Final
Prescribed Burn Air Sampling and Analysis Plan
Ranges 43-48
Former Fort Ord, California

Prepared for

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1325 J Street
Sacramento, California 95814-2922

MACTEC Project No. 56286 010404

Bruce L. Wilcer
Associate Geologist

Douglas E. Cover, REA, QEP
Vice President

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MACTEC Engineering and Consulting, Inc.
90 Digital Drive
Novato, CA 94949 - (415) 883-0112

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CONTENTS

TABLES

PLATES

APPENDIXES

A. USEPA COMPENDIUM METHOD 1O-2.1
B. USEPA COMPENDIUM METHOD 1O-3.1
C. USEPA COMPENDIUM METHOD 1O-3.4
D. USEPA COMPENDIUM METHOD TO-9A
E. USEPA COMPENDIUM METHOD TO-11A
F. USEPA COMPENDIUM METHOD TO-13A
G. USEPA COMPENDIUM METHOD TO-15
H. USACHPPM LAB SOP CAD 26.3
I. MIE DATARAM, HESE SOP-101
J. GMW PS-1 PUF, HESE SOP-102
K. GMW 2000H, HESE SOP-103
L. MINIVOL, HESE SOP-104
M. ANDERSON GUV-16H, HESE SOP-105
N. KSC PCXR4, HESE SOP-106
O. TSI Q-TRAK PLUS IAQ MONITOR OPERATION AND SERVICE MANUAL
P. RESPONSE TO COMMENTS

DISTRIBUTION

LIST OF ACRONYMS AND ABBREVIATIONS

AA	Atomic Absorption
agl	Above ground level
Army	U.S. Department of the Army
Basewide OE RI/FS	Basewide OE Remedial Investigation/Feasibility Study
BRAC	Base realignment and closure
CAAA	Clean Air Act Amendments
CalEPA	California Environmental Protection Agency
CDQMP	Chemical Data Quality Management Plan
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CO	Carbon Monoxide
COC	Chain-of-Custody
CO_2	Carbon Dioxide
COPCs	Chemicals of potential concern
DOD	U.S. Department of Defense
DQOs	Data quality objectives
DS	Data System
DTSC	Department Of Toxic Substances Control
EPA	Environmental Protection Agency
FORA	Fort Ord Reuse Authority
Fort Ord	The former Fort Ord
GC-ECD	Gas Chromatography with Electron Capture Detection
GC-MS	Gas Chromatography/Mass Spectrometry
GFAA	Graphite Furnace Atomic Absorption
GPS	Global Positioning System
H&S	Health and Safety
Harding ESE	Harding ESE, Inc. (formerly Harding Lawson Associates)
HE	High Explosive
HLA	Harding Lawson Associates
H_2O	Water
HPLC	High Performance Liquid chromatography
HPLCMS	High Performance Liquid Chromatography Mass Spectroscopy
HRGC	High Resolution Gas Chromatograph-

HRMS	High Resolution Mass Spectrometer
HV	High-Volume
IDW	Investigation-derived waste
Interim Action RD	Interim Action Remedial Design
Interim Action ROD	Interim Action Record of Decision
Interim Action RAWP	Interim Action Remedial Action Work Plan
LAW	Light Antitank Weapon
MACTEC	MACTEC Engineering and Consulting, Inc. (formerly Harding ESE, Inc.)
MBUAPCD	Monterey Bay Unified Air Pollution Control District
MQL	Minimum Quantitation Limit
MRA	Multi-Range Area
NDIR	Non-Dispersive Infrared
NEW	Net Explosive Weight
N_2	Nitrogen
NMHC	Non-Methane Hydrocarbons
NO	Nitric Oxide
NO_x	Nitrogen Dioxide
O_2	Oxygen
OB	Open Burning
OD	Open Detonation
OE	Ordnance and Explosives
OVS	OSHA Versatile Sampler
PAHs	Polycyclic Aromatic Hydrocarbons
pg/m^3	Picograms Per Cubic Meter
PM_{10}	Particulate Matter Non-Methane Hydrocarbons (NMHC)
POM	Polycyclic Organic Material
PRGs	Preliminary Remediation Goals
PUF	Polyurethane Foam
QA/QC	Quality Assurance/Quality Control
QC	Quality Control
QCSM	Quality Control System Manager
SAP	Sampling and Analysis Plan
scfm	standard cubic feet per minute
SPM	Suspended Particulate Matter

SSHP	Site Safety and Health Plan
SVOCs	Semi Volatile Organic Compounds
TACs	Toxic Air Contaminants
TSP	Total Suspended Particulate
TWA	Time Weighted Average
µg	microgram
$\mu g/m^3$	Micrograms per cubic meter
USACE	U.S. Department of the Army, Corps of Engineers
USACHPPM	US Army Center for Health Promotion and Preventive Medicine
USEPA	U.S. Environmental Protection Agency
UXO	Unexploded Ordnance
VOCs	Volatile Organic Compounds
XRF	X-ray fluorescence

FORWARD

This June 2003 revision to the Draft Final Prescribed Burn Air Sampling and Analysis Plan, Ranges 43-48, Former Fort Ord, California, (the Air SAP) has been prepared to document revisions to some of the sampling activities proposed for the 2003 burn season. This revision incorporates minor technical changes documented in two Field Change Notifications that were issued in the weeks leading up to the planned burn in 2002, and also includes revisions to the approach for background sampling.

Provided below is a general summary of the changes incorporated in this revised Air SAP. Details of these changes are provided in the sections which follow.

1. Revision to location of sampling sites (from Field Change Notification #1).

2. Real-time PM_{10} data will be collected at more sites (from Field Change Notification #1).

3. Particulate metal analysis on all filter samples will be performed using EPA Method IO-3.4 ICP (from Field Change Notification #1).

4. Energetic analysis will be done by USACHPPM using their Method 26.3 (from Field Change Notification #1).

5. Air samples for Acrolein will be collected in SUMMA canisters for subsequent analysis by GC/MS full scan following EPA Method TO-15.

6. Eliminate energetic compounds from baseline sampling in 2003 (a complete set of baseline samples for energetic compounds were collected in 2002).

7. Conduct 2003 baseline sampling after the burn day so that baseline sampling can be done under similar meteorological conditions as the day the burn is conducted.

8. Changes to the number of "Public" sampling sites and the analytes to be included at each "Public" site.

EXECUTIVE SUMMARY

From 1917 to 1993, the U.S. Department of the Army (Army) used Fort Ord, California, as a training and staging area for infantry troops. Among the activities conducted at Fort Ord prior to its closure in December 1994 were the firing and use of various types of ordnance and explosives (OE), including projectiles, rockets, mortars, hand grenades, practice land mines, pyrotechnics, detonators, and other explosive materials. These OE items were used at various sites in two main areas known as the Multi-Range Area (MRA) and the Inland Training Ranges. Both of these areas today contain sites where unexploded ordnance (UXO) are known or are suspected to exist. The location and removal of these OE are necessary before the land can be safely transferred for public use.

In November, 1998, the Army agreed to evaluate OE at former Fort Ord in an OE RI/FS consistent with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process. The Army is preparing the basewide OE Remedial Investigation/Feasibility Study (basewide OE RI/FS) for Fort Ord to address OE-related hazards, which will include input from the community and require regulatory agency review and approval. The basewide OE RI/FS will review and evaluate past investigative and removal actions, as well as recommend future response actions deemed necessary to protect human health and the environment on the basis of proposed reuses specified in the Fort Ord Reuse Authority (FORA) Reuse Plan or as amended or periodically updated. The basewide OE RI/FS is scheduled to be completed in 2005.

The Army, as the lead agency, has determined that an Interim Action is appropriate to protect human health from the imminent threat posed by OE at three Interim Action sites (Ranges 43-48, Range 30A, and Site OE-16) while an ongoing comprehensive study of OE cleanup needs at former Fort Ord is conducted under the basewide OE RI/FS. Interim Action remedial activities were evaluated in three parts: vegetation clearance, OE remedial action, and OE detonation, as described in the Interim Action OE RI/FS (*Harding ESE, 2002*).

The Army's Proposed Plan (*Army, 2002*) identified prescribed burning as the preferred alternative to clear vegetation, subsurface OE removal as the preferred OE remedial action alternative, and detonation with engineering controls as the preferred OE detonation alternative for the three Interim Action sites. The public comment period for the Proposed Plan ended on 13 May 2002. The final selection of vegetation clearance method, OE remedial action and OE detonation method to be used at the Interim Action sites will be made in the Interim Action Record of Decision (Interim Action ROD). The Interim Action ROD is expected to be complete in September 2002.

Although the final decision has not been made, the Army has proceeded with developing the Site Specific Interim Action Remedial Design / Remedial Action Work Plan (Interim Action RD/RAWP) for Ranges 43-48, because it has the highest priority of the three Interim Action sites. The Ranges 43-48 Interim Action RD/RAWP consists of four separately prepared plans. Each of the following four plans details task-specific inter-related work activities for implementing the Interim Action remedial activities. These four plans are described at the end of this Executive Summary.

(1) Fort Ord Prescribed Burn Plan of Ranges 43–48, August, (*Fire Stop, 2002*)

(2) Voluntary Relocation Plan, August, (*Creighton & Creighton, Inc., 2002*)

(3) Prescribed Burn Air Sampling, July, (*this document, July 2003*)

(4) Ranges 43-48 Site-Specific Work Plan, August, (*Parsons, 2002*).

If prescribed burning is selected for the Interim Action sites, the intense fire associated with prescribed burn conditions may result in the incidental detonation of surface or near-surface OE items. Detonation of OE has the potential to release air pollutants to the atmosphere. These air emissions may potentially include combustion products, volatile or semivolatile organic compounds, unburned or incompletely burned energetic material, and particulate metals and metal compounds from chemical components of the OE items. Available models and studies described in this Sampling and Analysis Plan (SAP) suggest that no significant amounts of criteria air pollutants or toxic air contaminants (TACs) would be released from the incidental OE detonations during prescribed burn activities conducted at the former Fort Ord. A Technical Memorandum prepared by Harding ESE (*Harding ESE, 2001*) documented the results of an investigation of ordnance-related air emissions from a proposed prescribed burn on Ranges 43-48. That investigation concluded that all ordnance-related air emission impacts would be well below human health-protective regulatory screening levels.

In addition to possible OE-related air emissions, the smoke generated from prescribed burning of vegetation may also contain air pollutants which could be a concern to adjacent populated areas. Inhalable particulate matter (suspended particles less than 10 microns in diameter [PM_{10}]) and other products of combustion can cause temporary respiratory distress to sensitive populations during the burn event. Smoke management techniques as described in the burn plan (*Fire Stop, 2002*) will be employed by the Army to minimize public exposure to smoke from prescribed burns at the former Fort Ord.

This SAP outlines procedures for the collection and analysis of air samples during a prescribed burn event for Ranges 43-48 at the former Fort Ord. The purpose of the sampling and analysis program described herein is to:

(1) Confirm or refine conclusions drawn from other studies that ground-level concentrations of ordnance-related air pollutants downwind of the prescribed burn will be below human health-protective regulatory screening levels, and

(2) Provide data to assess the adequacy of the of the burn prescription relative to smoke dispersion and downwind impacts.

Description of Other Inter-Related Plans

1. Fort Ord Prescribed Burn Plan of Ranges 43-48, August (*Fire Stop, 2002*)

This Burn Plan describes the objectives of the prescribed burn; the burn area; the range of environmental conditions under which the burn will be conducted; the manpower and equipment resources required to ignite, manage, and contain the fire; a smoke management plan; and establishment of communication procedures for the fire crew and to the public and other affected agencies. Procedures for conducting the burn within the window of environmental conditions established in the burn prescription are discussed in this Burn Plan. An escaped fire contingency plan also is included.

2. Voluntary Relocation Plan, August, (*Creighton & Creighton, Inc, 2002*)

This Voluntary Relocation Plan describes the Army's actions that will be implemented for those Monterey County residents who wish to temporarily relocate if the Army uses prescribed burns to clear vegetation in preparation of OE cleanup. This plan describes the roles and responsibilities of the various Army organizations and contractors, and local government and community organizations, prior to, during, and after prescribed burns. It also describes the responsibilities of those people who wish to relocate.

3. Prescribed Burn Air Sampling and Analysis Plan, Ranges 43-48, Former Fort Ord, California, August (*this document, revised July 2003*)

This Prescribed Burn Air Sampling and Analysis Plan outlines procedures for the collection and analysis of air samples during a prescribed burn. The primary purpose of collecting and analyzing air samples during a prescribed burn is to confirm or refine the conclusions of the Technical Memorandum, Air Emissions from Incidental Ordnance Detonation During a Prescribed Burn on Ranges 43 through 48, Former Fort Ord, California (*Harding ESE, 2001*) that ground-level concentrations of ordnance-related air pollutants downwind of the prescribed burn will be well below human health-protective regulatory screening levels. While the air sampling program is focused on detection and quantification of ordnance-related emissions, data from the air sampling program will also be used to assess the adequacy of the burn prescription and to assess downwind concentrations of selected vegetation-related emissions.

4. Ranges 43-48 Site-Specific Work Plan, August (*Parsons, 2002*)

This Site-Specific Work Plan describes the procedures, methods and resources that Parsons and its subcontractors will use while performing subsurface OE removal and OE detonation with engineering controls. Subsurface OE removal consists of identification (visual search and operation of OE detection equipment) and remediation (combined with follow-on detonation) of any OE found/detected on the ground surface and in the subsurface to depths determined in this plan. A depth analysis plan is included as part of this plan. OE detonation with engineering controls consists of applying additional detonating charges to single or consolidated OE items, and applying engineering controls (covering the OE with tamped dirt, sandbags, contained water, or other materials) prior to detonation to reduce the blast and any associated fragmentation, emissions, or noise.

An appendix to this Site-Specific Work Plan addresses site preparation activities to be performed prior to a prescribed burn to reduce smoke emissions during the prescribed burn and ensure the prescribed burn is contained within the site boundaries. Site preparation activities include removal of tires, structures, inactive utility poles, selected trees; maintenance of containment lines, establishment of staging areas and escape routes; and protection of existing structures outside of the site by removing nearby vegetation, applying fire suppressant foam, or installing irrigation sprinkler systems.

1.0 PROJECT ORGANIZATION

The MACTEC Engineering and Consulting, Inc. (MACTEC) project organization for this contract is presented in Section 2.0 of the *Draft Final Chemical Data Quality Management Plan (CDQMP), Engineering and Environmental Investigation Services, Former Fort Ord Complex, California*, dated July 22, 1997 (*HLA, 1997a*). The identity and responsibilities of key project personnel related to this plan are summarized below.

1.1 Program Manager

The MACTEC Program Manager for U.S. Department of the Army, Corps of Engineers (USACE) projects, Mr. Ed Ticken, has overall responsibility and authority for project coordination between the USACE and MACTEC.

1.2 Quality Control System Manager

The MACTEC Quality Control System Manager (QCSM), Mr. Donald Smallbeck, is responsible for independent review and approval of project-related documents as well as overall responsibility for quality control (QC) of field operations, data collection, laboratory activities, and implementation of a three-phase QC procedure (see Section 9.1). As well as reporting to the Program Manager, the QCSM reports to MACTEC's Chief Technical Quality Assurance/Quality Control (QA/QC) Officer and the MACTEC Bay Area Officer Manager. The QCSM may delegate review of all or portions of a document to other appropriate and qualified staff.

1.3 Project Manager

The MACTEC Project Manager for the former Fort Ord project, Mr. Bruce Wilcer, is responsible for the implementation of USACE and regulatory agency requirements for the project. These responsibilities may include oversight of the development of all delivery order documents and related activities as well as schedule and contract management, technical oversight, report generation, implementation of three-phase QC activities, and overall project quality.

1.4 Task Manager

The MACTEC Task Manager for the sampling program described in this SAP, Mr. Doug Cover, is responsible for implementation and oversight of activities related to project performance. This responsibility includes development of delivery order documents, implementation of project activities, management of the schedule and contract, oversight of technical issues, generation of reports, and implementation of the QC procedures specified in this SAP.

1.5 Project Chemist

The Project Chemist, Ms. Debbie Leibensberger, provides input for development of this SAP, as well as management of project tasks associated with sampling and preservation requirements, general oversight of field personnel in sampling activities, coordination of sample collection and analysis with the analytical laboratory, review of analytical data soon after they are received, and implementation of three-phase QC activities and corrective actions (as necessary). The Project Chemist will also conduct a project kick-off meeting with the analytical laboratory prior to sample collection or analysis.

2.0 PROJECT BACKGROUND AND PROBLEM DEFINITION

Project background and problem definition include a description of the facility, the prescribed burn operations, and potential impacts to air.

2.1 Facility History and Description

The following sections describe the facility in terms of location, history, and OE profile.

2.1.1 Location

The former Fort Ord (Fort Ord) is adjacent to Monterey Bay in northwestern Monterey County, California, approximately 80 miles south of San Francisco (Plate 1). The former Army base consists of approximately 28,000 acres adjacent to the cities of Seaside, Sand City, Monterey, and Del Rey Oaks to the south and Marina to the north. The Southern Pacific Railroad and Highway 1 pass through the western part of Fort Ord, separating the beachfront portions from the rest of the former base. Laguna Seca Recreation Area and Toro Regional Park border Fort Ord to the south and southeast, respectively, as well as several small communities such as Toro Park Estates and San Benancio.

2.1.2 Historical Use

Military training on the former Fort Ord began in approximately 1917 and continued until base closure in 1994. At its founding in 1917, the former Fort Ord served primarily as training and staging facility for infantry troops. From 1947 to 1974, the Installation was a basic training center. After 1974, the 7th Infantry Division occupied the Installation. The 7th Infantry Division was converted to a light division in 1983; light infantry troops operate without heavy tanks or armor. The former Fort Ord was selected in 1991 for base realignment and closure (BRAC), and the base was officially closed in September 1994.

In 1917, the Army bought a portion of the present-day Main Garrison and East Garrison, and nearby lands on the east south central side of the former Fort Ord to use as a maneuver and training ground for field artillery and cavalry troops stationed at the Presidio of Monterey. Before the Army's acquisition of the property, the area was agricultural, as is much of the surrounding land today. No permanent improvements were made until the late 1930s, when administrative buildings, barracks, mess halls, tent pads, and a sewage treatment plant were constructed.

In 1940, additional agricultural property was purchased for further development of the Main Garrison. At the same time, beachfront property was donated to the Army. Building construction in the Main Garrison began in 1940 and continued into the 1960s, starting in the northwest corner of the base and expanding southward and eastward. During the 1940s and 1950s, the Army constructed and maintained a small airfield within the Main Garrison in what became the South Parade Ground. In the early 1960s, when the Fritzsche Army Airfield was completed, the Main Garrison airfield was decommissioned and its facilities were redeveloped as motor pools and other facilities.

2.1.3 History of OE Use

Since 1917, portions of the Installation were used by infantry units for maneuvers, target ranges, and other purposes. OE that have been fired into, fired upon, or used on the facility include artillery and mortar projectiles, rockets and guided missiles, rifle and hand grenades, practice land mines,

pyrotechnics, and demolition materials. A wide variety of conventional unexploded ordnance (UXO) items have been located at sites throughout the former Fort Ord, including pyrotechnics and explosives.

2.2 Ranges 43–48 History and Site Description

In November, 1998, the Army agreed to evaluate OE at former Fort Ord in an OE RI/FS consistent with the CERCLA process. The Army is preparing the basewide OE RI/FS for Fort Ord to address OE-related hazards, which will include input from the community and require regulatory agency review and approval. The basewide OE RI/FS will review and evaluate past investigative and removal actions, as well as recommend future response actions deemed necessary to protect human health and the environment on the basis of proposed reuses specified in the Fort Ord Reuse Authority (FORA) Reuse Plan or as amended or periodically updated. The basewide OE RI/FS is scheduled to be completed in 2005.

The Army, as the lead agency, determined that an interim action is appropriate to protect human health from the imminent threat posed by OE at Ranges 43-48, Range 30A, and Site OE-16 in order to ensure public safety while the basewide OE RI/FS is being conducted. In March 2002, the Army issued the Final IA OE RI/FS report (*Harding ESE, 2002*) and presented the Interim Action Proposed Plan for Ranges 43–48, Range 30A, and Site OE-16 at former Fort Ord to the public for review and comment (*Army, 2002*). The Proposed Plan presented the preferred alternatives for each area and summarized information in the IA RI/FS and other documents in the Administrative Record. Prescribed burning is the Army's preferred alternative selected for vegetation clearance. Comments have been received on the Proposed Plan and are being considered. The final decision on vegetation clearance method(s) that will be used at the interim action sites will be made in the Record of Decision that is expected to be completed in September 2002.

If prescribed burning is selected as the vegetation clearance method for the IA sites, then Ranges 43–48 would be scheduled for vegetation clearance first with OE Site 16 and Range 30A scheduled for subsequent years.

2.2.1 Location

Ranges 43–48 cover approximately 483 acres to the south of Eucalyptus Road in the south-central portion of the former Fort Ord (Fort Ord) (Plate 2). Future reuse of the northern portion is development (11 acres). The southern portion is designated as habitat reserve and will remain undeveloped (472 acres).

These ranges were part of Fort Ord's Multi-Range area (MRA) and are categorized as firing ranges where personnel were trained in the use of live ammunition. The MRA is fenced and posted with signs warning of the dangers associated with OE. Vegetation at Ranges 43–48 mainly consists of Central Maritime Chaparral with some grassland areas.

2.2.2 History of OE use at Ranges 43-48

Training facilities maps indicate these ranges were used for a variety of live fire exercises from the 1940s through the 1990s. Records and recent field investigations indicate that the ammunition used at these ranges included 4.2-inch, 60mm, and 81mm mortars; 14.5mm subcaliber projectiles; 35mm subcaliber rockets; 90mm recoilless rifle rounds; 84mm incendiary projectiles; 40mm High Explosive (HE) grenades; 66mm light antitank weapon (LAW); small arms; anti-personnel mines; dragon guided missiles; and fragmentation hand grenades (*Harding ESE, 2002*).

2.2.3 Risks from OE at Ranges 43-48

In general, risks from physical contact with OE are acute and potentially catastrophic in nature, and may result in crippling injuries or death.

Areas in and around the former firing ranges contain sensitively fuzed, highly dangerous OE present on the ground surface or at shallow depths below the ground. As described above, numerous types of OE ranging from hand grenades to 90mm recoilless rifle rounds are known or suspected to be on the site. During recent limited investigations, thousands of unexploded and expended items were recovered at Ranges 43–48.

2.3 Prescribed Burn Operations

The Army recognizes that smoke produced by prescribed burn events has the potential to create short-term impacts on local air quality and potential impacts on public health downwind of the smoke, and is currently working with the regulatory agencies, local air pollution control agency and the public to develop effective smoke management measures. Additionally, procedures will be in place to inform the local communities prior to conducting prescribed burn events, and a provision for temporary relocation of smoke-sensitive individuals is planned. In light of the short-term impacts due to smoke, measures that will also be considered to accomplish smoke management include optimizing the ignition patterns for the burn and modifying parameters of the burn prescription.

A detailed Burn Plan has been prepared by the Army's burn contractor, Fire Stop (*Fire Stop, 2002*). That Plan describes the operational aspects of the proposed burn at Ranges 43-48, including all considerations for smoke management.

2.4 Problem Definition: Potential Impacts to Air

2.4.1 Incidental Detonation of OE

Prescribed burn activities in OE areas at the former Fort Ord may result in the incidental detonation of surface or near-surface OE items. Detonation of OE has the potential to release air pollutants to the atmosphere. These air emissions may potentially include combustion products, volatile or semivolatile organic compounds, unburned or incompletely burned energetic material, and particulate metals and metal compounds from chemical components of the OE items. Available models and studies described below suggest that no significant amounts of criteria air pollutants or TACs would be released from the incidental OE detonations during prescribed burn activities conducted at the former Fort Ord.

2.4.1.1 Pollutant Prediction Model

Data on characterization of TACs from detonation of military ordnance are not widely available. The USEPA document "Compilation of Air Pollution Emission Factors, 5th Edition (AP-42)" *(USEPA, 1996)* is limited to data regarding the detonation of industrial explosives and firing of small arms, and specifically excludes military applications.

Of the publicly available information on military applications, a reference document by Baroody *(1987)* and an associated computer program, POLU13L *(Baroody, 1994)*, developed by the Department of the Navy, Naval Surface Warfare Center, Indian Head, Maryland, provides the most comprehensive source of combustion product characterization for military ordnance. The POLU13L model calculates combustion products by solving a large set of nonlinear algebraic equations to estimate high temperature chemical equilibria, and has a library of over 1400 potential combustion products that are considered in the model

calculations. However, the model is limited to considering only those chemical components and additives in the explosive mixture; metals used in the casing or other structural components of OE items are expected to have little contribution to emissions and are not factored into the calculations. The model is also limited in that its library of potential combustion products, while quite large, does not include residual energetic materials and many TACs that may be produced in trace amounts.

The data provided by Baroody *(1987)* for military explosives is consistent with that in USEPA *(1996)* for conventional explosives in that the products of combustion for the most widely-used explosive mixtures are largely carbon dioxide (CO_2), carbon monoxide (CO), nitrogen (N_2), oxygen (O_2), and water (H_20). Both references suggest that only trace amounts of TACs are produced.

A set of worst-case assumptions were developed based on results of past OE sampling activities (*Army, 1998*), which would be considered high OE density areas, to quantify the total net explosive weight (NEW) of OE items that may detonate during a prescribed burn. Those assumptions are:

- Maximum live OE density = 10 per acre
- Fraction of live OE items detonated during a prescribed burn = 0.5 (i.e., 50%)
- Maximum prescribed burn area in a single day = 1,000 acres
- All OE items are either LAW rockets (0.5 lbs. Octol/item) or 81 mm mortars (1.29 lbs. Comp B/item). Comp B and Octol are the two most common energetic materials in the OE items found at the former Fort Ord.

These assumptions result in an upper bound estimate of 5,000 OE items detonated during a 1,000-acre prescribed burn. If all items were LAW rockets, then the total NEW would be 2,500 lbs. Octol. If all items were 81mm mortars, then the total NEW would be 6,450 lbs. Comp B.

The pollutant prediction model POLU13L was used to identify and quantify the pollution products from these two scenarios. The results of the POLU13L simulations are summarized in Table 1a.

The primary pollutant products were predicted to be N_2, O_2, CO/CO_2, and H_2O, with significantly smaller to trace amounts of particulate carbon, NO/NO_x, CH_4, and NH_3. Of the pollutant products predicted by the POLU13L model, only CO and NO_2 (as NO/NO_x) are regulated criteria air pollutants. None of the predicted pollutant products are regulated as TACs under either the 1990 Clean Air Act Amendments (CAAA) or the Monterey Bay Unified Air Pollution Control District (MBUAPCD) Rule 1000 (Permit Guidelines and Requirements For Sources Emitting Toxic Air Contaminants), nor do they have established EPA Region IX Preliminary Remediation Goals (PRGs).

2.4.1.2 BangBox Studies

A series of seven field studies funded by the U.S. Department of Defense (DOD) have been conducted to identify and quantify the pollutant species released to the air from detonating or burning energetic materials. These studies are commonly referred to as BangBox studies, because the tests were conducted inside large chambers. A total of 16 energetic materials were burned and 23 were detonated in the BangBox studies. An August 1998 USEPA report entitled "Emission Factors for the Disposal of Energetic Materials by Open Burning and Open Detonation (OB/OD)" (*USEPA, 1998*) provides an analysis and summary of all the BangBox studies.

Air samples from the BangBox tests were analyzed for more than 275 individual compounds, including volatile organic compounds (VOCs), energetic and other semi-volatile organic compounds (SVOCs),

particulate metals, and chlorinated dioxins and furans. Many of those compounds (103 of 108 SVOCs and over 65% of the VOCs) were never detected in any of the BangBox tests. Further, many of the analytes that were detected were observed at concentrations less than background or below the minimum quantitation limit (MQL), and were therefore considered "not detected" in the report. Of the 83 analytes for which emission factors are reported, most are non-hazardous compounds commonly found in ambient air.

The USEPA report was reviewed to identify those analytes which were associated with the types of OE at the former Fort Ord. Emission factors that were reported for analytes associated only with open burning of propellant wastes and other items or processes not encountered at the former Fort Ord are not considered relevant to the identification of air pollutant emissions from OE detonation at this location.

A brief discussion of the analytes detected in the BangBox studies applicable to the former Fort Ord are described below. Using the BangBox emission factors, Table 1b summarizes the type and estimated quantity of criteria air pollutant and TAC emissions that would be expected from the worst-case incidental detonation scenarios described above.

Criteria Air Pollutants

Criteria air pollutants observed during the BangBox studies were CO, NO_2, and PM_{10} (particulate matter less than 10 microns). Emission factors for CO and NO_2 are expressed as a percent of the total carbon (for CO) and total nitrogen (for NO_2) in the detonated charge. The CO emission factors averaged an order of 4 percent of total carbon, and NO_2 emissions averaged an order of 2 percent of total nitrogen. PM_{10} emissions were reported an order of 0.2 pounds per pound NEW.

Volatile Organic Compounds

A number of saturated VOCs (e.g., ethane, propane, butane) and unsaturated VOCs (e.g., ethylene, acetylene, and propene) were commonly associated with detonation of OE items. These compounds, however, are environmentally benign and are not regulated air pollutants or TACs. The only aromatic VOCs associated with detonation of common OE items are benzene, ethylbenzene, and toluene, which are regulated as TACs under the 1990 CAAA and MBUAPCD Rule 1000. Styrene, also a regulated TAC, was observed only with OE items which had polystyrene structural components. Emission factors reported for aromatic VOCs are on the order of 10E-06 pounds per pound NEW.

Energetic Analytes

Three energetic compounds (RDX, HMX, and PETN) were reported to be associated with OE detonations in the BangBox studies. These compounds are not specifically regulated as TACs; however, RDX and HMX are considered TACs for this investigation because they have established human health risk values. Mean emission factors reported for RDX and HMX are on the order of 1E-04 pounds per pound NEW.

Other Semivolatile Organic Compounds

Only one SVOC (diethylphthalate) was identified in some OE detonation samples, but only with OE items which contained phthalates (mainly some signal flares and fuzes). Diethylphthalate is regulated as a TAC by the MBUAPCD. Mean emission factors reported for diethylphthalate are on the order of 1E-05 pounds per pound NEW.

Dioxins and Furans

Furans were not detected above background levels in any of the BangBox studies. Only one dioxin isomer (OCDD) was reported and was associated only with detonation of M43A2 flares. The occurrence of OCDD was reported to have likely resulted from the reaction of chloride-containing compounds and the plastic materials in the flare. The mean emission factor reported for OCDD is very low, on the order of 1E-09 pounds per pound NEW.

Particulate Metals

Analytical results for metals in the BangBox studies were inconsistent and prevented development of valid emission factors even for OE items where metals were expected (e.g., signal flares containing powdered aluminum in the primary energetic material). As a conservative approach, the report suggests that any metals contained within the energetic material should be assumed to be entirely emitted to the atmosphere. Several metals (e.g., lead, cadmium, nickel) that may be contained in trace amounts in some OE items are regulated as TACs.

2.4.1.3 Range 43 through 48 Air Emissions Technical Memorandum

The Army is evaluating vegetation clearance methods, including prescribed burning of approximately 500 acres in Ranges 43-48 of the former Fort Ord, to facilitate the subsequent removal of OE. A detailed investigation was conducted in consultation with the U.S. Environmental Protection Agency (USEPA) Region IX, California Environmental Protection Agency Department of Toxic Substances Control (CalEPA/DTSC), U.S. Army Corps of Engineers (USACE) Sacramento District, and the Department of the Army (Army) to (1) quantify a reasonable upper bound estimate of air emissions from incidental detonation of OE in Ranges 43-48, (2) compare those emissions with those expected from burning of vegetation (biomass) on Ranges 43-48, and (3) compare screening level estimates of pollutant concentrations from OE to health-protective regulatory screening values.

The results of this investigation were documented in a Technical Memorandum (*Harding ESE, 2001*), and are summarized here in Table 2. The investigation revealed that reasonable upper bound estimates of air emissions from incidental OE detonation for combustion products and volatile organic compounds are much less than 0.1% (i.e., one one-thousandth) of the corresponding emissions from vegetation burning on Ranges 43-48. The only exception is for dioxin/furan toxicity equivalent emissions for which the reasonable upper bound OE contribution is about 1% (i.e., one one-hundredth) of that from vegetation. Reasonable upper bound emissions of all particulate metals except Beryllium from incidental OE detonation are equal to or less than 10% (i.e., one-tenth) those from vegetation burning. For all OE-related pollutants evaluated in this investigation, screening model estimates of pollutant concentrations are much less than health-protective regulatory screening values.

The conclusion of this investigation is that air pollutant emissions from incidental OE detonation during a prescribed burn on Ranges 43-48 will be minor compared to emissions contributed directly by vegetation burning, and will result in pollutant concentrations well below health-protective regulatory screening levels.

2.4.1.4 Contaminants of Potential Concern

The results of the POLU13L model and the BangBox studies suggest that little or no TACs are likely to be produced and released to the atmosphere from the incidental detonation of OE items during prescribed burns at the former Fort Ord. However, both the POLU13L model and the BangBox studies have limitations. Most notably, the pollutant prediction model does not address the possible emission

contribution of metals from OE structural components. It also fails to predict emissions of residual energetic material and several TACs which were observed at low levels during BangBox tests of common OE items. The results of the BangBox tests were useful in eliminating many TACs from the list of possible byproducts of OE detonation, but some results, such as for particulate metals, were inconclusive.

The results of the air emissions Technical Memorandum (*Harding ESE, 2001*) concludes that maximum downwind concentrations from OE emissions during a prescribed burn on Ranges 43-48 would occur at approximately 3,285 meters downwind and would be well below health-protective regulatory screening levels. This study also showed that emissions of all OE-related combustion products would be many orders of magnitude less than for the same pollutant produced from vegetation burning. For this reason, it would be impossible to distinguish any OE contribution to those combustion products which are also produced from the vegetation.

This air sampling program, therefore, will focus on those combustion products which are unique to OE detonation. Energetic materials and their likely breakdown products are the primary pollutant species which were shown in the previous studies to be clear signatures of OE emissions. The air emissions Technical Memorandum identified a few volatile organic compounds (VOCs) for which vegetation emissions were unknown, but not necessarily zero. These VOCs are also ubiquitous in low concentrations in urban areas and so would not provide a clear signature of OE emissions.

The other possible candidate for OE signature emissions are particulate metals. The previous studies indicated that OE detonation may result in the release of particulate metals, but there were several uncertainties in the emission factors. The BangBox studies, for example, were inconclusive with respect to metal emissions because of various sampling difficulties. The air emissions Technical Memorandum relied on reasonable upper bound assumptions regarding particulate metal emissions from OE detonation. Because of these uncertainties, it is prudent to include particulate metals in this investigation to determine if further assessment is warranted.

Dioxins and furans are estimated to occur in very low amounts from OE detonation, and only from certain types of OE with plastic components. However, dioxins and furans are included in this air sampling program because of the uncertainty in the emission estimate for those compounds.

2.4.2 Burning of Vegetation

Prescribed fire is an extremely diverse source and its emissions are therefore difficult to quantify. The diversity in the type and quantity of combustion products is due to many factors, including fuel (vegetation) type, moisture content, and the diversity of combustion processes which occur simultaneously within a fire. The primary combustion processes include flaming, smoldering, and glowing combustion.

Despite the wide variation in combustion emissions, prescribed burning is generally recognized as a significant source of particulate matter and carbon monoxide emissions. Emissions of toxic air contaminants are less understood, but can include nitrogen oxides, hydrocarbons, sulfur oxides, and polycyclic organic material (POM), which contains hundreds of other compounds in small quantities (*Peterson and Ward, 1989*).

Nitric oxide, the criteria air pollutant component of the larger category of nitrogen oxides, forms only at temperatures well above those occurring in prescribed fires and is generally not considered a significant emission from prescribed burning. Sulfur oxide emissions are typically negligible because of the low sulfur content of most biomass fuels. The hydrocarbons most often found are products of incomplete

combustion such as methane, ethylene, alkynes, aldehydes, furans, carboxylic acids, and polynuclear aromatic hydrocarbons (*Peterson and Ward, 1989*).

Peterson and Ward (*1989*) and Hardy (*1996*) have summarized the results of a number of field and laboratory prescribed burn smoke sampling programs, and have provided a method for estimating the quantity of air emissions produced from prescribed burns for a wide variety of fuel types. These data were used in the air emissions Technical Memorandum (*Harding ESE, 2001*) to estimate vegetation-related air emissions from a proposed prescribed burn on Ranges 43-48 at the former Fort Ord. Emission estimates for the primary combustion byproducts:

Pollutant Species	Emission Estimate (pounds per acre)
Carbon Dioxide (CO_2)	43,186
Carbon Monoxide (CO)	2,039
Particulate Matter (PM_{10})	268
Non-Methane Hydrocarbons (NMHC)	260
Nitrogen Oxides (NO_x)	63

CO and CO_2 are clearly produced in the greatest amounts from vegetation burning and are therefore the best choice for signature compounds to indicate whether and to what extent the sampling locations for this investigation are being impacted by the smoke from the prescribed burn. PM_{10} will also be included in the list of target analytes for this investigation because it may provide an opportunity to correlate with qualitative measures of smoke impact (e.g., subjective assessments of smoke density). This PM_{10} sampling will also fulfill the requirement in Title 17 of the California Code of Regulations for ambient particulate sampling for prescribed burns greater than 250 acres in Wildland/Urban interface areas.

Of the TACs likely to be produced by prescribed burning, aldehydes are the compounds which are generally associated with acute irritation in smoke-impacted public areas. Formaldehyde, acetaldehyde, and acrolein are the specific aldehydes of interest from vegetation burning. Accordingly, this sampling program will include sampling and analysis for formaldehyde, acetaldehyde, acrolein, and total aldehydes.

Table 3 summarizes the complete list of target analytes proposed for this investigation, including OE-specific compounds and smoke signature compounds. Table 4 summarizes the applicable regulatory screening levels that will be used for comparison to the sampling results.

3.0 PROJECT DESCRIPTION

This section describes the project briefly in terms of objective and scope, as well as schedule and reporting.

3.1 Objective and Scope

This SAP outlines procedures for collection and analysis of air samples in areas potentially affected by air emissions from a prescribed burn at Ranges 43-48. The results of other relevant studies and investigations have been applied in this SAP as an initial estimate of the type and quantity of chemicals of potential concern (COPCs) from incidental OE detonation. The purpose of the sampling and analysis program described herein is to:

(1) Confirm or refine conclusions drawn from those other studies that ground-level concentrations of ordnance-related air pollutants downwind of the prescribed burn will be below human health-protective regulatory screening levels, and

(2) Provide data to assess the adequacy of the of the burn prescription relative to smoke dispersion and downwind impacts. The air sampling program is therefore focused on detection and quantification of ordnance-related emissions and selected vegetation-related combustion products. Real-time data and smoke observations during the burn may also be used to allow the burn contractor to modify the burn tactics so as to reduce downwind smoke impacts.

The Army's burn contractor, Fire Stop, estimates that the prescribed burn at Ranges 43-48 may take from one to three days to complete. If active ignition is implemented on a second or third day to complete the burn, then air sampling will be conducted on each of those additional days.

3.2 Schedule and Reporting

The following report and schedule projections are based on the date the Preliminary Draft SAP is submitted and the duration of USACE and agency review. The agencies that will review this SAP are the California Department of Toxic Substances Control (DTSC) and the U.S. Environmental Protection Agency (USEPA).

ACTION ITEM	SCHEDULE
Agencies review Draft SAP	30 days after receipt of Draft SAP
Address agency comments and submit Draft Final SAP	30 days after review comments received
Agencies complete review of Draft Final SAP	15 days after receipt of Draft Final SAP
Address agency comments and submit Final SAP	15 days after review comments received
Agencies review 2003 Revised SAP	*7 days after receipt of 2003 Revised SAP*
Address agency comments and submit 2003 Final SAP	*7 days after review comments received*
Perform field work	Contingent on local weather conditions and fuel moisture content which meet the burn prescription
Submit Preliminary Draft Investigation Report to USACE	60 days after completion of field work
USACE completes review of Preliminary Draft Investigation Report	30 days after receipt of Preliminary Draft Investigation Report
Address USACE comments and submit Draft Investigation Report to agencies	2 weeks after review comments received
Agencies complete review of Draft Investigation Report	30 days after receipt of Draft Investigation Report
Address agency comments and submit Draft Final Investigation Report	2 weeks after review comments received

4.0 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) for the project are discussed in the sections below.

4.1 Statement of the Problem

The identity and quantity of products and residues emitted to the air from prescribed burn activities at the former Fort Ord can only be estimated from previous studies. Former Fort Ord-specific measurements of air pollutant concentrations are not adequate for the objectives of this SAP.

4.2 Identification of Decisions

The primary decisions related to this project are to (1) evaluate whether prescribed burns at the former Fort Ord result in downwind ambient concentrations of ordnance-related air pollutants that exceed human health-based screening levels, and (2) evaluate the adequacy of the burn prescription relative to smoke dispersion and downwind impacts to the public.

4.3 Identification of Inputs to Decisions

Inputs to decisions necessary for evaluating prescribed burn activities at former Fort Ord are as follows:

- Identify target list of COPCs
- Identify appropriate screening levels for COPCs in air (e.g., California Ambient Air Quality Standards, approved Fort Ord PRGs, (*HLA, 1994*) or EPA Region IX PRGs (*EPA, 1999*)
- Identify appropriate criteria for modifying burn tactics based upon real-time data collected during the burn (will require coordination between the burn contractor and the regulatory agencies)
- Assess baseline concentrations of COPCs
- Measure downwind concentrations of COPCs in air during a prescribed burn event
- Record field observations, including wind speed and direction during the event, and visually identify the downwind area that received smoke impacts
- Record size (acres) of the prescribed burn area and duration of the burn.

4.4 Definition of Study Boundaries

The study boundary is defined as the area downwind of the prescribed burn event that receives smoke impacts. Air samples will be collected on the day before, the day of, and the day after the prescribed burn event. The scale of decision relates to human health.

4.5 Development of Decision Rules

If real time air pollutant concentrations or visible smoke impacts exceed action criteria (to be developed jointly by the Army's burn contractor and the regulatory agencies), then burn tactics for the current burn will be altered to minimize these smoke impacts as specified in the Burn Plan (*Fire Stop, 2002*).

If measured concentrations of COPCs in air are less than established screening levels, then no modifications will be made to future prescribed burn operations.

If measured concentrations of COPCs in air are greater than or equal to established screening levels, then data will be evaluated in a human health risk assessment. If the results of the human health risk assessment show that COPCs in air may pose an unacceptable risk to human health, then modifications to future prescribed burn operations will be made.

4.6 Specification of Limits on Decision Errors

The null hypothesis is that, following this investigation, no modifications to future prescribed burn operations will be necessary ("future prescribed burn operations" in this context includes burn tactics for the balance of the Range 43-48 burn as well as separate burns at later dates).

A false positive decision error would be to conclude that modifications are necessary when, in fact, they are not. The consequence of this error would be that unnecessary modifications or limitations to future prescribed burn operations would be made, resulting in unnecessary cost to the government.

A false negative decision error would be to conclude that modifications are not necessary when, in fact, they are. The consequence of this error would be that future prescribed burn operations potentially harmful to human health would continue.

This investigation employs a biased sampling strategy designed to characterize areas of maximum impact. Consequently, confidence limits on decision errors are not applicable to this investigation. The expected COPC distribution is not random; hence, the judgmental sampling strategy proposed does not lend itself to statistically derived confidence levels for decision errors. However, decision errors will be controlled by adhering to the procedures specified in this SAP, including specific QA/QC procedures as defined in the sampling and analytical methods. In particular, analytical laboratory QA/QC acceptance criteria will be used to verify that measurements are capable of supporting project decisions.

4.7 Optimization of Investigation Design for Obtaining Data

The sampling investigation design includes the following factors:

- Number of air samples
- Location of air samples
- Sampling and analytical methods
- QC samples.

Rationale for the sampling investigation design includes the following factors and objectives:

- To obtain samples that confirm the presence or absence of ordnance-related COPCs
- To obtain samples that characterize the maximum vegetation-related COPC concentrations in air near the prescribed burn event and in downwind populated areas
- To collect real-time data for selected vegetation-related combustion products to document the temporal variation of smoke impact at selected sampling locations

- Because the downwind COPC concentration distribution is nonrandom within the study area, a judgmental sampling design is appropriate. Also, because decisions will not be made using mean concentrations compared to the screening level, probabilistic sampling design is not useful.

