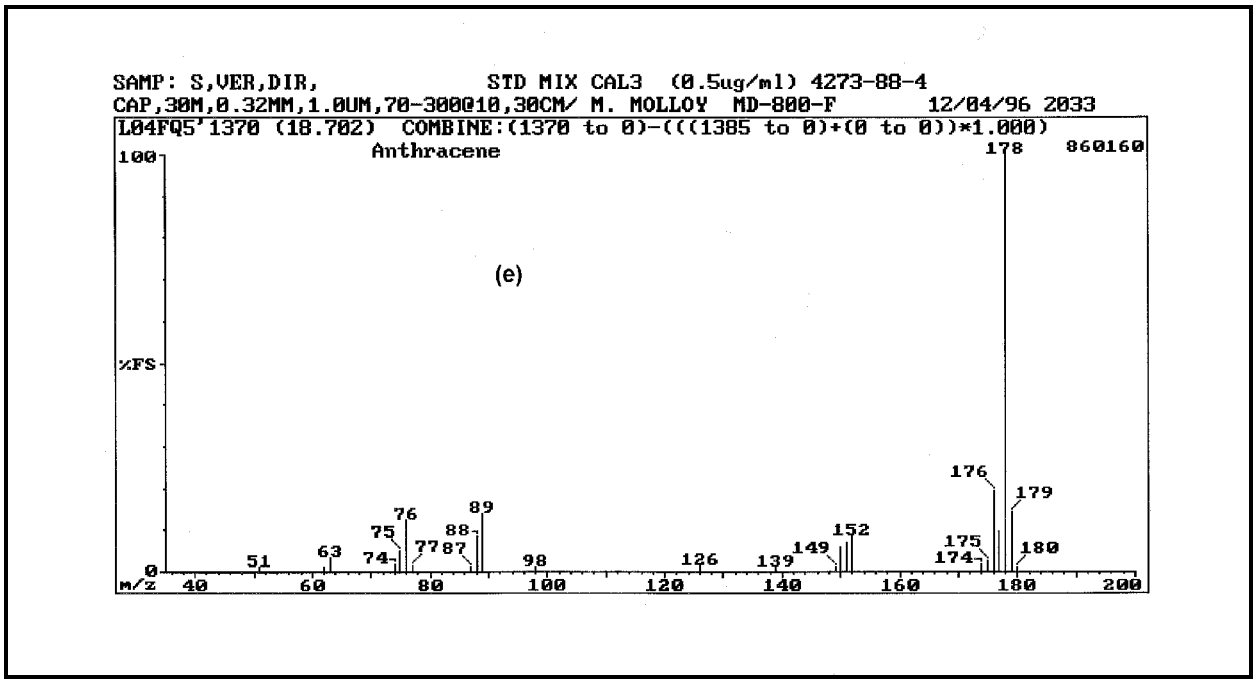


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (c) acenaphthene and (d) fluorene.



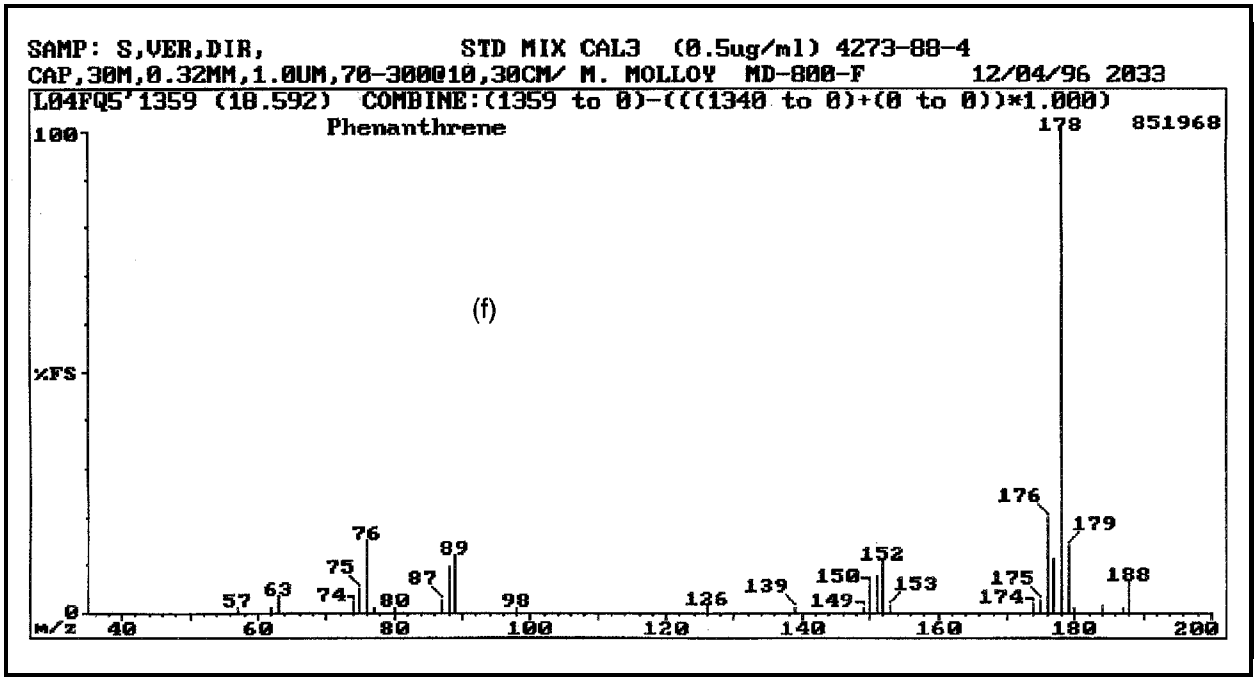
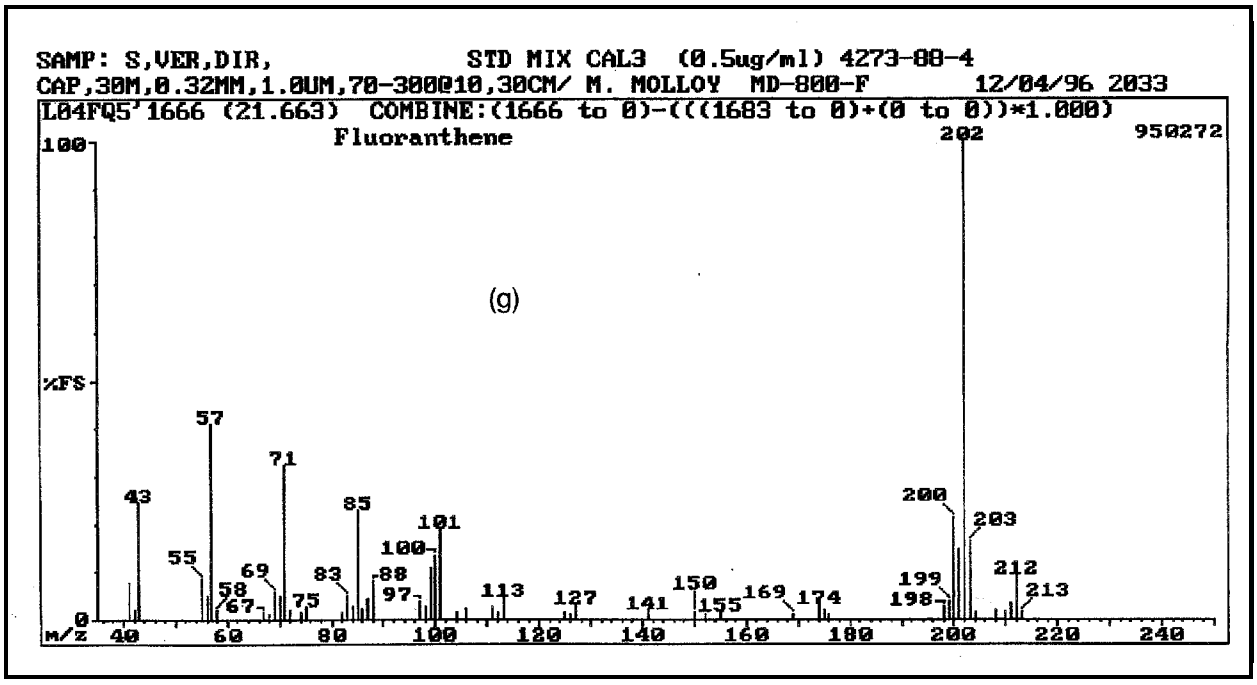


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (e) anthracene and (f) phenanthrene.



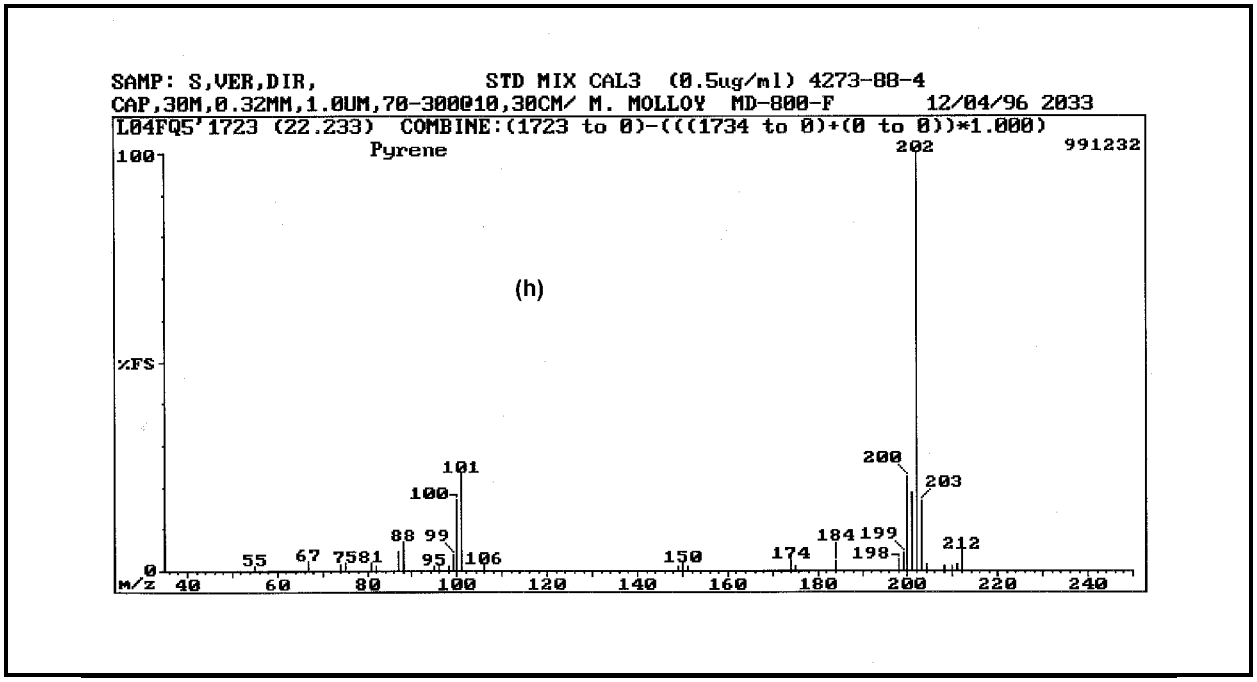


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (g) fluoranthene and (h) pyrene.

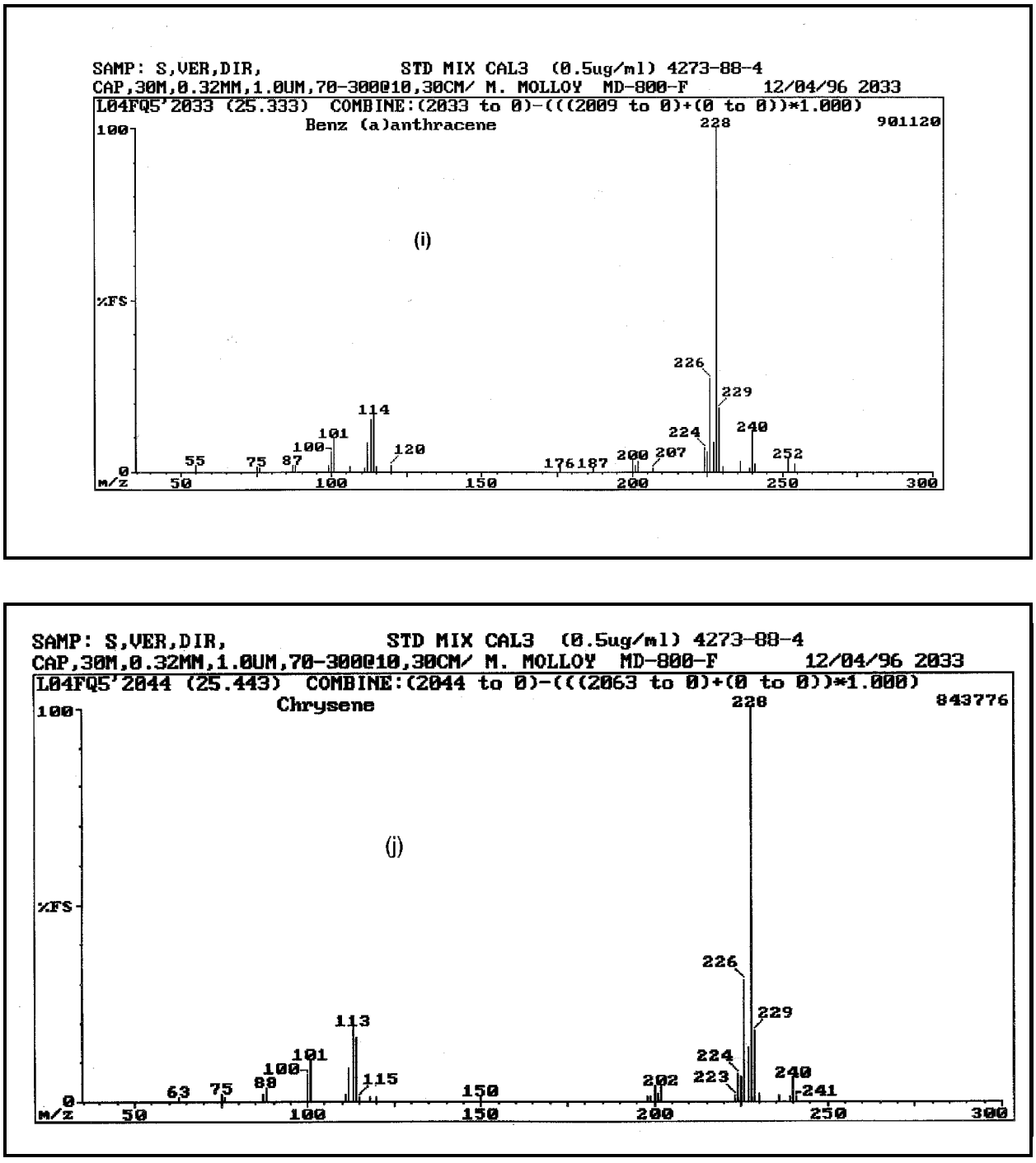
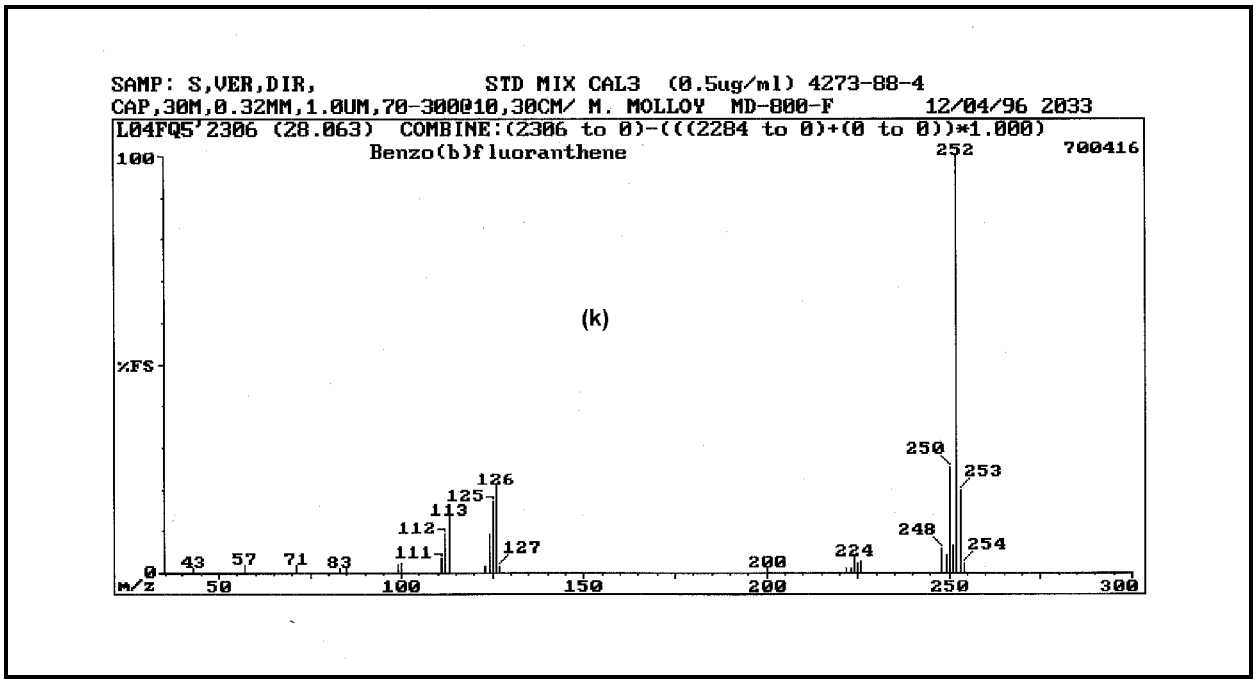


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (i) benz(a)anthracene and (j) chrysene.



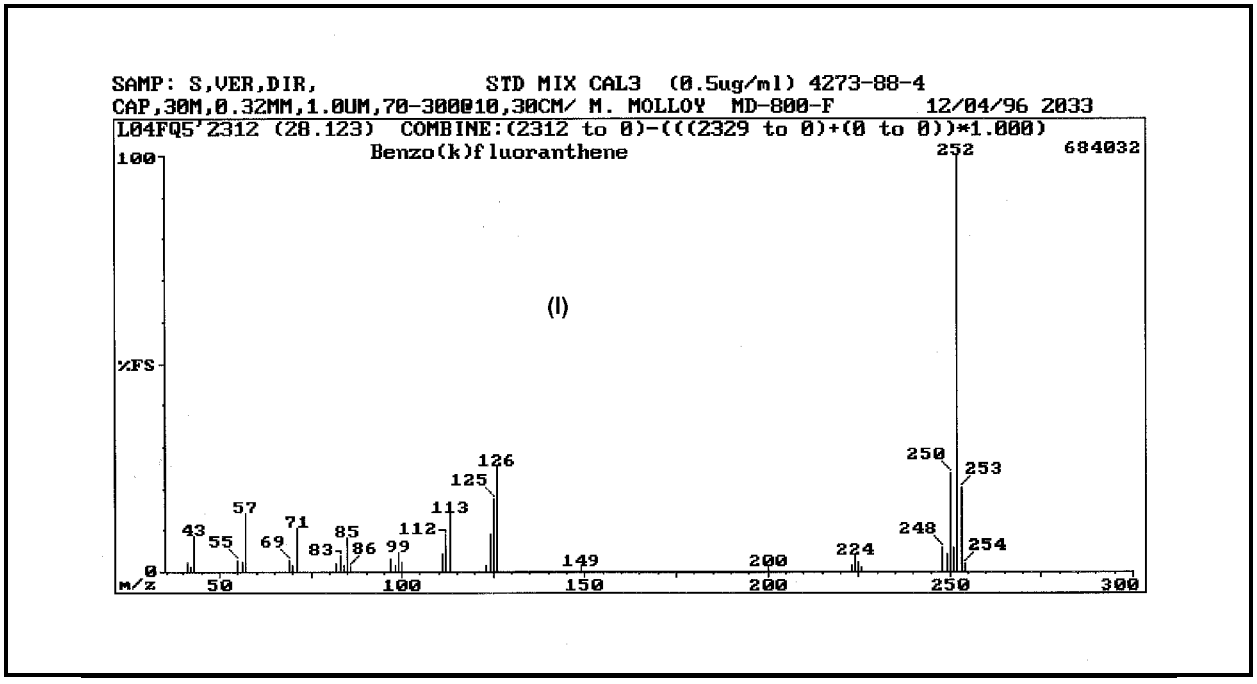
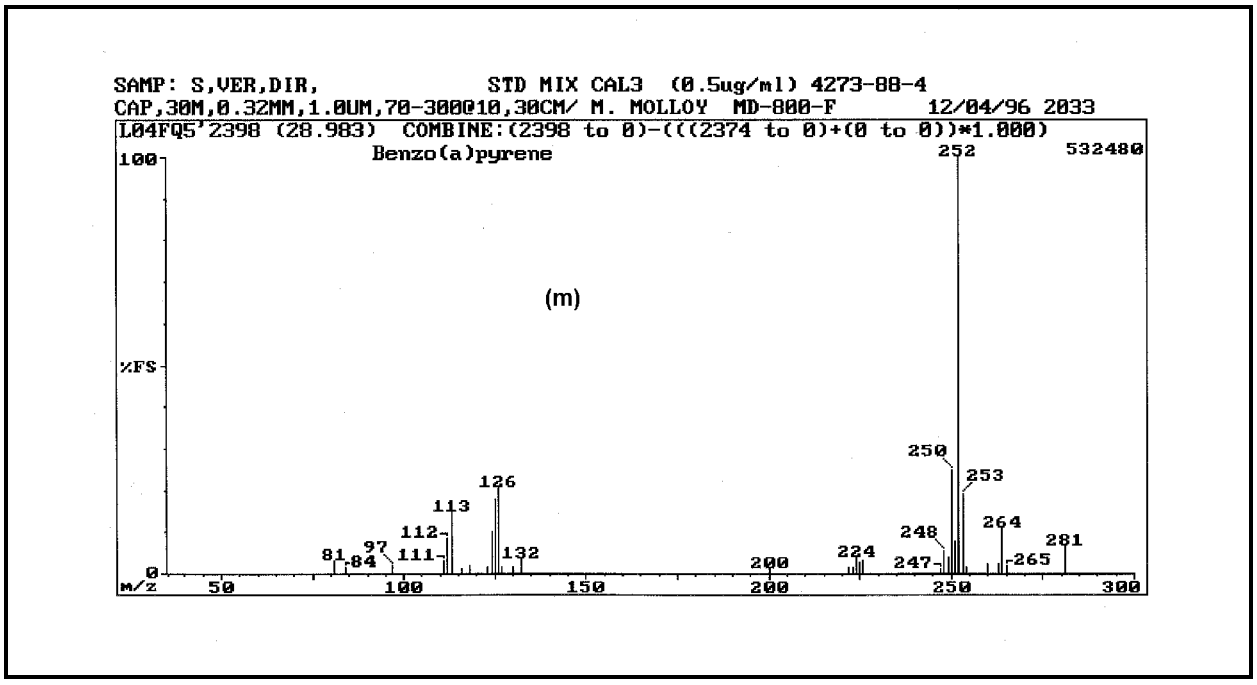


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (k) benzo(b)fluoranthene and (l) benzo(k)fluoranthene.



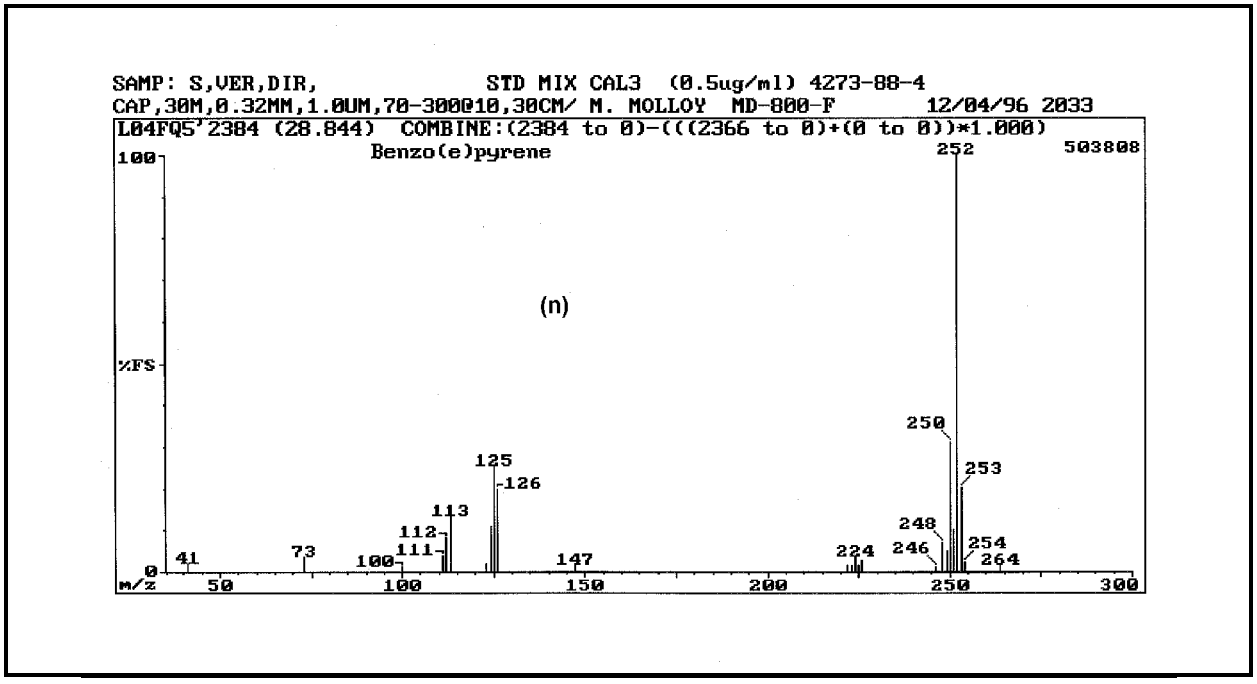
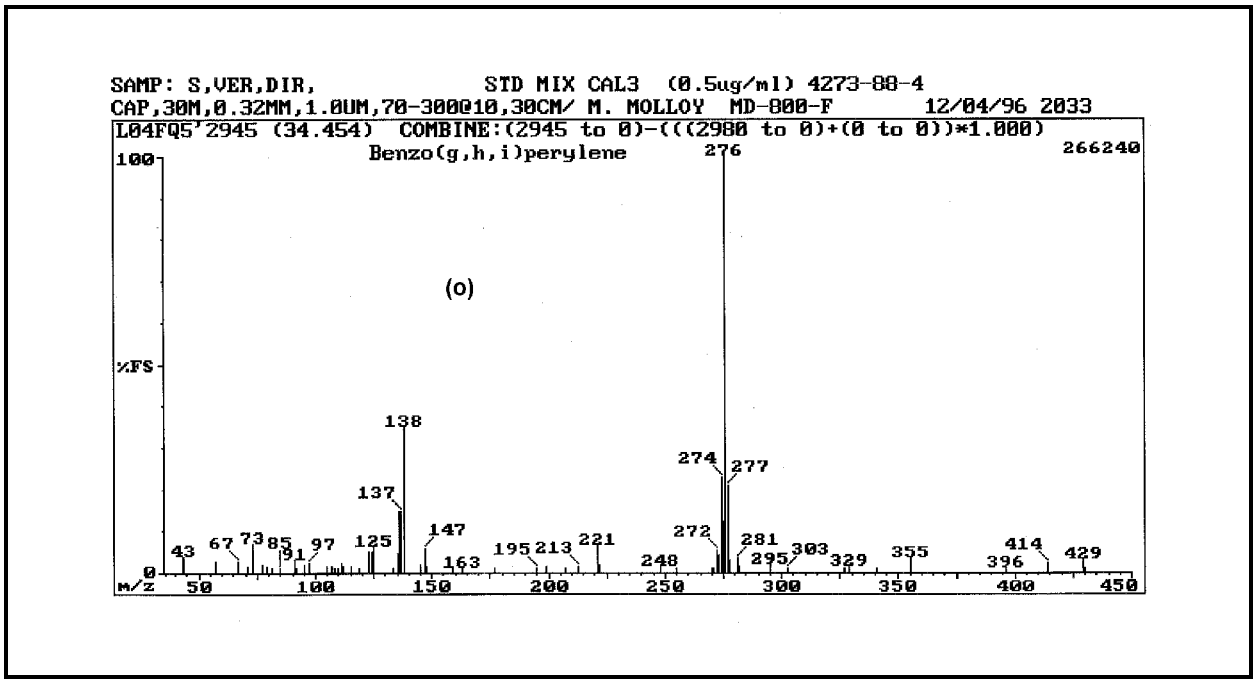