Factors to consider to optimize sampling investigation design include the following:

- Sampling during a prescribed burn event in an area of high UXO density will provide a "worst-case" scenario for OE emissions
- COPCs in air may occur as particulate, semivolatile, and/or volatile compounds
- The location of the highest concentrations of COPCs in air may vary during the event as meteorological conditions evolve throughout the day
- Field sampling methods should facilitate rapid mobilization to locations of smoke impact during the prescribed burn event.

The sampling strategy for COPCs in air will be to conduct the following activities:

- Collect air samples in multiple areas most likely to experience smoke impacts (based on observations from previous prescribed burn events, wind direction predictions for the specific burn day, pre-burn smoke dispersion modeling by the burn contractor, and/or real-time observations of smoke impacts)
- Collect air samples under similar meteorological conditions either before or after the burn to establish baseline conditions for COPCs
- Collect time weighted average (TWA) air samples from onset of the prescribed burn and lasting for about 8 to 10 hours
- Record real-time concentrations of selected COPCs during the prescribed burn event to establish peak-to-mean ratios and to support decisions regarding burn tactics
- Repeat TWA air samples and real-time monitoring for each day of active burn ignition, if the burn is not completed in one day
- Samples shall be measured/analyzed for the COPC compounds listed in Table 3.

5.0 SAMPLING PROCESS DESIGN

Results of the DQO process described in Section 4.0 were used to develop the sampling process design for this project. This section describes the details of the planned sampling, such as the number and location of samples. The rationale and assumptions used for sample process design are presented in Section 4.7. Section 6.0 provides a description of the sampling and analytical methods.

5.1 Objective and Basic Design

The primary objectives of this field investigation are to:

(1) Determine if ground-level concentrations of OE-related compounds in air downwind of a burn event are above or below human health-protective regulatory screening levels, and

(2) Assess the adequacy of the burn prescription for minimizing downwind smoke impacts to the public. The results of this investigation are intended to facilitate conclusions regarding public health that may be applied to the entire prescribed burn program at the former Fort Ord. Consequently, the prescribed burn during which this investigation is implemented should have the following desired characteristics:

- The size of the burn area should be typical of or larger than the burn areas planned for future prescribed burns
- The location of the burn area should be known to contain a high density of surface and near-surface UXO items, and preferably large NEW items (e.g., mortars or LAW rockets)
- The meteorological and fuel moisture conditions on the burn day should meet the prescription requirements.

To meet the stated objectives, this investigation will include pre- or post-burn baseline sampling, sampling during the burn on each day of active ignition, and sampling the day after active ignition is completed. Baseline samples are necessary because some of the target list of COPCs are ubiquitous in urban environments. If baseline sampling is conducted after the burn, it will be necessary to allow several days to elapse to ensure that any residual smoke has dispersed from the area. The baseline data will provide a comparison for the samples collected on the day(s) of the burn.

TWA air samples will be collected over the duration of active ignition during the prescribed burn event, which may take from one to three days to complete. The sample duration is expected to be on the order of 8 to 10 hours on each day of active ignition (baseline samples will be collected over a similar 8 to 10-hour duration). The sampling and analytical process and methods are described in Section 6 of this SAP. Real-time continuous monitoring for selected vegetation-related smoke compounds will be conducted to document the presence or absence of smoke impacts at several of the sampling locations. Visual observations and photographs will also be used to document the presence or absence of smoke impacts.

This air sampling program may include support and participation from a variety of Army and regulatory agency resources. Most sampling equipment and field personnel will be provided by MACTEC under subcontract to Parsons, who is contracted directly with the USACE. Sampling equipment and personnel for portions of the sampling activities have been offered by the US Army Center for Health Promotion and Preventive Medicine (USACHPPM), the Monterey Bay Unified Air Pollution Control District (MBUAPCD), and USEPA Region IX. Discussions are currently underway with the California Air

Resources Board (CARB) to assess their ability to provide sampling equipment and resources as well. These agencies, and CalEPA/DTSC, have provided comments and guidance in the development of the air sampling program, and will provide peer review of the results of the investigation.

This sampling locations and procedures described in this SAP will be followed to the maximum practicable extent during this field investigation. However, deviations from the SAP may be required because of unforeseen conditions. Any deviations must be approved by the Task Manager and will be documented in writing in a Field Change Notification.

5.2 Air Sampling Locations

A total of fifteen (15) sampling locations are proposed for this investigation, fourteen (14) fixed stations and one (1) mobile station. Two (2) of the fixed stations will be installed in locations that are immediately adjacent to the burn area, and will be collocated with the two meteorological stations currently being operated by the burn contractor. These two stations will characterize COPC concentrations as close as possible to the burn. Three (3) stations will be installed in on-base locations to characterize possible smoke impacts relatively close to the burn area. The remaining nine (9) stations will be located in residential areas surrounding the base to characterize any smoke impacts to the public.

Because the actual smoke impact areas cannot be known in advance, one (1) mobile air sampling station will be dispatched after the burn has progressed and smoke impact areas are observed. This mobile station will be located as near as possible to the apparent maximum offsite impact area, or, if the offsite fixed locations are suitably positioned in the impact area, the mobile station may be deployed to collect samples onsite close to the burn or at an offsite residential location further downwind. The decision on where to place the mobile station will be made by the Task Manager during the burn event based on the following considerations in order of priority:

1. Offsite, nearby residential smoke impact location: if the eight fixed stations are not experiencing smoke impacts, then an additional offsite location will be given priority

2. Onsite smoke impact location: if the three on-base stations are not experiencing smoke impacts, then an additional on-base location will be given priority

3. Offsite, further downwind residential smoke impact location: lowest priority.

Table 5 summarizes the number and location of the sampling locations, describes the sampling objectives, and shows the COPCs that will be sampled at each location. Plate 3 shows the approximate location of the sampling stations. These sampling locations were determined in consultation with the Army, USEPA, DTSC, and the MBUAPCD in September 2002. These locations are expected to be representative of the most likely smoke dispersal patterns under the burn prescription as determined by the Army's burn contractor. Smoke dispersion modeling currently being conducted by the MBUAPCD, if available, will also be considered in identifying potential sampling locations. Any changes to the sampling locations shown on Plate 3 will be documented in a Field Change Notification. Such changes may be warranted based on modifications to the burn prescription or refinements to the sampling approach. The exact coordinates of each sampling location used will be recorded using Global Positioning System (GPS) technology.

6.0 SAMPLING AND ANALYTICAL METHOD REQUIREMENTS

The proposed sampling program includes collecting the following types of samples for the COPCs as summarized in Table 5:

- Baseline air samples conducted under similar meteorological conditions as defined in the burn prescription. Baseline sampling may be conducted either before or several days after the burn. (Note: Baseline air samples for energetic analytes were collected during the 2002 burn season and will not be repeated in 2003 by mutual agreement with the regulatory agencies.)
- Air samples during each day of active burning
- Post-burn air samples on the day following the burn
- Duplicate (QC) air samples (one duplicate for each sampling method, per day)

Air samples will be collected at fifteen (15) locations during each of the baseline, burn day, and post burn sampling events:

- two (2) fixed stations adjacent to the burn area
- three (3) fixed on-base stations close to the burn area
- nine (9) fixed stations in surrounding residential communities
- one (1) mobile station.

Air samples for the COPCs will include both "real-time" samples using direct-reading instrumentation, and "integrated" TWA samples where samples are collected on or in a specific media for subsequent laboratory analysis. All TWA samples will be collected over the duration of active ignition during each day of the prescribed burn event, beginning at the initiation of each day's burn and terminating approximately 8 to 10 hours later (baseline and post-burn samples for these methods will be collected over a similar duration). Real-time, continuous air samples will be collected for selected vegetation-related combustion compounds to indicate the presence or absence of smoke impacts at the sampling locations. All samples will be collected at approximately two (2) meters above ground level (agl), which is at or near human adult breathing zone and within the probe siting criteria recommended by the USEPA (*USEPA, 1987*). USEPA guidance for spacing from obstructions will also be followed.

The air sampling and analytical methods that will be used in this investigation are summarized in Table 6 and described in the following sections. The analytical laboratories for this project will be USACE-validated and State of California certified, as applicable. All TWA sample media will be maintained under strict chain-of-custody (COC) control. Media will be uniquely identified and labeled, and the time, location, and duration of exposure will be recorded on COC forms. All COC forms will be completed and signed by the sampling technician before relinquishing the exposed media for shipment to the analytical laboratory. Trip blanks will be handled identically to exposed media, and will be submitted "blind" to the respective laboratory for analysis.

The sampling equipment proposed for the burn area and on-base sampling stations requires AC power to operate. Commercial electrical power is not available at the two burn area sampling locations, and may not be available at one or more of the three on-base sampling locations. Diesel generators will be used

where commercial electrical power is not available. To minimize any cross-contamination of the air samples from the diesel generator exhaust, a heavy-duty extension cord will be used to place the sampling equipment approximately 100 away from the generator. The sampling equipment proposed for the mobile station also requires AC power, which will be provided by a gasoline generator (also placed approximately 100 feet away from the sampling equipment). The sampling equipment proposed for the eight public sampling stations operates on batteries, so generator use is not necessary.

6.1 Energetic Analytes

Sampling Method

Air samples for energetic analytes will be collected via high-volume sampling system (e.g., GMW Model PS-1 PUF Sampler or equivalent). The sampling system is diagrammed in Figure 2 of Reference 1, USEPA Compendium Method TO-13A. The sampling procedure used for energetic compounds is the same as for Polycyclic Aromatic Hydrocarbons (PAHs). Sampling media for energetic analytes is polyurethane foam (PUF) cartridge that consists a quartz fiber particulate pre-filter followed by a sorbent bed separated by PUF layers. The sorbent bed selected for energetic analytes is XAD-2 resin.

The air sampler will be operated at a rate of approximately 8 standard cubic feet per minute (scfm) (0.225 stdm3/min), with an acceptable flow rate range within 10% of this value. Total sample volume of approximately 120 m^3 will be obtained over an 8- to 10-hour period. The sampler will be located in an unobstructed area, at least 2 meters from any obstacle to air flow. The exhaust hose will be stretched out in the downwind direct to prevent recycling of air into the sample head. Sampling operations will follow the procedure in Harding ESE, Inc. Standard Operating Procedure number HESE SOP102 that meets requirements established in Reference 1, USEPA Compendium Method TO-13A.

A filled Chain-of-Custody with cartridge number, surrogate concentration, data of cartridge certification, etc. will accompany the cartridge to the field and to the laboratory. After exposure, all samples will be shipped in environmentally controlled containers and stored in a refrigerator at <4°C until analysis.

Analysis Method

Integrated air samples collected on PUF cartridges will be analyzed for the target list of energetic analytes in Table 3 by using gas chromatography with electron capture detection (GC-ECD) in accordance with Reference 2, USACHPPM Standing Operating Procedure number CAD 26.3. This method directs the analysis of all listed energetic analytes by using GC-ECD. As PETN co-elutes with RDX on the chromatographic columns, a separated run will be performed for PETN using the same analytical procedures. The analysis is conducted using two chromatographic columns with dissimilar stationary phases. The primary column is to quantitate all standards and samples. The confirmation column is to confirm or quantitate those samples that have positive results on the primary column and/or where interfering compounds co-elute with analytes on the primary column. The PQL for this method is reported in the range of 1.3 to 3.6 microgram (µg) per sample, depending on the specific analyte. Sample volumes determined from field records will be used to calculate concentrations in micrograms per cubic meter (µg/m^3).

Performance Criteria and Quality Control

One field duplicate sample will be collected and analyzed per day of sampling, and field (trip) blanks will be submitted on a frequency of 10% of total samples (the field blank cartridge and filter will be shipped to the field and returned without drawing air through the sampler). Laboratory QA/QC samples, at a minimum, will be performed at the frequency specified in the analytical method. Analytical parameters

such as initial calibration and instrument conditions will be in compliance with the acceptance criteria as specified in the analytical method.

References

1. USEPA 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). EPA/625/R-96/010b, Center for Environmental Research Information, Cincinnati, Ohio. January 1999.

2. US Army Center for Health Promotion and Preventive Medicine (USACHPPM) Standard Operating Procedure CAD 26.3. Procedure for Analysis of Explosives in Ambient Air. September 2002.

3. Harding ESE Standard Operating Procedure for GMW Model PS-1 PUF Sampler. HESE SOP 102. August 2002.

6.2 Particulate Metals

Sampling Method

Integrated TWA air samples for particulate metals will be accomplished using both low volume and high volume sampling methods. At the two burn area sampling locations, total suspended particulate (TSP) samples will be collected on quartz fiber filter media using volumetric-flow-controlled high-volume samplers (e.g., GMW Model 2000H Sampler or equivalent). Flow control will be accomplished by a system. Sampling operations will follow the procedure in Harding ESE, Inc. Standard Operating Procedure number HESE SOP 103 that meets requirements established in Reference 1, USEPA Compendium Method IO-2.1. At these same two sampling locations, PM_{10} samples will be collected on quartz fiber filter media using volumetric-flow-controlled high-volume samplers with a size-selective inlet (e.g., Anderson Model GUV-16H Sampler or equivalent). Sampling operations will follow the procedure in Harding ESE, Inc. Standard Operating Procedure number HESE SOP 105 that meets requirements established in Reference 1, USEPA Compendium Method IO-2.1. Both the TSP and PM_{10} filters will be submitted for particulate metals analysis to establish a ratio between TSP metals and PM_{10} metals. Particulate metals at all other sampling locations will be analyzed from PM_{10} filter samples.

To maximize the flexibility of the sampling program, battery-operated low-volume sampling equipment (e.g., Airmetrics MiniVol® Sampler or equivalent) will be used to collect filter samples for PM_{10} particulate metals at the three on-base and nine public sampling locations, and at the one mobile station. Samples will be collected using Teflon® filter media. Sampling operation will follow the Harding ESE, Inc. Standard Operating Procedure number HESE SOP 104 that meets requirements established in Reference 1, USEPA Compendium Method IO-2.1 (modified for low volume sampling).

Analysis Method

Integrated air samples collected on quartz fiber filter by high-volume samplers (both TSP and PM_{10} filters), and integrated air samples collected on Teflon® filter media by low-volume samplers, will be analyzed for the target list of particulate metals shown in Table 3 by Inductively Coupled Plasma Spectroscopy (ICP) in accordance with Reference 2, USEPA Compendium Method IO-3.4. In ICP analysis, the sample is excited using an argon plasma torch. When the excited atoms return to their normal state, each element emits a characteristic wavelength of light. The wavelengths detected and their intensities indicate the presence and amounts of particular elements. The PQL for this method is reported

in the range of 0.0003 to 0.1 ng/m3, depending on the specific analyte. Sample volumes determined from field records will be used to calculate concentrations in $\mu g/m^3$ for each metal.

Performance Criteria and Quality Control

One field duplicate sample will be collected and analyzed per day of sampling, and field (trip) blanks will be submitted on a frequency of 10% of total samples (the field blank filter will be shipped to the field and returned without drawing air through the sampler). Laboratory QA/QC samples, at a minimum, will be performed at the frequency specified in the analytical method. Analytical parameters such as initial calibration and instrument conditions will be in compliance with the acceptance criteria as specified in the analytical method.

References

1. USEPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. Compendium Method IO-2.1. *Sampling of Ambient Air for Total Suspended Particulate Matter (SPM) and PM_{10} Using High-Volume (HV) Sampler*. EPA/625/R-96/010a, Center for Environmental Research Information, Cincinnati, Ohio. January 1999.

2. USEPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. Compendium Method IO-3.4. *Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy*. EPA/625/R-96/010a, Center for Environmental Research Information, Cincinnati, Ohio. June 1999.

3. Harding ESE *Standard Operating Procedure for GMW Model 2000H Sampler*. HESE SOP 103. August 2002.

4. Harding ESE *Standard Operating Procedure for MiniVol® Sampler*. HESE SOP 104. August 2002.

6.3 Particulate Matter Less than 10 Microns (PM_{10})

Sampling Method

Integrated TWA air samples for particulate matter less than 10 microns (PM_{10}) at the two burn area sampling locations will be collected on quartz fiber filter media using volumetric-flow-controlled high-volume samplers with a size-selective inlet (e.g., Anderson Model GUV-16H Sampler or equivalent). Sampling operations will follow the procedure in Harding ESE, Inc. Standard Operating Procedure number HESE SOP 105 that meets requirements established in Reference 1, USEPA Compendium Method IO-2.1.

To maximize the flexibility of the sampling program, battery-operated low-volume sampling equipment (e.g., Airmetrics MiniVol® Sampler or equivalent) will be used to collect filter samples for PM_{10} at the three on-base and nine public sampling locations, and at the one mobile station. Samples will be collected using Teflon® filter media. Sampling operation will follow the Harding ESE, Inc. Standard Operating Procedure number HESE SOP 104 that meets requirements established in Reference 1, USEPA Compendium Method IO-2.1 (modified for low volume sampling).

Analysis Method

Filter mass concentration of both high-volume air samplers and low-volume air sampler will be determined gravimetrically. Pre- and post-exposure filter weights will be assessed with a microbalance. The total volume of air sampled, corrected to USEPA reference condition, is determined from the

measured air flow rate and the sample time. The mass concentration of PM_{10} in the ambient air is computed as the total mass of captured particles in the PM_{10} size range divided by the volume of air sampled, and is expressed in $\mu g/m^3$. Filter weighing procedures will be conducted by an analytical laboratory and will meet requirements specified in Reference 2, USEPA Compendium Method IO-3.1

Performance Criteria and Quality Control

One field duplicate sample will be collected and analyzed per day of sampling, and field (trip) blanks will be submitted on a frequency of 10% of total samples (the field blank filter will be shipped to the field and returned without drawing air through the sampler). Laboratory QA/QC samples, at a minimum, will be performed at the frequency specified in the analytical method. Analytical parameters such as initial calibration and instrument conditions will be in compliance with the acceptance criteria as specified in the analytical method.

Measurement Using Real-time PM_{10} Monitor

Real-time monitoring for PM_{10} for smoke signature will be accomplished using MIE Personal DataRAM™ 1000 direct reading aerosol monitors (or equivalent). The MIE DataRAM™ is a portable, battery-operated instrument that can measure PM_{10} concentrations over a wide range from 0.0001 to 400 mg/m^3. It has a built-in data logging capability that can store concentration data for later downloading and analysis. Data will be recorded for both short-term (e.g., 1-minute) and TWA concentrations over the burn event. The operation of real-time PM_{10} monitor will meet specification established in Reference 5, Harding ESE, Inc. Standard Operating Procedure number HESE SOP 101.

At the end of each day's sampling event, PM_{10} data collected using real-time instrumentation will be downloaded to computer storage for QC and data analysis. No laboratory analyses are required for these data.

References

1. USEPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. Compendium Method IO-2.1. Sampling of Ambient Air for Total Suspended Particulate Matter (SPM) and PM_{10} Using High-Volume (HV) Sampler. EPA/625/R-96/010a, Center for Environmental Research Information, Cincinnati, Ohio. June 1999.

2. USEPA Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air. Compendium Method IO-3.1. Selection, Preparation and Extraction of Filter Material. EPA/625/R-96/010a, Center for Environmental Research Information, Cincinnati, Ohio, June 1999.

3. Harding ESE, Inc. Standard Operating Procedure for Anderson Model GUV-16H PM_{10} Sampler. HESE SOP 105. August 2002.

4. Harding ESE, Inc. Standard Operating Procedure for Airmetrics MiniVol® Sampler. HESE SOP 104. August 2002.

5. Harding ESE, Inc. Standard Operating Procedure for MIE Personal DataRAM™ 1000 Real-Time PM_{10} Monitor. HESE SOP 101. August 2002.

6.4 Carbon Monoxide/Carbon Dioxide (CO/CO_2)

Measurement Using Real-Time CO/CO_2 Monitor

Real-time concentrations of CO/CO_2 for smoke signature will be measured and recorded using TSI Model 8552/8554 Q-Trak™ Plus IAQ Monitor (or equivalent) direct-reading instruments. The TSI Model 8552/8554 Q-Trak™ Plus IAQ Monitor utilizes Non-Dispersive Infrared (NDIR) sensor for CO_2 measurement and Electro-Chemical sensor for CO measurement. Concentrations measured by TSI Model 8552/8554 Q-Trak™ Plus IAQ Monitor have a wide range from 0 to 5000 ppm for CO_2 and from 0 to 500 for CO. It has a built-in data logging capability that can store concentration data for later downloading and analysis. Data will be recorded for both short-term (e.g., 1-minute) and TWA concentrations over the burn event. Operation of the real-time CO/CO_2 monitor will be in accordance with Reference 1, TSI Operating and Service Manual for Model 8552/8554 Q-Trak™ Plus IAQ Monitor.

At the end of each day's sampling event, CO/CO_2 data will be downloaded to computer storage for QC and data analysis. No laboratory analyses are required for these data.

References

1. TSI Incorporated Operating and Service Manual for Model 8552/8554 Q-Trak TM Plus IAQ Monitor. February 2002.

6.5 Aldehydes

Sampling Method

Air samples for aldehydes will be collected on sorbent sampling media via low-volume sampling pumps (e.g., SKC Model PCXR4 or equivalent). The sampling system is diagrammed in Figure 3 of Reference 1, USEPA Compendium Method TO-11A. The sorbent tubes for aldehyde sampling will be commercially prepared low-pressure drop DNPH (2,4-dinitrophenyhyrazine) impregnated cartridges. Sampling operations will follow the procedure in Harding ESE, Inc. Standard Operating Procedure number HESE SOP 106 that meets requirements established in Reference 1, USEPA Compendium Method TO-11A.

Analysis Method

Integrated air samples collected on DNPH impregnated cartridges will be analyzed for the target list of aldehydes in Table 3 by using high performance liquid chromatography (HPLC) in accordance with Reference 1, USEPA Compendium Method TO-11A. The PQL will be determined using the procedures in Section 13.5 of Reference 1. Sample volumes determined from field records will be used to calculate aldehyde concentrations in $\mu g/m^3$.

Performance Criteria and Quality Control

One field duplicate sample will be collected and analyzed per day of sampling, and field (trip) blanks will be submitted on a frequency of 10% of total samples (the field blank sorbent cartridge will be shipped to the field and returned without drawing air through the sampler). Laboratory QA/QC samples, at a minimum, will be performed at the frequency specified in the analytical method. Analytical parameters such as initial calibration and instrument conditions will be in compliance with the acceptance criteria as specified in the analytical method.

References

1. USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Second Edition, Compendium Method TO-11A. Determination of Formaldehyde in Ambient Air Using HPLC. EPA/625/R-96/010b, Center for Environmental Research Information, Cincinnati, Ohio. January 1999.

2. Harding ESE, Inc. Standard Operating Procedure for SKC Model PCXR4 Air Sampling Pump Sampler. HESE SOP 106. August 2002.

6.6 Acrolein

Sampling Method

Air samples for acrolein will be collected in 6-liter SUMMA canisters equipped with mass flow controllers. The flow controllers will be pre-set for a 10-hour sample duration, such that the canisters will be filled to about 80% (approximately 4.8 liters) of the total volume. Leaving a slight vacuum in each canister will confirm that the sample was integrated over the intended sampling interval, and upon canister receipt at the lab will provide assurance that the sample was not compromised during shipping. The canisters will be secured at each sampling location such that the inlet will be approximately two meters above ground level. Each canister will have a dedicated flow controller (i.e., each flow controller will be used only once) to avoid any cross contamination between samples. Other aspects of the sampling will be in accordance with Reference 1, USEPA Compendium Method TO-15.

Analysis Method

Air samples collected in SUMMA canisters will be analyzed for acrolein by using GC/MS full scan in accordance with Reference 1, USEPA Compendium Method TO-15. The PQL for this method is reported to be 0.92 $\mu g/m^3$.

Performance Criteria and Quality Control

One field duplicate sample will be collected and analyzed per day of sampling, and field (trip) blanks will be submitted on a frequency of 10% of total samples (the field blank will be a SUMMA canister shipped to the field and returned without drawing air into the canister). Laboratory QA/QC samples, at a minimum, will be performed at the frequency specified in the analytical method. Analytical parameters such as initial calibration and instrument conditions will be in compliance with the acceptance criteria as specified in the analytical method.

References

1. USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15. Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS). EPA/625/R-96/010b. January 1999.

6.7 Dioxins/Furans

Sampling Method

Air samples will be collected at the two burn area locations and at the mobile station for dioxins/furans via high-volume sampling system (e.g., GMW Model PS-1 PUF Sampler or equivalent). The sampling system will meet requirements established in Reference 1, USEPA Compendium Method TO-9A. Sampling media for dioxins/furans is a polyurethane foam (PUF) cartridge that consists of a quartz fiber particulate pre-filter followed by a PUF sorbent bed. The air sampler will be operated at a rate of approximately 8 standard cubic feet per minute (scfm) (0.225 stdm3/min), with an acceptable flow rate range within 10% of this value. Total sample volume of approximately 120 m^3 will be obtained over an 8- to 10-hour period. The sampler will be located in an unobstructed area, at least 2 meters from any obstacle to air flow. The exhaust hose will be stretched out in the downwind direct to prevent recycling of air into the sample head. Sampling operations will follow the procedure in Harding ESE, Inc. Standard Operating Procedure number HESE SOP 102 that meets requirements established in Reference 1, USEPA Compendium Method TO-9A.

Analysis Method

Integrated air samples collected on PUF cartridges will be analyzed for dioxins/furnas by using High Resolution Gas Chromatograph-High Resolution Mass Spectrometer-Data System (HRGC-HRMS-DS) in accordance with Reference 1, USEPA Compendium Method TO-9A. The PQL for this method is reported in the range of 0.02 to 0.25 picograms per cubic meter (pg/m3), depending on the specific analyte The PQL will be determined using the procedures in Section 14.5 of Reference 1, USEPA Compendium Method TO-9A. Sample volumes determined from field records will be used to calculate concentrations in $\mu g/m^3$.

Performance Criteria and Quality Control

One field duplicate sample will be collected and analyzed per day of sampling, and field (trip) blanks will be submitted on a frequency of 10% of total samples (the field blank filter and PUF cartridge will be shipped to the field and returned without drawing air through the sampler). Laboratory QA/QC samples, at a minimum, will be performed at the frequency specified in the analytical method. Analytical parameters such as initial calibration and instrument conditions will be in compliance with the acceptance criteria as specified in the analytical method.

References

1. USEPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Second Edition, Compendium Method TO-9A. Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-Dioxins and Dibenzofurans in Ambient Air. EPA/625/R-96/010b, Center for Environmental Research Information, Cincinnati, Ohio. January 1999.

2. Harding ESE, Inc. Standard Operating Procedure for GMW Model PS-1 PUF Sampler. HESE SOP 102. August 2002.

6.8 Decontamination Procedures

Each air sample will be collected on individual sampling media specific to the analyte class being investigated. Decontamination procedures will not be required because all sample tubing and pumps will be downstream of the collection media.

7.0 INVESTIGATION-DERIVED WASTE

Investigation-derived waste (IDW) consists of tools, personal protective equipment, soil cuttings, wash water, and other disposable items that may have come into contact with site contaminants. IDW is not expected as part of this investigation.

8.0 QUALITY CONTROL

Contractor QC activities relative to the acquisition and reporting of chemical data are described in the CDQMP (*HLA, 1997a*). The task managers for this project are described in Section 1.0 of this SAP. This section describes the QC procedures specific to the prescribed burn air sampling.

8.1 Three-Phase Quality Control Process

The three-phase QC process, as described below, will be implemented for the ordnance and explosives removal activities. Each phase of QC is important for obtaining a quality product. However, the preparatory and initial inspections are particularly valuable in preventing problems. Production work is not to be performed on a definable feature of work until a successful preparatory and initial phase inspection have been completed.

During these inspections, the Project Manager will verify implementation of the requirements of this SAP and the relevant requirements of the CDQMP.

8.1.1 Preparatory Phase Inspection

Before conducting a feature of work, the Project Manager shall check that technical requirements have been planned for and that work prerequisites have been identified and met. The Project Manager's responsibility is to check that lessons learned during previous similar work have been incorporated as appropriate into the project procedures to prevent recurrence of past problems. Minimum review criteria for a preparatory phase inspection are contained in Table 2 of Part II of the CDQMP. Discrepancies among existing conditions and approved plans/procedures are to be resolved, and completion of corrective actions for unsatisfactory and nonconforming conditions identified during a preparatory inspection is to be verified by the Project Manager or designee prior to granting approval to begin work. In addition, the Project Chemist will hold a project kick-off meeting with each analytical laboratory to discuss the SAP and the CDQMP requirements for this project. Results of this meeting will be documented in the preparatory inspection checklist and reported to the USACE in a letter report. Technical systems audits will be performed as needed to resolve discrepancies noted during the project kickoff meetings. Laboratory kick off meetings and necessary technical systems audits will be completed prior to the submittal of samples for analysis.

8.1.2 Initial Phase Inspection

The second QC phase consists of checks performed during the initial field activities. During the first full day of field work, the Project Manager or designee will monitor the work and verify compliance with the specifications and requirements of the contract, delivery order, and approved plan and procedures. Minimum review criteria for the initial phase inspection are provided in Table 2 of Part II of the CDQMP. The Project Manager is also responsible for verifying that a daily health and safety (H&S) inspection is performed and documented as prescribed in the site safety and health plan (SSHP). The Project Manager or designee is responsible for ensuring that discrepancies between site practices and approved specifications are identified and resolved. Discrepancies between site practices and approved plans/procedures are to be resolved and corrective actions for unsatisfactory and nonconforming conditions or practices are to be verified by the Project Manager or designee prior to granting approval to proceed. Client notification is required at least 72 hours in advance. Results will be summarized in the daily QC report.

8.1.3 Follow-Up Phase Inspection

During each day of field activities, the Project Manager or designee is responsible for onsite monitoring of the practices and operations taking place and verifying continued compliance with the specifications and requirements of the contract, delivery order, and approved project plans and procedures. Minimum review criteria for the follow-up phase inspections are provided in Table 2 of Part II of the CDQMP. Discrepancies among site practices and approved plans/procedures are to be resolved and corrective actions for unsatisfactory and nonconforming conditions or practices are to be verified by the Project Manager or designee prior to granting approval to continue work. Follow-up inspection results will be summarized in the daily QC report.

8.2 Additional Inspections

Additional inspections performed on the same definable feature of work may be required at the discretion of the USACE or the Project Manager. Additional preparatory and initial inspections are generally warranted under any of the following conditions: unsatisfactory work, as determined by program or project management or USACE; changes in key personnel; resumption of work after a substantial period of inactivity (e.g., 2 weeks or more); and changes to the project scope of work/specifications. Results are to be summarized in the daily field report.

8.3 Completion/Acceptance Inspection

Upon conclusion of the feature of work and prior to close-out, a completion inspection is to be performed to verify that project requirements relevant to the particular feature of work are satisfied. Outstanding and nonconforming items are to be identified. As each item is resolved, it is to be so noted on the checklist. Client acceptance and close-out of each definable feature of work is a prerequisite to project close-out.

8.4 Nonroutine Occurrences

Implementation of three-phase QC activities may not prevent all potential occurrences that impact the project performance. Nonroutine occurrences are project-related events or activities that significantly impact the cost of work, schedule of work, quality of work, and quality of environmental analytical data. In the event that nonroutine events occur, MACTEC will send a written report to the USACE within 48 hours of occurrence of the event.

8.5 Deliverables

USACE analytical data reporting and deliverable requirements are specified in the CDQMP and will be followed for this project. Specifically, the following deliverables will be prepared:

- Daily QC reports, compiled weekly
- Comprehensive certificate of analysis.

8.6 Data Validation

Data validation procedures and reporting requirements are described in detail in the CDQMP *(HLA, 1997a)*. The Project Chemist will be responsible for coordinating data validation efforts.

9.0 REFERENCES

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U.S. Environmental Protection Agency, 1987. *Ambient Monitoring Guidelines for Prevention of Significant Deterioration (EPA-450/4-87-007)*; Office of Air Quality Planning and Standards.

U.S. Environmental Protection Agency, 1996. *Compilation of Air Pollutant Emission Factors, 5th Edition (AP-42)*; Office of Air Quality Planning and Standards.

U.S. Environmental Protection Agency, 1998. *Emission Factors for the Disposal of Energetic Materials by Open Burning and Open Detonation (OB/OD)*; MD-46: Research Triangle Park, NC. EPA/600/R-98/103.

TABLES

Table 1a. POLU13L-Predicted Total Emissions (pounds)
For a 1,000-Acre Prescribed Burn
Prescribed Burn Air Sampling and Analysis Plan
Former Fort Ord, California

Pollutant Species	Octol (2,500 lbs. NEW)	Comp B (6,450 lbs. NEW)
CO	369.9	1,256.5
N_2	18,566.2	47,714.4
CO_2	1,961.9	5,799.0
H_2O	580.1	1,453.0
H_2	35.2	95.5
N_2O_5	< 0.1	0.1
O_2	3,891.8	9,534.3
NO	< 0.1	0.1
CH_4	27.6	61.3
NH_3	0.1	0.3
C (particulate)	112.0	439.1

Table 1b. BangBox-Predicted Total Emissions (pounds)
For a 1,000-Acre Prescribed Burn
Prescribed Burn Air Sampling and Analysis Plan
Former Fort Ord, California

Pollutant Species	Octol (2,500 lbs. NEW)	Comp B (6,450 lbs. NEW)
CO	50.0	129.0
NO_2	33.3	64.5
PM_{10}	500.0	1,290.0
Aromatic VOCs	2.5 E-02	6.4 E-02
RDX	2.5 E-01	6.4 E-01
HMX	2.5 E-01	6.4 E-01
Diethylphthalate*	2.5 E-02	6.4 E-02
OCDD (a dioxin isomer)*	2.5 E-06	6.4 E-06

* These pollutant species were observed only with a limited type of OE item (see text).

Table 2. ISCST3 Model Concentrations of OE Emissions Compared to Regulatory Screening Levels Ranges 43 through 48 Former Fort Ord, California

	Air Contaminant	Air Emissions (lbs) from Ordnance Detonation	Modeled Max 1-Hr Air Concentration [1] ($\mu g/m^3$)	Air Screening Level ($\mu g/m^3$)	Air Concentration as a % of the Screening Level [8]	Screening Level Reference
Combustion Products and VOCs:	Carbon Monoxide	1.01E+01	7.87E-02	2.30E+04	0.0003%	California AAQS [6]
	Carbon Dioxide	2.98E+02	2.31E+00	2.14E+04	0.0108%	MBUAPCD Rule 1000
	Nitrogen Oxides (as NO_2)	3.33E+00	2.59E-02	4.70E+02	0.0055%	California AAQS
	Non-Methane Hydrocarbons	3.20E-01	2.49E-03	N/A [7]	N/A	N/A
	Particulate Matter < 10 microns	5.82E+01	4.52E-01	5.00E+01	0.9042%	California AAQS
	1,3-Butadiene	1.86E-03	1.44E-05	5.24E+00	0.0003%	MBUAPCD Rule 1000
	n-Hexane	1.07E-03	8.30E-06	4.29E+02	0.0000%	MBUAPCD Rule 1000
	Methyl Chloride	6.96E-04	5.41E-06	2.50E+02	0.0000%	MBUAPCD Rule 1000
	Benzene	2.25E-02	1.74E-04	1.30E+03	0.0000%	OEHHA Acute REL
	Carbon Tetrachloride	4.78E-04	3.71E-06	1.90E+03	0.0000%	OEHHA Acute REL
	Methylene Chloride	5.90E-02	4.58E-04	1.40E+04	0.0000%	OEHHA Acute REL
	Tetrachloroethylene	2.25E-03	1.75E-05	2.00E+04	0.0000%	OEHHA Acute REL
	Toluene	8.24E-03	6.41E-05	3.70E+04	0.0000%	OEHHA Acute REL
	Vinyl Chloride	1.31E-03	1.02E-05	1.80E+05	0.0000%	OEHHA Acute REL [2]
	Dioxin/Furan TEQ	4.23E-07	3.29E-09	4.48E-08	7.3357%	EPA Region 9 PRG [4]
Energetics:	RDX	3.85E-02	2.99E-04	3.57E+00	0.0084%	MBUAPCD Rule 1000 [3]
	HMX	5.89E-04	4.58E-06	1.80E+02	0.0000%	EPA Region 9 PRG [4]
	PETN	1.60E-04	1.24E-06	1.19E+00 [5]	0.0000%	MBUAPCD Rule 1000
	TNT	4.40E-05	3.42E-07	1.19E+00	0.0000%	MBUAPCD Rule 1000
Metals:	Aluminum	1.05E+02	8.18E-01	2.38E+01	3.4355%	MBUAPCD Rule 1000
	Antimony	1.24E-01	9.67E-04	1.19E+00	0.0812%	MBUAPCD Rule 1000
	Barium	4.14E+00	3.22E-02	1.19E+00	2.7046%	MBUAPCD Rule 1000
	Beryllium	9.56E-03	7.43E-05	4.76E-03	1.5602%	MBUAPCD Rule 1000
	Cadmium	3.96E-01	3.08E-03	1.19E-02	25.8587%	MBUAPCD Rule 1000
	Chromium (total)	4.73E-01	3.68E-03	1.19E+00	0.0043%	MBUAPCD Rule 1000
	Cobalt	2.62E-03	2.04E-05	4.70E-02	0.0171%	MBUAPCD Rule 1000
	Copper	4.34E+00	3.37E-02	1.00E+02	0.0337%	OEHHA Acute REL
	Lead	1.69E+00	1.31E-02	1.50E+00	0.8730%	California AAQS
	Manganese	1.21E-01	9.41E-04	4.70E-01	0.2002%	MBUAPCD Rule 1000
	Mercury	7.65E-03	5.94E-05	1.80E+00	0.0033%	OEHHA Acute REL
	Molybdenum	4.62E-04	3.59E-06	2.38E+01	0.0000%	MBUAPCD Rule 1000
	Nickel	2.54E-01	1.98E-03	6.00E+00	0.0329%	OEHHA Acute REL
	Zinc	2.95E+01	2.29E-01	1.19E+01	1.9277%	MBUAPCD Rule 1000

Source: Technical Memorandum, Air Emissions from Incidental Ordnance Detonation During a Prescribed Burn on Ranges 43 through 48, Former Fort Ord, California (*Harding ESE, 2001*)

[1] Maximum 1-hour average air concentrations were modeled with the ISCST3 dispersion model using 5 years of meteorological data from the Monterey Peninsula. The model predicted that maximum concentrations would occur 3,285 meters from the burn area.

[2] Office of Environmental Health Hazard Assessment Acute Reference Exposure Levels (http://www.oehha.ca.gov/air/acute_rels/allAcRELs.html)

[3] Monterey Bay Unified Air Pollution Control District Rule 1000 (screening values shown are 1/420th of the OSHA Permissible Exposure Limit)

[4] U.S. Environmental Protection Agency, Region 9, Preliminary Remediation Goals (these are chronic screening values; acute screening values are not available for these chemicals)

[5] A chemical-specific screening level does not exist for PETN, so the most restrictive screening level from the other energetic compounds (TNT) was used.

[6] California Ambient Air Quality Standard

[7] No screening level exists for this general class of hydrocarbons. Refer to the specific listed VOCs for screening level comparisons.

[8] (Modeled Air Concentration) / (Screening Level) * 100%. Values less than 100% indicate that the screening level will not be reached or exeeded, and adverse health effects are unlikely.

Table 3. Target Analytes for Investigation of Air Pollutant Emissions from Prescribed Burns Prescribed Burn Air Sampling and Analysis Plan Former Fort Ord, California

Analyte Class	Analyte	Rationale
Vegetation-Related Combustion Compounds		
Gaseous Species	Carbon Monoxide (CO) and Carbon Dioxide (CO_2)	CO/CO_2 are the combustion species produced in the greatest amounts from vegetation burning. CO/CO_2 data will indicate the presence or absence of smoke impacts at the sampling locations.
Particulate Matter	Particulate Matter less than 10 microns (PM_{10})	PM_{10} may also be produced in large amounts from vegetation burning. PM_{10} data will provide a relative indication of smoke impact at the sampling locations.
Aldehydes	Formaldehyde, Acetaldehyde, Acrolein, and Total Aldehydes	Aldehydes are commonly associated with acute eye and respiratory system irritation in smoke-impacted areas.
OE-Related Combustion Species		
Energetic Analytes	HMX Nitrobenzene RDX PETN 1,3 Dinitrobenzene 1,3,5 Trinitrobenzene 2,4 Dinitrotoluene 2,4,6 Trinitrotoluene 2,6 Dinitrotoluene	Energetic materials and their likely breakdown products are not produced by vegetation burning. Consequently, if present in the smoke plume, their concentrations can be directly attributed to OE emissions.
Particulate Metals	Aluminum Antimony Barium Beryllium Cadmium Chromium (total) Cobalt Copper Lead Manganese Mercury Molybdenum Nickel Zinc	Particulate metals may be produced both from OE detonation and from vegetation burning, so their presence in smoke is not necessarily a positive signature of emissions from OE. Measurement of particulate metals is included here nonetheless because of the uncertainty in the metal emission factors for OE. The presence of any metal above its regulatory screening level will require further investigation to assess the possible contribution from OE.
Dioxins and Furans	Total Dioxin and Furan Toxicity Equivalent (TEQ)	Dioxins and furans may be produced both from OE detonation and from vegetation burning, so their presence in smoke is not necessarily a positive signature of emissions from OE. Measurement of dioxins and furans is included here nonetheless because of the uncertainty in the emission factors for OE. The presence of dioxins and furans above a regulatory screening level will require further investigation to assess the possible contribution from OE.

Table 4. Screening Levels for the Target Analytes
Prescribed Burn Air Sampling and Analysis Plan
Former Fort Ord, California

Analyte Class	Analyte	Air Screening Level ($\mu g/m^3$)		Screening Level Reference
Vegetation-Related Combustion Compounds				
Gaseous Species	Carbon Monoxide (CO) and Carbon Dioxide (CO_2)	N/A		N/A
Particulate Matter	Particulate Matter less than 10 microns (PM_{10})	50	(24-hour)	California AAQS [1]
Aldehydes	Formaldehyde	94	(1-hour)	OEHHA Acute REL [2]
	Acetaldehyde	9	(long term)	OEHHA Chronic REL [3]
	Acrolein	0.19	(1-hour)	OEHHA Acute REL
OE-Related Combustion Species				
Energetic Analytes	HMX	180	(long term)	EPA Region 9 PRG [4]
	Nitrobenzene	2.10	(1-hour)	EPA Region 9 PRG
	RDX	3.57	(1-hour)	MBUAPCD Rule 1000 [5]
	PETN	1.19	(1-hour) [6]	MBUAPCD Rule 1000
	1,3 Dinitrobenzene	0.37	(1-hour)	EPA Region 9 PRG
	1,3,5 Trinitrobenzene	110	(long term)	EPA Region 9 PRG
	2,4 Dinitrotoluene	7.30	(1-hour)	EPA Region 9 PRG
	2,4,6 Trinitrotoluene	1.19	(1-hour)	MBUAPCD Rule 1000
	2,6 Dinitrotoluene	3.70	(1-hour)	EPA Region PRG
Particulate Metals	Aluminum	23.8	(1-hour)	MBUAPCD Rule 1000
	Antimony	1.19	(1-hour)	MBUAPCD Rule 1000
	Barium	1.19	(1-hour)	MBUAPCD Rule 1000
	Beryllium	0.0047	(1-hour)	MBUAPCD Rule 1000
	Cadmium	0.0119	(1-hour)	MBUAPCD Rule 1000
	Chromium (total)	1.19	(1-hour)	MBUAPCD Rule 1000
	Cobalt	0.047	(1-hour)	MBUAPCD Rule 1000
	Copper	100	(1-hour)	OEHHA Acute REL
	Lead	1.5	(3-month)	California AAQS
	Manganese	0.47	(1-hour)	MBUAPCD Rule 1000
	Mercury	1.8	(1-hour)	OEHHA Acute REL
	Molybdenum	23.8	(1-hour)	MBUAPCD Rule 1000
	Nickel	6	(1-hour)	OEHHA Acute REL
	Zinc	11.9	(1-hour)	MBUAPCD Rule 1000
Dioxins and Furans	Total Dioxin and Furan Toxicity Equivalent (TEQ)	4.0E-05	(long term)	OEHHA Chronic REL

[1] California Ambient Air Quality Standard

[2] Office of Environmental Health Hazard Assessment Acute Reference Exposure Levels (http://www.oehha.ca.gov/air/acute_rels/allAcRELs.html)

[3] Office of Environmental Health Hazard Assessment Chronic Reference Exposure Levels (http://www.oehha.ca.gov/air/chronis_rels/allChRELs.html)

[4] U.S. Environmental Protection Agency, Region 9, Preliminary Remediation Goals

[5] Monterey Bay Unified Air Pollution Control District Rule 1000 (screening values shown are 1/420th of the OSHA Permissible Exposure Limit)

[6] A chemical-specific screening level does not exist for PETN, so the most restrictive acute screening level from the other energetic compounds (TNT) was used.