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (m) benzo(a)pyrene and (n) benzo(e)pyrene.



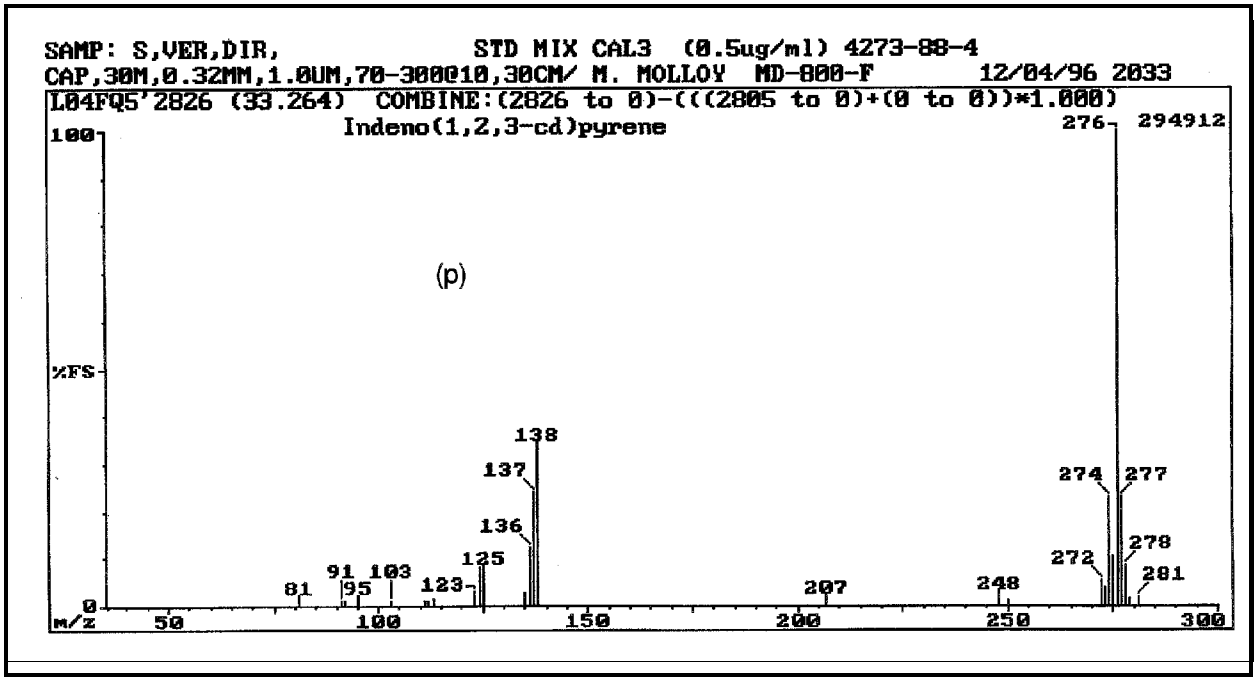


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (o) benzo(g,h,i)perylene and (p) indeno(1,2,3-cd)pyrene.

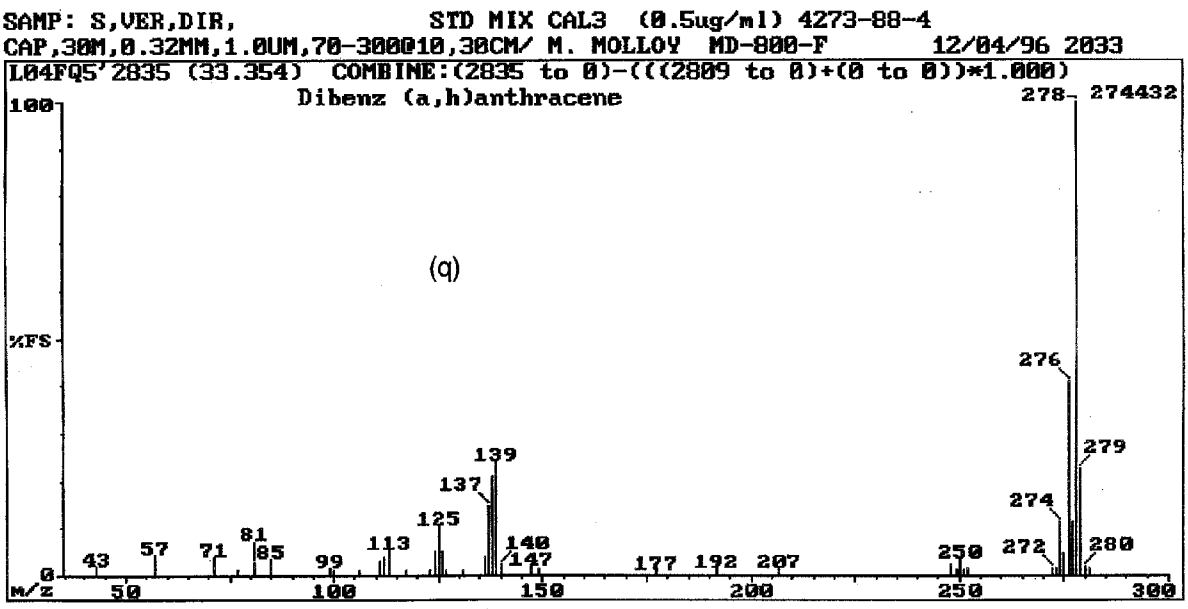


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (q) dibenz(a,h)anthracene.

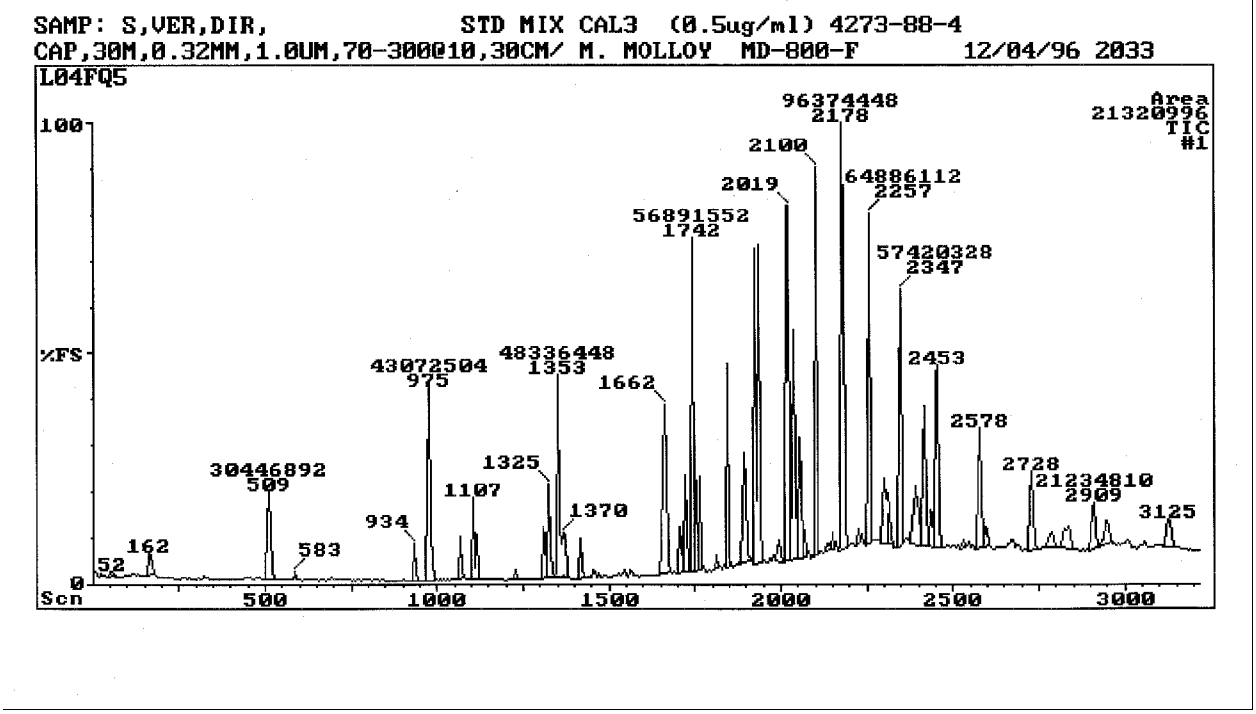


Figure 16. Total ion chromatogram (TIC) of Compendium Method TO-13A target PAHs.

This page intentionally left blank

APPENDIX H
EPA METHOD 625

This page intentionally left blank.

United States Environmental Protection Agency

www.epa.gov Promulgated 1984

Method 625: Base/Neutrals and Acids

APPENDIX A TO PART 136
METHODS FOR ORGANIC CHEMICAL ANALYSIS OF MUNICIPAL AND INDUSTRIAL WASTEWATER

METHOD 625—BASE/NEUTRALS AND ACIDS

1. Scope and Application

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method[2,14] applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR Part 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1)[1] for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR Parts 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1 L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor.[2] The methylene chloride extract is dried,

concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using internal standard techniques with a single characteristic m/z.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current 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 as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400°C for 15-30 minutes. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

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

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chrysene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 610.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of

CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method have 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 OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified[4-6] for the information of the analyst.

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

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composit sampling.

5.1.1 Grab sample bottle—1 L or 1 qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be throughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.)

5.2.1 Separatory funnel—2 L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit

5.2.3 Concentrator tube, Kuderna-Danish—10 mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500 mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three all macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10-15 mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid-liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400°C for 30 minutes of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.6.2 Column for base/neutrals—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35-450 amu every seven seconds or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows 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 specific m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methlylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray.

6.7 Stock standard solutions (1.00 µg/µL)—standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10 mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 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.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 µg/mL in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 µg/L of each surrogate standard. Store the spiking solution at 4°C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 µg/mL solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 8. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense m/z quantities for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2-5 µL, analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$

where:
A_s = Area of the characteristic m/z for the parameter to be measured.
A_{is} = Area of the characteristic m/z for the internal standard.
C_{is} = Concentration of the internal standard.
C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s / A_{is}, vs. concentration ratios C_s / C_{is}*.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to 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 data quality. The laboratory must maintain records to document the quality of data that is 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 atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occuring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

---

*This equation corrects an error made in the original method publication (49 FR 43234, October 26, 1984). This correction will be formalized through a rulemaking in FY97.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 µg/mL in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 µg/L by adding 1.00 mL of QC check sample concentrate to each of four 1 L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

NOTE: The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to 20 samples per month, at least one spiked sample per month is required.

8.3.1. The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or one to five times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 µg/L or one to five times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either five times higher than the expected background concentration or 100 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as 100 (A-B)%/T, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were

calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.[7] If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (X′) using the equation in Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S′) using the equation in Table 7, substituting X′ for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100 X′/T) ±2.44(100 S′/T)%.[7]

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Section 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_S) as 100 (A/T)%, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy

assessment as a percent interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}$=90% and s_p=10%, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g., after each 5-10 new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[8] should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4°C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.[9] Field test kits are available for this purpose.

9.3 All samples must be extracted within seven days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250 mL, 100 mL, and 100 mL volumes of methylene chloride for the serial extraction of the base/neutrals and 200 mL, 100 mL, and 100 mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH >11 with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 11.3.

10.4 Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60 mL aliquots of methylene chloride. Collect and combine the extracts in a 250 mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20-30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°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 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5 mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K-D apparatus on a hot

water bath (60-65°C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. 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 about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH >11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50-100 mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200-500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 hours. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.[10] Each day that benzidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy:	70 V (nominal)
Mass Range:	35-450 amu
Scan Time:	To give at least five scans per peak but not to exceed seven seconds per scan.

12.3 DFTPP performance test—At the beginning of each day, inject 2 µL (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. Inject 100 ng of benzidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benzidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.[11] Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by these columns are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 The internal standard must be added to sample extract and mixed thoroughly immediately before it is injected into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2-5 µL of the sample extract or standard into the GC/MS system using the solvent-flush technique.[12] Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ±30 seconds of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within ±20% of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 seconds difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 2.

Equation 2

$$\text{Concentration } (\mu g/L) = \frac{(A_s)\ (I_s)}{(A_{is})\ (RF)\ (V_o)}$$

where:

A_s = Response for the parameter to be measured.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract (µg).
V_o = Volume of water extracted (L).

15.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[1] The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.[13] The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1300 µg/L.[14] Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 mL.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.6.2) to 220°C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5-7 µL of the base/neutral extract. Collect SIM data for a total of 10 minutes.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures.

References

1. 40 CFR Part 136, Appendix B.

2. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1977, Revised April 1977. Available from Effluent Guidelines Division, Washington, DC 20460.

3. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.

4. "Carcinogens-Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

5. "OSHA Safety and Health Standards, General Industry," (29 CFR Part 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. Provost, L.P. and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

8. ASTM Annual Book of Standards, Part 31, D3370-76. "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.

9. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

10. Eichelberger, J.W., Harris, L.E., and Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectometry," *Analytical Chemistry*, 47, 995 (1975).

11. McNair, N.M. and Bonelli, E.J. "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1969.

12. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists, 48,* 1037 (1965).

13. Olynyk, P., Budde, W.L. and Eichelberger, J.W. "Method Detection Limit for Methods 624 and 625," Unpublished report, May 14, 1980.

14. "EPA Method Study 30, Method 625, Base/Neutrals, Acids, and Pesticides," EPA 600/4-84-053, National Technical Information Service, PB84-206572, Springfield, Virginia 22161, June 1984.

Table 1—Base/Neutral Extractables

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Aldrin	39330	309-00-2
Benzo(a)anthracene	34526	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(ghi)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
β-BHC	39338	319-85-7
δ-BHC	34259	319-86-8
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Bis(2-chloroisopropyl)ether[a]	34283	108-60-1
4-Bromophenyl phenyl ether[a]	34636	101-55-3
Chlordane	39350	57-74-9
2-Chloronaphthalele	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dibenzo(a,h)anthracene	34556	53-70-3
Di-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-94-1
Dieldrin	39380	60-57-1
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2

Table 1—Base/Neutral Extractables

Parameter	STORET No.	CAS No.
2,6-Dinitrotoluene	34626	606-20-2
Di-n-octylphthalate	34596	117-84-0
Endosulfan sulfate	34351	1031-07-8
Endrin aldehyde	34366	7421-93-4
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Heptachlor	39410	76-44-8
Heptchlor epoxide	39420	1024-57-3
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloroethane	34396	67-72-1
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Toxaphene	39400	8001-35-2
1,2,4-Trichlorobenzene	34551	120-82-1

[a]The proper chemical name is 2,2'-oxybis(1-chloropropane).

Table 2--Acid Extractables

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	34694	108-95-2
2,4,6-Trichlorophenol	34621	88-06-2

Table 3—Additional Extractable Parameters[a]

Parameter	STORET No.	CAS No.	Method
Benzidine	39120	92-87-5	605
β-BHC	39337	319-84-6	608
δ-BHC	39340	58-89-8	608
Endosulfan I	34361	959-98-8	608
Endosulfan II	34356	33213-65-9	608
Endrin	39390	72-20-8	608
Hexachlorocylopentadiene	34386	77-47-4	612
N-Nitrosodimethylamine	34438	62-75-9	607
N-Nitrosodiphenylamine	34433	86-30-6	607

[a]See Section 1.2.

Table 4—Chromatographic Conditions, Method Detection Limits, and Characteristic Masses for Base/Neutral Extractables

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether[a]	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether[a]	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propylamine	.....	.....	130	42	101	.....	.....	.....

Table 4—Chromatographic Conditions, Method Detection Limits, and Characteristic Masses for Base/Neutral Extractables

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
Nitrobenzene	11.1	1.9	77	123	65	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	209
Isophorone	11.9	2.2	82	95	138	139	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	137
Hexachlorocyclopentadiene[a]	13.9	.....	237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141	.....	.....	.....
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethyl phthalate	20.1	1.9	149	177	150	177	223	251
N-Nitrosodiphenylamine[b]	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	288
β-BHC[b]	21.1	.....	183	181	109	.....	.....	.....
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
δ-BHC[b]	22.4	.....	183	181	109	.....	.....	.....
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109	.....	.....	.....
Heptachlor	23.4	1.9	100	272	274	.....	.....	.....
δ-BHC	23.7	3.1	183	109	181	.....	.....	.....
Aldrin	24.0	1.9	66	263	220	.....	.....	.....
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351	.....	.....	.....
Endosulfan I[b]	26.4	.....	237	339	341	.....	.....	.....
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279	.....	.....	.....
4,4'-DDE	27.2	5.6	246	248	176	.....	.....	.....
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin[b]	27.9	.....	81	263	82	.....	.....	.....
Endosulfan II[b]	28.6	.....	237	339	341	.....	.....	.....
4,4'-DDD	28.6	2.8	235	237	165	.....	.....	.....

Table 4—Chromatographic Conditions, Method Detection Limits, and Characteristic Masses for Base/Neutral Extractables

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
Benzidine[b]	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165	.....	.....	.....
Endosulfan sulfate	29.8	5.6	272	387	422	.....	.....	.....
Endrin aldehyde	.....	.....	67	345	250	.....	.....	.....
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149	.....	.....
Chrysene	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126	.....	.....	.....
Di-n-octyl phthalate	32.5	2.5	149	.....	.....	.....	.....	.....
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281
Indeno(1,2,3-cd) pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h) anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethyl-amine[b]	.....	.....	42	74	44	.....	.....	.....
Chlordane[c]	19-30	.....	373	375	377	.....	.....	.....
Toxaphene[c]	25-34	.....	159	231	233	.....	.....	.....
PCB 1016[c]	18-30	.....	224	260	294	.....	.....	.....
PCB 1221[c]	15-30	30	190	224	260	.....	.....	.....
PCB 1232[c]	15-32	.....	190	224	260	.....	.....	.....
PCB 1242[c]	15-32	.....	224	260	294	.....	.....	.....
PCB 1248[c]	12-34	.....	294	330	262	.....	.....	.....
PCB 1254[c]	22-34	36	294	330	362	.....	.....	.....
PCB 1260[c]	23-32	.....	330	362	394	.....	.....	.....

[a]The proper chemical name is 2,2'-bisoxy(1-chloropropane).
[b]See Section 1.2.
[c]These compounds are mixtures of various isomers (See Figures 2 through 12). Column conditions: Supelcoport (100/120 mesh) coated with 3% SP-2250 packed in a 1.8 m long x 2 mm ID glass column with helium carrier gas at 30 mL/min. flow rate. Column temperature held isothermal at 50°C for four minutes, then programmed at 8°C/min. to 270°C and held for 30 minutes.

Table 5—Chromatographic Conditions, Method Detection Limits, and Characteristic Masses for Acid Extractables

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.6	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinitrophenol	15.9	42	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Column conditions: Supelcoport (100/120 mesh) coated with 1% SP-1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min. flow rate. Column temperature held isothermal at 70°C for two mintues then programmed at 8°C/min. to 200°C.

Table 6—QC Acceptance Criteria—Method 625

Parameter	Test conclusion (µg/L)	Limits for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P_s (Percent)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27-133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether[a]	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl) phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158

Table 6—QC Acceptance Criteria—Method 625

Parameter	Test conclusion (µg/L)	Limits for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P_s (Percent)
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4,-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dhlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octyl phthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26-155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Dichlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132

Table 6—QC Acceptance Criteria—Method 625

Parameter	Test conclusion (µg/L)	Limits for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P_s (Percent)
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

$\bar{s}$ = Standard deviation for four recovery measurements, in µg/L (Section 8.2.4).
$\bar{X}$ = Average recovery for four recovery measurements, in µ/L (Section 8.2.4).
P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).
D = Detected; result must be greater than zero.
NOTE: These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limts to concentrations below those used to develop Table 7.
[a]The proper chemical name is 2,2'oxybis(1-chloropropane).

Table 7—Method Accuracy and Precision as Functions of Concentration—Method 625

Parameter	Accuracy, as recovery, X′ (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S′ (µg/L)
Acenaphthene	0.96C+0.19	0.15$\bar{X}$-0.12	0.21$\bar{X}$-0.67
Acenaphthylene	0.89C+0.74	0.24$\bar{X}$-1.06	0.26$\bar{X}$-0.54
Aldrin	0.78C+1.66	0.27$\bar{X}$-1.28	0.43$\bar{X}$+1.13
Anthracene	0.80C+0.68	0.21$\bar{X}$-0.32	0.27$\bar{X}$-0.64
Benzo(a)anthracene	0.88C-0.60	0.15$\bar{X}$+0.93	0.26$\bar{X}$-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22$\bar{X}$+0.43	0.29$\bar{X}$+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19$\bar{X}$+1.03	0.35$\bar{X}$+0.40
Benzo(a)pyrene	0.90C-0.13	0.22$\bar{X}$+0.48	0.32$\bar{X}$+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29$\bar{X}$+2.40	0.51$\bar{X}$-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18$\bar{X}$+0.94	0.53$\bar{X}$+0.92
β-BHC	0.87C-0.94	0.20$\bar{X}$-0.58	0.30$\bar{X}$-1.94
δ-BHC	0.29C-1.09	0.34$\bar{X}$+0.86	0.93$\bar{X}$-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35$\bar{X}$-0.99	0.35$\bar{X}$+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16$\bar{X}$+1.34	0.26$\bar{X}$+2.01
Bis(2-chloroisopropyl)ether[a]	1.03C-2.31	0.24$\bar{X}$+0.28	0.25$\bar{X}$+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26$\bar{X}$+0.73	0.36$\bar{X}$+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13$\bar{X}$+0.66	0.16$\bar{X}$+0.66
2-Chloronaphthalene	0.89C+0.01	0.07$\bar{X}$+0.52	0.13$\bar{X}$+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20$\bar{X}$-0.94	0.30$\bar{X}$-0.46
Chrysene	0.93C-1.00	0.28$\bar{X}$+0.13	0.33$\bar{X}$-0.09
4,4'-DDD	0.56C-0.40	0.29$\bar{X}$-0.32	0.66$\bar{X}$-0.96
4,4'-DDE	0.70C-0.54	0.26$\bar{X}$-1.17	0.39$\bar{X}$-1.04
4,4'-DDT	0.79C-3.28	0.42$\bar{X}$+0.19	0.65$\bar{X}$-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30$\bar{X}$+8.51	0.59$\bar{X}$+0.25