Table 5. Summary of Sampling Locations and Rationale
Prescribed Burn Air Sampling and Analysis Plan
Former Fort Ord, California

Location	Number	Station Designation *	Sampling Objective	COPCs to be Sampled								
					Metals		PM_{10}					
				Energetics	TSP	PM_{10}	HV	LV	RT	CO/CO_2	Acrolein & Aldehydes	Dioxins / Furans
Burn Area	2	BA1, BA2	The Burn Area stations will be co-located with the existing meteorological monitoring stations operated by Fire Stop at Ranges 43 and 46. The objective is to collect samples in an area that receives substantial smoke impact as close to the burn polygon as possible.	✓	✓	✓	✓		✓		✓	✓
On Base	3	OB1, OB2, OB3	The On Base stations will be located in areas near the burn polygon where smoke impacts may be observed. The objective is to collect samples from the smoke as it begins to disperse downwind.	✓		✓		✓	✓	✓	✓	
Public Areas	9	PS1, PS2, PS3, PS4, PS5, PS6, PS7, PS8, PS9	The Public Area stations will be located in the communities surrounding Fort Ord. The objective is to characterize selected constituents of smoke in areas where public exposure may occur.			✓		✓	✓ (2)		✓	
Mobile Station	1	MS1	The Mobile Station will be deployed on the day of the prescribed burn after the smoke dispersion pattern is observed. The objective is to locate in an area of observed smoke impact, either on base or in a public area, that may not be adequately characterized by the fixed stations described above.	✓		✓		✓	✓	✓	✓	✓

*Locations for the fixed sampling stations are shown on Plate 3.

TSP - Total Suspended Particulates
PM_{10} - Particulate Matter less than 10 microns in diameter
HV - High Volume Sampling
LV - Low Volume Sampling
RT - Real Time Sampling
CO/CO_2 - Carbon Monoxide/Carbon Dioxide

Table 6. Summary of Sampling and Analytical Methods and QA/QC Requirements
Prescribed Burn Air Sampling and Analysis Plan
Former Fort Ord, California

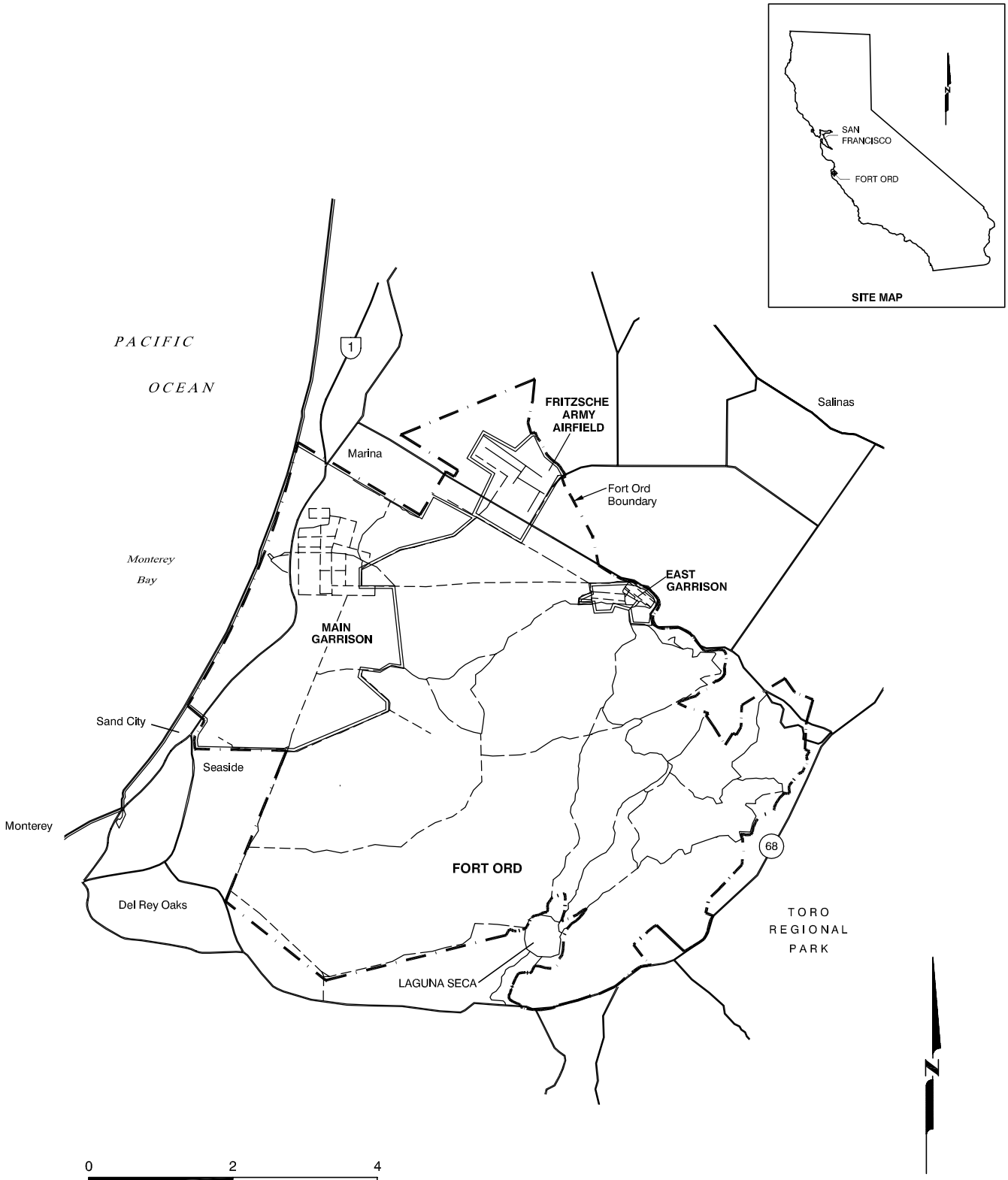
Pollutant	Sampling Equipment	Sampling Method	Analytical Method	Quality Assurance / Quality Control		
				Field Duplicates	Field Blanks	Lab QA/QC
Energetic Compounds	High Volume PUF Sampler equipped with quartz fiber particulate filter and XAD-2 resin packed cartridge (GMW PS-1 Sampler)	USEPA Compendium Method TO-13A	USACHPPM Laboratory SOP CAD 26-2	One per day of sampling	10%	See Note 1.
Particulate Metals	High Volume TSP Sampler equipped with quartz fiber filter (GMW 2000H Sampler)	USEPA Compendium Method IO-2.1, modified for less than 24 hour sampling	USEPA Compendium Method IO-3.4 (ICP)	One per day of sampling	10%	See Note 1.
	Low Volume PM_{10} Sampler with Size-Selective Inlet equipped with Teflon filter (Airmetrics MiniVol)	USEPA Compendium Method IO-2.1, modified for low volume and less than 24 hour sampling	USEPA Compendium Method IO-3.4 (ICP)	One per day of sampling	10%	See Note 1.
	High Volume Sampler with Size-Selective Inlet equipped PM_{10} with quartz fiber filter (Anderson GUV-16H Sampler)	USEPA Compendium Method IO-2.1, modified for less than 24 hour sampling	USEPA Compendium Method IO-3.4 (ICP)	One per day of sampling	10%	See Note 1.
Particulate Matter < 10 microns (PM_{10})	High Volume Sampler with Size-Selective Inlet equipped with quartz fiber filter (Anderson GUV-16H Sampler)	USEPA Compendium Method IO-2.1, modified for less than 24 hour sampling	USEPA Compendium Method IO-3.1	One per day of sampling	10%	See Note 1.
	Low Volume Sampler with Size-Selective Inlet equipped with Teflon filter (Airmetrics MiniVol)	USEPA Compendium Method IO-2.1, modified for low volume and less than 24 hour sampling	USEPA Compendium Method IO-3.1	One per day of sampling	10%	See Note 1.
	Real-Time Aerosol Monitor with Size-Selective Inlet (MIE DataRAM 1000)	Harding ESE, Inc. Standard Operating Procedure HESE SOP-101	N/A	N/A	N/A	N/A
Carbon Monoxide / Carbon Dioxide (CO/CO_2)	Real-Time Monitor (TSI Q-Trak 8552)	TSI Operations Manual	N/A	N/A	N/A	N/A
Aldehydes	Low Volume Sample Pump with DNPH-impregnated Sorbent Tube (SKC PCXR4 Pump)	USEPA Compendium Method TO-11A	USEPA Compendium Method TO-11A	One per day of sampling	10%	See Note 1.

Table 6. Summary of Sampling and Analytical Methods and QA/QC Requirements
Prescribed Burn Air Sampling and Analysis Plan
Former Fort Ord, California

Pollutant	Sampling Equipment	Sampling Method	Analytical Method	Quality Assurance / Quality Control		
				Field Duplicates	Field Blanks	Lab QA/QC
Aerolein	SUMMA Canisters with 10-hour mass flow controller	USEPA Compendium Method TO-15	USEPA Compendium Method TO-15 with GC/MS Full Scan	One per day of sampling	10%	See Note 1.
Dioxins/Furans	High Volume PUF Sampler equipped with quartz fiber particulate filter and PUF packed cartridge (GMW PS-1 Sampler)	USEPA Compendium Method TO-9A	USEPA Compendium Method TO-9A	One per day of sampling	10%	See Note 1.

Note 1: Laboratory QA/QC samples, at a minimum, will be performed at the frequency specified in the analytical method. Analytical parameters such as initial calibrations and instrument conditions will be in compliance with the acceptance criteria as specified in the analytical method.

PLATES



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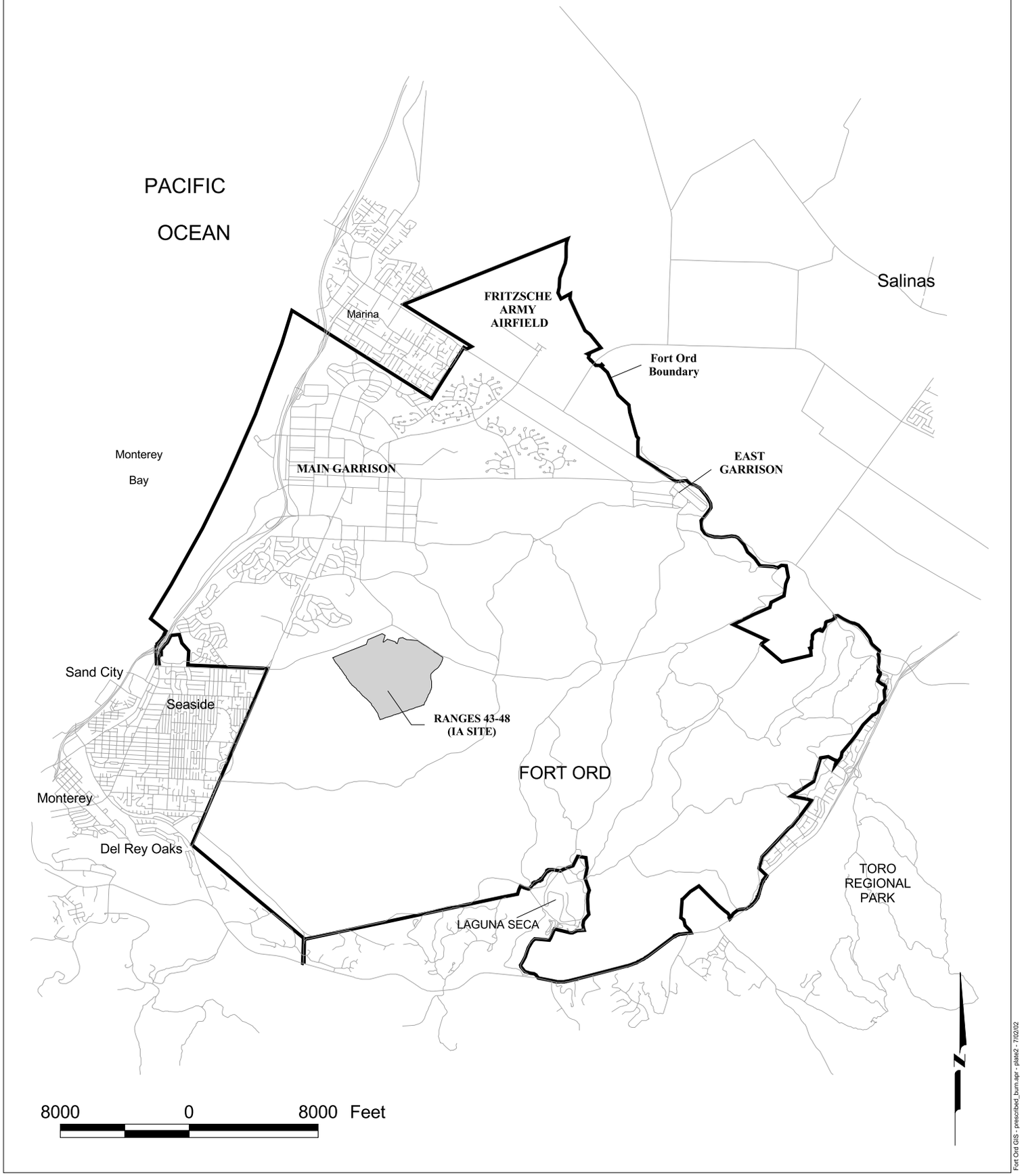
Harding ESE
A MACTEC COMPANY

SIte LocatIon Map
Prescribed Burn
Air Sampling and Analysis Plan
Former Fort Ord, California

PLATE
1

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
TJH	46310 00117		7/02	



Fort Ord GIS - prescribed_burn.apr - plate2 - 7/02/02

Harding ESE
A MACTEC COMPANY

Ranges 43 through 48
Prescribed Burn
Air Sampling and Analysis Plan
Former Fort Ord, California

PLATE
2

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
JCB	46310 00117		7/02	

N
W E
S

Marina
Salinas
Pacific Ocean
Seaside
Monterey
Del Rey Oaks
Laguna Seca
Housing Area
Toro Park
Estates
Spreckles
Gonzales

PS 1
PS 2
PS 3
PS 4
PS 5
PS 6
PS 7
PS 8
PS 9
OB 1
OB 2
OB 3
BA 1
BA 2

Watkins Gate Road
EUCALYPTUS RD (WEST)
EUCALYPTUS RD (EAST)
WATKINS GATE RD
BOUNDARY ROAD (INTERIOR)
S BOUNDARY ROAD (EAST)
CRESCENT BLUFF RD
HENNEKENS RANCH RD
BARLOY CANYON ROAD
IMPOSSIBLE CANYON RD
BARLOY CANYON RD
ENGINEER CANYON RD
JACKS RD
SKYLINE RD
OIL WELL RD
ROBERTOS CANYON RD
PARKER FLATS
Parker Flats Cutoff
101
68

Legend

- Burn Area Stations (BA 1, BA 2)
- On Base Stations (OB 1, OB 2, OB 3)
- Public Sampling Stations (PS 1 through PS 9)

Road Classification

- Limited Access Higwhay
- Highway
- Roads
- Pacific Coast

- Multi-Range Area
- Ranges 43-48 Original IA Boundary
- Fort Ord Boundary

4,000 0 4,000 Feet

Fort Ord GIS - Air_SAP_sample_locations.mxd - 8/19/02

MACTEC

Sampling Locations

Prescribed Burn
Air Sampling and Analysis Plan
Former Fort Ord, California

PLATE 3

DRAWN	JOB NUMBER	APPROVED	DATE	REVISED DATE
JCF	56286 010404		06/03	07/03

APPENDIX A

USEPA Compendium Method IO-2.1

EPA/625/R-96/010a

Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Compendium Method IO-2.1

SAMPLING OF AMBIENT AIR FOR TOTAL SUSPENDED PARTICULATE MATTER (SPM) AND PM_{10} USING HIGH VOLUME (HV) SAMPLER

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

June 1999

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Author(s)

- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

Peer Reviewers

- David Brant, National Research Center for Coal and Energy, Morgantown, WV
- John Glass, SC Department of Health and Environmental Control, Columbia, SC
- Jim Cheney, U.S. Army Corps of Engineers, Omaha, NE
- Margaret Zimmerman, Texas Natural Resource Conservation Commission, Austin, TX
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DISCLAIMER

Method IO-2.1
Sampling of Ambient Air for Total Suspended Particulate Matter (SPM) and PM_{10} Using High Volume (HV) Sampler

TABLE OF CONTENTS

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Chapter IO-2
Integrated Sampling of Suspended Particulate Matter (SPM)

Method IO-2.1
SAMPLING OF AMBIENT AIR FOR TOTAL SUSPENDED PARTICULATE MATTER (SPM) AND PM_{10} USING HIGH VOLUME (HV) SAMPLER

1. Scope

1.1 Suspended particulate matter (SPM) in air generally is a complex, multi-phase system of all airborne solid and low vapor pressure liquid particles having aerodynamic particle sizes from below 0.01-100 µm and larger. Historically, SPM measurement has concentrated on total suspended particulates (TSP), with no preference to size selection.

1.2 The U. S. Environmental Protection Agency (EPA) reference method for TSP is codified at 40 CFR 50, Appendix B. This method uses a high-volume sampler to collect particles with aerodynamic diameters of approximately 100 µm or less. The high-volume samples 40-60 ft^3/min of air with the sampling rate held constant over the sampling period. The high-volume design causes the TSP to be deposited uniformly across the surface of a filter located downstream of the sampler inlet. The TSP high-volume can be used to determine the average ambient TSP concentration over the sampling period, and the collected material subsequently can be analyzed to determine the identity and quantity of inorganic metals present in the TSP.

1.3 Research on the health effects of TSP in ambient air has focused increasingly on particles that can be inhaled into the respiratory system, i.e., particles of aerodynamic diameter less than 10 µm. The health community generally recognizes that these particles may cause significant adverse health effects. Recent studies involving particle transport and transformation strongly suggest that atmospheric particles commonly occur in two distinct modes: the fine (< 2.5 µm) mode and the coarse (2.5-10.0 µm) mode. The fine or accumulation mode (also termed the respirable particulate matter) is attributed to growth of particles from the gas phase and subsequent agglomeration, while the coarse mode is made of mechanically abraded or ground particles. Particles that have grown from the gas phase (either because of condensation, transformation, or combustion) occur initially as very fine nuclei--0.05 µm. These particles tend to grow rapidly to accumulation mode particles around 0.5 µm which are relatively stable in the air. Because of their initially gaseous origin, particle sizes in this range include inorganic ions such as sulfate, nitrate, ammonia, combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, are produced mainly by mechanical forces such as crushing and abrasion. Coarse particles, therefore, normally consist of finely divided minerals such as oxides of aluminum, silicon, iron, calcium, and potassium. Coarse particles of soil or dust mostly result from entrainment by the motion of air or from other mechanical action within their area. Since the size of these particles is normally > 2.5 µm, their retention time in the air parcel is shorter than the fine particle fraction.

1.4 On July 1, 1987, the U. S. Environmental Protection Agency (EPA) promulgated a new size-specific air quality standard for ambient particulate matter. This new primary standard applies only to particles with aerodynamic diameters #10 micrometers (PM_{10}) and replaces the original standard for TSP. To measure concentrations of these particles, the EPA also promulgated a new federal reference method (FRM). This method is based on the separation and removal of non-PM_{10} particles from an air sample, followed by filtration and gravimetric analysis of PM_{10} mass on the filter substrate.

1.5 The new primary standard (adopted to protect human health) limits PM_{10} concentrations to 150 µg/std. m^3 averaged over a 24-h period. These smaller particles are able to reach the lower regions of the human respiratory tract and, therefore, are responsible for most of the adverse health effects associated with suspended particulate pollution. The secondary standard, used to assess the impact of pollution on public welfare, has also been established at 150 µg/std. m^3.

1.6 Ambient air SPM measurements are used (among other purposes) to determine whether defined geographical areas are in attainment or non-attainment with the national ambient air quality standards (NAAQS) for PM_{10}. These measurements are obtained by the States in their State and local air monitoring station (SLAMS) networks as required under 40 CFR Part 58. Further, Appendix C of Part 58 requires that the ambient air monitoring methods used in these EPA-required SLAMS networks must be methods that have been designated by the EPA as either reference or equivalent methods.

1.7 Monitoring methods for particulate matter are designated by the EPA as reference or equivalent methods under the provisions of 40 CFR Part 53, which was amended in 1987 to add specific requirements for PM_{10} methods. Part 53 sets forth functional specifications and other requirements that reference and equivalent methods for each criteria pollutant must meet and explicit test procedures by which candidate methods or samplers are to be tested against those specifications. General requirements and provisions for reference and equivalent methods are also given in Part 53, as are the requirements for submitting an application to the EPA for a reference or equivalent method determination.

1.8 Several methods are available for measuring SPM in ambient air. As mentioned earlier, the most commonly used device is the high-volume sampler, which consists essentially of a blower and a filter, and which is usually operated in a standard shelter to collect a 24-h sample. The sample is weighed to determine concentration and may be analyzed chemically. The high volume sampler is considered a reliable instrument for measuring the mass concentration of TSP in ambient air. When EPA first regulated TSP, the NAAQS was stated in terms of SPM captured on a filter with aerodynamic particle size of < 100 µm as defined by the TSP sampler; therefore, the TSP sampler was used as the reference method.

1.9 Under Part 53 requirements, reference methods for PM_{10} must be shown to use the measurement principle and meet other specifications set forth in 40 CFR 50, Appendix J. They must also include a PM_{10} sampler that meets the requirements specified in Subpart D of 40 CFR 53. Appendix J specifies a measurement principle based on extracting an air sample from the atmosphere with a powered sampler that incorporates the inertial separation of PM_{10} size range particles followed by the collection of PM_{10} particles on a filter over a 24 h period. The average PM_{10} concentration for the sample period is determined by dividing the net weight gain of the filter over the sample period by the total volume of air sampled, corrected to EPA's standard temperature (25EC) and standard pressure (760 mm Hg). Other specifications for flow rate control and measurement, flow rate measurement device calibration, filter media characteristics and performance, filter conditioning before and after sampling, filter weighing, sampler operation, and correction of sample volume to EPA reference temperature and pressure are prescribed in Appendix J. In addition, sampler performance requirements in Subpart D of Part 53 include sampling effectiveness (the accuracy of the PM_{10} particle size separation capability) at each of the three wind speeds and at "50% cutpoint" (the primary measure of 10-µm particle size separation). Field tests for sampling precision and flow rate stability are also specified. In spite of the instrumental nature of the sampler, this method is basically a manual procedure, and all designated reference methods for PM_{10} are therefore defined as manual methods.

1.10 This document describes the procedures for sampling SPM in ambient air for both TSP and PM_{10} based upon active sampling using a high volume air sampler. The ambient particles are collected on quartz fiber filters. The sampler collects TSP or PM_{10} ambient particles depending upon the type of inlet selected.

2. Applicable Documents

2.1 ASTM Documents

- D4096 *Application of the High Volume Sample Method for Collection and Mass Determination of Airborne Particulate Matter*.
- D1356 *Definition of Terms Related to Atmospheric Sampling and Analysis*.
- D1357 *Practice for Planning the Sampling of the Ambient Atmosphere*.
- D2986 *Method for Evaluation of Air Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test*.

2.2 Other Documents

- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance*, EPA/600/R-94/038a.
- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA/600/R-94/038b.
- *Reference Method for the Determination of Particulate Matter in the Atmosphere*, 40 CFR 50, Appendix J.
- *Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)*, 40 CFR 50, Appendix B.
- *Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air*, 40 CRF 50, Appendix G.
- *Reference Method for this Determination of Suspended Particulates in the Atmosphere (PM_{10} Method)*, 40 CFR 50, Appendix J.

3. Summary of Method

3.1 The sampling of a large volume of atmosphere, 1,600-2,400 m^3 (57,000-86,000 ft^3), with a high-volume blower, typically at a rate of 1.13-1.70 m^3/min (40-60 ft^3/min), is described in this method. The calibration and operation of typical equipment used in this sampling is also described.

3.2 Air is drawn into the sampler and through a glass fiber or quartz filter by means of a blower, so that particulate material collects on the filter surface. Without a 10 µm size-selective inlet, particles of 100 µm size and less enter the sampling inlet and are collected on the downstream filter. The collection efficiencies for particles larger than 20 µm decreases with increasing particle size, and it varies widely with the angle of the wind with respect to the roof ridge of the sampler shelter. When glass fiber filters are used, particles 100-0.1 µm or less in diameters are ordinarily collected. With a size-select inlet, particles 10 µm diameter or less are collected on the quartz filter.

3.3 The upper limit of mass loading is determined by plugging the filter medium with sample material, which causes a significant decrease in flow rate. For very dusty atmospheres, shorter sampling periods will be necessary.

3.4 The volume of air sampled is determined by a flow-rate indicator. The instrument flow-rate indicator is calibrated against a reference orifice meter. The latter is a working standard which, in turn, has been calibrated against a master flow meter certified by the National Institute of Standards and Technology (NIST).

3.5 Airborne particulate matter retained on the filter may be examined or analyzed chemically by a variety of methods (ICP, ICP/MS, AA, GFAA, and NAA) as delineated in Inorganic Compendium Methods IO-3.2 through IO-3.7.

4. Significance

4.1 The area of toxic air pollutants has been the subject of interest and concern for many years. Recently the use of receptor models has resolved the elemental composition of atmospheric aerosol into components related to emission sources. The assessment of human health impacts resulting in major decisions on control actions by federal, state and local governments is based on these data. Accurate measures of toxic air pollutants at trace levels is essential to proper assessments.

4.2 The high volume sampler is commonly used to collect the airborne particulate component of the atmosphere. A variety of options available for the sampler provides broad versatility and allows the user to develop information about the size and quantity of airborne particulate material and, using subsequent chemical analytical techniques, information about the chemical properties of the particulate matter. The advent of inductively coupled plasma spectroscopy has improved the speed and performance of metals analysis in many applications.

5. Definitions

[Note: Definitions used in this document are consistent with those used in ASTM Methods. All pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 High-Volume Air Sampler (HV). A device for sampling large volumes of an atmosphere for collecting the contained particulate matter by filtration. Consists of a high-capacity blower, a filter to collect suspended particles, and a means for measuring the flow rate.

5.2 Working Flow-Rate Standard. A flow-rate measuring device, such as a standard orifice meter, that has been calibrated against a master flow-rate standard. The working flow-rate standard is used to calibrate a flow measuring or flow rate indicating instrument.

5.3 Master Flow-Rate Standard. A flow-rate measuring device, such as a standard orifice meter, that has been calibrated against a primary standard.

5.4 Primary Flow-Rate Standard. A device or means of measuring flow rate based on direct primary observations such as time and physical dimensions.

5.5 Spirometer. A displacement gasometer consisting of an inverted bell resting upon or sealed by liquid (or other means) and capable of showing the amount of gas added to or withdrawn from the bell by the displacement (rise or fall) of the bell.

5.6 Absolute Filter. A filter or filter medium of ultra-high collection efficiency for very small particles (submicrometer size) so that essentially all particles of interest or of concern are collected. Commonly, the efficiency is 99.95% or higher for a standard aerosol of 0.3 µm diameter.

5.7 Calibration. The process of comparing a standard or instrument with one of greater accuracy (small uncertainty) to obtain quantitative estimates of the actual values of the standard being calibrated, the deviation of the actual value from a nominal value, or the difference between the value indicated by an instrument and the actual value.

5.8 Differential Pressure Meter. Any flow measuring device that operates by restricting air flow and measuring the pressure drop across the restriction.

5.9 Emissions. The total of substances discharged into the air from a stack, vent, or other discrete source.

5.10 Flowmeter. An instrument for measuring the rate of flow of a fluid moving through a pipe or duct system. The instrument is calibrated to give volume or mass rate of flow.

5.11 Impaction. A forcible contact of particles of matter. A term often used synonymously with impingement.

5.12 Impactor. A sampling device that employs the principle of impaction (impingement).

5.13 Impingement. The act of bringing matter forcibly in contact. As used in air sampling, refers to a process for the collection of particulate matter in which the gas being sampled is directed forcibly against a surface.

5.14 Inhalable Particles. Particles with aerodynamic diameters of < 10 µm that are capable of being inhaled into the human lung.

5.15 Interference. An undesired positive or negative output caused by a substance other than the one being measured.

5.16 Mass Flowmeter. Device that measures the mass flow rate of air passing a point, usually using the rate of cooling or heat transfer from a heated probe.

5.17 Matter. The substance of which a physical object is composed.

5.18 Orifice Meter. A flowmeter, employing as the measure of flow rate the difference between the pressures measured on the upstream and downstream sides of the orifice (that is, the pressure differential across the orifice) in the conveying pipe or duct.

5.19 Aerodynamic Diameter (a.d.). The diameter of a unit density sphere having the same terminal settling velocity as the particle in question. Operationally, the size of a particle as measured by an inertial device.

5.20 Particle. A small discrete mass of solid or liquid matter.

5.21 Particulate. Solids of liquids existing in the form of separate particles.

5.22 Precision. The degree of mutual agreement between individual measurements, namely repeatability and reproducibility.

5.23 Pressure Gage. The difference in pressure existing within a system and that of the atmosphere. Zero gage pressure is equal to atmospheric pressure.

5.24 Rotameter. A device, based on the principle of Stoke's law, for measuring rate of fluid flow. It consists of a tapered vertical tube having a circular cross section, and containing a flow that is free to move in a vertical path to a height dependent upon the rate of fluid flow upward through the tube.

5.25 Sampling. A process consisting of the withdrawal or isolation of a fractional part of a whole. In air or gas analysis, the separation of a portion of an ambient atmosphere with or without the simultaneous isolation of selected components.

5.26 Standard. A concept that has been established by authority, custom, or agreement to serve as a model or rule in the measurement of quantity of the establishment of a practice or procedure.

5.27 Traceability to NIST. Documented procedure by which a standard is related to a more reliable standard verified by the National Institute of Standards Technology (NIST).

5.28 Uncertainty. An allowance assigned to a measured value to take into account two major components of error: The systematic error and the random error attributed to the imprecision of the measurement process.

6. Apparatus Description

6.1 General Description

6.1.1 The essential features of a typical non size-specific TSP high-volume sampler are shown in Figure 1. The high volume sampler is a compact unit consisting of a protective housing; an electric motor driven; a high-speed, high-volume blower; a filter holder capable of supporting a 203 x 254-mm (8 in. by 10 in.) filter; and a flow-controller for controlling the air-flow rate through the instrument at 40-60 ft^3/min.

6.1.2 In operation, this traditional TSP sample draws ambient air into the sampler through the air inlet gap between the cover and the sampler housing walls (see Figure 2). The air inlet is uniform on all sides of the sampler to provide an effective particle capture air velocity between 20-35 cm/sec. at the recommended flow rate between 40-60 ft^3/min. The gable roof design of the sampler allows the sampled air to be evenly distributed over the surface of a downstream filter, where TSP is collected.

6.1.3 For PM_{10} measurement, the traditional gable roof of the TSP sampler is replaced with an impactor design size-select inlet, as illustrated in Figure 3. For the impaction design, an air sample enters a symmetrical (therefore wind-direction insensitive) hood and is deflected upward into a buffer chamber. The buffer chamber is evacuated at a rate of 68 m^3/h (40 cfm) through multiple circular nozzles. Particles are accelerated as they pass through the nozzles to an impaction chamber (see Figure 4). Because of their momentum, particles having diameters larger than the inlet's 10-µm cut design impact the surface of the

impaction chamber. Smaller particles rise through the impaction chamber at speeds slow enough to minimize reentrainment of the impacted particles and then pass through multiple vent tubes to the high-volume sampler's filter where they are collected.

6.1.4 The second size-select design for PM_{10} measurement is the cyclone inlet, as illustrated in Figure 5. The omnidirectional cyclone used for fractionation in this inlet allows particles to enter from all angles of approach. An angular velocity component is imparted to the sample air stream and the particles contained in it by a series of evenly spaced vanes. Larger particle removal occurs in an inner collection tube. This tube incorporates a "perfect absorber," which is an oil-coated surface to eliminate particle bounce and reentrainment. The sample flow (with the unremoved smaller particles) then enters an intermediate tube, where the trajectory is altered to an upward direction. An additional turn is then made to alter the flow to a downward trajectory to allow the remaining particles (i.e., PM_{10} fraction) to deposit on a filter for subsequent analysis. As with the impaction inlet, control of air velocities in the cyclonic inlet is critical to maintain the correct particle size cutpoint. Maintaining the correct design volumetric flow rate through the inlet is important. This design flow rate is specified by the manufacturer in the instruction manual. For example, a popular cyclonic impaction inlet has a design flow rate of 1.13 m^3/min.

6.2 Filter Medium

6.2.1 Selecting a filtration substrate for time-integrated SPM monitoring must be made with some knowledge of the expected characteristics and a pre-determined analytical protocol. For any given standard test method, the appropriate medium will normally be specified.

6.2.2 Of the various types of filters listed in Table 1 of Chapter IO-2 Overview, four general types of filter material have been used to capture SPM. They include cellulose fiber, quartz/glass fiber, mixed fiber and membrane filter types. Selecting a filter depends upon variables such as background metal content, artifact formation, and affinity for moisture. The basic characteristics of the types of filter material used in air monitoring are outlined in Table 1, while useful filter properties are identified in Table 2. Several characteristics are important in selection of filter media. They are:

- **Particle Sampling Efficiency.** Filters should remove more than 99% of SPM from the air drawn through them, regardless of particle size or flow rate.
- **Mechanical Stability.** Filters should be strong enough to minimize leaks and wear during handling.
- **Chemical Stability.** Filters should not chemically react with the trapped SPM.
- **Temperature Stability.** Filters should retain their porosity and structure during sampling.
- **Blank Correction.** Filters should not contain high concentrations of target compound analytes.

6.2.3 Quartz fiber filters are the most commonly used filters for SPM sampling for determining mass loading. Typical characteristics of quartz fiber filters are (1) a fiber content of high purity quartz, (2) a binder of below 5% (zero for binderless types), (3) a thickness of approximately 0.5 mm, (4) a surface with no pinholes, and (5) an allowance of no more than 0.05% of smoke particles to pass through the filter at a pressure of 100 mm of water with a flow rate of 8.53 m/min (28 ft/min), as determined by a DOP smoke test (see ASTM Method D2986).

6.2.4 Quartz fiber filters are made from finely spun glass fiber by combining the fiber with an organic binder and compressing this material in a paper machine. These filters are increasingly used in air sampling. These filters have the ability to withstand high temperatures (up to 540EC). They are further typified by high-collection efficiency. In some cases, the organic binder may interfere with subsequent analysis, so the filter is flash-fired to remove the binder material. This action causes some loss in tensile strength and usually requires that a backing material be used during sampling. The quartz filters are nonhydroscopic, thus allowing them to be used in areas where humidity is high. Because they are glass, they are the filter choice for most corrosive atmospheres. All the filters in this category are fragile and must be handled with care. Quartz fiber filters, because of the high silicate content, are extremely difficult to ash by chemicals or heat.

Therefore, extraction procedures are performed on these filters to remove the sample for subsequent chemical analysis. For this reason, flash-fired quartz filters are the major atmospheric sampling filters.

6.3 Flow Control System

The high-volume sampler employs two basic types of flow control systems. One is a mass-flow-control (MFC) system; the other is a volumetric-flow-control (VFC) system. Because the calibration and standard operating procedures differ considerably between these two types of flow-control systems, this method presents procedures that are control-system-specific. PM_{10} inlets can be used with either the MFC and VFC systems.

6.3.1 Mass-flow-control (MFC) system. The flow rate in a MFC system is actively sensed and controlled at a predetermined set point. Air is pulled through the filter into the intake of a blower and subsequently exits the sampler through an exit orifice, which facilitates measurement of the flow with a manometer or pressure recorder. The flow rate is controlled by an electronic mass-flow controller, which uses a flow sensor installed below the filter holder to monitor the mass flow rate and related electronic circuitry to control the speed of the motor accordingly to provide a constant sampling rate. The controlled flow rate can be changed by an adjustment knob on the flow controller.

6.3.2 Volumetric-flow-control (VFC) system. A VFC system maintains a constant volumetric flow rate through the inlet, rather than a constant mass flow rate as in the MFC system. In a popular commercial VFC system, a choked-flow venturi is operated such that the air attains sonic velocity in the throat of the device. In this "choked" mode, the flow rate is unaffected by downstream conditions, such as motor speed or exit pressure and is a predictable function of upstream conditions, such as the stagnation pressure ratio and temperature. Thus, the volumetric flow is controlled without any moving parts or electronic components. In this type of flow control system, no means is provided for adjusting the controlled flow rate. The controlled flow rate is set by the manufacturer through engineering design of the venturi.

7. Calibration

7.1 Introduction

[Note: All sampling equipment must be properly calibrated. Calibration is the relationship between an instrumental output and the input of a known reference standard. The objective of this section is to provide technically sound flow-rate calibration procedures for the MFC and VFC HV samplers.]

[Note: Consistency of temperature and barometric pressure is required. All temperatures should be expressed in kelvin (K = EC + 273). All barometric pressures should be expressed in mm Hg. Avoid calibrating an HV sampler using one set of units and then performing sample calculations using another set.]

7.1.1 HV sampler inlet. Two types of size-selective inlets available are impaction and cyclonic for monitoring inhalable particles (< 10 µm). The particle size discrimination characteristics of both the impaction and cyclonic type inlets depend critically on maintaining certain air velocities within the inlet; a change in velocity will result in a change in the nominal particle size collected. For this reason, the flow rate through the inlet must be maintained at a constant value that is as close as possible to the inlet's design flow rate. The design flow rate for a given sampler is specified in the sampler's instruction manual. The manual may also provide tolerance limits (or upper and lower limits) within which the sampler flow must be maintained. If the tolerance is not specified by the manufacturer, it should be assumed to be ± 10%.

7.1.1.1 The symmetrical design of the impaction inlet (see Figure 4) ensures wind-direction insensitivity. Ambient air that is drawn into the inlet is evacuated from the buffer chamber through nine acceleration nozzles into the first impaction chamber, where initial particle separation occurs. The air is then accelerated through an additional 16 jets into a second impaction chamber. The acceleration jets have critical diameters calculated by the manufacturer to provide the necessary changes in velocity to effect correct particle size fractionation within the impaction chambers. The air flow finally exits the inlet through nine vent tubes onto a sample filter. Because air velocities are critical to maintain the correct particle size cutpoint within the inlet, maintaining the correct design flow rate through the inlet is important. This design flow rate is specified by the manufacturer in the instruction manual. For example, the design flow rate for one popular impaction inlet is 1.13 m^3/min.

7.1.1.2 The omnidirectional cyclone inlet (see Figure 5) used for fractionation allows particles to enter from all angles of approach. A angular velocity component is imparted to the sample air stream and the particles contained in it by a series of evenly spaced vanes. Larger particle removal occurs in an inner collection tube. This tube incorporates a "perfect absorber," an oil-coated surface to eliminate particle bounce and reentrainment. The sample flow (with the unremoved smaller particles) then enters an intermediate tube, where the trajectory is altered to an upward direction. An additional turn is then made to alter the flow to a downward trajectory to allow the remaining particles (i.e., PM_{10} fraction) ultimately to deposit on a filter for subsequent analysis. As with the impaction inlet, control of air velocities in the cyclonic inlet is critical to maintain the correct particle size cutpoint. Maintaining the correct design volumetric flow rate through the inlet is important. This design flow rate is specified by the manufacturer in the instruction manual. For example, as in the case of the impaction inlet, a popular cyclonic inlet also has a design flow rate of 1.13 m^3/min.

7.1.2 Total suspended particulate (TSP). As illustrated in Figure 2, particles of less than 100 µm are collected at a flow rate of 1.13-1.70 m^3/min (40-60 ft^3/min) using the conventional high-volume sampler, without size selection.

7.2 Summary of Calibration Procedures

[Note: During calibration, a closure plate perforated with a number of circular orifices is connected to the inlet of the sampler. The pressure drop across this orifice plate provides a measure of instrument air flow rate at any time. This pressure drop may be indicated by a rotameter, manometer, or other pressure-responsive device traceable to an NIST certified standard.]

7.2.1 A simple and sufficiently accurate method of calibrating is to compare the sampler meter with an orifice meter (working standard) that has been calibrated against a primary or master standard such as a Roots meter.

7.2.2 The preferable primary standard is a Roots meter of sufficient capacity to allow an accurate time-volume reading, which would be at least 30 s.

7.2.3 A positive displacement pump or blower may be used as a master flow-rate standard. In this case, the delivery rate of the master standard must be known accurately and the equipment must be in sound mechanical condition (no bypass leakage).

7.3 Certification of an Orifice Transfer Standard

[Note: The following certification procedure is applicable to an orifice transfer standard such as those that have been used previously in the calibration of both the traditional HV sampler and the PM_{10} samplers. Two common types of orifice devices are available: one equipped with a set of fixed resistance plates (e.g., a reference flow [Ref] device or a top-hat orifice) and one with an externally variable resistance valve. The

series of plates normally provided by the orifice manufacturer include an 18-, 13-, 10-, 7-, and 5-hole plate. Unfortunately, the 5-hole plate provides too low a flow rate to be useful for HV calibration, and other plates may produce flow rates substantially outside the design flow-rate range of the commercially available HV inlets. One may opt to fabricate or procure a different series of resistance ranges or use the variable-resistance type orifice device.]

7.3.1 Orifice Calibration Procedure.

7.3.1.1 Assemble the following equipment (see Figure 6):

- Orifice transfer standard (i.e., top-hat orifice, variable orifice, or ReF device) to be calibrated.
- Water or oil manometer with a 0-400 mm (0-16") range and minimum scale divisions of 1 mm (0.1"). This manometer should be permanently associated with the orifice transfer standard.
- Variable voltage transformer, a set of resistance plates, or available flow orifice (see Figure 7).
- Calibrated positive displacement, standard volume meter (such as a Roots Meter®) traceable to National Institute of Standards and Technology (NIST).

  [Note: As they are sold, standard volume meters may not be traceable to NIST. Traceability can be established directly through NIST or indirectly through the meter manufacturer's repair department. Periodic recertification is not normally required under clean service conditions unless the meter has been damaged and must be repaired. In general, damage will be indicated by a substantial (e.g., 50%) increase in the pressure drop across the meter. The meter's traceability certificate should contain a graph of the pressure drop as a function of flow rate.]

- High-volume air mover (e.g., a blower motor from a HV sampler).
- Accurate stopwatch.
- Mercury manometer, with a 0-200 mm (0-8") range and minimum scale divisions of 1 mm (0.1").
- Thermometer, capable of accurately measuring temperatures over the range of 0-50EC (273-323 K) to the nearest ±1EC and referenced to an NIST or ASTM thermometer within ±2EC at least annually.
- Barometer, capable of accurately measuring ambient barometric pressure over the range of 500-800 mm Hg (66-106 kPa) to the nearest mm Hg and reference within ±5 mm Hg of a barometer of known accuracy at least annually.
- Orifice transfer standard certification worksheet (see Figure 8).

7.3.1.2 Record on the orifice transfer standard certification worksheet the standard volume meter's serial number; orifice transfer standard's type, model, and serial number; the person performing the certification; and the date.

7.3.1.3 Observe the barometric pressure and record it as Pa. Read the ambient temperature in the vicinity of the standard volume meter and record it as Ta (K = EC + 273).

7.3.1.4 Connect the orifice transfer standard to the inlet of the standard volume meter. Connect the mercury manometer to measure the pressure at the inlet of the standard volume meter. Connect the orifice (water or oil) manometer to the pressure tap on the orifice transfer standard. Connect a high-volume air mover to the outlet side of the standard volume meter. Make sure that all gaskets are present and are in good condition.

7.3.1.5 Check that the standard volume meter table is level and adjust its legs if necessary.

7.3.1.6 Check for leaks by temporarily clamping both manometer lines (to avoid fluid loss) and blocking the orifice with a large-diameter rubber stopper, wide duct tape, or other suitable means. Start the high-volume air mover and note any change in the standard volume meter's reading. The reading should

remain constant. If the reading changes, locate any leaks by listening for a whistling sound and/or retightening all connections, making sure that all gaskets are properly installed.