Table 7—Method Accuracy and Precision as Functions of Concentration—Method 625

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S' (µg/L)
Di-n-butyl phthalate	0.59C+0.71	0.13$\bar{X}$+1.16	0.39$\bar{X}$+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20$\bar{X}$+0.47	0.24$\bar{X}$+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25$\bar{X}$+0.68	0.41$\bar{X}$+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24$\bar{X}$+0.23	0.29$\bar{X}$+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28$\bar{X}$+7.33	0.47$\bar{X}$+3.45
Dieldrin	0.82C-0.16	0.20$\bar{X}$-0.16	0.26$\bar{X}$-0.07
Diethyl phthalate	0.43C+1.00	0.28$\bar{X}$+1.44	0.52$\bar{X}$+0.22
Dimethyl phthalate	0.20C+1.03	0.54$\bar{X}$+0.19	1.05$\bar{X}$-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12$\bar{X}$+1.06	0.21$\bar{X}$+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14$\bar{X}$+1.26	0.19$\bar{X}$+0.35
Di-n-octyl phthalate	0.76C-0.79	0.21$\bar{X}$+1.19	0.37$\bar{X}$+1.19
Endosulfan sulfate	0.39C+0.41	0.12$\bar{X}$+2.47	0.63$\bar{X}$-1.03
Endrin aldehyde	0.76C-3.86	0.18$\bar{X}$+3.91	0.73$\bar{X}$-0.62
Fluoranthene	0.81C+1.10	0.22$\bar{X}$-0.73	0.28$\bar{X}$-0.60
Fluorene	0.90C-0.00	0.12$\bar{X}$+0.26	0.13$\bar{X}$+0.61
Heptachlor	0.87C-2.97	0.24$\bar{X}$-0.56	0.50$\bar{X}$-0.23
Heptachlor epoxide	0.92C-1.87	0.33$\bar{X}$-0.46	0.28$\bar{X}$+0.64
Hexachlorobenzene	0.74C+0.66	0.18$\bar{X}$-0.10	0.43$\bar{X}$-0.52
Hexachlorobutadiene	0.71C-1.01	0.19$\bar{X}$+0.92	0.26$\bar{X}$+0.49
Hexachloroethane	0.73C-0.83	0.17$\bar{X}$+0.67	0.17$\bar{X}$+0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{X}$+1.46	0.50$\bar{X}$+0.44
Isophorone	1.12C+1.41	0.27$\bar{X}$+0.77	0.33$\bar{X}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{X}$-0.41	0.30$\bar{X}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{X}$+0.92	0.27$\bar{X}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{X}$+0.68	0.44$\bar{X}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{X}$+3.61	0.43$\bar{X}$+1.82
Phenanthrene	0.87C-0.06	0.12$\bar{X}$+0.57	0.15$\bar{X}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{X}$+0.06	0.15$\bar{X}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{X}$+0.85	0.21$\bar{X}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{X}$+0.75	0.29$\bar{X}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{X}$+1.46	0.28$\bar{X}$+0.97
2,4-Dichlorophenol	0.87C+0.13	0.15$\bar{X}$+1.25	0.21$\bar{X}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{X}$+1.21	0.22$\bar{X}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{X}$+2.36	0.42$\bar{X}$+26.29
2-Methyl-4,6-Dinitrophenol	1.04C-28.04	0.05$\bar{X}$+42.29	0.26$\bar{X}$+23.10
2-Nitrophenol	1.07C-1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{X}$+2.57	0.44$\bar{X}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{X}$+3.03	0.30$\bar{X}$+4.33

Table 7—Method Accuracy and Precision as Functions of Concentration—Method 625

Parameter	Accuracy, as recovery, X′ (µg/L)	Single analyst precision, s_r' (µg/L)	Overall precision, S′ (µg/L)
Phenol	0.43C+1.26	$0.26\bar{X}+0.73$	$0.35\bar{X}+0.58$
2,4,6-Trichlorophenol	0.91C-0.18	$0.16\bar{X}+2.22$	$0.22\bar{X}+1.81$

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.
s_r' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.
$\bar{C}$ = True value for the concentration, in µg/L.
$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.
[a]The proper chemical name is 2,2'oxybis(1-chloropropane).

Table 8—Suggested Internal and Surrogate Standards

Base/neutral fraction	Acid fraction
Aniline-d_5	2-Fluorophenol
Anthracene-d_{10}	Pentafluorophenol
Benzo(a)anthracene-d_{12}	Phenol-d_5
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2′-Difluorobiphenyl	
4-Fluoroaniline	
1-Fluoronaphthalene	
2-Fluoronaphthalene	
Naphthalene-d_8	
Nitrobenzene-d_5	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene-d_{10}	
Pyridine-d_5	

Table 9—DFTPP Key Masses and Abundance Criteria

Mass	m/z Abundance criteria
51	30-60 percent of Mass 198.
68	Less than 2 percent of Mass 69.
70	Less than 2 percent of Mass 69.
127	40-60 percent of Mass 198.
197	Less than 1 percent of Mass 198.
198	Base peak, 100 percent relative abundance.
199	5-9 percent of Mass 198.
275	10-30 percent of Mass 198.
365	Greater than 1 percent of Mass 198.
441	Present but less than Mass 443.
442	Greater than 40 percent of Mass 198.
443	17-23 percent of Mass 442.

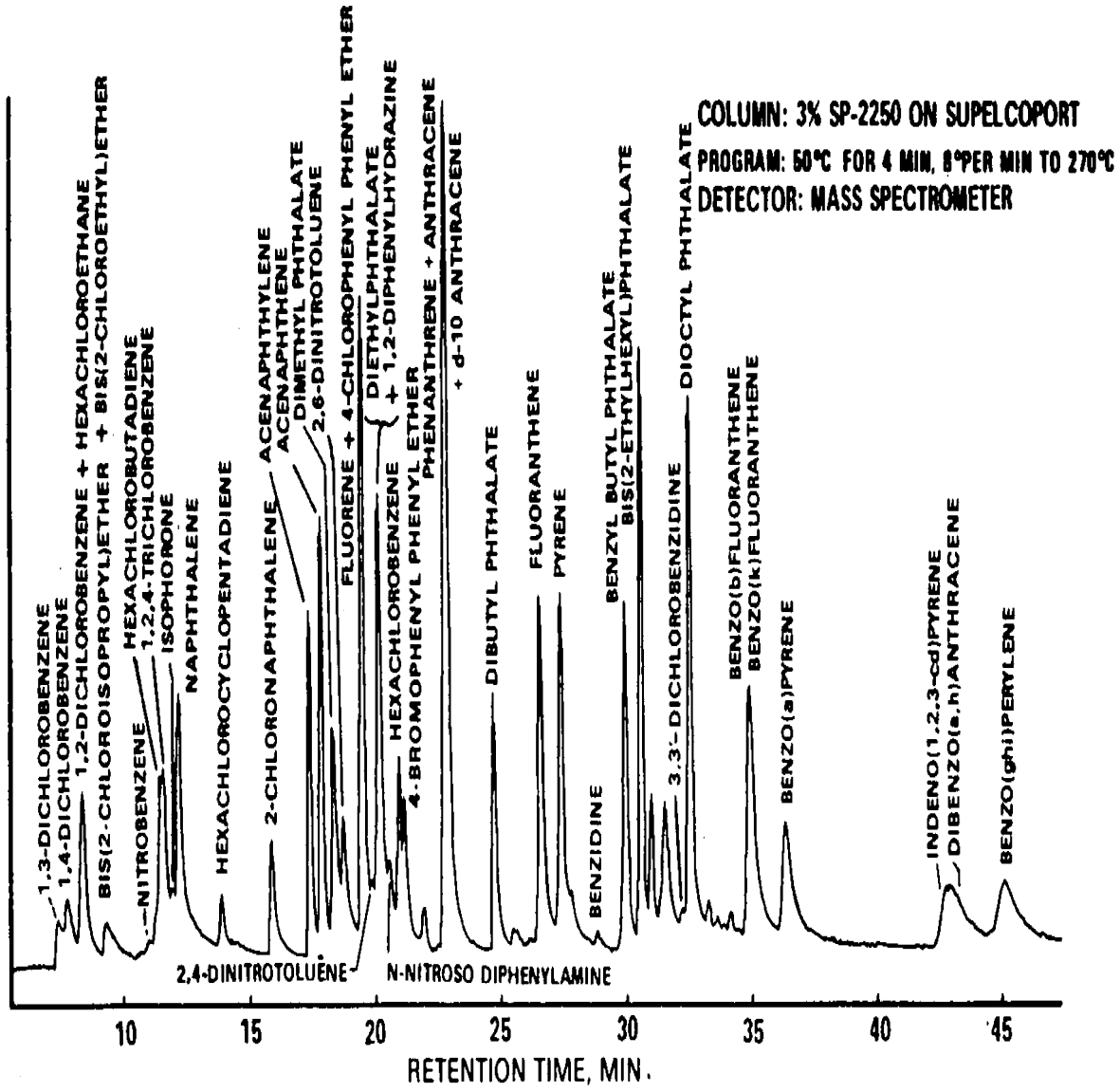


Figure 1. Gas chromatogram of base/neutral fraction.

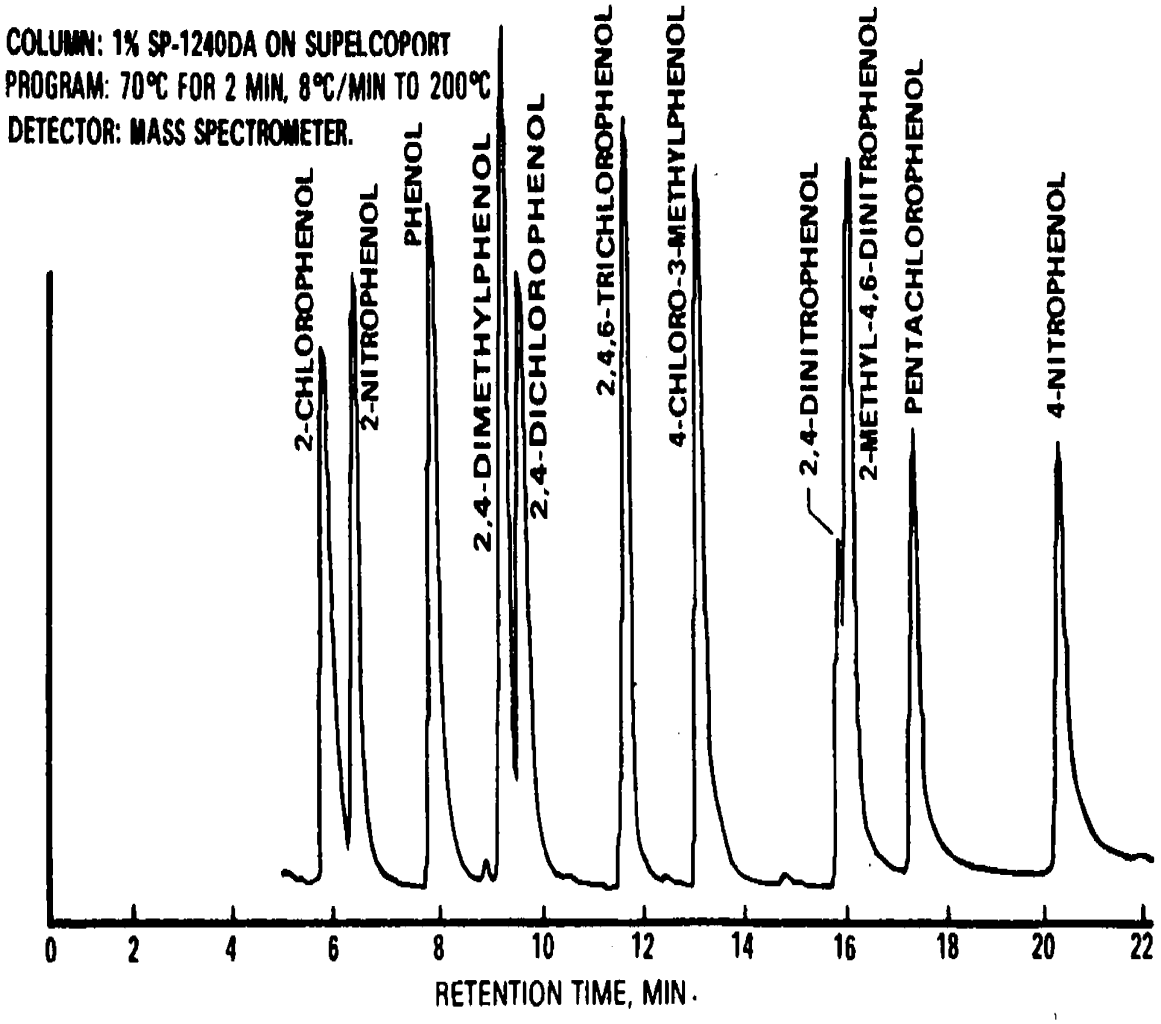


Figure 2. Gas chromatogram of acid fraction.