[Note: Avoid running the sampler for longer than 30 s at 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 motor's lifetime; it can raise temperatures to the point of defeating the electrical insulation which could result in fire or electric shock to the user.]

7.3.1.7 After satisfactorily completing the leak check, turn off the high-volume air sampler, unblock the orifice, and unclamp both manometer lines. Zero the water and mercury manometers by sliding their scales so that their zero lines are even with the bottom of the meniscuses.

7.3.1.8 Turn on the high-volume air sampler. Adjust the variable voltage transformer to achieve an appropriate flow rate (i.e., within the approximate range of 0.9-1.3 m^3/min (32-46 ft^3/min)). If necessary, use fixed resistance plates or the variable resistance valve to achieve the appropriate flow rate (see Figure 7). The use of fixed resistance plates is discouraged (but not prohibited) because the leak check must be repeated each time that a plate is installed.

7.3.1.9 After setting a flow rate, allow the system to run for at least 1 min to attain a constant motor speed. Observe the standard volume meter dial reading and simultaneously start the stopwatch. Error in reading the meter dial can be minimized by starting and stopping the stopwatch on whole number dial readings (e.g., 4091.00).

7.3.1.10 Record the initial volume that the meter dial indicated when the stopwatch was started. Maintain this constant flow rate until at least 3 m^3 of air have passed through the standard volume meter. Record the standard volume meter's inlet pressure manometer reading as) Hg and the orifice manometer reading as) H_2O. If) H_2O changes significantly during the run, abort the run and start again.

7.3.1.11 When at least 3 m^3 of air have passed through the system, note the standard volume meter reading and simultaneously stop the stopwatch. Record the final volume that the meter dial was indicating when the stopwatch was stopped. Record the elapsed time (Time) indicated on the stopwatch.

7.3.1.12 Calculate the volume measured by the standard volume meter (Vol.) using the following equation:

$$) \text{ Vol.} = \text{Final Volume} - \text{Initial Volume}$$

7.3.1.13 Correct this volume to ambient atmosphere pressure.

$$Va =) \text{ Vol.} (Pa -) \text{ Hg})/Pa$$

where:

Va = actual volume at ambient barometric pressure, m^3.
) Vol. = actual volume measured by the standard volume meter, m^3.
Pa = ambient barometric pressure during calibration, mm Hg.
) Hg = differential pressure at inlet to volume meter, mm Hg.

7.3.1.14 Calculate the actual volumetric flow rate (m^3/min).

$$Qa = Va/) \text{ Time}$$

where:

Qa = actual volumetric flow rate through the orifice, m^3/min.
) time = elapsed time, min.

7.3.1.15 Repeat Sections 7.3.1.8 through 7.3.1.14 for at least four additional flow rates within the approximate range of 0.9-1.3 m^3/min (32-46 ft^3/min). At least five evenly distributed different flow rates are required, and at least three flow rates must be in the specified inlet flow-rate interval (1.02-1.24 m^3/min [36-44 ft^3/min]). Better calibration precision may be obtained by running additional flow rates or repeating the flow rates.

7.3.1.16 For each flow, compute $[(\ ) H_2O)(Ta/Pa)]^{½}$, and plot these values against the corresponding values of Qa. Draw the orifice transfer standard's certification curve. For the model $[(\ ) H_2O)(Ta/Pa]^{1/2}$ = m (Qa) + b, calculate the linear least squares regression's slope (m), intercept (b), and correlation coefficient (r) of the certification relationship. Plot the regression line on the same graph as the calibration data, as illustrated in Figure 9. A certification graph should be readable to 0.02 m^3/min.

7.3.1.17 If any calibration point does not fall within ± 2% of the line, rerun the point, recalculate, and replot.

7.3.1.18 For subsequent use of the orifice transfer standard, calculate Qa from the calibration relationship as:

$$Qa(orifice) = \{[(\ ) H_2O)(Ta/Pa)]^{½} - b\} \{l/m\}$$

where:

Qa(orifice) = actual volumetric flow rate as indicated by the orifice transfer standard, m^3/min
) H_2O = pressure drop across the orifice, mm H_2O.
Ta = ambient temperature during use, K (K = EC + 273).
b = intercept of the orifice calibration relationship.
m = slope of the orifice calibration relationship.

7.3.2 Orifice Transfer Standard Calibration Frequency. Upon receipt and at l-yr intervals, the calibration of the orifice transfer standard should be certified with a standard volume meter (such as a Roots Meter®) traceable to NIST. An orifice transfer standard should be visually inspected for signs of damage before each use and should be recalibrated if the inspection reveals any nicks or dents.

7.4 Procedure for a Mass-Flow-Controlled (MFC) High Volume Sampler

The MFC sampler calibration procedure presented in this section relates known flow rates to the pressure in the exit orifice plenum. The known flow rates are determined by an orifice transfer standard that has been certified according to the procedure presented in Section 7.3.1. The exit orifice plenum is the area within the motor housing (below the motor unit) that contains the air flow just before it is exhausted to the atmosphere through the exit orifice. This exit orifice plenum pressure should be measured with a 25-cm (10") water or oil manometer. Also, each sampler should have its own dedicated manometer, which can be conveniently mounted to the side of the sampler housing. Other types of pressure measurement devices may be used provided they have comparable accuracy. The 4" continuous pressure (flow) recorders of the type often supplied with high volume PM_{10} samplers are generally not sufficiently accurate and are not recommended for quantitative sampler pressure or flow measurements. These flow recorders should be used only for nonquantitative determination that the flow was approximately constant and uninterrupted over the sample period. The flow recorder may be connected in parallel with the manometer or other pressure

measuring device, using a tee or "y" tubing connection. For this MFC calibration procedure, the following conditions are assumed:

- The high volume PM_{10} sampler is equipped with a mass flow controller to control its sample flow rate.
- The sampler flow rate is measured by measuring the exit orifice plenum pressure, using a water or oil manometer [or, if necessary, a continuous-flow recording device using square-root-scale chart paper].
- The transfer standard for the flow-rate calibration is an orifice device equipped with either a series of resistance plates or an integral variable-resistance valve. The pressure drop across the orifice is measured by an associated water or oil manometer.

[Note: Because flow recorders are still widely used for quantitative flow measurements, the calibration procedure includes specific instructions for quantitatively calibrating a flow recorder. These flow recorder instructions are enclosed in brackets [ ] and should be used only when a manometer or other pressure measurement device cannot be used.]

7.4.1 Calibration Equipment.

7.4.1.1 Orifice transfer standard with calibration traceable to NIST (see Section 7.3).

7.4.1.2 An associated water or oil manometer, with a 0-400 mm (0-16") range and an minimum scale division of 2 mm (0.1")

[Note: Digital manometers may also be used in place of water or oil manometers, especially in cold/frigate climates. Ensure the battery in the manometer is new before use.]

7.4.1.3 A water or oil manometer, with a 0-400 mm (0-16") range and a minimum scale division of 2 mm (0.1") for measurement of the sampler exit orifice plenum pressure. This manometer should be associated with the sampler.

[*Note: Manometers used for field calibration may be subject to damage or malfunction and should thus be checked frequently.*]

7.4.1.4 Thermometer, capable of accurately measuring temperature over the range of 0-50EC (273-323 K) to the nearest ± 1 EC and referenced to an NIST or ASTM thermometer within ± 2 EC at least annually.

7.4.1.5 A portable aneroid barometer (e.g., a climber's or engineer's altimeter) capable of accurately measuring ambient barometric pressure over the range of 500-800 mm Hg (66-106 kPa) to the nearest mm Hg and referenced within ± 5 mm Hg of a barometer of known accuracy at least annually.

7.4.1.6 Miscellaneous handtools, calibration data sheets or station log book, and 51 mm (2") duct tape.

7.4.2 Multipoint Flow-Rate Calibration. The procedure presented here is basic and generic, given the assumptions listed in Section 7.4. More detailed calibration procedures, variations, or alternative procedures may be presented in the manufacturer's instruction manual. The manual should be reviewed carefully and the various calibration variations or alternative procedures should be evaluated. In-house equipment and personnel, procedural simplicity and uniformity, and subsequent data applications should be considered in establishing the specific, detailed calibration procedure to be implemented.

[Note: Do not attempt to calibrate the MFC sampler under windy conditions. Short-term wind velocity fluctuations will produce variable pressure readings by the orifice transfer standard's manometer. The calibration will be less precise because of pressure variations.]

7.4.2.1 Set up the calibration system as recommended by the manufacturer. A typical MFC PM_{10} sampler calibration configuration is illustrated in Figure 10. MFC samplers are calibrated without a filter or filter cassette installed.

7.4.2.2 Disconnect the motor from the flow controller and plug it directly into a stable line voltage source (i.e., the sampler's on-off timer, if so equipped, or other source of the line voltage).

7.4.2.3 Install the orifice transfer standard and its adapter faceplate on the sampler. Check all gaskets and replace any questionable ones.

[Note: Tighten the faceplate nuts evenly on alternate corners to properly align and seat the gaskets. The nuts should be only hand-tightened because too much compression can damage the sealing gasket.]

7.4.2.4 Select the first calibration flow rate and install the appropriate resistance plate or adjust the variable orifice valve. At least four flow rates are required to define the calibration relationship. For resistance plate orifices, make sure that the orifice and resistance plate gaskets are in place and the orifice is not cross-threaded on the faceplate.

7.4.2.5 To leak check, block the orifice with a large-diameter rubber stopper, wide duct tape, or other suitable means. Seal the pressure port with a rubber cap or similar device. Turn on the sampler. 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 in the sampler's exit orifice manometer or flow recorder. Leaks are usually caused either by a damaged or missing gasket between the orifice transfer standard and the faceplate or by cross-threading of the orifice transfer standard on the faceplate. All leaks must be eliminated before proceeding with the calibration. When the system is determined to be leak-free, turn off the sampler and unblock the orifice.

[Note: Avoid running the sampler for longer than 30 s at 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 motor's lifetime and can raise temperatures to the point of defeating the electrical insulation, which could result in fire or electric shock to the user.]

7.4.2.6 Inspect the connecting tubing of both manometers for crimps or cracks. Open the manometer valves (if present) and blow gently through the tubing, watching for the free flow of the fluid.
Adjust the manometers' sliding scales so that their zero lines are at the bottom of the meniscuses. Connect the orifice transfer standard manometer to the orifice transfer standard. Connect the sampler's exit orifice manometer [and the continuous-flow recorder, if used] to the exit orifice plenum port. Ensure that one side of each manometer is open to atmospheric pressure. Make sure that the tubing fits snugly on the pressure ports and on the manometer.

7.4.2.7 If a continuous flow recorder is to be used quantitatively in lieu of a manometer, record the site location, sampler S/N, date, and the operator's initials on the blank side of a clean recorder chart. Make sure the chart has a square-root scale. Open the front door of the sampler and install the clean recorder chart.

7.4.2.8 Read and record the following parameters on the HV data sheet. An example calibration data sheet for the MFC sampler is illustrated in Figure 11.

- Date, location, and operator's signature.
- Sampler S/N and model.
- Ambient Pa, mm Hg.
- Ambient temperature (Ta), K (K = EC + 273).
- Orifice S/N and calibration relationship.

[Note: Consistency of temperature and barometric pressure units is required. All temperatures should be expressed in kelvin (K = EC + 273). Also, all barometric pressures should be expressed in mm Hg. Avoid calibrating a sampler using one set of units and then performing sampler calculations using another set.]

[Note: Ideally, the temperature of the air in the exit orifice plenum should be measured because it will be somewhat higher than ambient temperature. However, an adequate approximation of this temperature may be obtained by adding 30 K to the ambient temperature. This addition is incorporated in the calculations given in Section 7.4.3.]

7.4.2.9 Turn on the sampler and allow it to warm up to operating temperature (3-5 min). Then read and record the orifice transfer standard's manometer deflection,) H_2O (in. H_2O), and the corresponding sampler's manometer deflection,) Pex [or flow recorder chart reading, I].

[Note: The sampler inlet may be partially lowered over the orifice transfer standard to act as a draft shield (if a shield is not otherwise provided). Use a block to provide at least 2" of clearance at the bottom for air flow and for the manometer tubing.]

7.4.2.10 Install the other resistance plates or adjust the variable orifice value to obtain each of the other calibration flow rates and repeat Section 7.4.2.9 for each. At least four calibration flow rates are required.

7.4.2.11 Plot the calibration data on a sheet of graph paper as specified in Section 7.4.3.4.

[Note: The data should be plotted in the field as the calibration is occurring, rather than afterwards back at the laboratory.]

Repeat Section 7.4.2.9 for any data that are questionable on the plot.

[Note: Running additional calibration points at differing flow rates or repeating the calibration points at the same flow rates is encouraged to improve the precision of the calibration.]

7.4.2.12 Turn off the sampler and remove the orifice transfer standard.

7.4.2.13 Reconnect the sampler motor to the flow controller.

7.4.2.14 Perform the calibration calculations presented in the following section. The data generated will be used to set the mass flow controller (see Section 7.4.4) to a value that will result in optimal volumetric flow based on the seasonal average temperature and barometric pressure at the monitoring site.

7.4.3 Calibration Calculations. Gather all calibration data, including the orifice calibration information and the sampler calibration data sheet (and, if used, the flow recorder chart, which should graphically display the various calibration flow rates).

[Note: These calculations should be done at the time of the calibration, rather than later. This approach will allow additional calibration points to be taken if questions arise about the data that have already been obtained.]

7.4.3.1 Verify that the orifice transfer standard calibration relationship is current and traceable to an acceptable primary standard.

7.4.3.2 Calculate and record Qa for each calibration point from the orifice calibration information using the following equation.

$$Qa(orifice) = \{\Delta H_2O(Ta/Pa)\}^{1/2} - b\} \{l/m\}$$ where:

Qa(orifice) = actual volumetric flow rate as indicated by the transfer standard orifice, m^3/min
ΔH_2O = pressure drop across the orifice, in. H_2O.
Ta = ambient temperature during use, K (K = EC + 273).
Pa = ambient barometric pressure during use, mm Hg.
b = intercept of the orifice calibration relationship.
m = slope of the orifice calibration relationship.

7.4.3.3 Calculate and record the quantity for each calibration point as:

$$\Delta Pext = [\Delta Pex(Ta + 30)/Pa]^{1/2}$$

where:

Δ Pext = transformed manometer reading.
Δ Pex = sampler manometer reading, in. H_2O Ta = ambient temperature, K (K = EC + 273).
Pa = ambient barometric pressure, mm Hg.

[If a continuous-flow recorder is used quantitatively, calculate and record the quantity [It] as follows:

$$[It] = I[Ta + 30)/Pa]^{1/2}$$

where:

[It] = transformed flow recorder chart reading.
I = flow recorder chart reading, arbitrary units on square root scale.

[Note: If recorder charts with linear scales are used, substitute $(I)^{1/2}$ for I in the above equation.]

7.4.3.4 On a sheet of graph paper, plot the calculated Qa(orifice) flow rates on the x-axis and the transformed sampler manometer response, Δ Pext [or the transformed flow recorder reading, It], on the y-axis.

Because determining the sampler's average operational flow rate (Qa) during a sample period depends on the ambient average temperature and pressure, using a graphic plot of the calibration relationship is not recommended for subsequent data reduction. This plot is used only to visually assess the calibration points to see if any should be rerun. Plot the regression line on the same graph paper as the calibration data. For the regression model y = mx + b, let y + 2 Δ Pext and x = Qa(Orifice) so that the model is given by:

$$\Delta Pext = m[Qa(orifice)] + b$$

For the flow recorder, the model is:

$$It = m[Qa(orifice)] + b]$$

Using a programmable calculator or a calculation data form, determine the linear regression slop (m), intercept (b), and correlation coefficient (r) and record them on the data sheet. A five-point calibration should yield a regression equation with a correlation coefficient of $r > 0.990$, with no point deviating more

than ± 0.04 m^3/min from the value predicted by the regression equation. Plot the regression line on the same graph paper that has the individual calibration points.

7.4.3.5 For subsequent sample periods, the sampler's average actual operational flow rate, $\overline{\overline{Qa}}$, is calculated from the calibration slope and intercept using the equation.

$$\overline{\overline{Qa}} = \{) \overline{\overline{Pex}}(Tav + 30)/Pav]^{1/2} - b\} \{l/m\}$$

where:

$\overline{\overline{Qa}}$ = the sampler's average actual flow rate, m^3/min.
) $\overline{\overline{Pex}}$ = average of initial and final sampler manometer readings ( ) Pex_i +) Pex_f), mm Hg.
Tav = average ambient temperature for the sample period, K(K = EC + 273).
Pav = average ambient pressure for the sampling period, mm Hg.
b = intercept of the sampler calibration relationship.
m = slope of the sampler calibration relationship.

[For the flow controller,

$$\overline{\overline{Qa}} = \{\overline{I}(Tav + 30)/Pav]^{1/2} - b\} \{l/m\}$$

where:

$\overline{I}$ = average flow recorder reading for the sample period.]

[*Note: If recorder charts with linear scales are used, substitute* $(I)^{1/2}$ *for (I) in the above equation.]*

7.4.4 Mass Flow Controller Adjustment Procedure. The controlled flow rate of an MFC sampler is adjustable and must be set to the proper design flow rate. The constant mass flow maintained by the MFC causes the actual volumetric flow rate through the inlet to fluctuate as the ambient temperature and barometric pressure change at the monitoring site. Normally, the range of these fluctuations is within the allowable tolerance limits for the inlet. However, the flow-rate set point of the mass flow controller must be correctly adjusted so that the deviations are "centered" with respect to the seasonal average temperature and barometric pressure at the site, not the temperature and pressure prevailing at the time of setting. The correct seasonal volumetric setpoint flow rate (SFR) at Ta and Pa has had the same mass flow rate as the inlet design volumetric flow rate at Ts and Ps.

[Note: The correct SFR may differ from day to day and may be somewhat higher or lower than the inlet design flow rate on any particular day.]

7.4.4.1 Determine the seasonal average temperature (Ts) and seasonal average pressure (Ps) at the site and record them on the calibration data sheet. (Determination of the number of "seasons," i.e., the number of different seasonal average temperatures needed for the year, is left to the discretion of the operator.)

7.4.4.2 Calculate SFR and record on the calibration data sheet:

$$SFR = (1.13)\,(Ps/Pa)(Ta/Ts)$$

where:

SFR = set-point actual volumetric flow rate for adjustment of the mass flow controller, based on seasonal average temperature and average pressure at site, m^3/min.
1.13 = inlet design flow rate (as specified by the manufacturer), m^3/min.
Ps, Pa = seasonal average and current ambient barometric pressure at the site, respectively, mm Hg.
Ts, Ta = seasonal average and current ambient temperature, respectively, K (K = EC + 273).

7.4.4.3 Calculate and record on the sampler's calibration data sheet the sampler set-point manometer reading [or flow recorder reading] that corresponds to the SFR calculated in Section 7.4.4.2.

$$SSP = [Pa/(Ta + 30)][m(SFR) + b]^2$$

where:

SSP = sampler set-point manometer reading, in H_2O.
Pa = ambient barometric pressure, mm Hg.
Ta = ambient temperature, K (K = EC + 273).
m = slope of the sampler's calibration relationship.
SFR = set-point flow rate from 7.4.4.2, m^3/min.
b = intercept of the sampler's calibration relationship.

[For the flow recorder,

$$SSP = [m(SFR) + b]\,[Pa/(Ta + 30)]^{½}]$$

7.4.4.4 Visually check to make sure the motor is connected to the mass flow controller and the manometer is properly connected.

7.4.4.5 Install a clean filter (in a filter cassette) in the sampler according to the manufacturer's instructions. [If the continuous flow recorder is used quantitatively, install a clean chart and verify that the recorder is zeroed (i.e., the pen rests on the innermost circle of the chart).]

7.4.4.6 Turn on the sampler and allow it to warm up to operating temperature (3-5 min).

7.4.4.7 Following the manufacturer's instructions, adjust the mass flow controller until the manometer reading [or flow recorder response] indicates the sampler set point (SSP) as calculated in Section 7.4.4.3.

7.4.4.8 Verify that the flow controller will maintain this flow rate for at least 10 min. Turn off the sampler.

7.4.4.9 The sampler can now be prepared for the next sample run day.

7.5 Procedure for a Volumetric-Flow-Controlled (VFC) Sampler

The VFC sampler calibration procedure presented in this section relates known flow rates (Qa, as determined by an orifice transfer standard) to the ratio of the stagnation pressure to the ambient barometric pressure (Pl/Pa). The stagnation pressure (Pl) is the air pressure inside the sampler in the area just under the filter. VFC samplers have a stagnation pressure tap or port through which the stagnation pressure can be measured. A VFC sampler may also have an exit orifice below the motor similar to those in MFC samplers. In this case, the sampler flow rate can be measured and calibrated using the exit orifice plenum pressure generally described in Section 7.4. However, using the stagnation pressure generally provides a more accurate

indication of sampler flow rate. Additionally, a continuous-flow recorder may be connected to the exit orifice pressure tap for nonquantitative determination that the flow rate was constant and uninterrupted over the sample period.

The stagnation pressure should be measured with a 0-1000 mm (0-36") oil, water, or digital manometer. Also, each sampler should have its own dedicated manometer, which can be conveniently mounted to the side of the sampler housing. Other types of pressure measurement instruments may be used provided they have comparable accuracy. However, the 4" continuous pressure (i.e., flow) recorders often supplied with HV samplers are generally not sufficiently accurate and are **not recommended** for quantitative sampler pressure or flow rate measurements.

The VFC sampler's flow control system is a choke-flow venturi. This system must be precisely sized for a given average annual temperature and pressure because no means is provided for the user to adjust the operational flow rate. Therefore, the purchasing agency should notify the manufacturer of the **operational** location of the sampler; differences in temperature and pressure between the shipping address and the monitoring site may result in an incorrect operational flow rate. As with the MFC sampler, both the ambient temperature and barometric pressure readings must be determined or estimated during the sampling period for the subsequent calculation of total sampler volume in standard volume units.

For this VFC calibration procedure, the following conditions are assumed:

- The VFC sampler uses a choked-flow venturi to control the actual volumetric flow rate.
- The sampler flow rate is measured by measuring the stagnation pressure ratio, and the sampler is not equipped with a continuous flow recorder.
- The sampler inlet is designed to operate at a constant actual volumetric flow rate of 1.13 m^3/min.
- The transfer standard for the flow-rate calibration is an orifice device equipped with either a series of resistance plates or an integral variable-resistance valve. The pressure drop across the orifice is measured by an associated water or oil manometer.
- The sampler will be calibrated in actual volumetric flow-rate units (Qa), and the orifice transfer standard is also calibrated in Qa, as specified in Section 7.3.

7.5.1 Calibration Equipment.

7.5.1.1 Orifice transfer standard with proper calibration traceable to NIST (see Section 7.3).

7.5.1.2 An associated water, oil, or digital manometer, with a 0-400 mm (0-16") range and minimum scale divisions of 2 mm (0.1").

7.5.1.3 An oil, water, or digital manometer, with a 0-1000 mm (0-36") range and minimum scale divisions of 2 mm (0.1") or other pressure measurement device for measurement of the sampler stagnation pressure. Ideally, this manometer (or other pressure instrument) should be associated with the sampler.

[Note: Manometers used for field calibration may be subject to damage or malfunction and should thus be checked frequently.]

7.5.1.4 Thermometer, capable of accurately measuring temperature over the range of 0-50EC (273-323 K) to the nearest ± 1EC and referenced to an NIST or ASTM thermometer within ± 2EC at least annually.

7.5.1.5 A portable, aneroid barometer (e.g., a climber's or engineer's altimeter) capable of accurately measuring ambient barometric pressure over the range of 500-800 mm Hg to the nearest mm Hg and referenced within ± 5 mm Hg to a barometer of known accuracy at least annually.

7.5.1.6 Calibration data sheets or the station log book and 51 mm (2")-wide duct tape.

7.5.1.7 A clean filter.

7.5.2 Multipoint Flow-Rate Calibration Procedure - VFC Sampler. The procedure presented here is basic and intended to be generic, given the assumptions listed in Section 7.5. More detailed calibration procedures, variations, or alternative procedures may be presented in the manufacturer's instruction manual. The manual should be reviewed carefully and that the various calibration variations or alternative procedures be evaluated. In-house equipment and personnel, procedural simplicity and uniformity, and subsequent data applications should be considered in establishing the specific, detailed calibration procedure to be implemented.

[Note: The calibration of some VFC samplers may be affected by changes in line voltage, particularly if the line voltage is below normal (normal is about 115 V). For this reason, VFC samplers should always be calibrated at the monitoring site. Further, if the line voltage at the site is low and likely to fluctuate significantly, a line voltage booster or regulator may be advisable. Also, be sure that replacement blower motors are of the correct type.]

[Note: Do not attempt to calibrate the VFC sampler under windy conditions. Short-term velocity fluctuations will produce variable pressure readings by the orifice transfer standard's manometer. The calibration will be less precise because of the pressure variations.]

7.5.2.1 Set up the calibration system as recommended by the manufacturer. A typical VFC sampler calibration configuration is illustrated in Figure 12. The VFC sampler manufacturer may specify that the sampler be calibrated with a filter installed, which generally precludes calibration flow rates higher than normal operating flow rate. Additional calibration flow rates obtained without a filter may be appropriate, as discussed in Section 7.5.2.8.

7.5.2.2 Install the orifice transfer standard and its adapter faceplate on the sampler. First inspect all gaskets and seals and replace any doubtful ones.

[Note: Tighten the faceplate nuts evenly on alternate corners to properly align and uniformly seat the gaskets. The nuts should be hand-tightened only; too much compression can damage the sealing gasket.]

7.5.2.3 Select a calibration flow rate and install the appropriate resistance plate (or no plate) or adjust the variable resistance valve. At least four flow rates are required to define the calibration relationship. At least three flow rates should be within the acceptable flow-rate range (i.e., 1.02-1.24 m^3/min) for the sampler inlet. For resistance plate orifices, make sure the orifice and resistance plate gaskets are in place and the orifice is not cross-threaded on the faceplate.

7.5.2.4 Leak check the system by blocking the orifice with a large-diameter rubber stopper, wide duct tape, or other suitable means. Seal the pressure port with a rubber cap or similar device. Turn on the sampler. Gently rock the orifice transfer standard and listen for a whistling sound that would indicate a leak in the system. Leaks are usually caused either by a damaged or missing gasket between the orifice transfer standard and the faceplate or by crossthreading of the orifice transfer standard on the faceplate. All leaks must be eliminated before proceeding with the calibration. When the system is determined to be leak-free, turn off the sampler and unblock the orifice.

[Note: Avoid running the sampler for longer than 30 s at 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 motor's lifetime. It can raise temperatures to the point of defeating the electrical insulation, which could result in fire or electric shock to the user.]

7.5.2.5 Inspect the connecting tubing of the manometers for crimps or cracks. Open the manometer valves (if present) and blow gently through the tubing, watching for the free flow of the fluid. Adjust the manometers' sliding scales so that their zero lines are at the bottom of the meniscuses. Connect the transfer standard manometer to the transfer standard and the sampler stagnation pressure manometer (or other pressure instrument) to the stagnation pressure port. Ensure that one side of each manometer is open to atmospheric pressure. Make sure the tubing fits snugly on the pressure ports and on the manometers.

7.5.2.6 Read and record the following parameters on the VFC Sampler Data Sheet. An example calibration data sheet for the VFC sampler is illustrated in Figure 13.

- Date, location, and operator's signature.
- Sampler S/N and model.
- Ambient barometric pressure (Pa), mm Hg.
- Ambient temperature (Ta), EC and K (K = EC + 273).
- Orifice S/N and calibration relationship.

[Note: Consistency of temperature and barometric pressure units is required. All temperatures should be expressed in kelvin (K = EC + 273). Also, all barometric pressures should be expressed in mm Hg. Avoid calibrating a HV sampler using one set of units and then performing sampler calculations using another set.]

7.5.2.7 Turn on the sampler and allow it to warm to operating temperature (3-5 min). Read and record the orifice transfer standard's manometer reading, H_2O, and the corresponding sampler relative stagnation pressure manometer reading, Pstg, on the data sheet. (Relative stagnation pressure is a negative pressure [i.g., a vacuum] relative to atmospheric pressure as measured by a manometer with one leg open to the atmosphere.) Be sure to convert the manometer reading to mm Hg using the following equation before recording the reading on the calibration data sheet:

$$\text{mm Hg} = 25.4 \text{ (in. } H_2O/13.6)$$

[Note: The sampler inlet may be partially lowered over the orifice transfer standard to act as a draft shield (if a shield is not otherwise provided). Use a block to provide at least 2" of clearance at the bottom of air flow and for the manometer tubing).]

7.5.2.8 Install the other resistance plates or adjust the variable orifice value to obtain each of the other calibration flow rates and repeat Section 7.5.2.7 for each. At least four calibration flow rates are required with at least three in the acceptable flow-rate range. Difficulties may be encountered in obtaining flow rates in the acceptable range. Even with modified resistance plates (or with no plates) installed, it may be impossible to obtain three acceptable flow rates with a filter mounted on the sampler. Lower flow rate calibration points may be used by extrapolation into the acceptable range without a filter installed in the sampler. If additional calibration points are obtained without a filter, they should be examined carefully to make sure they are consistent with the calibration points obtained with a filter (i.e., they fall on a smooth curve through all the calibration points).

7.5.2.9 Plot the calibration data on a sheet of graph paper as specified in Section 7.5.3.5 of the next section. Repeat Section 7.5.2.7 for any data that are questionable on the plot. Running additional calibration points at differing flow rates or repeating the calibration points at the same flow rates is encouraged to improve the precision of the calibration.

[Note: The data should be plotted in the field as the calibration is occurring, rather than afterwards back at the laboratory.]

7.5.2.10 Turn off the sampler and remove the orifice transfer standard.

7.5.2.11 Install a clean filter on the sampler in the normal sampling mode (use a filter cassette if one is normally used). Turn on the sampler and allow it to warm up to operating temperature.

7.5.2.12 Read the relative stagnation pressure as in Section 7.5.2.7 and record it on the data sheet in the row for the operational flow rate.

7.5.2.13 Perform the calibration calculations presented in the following sections.

7.5.3 Calibration Calculations. Gather together all the calibration data, including the orifice transfer standard's calibration information and the sampler calibration data sheet.

[Note: These calculations should be done at the time of the calibration, rather than later. This approach will allow additional calibration points to be taken if questions arise about the data that have already been obtained.]

7.5.3.1 Verify that the orifice transfer standard calibration relationship is current and traceable to an acceptable primary standard.

7.5.3.2 Calculate the record Qa(orifice) for each calibration point from the orifice calibration information and the equation.

$$Qa(orifice) - \{[\ ) H_2O(T_a/Pa)]^{½} - b\} \{l/m\}$$

where:

Qa(orifice) = actual volumetric flow rate as indicated by the transfer standard orifice, m^3/min.
) H_2O = pressure drop across the orifice, in. H_2O.
Ta = ambient temperature during use, K (K = EC + 273).
Pa = ambient barometric pressure during use, mm Hg.
b = intercept of the orifice transfer standard's calibration relationship.
m = slope of the orifice transfer standard's calibration relationship.

7.5.3.3 Calculate and record the value of the absolute stagnation pressure ratio, [Pl], for each calibration point:

$$[Pl] = Pa -) Pstg$$

where:

[Pl] = absolute stagnation pressure, mm Hg.
Pa = ambient barometric pressure, mm Hg.
) Pstg = relative stagnation pressure, mm Hg.

7.5.3.4 Calculate and record the stagnation pressure ratio:

$$\text{Stagnation pressure ratio} = Pl/Pa$$

7.5.3.5 On a sheet of graph paper, plot the calculated orifice transfer standard's flow rates, Qa(orifice), on the x-axis vs. the corresponding stagnation pressure ratios, Pl/Pa, on the y-axis. Draw a smooth curve through the plotted data. If necessary, extrapolate the curve to include the acceptable flow-rate range.

7.5.3.6 If the sampler manufacturer has provided a factory calibration table (i.e., the lookup table) for the sampler, compare Qa(orifice) for several points on the calibration plot with Qa(sampler) determined from the factory calibration. Calculate the percentage difference between Qa(orifice) and Qa(sampler) using the following equation.

$$\% \text{ Difference} = \frac{Qa(\text{sampler}) - Qa(\text{orifice})}{Qa(\text{orifice})} \times [100]$$

If the agreement is within a few (i.e., 2 or 4) percent, the factory calibration is validated and may be used for subsequent sample periods. Proceed to Section 7.5.5.

7.5.3.7 If the agreement is not within a few percentage points, recheck the accuracy of the orifice transfer standard and recheck the calibration procedure. Look for leaks, manometer reading errors, incorrect temperature or pressure data, or miscalculations. Also check for abnormally low line voltage at the site (it should be at least 110 V ac), for the correct blower motor, and for the presence of a gasket between the motor and the choked-flow venturi. A factory calibration is not likely to be substantially incorrect, and any discrepancy of more than a few percent is probably due to some problem with the sampler or with the calibration procedure. However, if no errors or problems with the sampler or with the calibration can be found, or if no factory calibration is provided by the manufacturer, proceed as described in Section 7.5.4.

7.5.4 Generation of Calibration Relationship - VFC Sampler.

7.5.4.1 For each calibration point, calculate and record the quantity,

$$[Pl/Pa)Ta]^{1/2}$$

where:

Pl/Pa = stagnation pressure ratio from the equation in Section 7.5.3.
Ta = ambient temperature during sampler calibration, K (K = EC + 273).

7.5.4.2 For the general linear regression model, $y = mx + b$, let $y = [(Pl/Pa)Ta]^{1/2}$ and let $x = Qa(\text{orifice})$, such that the model is given by:

$$[(Pl/Pa)Ta]^{1/2} = m[Qa(\text{orifice})] + b$$

Calculate the linear regression slope (m), intercept (b), and correlation coefficient (r).

[Note: Inspect the plotted calibration curve to determine whether any of the calibration points that are substantially outside of the acceptable flow-rate range need to be eliminated so that they do not result in an inappropriate linear regression line.]

7.5.4.3 For subsequent sample periods, the sampler's average actual operating flow rate, Qa, is calculated from the calibration slope and intercept using the following equation.

$$\overline{Qa}(\text{sampler}) = \{[\overline{P1}/Pav)Tav]^{1/2} - b\} \{l/m\}$$

where:

$\overline{Qa}$(sampler) = the sampler's average actual flow rate, m^3/min.
$\overline{P1}$/Pav = average stagnation pressure ratio for the sampling period.
Tav = average ambient temperature for the sampling period, K (K = EC + 273).
b = intercept of the sampler calibration relationship.
m = slope of the sampler calibration relationship.

[Note: The average value for Pl should be calculated from stagnation pressure measurements taken before and after the sampling period. Pav should be estimated from barometric pressure for the sampling period. See also Section 9.4 for additional information.]

7.5.4.4 If a calibration (Lookup) table is desired, evaluate the above equation for various appropriate values of Pl/Pa and Ta and list the corresponding values of Qa(sampler) in tabular form.

7.5.5 Single-Point Operational Flowrate Ventilation. This procedure compares the VFC sampler's normal operating flow rate to the design flow rate of the inlet (e.g., 1.13 m^3/min).

7.5.5.1 Determine the value of Pl/Pa for the operational flow rate obtained with only the filter cassette installed (see Section 7.5.2.11 and Section 7.5.2.12).

7.5.5.2 Determine the new sampler flow rate, Qa(sampler) from the lookup table that corresponds to this value of Pl/Pa. Use the manufacturer's calibration table if it has been validated in 7.5.3.6; otherwise, use the equation in Section 7.5.4.3.

7.5.5.3 Compare Qa(sampler) with the inlet design flow rate (e.g., 1.13 m^3/min) using the following equation:

$$\text{Design flow rate\% difference} = \frac{\text{Qa(sampler)} - 1.13}{1.13} \times 100$$

This design flow rate percentage difference must be less than the allowable flow rate tolerance (i.e., ± 10, if not otherwise specified by the manufacturer). However, this value should be well within ± 7 to allow for some variation with ambient temperature. If this value is not within ± 7, recheck the calibration procedure and data for errors. Check the sampler for leaks, bad motor brushes, missing gaskets, incorrect motor type, or abnormally low line voltage. Because the VFC flow rate is not adjustable, the VFC manufacturer must be consulted to resolve cases of substantially incorrect VFC flow rates.

7.6 Sampler Calibration Frequency

To ensure accurate measurement calibrate HV samplers upon installation and recalibrate as follows:

7.6.1 At least quarterly or annually (see 40 CFR 58, Appendix A for a description of the quality assurance requirements);

7.6.2 After any repairs that might affect sampler calibration (e.g., replacing the motor);

7.6.3 After relocation of the sampler to a different site;

7.6.4 If the results of a field flow-check exceed quality control limits (e.g., greater than $\pm 7\%$ from the sampler's indicated flow rate); or

7.6.5 Whenever a field flow-check or performance audit indicates that the sampler is out (or nearly out) of the acceptable flow-rate range.

[Note: Multipoint flow-rate calibrations should be distinguished from single-point, quality control flow checks (see Section 13). The latter are done more frequently than calibrations and are intended to check if the sampler flow rate, Qa(sampler), or the calibration relationship has changed significantly since the last calibration.]

8. Filters

8.1 Pre-weighing of Filters

8.1.1 Filters ready for field use have been pre-weighed in the laboratory, under prescribed climate control conditions of temperature and relative humidity, using Inorganic Compendium Method IO-3.1, *Selection, Extraction and Preparation of Filter Material*.

8.1.2 Within Method IO-3.1, the user is provided guidance on proper selection of filter material in order to meet project specific data quality objectives (DQOs), how to visually inspect a new lot of filters for consistency and identification of defects, and initial weighing of the filters so a net concentration of particulate matter can be calculated after sampling.

8.1.3 The user should follow the procedures outlined within Method IO-3.1 as part of meeting the program's standard operating procedures (SOPs) and quality control (QC) requirements.

8.2 Filter Handling

8.2.1 Filter material may be brittle and subject to shearing and breakage. Laboratory and field personnel must be aware of these characteristics and handle sample filters with care.

8.2.2 For convenience, filters can be packed in groups of 50 or less in their original containers or in a box of comparable size. The filters should be separated by a sheet of 8 ½ x 11" tracing paper. Filter inventory can be controlled by stacking the filters in numerical order so that the operator will use the proper filter first. One side of the shipping box can be cut away to allow the operator to remove the filter easily without damaging the corners.

8.2.3 A filter identification number must be assigned to each filter. Because of difficulty in seeing the "up" side (i.e., the side with the slightly rougher texture) of the filter, consistency in labeling these filters will allow the operator easy access to the filter ID number for documentation and cross-referencing laboratory data forms. This consistency will also eliminate confusion in loading the filter cassettes for subsequent sampling. If the filter ID number is embossed by the operating agency, gentle pressure must be used to avoid filter damage, and extreme care must be taken to avoid duplication or missed numbers.

8.2.4 If samples are to be mailed, the field operator should be supplied with reinforced envelopes and manila folders for protection of the exposed filters during their return to the analytical laboratory. These manila folders may be printed to serve as sample data sheets.

8.3 Visual Filter Inspection

All filters must be visually inspected for defects, and defective filters must be rejected if any are found. Batches of filters containing numerous defects should be returned to the supplier.
The following are specific defects to look for:

- **Pinhole** - a small hole appearing as a distinct and obvious bright point of light when examined over a light table or screen, or as a dark spot when viewed over a black surface.
- **Loose material** - any extra loose material or dirt particles on the filter that must be brushed off before the filter is weighed.
- **Discoloration** - any obvious visible discoloration that might be evidence of a contaminant.
- **Filter nonuniformity** - any obvious visible nonuniformity in the appearance of the filter when viewed over a light table or black surface that might indicate gradations in porosity across the face of the filter.
- **Other** - a filter with any imperfection not described above, such as irregular surfaces or other results of poor workmanship.

9. Sampling Procedure

[Note: This section describes routine operation of a monitoring site using an HV sampler and covers an array of topics, ranging from initial site selection to final data documentation. The procedures herein are intended to serve as guidelines for developing a monitoring program that will accurately reflect trends in local or regional air quality. The effectiveness of the monitoring program depends on responsible day-to-day operation of the monitoring site. The operators who conduct sampling activities offer a unique perspective on the sampler's performance, and their awareness and attention to detail will salvage data that may otherwise be lost. Note, however, that "routine" does not mean "unimportant." The site operator provides cohesiveness in a sampling program.]

9.1 Summary

9.1.1 The PM_{10} sampler can be used in a number of ways. Procedure variations may include the kind of filter medium, the surface area of the filter, prescreening to exclude particles up to a given size, and the manner of placing and exposing the filter during the test. The procedure most commonly used will be described here.

9.1.2 Calibrate the sampler as described in the Section 7. Do not make any change or adjustment on the sampler flow indicator after calibrating. Remove the calibrating orifice. The filters may be packed into a box with sheets of glassine between the filters, or they may be individually packed in self-sealing plastic bags for transportation to the field.

9.1.3 Mount the filter sheet in the filter holder taking care not to lose any of the fiber. Clamp it in place by means provided. Seal into place easier by facing the smooth side into the housing if there is a difference in texture. If the filter holder is separate from the sampler, mount the holder on the intake port, making sure that the coupling gasket is in place and that it is tight.

9.1.4 Place the sampler in the position and location called for in the test, which is with the filter face up, in a horizontal plane, and inside a housing. The dimensions and clearances specified are intended to provide uniformity in sampling practice.

9.1.5 Start the sampler motor and record the time and date. Read the flow-rate indicator and record this reading and the corresponding flow rate as read from the calibration curve. Note also the temperature and barometric pressure. An electric clock should be connected to the same line as the motor so as to detect any loss of test time due to power interruption. A continuous record of the sampling flow rate and sampling time can be obtained by the use of a continuous pressure (or flow rate) recorder.

9.1.6 Allow the sample to run for the specified length of time, which is commonly 24 h, $\pm$ 1 h. During this period several readings of flow rate, temperatures, barometric pressure, and time should be taken if this is feasible. A final set of reading is taken at the end of the test period. If only initial and final readings are made, assume that change of readings is linear over the period of test. Intermediate readings will improve the accuracy of volume measurement.

9.1.7 At the end of the sampling period, record all final readings. Remove the filter from the mount very carefully so as not to lose any of the fiber material or collected particulate matter. Fold the filter in half upon itself with the collected material enclosed within. Place the folded filter in a clean tight envelope and mark it for identification. In some applications it may be desirable to place the used filter in a tight metal container to prevent any loss or damage to the filter.

9.1.8 In the laboratory remove the filter from its container. Tap the container and knock any loose fiber or particulate matter onto the inside surface of the folded filter. Examine the inside surface and, with a pair of tweezers, remove any accidental objects such as insects.

9.2 Siting Requirements

9.2.1 As with any type of air monitoring study in which sample data are used to draw conclusions about a general population, the validity of the conclusions depends on the representativeness of the sample data. Therefore, the primary goal of a monitoring project is to select a site or sites where the collected particulate mass is representative of the monitored area.

9.2.2 Basic siting criteria for the placement of high-volume sampler (either TSP or PM_{10}) are documented in Table 3. This list is not a complete listing of siting requirements; instead, an outline to be used by the operating agency to determine a sampler's optimum location. Complete siting criteria are presented in 40 CFR 58, Appendix E.

9.2.3 Additional factors not specified in the Code of Federal Regulations (CFR) must be considered in determining where the sampler will be deployed. These factors include accessibility under all weather conditions, availability of adequate electricity, and security of the monitoring personnel and equipment. The sampler must be situated where the operator can reach it safely despite adverse weather conditions. If the sampler is located on a rooftop, care should be taken that the operator's personal safety is not jeopardized by a slippery roof surface during inclement weather. Consideration also should be given to the fact that routine operation (i.e., calibrations, filter installation and recovery, flow checks, and audits) involves transporting supplies and equipment to and from the monitoring site.

9.2.4 To ensure that adequate power is available, consult the manufacturer's instruction manual for the sampler's minimum voltage and power requirements. Lack of a stable power source can result in the loss of many samples because of power interruptions.

9.2.5 The security of the sampler itself depends mostly on its location. Rooftop sites with locked access and ground-level sites with fences are common. In all cases, the security of the operating personnel as well as the sampler should be considered.

9.3 Sampler Installation Procedures

9.3.1 On receipt of a high-volume sampler (TSP or PM_{10}) from the manufacturer, visually inspect it and account for all components. Compare the equipment delivered with the enclosed packing slip. Notify the manufacturer immediately of any missing or damaged equipment.

9.3.2 Perform a laboratory check to determine if the sampler is operational. Turn on the sampler and observe the vacuum motor performance and shift the recorder response (if so equipped).

9.3.3 Carefully transport the sampler to the field site. If possible, install the sampler in the center of the site platform. This practice will ensure easy access to the sampler's inlet during maintenance procedures and will reduce inlet damage if the sampler should topple over.

9.3.4 Following manufacturer's instructions, carefully assemble the base and inlet of the sampler. The sampler must be bolted down to a secure mounting surface.

9.3.5 Check all tubing and power cords for crimps, cracks, or breaks.

9.3.6 Plug the power cord into a line voltage outlet. If possible, this outlet should be protected by a ground fault interrupter (GFI) for the operator's safety. The use of waterproof interlocking electrical connectors is also recommended to ensure operator safety and to avoid shorts or power interruptions. Do not allow any electrical connections to be submerged during periods of inclement weather.

9.3.7 Turn on the sampler and make sure that it is still working properly. Investigate and correct any malfunctions before proceeding. Operate the sampler for approximately 30 min to ensure that the motor brushes are properly seated and that the motor is operating at full performance.

9.3.8 Perform a multipoint flow-rate calibration, as described in Section 7.

9.4 Sampling Operations

9.4.1 General.

9.4.1.1 Operational procedures will vary according to the sampler model and options (e.g., the types of flow-rate controller and timer) selected for use in the monitoring program. Consult the instrument manual before putting the sampler into operation. Significant differences exist in the field operation of the two types of flow-controlling systems and, hence, in the determination of operational flow rates. The following assumptions are made in this section:

- The flow rate through a sampler that is equipped with a mass-flow controller is indicated by the exit orifice plenum pressure. This pressure is measured with a manometer (or a flow recorder).
- The flow rate through a sampler that is equipped with a volumetric-flow controller is indicated by the stagnation pressure. This pressure is measured with a manometer.
- The sampler has been calibrated according to procedure presented in Section 7.

9.4.1.2 The sampler has been calibrated according to procedures presented in Section 7.

9.4.1.3 The average actual flow rate for MFC samplers is calculated by determining the following:

- The average of the initial and final manometer readings of the exit orifice plenum pressure (or the average flow recorder reading).
- The average ambient temperature (Tav).
- The average ambient barometric pressure (Pav) during the sampling period.

These values are then applied to the sampler's calibration relationship. The 4" pressure flow recorders often supplied with HV samplers generally are not sufficiently accurate and are *not recommended* for quantitative sampler pressure or flow rate measurements. These flow recorders should be used only for nonquantitative determination that the flow was approximately constant and uninterrupted over the sampling period. The flow recorder may be connected in parallel with the manometer or other pressure measuring device using a tee or "Y" tubing connector.

[Note: Because flow recorders are still widely used for quantitative flow rate measurements, the procedures in this section include specific instructions for the use of a flow recorder. These flow recorder instructions are enclosed in brackets.]

9.4.1.4 The average actual flow rate for VFC samplers is calculated by determining the following:

- The average of the initial and final relative stagnation pressures (Pstg).
- The average ambient temperature (Tav).
- The average barometric pressure (Pav) during the sampling period and then by applying these values to the calibration relationship.

*[Note: Consistency of temperature and barometric pressure units is required. All temperatures should be expressed in kelvin (K = EC + 273). Also, all barometric pressures should be expressed in either mm Hg or kPa (**but don't mix the two units**). Avoid calibrating a PM_{10} sampler using one set of units and then performing sample calculations using another set.]*

9.4.2 Presampling Filter Preparation Procedures.

9.4.2.1 Most high-volume samplers (TSP or PM_{10}) have been designed to accept filter cassettes. Loading these cassettes in the laboratory will minimize damage; however, if extreme care is exercised, they can be loaded at the site when ambient conditions permit. Wear protective gloves when handling filters to avoid contaminating the filters with body oils and moisture. Keep the filters in protective folders or boxes. Never bend or fold unexposed filters. The analytical laboratory (and/or filter manufacturer) will give each filter an ID number. Because it is extremely difficult to see the "up" side of a quartz filter (i.e., the side with the slightly rougher texture), the filters should be consistently labeled on one side. When a filter that has

been labeled on its "down" side is folded for transport to the laboratory, its sample number will be readily accessible for documentation on laboratory log sheets upon arrival at the laboratory.

9.4.2.2 Following the manufacturer's instructions, carefully load the pre-weighted filter in the filter cassette. The filter should be centered on the wire screen so that the gasket will form an airtight seal on the outer edge of the filter when the faceplate is in place. Poorly aligned filters show uneven white borders after exposure. Care should be taken to ensure that the filter cassette is not excessively tightened, as the filer may stick or the gasket may be permanently damaged. Check that the gasket is in good condition and has not deteriorated.

9.4.3 Sampling Procedures--MFC Sampler.

9.4.3.1 Filter Installation Procedure.

9.4.3.1.1 Following the manufacturer's instructions, loosen the nuts that secure the inlet to the base and gently tilt back the inlet to allow access to the filter support screen.

9.4.3.1.2 Examine the filter support screen. If the screen appears dirty, wipe it clean. If the filter cassette is equipped with a protective cover, remove it and place the loaded cassette in position on the sampler support screen. Tighten the thumb nuts to hold the filter cassette securely. Check that the gasket is in good condition and has not deteriorated.

Caution: Tighten the thumb nuts evenly on alternate corners to properly align and seat the gasket. The nuts should be only hand-tightened because too much compression can damage the sealing gasket.

9.4.3.1.3 If an inlet is being used, lower the sample inlet. Inspect the sample inlet to make sure that it is resting on the filter cassette and not on the sampler's frame. Secure the sample inlet to the sampler base.

9.4.3.1.4 Open the front door of the sample and examine the flow recorder. Remove any moisture inside by wiping it with a clean cloth. Record the sampler S/N, filter ID number, site location, and sampling data on the back of a clean chart and install the chart in the flow recorder.

[Note: Charts used for PM_{10} samplers normally have square-root-function scales; however, linear-function scales may be used. If charts with linear-function scales are used, Equations in Section 7.4.3.3 and Section 7.4.3.5 will have to be modified from their current form by replacing I with $(I)^{½}$]

[Note: While installing the chart, do not bend the pen arm beyond its limits of travel. Raise the pen head by pushing on the very top of the pen air (or by using the pen lift). Be sure that the chart tab is centered on the slotted drive to ensure full 360E rotation in 24 h. Make sure that the chart edges are properly located beneath the retainers. Lower the pen arm and tap the recorder face lightly to make certain that the pen is free.]

[Note: During periods of inclement weather, the chart tends to stick to the recorder face. Two charts can be installed simultaneously to enable the sample (top, annotated) chart to rotate freely.]

9.4.3.1.5 Using a coin or slotted screwdriver, advance the chart and check to see that the pen rests on zero--the smallest circle diameter. If necessary, adjust the zero set screw while gently tapping on the side of the flow recorder. If a chart with a linear function scale is used, some positive zero offset may be desirable to allow for normal variation in the zero readings.

9.4.3.1.6 Turn on the sampler and allow it to equilibrate to operating temperature (3-5 min).

9.4.3.1.7 While the sampler is equilibrating, record the following parameters on the MFC Sampler Field Data Sheet (see Figure 14):

- Site Location.
- Sample date.
- Filter ID number.
- Sampler model and S/N.
- Operator's initials.

9.4.3.1.8 Inspect the manometer for crimps or cracks in its connecting tubing. Open the valves and blow gently through the tubing of the manometer while watching for the free flow of the fluid. Adjust the manometer's sliding scale so that its zero line is at the bottom of the meniscuses.

9.4.3.1.9 Measure the initial exit orifice plenum pressure (Pex) using an oil or water manometer, with a 0-200-mm (0-8") range and a minimum scale division of 1 mm (0.1"). Record the initial Pex on the MFC Sampler Field Data Sheet. If Pex is substantially different than for previous samples or otherwise appears abnormal, carry out a Quality Control (QC) flow check as described in Section 13.1.

9.4.3.1.10 Verify that the flow recorder (if used) is operational and that the pen is inking. Note the flow recorder reading. If it is substantially different than for previous samples or otherwise appears abnormal, carry out a QC flow-check as described in Section 13.1.

9.4.3.1.11 Turn the sampler off.

9.4.3.1.12 Check the time indicated by the time-set pointer on the flow recorder. If it is in error, rotate the chart clockwise by inserting a screwdriver or coin in the slotted drive in the center of the chart face until the correct time is indicated.

9.4.3.1.13 Reset the elapsed time meter to 0000 min and the sampler timer for the next run day. Close the sampler door, taking care not to crimp the vacuum tubing or any power cords. The sampler is now ready to sample ambient air.

9.4.3.2 Filter Recovery Procedure. As soon as possible after sampling, the operator should return to the monitoring site to retrieve the exposed filter. Particle loss or filter damage will result if the filter is left in the sampler for extended periods.

9.4.3.2.1 Turn on the sampler and allow it to equilibrate to operating temperature (3-5 min).

9.4.3.2.2 Measure the final Pex and record it on the MFC Sampler Field Data Sheet.

9.4.3.2.3 Turn off the sampler.

9.4.3.2.4 Open the door of the sampler, remove the flow recorder chart, and examine the recorder trace. If the trace indicates extensive flow fluctuations, investigate and correct before the next sampling day.

9.4.3.2.5 Record the following parameters on the MFC Sampler Field Data Sheet:

- Elapsed time of the sampling period, min.
- Average recorder response, arbitrary units.
- Average ambient temperature for the run day (Tav), K (K = EC + 273).
- Average ambient barometric pressure for the run day (Pav), mm Hg or kPa.

[Note: Tav and Pav readings may be recorded or estimated on site or may be obtained from a nearby U.S. National Weather Service Forecast Office or airport weather station. Barometric pressure readings obtained from remote sources must be at station pressure (not corrected to sea level), and they may have to be corrected for differences between the evaluation are not available, seasonal average temperature (Ts) and barometric pressure (Ps) may be substituted for Tav and Pav, respectively. Care must be taken, however, that the actual conditions at the site can be reasonably represented by such averages. Therefore, seasonal values may represent actual values within 20EC and 40 mm Hg.]

The calculations presented in this section assume that the sampler has been calibrated in terms of actual temperature and barometric pressure and that the substitution of seasonal values is used only to determine the sampler's operational flow rate during a sample period. Although additional calculations to convert the sampler's calibration curve to seasonal can be made, the error represented by this method is negligible.

9.4.3.2.6 Calculate and record the average actual flow rate (as determined by the sampler's calibration relationship) on the MFC Sampler Field Data Sheet and on the back of the chart. Attach the chart to the data sheet.

$$Qa = \{[\ ) \ \overline{\overline{Pex}}(Tav + 30)/Pa]^{1/2} - b\} \{l/m\}$$

or for the flow recorder,

$$\overline{\overline{Qa}} = \{[\overline{I}(Tav + 30)/Pa]^{1/2} - b\} \{1/m\}$$

where:

$\overline{\overline{Qa}}$ = average sampler flow rate, actual m^3/min.
$\overline{\overline{Pex}}$ = average exit orifice plenum pressure, mm Hg.
I = average flow recorder response, arbitrary units.
Tav = average ambient temperature for the run day, K.
Pav = average ambient pressure for the run day, mm Hg.
b = intercept of the MFC sampler calibration relationship.
m = slope of the MFC sampler calibration relationship.

[Note: If charts with linear-function scales are used, substitute $(I)^{½}$ for I.]

9.4.3.2.7 Observe conditions around the monitoring site; note any activities that may affect filter particle loading (e.g., paving, mowing, fire) and record this information on the MFC Sampler Field Data Sheet.

9.4.3.2.8 Raise the sampler inlet and remove the filter cassette. Replace the cassette protective cover (if so equipped). To avoid particle loss, be careful to keep the cassette as level as possible.

9.4.3.2.9 The sampler may now be readied for the next run day.

9.4.3.2.10 Keeping the filter cassette level, carefully transport it, the data sheet, and the flow recorder chart to the laboratory sample custodian.

9.4.4 Sampling Procedures--VFC Sampler.

9.4.4.1 Filter Installation Procedure.

9.4.4.1.1 Following the manufacturer's instructions, loosen the nuts that secure the inlet to the base and gently tilt back the inlet to allow access to the filter support screen.

9.4.4.1.2 Examine the filter support screen. If the screen appears dirty, wipe it clean. If the filter cassette is equipped with a protective cover, remove it and place the loaded cassette in position on the sampler support screen. Tighten the thumb nuts sufficiently to hold the filter cassette securely. Check that the gasket is in good condition and has not deteriorated.

Caution: Tighten the thumb nuts evenly on alternate corners to properly align and seat the gasket. The nuts should be only hand-tightened because too much compression can damage the sealing gasket.

9.4.4.1.3 If an inlet is used, lower the sample inlet and secure it to the sampler base. For impaction inlets, inspect the sample inlet to make sure that it is resting on the filter cassette and not on the sampler's frame. Secure the sampler inlet to the sampler base.

9.4.4.1.4 Record the following parameters on the VFC Sampler Field Data Sheet (see Figure 15):
- Site location.
- Sample date.
- Filter ID number.
- Sampler model and S/N.
- Operator's initials.

9.4.4.1.5 Turn on the sampler and allow it to reach a stable operating temperature (3-5 min).

9.4.4.1.6 Bring an oil or water manometer to the side of the sampler. This manometer should have a range of 0-400 mm (0-16") and a minimum scale division of 1 mm (0.1").

[Note: Be sure to convert the manometer reading to mm Hg using the following equation before recording the reading on the VFC Sampler Field Data Sheet.]

$$\text{mm Hg} = (25.4)\ (\text{in. } H_2O/13.6)$$

Inspect the manometer for crimps or cracks in its connecting tubing. Open the valves and blow gently through the tubing of the manometer, while watching for the free flow of the fluid.
Adjust the manometer's sliding scale so that its zero line is at the bottom of the meniscuses.

9.4.4.1.7 Remove the vacuum cap from the stagnation pressure port located on the side of the sampler base. Using the connecting tubing, attach one side of the manometer to the port. Leave the other side of the manometer open to atmospheric pressure. Make sure the tubing snugly fits the port and the manometer.

9.4.4.1.8 Measure the initial relative stagnation pressure ( ) Pstg) and record this reading on the VFC Sampler Field Data Sheet.

9.4.4.1.9 Turn off the sampler, disconnect the manometer, and replace the vacuum cap on the stagnation pressure port.

9.4.4.1.10 Reset the elapsed-time meter to 0000 min and the sampler timer for the next run day. The sampler is now ready to sample ambient air.

9.4.4.2 Filter Recovery Procedure. As soon as possible after sampling, the operator should return to the monitoring site to retrieve the exposed filter. Particle loss or filter damage will result if the filter is left in the sampler for extended periods.

9.4.4.2.1 Turn on the sampler and allow it to warm up to operating temperature (3-5 min).

9.4.4.2.2 While the sampler is equilibrating, record the following parameters on the VFC Sampler Field Data Sheet:
- Elapsed time of the sampling period, min.
- Average ambient temperature for the run day (Tav), EC and K.
- Average ambient barometric pressure for the run day (Pav), mm Hg.

[Note: Tav and Pav readings may be recorded or estimated on site or may be obtained from a nearby U.S. National Weather Service Forecast Office, National Weather Service (NWS) station, or an airport weather station. Barometric pressure readings obtained from remote sources must be at station pressure (not corrected to sea level), and they may have to be corrected for differences between the elevation of the monitoring site and that of the airport. If Tav and Pav readings are not available, seasonal average temperature (Ts) and barometric pressure (Ps) can be substituted. Care must be taken, however, that the actual conditions at the site can be reasonably represented by such averages. Therefore, seasonal values may represent actual values within 20EC and 40 mm Hg.]

9.4.4.2.3 Inspect the manometer for crimps or cracks in its connecting tubing. Open the valves and blow gently through the tubing of the manometer, while watching for the free flow of the fluid. Adjust the manometer sliding scale so that its zero line is at the bottom of the meniscuses.

9.4.4.2.4 Remove the vacuum cap from the stagnation pressure port located on the side of the sampler base. Using the connecting tubing, attached one side of the manometer to the port. Make sure that the tubing snugly fits the port and the manometer. Leave the other side open to atmospheric pressure.

9.4.4.2.5 Record the final Pstg on the VFC Sampler Field Data Sheet. Turn off the sampler and replace the vacuum cap.

[Note: Be sure to convert the manometer reading to mm Hg using the following equation before recording the reading on the Sampler Field Data Sheet.]

$$\text{mm Hg} = 25.4 \text{ (in. } H_2O/13.6)$$

9.4.4.2.6 Calculate the average relative stagnation pressure ($\overline{)\text{Pstg}}$) and record it on the data sheet.

9.4.4.2.7 Calculate the average absolute stagnation pressure ($\overline{\text{P1}}$) for the sample run day and record it on the data sheet.

$$\overline{\text{P1}} = \text{Pav} - \overline{)\text{Pstg}}$$

where:

$\overline{\text{P1}}$ = average absolute stagnation pressure, mm Hg.
Pav = average ambient barometric pressure for the run day (not the retrieval day), mm Hg.
$\overline{)\text{Pstg}}$ = average stagnation pressure drop, mm Hg.

9.4.4.2.8 Calculate and record the average stagnation pressure ratio:

$$\text{Average stagnation pressure ratio} = \text{P1/Pav}$$

where:

Pl = average absolute stagnation pressure, mm Hg.
Pav = average ambient barometric pressure on the sample run day, mm Hg.

9.4.4.2.9 Using the manufacturer's lookup table (or an alternate calibration relationship as described in Section 7.5.4), locate the column and row corresponding to $\overline{\text{P1}}$/Pav and the Tav value for the sample run day. Read and record the indicated $\overline{\text{Qa}}$ value.

9.4.4.2.10 Observe conditions around the monitoring site; note any activities that may affect filter particle loading (paving, mowing, fire) and record this information on the VFC Sampler Field Data Sheet.

9.4.4.2.11 Raise the sampler inlet and remove the filter cassette. Replace the cassette protective cover (if so equipped). To avoid particle loss, be careful to keep the cassette as level as possible.

9.4.4.2.12 The sampler may now be readied for the next sampling period.

9.4.4.2.13 Keeping the filter cassette level, carefully transport it and the Sampler Field Data Sheet to the laboratory sample custodian.

9.4.5 Post-Sampling Filter Handling Procedures. If a sample will not be analyzed immediately, the sample custodian should store the filter within a protective covering. Because filter cassettes often prove too expensive and unwieldy for storage purposes, the use of a manila folder and a protective envelope of comparable size to that of the filter is recommended. Laboratory personnel should adhere to the following procedure:

9.4.5.1 Following the manufacturer's instructions, remove the top frame of the filter cassette.

9.4.5.2 Conduct a secondary check of a sample's validity as presented in "Laboratory Validation Criteria" (see Section 9.5).

9.4.5.3 Carefully slip a manila folder underneath the edge of the exposed filter. The filter may stick in the cassette because of overcompression of the filter cassette gasket. Be extremely careful to avoid damage to the brittle quartz filter.

9.4.5.4 Center the filter on the folder. If the filter must be touched, do not touch or jar the deposit. Fold the manila folder lengthwise at the middle with the exposed side of the filter in. If the collected sample is not centered on the filter (i.e., the unexposed border is not uniform around the filter), fold it so that only deposit touches deposit. **Do not crease the folder**--the sample filter may tear. If the filter shears or breaks, ensure that all pieces of the filter are included within the folder.

9.4.5.5 Insert the folder into the protective envelope.

9.4.5.6 Deliver the filter in its protective folder and envelope, accompanied by the completed data sheet, to the analytical laboratory.

9.5 Sample Validation and Documentation

9.5.1 Field Validation Criteria. After each sampling period, calculate the percentage difference between Qa and the design flow rate (1.13 m^3/min) using the following formula:

$$\% \text{ Difference } = 100 \frac{\overline{Qa} - 1.13}{1.13}$$

Record this value on a control chart for the field validation of the sampler's actual volumetric flow rate as is shown in Figure 16.

- Decreases in flow rate during sampling (due to mechanical problems) of more than 10% from the initial set point result in sample invalidation. Recalibrate the sampler. A sample flow rate may also fluctuate due to heavy filter loading. If a high concentration is suspected, the operator should indicate this on the field data sheet. The laboratory supervisor will make the final decision regarding the sample's validity.
- Changes in flow-rate calibration of more than 10%, as determined by a field QC flow-rate check (see Section 13), will invalidate all samples collected back to the last calibration or valid flow check. Recalibrate the sample.

9.5.2 Laboratory Validation Criteria.

9.5.2.1 Upon receiving the filter from the field, check the filter for signs of air leakage by observing the border around the filter. If the border is clear, then the gasket on the sampler is still usuable. However, if particulate matter is on the border, then air leakage has occurred and the gasket on the sampler should be changed. Leakage may result from a worn or improperly installed faceplate gasket. A gasket generally deteriorates slowly. The sample custodian should be able to decide well in advance (by the increased fuzziness of the sample outline) when to change the gasket before total gasket failure results. If signs of leakage are observed, void the sample, determine the cause, and instruct the operator to take corrective actions before starting another sampling period.

9.5.2.2 Check the exposed filter for physical damage that may have occurred during or after sampling. Physical damage after sampling would not invalidate the sample if all pieces of the filter were put in the

folder; however, complete losses of loose particulate after sampling (e.g., loss when folding the filter) would void the sample. Mark such samples as "void" on the HV data sheet.

9.5.2.3 Check the appearance of the particles. Any changes from normal color may indicate new emission sources or construction activity in the area. Note any change on the data sheet.

9.5.2.4 The filters should be weighed according to the procedures described in Inorganic Compendium Method IO-3.1, Section 5, *Gravimetric Analysis*.

9.5.3 Data Documentation. Recordkeeping is a critical part of the QA program. Careful documentation of sampling data will salvage samples that may otherwise be lost. The sheer repetition of recording data may result in errors; however, this cross-referencing between data sheets, log books, and (for those samplers so equipped) the continuous-flowrecorder charts will allow the operator to pinpoint discrepancies that may result in a sample's invalidation.

[Note: The use of log books at monitoring sites is highly encouraged.]

9.5.3.1 Presampling Documentation and Inspection. The following information should be recorded on the Sampler Field Data Sheet (SFDS), sampler recorder chart (RC), flow-rate control chart (CC), and in the site log book (LB):

- Site Location.
- Sample Date.
- Filter ID number.
- Sample model and S/N.
- Operator's initials.

9.5.3.2 Post-Sampling Documentation and Inspection. Upon receipt of exposed filters from the field, the sample custodian should adhere to the following procedures.

9.5.3.2.1 Examine the field data sheet. Determine whether all data needed to verify sample validity and to calculate mass concentration are provided (e.g., average flow rate, ambient temperature, barometric pressure, and elapsed time). Void the sample if data are missing or unobtainable from a field operator or if a sampler malfunction is evident.

9.5.3.2.2 If the exposed filter was packaged for shipment, remove the filter from its protective envelope and examine the shipping envelope. If sample material has been dislodged from a filter, recover as much as possible by brushing it from the envelope onto the deposit on the filter with a soft camel's-hair brush.

9.5.3.2.3 Match the filter ID number with the correct laboratory data/coding form on which the original balance ID number, filter ID number, filter tare weight, and other information are inscribed. The sample custodian should group filters according to their recorded balance ID numbers. Initial separation of filters by balance ID number will decrease the probability of a balance error that could result from the use of different balances for tare and gross weights.

9.5.3.2.4 Remove the filter from the protective manila folder. Should the filter be retained in its filter cassette, loosen the nuts on the top and remove the filter. Overtightening the nuts may cause the filter to adhere to the cassette gasket. Gently remove it by the extreme corners to avoid damage. Inspect the filters for any damage that may have occurred during sampling. Conduct a secondary check of a sample's validity (as presented in Section 9.4). If insects are embedded in the sample deposit, remove them with Teflon®-tipped tweezers and disturb as little of the sample deposit as possible. If more than 10 insects are observed, refer the sample to the supervisor for a decision on acceptance or rejection of the filter for analysis.

9.5.3.2.5 Place defect-free filters in protective envelopes and forward them to the laboratory for weighing and analysis. File the data sheets for subsequent mass concentration calculations.

9.5.3.2.6 Place defective filters, with the type of defect(s) listed, in separate clean envelopes. Label the envelopes and submit them to the laboratory supervisor for final approval of filter validity.

10. Interferences

10.1 Large extraneous objects, such as insects, may be swept into the filter.

10.2 Liquid aerosols, such as oil mists and fog droplets, are retained by the filter. If the amount of liquid so collected is sizeable, the filter can become wet and its function may be impaired.

10.3 Any gaseous or vaporous constituent of the atmosphere under test that is reactive with or absorbed on the filter will be retained.

10.4 As the filter becomes loaded with collected matter, the sampling rate is reduced. If a significant drop in flow rate occurs, the average of the initial and final flow rate will not give an accurate estimate of total flow during the sampling period. The magnitude of such errors will depend on the amount of reduction of airflow rate and on the variation of the mass concentration of dust with time during the 24-h sampling period. As an approximate guideline, any sample should be suspect if the final flow rate is less than one-half the initial rate.

10.5 Power failure or voltage change during the test period will lead to an error, depending on the extent and time duration of such failure.

10.6 The passive loading of the filter left in place for any time prior to or following a sampling period can introduce an error. The timely installation and removal of the filter is advisable, or a sampler with shutters may be used.

10.7 If two or more samplers are used at a given location, they should be placed at least 2 meters apart so that one sampler will not affect the results of an adjacent sampler.

10.8 Recent wind tunnel studies have shown significant possible sampling errors as a function of sampler orientation in atmospheres containing high relative concentrations of large particles.

10.9 Metal dusts from motors, especially copper, may significantly contaminant samples under some conditions.

10.10 Under some conditions, atmospheric SO_2 and NO_x may interfere. Artifact formation errors are caused by the retention of sulfur dioxide in the form of sulfate particulate on alkaline filters. Experiments involving a variety of filters indicate that sulfate loading errors of 0.3-3.0 $\mu g/m^3$ can be expected with the use of common glass fiber filters under normal sampling conditions and that larger sulfate errors are possible under extreme sampling conditions. A neutral or low-alkalinity filter medium will eliminate excessive artifact formation.

10.11 Guidelines to help prevent post-sampling particle loss are presented in Section 8.

11. Calculations, Validations, and Reporting of TSP and PM_{10} Data

11.1 Basic Information Used for Calculations

11.1.1 The design flow rate is specified as an actual volumetric flow rate (Qa), measured at existing conditions of temperature (Ta) and pressure (Pa). The sampler's operational flow rate should be very close to the design flow rate. All samplers have some means for measuring the operational flow rate, and that flow rate measurement system must be calibrated periodically with a certified flow rate transfer standard. Usually, measurements (or estimates) of ambient temperature and barometric pressure are required to get an accurate indication of the operational flow rate. To determine the average sampler flow rate over a sample period, use the average temperature (Tav) and average barometric pressure (Pav) over the sample period. However, if average temperature and pressure values (or reasonable estimates) cannot be obtained for each sample period, seasonal average temperature (Ts) and barometric pressure (Ps) for the site may be substituted.

[Note: Tav and Pav readings may be recorded on site or estimated from data obtained from a nearby U.S. National Weather Service Forecast Office, NWS station, or local airport weather station. Barometric pressure readings obtained from airports or other sources must be at station pressure (i.e., not corrected to sea level), and they may have to be corrected for differences between the elevation of the monitoring site and that of the airport. If individual Tav and Pav readings cannot be obtained for each sample period and seasonal averages for the site are routinely substituted, care must be taken to ensure that the actual temperature and barometric pressure at the site are reasonably represented by such averages. Therefore, seasonal average temperature and pressure values (Ts and Ps) for the site by should be used only when these values are within 20 K and 40 mm Hg (5 kPa) of the actual average temperature and barometric pressure (Tav and Pav) for the sample period.]

11.1.2 The calculations presented in this section assume that the sampler has been calibrated in actual volumetric flow rate units (Qa) and that individual average temperature and barometric pressure values are used for each sample period. If seasonal average temperature and pressure values for the site are to be used, Ts may be substituted for Tav, and Ps may be substituted for.

11.1.3 The true or actual flow rate through the sampler inlet must be known and controlled. A common source or error in a monitoring program is confusion of various air volume flow-rate measurement units. Although the sampler's operational flow rate must be monitored in terms of actual volume flow rate units (Qa), sampler flow rates can be corrected to standard volume flow rate units (Qstd) at EPA standard conditions of temperature (25EC) and pressure (760 mmHg).

- $\overline{Qa}$: Actual volumetric air flow rates, measured and expressed at existing conditions of temperature and pressure and denoted by Qa (Qactual). Typical units are L/min and m^3/min. Inlet design flow rates for PM_{10} samplers are always given in actual volumetric flow rate units.
- Qstd: Airflow rates that have been corrected to equivalent standard volume flow rates at EPA standard conditions of temperature and pressure (25EC or 298 K and 760 mm Hg or 101 kPa) and denoted by Qstd (Qstandard). Typical units are std. L/min, and std. m^3/min. Standard volume flow-rate units are often used by engineers and scientists because they are equivalent to mass flow units.

11.1.4 The Qa and Qstd measurement units must not be confused or interchanged. The flow-rate units can be converted as follows, provided the existing temperature and pressure (or in some cases the average temperature and pressure over a sampling period) are known:

$$\overline{Qstd} = \overline{Qa}(Pa/Pstd)(Tstd/Ta)$$
$$Qstd = (Pav/Pstd)(Tstd/Tav)$$
$$Qa = Qstd(Pstd/Pa)(Ta/Tstd)$$

where:

Qstd = standard volume flow rate, std m^3/min.
Qa = actual volume flow rate, actual m^3/min.
Pa = ambient barometric pressure, mm Hg.
Pstd = EPA standard barometric pressure, 760 mm Hg.
Tstd = EPA standard temperature, 298 K.
Ta = standard temperature, K (K = EC + 273).
Qstd = average standard volume flow rate for the sample period, std. m^3/min.
$\overline{Qa}$ = average actual volume flow rate for the sample period, m^3/min.
Pav = average ambient barometric pressure during the sample period, mm Hg.
Tav = average ambient temperature during the sample period, K.

Inorganic Compendium Method IO-2.4 provides guidance on calculating sample volume corrected to EPA standard temperature and pressure.

11.2 Flow-Rate Calculations. Because flow control methods (and hence, calibration procedures) vary among different sampler models, the calculations necessary to determine the average actual flow rate during a sample run will also differ. The following general procedures are recommended for calculating the average ambient flow rate of the sampler. In this section, it is assumed that the samplers have been calibrated according to procedures outlined in Section 7.

[Note: Consistency in units is required. Adoption of uniform designations of K for temperature and mm Hg (or kPa) for pressure is recommended in all calculations.]

11.2.1 MFC Sampler.

11.2.1.1 The average actual flow rate for sample period is calculated by determining:

- The average of the initial and final manometer readings ($\overline{)Pex}$) [or the average flow recorder trace];
- The average ambient temperature (Tav); and
- The average ambient barometric pressure (Pav) during the sampling period and applying these values to the calibration relationship.

11.2.1.2 Each sampler's flow measurement system should be calibrated periodically, and the calibration should be described by a mathematical expression (e.g., a least-squares linear regression equation) that indicates the slope and intercept of the calibration relationship. Following the procedure in Section 7, this expression is in the form of:

$$\overline{Qa} = \{[\overline{Pex}(Tav + 30)/Pav)]^{½} - b\} \{l/m\}$$

where:

$\overline{Qa}$ = the sampler's average actual flow rate for the sample period, m^3/min.
$\overline{Pex}$ = average of initial and final sampler manometer readings, ( ) Pex_i +) Pex_f)/2, in. H_2O.
Tav = average barometric pressure for the sample period, K (K = EC + 273).
Pav = average barometric pressure for the sample period, mm Hg.
b = intercept of the sampler calibration relationship.
m = slope of the sampler calibration relationship.

For the flow recorder,

$$\overline{Qa} = \{[\bar{I}(Tav + 30)/Pav]^{1/2} - b\} \{l/m\}$$

where:

$\bar{I}$ = average flow recorder reading for the sample period.

11.2.1.3 The average actual flow rate is then corrected to EPA-standard conditions, calculated as:

$$\overline{Qstd} = \overline{Qa}(Pav/Pstd)(Tstd/Tav)$$

where:

$\overline{Qstd}$ = average sampler flow rate corrected to EPA-standard volume flow rate units, std. m^3/min.
$\overline{Qa}$ = average actual sampler flow rate for the sample period, m^3/min.
Pstd = standard barometric pressure, 760 mm Hg.
Tstd = standard temperature, 288 K.

11.2.2 VFC Sampler.

11.2.2.1 The average actual flow rate for the sample period is calculated by determining the ratio of the average absolute stagnation pressure of the average ambient barometric pressure ($\overline{P1}$/Pav) and the ambient average temperature (Tav) for the sampler period.

11.2.2.2 Calculate the value of Pl in mm Hg:

$$\overline{P1} = Pav - \overline{)Pstg}$$

where:

Pl = average absolute stagnation pressure for the sample period, mm Hg .
Pav = average barometric pressure for the sample period, mm Hg.
$\overline{)Pstg}$ = average of initial and final relative stagnation pressure readings, mm Hg.

[Note: Be sure to convert a water manometer reading to mm Hg using the following equation before recording the reading on the data sheet:]

$$mmHg = 25.4 ( ) H_2O/13.6)$$

11.2.2.3 Calculate and record the value of the average stagnation pressure ratio.

$$\text{Average stagnation pressure ratio} = (\overline{P1}/Pav)$$

11.2.2.4 Use the manufacturer's lookup table (or alternate calibration relationship; see Section 7) to determine Qa from the average stagnation pressure ratio ($\overline{P1}/Pav$) and Tav for the sample period. The value of $\overline{Qa}$ is the average volumetric flow rate for the sampler period.

11.2.2.5 The average actual flow rate is then corrected to EPA-standard conditions using the following equation:

$$\overline{Qstd} = \overline{Qa}(Pav/Pstd)(Tstd/Tav)$$

where:

$\overline{Qstd}$ = average sampler flow rate corrected to EPA-standard volume flow rate units, std. m^3/min.
$\overline{Qa}$ = average actual sampler flow rate for the sample period, m^3/min.
Pstd = standard barometric pressure, 760 mm Hg.
Tstd = standard temperature, 298 K.

11.3 The total standard volume of air sampled is calculated by the following equation:

$$Vstd = (\overline{Qstd})(t)$$

where:

Vstd = total volume of air sampled in standard volume units, std m^3.
$\overline{Qstd}$ = average sampler flow rate corrected to EPA-standard conditions, std m^3/min.
t = total elapsed sampling time, min.

11.4 Percent Difference

11.4.1 After each sampling period, calculate the percentage difference between Qa and the design flow rate (1.13 m^3/min) using the following formula:

$$\% \text{ Difference } = 100 \frac{Qa - 1.13}{1.13}$$

Record this value on a control chart for the field validation of the sampler's actual volumetric flow rate as is shown in Figure 14.

11.4.2 The following criteria should be used as the basis for determining a sample's validity:

- Decreases in flow rate during sampling (due to mechanical problems) of more than 10% from the initial set point cause sample invalidation. A sample flow rate may also fluctuate due to heavy filter loading. If a high concentration is suspected, the operator should indicate it on the field data sheet. The laboratory supervisor will make the final decision regarding the sample's validity.
- Changes in flow-rate calibration of more than 10%, as determined by a field QC flow-rate check, will invalidate all samples collected back to the last calibration or valid flow check.

12. Records

12.1 MFC Sampler

Record the following parameters on the MFC Sampler Field Data Sheet (see Figure 14):

- Final Pex.
- Elapsed time of the sampling period, min.
- Average record response, arbitrary units.
- Tav for the run day K (K = EC + 273).
- Pav for the run day, mm Hg.

12.2 VFC Sampler

Record the following parameters on the VFC Sampler Field Data Sheet (see Figure 15):

- Site location.
- Sample date.
- Filter ID number.
- Sampler model and S/N
- Operator's initials.
- Initial Relative Stagnation Pressure (Pstg).
- Elapsed time of the sampling period, min.
- Tav for the run day Tav, EC and K.
- Pav for the run day Pav, mm Hg.
- Pstg, mm Hg.
- Relative Stagnation Pressure.
- Absolute Stagnation Pressure.
- Qa value (from chart generated in Section 7.5.4.).

12.3 Tav and Pav readings may be recorded or estimated on site or may be obtained from a nearby U.S. National Weather Service Forecast Office or airport weather station. Barometric pressure readings obtained from remote sources must be at station pressure (not corrected to sea level); they may have to be corrected for differences between elevation of the monitoring site and that of the airport. If Tav and Pav readings are not available, seasonal average temperature (Ts) and barometric pressure (Ps) may be substituted for Tav and Pav, respectively. Care must be taken, however, that the actual conditions at the site can be reasonably represented by such averages. Therefore, seasonal values should represent actual values within 20EC and 40 mm Hg.

12.4 Observe conditions around the monitoring site; note any activities that may affect filter particle loading (paving, mowing, fire) and record this information on the VFC Sampler Field Data Sheet.
Document any factors that may cause a sample's invalidation on the sample data sheet. Forward the data sheet and the filter to the laboratory supervisor, who will make the final decision regarding the sample's validity.

12.5 Record the percentage difference between Qa and the design flow rate on Figure 16.
12.6 Recordkeeping is a critical part of the QA program. Careful documentation of sampling data will salvage samples that may otherwise be lost. The sheer repetition of recording data may result in errors;

however, this cross-referencing between data sheets, log books, and (for those samplers so equipped) the continuous-flow-recorder charts will allow the operator to pinpoint discrepancies that may result in a sample's invalidation.

[Note: The use of log books at monitoring sites is highly encouraged. The following information should be recorded on the Sampler Field Data Sheet (SFDS), sampler recorder chart (RC), in the site log book (LB), and on the flow-rate control chart (CC).]

12.6.1 The following information should be recorded by the operator who starts the sample. (The designation in parentheses indicates where the data must be inscribed):

- Site designation and locations (SFDS)(RC)(LB). This information should be recorded in the log book only once, at the initiation of a monitoring program.
- Sampler model and S/N (SFDS)(RC)(LB). This information needs to be recorded in the log book only at the commencement of monitoring, unless there is more than one sampler or a new sampler has been deployed.
- Filter ID number (SFDS)(RC)(LB).
- Sample date (SFDS)(RC)(LB).
- Initial Pex for MFC or initial) Pstg for VFC (SFDS)(LB).
- Unusual conditions that may affect the results (e.g., subjective evaluation of pollution that day, construction activity, weather conditions) (SFDS)(LB).
- Operator's initials (SFDS).
- Signature (LB).

12.6.2 The following information should be recorded by the operator who removes the samples.

- Elapsed time of the sample run (SFDS)(RC)(LB).
- Final) Pex [or mean I] for MFC or final) Pstg, $\overline{P1}$, and $\overline{P1}$/Pav for VFC (DS)(LB)[RC].
- The calculated standard average flow rate (Qstd) in std m^3/min (SFDS)(LB).
- The percentage difference between the actual and design flow rates (CC).
- Average ambient temperature and barometric pressure on the sample run day (SFDS)(LB).
- Seasonal average temperature and pressure, if needed (SFDS/LB). This information needs to be recorded in the logbook once, at the change of each season.
- Existing conditions that may affect the results (SFDS)(LB).
- Explanations for voided or questionable samples (SFDS)(LB).
- Operator's initials (SFDS).
- Signature (LB).

13. Field QC Procedure

For HV samplers, a field-calibration check of the operational flow rate is recommended at least once per month. The purpose of this check is to track the sampler's calibration stability. A control chart (e.g., Figure 14) that contains the percentage difference between a sampler's indicated and measured flow rates should be maintained. This chart is a quick reference of instrument flow-rate drift problems and is useful for tracking the performance of the sampler. Either the sampler log book or a data sheet must be used to document flow-check information. This information includes, but is not limited to, instrument and transfer standard model and serial numbers, ambient temperature and pressure conditions, and collected flow-check data.

In this section, the following is assumed:

- The flow rate through sampler that is equipped with a mass-flow controller is indicated by the exit orifice plenum pressure. This pressure is measured with a manometer [or a flow recorder].
- The flow rate through a sampler that is equipped with a volumetric flow controller is indicated by the stagnation pressure. This pressure is measured with a manometer.
- The acceptable flow-rate fluctuation range is 10% of the design flow rate.
- The transfer standard will be an orifice device equipped with a water or oil manometer.
- The orifice transfer standard's calibration relationship is in terms of the actual volumetric flow rate (Qa).

13.1 QC Flow-Check Procedure--MFC Sampler. The indicated flow rate [Qa (sampler)] for MFC samplers is calculated by determining:

- The manometer reading of the exit orifice plenum pressure [or the flow recorder reading],
- The ambient temperature (Ta), and
- The barometric pressure (Pa) during the flow check.

These values are then applied to the sampler's calibration relationship. The 4" pressure (flow) recorders of the type often supplied with high-volume PM_{10} samplers are generally not sufficiently accurate and are not recommended for quantitative sampler pressure or flow measurements. The flow recorder may be connected in parallel with the manometer or other pressure measuring device, using a tee or "Y" tubing connector. An alternate QC flow-check procedure may be presented in the manufacturer's instruction manual. The manual should be reviewed and the various methods evaluated. Inhouse equipment and procedural simplicity should be considered in determining which method to use.

[Note: Do not attempt to conduct a flow check of samplers under windy conditions. Short-term wind velocity fluctuations will produce variable pressure readings by the orifice transfer standard's manometer. The flow check will be less precise because of the pressure variations.]

13.1.1 Collect the following equipment and transport it to the monitoring station:

[Note: An independent person should perform the QC flow check, with an outside observer present.]

- A water, oil, or digital manometer with a 0-200 mm (0-8") range and a minimum scale division of 1 mm (0.1") for measuring the sampler's exit orifice plenum pressure. This manometer should be the same as is used routinely for sampler flow rate measurements.
- An orifice transfer standard and its calibration relationship (different from initial orifice standard).
- An associated water or oil manometer with a 0- to 400-mm (0- to 16") range and a minimum scale division of 1 mm (0.1") for measuring the orifice transfer standard.
- A thermometer capable of accurately measuring temperature 0-50EC (273-323 K) to the nearest ± 1EC and referenced to an NIST or ASTM thermometer within ± 2EC at least annually.
- A portable aneroid barometer (e.g., a climber's or engineer's altimeter) capable of accurately measuring ambient pressure 500-800 mm Hg (66-106 kPa) to the nearest millimeter Hg and referenced within ± 5 mm Hg of a barometer of known accuracy at least annually.
- The sampler's calibration information.
- Spare recorder charts and a clean flow-check filter.
- MFC Sampler Flow-Check Data Sheet or site log book.

13.1.2 Record the site location, sampler S/N, and date on the back of a clean chart and install it in the flow recorder. While installing the chart, do not bend the pen arm beyond its limits of travel. Raise the pen head by pushing on the very top of the pen arm (or by using the pen lift) and simultaneously insert the chart.

13.1.3 Lower the pen arm and tap the recorder face lightly to make certain that the pen can move freely.

13.1.4 Using a coin or slotted screwdriver, advance the chart and check to see that the pen head rests on zero (i.e., that smallest diameter circle). If necessary, adjust the zeroset screw while gently tapping on the side of the recorder. A quarter turn of the set screw usually results in large offsets; adjust the set screw carefully.

13.1.5 Set up the flow-check system as previously illustrated in Figure 10. MFC samplers are normally flow-checked with a filter in line (i.e., between the orifice transfer standard and the motor). Install a clean filter in the sampler. Place the filter directly upon the sampler's filter screen. Do not use a filter cassette. A flow-check filter should never be used for subsequent sampling because particles larger than 10 Fm can be collected on the filter while the inlet is raised. The sample mass will be biased as a result of using a filter for both a flow check and subsequent sampling.

13.1.6 Install the orifice transfer standard and its faceplate on the sampler. Do not restrict the flow rate through the orifice (i.e., by using fixed resistance plates or closing the variable-resistance valve).
Caution: Tighten the faceplate nuts on alternate corners first to eliminate leaks and to ensure even tightening. The nuts should be hand-tightened; too much compression can damage the sealing gasket. Make sure the orifice transfer standard gasket is in place and the orifice transfer standard is not cross-threaded on the faceplate.