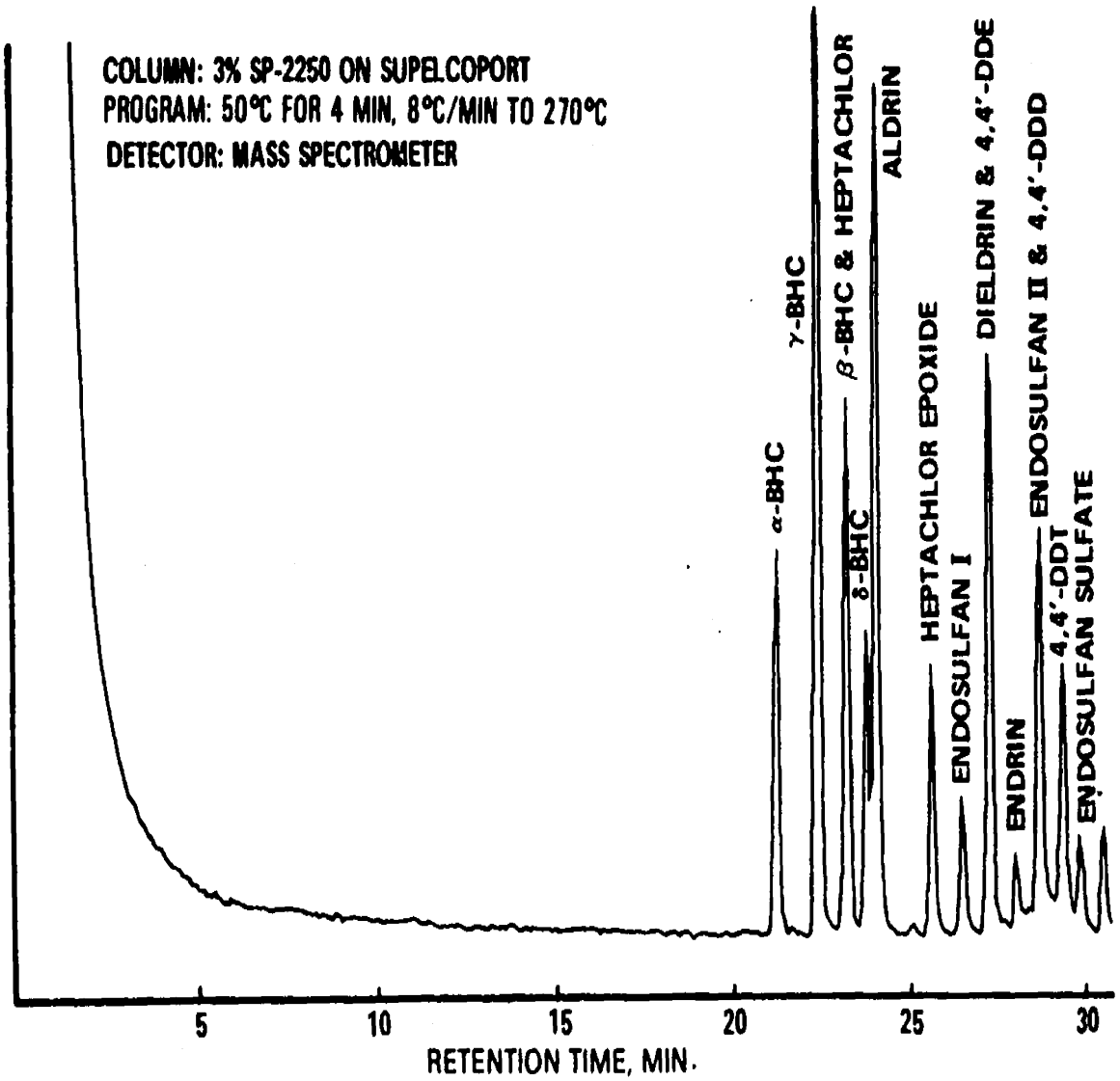


Figure 3. Gas chromatogram of pesticide fraction.

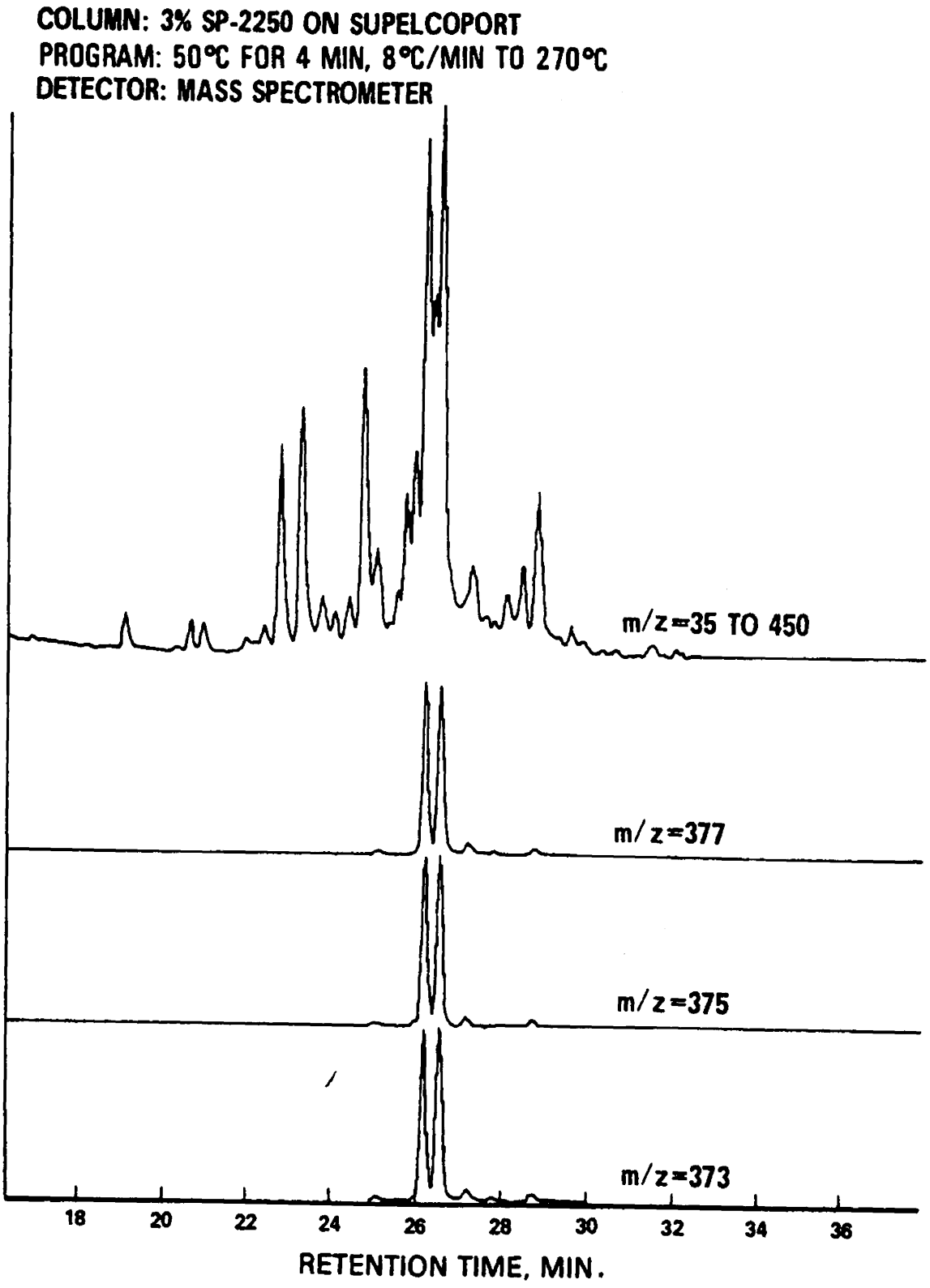


Figure 4. Gas chromatogram of chlordane.

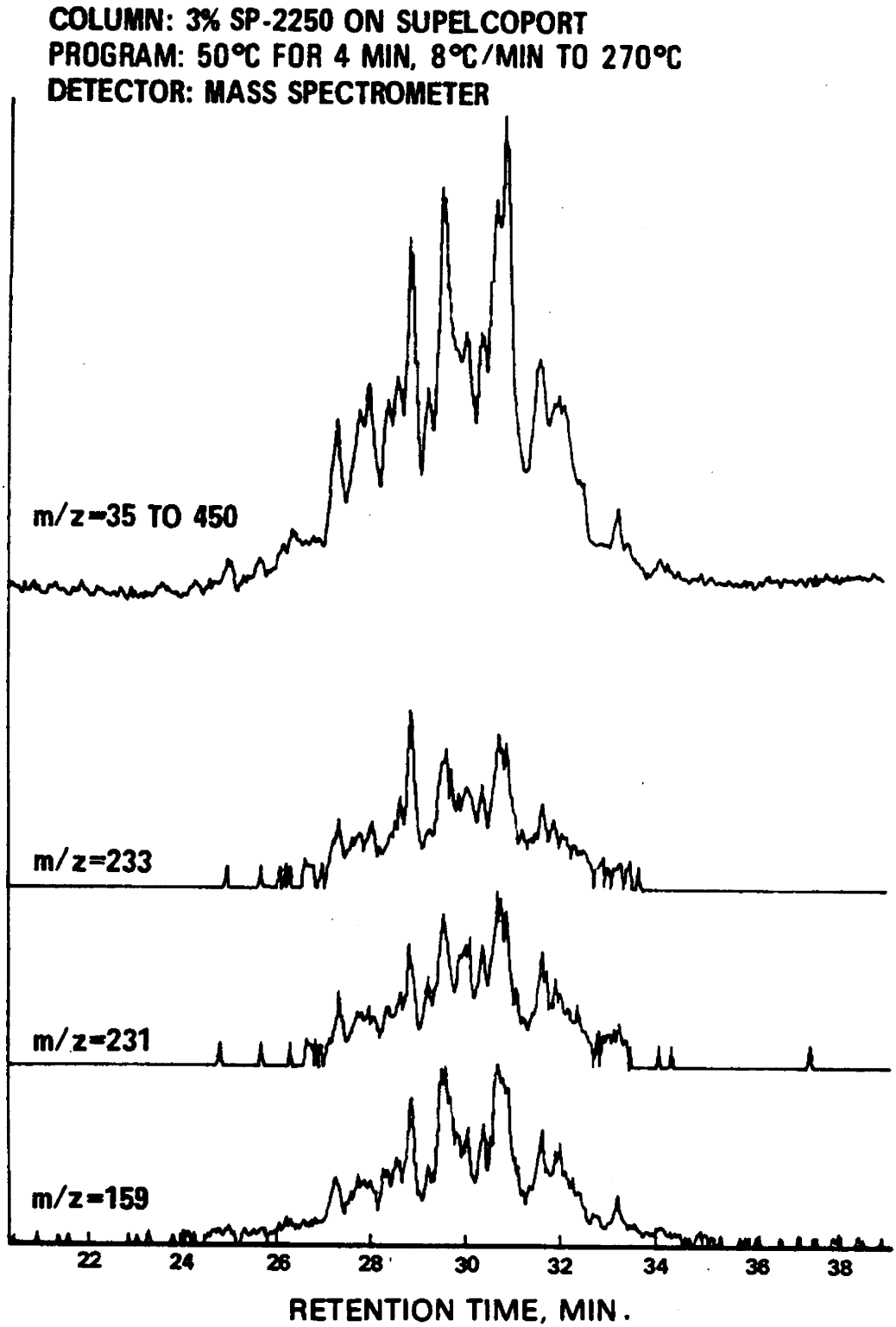


Figure 5. Gas chromatogram of toxaphene.

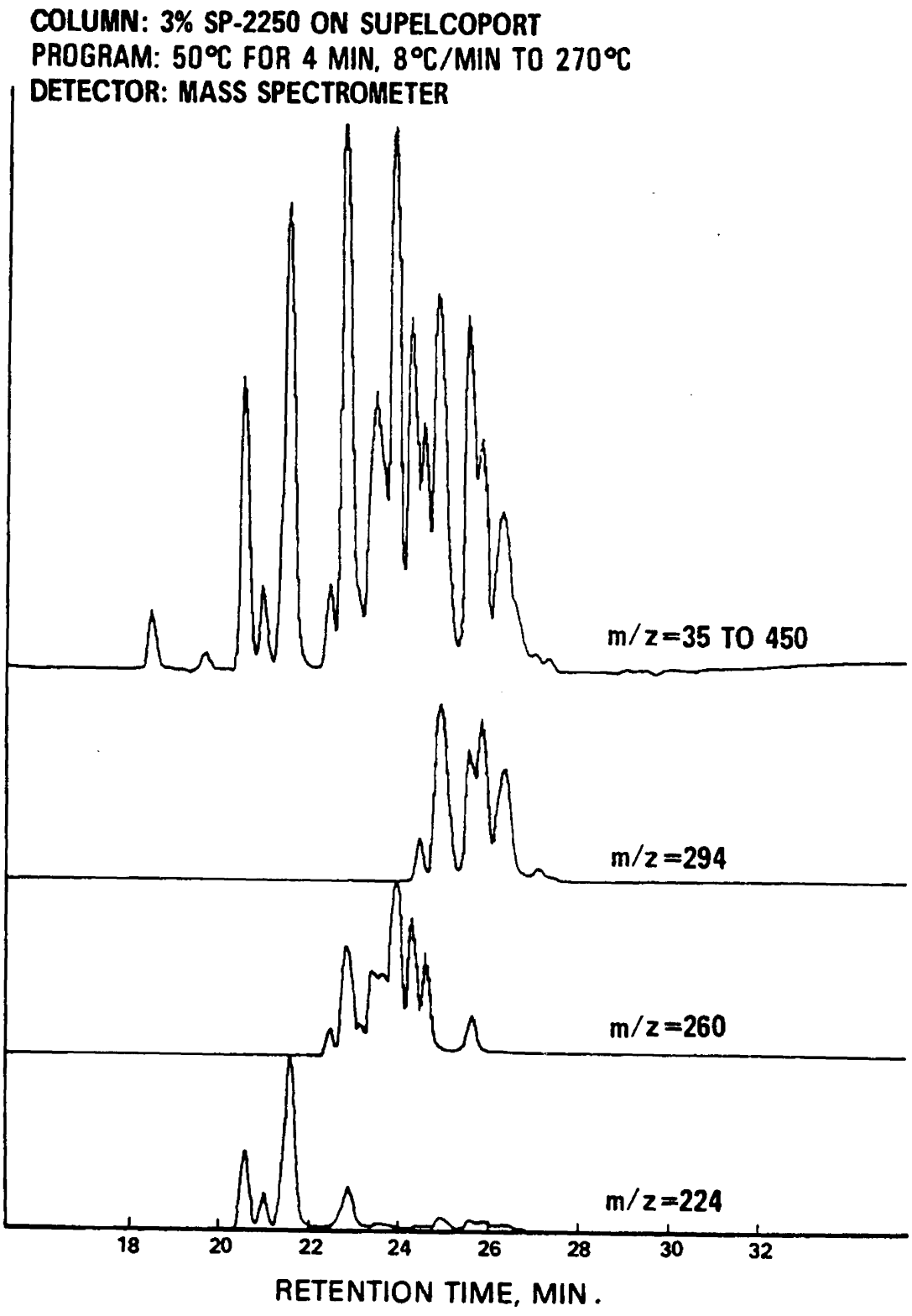


Figure 6. Gas chromatogram of PCB-1016.