13.1.7 Connect the orifice manometer to the pressure port of the orifice transfer standard and the sampler manometer to the sampler's exit orifice plenum. Inspect the manometers' connecting tubings for crimps and cracks. Open the manometer valves and blow gently through the tubings. Watch for the free flow of fluid. Adjust the manometers' scales so that their zero lines are at the bottom of the meniscuses. Make sure that the connecting tubing snugly fits the manometer and the pressure port.

13.1.8 Turn on the sampler and allow it to warm up to operating temperature (3-5 min).

[Note: The sampler inlet may be partially lowered over the orifice transfer standard to act as a draft shield (if a shield is not otherwise provided). Use a block to provide at least 2" of clearance at the bottom for air flow and for the manometer tubing.]

13.1.9 Read and record the following parameters on the MFC Sampler Flow-Check Data Sheet:
- Sampler location and date.
- Sampler model and S/N.
- Ambient temperature (Ta), EC and K.
- Ambient barometric pressure (Pa), mm Hg.
- Unusual weather conditions.
- Orifice transfer standard S/N and calibration relationship.
- Operator's signature.

13.1.10 Observe the) H_2O across the orifice by reading the manometer deflection. Record the manometer deflection on the MFC Sampler Flow-Check Data Sheet (see Figure 11).

13.1.11 Measure the exit orifice plenum pressure ( ) Pex) by reading the manometer deflection. Record the manometer deflection on the MFC Sampler Flow-Check Data Sheet.

13.1.12 Using a coin or small screwdriver, advance the recorder chart to read the sampler's corresponding response (I) and record on the data sheet. A gentle tap on the recorder face is often necessary to ensure that the pen is not sticking to the chart.

13.1.13 Turn off the sampler and remove the orifice transfer standard, but not the filter. Turn on the sampler and repeat Section 13.1.11 [or Section 13.1.12] to check the flow rate under normal operating conditions. Turn off the sampler and remove the filter.

13.1.14 Calculate and record Qa(orifice) at actual conditions using the following equation:

$$Qa(orifice) = \{[(\Delta H_2O)(Ta/Pa)]^{½} - b\} \{l/m\}$$

where:

Qa(orifice) = actual volumetric flow rate as indicated by the orifice transfer standard, m^3/min
ΔH_2O = pressure drop across the orifice, in. H_2O.
Ta = ambient temperature, K.
Pa = ambient barometric pressure, mm Hg.
b = intercept of the orifice calibration relationship.
m = slope of the orifice calibration relationship.

13.1.15 Calculate and record the corresponding sampler flow rate at actual conditions using the following equation:

$$Qa(sampler) = \{\Delta Pex\ (Ta + 30)/Pa]^{1/2} - b\} \{l/m\}$$

or use the following if a flow recorder is being used to measure the exit orifice plenum pressure:

$$Qa(sampler) = \{I(Ta + 30)/Pa]^{1/2} - b\} \{l/m\}$$

where:

Qa(sampler) = sampler flow rate, actual m^3/min.
ΔPex = exit orifice plenum pressure, in. H_2O.
Ta = ambient temperature during the flow check, K (K = EC + 273).
Pa = ambient barometric pressure during the flow check, mm Hg.
b = intercept of the MFC sampler calibration relationship.
m = slope of the MFC sampler calibration relationship.

[Note: If charts with linear-function scales are used, substitute $(I)^{½}$ for I.]

13.1.16 Using this information and the formulas provided on the MFC Sampler Flow-Check Data Sheet, calculate the QC check percentage differences.

$$QC\&check\ \%\ difference = \frac{[Qa(sampler)\ \&\ Qa(orifice)]}{Qa(orifice)}\ [100]$$

where:

Qa(sampler) is measured with the orifice transfer standard being installed.

Record this value on the MFC Sampler Flow-Check Data Sheet and plot on the QC control chart. If the sampler flow rate is within 93-107% (±7% difference) of the calculated Qa(orifice) flow rate (in actual volumetric units), the sampler calibration is acceptable. If these limits are exceeded, investigate and correct any malfunction. Recalibrate the sampler before sampling is resumed. Differences exceeding ±10% may result in the invalidation of all data collected subsequent to the last calibration or valid flow check. Before invalidating any data, double-check the orifice transfer standard's calibration and all calculations.

13.1.17 Calculate the corrected sampler flow rate, Qa(corr. sampler), using the following equation:

$$\text{Qa(corr. sampler } = \text{[Qa(sampler)]} \frac{\text{[(100 \& \% difference)]}}{100}$$

where:

Qa(sampler) is measured without the orifice transfer standard being installed and where the QC-check percentage difference was obtained from the equation above.

[Note: Take care to use the correct sign (i.e., positive or negative) for the percent difference.]

13.1.18 Calculate and record on the MFC Sampler Flow-Check Data Sheet the percentage difference between the inlet's design flow rate and the corrected sampler flow rate as:

$$\text{Design flow rate \% difference } = \frac{\text{[Qa(corr. sampler) \& 1.13]}}{1.13)}[100]$$

[Note: The author assumes in this section that the inlet is designed to operate at a flow rate of 1.13 actual m^3/min. If the design flow rate percentage difference is less than or equal to ±7%, the sampler calibration is acceptable. If the difference is greater than ±7%, investigate potential error sources and correct any malfunction. Recalibrate the sampler before sampling is resumed. Differences exceeding ±10% may invalidate all data collected subsequent to the last calibration or valid flow check. Before invalidating any data, double-check the sampler's calibration, the orifice transfer standard's certification, and all calculations.]

[Note: Deviations from the design flow rate may be caused in part by deviations in the site temperature and pressure from the seasonal average conditions. Recalculate the optimum set-point flow rate (SFR) according to Section 7.4.4 to determine if the flow controller should be adjusted.]

13.1.19 Set up the sampler for the next sampling period according to the operating procedure in Section 9.4.

13.2 QC Flow-Check Procedure--VFC Sampler

The indicated flow rate (Qa (sampler)) for VFC samplers is calculated by determining:

- The relative stagnation pressure (Pstg),
- The ambient temperature (Ta), and
- The barometric pressure (Pa) during the flow check.

These values are then applied to the sampler's calibration relationship. An alternative QC flow-check procedure may be presented in the manufacturer's instruction manual. The manual should be reviewed and the various methods evaluated. Inhouse equipment and procedural simplicity should be considered in determining which method to use.

[Note: Do not attempt to conduct a flow check of samplers under windy conditions. Short-term wind velocity fluctuations will provide variable pressure readings by the orifice transfer standard's manometer.]

The flow check will be less precise because of the pressure variations.

13.2.1 Collect the following equipment and transport it to the monitoring station:

- An orifice transfer standard and its calibration relationship in actual volumetric flow units (Qa).
- An associated oil, water, or digital manometer, with a 0-400 mm (0-16") range and minimum scale divisions of 1 mm (0.1").
- An oil, water, or digital manometer, with a 0-400 mm (0-16") range and minimum scale divisions of 1 mm (0.1") or other pressure measurement device for measurement of the sampler stagnation pressure. Ideally, this manometer (or other pressure measurement device) should be associated with the sampler.

[Note: Manometers used for QC flow-checks may be subject to damage or malfunction and thus should be checked frequently.]

- A thermometer capable of accurately measuring temperature from 0E-50EC (273-323 K) to the nearest ± 1EC and referenced to an NIST or ASTM thermometer within 2EC at least annually. To calculate the orifice flow rates, convert EC to K.
- A portable aneroid barometer (e.g., a climber or engineer's altimeter) capable of accurately measuring ambient barometric pressure over the range of 500-800 mm Hg to the nearest millimeter Hg and referenced within 5 mm Hg of a barometer of known accuracy at least annually.
- The sampler's calibration relationship (i.e., lookup table or alternative calibration relationship).
- A clean flow-check filter loaded into a filter cassette.
- A VFC Sampler Flow-Check Data Sheet (see Figure 13) or a site log book.

13.2.2 Set up the flow-check system as previously illustrated in Figure 12. VFC samplers are normally flow-checked with a loaded filter cassette in line (i.e., between the orifice transfer standard and the motor). The orifice transfer standard should be installed without fixed resistance plates or with the adjustable resistance value fully open. A flow-check filter should never be used for subsequent sampling because particles larger than 10 Fm can be collected on the filter while the inlet is raised. The sample mass will be biased as a result of using a filter for both a flow check and subsequent sampling.
Caution: Tighten the faceplate nuts on alternate corners first to eliminate leaks and to ensure even tightening. The fittings should be hand-tightened; too much compressing can damage the sealing gasket. Make sure the orifice gasket is in place and the orifice transfer standard is not cross-threaded on the faceplate.

13.2.3 Turn on the sampler and allow the sampler to warm up to operating temperature (3-5 min).

[Note: The sampler inlet may be partially lowered over the orifice transfer standard to act as a draft shield (if a shield is not otherwise provided). Use a block to provide at least 2" of clearance at the bottom for air flow and for the manometer tubing.]

13.2.4 Read and record the following parameters on the VFC Sampler Flow-Check Data Sheet (see Figure 13):

- Sampler location and date.
- Sampler S/N and model.
- Ambient temperature (Ta), EC and K.
- Ambient barometric pressure (Pa), mm Hg.
- Unusual weather conditions.
- Orifice transfer standard S/N and calibration relationship.
- Operator's signature.

13.2.5 Inspect the manometers for crimps or cracks in the connecting tubing. Open the valves and blow gently through the tubing, watching for the free flow of the fluid.
Adjust the manometers' sliding scales so that the zero lines are at the bottom of the meniscuses.

13.2.6 Connect the orifice manometer to the orifice transfer standard and the sampler manometer to the sampler stagnation pressure port located on the side of the sampler base. Ensure that one side of each manometer is open to atmospheric pressure. Be sure that the connecting tubing snugly fits the pressure ports and the manometers.

13.2.7 Read the pressure drop as indicated by the orifice manometer ( ) H_2O) and record the value on the VFC Sampler Flow-Check Data Sheet. Read the stagnation pressure drop and record it as) Pstg (mm Hg) on the data sheet.

[Note: Be sure to convert the manometer reading to mm Hg using the following equation before recording the reading on the data sheet.]

$$\text{mm Hg} = 25.4(\text{in. } H_2O/13.6)$$

13.2.8 Turn off the sampler and remove the orifice transfer standard.

13.2.9 With only a loaded filter cassette in line, turn on the sampler and allow it to warm up to operating temperature.

13.2.10 Read and record the stagnation pressure drop ( ) Pstg) for the normal operating flow rate. Turn off the sampler. Replace the vacuum cap on the stagnation pressure port.

13.2.11 Calculate and record Qa(orifice) flow rate for the flow-check point, as in the equation, reproduced below:

$$Qa(\text{orifice}) = \{[(\ ) H_2O)(Ta/Pa)]^{½} - b]\ [l/m]$$

where:

Qa(orifice) = actual volumetric flow rate as indicated by the transfer standard orifice, m^3/min.
) H_2O = pressure drop across the orifice, in. H_2O.
Ta = ambient temperature, K (K = EC + 273).
Pa = ambient barometric pressure, mm Hg.
b = intercept of the orifice calibration relationship.
m = slope of the orifice calibration relationship.

13.2.12 Calculate and record the value of Pl (mm Hg) for the measurements, with and without the orifice installed, according to the following equation:

$$Pl = [Pa- \ ) Pstg\ ]$$

where:

Pl = stagnation pressure, mm Hg.
Pa = ambient barometric pressure, mm Hg.
) Pstg = stagnation pressure drop, mm Hg.

13.2.13 Calculate and record the stagnation pressure ratio for the measurements, with and without the orifice installed, according to the following equation:

$$\text{Stagnation pressure ratio} = Pl/Pa$$

where:

Pl = stagnation pressure, mm Hg.
Pa = ambient barometric pressure, mm Hg.

13.2.14 Refer to the instrument manufacturer's lookup table (or alternative calibration relationship as described in Section 7.5.4) and determine the Qa(sampler) flow rates (m^3/min) for the measurements with

and without the orifice installed as indicated for the ratio of Pl/Pa and ambient temperature in EC. Record these values on the VFC sampler flow check data sheet.

13.2.15 Using Qa(orifice) and Qa(sampler) for the measurements with the orifice installed, calculate the QC-check percentage difference as:

$$\text{QC\&check \% difference} = \frac{[\text{Qa(sampler)} - \text{Qa(orifice)}]}{\text{Qa(orifice)}} [100]$$

Record this value on the VFC Sampler Flow-Check Data Sheet and plot it on the control chart for QC flow checks. If the QC-check percentage difference is less than or equal to ± 7%, the sampler calibration is acceptable. Those differences exceeding ± 7% will require recalibration. Differences exceeding ± 10% may invalidate all data collected subsequent to the last calibration or valid flow check. Before invalidating any data, double-check the sampler's calibration, the orifice transfer standard's certification, and all calibrations.

13.2.16 Using this percentage difference and Qa (sampler) from the measurements without the orifice installed (i.e., for the normal operating flow rate), calculate the corrected sampler flow rate as:

$$\text{Qa(corr. sampler} = [\text{Qa(sampler)}] \frac{[(100 - \text{\% difference})]}{100}$$

Record Qa (corr. sampler) on the VFC Sampler Flow-Check Data Sheet.

13.2.17 Determine the design flow rate percentage difference between the PM_{10} sampler inlet design flow rate (e.g., 1.13 m^3/min) and Qa (corr. sampler) as:

$$\text{QC\&check \% difference} = \frac{[\text{Qa(sampler)} - \text{Qa(orifice)}]}{\text{Qa(orifice)}} [100]$$

Record this design flow rate percentage difference on the VFC Sampler Flow-Check Data Sheet and plot it on the control chart for the field validation of flow rates. When plotting this value, use a different symbol than is normally used for plotting values that are obtained during sampling periods. If the design flow rate percentage difference is less than or equal to ± 7%, the sampler calibration is acceptable. Those differences exceeding ± 7% will require recalibration. Differences exceeding ± 10% may invalidate all data obtained subsequent to the last calibration or valid flow check. Before invalidating any data, double-check the sampler's calibration, the orifice transfer standard's certification, and all calculations.

14. Maintenance

Maintenance is defined as a program of positive actions aimed toward preventing failure of monitoring and analytical systems. The overall objective of a routine preventive maintenance program is to increase measurement system reliability and provide more complete data acquisition. The general maintenance procedures for HV samplers are outlined in this section. For more complete information on a particular sampler or on laboratory equipment maintenance, refer to the manufacturer's instruction manual for the individual instrument. Maintenance activities for the HV sampler are summarized in Table 4. Records should be maintained for the maintenance schedule of each HV sampler. Files should reflect the history of maintenance, including all replacement parts, suppliers, costs, expenditures, and in inventory of on-hand spare equipment for each sampler. Check sheets should be used to record preventive and/or corrective maintenance activities and the subsequent sampler calibration curve.

14.1 Maintenance Procedures

The HV sampler is comprised of two basic components: the inlet and the flow control system. Because of the differences between sampler models, refer to the manufacturer's instruction manual for specific maintenance guidelines and necessary supplies.

14.2 Recommended Maintenance Schedules

14.2.1 MFC Base. The MFC base is equipped with the following items:

14.2.1.1 Connecting tubing and power lines, which must be checked for crimps, cracks, or obstructions on sample recovery days. Fittings should be inspected periodically for cross-threading and tightness.

14.2.1.2 A filter screen, which should be inspected on sample recovery days for any impacted deposits.

14.2.1.3 Filter cassette gaskets, which need to be inspected each time a cassette is loaded. A worn cassette gasket is characterized on exposed filters by a gradual blending of the boundary between the collected particulate and the filter border.

14.2.1.4 Motor and housing gaskets, which should be checked at 3-month intervals and replaced as necessary.

14.2.1.5 Blower motor brushes, which should be replaced before they become worn to the point that damage may occur. Although motor brushes usually require replacement after 600-1,000 hours of operation, the optimum replacement interval must be determined by experience. A pumice stone can be used against the motor's contacts to ensure high conductivity. Change the brushes according to manufacturer's instructions and perform the operator's field-calibration check as presented in Section 13. If the sampler's indicated flow rate exceeds the manufacturer-specified design-flow-rate range, adjust the sampler before the next run day.

To achieve the best performance, new brushes should be properly seated on the motor's commutator before full voltage is applied to them. After the brushes have been changed, operate the sampler at 50-75% of normal line voltage for approximately 30 min. The motor should return to full performance after an additional 30-45 min at normal line voltage.

[Note: The motors that are used for HV samplers are higher-current versions of the motors that have been used for HV total suspended particulate samplers. The brushes for the two types of motors are different. Make sure that the correct replacement brushes are used for the maintenance of HV samplers. If a motor needs to be replaced, be sure to use the higher-current versions that are needed for HV sampling. When lower-current motors are installed in HV samplers, the flow rate has been found to vary with changes in the line voltage.]

14.2.1.6 A flow controller should be replaced if the flow recorder indicates no flow, low flow, excessive flow, or erratic flow. Minor adjustments can be made to alter sampling flow rates; however, the controller generally cannot be repaired in the field.

[Note: A flow recorder requires very little maintenance, but does deteriorate with age. Difficulty in zeroing the recorder and/or significant differences (i.e., greater than 0.3 m^3/min) in average flow rates obtained from consecutive sampling periods usually indicate a faulty recorder. The recorder pens should be replaced every 30 recording days. In dry climates, a more frequent replacement schedule may be required.]

14.2.2 VFC Base. The VFC base is equipped with the following items:

14.2.2.1 Power lines, which must be checked for crimps or cracks on sample recovery days. Fittings should be inspected periodically for cross-threading and tightness.

14.2.2.2 A filter screen at the throat of the choked-flow venturi, which should be inspected on sample recovery days for any impacted deposits.

14.2.2.3 Filter cassette gaskets, which should be checked each time a filter is installed. A worn casket gasket is characterized on exposed filters by a gradual blending of the boundary between the collected particulates and the filter border.

14.2.2.4 Motor and housing gaskets, which should be checked at 3-month intervals and replaced as necessary.

14.2.2.5 Blower motor brushes, which should be replaced before they become worn to the point that damage may occur. Although motor brushes usually require replacement after 600-1,000 hours of operation, the optimum replacement interval must be determined by experience. A pumice stone can be used against the motor's contacts to ensure high conductivity. Change the brushes according to manufacturer's instructions, and perform the operator's field-calibration check as presented in Section 13. If the sampler's indicated flow rate exceeds the manufacturer-specified design flow-rate range, recalibrate the sampler before the next run day.

To achieve the best performance, new brushes should be seated properly on the motor's commutator before full voltage is applied to them. After the brushes have been changed, operate the sampler at 50-75% of normal line voltage for approximately 30 min. The motor should return to full performance after an additional 30-45 min at normal line voltage.

Caution: Motors that are used for HV PM_{10} samplers are higher-current versions of the motors that have been used for HV total suspended particulate samplers. The brushes for the two types of motor are different. Make sure that the correct replacement brushes are used for the maintenance of HV PM_{10} samplers.

14.2.2.6 If a motor needs to be replaced, be sure to use the higher-current versions that are needed for HV PM_{10} sampling. When lower-current motors are installed in HV PM_{10} samplers, the flow rate has been found to vary with changes in the line voltage.

14.3 Refurbishment of HV Samplers

If operated in the field for extended periods, HV PM_{10} samplers may require major repairs or complete refurbishment. If so, refer to the manufacturer's instrument manual before work is undertaken. A sampler that has undergone major repairs or refurbishment must be leak-checked and calibrated prior to sample collection.

15. REFERENCES

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TABLE 1. EXAMPLE OF BASIC CHARACTERISTICS OF SOME COMMON FILTER MATERIAL

QUARTZ FIBER FILTER (Glass Spun with Organic Binder)
! Whatman QMA Filter ! Maximum temperature of up to 540EC ! High Collection Efficiency ! Non-hydroscopic ! Good for Corrosive Atmospheres ! Fragile ! Lowest background metals content
CELLULOSE FIBER FILTER (Cellulose Pulp)
! Whatman # 41/MSA "s" ! Low Ash ! Maximum Temperature of 150EC ! High Affinity for Water ! Enhanced Artifact Formation for $SO_4^=$ and NO_3 ! Good for X-Ray/Neutron Activation Analysis ! Low Metal Content
MEMBRANE FILTER (Dry Gel of Cellulose Esters)
! Whatman #41 ! Fragile, Therefore Requires Support Pad ! High Pressure Drop ! Low Residue when Ashed

TABLE 2. EXAMPLE OF SUMMARY OF USEFUL FILTER PROPERTIES

Filter and Filter Composition	Density mg/cm^2	pH	Filter Efficiency %
Teflon® (Membrane) $(CF_2)_n$(2µm Pore Size)	0.5	Neutral	99.95
Cellulose (Whatman 41) $(C_6H_{10}O_5)_n$	8.7	Neutral (Reacts with HNO_3)	58% at 0.3 µm
Glass Fiber (Whatman GF/C)	5.16	Basic pH - 9	99.0
"Quartz" Gelman Microquartz	6.51	pH - 7	98.5
Polycarbonate (Nuclepore) $C_{15}H_{14} + CO_3$ (0.3µm Pore Size	0.8	Neutral	93.9
Cellulose Acetate/Nitrate Millipore $(C_9H_{13}O_7)_n$(1.21 µm Pore Size)	5.0	Neutral (Reacts with HNO_3)	99.6

TABLE 3. EXAMPLE OF MINIMUM SAMPLER SITING CRITERIA

Scale	Height above ground, meters	Distance from supporting structure, meters		Other spacing criteria
		Vertical	Horizontal[a]	
Micro	2 to 7	> 2	> 2	1. Should be > 20 meters from trees. 2. Distance from sampler to obstacle, such buildings, must be twice the height and the obstacle protrudes above the sampler. 3. Must have unrestricted airflow 270 degrees around the sampler inlet. 4. No furnace or incineration flues should be nearby.[b] 5. Spacing from roads varies with traffic (see 40 CFR 58, Appendix E). 6. Sampler inlet is at least 2 m but not greater than 4 m from any collocated PM_{10} sampler. (See 40 CFR 58, Appendix E.)
Middle, neighborhood, urban, and regional scale	2 to 15	> 2	> 2	

[a]When inlet is located on rooftop, this separation distance is in reference to walls, parapets, or penthouses located on the roof.

[b]Distance depends on the height of furnace or incineration flues, type of fuel or waste burned, and quality of fuel (sulfur, ash, or lead content). This is to avoid undue influences from minor pollutant sources.

TABLE 4. EXAMPLE OF ROUTINE MAINTENANCE ACTIVITIES FOR SAMPLERS

Equipment	Frequency and/or method	Acceptance limits	Action if requirements are not met
Sampler inlet	Dismantle and clean at manufacturer-specified internals	No obvious particulate deposits or damage	Clean, replace damaged equipment before sampling
Sampler base			
Power lines	Check for crimps or cracks	No obvious damage	Replace as necessary
Filter screen and throat	Visually check on sample-recovery days	No obvious deposits; clean with wire brush	Clean
Gaskets	At 3-mo intervals, inspect all gaskets in the sampler	No leaks; no compression damage evident	Replace as necessary
Brushes	Replace after 600-1,000 h of operation	Stable flow rate	Replace as necessary
Motor	Replace if needed	Correct model must be used	Obtain correct model
Flow controller	Check when flowrate changes are evident	Stable flow rate throughout sample run	Replace or repair if possible
Recording device	Inspection with experiencing difficulty in zeroing, or when large changes in flow rates occur	Recorder stays zeroed; chart advances; pen inks	Replace or repair if possible
Tubing, fittings	Visually inspect on sample-recovery days	No crimps, cracks, or obstructions; no crossthreading	Replace as necessary.

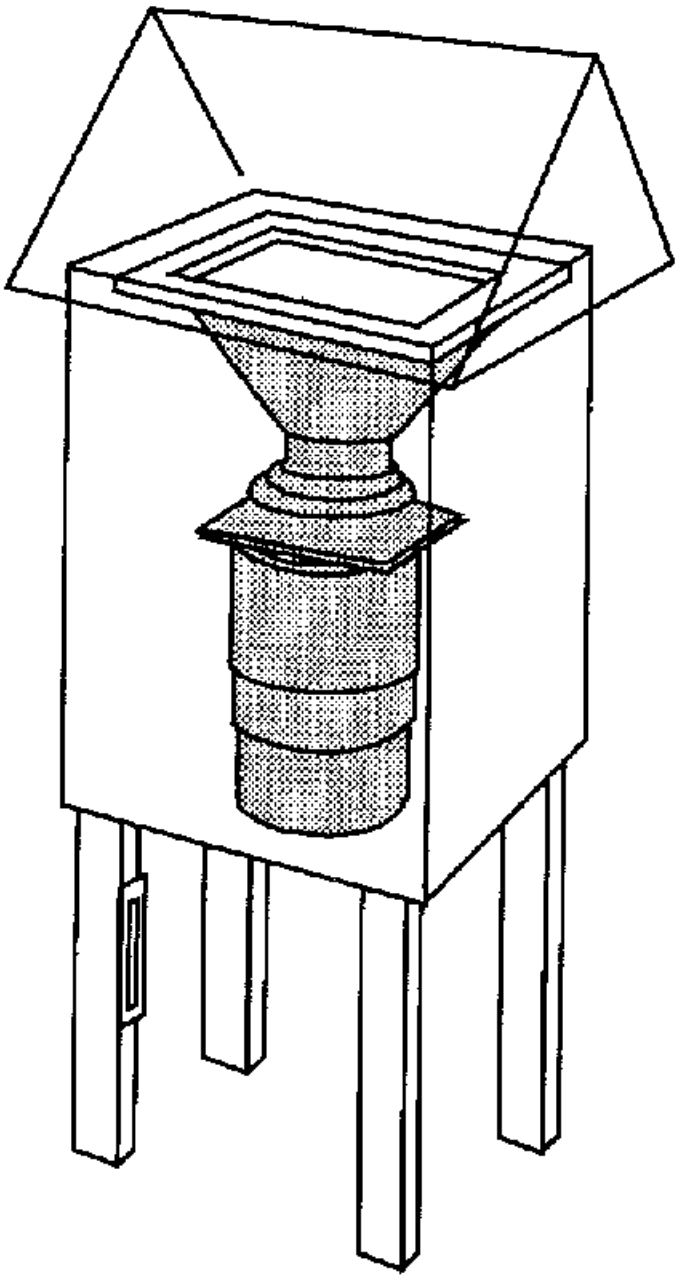


Figure 1. High-volume sampler with shelter.

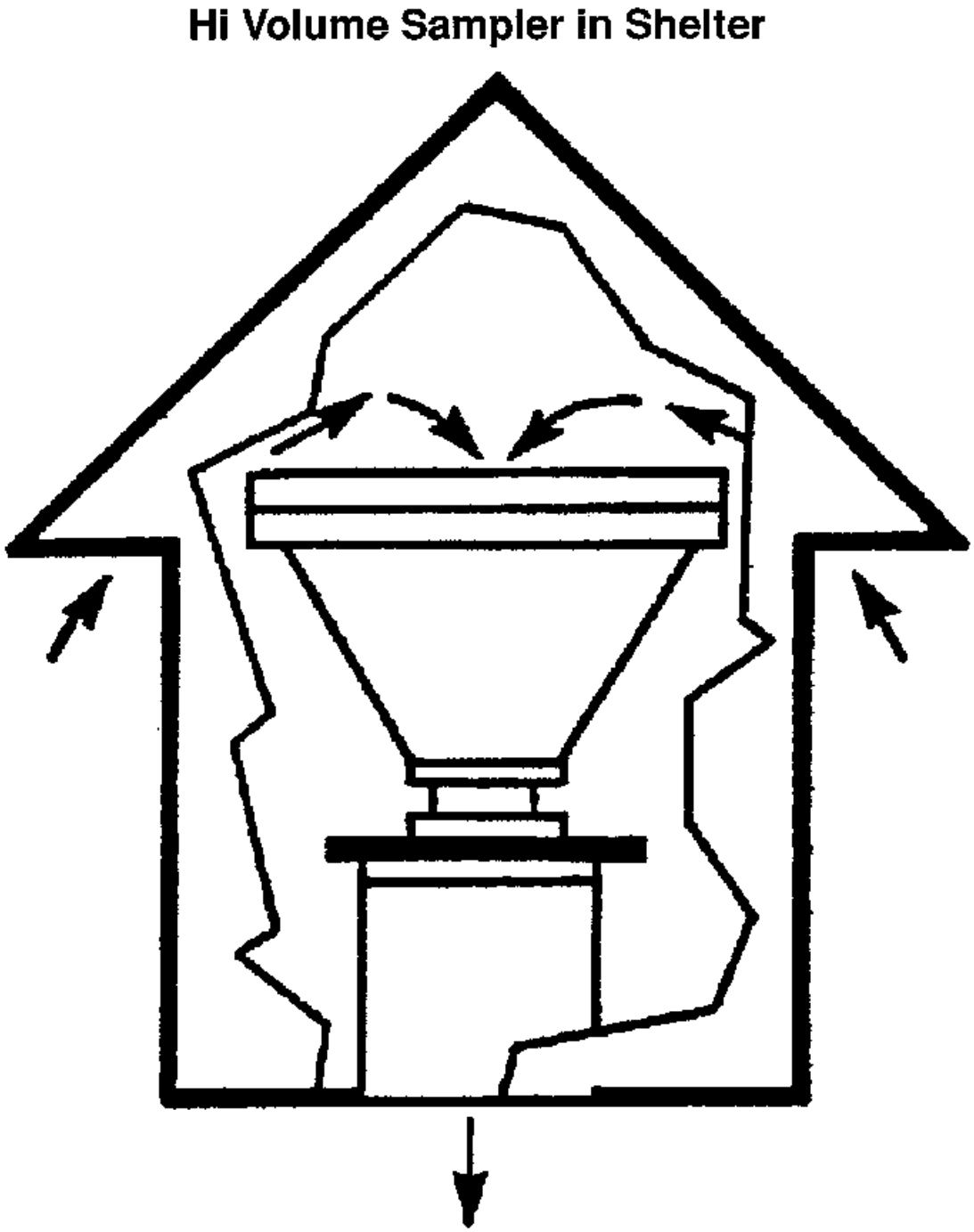


Figure 2. Inlet to EPA approved high volume sampler.

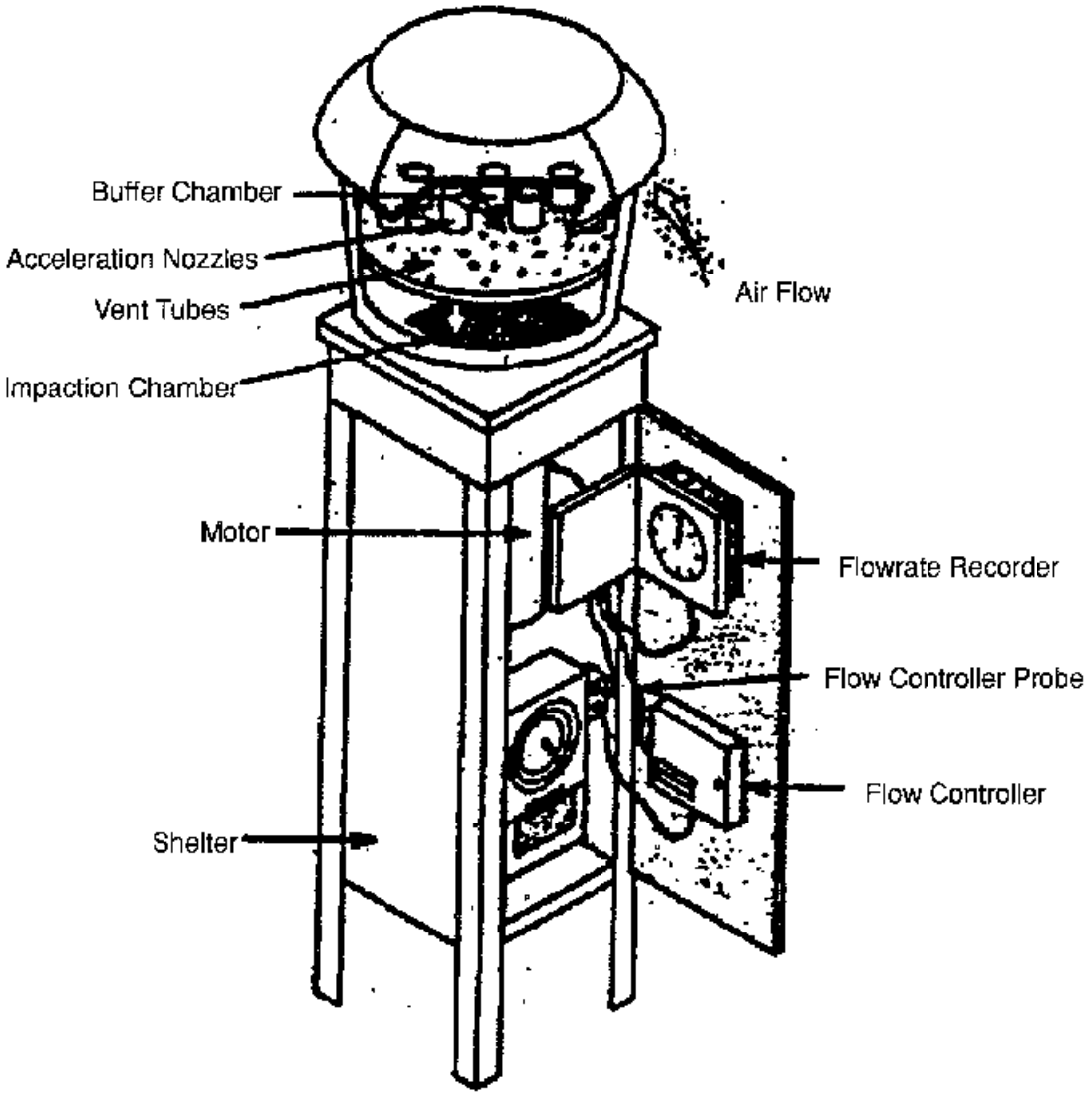


Figure 3. High-volume sampler with mass flow controller and impactor design size select inlet.

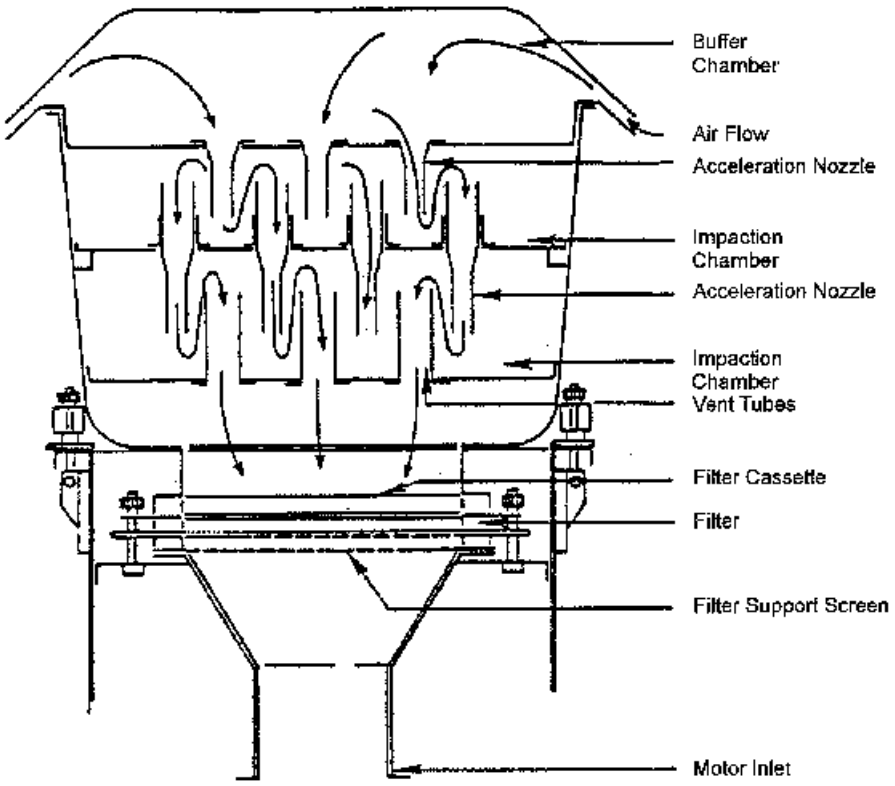


Figure 4. Schematic diagram of an impaction inlet for size select sampling for particulate matter.

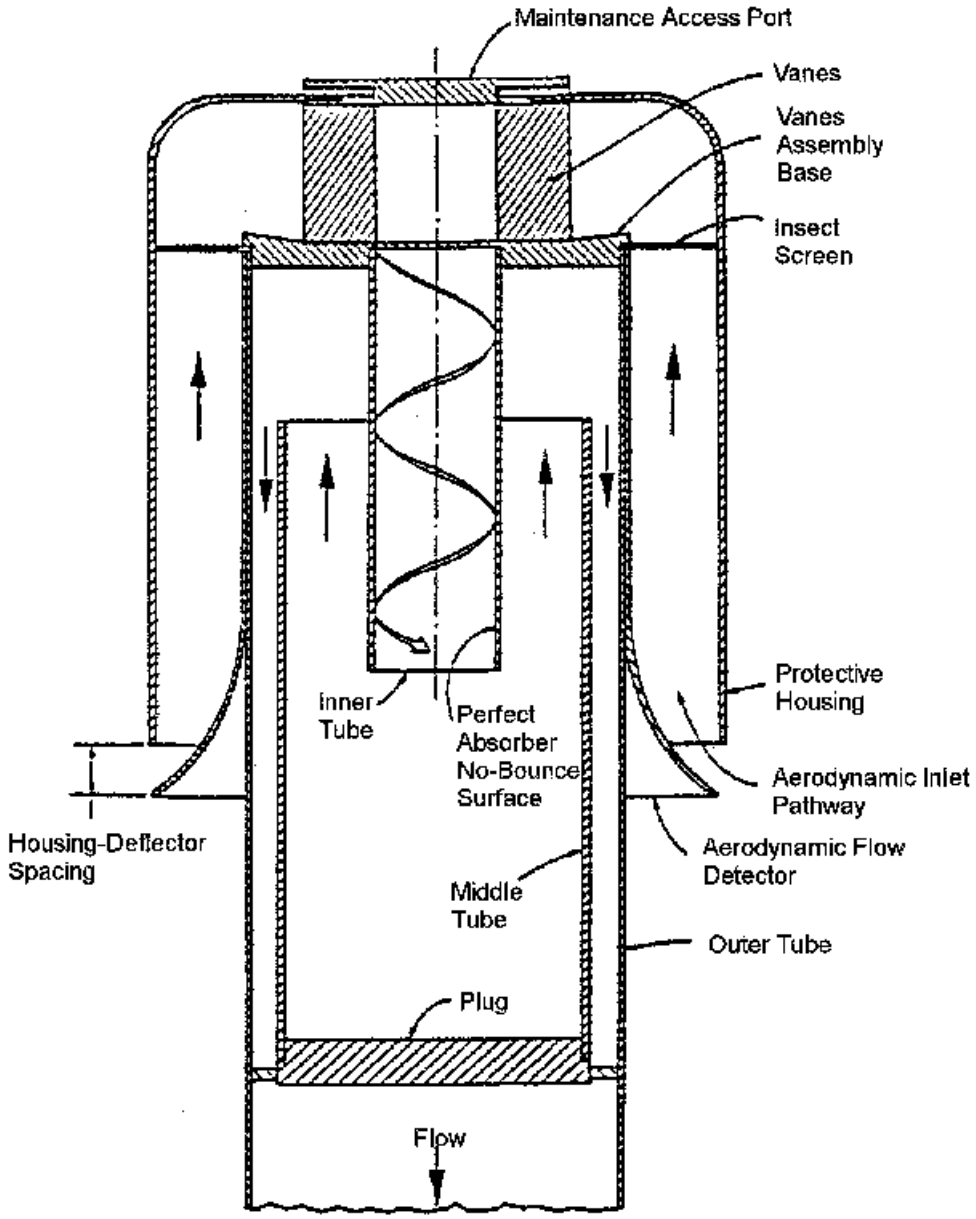


Figure 5. Schematic diagram of a cyclonic inlet for size select sampling for particulate matter.

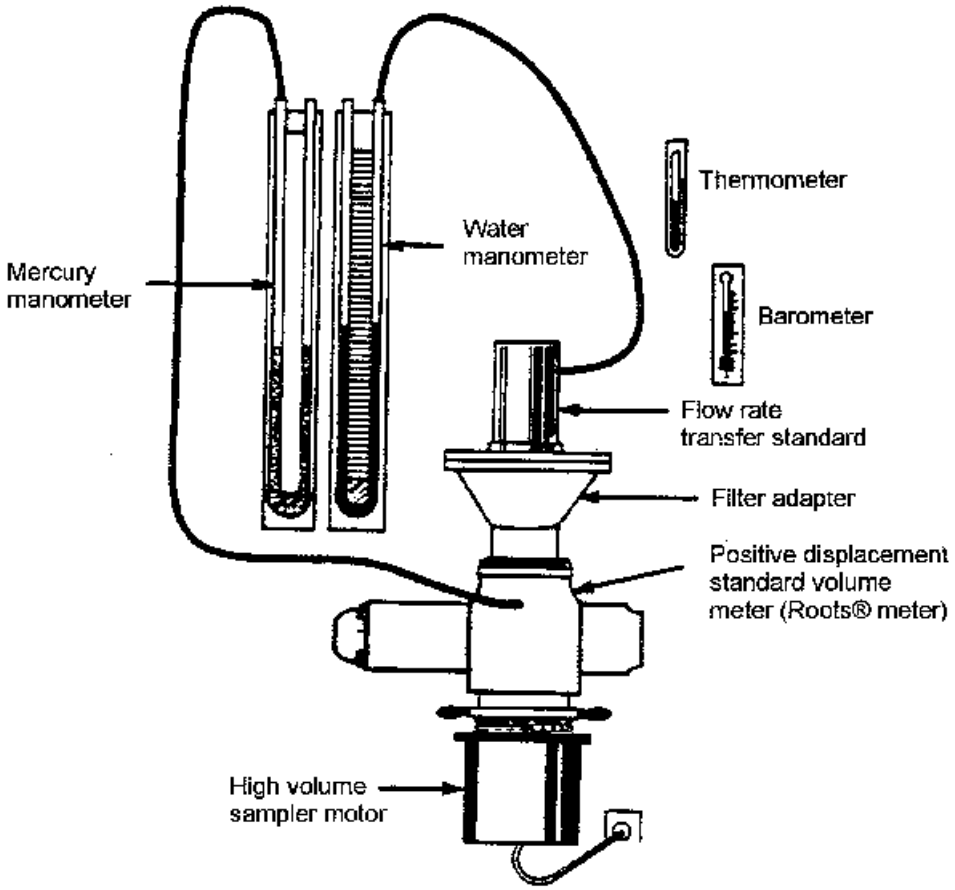


Figure 6. Flow rate transfer standard calibration setup.

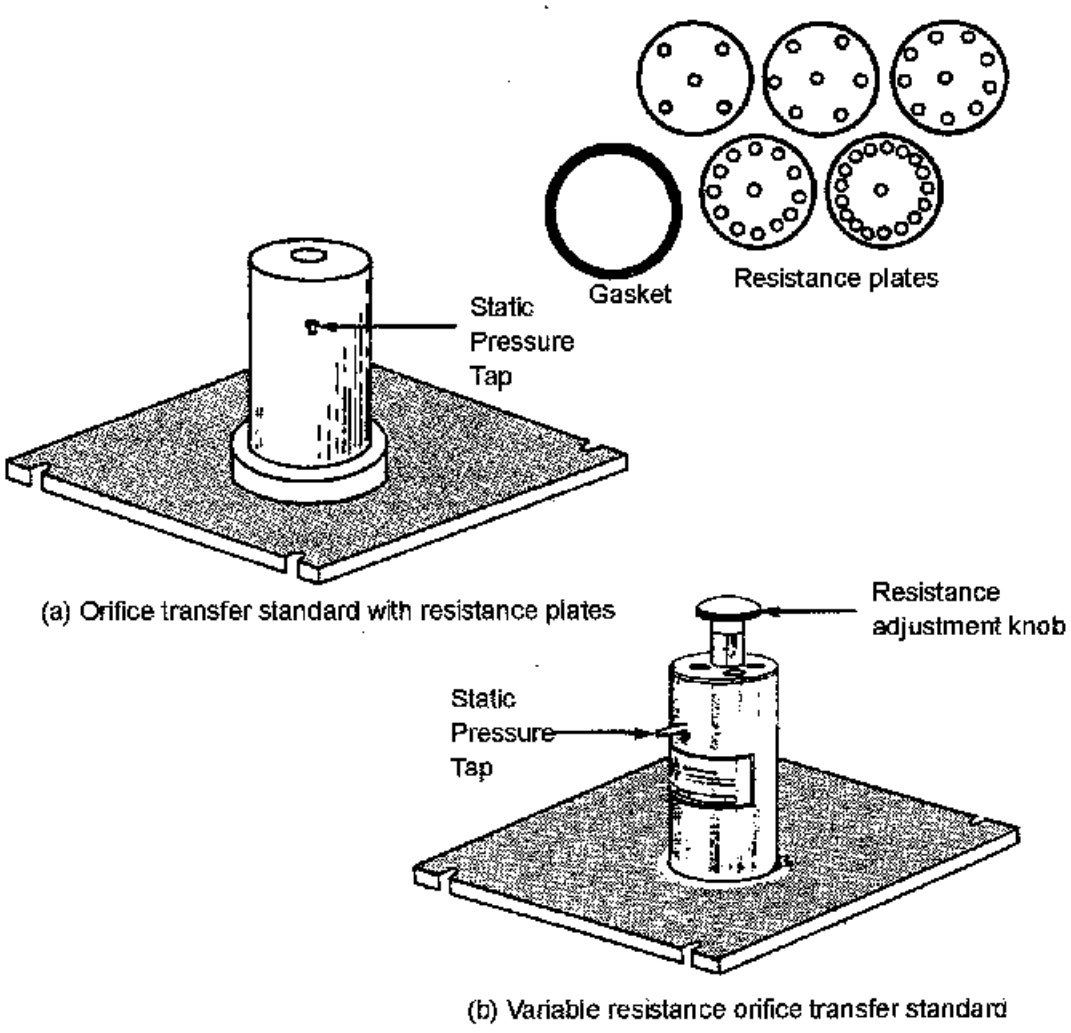


Figure 7. Typical orifice-type flow rate transfer standards.

ORIFICE TRANSFER STANDARD CERTIFICATION WORKSHEET

Date: Roots meter S/N: Ta: K

Operator: Orifice S/N: Pa: mm Hg

Plate or Volts AC	Initial Volume	Final Volume	Δ Vol.	ΔTime (min)	ΔHg (mm)	ΔH_2O (in.)

DATA TABULATION

Vstd	(x-axis) Qstd	(y-axis) $[\Delta H_2O\ (Pa/Ta)]^{1/2}$	Va	(x-axis) Qa	(y-axis) $[\Delta H_2O\ (Ta/Pa)]^{1/2}$
	m =			m =	
	b =			b =	
	r =			r =	

CALCULATIONS

Vstd = Δ Vol [(Pa − ΔHg)/760] (298/Ta)*
Qstd = Vstd/ΔTime*
y = mx + b

Va = ΔVol [(Pa − ΔHg)/Pa]
Qa = Va/ΔTime
y = mx + b

For subsequent flow rate calculations:

Qstd = $\{[\Delta H_2O\ (Pa/Ta)]^{1/2} - b\}\ \{1/m\}$*

Qa = $\{[\Delta H_2O\ (Ta/Pa)]^{1/2} - b\}\ \{1/m\}$

*NOTE: For PM10 monitoring, a calibration curve corrected to standard conditions is optional.

Figure 8. Example orifice transfer standard certification worksheet.

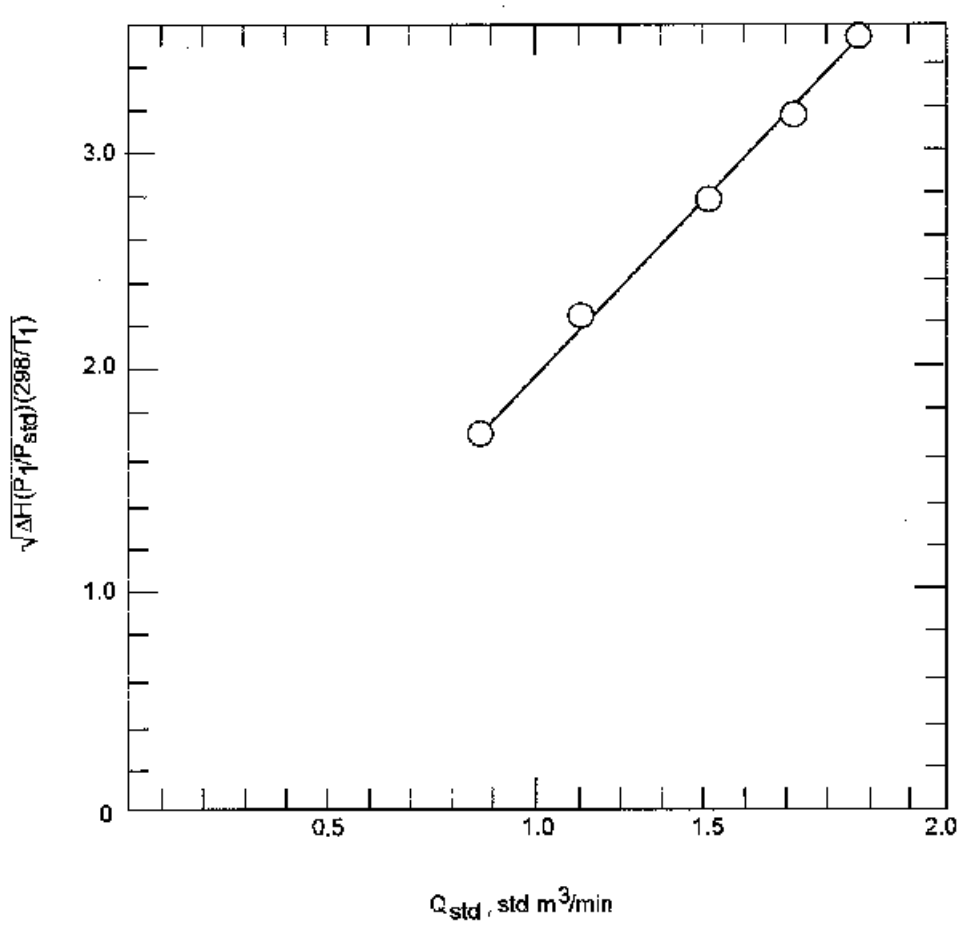


Figure 9. Typical calibration curve for a flow rate transfer standard.

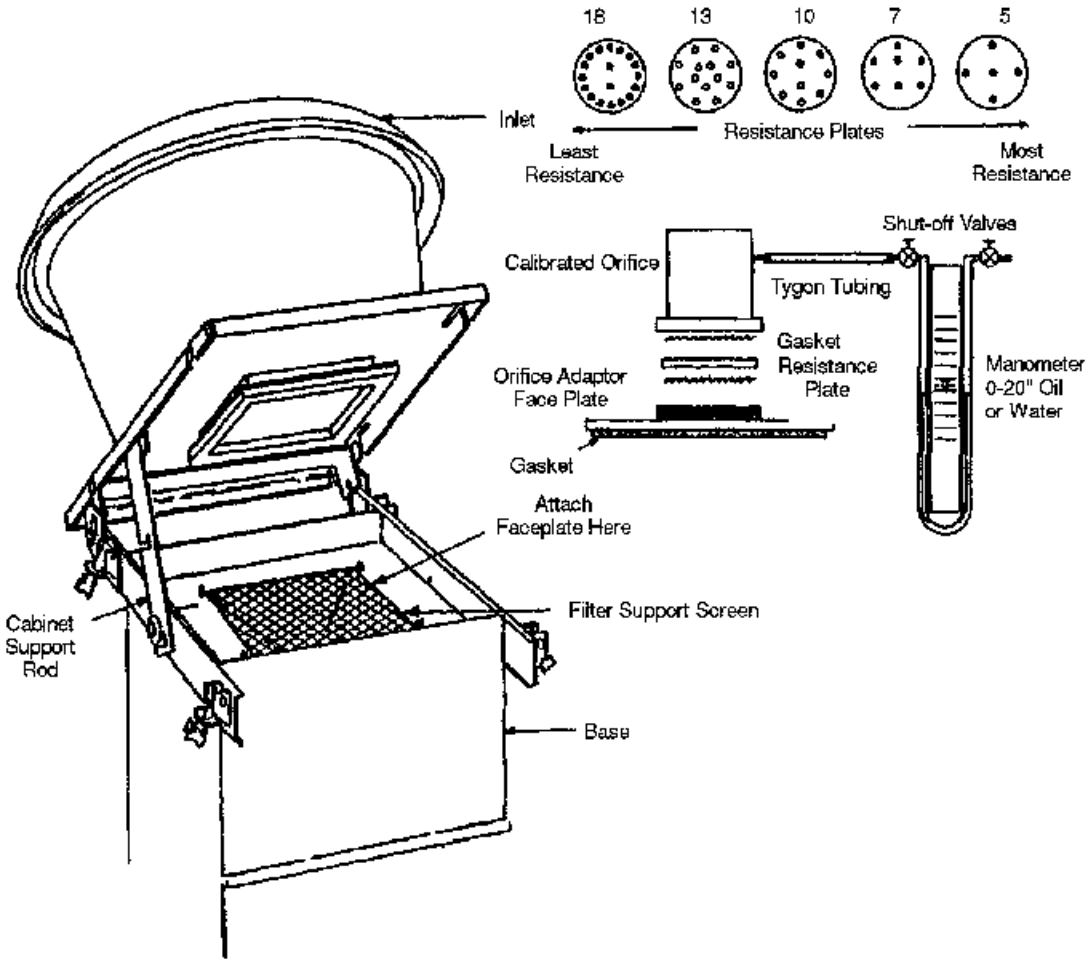


Figure 10. Typical calibration set-up for a mass flow controller (MFC).

MFC SAMPLER CALIBRATION DATA SHEET

Station Location _____ Date _____ Time _____

Sampler Model _____ S/N _____ Operator _____

Pa _____ mm Hg, Ta _____ °C _____ K, Unusual conditions: _____

Ps* _____ mm Hg, Ts* _____ °C _____ K, (*seasonal average Ta and Pa)

Orifice S/N _____ Orifice Calibration Date _____

Orifice calibration relationship: m = _____ b = _____ r = _____

Plate Number	Total ΔH_2O (in.)	X-Axis = Qa (orifice) flow rate[a] (m^3/min)	Sampler ΔPex (in. H_2O) [or I for flow recorders]	Y-Axis = Sampler ΔPext[b] [or It for flow recorders][c]

[a] $Qa = \{[(\Delta H_2O)(Ta/Pa)]^{1/2} - b\}\ \{1/m\}$

[b] $\Delta Pext = \{\Delta Pex(Ta + 30)/Pa)\}^{1/2}$

[c] $It = [I]\ [(Ta + 30)/Pa]^{1/2}$ if a flow recorder is used

Sampler Calibration Relationship (Qa on x-axis; ΔPext or [It] on y-axis):
$\Delta Pext = m[Qa\ (Orifice)] + b$ or $It = m[Qa(Orifice)] + b$

m = _____ b = _____ r = _____

For subsequent calculation of sampler flow rate:
$\overline{Qa} = \{[\text{mean } \Delta Pex\ (Tav + 30)/Pav]^{1/2} - b\}\ \{1/m\}$
or $\overline{Qa} = \{\text{mean } I[(Tav + 30)/Pav]^{1/2} - b\}\ \{1/m\}$

Set point flow rate (SFR) _____
$SFR = 1.13\ (Ps/Pa)\ (Ta/Ts)$

Sampler set point (SSP) _____
$SSP = [Pa/(Ta + 30)]\ [m(SFR) + b]^2$
or $SSP = [Pa/(Ta + 30)]^{1/2}\ [m(SFR) + b]$ for flow recorders

Figure 11. Example MFC sampler calibration data sheet.

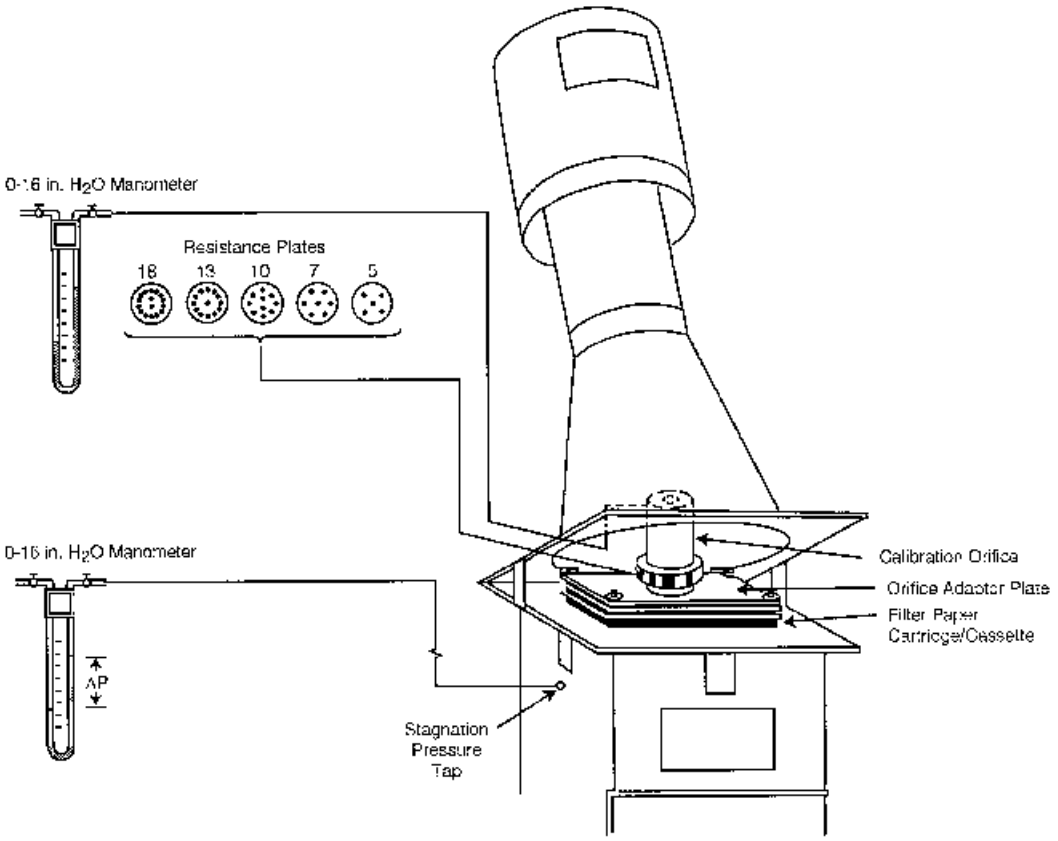


Figure 12. Calibration of a typical volumetric flow controller (VFC).

VFC SAMPLER CALIBRATION DATA SHEET

Station Location _____ Date _____ Time _____

Sampler Model _____ S/N _____ Operator _____

Pa _____ mm Hg, Ta _____ °C _____ K, Unusual Conditions _____

Orifice S/N _____, Orifice Calibration Date _____

Orifice Calibration Relationship: m = _____ b = _____ r = _____

Plate No.	ΔH_2O (in.)	ΔPstg (mm Hg)[a]	P1=Pa−ΔPstg (mm Hg)	P1/Pa (mm Hg)	Qa (orifice) flow rate[b] (m^3/min)	$\frac{Qa\ (orifice)}{[Ta]^{1/2}}$
Operational Flow Rate						

[a] mm Hg = 25.4 (in. H_2O/13.6)

[b] Qa (orifice) = 1/m {[(ΔH_2O) (Ta/Pa)]$^{1/2}$ − b}

[c] % Difference = $\left[\frac{Qa\ (sampler) - Qa\ (orifice)}{Qa\ (orifice)}\right]$ [100]

Qa (Orifice)	Qa (sampler) (Lookup Table)	% Difference[c]

Sampler Calibration Relationship

☐ Lookup Table Validated (i.e., % difference ≤ 4)

☐ New calibration relationship:

$X = \frac{Qa\ (orifice)}{[Ta]^{1/2}}$, Y = (P1/Pa)

m = _____ b = _____ r = _____

For subsequent calculation of sampler flow rate:

$Qa = \{[P1/Pa - b][Ta]^{1/2}\}\ \{1/m\}$

Operational Flow Rate _____ m^3/min

Figure 13. Example VFC sampler calibration data sheet.

MFC SAMPLER FIELD DATA SHEET

Station
Location _____ Date _____ SAROAD# _____

Sampler Model _____ S/N _____

Filter ID No. _____ Pav _____ mm Hg. Tav _____ °C _____ K

Sampler Manometer Readings **Flow Recorder Readings**

Initial ΔPex _____ in. H_2O Mean I _____

Final ΔPex _____ in. H_2O

Mean ΔPex _____ in. H_2O

Sampler Calibration Relationship: m = _____ b = _____ r = _____

$\overline{Qa}$ _____ m^3/min Elapsed Time _____ min

$\overline{Qa}$ = {[mean ΔPex (Tav + 30)/Pav]$^{1/2}$ − b} {1/m}
$\overline{Qa}$ = {mean I [(Tav + 30)/Pav]$^{1/2}$ − b} {1/m} for flow recorders

Operator _____

Comments: _____

_____

_____

_____

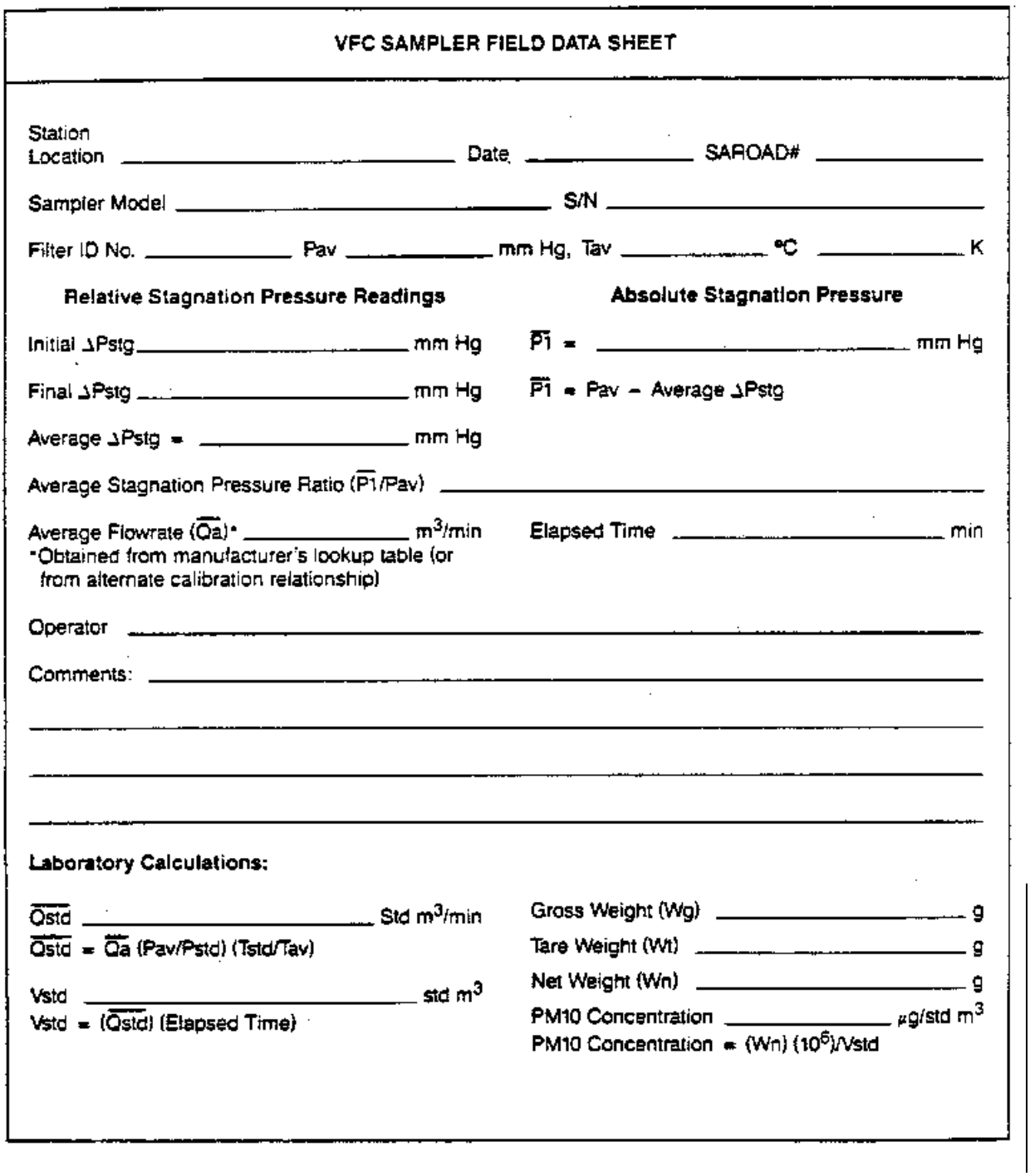
Laboratory Calculations:

$\overline{Qstd}$ _____ std m^3/min
$\overline{Qstd}$ = $\overline{Qa}$ (Pav/Pstd) (Tstd/Tav)

Vstd _____ std m^3
Vstd = ($\overline{Qstd}$) (elapsed time)

Gross weight (Wg) _____ g
Tare weight (Wt) _____ g
Net Weight (Wn) _____ g
PM10 Concentration _____ μg/std m^3
PM10 Concentration = (Wn) (10^6)/Vstd

Figure 14. Example MFC sampler field data sheet.



VFC SAMPLER FIELD DATA SHEET

Station Location _____ Date _____ SAROAD# _____

Sampler Model _____ S/N _____

Filter ID No. _____ Pav _____ mm Hg, Tav _____ °C _____ K

Relative Stagnation Pressure Readings

Initial ΔPstg _____ mm Hg

Final ΔPstg _____ mm Hg

Average ΔPstg = _____ mm Hg

Absolute Stagnation Pressure

$\overline{P1}$ = _____ mm Hg

$\overline{P1}$ = Pav − Average ΔPstg

Average Stagnation Pressure Ratio ($\overline{P1}$/Pav) _____

Average Flowrate ($\overline{Qa}$)* _____ m^3/min

*Obtained from manufacturer's lookup table (or from alternate calibration relationship)

Elapsed Time _____ min

Operator _____

Comments: _____

Laboratory Calculations:

$\overline{Qstd}$ _____ Std m^3/min

$\overline{Qstd}$ = $\overline{Qa}$ (Pav/Pstd) (Tstd/Tav)

Vstd _____ std m^3

Vstd = ($\overline{Qstd}$) (Elapsed Time)

Gross Weight (Wg) _____ g

Tare Weight (Wt) _____ g

Net Weight (Wn) _____ g

PM10 Concentration _____ μg/std m^3

PM10 Concentration = (Wn) (10^6)/Vstd

Figure 15. Example VFC sampler field data sheet.

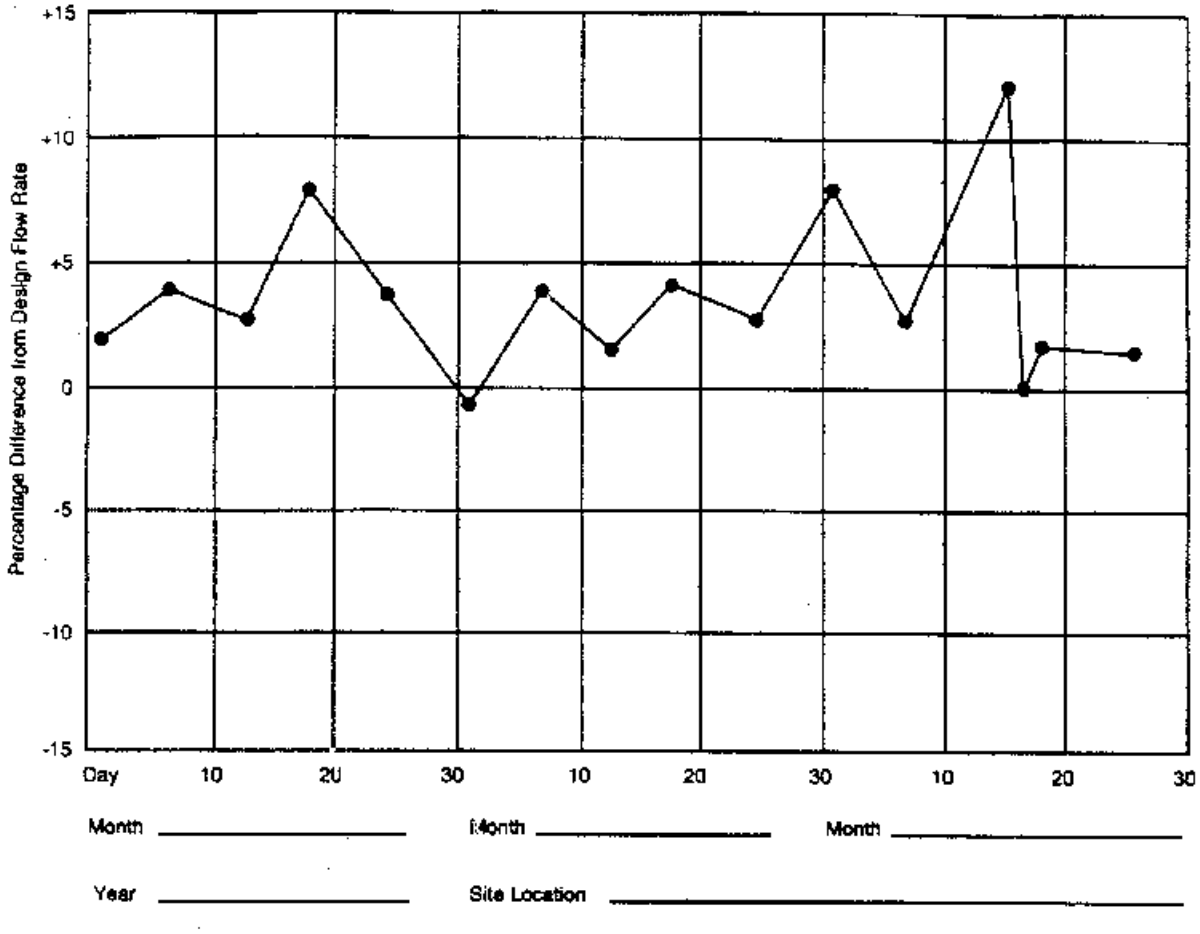


Figure 16. Field data control chart.

APPENDIX B

USEPA Compendium Method IO-3.1

EPA/625/R-96/010a

Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Compendium Method IO-3.1

SELECTION, PREPARATION AND EXTRACTION OF FILTER MATERIAL

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

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- James L. Cheney, U.S. Army Corps of Engineers, Omaha, NE
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- Frank F. McElroy, U.S. EPA, NERL, RTP, NC
- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

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

Author(s)

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

Peer Reviewers

- David Brant, National Research Center for Coal and Energy, Morgantown, WV
- John Glass, SC Department of Health and Environmental Control, Columbia, SC
- Jim Cheney, U.S. Army Corps of Engineers, Omaha, NE
- Dewayne Ehman, Texas Natural Resource Conservation Committee, Austin, TX
- Gary Wester, Midwest Research Institute, Kansas City, MO
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

DISCLAIMER

Method IO-3.1
Selection, Preparation and Extraction of
Filter Material

TABLE OF CONTENTS

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Chapter IO-3
CHEMICAL SPECIES ANALYSIS OF FILTER-COLLECTED SUSPENDED PARTICULATE MATTER (SPM)

Method IO-3.1
SELECTION, PREPARATION AND EXTRACTION OF FILTER MATERIAL

1. Scope

1.1 This methodology consists of (1) filter media selection, (2) numbering and pre-field tare weighing of filters, (3) post-field final weighing of filters, (4) microwave or hot acid extraction, and (5) analysis for metal analysis by ICP, FAA, ICP/MS or GFAA.

1.2 Pre-field filters are conditioned in a room of constant humidity and temperature and are gravimetrically tared. After air samples have been collected, the filters are returned to the laboratory and conditioned as before and weighed. The final filter weight minus the tare weight is calculated. The procedure for the weighing of filters is based on 40 CFR 50, Appendix B, entitled "*Reference Method for the Determination of Suspended Matter in the Atmosphere (High-Volume Method)*."

1.3 After the post-field filter final weights have been obtained, the filter is subsampled by cutting a filter strip consisting of one-ninth of the overall filter and digested using a microwave or hot acid extraction technique; these extracts are then analyzed by one of many analytical techniques. The results are multiplied by a factor of 9 to obtain the actual total µg of each metal found on the entire 8" x 10" filter. Based upon the analysis of a blank filter, background metal concentration may be subtracted from the total metal concentration to get a net value. Therefore, the analytical results represent the total µg found on the 8" x 10" filter but do not represent the volume of air sampled.

1.4 Sectioning the filter for extraction is based on 40CFR50, Appendix B entitled "*Determination of Lead in Suspended Particle Matter Collected From Ambient Air*." The procedure for the microwave extraction is based on a method developed by EPA entitled *Microwave Extraction of Glass-Fiber Filters*, as identified in Section 2.2. This procedure has been modified for extracting quartz fiber filters.

2. Applicable Documents

2.1 ASTM Documents

- D4096 *Application of the High Volume Sample Method for Collection and Mass Determination of Airborne Particle Matter*.
- D1356 *Definition of Terms Related to Atmospheric Sampling and Analysis*.
- D1357 *Practice for Planning the Sampling of the Ambient Atmosphere*.
- D2986 *Method for Evaluation of Air Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test*.

2.2 Other Documents

- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance*, EPA-600/R-94/038a.
- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA-600/R-94/038b.
- *Reference Method for the Determination of Particulate Matter in the Atmosphere*, Code of Federal Regulations (40 CFR 50, Appendix J).
- *Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)*, Code of Federal Regulations (40 CFR 50, Appendix B).
- *Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air*, Federal Register 43 (194): 46258-46261.
- U. S. Environmental Protection Agency, *Microwave Extraction of Glass Fiber Filters*, Method Research and Development Division, RTP, NC 1989.

3. Apparatus

3.1 Equipment For Gravimetric Analysis

3.1.1 Controlled Temperature. Temperature between 15 and 30EC with less than ±2EC variation during equilibration period.

3.1.2 Controlled Humidity. Less than 50% relative humidity, constant within ±5%

3.1.3 Analytical Balance. Sensitive to 0.1 mg, with weighing chamber designed to accept an unfolded 20.3 x 25.4 cm (8" x 10") filter.

3.1.4 Area Light Source. Similar to X-ray film viewer to backlight filters for visual inspection.

3.1.5 Numbering Device. Capable of printing identification numbers on the filters before they are placed in the filter conditioning environment if not numbered by the supplier.

3.1.6 Hygrothermograph. Capable of recording temperature and relative humidity in the weighing room.

3.2 Microwave Digestion Apparatus and Materials

3.2.1 Microwave Digestive System and Capping Station. With programmable power settings up to 600 watts, best source.

[Note: Commercial kitchen or home-use microwave should NOT be used for digesting samples. The oven cavity must be corrosion resistant and well ventilated. All electronics must be protected against corrosion for safe operation.]

3.2.2 PFA Teflon® Digestion Vessels. Capable of withstanding pressures of up to 120 psi. Pressure vessels capable of controlled pressure relief at pressures exceeding 120 psi (60-120 mL capacity), best source.

3.2.3 Teflon® PFA Overflow Vessel. Double ported (60-120 mL capacity), best source.

3.2.4 Rotating Table. Uniform exposure of samples within the oven.

3.2.5 Volumetric Glassware. 50-100 mL capacity (Class A borosilicate).

3.2.6 Bottles, Linear Polyethylene or Polypropylene with Leakproof Caps, for Storing Samples. Teflon® bottles for storing multielement standards (500 mL, 125 mL, and 30 mL), best source.

3.2.7 Centrifuge Tubes. Oak Ridge polysulfone tubes with screw caps of polypropylene, 30 mL.

3.2.8 Nylon or Teflon® 0.45 µm Syringe Filters. Acrodisc® No. 4438 or equivalent and syringes for rapid nonmetals contributing filtering.

3.2.9 Sterile Polypropylene Tubes with Screw Caps of Polypropylene, 15 mL Capacity. Best source.

3.2.10 Pipette. Automatic dispensing with an accuracy of setting 0.1 mL or better and repeatability of 20 FL, Grumman Automatic Dispensing Pipette, Model ADP-30DT or equivalent.

3.2.11 Particle Mask. 3M, No. 8500, to be worn while cutting and handling glass-fiber filters.

3.2.12 Template. Aid in sectioning the glass fiber filter. Federal Register 43 (194): 46258-46261.

3.2.13 Pizza Cutter, Thin Wheel. Clean razor blade (< 1 mm).

3.2.14 Vortex Mixer. VWR2 variable speed or equivalent.

3.2.15 Hydrochloric Acid. Baker Instra-Analyzed, concentrated (sp.gr.1.19) or equivalent, for preparing samples.

3.2.16 Nitric Acid. Baker Instra-Analyzed, concentrated (sp.gr.1.41) or equivalent, for preparing samples.

3.2.17 ASTM Type I Water. ASTM D193.

3.2.18 Extraction Solution (5.55% HNO_3/16.75% HCl). Prepare by adding in ~ 500 mL of Type I DI water, 55.5 mL of concentrated HNO_3, and 167.5 mL of concentrated HCl, dilute to one liter with Type I DI water.

3.3 Hot Acid Extraction Apparatus and Materials

3.3.1 Thermolyne Model 2200 Hot-Plate or Equivalent.

[Note: Temperature of the extracts may be monitored by the use of a beaker containing a thermometer and similar reagents as the samples.]

3.3.2 Volumetric Glassware. 50-100 mL capacity (Class A borosilicate).

3.3.3 Bottles, Linear Polyethylene or Polypropylene with Leakproof Caps, for Storing Samples. Teflon® bottles for storing multielement standards (500 mL, 125 mL, and 30 mL).

3.3.4 Centrifuge Tubes. Polypropylene or Oak Ridge polysulfone tubes with screw caps of polypropylene, 30 mL (Nalgene 3119-0050/3115-0030 or equivalent).

3.3.5 Nylon or Teflon® 0.45 µm Syringe Filters. Acrodisc® No. 4438 or equivalent and syringes for rapid nonmetals contributing filtering.

3.3.6 Sterile Polypropylene Tubes with Screw Caps of Polypropylene, 15 mL capacity. Falcon Model No. 2099 or equivalent.

3.3.7 Pipette. Automatic dispensing with an accuracy of setting 0.1 mL or better and repeatability of 20 FL. (Grumman Automatic Dispensing Pipette, Model ADP-30DT or equivalent).

3.3.8 Particle Mask. 3M, No. 8500. To be worn while cutting and handling glass-fiber filters.

3.3.9 Vortex Mixer. VWR2 variable speed or equivalent.

3.3.10 Hydrochloric Acid. Baker Instra-Analyzed, concentrated (36.5%-38%/12.3 M) or equivalent, for preparing samples.

3.3.11 Nitric Acid. Baker Instra-Analyzed, concentrated (70% 16M) or equivalent, for preparing samples.

3.3.12 ASTM Type I Water. ASTM D193.

4. Filter Medium Selection

4.1 Introduction

4.1.1 In general, the filter medium depends on the purpose of the test. For any given standard test method, the appropriate medium will be specified. However, it is important to be aware of certain filter characteristics that can affect selection and use.

4.1.2 Selecting a filtration substrate for time-integrated SPM monitoring must be made with some knowledge of the expected characteristics and a pre-determined analytical protocol. For any given standard test method, the appropriate medium will normally be specified.

4.1.3 In high-volume sampling, four types of filter material to capture SPM are commonly used. They include cellulose fiber, quartz/glass fiber, mixed fiber, and membrane filter types. Selecting a filter depends upon variables such as background metal content, artifact formation, and affinity for moisture. The basic characteristics of the types of filter material used in high volume are outlined in Table 1 sampling. Useful filter properties are described in Table 2. Several characteristics are important in the selection of filter media. They are:

- **Particle Sampling Efficiency**. Filters should remove more than 99% of SPM drawn through them, regardless of particle size or flow rates.
- **Mechanical Stability**. Filters should be strong enough to minimize leaks during sampling and wear during handling.
- **Chemical Stability**. Filters should not chemically react with the trapped SPM.
- **Temperature Stability**. Filters should retain their porosity and structure during sampling.
- **Blank Correction**. Filters should not contain high concentrations of target compound analytes.

Quartz fiber filter medium is most widely used for determining mass loading. Weight stability with respect to moisture is an attractive feature. Quartz fiber filters provide high efficiency and collect airborne particles of practically every size and description. Typical characteristics of quartz fiber filters are (1) a fiber content of high purity quartz, (2) a binder of below 5% (zero for binderless types), (3) a thickness of approximately 0.5 mm, (4) a surface with no pinholes, and (5) an allowance of no more than 0.05% of smoke particles to pass through the filter at a pressure of 100mm of water with a flow rate of 8.53 m/min (28 ft/min), as determined by ASTM-D2986, *Method for Evaluation of Air Assay Media by the Monodisperse DOP (Dioctyl Phthalate) Smoke Test*.

Particulate matter collected on quartz fiber filters can be analyzed for many constituents. If chemical analysis is anticipated, binderless filters should be used. Glass is a commercial product generally containing test-contaminating materials; therefore, appropriate background corrections should be made. Background concentration of various metals associated with different grades of quartz fiber filters are documented in Table 3.

4.1.4 Silica fiber filters are used when it may be required or desirable to use a mineral fiber filter, which may later be extracted by strong reagents. These fibers are usually made by leaching glass fibers with strong mineral acids followed by washing with deionized water. The fibers are rather weak but can be formed into filter sheets using little or no binder. These filters have been recently developed and are commercially available.

4.1.5 For some purposes, airborne particles may be collected on cellulose fiber filters. Cellulose low-ash filters are especially useful when the filter is to be destroyed by ignition or chemical digestion. However, these filters have higher flow resistance (lower sampling rate) and have been reported to have much poorer

collection efficiency than the glass fiber media. Furthermore, cellulose is very sensitive to moisture conditions, and even with very careful conditioning before and after sampling, accurately weighing the collected particles is difficult. The filter should be enclosed in a lightweight metal can with a tight lid and weighed.

4.1.6 As documented in the 40 CFR Part 58, Appendices A and B, identify the filter specifications when used as part of the *Federal Reference Method for Particulate Matter in Ambient Air*. These specifications include (1) a quartz-fiber, nonhydroscopic filter, (2) a size of approximately 8" x 10", (3) an exposure area of approximately 63 $in.^2$, (4) a 99% collection efficiency as measured by ASTM-2986 (DOP test) for particles 0.3 µm diameter, (5) a pressure drop range of 42-54 mm Hg at a flow rate of 1.5 m^3/min through the nominal exposed area, (6) a pH of 6 to 10, and (7) a maximum weight integrity of 2.4 mg.

4.2 Visual Filter Inspection

4.2.1 After purchased, all filters must be visually inspected for defects, and defective filters must be rejected if any are found. Batches of filters containing numerous defects should be returned to the supplier.

4.2.2 The following are specific defects to look for:

4.2.2.1 Pinhole. A small hole appearing as a distinct and obvious bright point of light when examined over a light table or screen, or as a dark spot when viewed over a black surface.

4.2.2.2 Loose material. Any extra loose material or dirt particles on the filter that must be brushed off before the filter is weighed.

4.2.2.3 Discoloration. Any obvious visible discoloration that might be evidence of a contaminant.

4.2.2.4 Filter nonuniformity. Any obvious visible nonuniformity in the appearance of the filter when viewed over a light table or black surface that might indicate gradations in porosity across the face of the filter.

4.2.2.5 Other. A filter with any imperfection not described above, such as irregular surfaces or other results of poor workmanship.

4.2.3 Visually inspect each filter in front of an area light and observe for any specific defects listed above.

4.2.4 Use a renumbering stamp to code the filter on its noncollection side with a 7-digit code before tare weighing. The noncollection side of the filter is designated by the manufacturer printed number and by a mesh texture. The number code might be as follows:

Example: Filter Number Code = ***9622001***

First 2 digits = yr, such as ***96*** for 1996
Third digit = project, such as ***2***
Fourth digit = filter type, such as ***2*** for 8" x 10" quartz fiber, Whatman QMA type
Last 3 digits = filter number, such as ***001***

5. Gravimetric Determination

5.1 Introduction

5.1.1 The filter is weighed (after moisture equilibration) before and after use to determine the net weight (mass) gain. The total volume of air sampled corrected to EPA standard conditions (25EC, 760 mm Hg) is determined from the measured flow rate and the sampling time. The concentration of TSP matter in the ambient air is computed as the mass of collected particles divided by the volume of air sampled (corrected to standard conditions) and expressed in µg/std m^3 (see Inorganic Compendium Method IO-2.4). For samples collected at temperatures and pressures significantly different than standard conditions, the corrected

concentrations may differ substantially from actual concentrations Fg/m^3, particularly at high elevations. The actual particulate matter concentration can be calculated from the corrected concentration using the actual temperature and pressure during the sampling period.

5.1.2 Verify that the weighing room conditions are within the limits. Filter equilibrium and weighing should be performed under controlled atmospheric conditions--a temperature of 25 ± 10EC and a relative humidity < 50% (normally 50 ± 5% humidity).

5.1.3 Use the results from the motorized psychrometer to verify the temperature and relative humidity indicated by the hygrothermograph. Record the psychrometer values on the strip chart, along with the date, time, and your initials.

[Note: For traceability purposes, document your initials and full name in the front of the weighing room notebook.]

5.1.4 Record the room equilibration data on the Weighing Room Atmospheric Condition Form (see Table 4).

5.2 High Volume Filter Weighing Procedure

5.2.1 Filter Handling Procedure.

5.2.1.1 Filters should only be handled with finger cots or vinyl (nonpowdered) gloves. This procedure applies to filter handling in the field as well as in the weigh room.

5.2.1.2 Avoid using metal tweezers since the filters later will be used for metals analysis. When handling filter with gloved fingers or with any type of tweezers, avoid touching the sampled area.

5.2.2 Initial Weighing of High Volume Filter.

5.2.2.1 Upon receipt of new high volume filters (8" x 10" quartz fiber), take them to the climate controlled room, remove the paper and plastic envelope (wearing clean plastic gloves), place each on edge in a clean metal file rack, and cover with clean white paper towels.

5.2.2.2 Allow the filters to equilibrate in the metal file rack in the weighing room atmosphere for at least 24 h. Humidity and temperature must be within Federal Reference method specification, (i.e., < 50% and 15-35EC, respectively).

5.2.2.3 Zero the high volume balance before weighing.

5.2.2.4 Manually calibrate the balance. However, checks against two working NIST traceable weights (Class S) standards should be conducted before the daily weighing. If the difference between the traceable weights is more than 0.5 mg, do not use the balance until it has been repaired.

5.2.2.5 Record the results on the Weighing Balance Check Form (see Table 5).

5.2.2.6 Weigh each filter and record filter numbers and tare weights on the Filter Weighing Form (see Table 6).

5.2.2.7 Return the weighed filters to the plastic and paper envelopes.

5.2.2.8 Weigh filters in lots of approximately 100, if possible. After every tenth weighing, recheck the zero of the balance. The balance response should be ± 1 mg from 0. All differences should be corrected. Any difference exceeding 1 mg requires reweighing the previous ten filters. Any filter weight outside the normal range of 3.5-5.0 g requires immediate investigation. In addition, after every tenth filter weighing, the analyst should review at least one of the working standards. Once again, if this measurement disagrees from the verified value by more than 0.5 mg, reweigh the standard. If the two measurements still disagree, troubleshoot and take appropriate corrective action, which may include (1) reweighing some or all of the previously weighed filters, (2) recertifying the working standards against the laboratory primary standards, and/or (3) having a service technician repair the balance. At the end of the weighing session, reweigh both

working standards. Record the measurements on the Weighing Balance Check Form. If both do not agree within 0.5 mg, then all weighings from the previous acceptable check must be repeated.

5.2.2.9 A second analyst should reweigh 10% of the filters. If the difference between the weights is less than 1.0 mg, the results are acceptable.

5.2.2.10 If the difference is greater than this limit, wait another 24 h and reweigh them.

5.2.2.11 If the results are still outside acceptable limits, wait another 24 h and reweigh them again. Then report the last reweigh values as the pre-field tare weights.

5.2.3 Final Weighing of High Volume Filter.

5.2.3.1 Exposed filters should be logged into the laboratory computer and received in individual manila folders, with computer printed identification labels affixed. No exposed filter should be touched until this label is affixed.