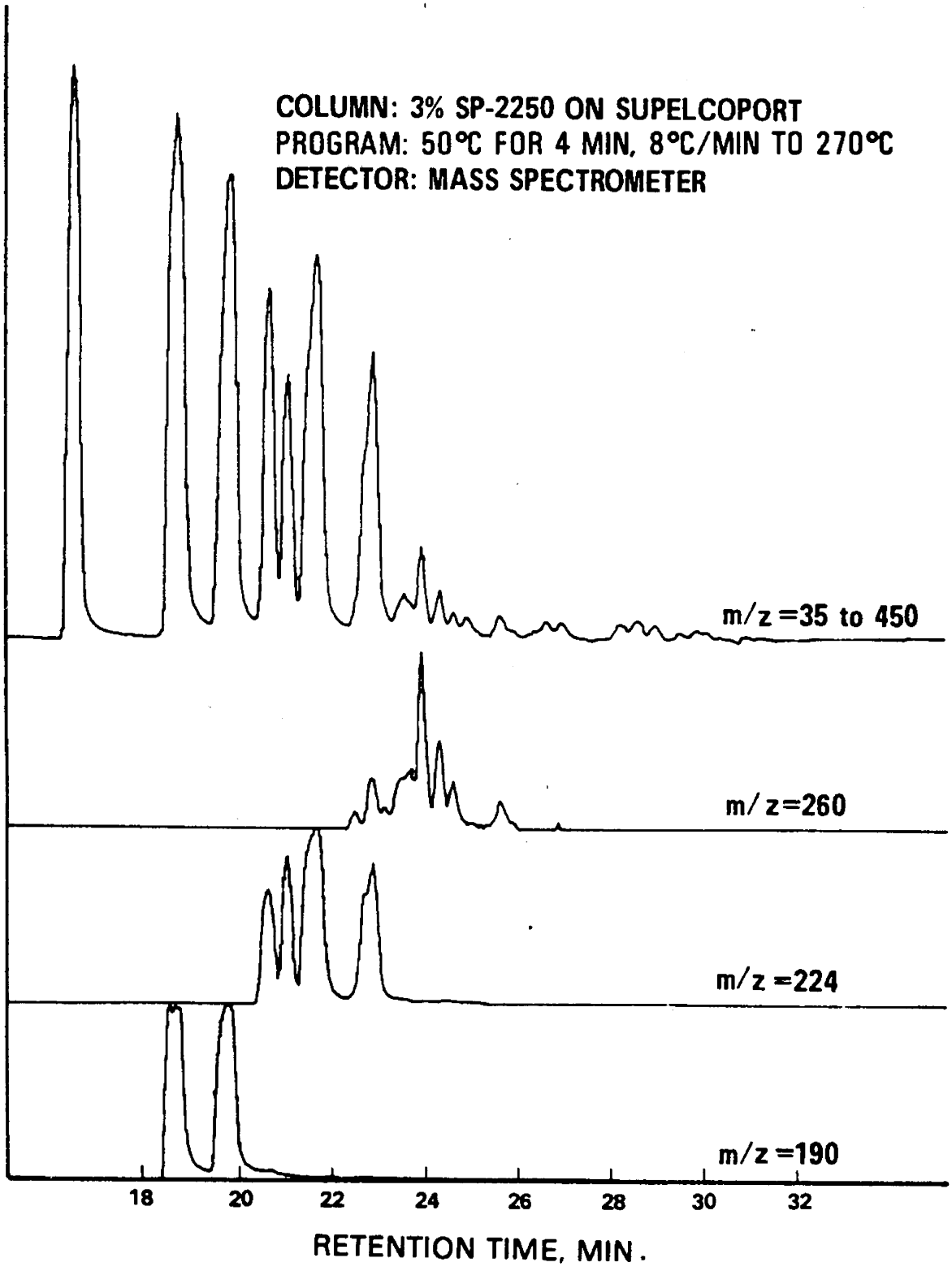


Figure 7. Gas chromatogram of PCB-1221.

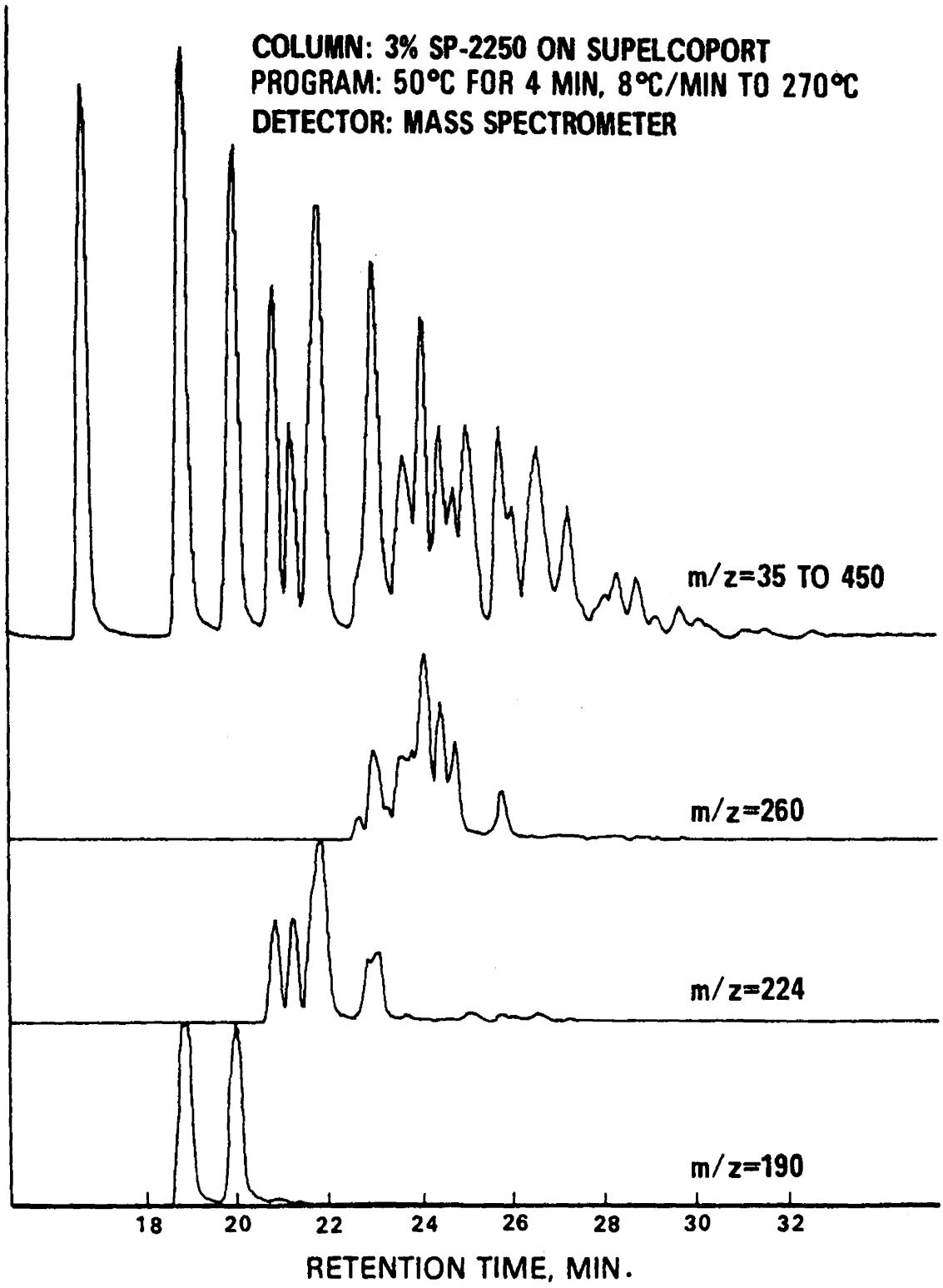


Figure 8. Gas chromatogram of PCB-1232.

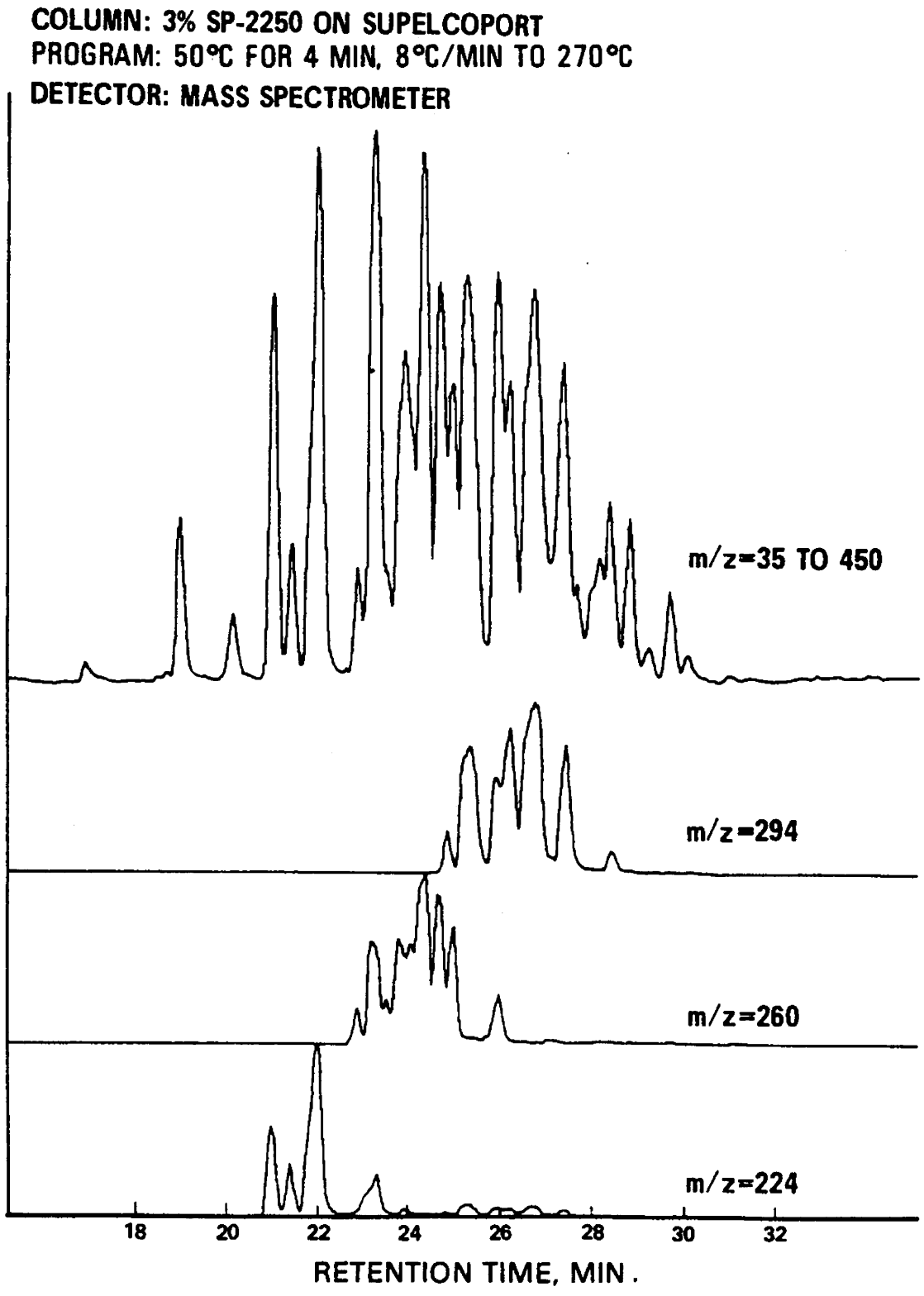


Figure 9. Gas chromatogram of PCB-1242.

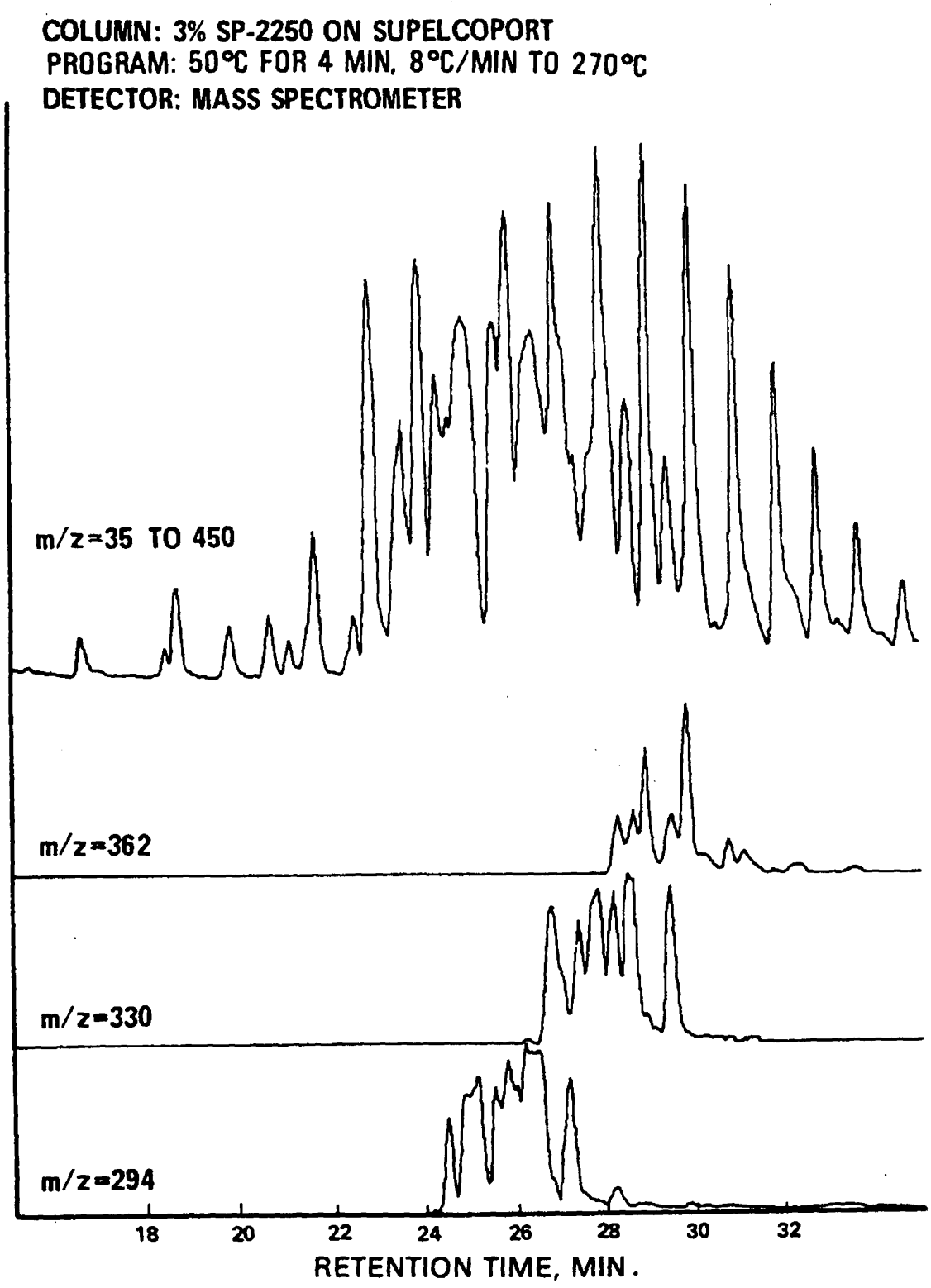


Figure 10. Gas chromatogram of PCB-1248.

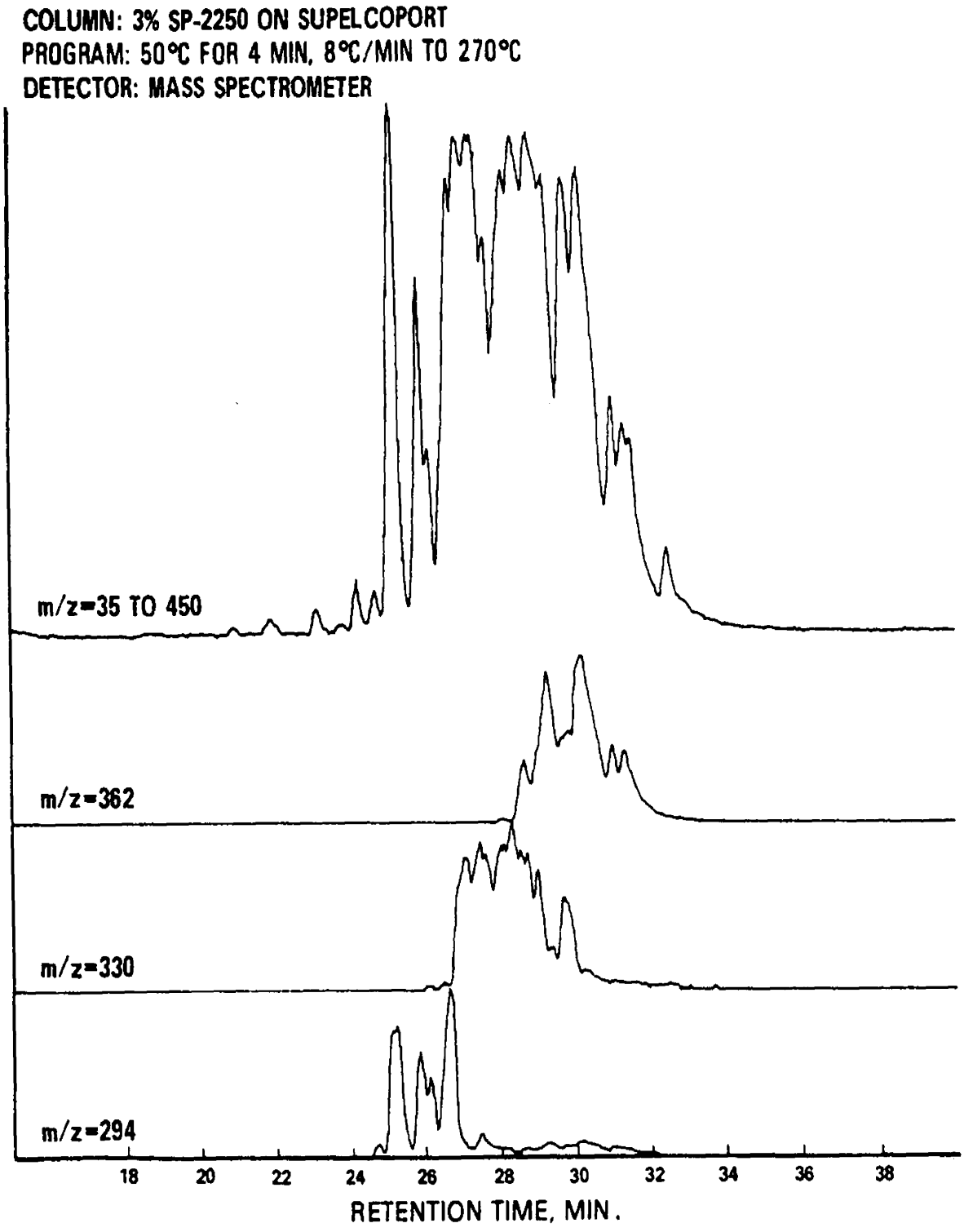


Figure 11. Gas chromatogram of PCB-1254.

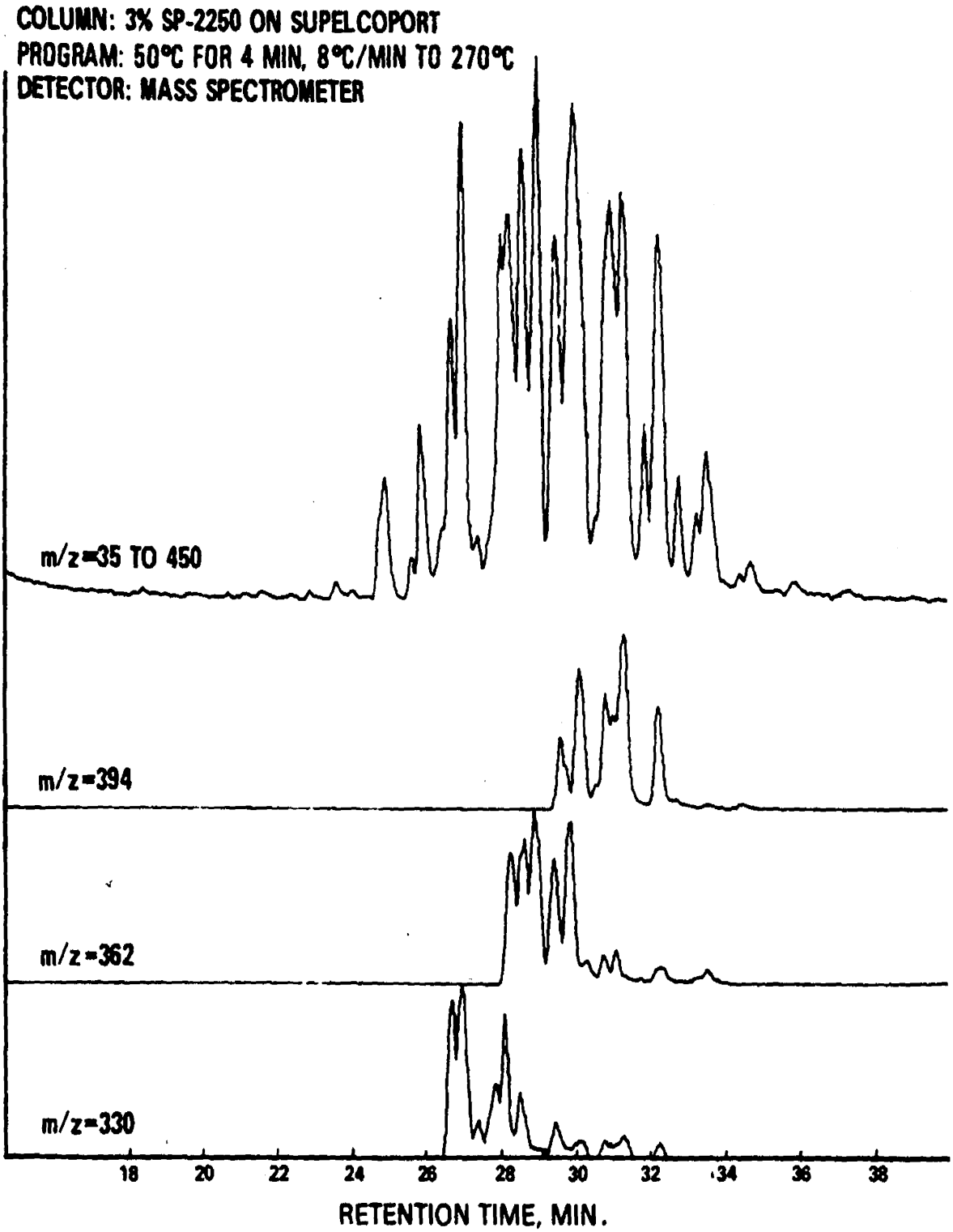
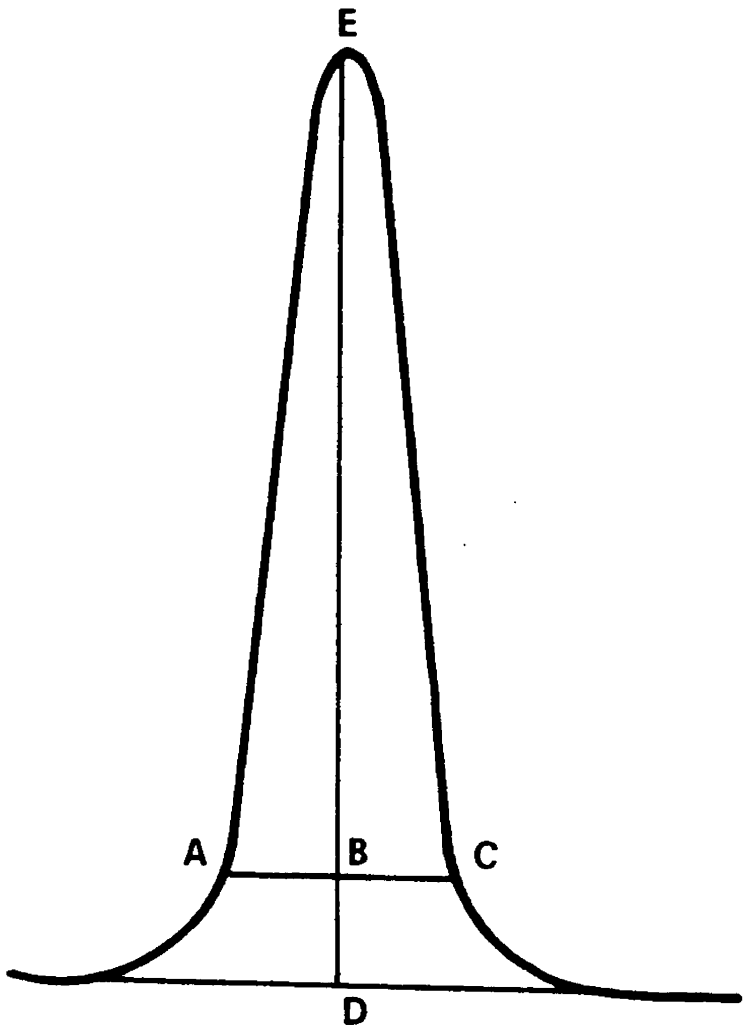


Figure 12. Gas chromatogram of PCB-1260.

$$RF = \frac{(A_s)\ (C_{is})}{(A_{is})\ (C_s)}$$



TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

Figure 13. Tailing factor calculation.