5.2.3.2 Condition all filters in the manner specified by the Federal Reference Method, as documented in Sections 5.1.2 and 5.2.2.

5.2.3.3 Weigh all filters according to the Tare Weighing Procedure in Section 5.2.2. Record final weights on the Filter Weighing Form (see Table 6).

5.2.3.4 For filters not to be analyzed, put an asterisk in the space preceding the four-letter code. Leave this space blank for samples to be analyzed. Sign and date the forms.

5.2.3.5 Archive asterisked high volume filters.

5.2.3.6 Have a second analyst reweigh 10% of the filters and verify that the weights have not changed.

- If the difference between the weights is less than 2.0 mg, the results are acceptable. Use the results from the first weighing.
- If the difference is greater than this limit, reweigh 100% of that lot and use the last reweigh weight.

5.2.3.7 Calculate and report the particulate matter concentrations as:
where:

$$SPM = \frac{(W_f - W_i) \times 10^6}{V_{std}}$$

SPM = mass concentration of suspended particulate matter (TSP or PM_{10}), µg/std m^3.
W_i = initial weight of clean filter, g.
W_f = final weight of exposed filter, g.
V_{std} = air volume sampled, converted to standard conditions (25EC and 760 mm Hg), std m^3.
10^6 = conversion of g to µg.

5.3 Dichotomous and Partisol® Filter Weighing Procedure

5.3.1 Initial Weighing of Dichotomous or Partisol® Filters.

5.3.1.1 Fabric filters, 37-mm or 47 mm (as appropriate for the samples) in diameter, with a circumferential plastic reinforcing ring are usually supplied in small boxes. Open the boxes in the climate-controlled room under conditions suitable for high volume weighing. Cover with a clean paper towel and allow to equilibrate for 24 h.

5.3.1.2 Weigh filters on a Mettler microbalance; each balance is identified by a balance number.

5.3.1.3 Assign each balance a block of 7-digit sample numbers to be used sequentially. Assign a sample number to each filter when it is tared.

[Note: Inaccuracies in this aspect of the procedure will cause irremedial sample loss.]

5.3.1.4 Turn on the microbalance and allow it to warmup for at least 15 min. If the balance is used daily, leave it on at all times.

5.3.1.5 Manually calibrate the microbalance with two working NIST traceable weight (Class S) standards (for example, a 100-mg standard and a 200-mg standard). If the difference between the traceable weights is more than 3 µg, reweigh the working standards. Record the Results on the Weighing Balance Check Form (see Table 7).

5.3.1.6 If the values still disagree, troubleshoot and take appropriate corrective action, which may include (1) recertifying the working standards against the laboratory primary standards, and/or (2) having a service technician repair the microbalance.

5.3.1.7 Using clean nonserrated tweezers that will not damage the filter, remove the filter from the Lexan jig or filter cassette and place it on the weighing pan. Turn the release lever to "1" and dial in tare weights until a reading between 0.000 and 7.000 is obtained. Allow the reading to stabilize (which may require 2 to 4 min). Record the reading and the dialed-in tare weight on the Filter Weighing Form (see Table 8). Return the release lever to "0" and remove the filter from the weighing pan.

[Note: Do not use metal tweezers.]

5.3.1.8 Place a white label on a clean 50-mm diameter plastic petri dish (tight fitting lid type).

5.3.1.9 Assign a sample number to each filter (from those assigned to that balance), taking extreme care to avoid duplication or missed numbers.

5.3.1.10 Record the assigned sample number on the petri dish label, leaving sufficient room for one more letter to be written following the number. Do not record the balance number on this label.

5.3.1.11 Record the balance number, the assigned sample number, the dialed-in tare weight, and the digital-displayed tare weight on the sample form. Number each sheet of the form sequentially in the upper right-hand corner. Write "Tare Weight, Dichot or Partisol® Filters" on the top of each sheet. When bound, these forms may serve as the laboratory notebook.

5.3.1.12 Place the weighed filter in its numbered petri dish for future use.

5.3.1.13 After every tenth filter weighing, the analyst should check the “zero” and reweigh at least one of the working standard. Record the measurement on the Weighing Balance Check Form. Once again, if this measurement disagrees from the verified value by more than 3 µg, reweigh the standard. If the two measurements still disagree, troubleshoot and take appropriate corrective action, which may include (1) reweighing some or all of the previously weighed filters, (2) recertifying the working standards against the laboratory primary standards, and/or (3) having a service technician repair the balance. At the end of the weighing session, reweigh both working standards. Record the measurements on the Weighing Balance Check Form. If both do not agree within 3 µg then all weighings from the previous acceptable check must be repeated.

5.3.1.14 At the end of the weighing session, at least 10% of the filters should be reweighed by a second analyst. Record the replicate measurement on the Filter Weighing Form (see Table 6). If the replicate measurement disagrees from the original measurement by more than 15 µg, reweigh the filter. If the measurements still disagree, troubleshoot and take appropriate corrective action, which may include (1) reweighing all or some of the previously weighed filters, (2) reweighing the working standards, or (3) having a service technician repair the microbalance. The analyst should not attempt to repair the microbalance.

5.3.1.15 Return the filter to the filter-handling container, replace the lid, and return it to conditioning chamber to protect it from contamination prior to sampling.

5.3.2 Final Weighing of Dichotomous or Partisol® Filter.

5.3.2.1 Filters should be returned from the field with a computer printed label affixed to the petri dish. The label should contain a five-character identification code that is different from the original sample number, a balance ID, the balance tare, and other information. All filters should be accompanied by extra labels. Some will have the words "To Be Analyzed" on the labels. The filter in each petri dish should rest in a Lexan jig or filter cassette.

5.3.2.2 Weigh each filter on the balance on which its tare weight was obtained. In the climate-controlled room, group the filters according to recorded balance numbers. Open the petri dishes, making certain that lids are placed under the bottoms and that no mixup occurs. Cover with a clean white paper towel and allow to equilibrate.

5.3.2.3 Repeat Section 5.3.1.4 to 5.3.1.6 of the filter tare weighing procedure.

5.3.2.4 Using clean, nonserrated tweezers that will not damage the filter, remove the filter from the Lexan jig or filter cassette and place it on the weighing pan. Dial in the tare weight recorded on the information label and turn the release lever to"1." Allow the reading to stabilize (which may require 2 to 4 min). Record the reading and the dialed-in tare weight. Return the release lever to “0" and remove the filter from the weighing pan.

5.3.2.5 After every tenth filter weighing, the analyst should check the “zero” and reweigh at least one of the working standards. Record the measurement on the Weighing Balance Check Form. Once again, if this measurement disagrees from the verified value by more than 3 ug, review the standard. If the two measurements still disagree, troubleshoot and take appropriate corrective action, which may include (1) reweighing some or all of the previously weighed filters, (2) recertifying the working standards against the laboratory primary standards, and/or (3) having a service technician repair the balance. At the end of the weighing session, reweigh both working standards. Record the measurements on the Weighing Balance Check Form. If both do not agree within 3 µg, then all weighings from the previous acceptable check must be repeated.

5.3.2.6 At the end of the post weighing session, at least 10% of the filters should be reweighed by a second analyst. Record the replicate measurement on the Filter Weighing Form (see Table 8). If the replicate measurement disagrees from the post measurement by more than 15 µg, reweigh the filter. If the measurements still disagree, troubleshoot and take appropriate corrective action, which may include (1) reweighing all or some of the previously weighed filters, (2) reweighing the working standards, and/or (3) having a service technician repair the microbalance. The analyst should not attempt to repair the microbalance.

5.3.2.7 If the dichotomous filter is not to be analyzed, use the tweezers to place it in a small glass envelope to which one of the extra labels has been affixed. Place an asterisk before the five-character code on the form. Deliver these filters to the filter bank for archiving.

5.3.2.8 If the filter is to be analyzed, use tweezers to carefully put it back into the petri dish. Place the petri dish **carefully** in a box.

5.3.2.9 Place a label on a sheet of 8 ½" x 11" paper for NAA, XRF, or other analysis as appropriate. Indicate the page number and balance number on each list. Keep the samples in the box in an order corresponding with the lists.

5.3.2.10 Without jostling the box, deliver it, the two lists, and the original Field Test Data Sheets with two copies of each to the sample custodian who will initial the original forms and return them upon receipt.

5.3.2.11 Calculate and report the particulate matter concentration for both fine and coarse samples utilizing the following equation:

$$PM = \frac{(W_f - W_i) \times 10^6}{V_{std}}$$

where:

PM = mass concentration of particulate matter (TSP, fine or coarse friction), µg/std m^3.

W_i = average initial weight of clean filter, g.

W_f = average final weight of exposed filter, g.

V_{std} = air volume sampled, converted to standard conditions, std m^3 (see Inorganic Compendium Method IO-2.4).

10^6 = conversion of g to µg.

5.4 Transport of Filters

5.4.1 After collecting samples, transport the filters to the laboratory, taking care to minimize contamination and loss of the sample. Glass fiber filters should be transported or shipped in a shipping envelope. Cover the exposed surface of the membrane filters with an unexposed filter and seal the filter in plastic filter holders.

5.4.2 Assign numbers to the filters and log them into the data record form, ensuring that any necessary sampling information is included (Untreated filter samples may be stored indefinitely.)

5.4.3 Provide one blank sample with every 10 actual samples. No air is drawn through the blank filter, but it is subjected to the same handling and shipping manipulations as the actual samples.

6. Extraction of Glass Fiber Filters in Preparation for Metal Analysis

6.1 Introduction

This section describes both a microwave-extraction procedure and a hot-acid extraction procedure to extract inorganics from the particulate quartz glass-fiber filter. Following extraction, target analytes are analyzed by ICP, ICP/MS, FAA, or GFAA.

6.1.1 Ambient air quartz fiber filters should be received folded in half lengthwise with the particulate material inward and enclosed in protective envelopes. Store these protective envelopes approximately 15E-30EC until analysis.

6.1.2 The maximum sample holding times is usually 180 days. Analyze the samples within 180 days, even if these times are less than the maximum data submission times allowed.

6.2 Microwave Extraction Procedure

6.2.1 Filter Cutting Procedure.

6.2.1.1 Cut a 1" x 8" strip from the 8" x 10" filter using a template (see Figure 1) and cutting tool (see Figure 2) as described in the Federal Reference Method for lead. Use a laboratory microwave extraction system to extract the metals with a hydrochloric/nitric acid solution. After cooling, mix the digestate and use

Acrodisc® syringe filters to remove any insoluble material. Microwave extraction is used to prepare samples for ICP, ICP/MS, FAA, or GFAA.

6.2.1.2 Prior to use, acid wash the plexiglass filter template, the polysulfone centrifuge tubes and caps, and all other laboratory equipment that will come into contact with the filter samples to prevent contamination.

6.2.1.3 Using vinyl gloves, place the acid-cleaned filter template and cover inside a balance hood for cutting quartz fiber filters.

6.2.1.4 Wipe plexiglass template base, cover, and cutting blade with a clean, dry Kimwipe® to prevent sample cross-contamination.

6.2.1.5 Unfold the 8" x 10" quartz filter to be sectioned and carefully place sampled side up (numbered side down) within the plexiglass template filter margins.

6.2.1.6 Carefully (without disturbing sampled area of filter) place the grooved cover, notch side down, within the margins of the base template. Use a clear cutting blade to cut a 1" x 8" strip.

6.2.1.7 Using gloved fingers, accordion-fold or tightly roll the filter strip and transfer on edge to an acid cleaned polysulfone® tube, labeled with wax pencil. DO NOT use barcodes or tape in microwave.

6.2.1.8 Clean filter template between samples with dry Kimwipes®. (Gloves should be changed after 50 filters to minimize cross-contamination.)

6.2.1.9 Duplicate sample frequency is normally 1 per 20 field samples (see Table 9). Prepare a sample filter duplicate by moving the template cover to a second portion of the field collected filter. Cut an additional filter strip by moving the template cover to a second section of the filter and repeat Sections 6.2.1.6 through 6.2.1.8 above using a separate polysulfone tube.

6.2.1.10 Select a field collected filter for matrix spiking. In addition to the filter strip cut for determining metals, section a second portion of the filter, and fortify (spike) with target metals.

6.2.1.11 Prepare matrix spike samples at a frequency of 1 per 20 field samples or a minimum of 1 per extraction day (see Table 9). Move the template to a second section of the filter and repeat Sections 6.2.1.6 through 6.2.1.8, using a separate polysulfone tube and spike as shown in Table 9.

6.2.2 Microwave Calibration Procedure. Calibration of the microwave unit is a critical step prior to its use. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined, which allows the analyst to relate power in Watts to the partial power setting of the unit (% Power).

Calibration of a laboratory microwave unit (see Figure 3) depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, the calibration can be a three-point calibration in the range of 50% to 100% power. If the unit does not prove linear ($\pm$10 W) using the three-point technique, a multiple-point calibration is necessary. A bracketed calibration range of the digesting power to be used is recommended for determining the calibration points. If the unit power calibration needs multiple-point calibration, the point where the linearity begins must be identified. For example, a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, and 50% power settings can be applied and the data plotted. The nonlinear portion of the calibration curve can be excluded or restricted. Each percent is equivalent to approximately 5.5-6.5 W and becomes the smallest unit of power that can be controlled. If 20-40 W are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

6.2.3 Microwave Power Evaluation. The equation in the following section evaluates the power available for heating in a microwave cavity. The variables are determined by measuring the temperature rise in 1 kilogram of water exposed to electromagnetic radiation for a fixed period of time. The following procedure is used for evaluating each calibration point, represented as % power output for each microwave.

6.2.3.1 Measure and record a 1 kilogram (1,000 g ± 0.1 g) sample of room temperature (23E ± 2EC) distilled water in a thick-walled microwave transparent (Teflon®) beaker for each calibration point.

6.2.3.2 Measure and record the initial temperature of the water, (T_i), to within 0.1EC. The starting temperature should be between 22 and 26EC.

6.2.3.3 Place the Teflon® beaker in microwave and irradiate at full power (100% point) for 2 min (120 s). Each calibration point (i.e., 100%, 50% or multi-points) requires a separate clean beaker containing water at room temperature.

6.2.3.4 Remove beaker from the microwave and measure and record the maximum final temperature (T_f) to 0.1EC, within 30 s of the end of irradiation. This process should be done while stirring continuously (an electronic stirrer using a large stir bar works best).

Calculate the microwave power according to the following formula:

$$\text{Power} = \frac{K \times C_p \times M \times \Delta T}{t}$$

$$\frac{K \times C_p \times M}{t} = 34.87$$

$$\text{Power} = 34.87 \times \Delta T$$

where:

Power = The apparent power absorbed by the sample, watts (W = joule-s^{-2}).
K = The conversion factor for thermochemical calories-s^{-1} to W = 4.184.
C_p = The heat capacity, thermal capacity, or specific heat (cal-g^{-1}-EC^{-1} = 1.0 for water).
M = The mass of the sample, grams.
ÎT = $T_f - T_i$, EC.
t = Time, s.

6.2.3.5 Derive an equation for the linear portion of the calibration range and determine the equivalent value in watts of the arbitrary setting scale. Use the actual power in watts to determine the appropriate setting of the particular microwave unit being used. Each microwave unit will have its own (% power) setting that corresponds to the actual power (in wattage) delivered to the samples.

6.2.3.6 An initial multipoint power evaluation should be performed for each microwave unit. If linear, the calibration should be checked on a regular basis, using the 3-point calibration verification routine. A single point verification may be appropriate when utilizing a single power output for digestion. If any part of the power source to the microwave has been serviced or altered, the entire calibration must be reevaluated.

6.2.4 Cleaning Procedure for PFA Vessels. All digestion vessels must be acid cleaned and rinsed with reagent water prior to use to prevent contamination.

6.2.4.1 Wash each PFA vessel with deionized detergent and rinse with reagent water.

6.2.4.2 Add 10 mL concentrated HNO_3 to each of 12 vessels, cap, and place in microwave.

6.2.4.3 Heat vessels at 100% power in microwave for 10 min as recommended by CEM (microwave manufacturer). Rinse the vessels with copious amounts of deionized, distilled water prior to use for any

analyses. If only 6 vessels are to be cleaned, 70% power may be utilized, which corresponds to approximately 5% per vessel.

6.2.5 Digestion Procedure for Microwave Extraction For Ambient Filter Samples.

[Note: Nitric and hydrochloric acid fumes are toxic. Prepare in a well-ventilated fume hood. Mixing results in an exothermic reaction. Stir slowly.]

6.2.5.1 Using vinyl gloves or plastic forceps, retrieve the filter strip from Section 6.2.1 and place on its edge in a labeled centrifuge tube. Using the plastic forceps, crush the filter strip down into the lower portion of the centrifuge tube to ensure acid volume will cover entire filter.

[Note: A breathing mask and vinyl gloves are required for safety of personnel handling dry glass-fiber filters. The breathing mask prevents the inhalation of minute glass shards and particulate material. The gloves protect the skin from the same materials and also prevent contamination of the sample by skin secretions. A recommended alternate to the use of a breathing mask would be performing cutting and transfer operations involving sample filters in a laminar flow hood, if available.]

[Note: More than one strip from a filter should be extracted to ensure adequate sample volume for sample and QC sample analysis. Blank filter samples should be extracted and analyzed, and digestion blanks should be run to ensure low levels of metals in the reagents used.]

6.2.5.2 Using a preset calibrated automatic dispensing pipette or Class A glass pipette, add 10.0 mL of the extraction solution to each of the centrifuge tubes. The acid should cover the strip completely. The sequence of adding the filter strip and acid to the centrifuge tube may be reversed, if more convenient, without affecting the results. Place the centrifuge tube in a Teflon® PFA vessel containing 31 mL of deionized water. Continue this process for a total of 12 samples to maximize microwave capacity.

6.2.5.3 Place the PFA vessel caps with the pressure release valves on the vessels hand-tight and tighten using the capping station to a constant torque of 12 ft-lb. Weigh and record the capped vessel assembly to the nearest 0.01 g. Place the vessels in the microwave carousel. Connect each sample vessel to the overflow vessel using the Teflon® PFA connecting tubes (see Figure 3).

6.2.5.4 Place the carousel containing the 12 vessels onto the turntable of the microwave unit. Any vessels containing 10 mL of acid solution for analytical blank purposes are counted as sample vessels. Irradiate the sample vessels at 486 W (power output) for 23 min. (Based on the calibration of the microwave as previously described). If fewer than 12 samples are to be digested, adjust the microwave system by reducing the power so that equivalent digesting power is delivered to the smaller sample batch. Generally, each vessel represents approximately 5% power. Therefore, a reduction in W would be reduced by 30% if only 6 vessels are digested. This reduction is only approximate, and each microwave unit will produce a different level of power output.

6.2.5.5 At the end of the microwave program, allow the pressure to dissipate (venting may be utilized with caution), then remove the carousel containing the vessels and cool in tap water for 10 min. Weigh the capped vessels assembly to the nearest 0.01 g and compare to the initial weight to verify no loss of sample. The initial and final weights should compare within 0.1 g. If the initial and final weights do not agree within 0.01 g, the appropriate action must be taken which may include rejecting the digested sample. Using the capping station uncap the microwave vessels, remove the labeled centrifuge tubes containing samples and discard the water in the PFA vessels.

6.2.5.6 Using a calibrated automatic dispensing pipette or a Class A glass pipette, add 10 mL of deionized distilled water to each centrifuge tube. Cap the centrifuge tube tightly and vortex (mix) the contents thoroughly for 2-3 minutes to complete extraction. Using a nylon or teflon syringe pull-up a volume

of sample from the centrifuge tube, place Acrodisc filter on syringe and dispense into a prelabeled sterile 15 mL centrifuge tube. Continue until centrifuge tube contains 10 mL of filtered digestate.

6.2.5.7 The final extraction volume is 20 mL based upon the above procedure. The final extraction solution concentration is 3% HNO_3/8% HCl. The filtered sample is now ready for analysis. Store for subsequent analysis by one or more of the Inorganic Compendium methods.

6.3 Hot Acid Extraction Procedure

6.3.1 Introduction. A hot extraction procedure to solubilize metals from the glass-fiber filter for subsequent analysis by ICP, ICP/MS, FAA, or GFAA is described in this method. An acid extraction solution is used to extract the metals from the quartz filter on a hot-plate.

6.3.2 Summary of Method.

6.3.2.1 Use the hot-acid extraction procedure as an alternate when microwave technology is not available.

6.3.2.2 Cut a 1" x 8" strip from the 8" x 10" filter as described in Federal Reference Method for lead. The inorganics are extracted from the filter strip by a HCl/HNO_3 acid solution using a hot acid extraction procedure. After cooling, pour the digestate rinses to a volumetric flask and dilute to volume. Filter to remove any insoluble material.

6.3.3 Hot Acid Extraction Procedure.

6.3.3.1 Using vinyl gloves or plastic forceps, retrieve the strip from Section 6.2.1 and place it in a labeled 150 mL Griffin beaker. Place the filter strip down into the lower portion of the beaker to ensure acid volume will cover entire filter.

[Note: More than one strip from a filter should be extracted to ensure adequate sample volume for sample and QC sample analysis. Blank filter samples should be extracted and analyzed and digestion blanks should be run to ensure low levels of metals in the reagents used.]

6.3.3.2 Using a preset calibrated automatic dispensing pipette or Class A glass pipette, add 10 mL of extracting acid (see Section 6.2.5.2) for analysis.

[Note: The acid should cover the strip completely.]

6.3.3.3 Place beaker on the hot-plate, contained in a fume hood, and reflux gently while covered with a watch glass for 30 min. Do not allow sample to dry. Remove the beakers from the hot-plate and allow to cool.

[Caution: Nitric acid fumes are toxic.]

6.3.3.4 Rinse the beaker walls and wash with D.I. water. Add approximately 10 mL reagent water to the remaining filter material in the beaker and allow to stand for at least 30 min. This critical step must not be deleted; it allows the acid to diffuse from the filter into the rinse. Transfer the extraction fluid in the beaker to a 20 mL volumetric flask or other graduated vessel. Rinse the beaker and any remaining solid material with Type I water and add the rinses to the flask. Some solids from the filter may be transferred to the flask with the rinses; this is acceptable. Dilute to the mark with Type I water and shake.

6.3.3.5 Using a nylon or Teflon® syringe, pull-up a volume of sample from the centrifuge tube, place disc filter on syringe, and dispense into a prelabeled sterile 15 mL centrifuge tube. Continue until centrifuge tube contains 10 mL of filtered digestate.

6.3.3.6 The final extraction volume is 20 mL based upon the above procedure. The final extraction solution concentration is 3 % HNO_3/8% HCl. The filtered sample is now ready for analysis. Store for subsequent analysis by one or more of the Inorganic Compendnium methods.

TABLE 1. CHARACTERISTICS OF FILTER MEDIUM

Cellulose Fiber (Cellulose Pulp)
• Low ash • Maximum temperature of 150EC • High affinity for water • Enhances artifact formation for $SO^{=}_{4}$ and NO^{-}_{3} • Good for x-ray/neutron activation analysis • Low metal content
Quartz Fiber (Quartz spun with/without organic binder)
• Maximum temperature up to 540EC • High collection efficiency • Non-hydroscopic • Good for corrosive atmospheres • Very fragile however • Difficult to ash; good with extraction
Synthetic Fiber (Teflon® and Nylon®)
• Collection efficiency > 99% for 0.01 µm particles • Low artifact formation • Low impurities • Excellent for X-ray analysis • Excellent for determining total mass due to non-hydroscopic nature • Nylon fiber good for HNO_3 collection
Membrane Fiber (Dry gel of cellulose esters)
• Fragile; requires support pad during sampling • High pressure drop • Low residue when ashed

TABLE 2. SUMMARY OF USEFUL PHYSICAL PROPERTIES OF VARIOUS FILTER MEDIUMS

Filter and Filter Composition	Density, mg/cm^2	pH	Filter Efficiency %
Teflon® (Membrane) $(CF_2)_n$(2 µm Pore Size)	0.5	Neutral	99.95
Cellulose (Whatman 41) $(C_6H_{10}O_5)_n$	8.7	Neutral (Reacts with HNO_3)	58% at 0.3 µm
Glass Fiber (Whatman GF/C)	5.16	Basic pH - 9	99.0
"Quartz" Gelman Microquartz	6.51	pH - 7	98.5
Polycarbonate (Nuclepore) $C_{15}H_{14}$ + CO_3 (0.3 µm Pore Size)	0.8	Neutral	93.9
Cellulose Acetate/Nitrate Millipore $(C_9H_{13}O_7)_n$ (1.21 µm Pore Size)	5.0	Neutral (Reacts with HNO_3)	99.6

TABLE 3. EXAMPLE OF TYPICAL BACKGROUND METAL CONCENTRATION (µg/FILTER) OF VARIOUS GRADES AND TYPES OF FILTERS

Metal	1	41	42	542	Filter 17ch	Grades GF/A	EPM 2K	934QH	QMA	QMB
Al	1	2	2	1	--	4,300	170	2,950	4	--
Ag	--	--	--	--	--	< 1	< 1	--	< 1	--
As	< 0.02	< 0.02	< 0.02	< 0.02	--	< 6	< 6	--	< 6	--
B	1	< 2	2	2	--	6,100	42	--	42	--
Ba	< 1	< 1	< 1	< 1		8,500	50	< 1	10	--
Be	--	--	--	--	--	0.2	< 1	0.1	< 1	< 1
Bi	--	--	--	--	--	0.3	< 4	0.8	< 4	7
Ca	185	13	13	9	29	2,500	540	7,000	85	--
Cd	--	--	--	--	--	1	< 1	0.8	0.2	< 1
Co	--	--	--	--	--	11	< 1	5.5	1.1	< 1
Cr	0.3	0.3	0.3	0.7	--	0.2	4.5	3.0	1.6	0.7
Cu	1.2	0.1	0.4	0.2	0.6	56.0	1	7	3.4	3.4
Fe	5.0	6.0	6.0	3.0	5.0	100	15	265	23	29
Mg	< 0.005	--	< 0.005	< 0.005	--	--	--	--	--	--
K	4.0	1.5	1.5	0.6	7	775	573	125	--	--
Mg	7	1.8	1.8	1.0	6	1,090	238	2,800	--	--
Mn	0.1	< 0.05	< 0.05	< 0.05	--	8.0	< 1	2	0.5	< 1
Mo	--	--	--	--	--	2.0	< 2	4	< 2	< 1
N	28	--	12	260	--	--	--	--	--	--
Na	160	40	37	8	30	1,830	1,020	1,100	280	--
Ni	--	--	--	--	--	6.0	--	2.5	3.4	2.2
Pb	0.4	0.2	0.2	0.1	1	10	2.5	2.0	2.3	8.3
S	17	< 5	< 5	< 5	--	26	--	--	--	--
Sb	< 0.02	< 0.02	< 0.02	< 0.02	--	< 4	< 4	--	< 4	--
Si	15	< 2	< 2	< 2	--	--	--	--	--	--
Ti	--	--	--	--	--	0.1	< 1	< 30	< 1	< 4
V	--	--	--	--	--	0.1	--	10	--	< 4
Sn	2.5	0.6	0.6	0.3	--	5,500	15	34	10	13

TABLE 4. EXAMPLE WEIGHING ROOM ATMOSPHERIC CONDITION FORM

Equilibrium Period				Temperature Limits = 15EC to 35EC			Relative Humidity Limits = < 50%			Name
Begin Date	Begin Time	End Date	End Time	Max-Min	Avg	Limits met?	Max-Min	Avg	Limits met?	

TABLE 5. EXAMPLE WEIGHING BALANCE CHECK FORM

Date	Time	Balance Type	Balance ID	Class S Weights Serial No. or ID	mg			Limit = 0.5 mg Limits met?	Name
					Class S weight	Balance weight	Difference		

TABLE 6. EXAMPLE FILTER WEIGHING FORM

Filter No.	Pre-field Initial Weighing		10% Second Weighing by Second Analyst (Limit = 1.0 mg)			Post-field Final Weighing		10% Second Weighing by Second Analyst (Limit = 2.0 mg)			
	Weight (mg)	Name-Date	Weight (mg)	Diff. (mg)	Limit met?	Name-Date	Weight (mg)	Name-Date	Weight (mg)	Diff. (mg)	Limit met?	Name-Date

TABLE 7. EXAMPLE WEIGHING BALANCE CHECK FORM

Date	Time	Balance Type	Balance ID	Class S Weights Serial No. or ID	mg			Limit = 3 ug Limits met?	Name
					Class S weight	Balance weight	Difference		

TABLE 8. EXAMPLE FILTER WEIGHING FORM

Filter No.	Pre-field Initial Weighing		10% Second Weighing by Second Analyst (Limit = 15 Fg)				Post-field Final Weighing		10% Second Weighing by Second Analyst (Limit = 15 Fg)			
	Weight (mg)	Name-Date	Weight (mg)	Diff. (mg)	Limit met?	Name-Date	Weight (mg)	Name-Date	Weight (mg)	Diff. (mg)	Limit met?	Name-Date

TABLE 9. EXAMPLE QUALITY CONTROL SAMPLES

Type	Frequency	Contains 1"x8" filter strip	Comments[a]
Method Blank	1 per 20 samples	No	Containing reagents only, to evaluate background contributions from reagents.
Filter Lot Blank	1 per filter lot change	Yes	Analyzed prior to use of new filter lot.
Filter Duplicate	1 per 20 samples	Yes	This is a second 1"x8" filter strip cut from a single field sample.
Matrix Spike[b]	1 per 20 samples	Yes	See individual methods.
LCS[c]	1 per extraction day	Yes	See individual methods.

[a]These multimetal stock standards can be acquired from Spex Industries, Inc., Inorganic Ventures Inc., or equivalent.
[b]The matrix spike (MS) is a 1"x8". strip cut from a field sample filter and spiked at a target level.
[c]The Lab Control Sample (LCS) is a blank filter spiked with the same concentration of metals as the matrix spike.

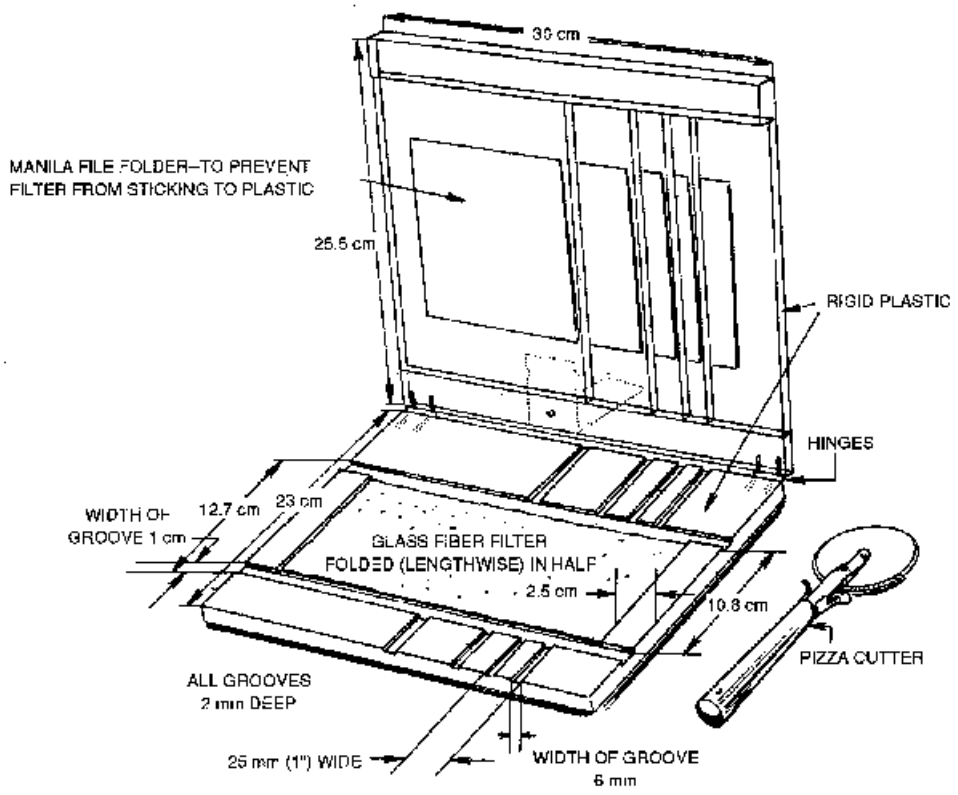

Figure 1. Example of templates for cutting filters.

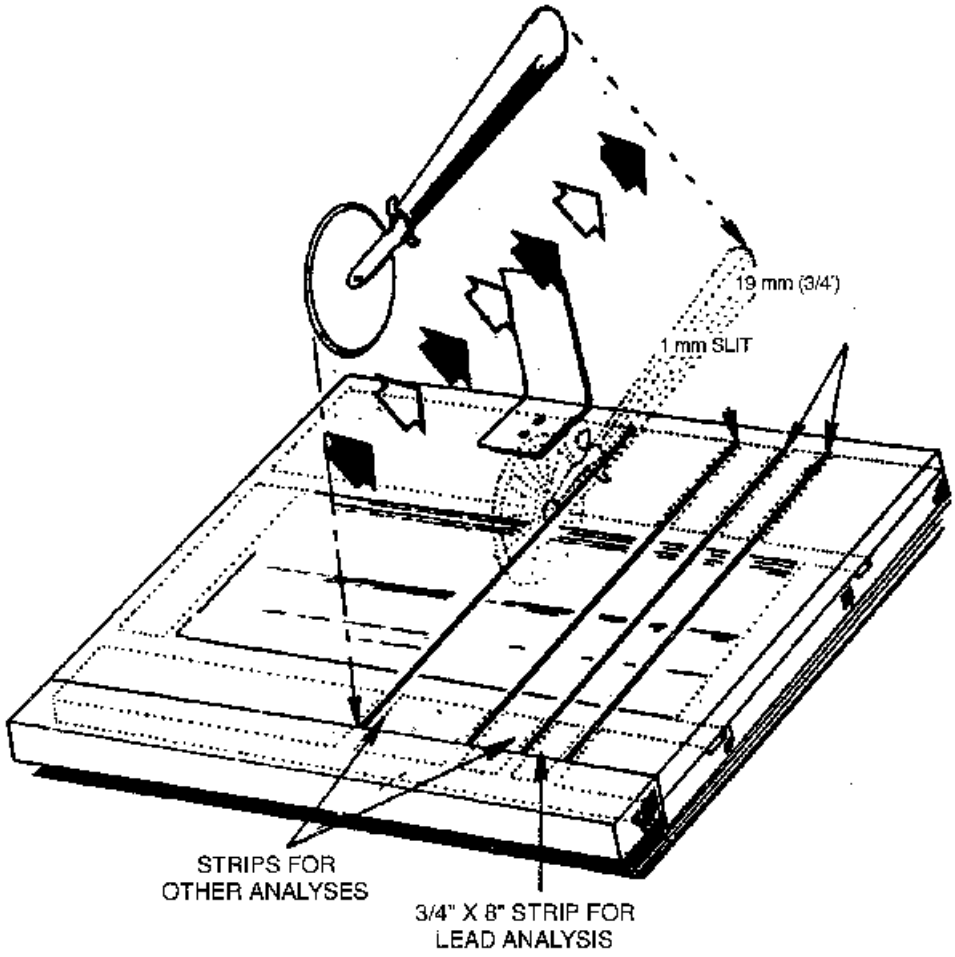

Figure 2. Diagram of filter cutting procedure.

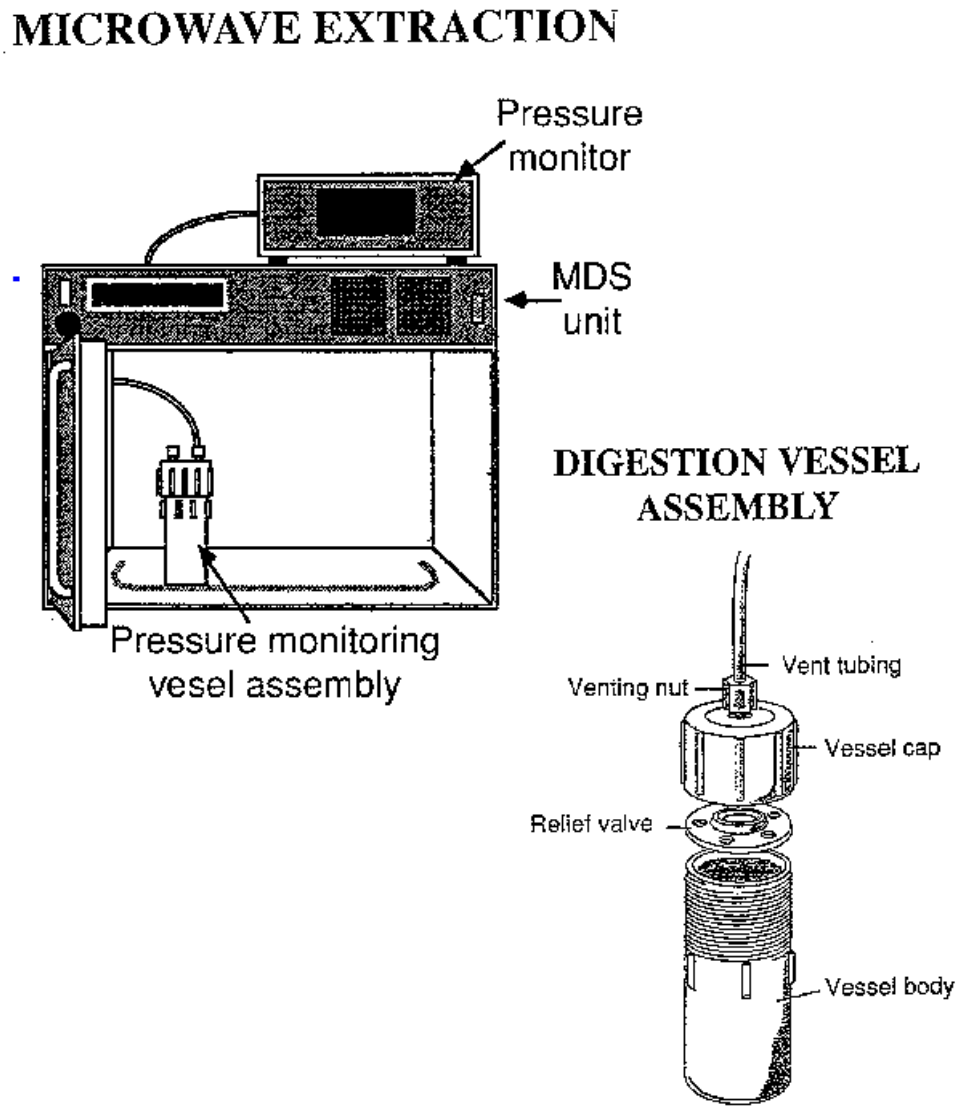

Figure 3. Example of microwave digestion system.

APPENDIX C

USEPA Compendium Method IO-3.4

EPA/625/R-96/010a

Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air

Compendium Method IO-3.4

DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA (ICP) SPECTROSCOPY

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

June 1999

Method IO-3.4

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Author(s)

- William T. "Jerry" Winberry, Jr., EnviroTech Solutions, Cary, NC

Peer Reviewers

- Dewayne Ehman, Texas Natural Resource Conservation Committee, Austin, TX
- David Harlos, Environmental Science and Engineering, Gainesville, FL
- Doug Duckworth, Lockheed-Martin Energy Research, Oak Ridge, TN
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

DISCLAIMER

Method IO-3.4
Determination of Metals in Ambient Particulate Matter Using Inductively Coupled Plasma (ICP) Spectroscopy

TABLE OF CONTENTS

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Chapter IO-3
CHEMICAL SPECIES ANALYSIS
OF FILTER-COLLECTED SPM

Method IO-3.4
DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING INDUCTIVELY COUPLED PLASMA (ICP) SPECTROSCOPY

1. Scope

1.1 Suspended particulate matter (SPM) in air generally is a complex multi-phase system consisting of all airborne solid and low vapor pressure liquified particles having aerodynamic particle sizes ranging from below 0.01-100 µm and larger. Historically, SPM measurement has concentrated on total suspended particulates (TSP), with no preference to size selection.

1.2 On July 1, 1987, the U. S. Environmental Protection Agency (EPA) promulgated a new size-specific air quality standard for ambient particulate matter. This new primary standard applies only to particles with aerodynamic diameters $\leq$10 µm (PM_{10}) and replaces the original standard for TSP. To measure concentrations of these particles, the EPA also promulgated a new federal reference method (FRM). This method is based on the separation and removal of non-PM_{10} particles from an air sample followed by filtration and gravimetric analysis of PM_{10} mass on the filter substrate. In 1997, the PM_{10} standard was replaced with the national ambient air quality standard (NAAQS) for $PM_{2.5}$.

1.3 The new primary standard (adopted to protect human health) limits $PM_{2.5}$ concentrations to 50 µg/m^3, averaged over a 24-h period. These smaller particles are able to reach the lower regions of the human respiratory tract and, therefore, are responsible for most of the adverse health effects associated with suspended particulate pollution. The secondary standard, used to assess the impact of pollution on public welfare, has also been established at 15 µg/m^3 for an annual average.

1.4 Ambient air SPM measurements are used (among other purposes) to determine whether defined geographical areas are in attainment or non-attainment with the NAAQS for $PM_{2.5}$. These measurements are obtained by the states in their state and local air monitoring station (SLAMS) networks as required under 40CFR Part 58. Further, Appendix C of Part 58 requires that the ambient air monitoring methods used in these EPA-required SLAMS networks must be methods that have been designated by EPA as either reference or equivalent methods.

1.5 The procedure for analyzing the elemental metal components in ambient air particulate matter collected on high volume filter material is described in this method. The high volume filter material may be associated with either the TSP or PM_{10} sampler, as delineated in Inorganic Compendium Method IO-2.1.

1.6 Filters are numbered, pre-weighed, field deployed and sampled, returned to the laboratory, extracted using microwave or hot acid, then analyzed by inductively coupled plasma (ICP) spectroscopy. The extraction procedure is accomplished by following Inorganic Compendium Method IO-3.1.

1.7 This method should be used by analysts experienced in the use of ICP, the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of 6-months experience with commercial instrumentation is required.

1.8 Those metals and their associated method detection limit (MDL) applicable to this technology are listed in Table 1.

2. Applicable Documents

2.1 ASTM Standards

- D1356 *Definition of Terms Related to Atmospheric Sampling and Analysis.*
- D1357 *Planning the Sampling of the Ambient Atmosphere.*
- D4096 *Application of the High Volume Sample Method for Collection and Mass Determination of Airborne Particle Matter.*

2.2 Other Documents

- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide for Environmental Quality Assurance*, EPA-600/R-94/038a.
- U. S. Environmental Protection Agency, *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods (Interim Edition)*, EPA-600/R-94/038b.
- *Reference Method for the Determination of Particulate Matter in the Atmosphere*, 40 CFR 50, Appendix J.
- *Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)*, 40 CFR 50, Appendix B.
- *Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air, Federal Register* 43 (194): 46258-46261.
- U. S. EPA Project Summary Document (1).
- U. S. EPA Laboratory Standard Operating Procedures (2).
- Scientific Publications of Ambient Air Studies (3-7).

3. Summary of Method

3.1 Instrument Description

3.1.1 The analytical system is an inductively coupled plasma atomic emission spectrometer, as illustrated in Figure 1. The plasma is produced by a radio frequency generator. The current from the generator is fed to a coil placed around a quartz tube through which argon flows. The oscillatory current flowing in the coil produces an oscillating magnetic field with the lines of force aligned axially along the tube. The argon is seeded with electrons by momentarily connecting a Tesla coil to the tube where the plasma forms inside. The ions in the gas tend to flow in a circular path around the lines of force of the oscillatory magnetic field and the resistance to their flow produces the heat. To avoid melting the silica tube, a flow of argon is introduced tangentially in the tube, which centers the plasma away from the walls of the tube. The plasma is formed in the shape of a toroid or doughnut, and the sample is introduced as an aerosol through the middle of the toroid. The hottest part of the plasma is in the ring around the center of the toroid, where temperatures of about 10,000 K are achieved. Through the center of the toroid where the sample is introduced, the temperature is somewhat lower, and the sample is subjected to temperatures of about 7,000 K. From the very hot region in the plasma and just above it, a continuum is radiated because of the high electron density. Above this

region, the continuum emission is reduced as the temperature falls and the spectral lines of the elements in the sample may be observed. Since this plasma is generated in an inert atmosphere, few chemical interferences exist.

3.1.2 The spectrum is resolved in a spectrometer. The relative intensities and concentrations of the elements are calculated by a small computer or processor. Samples containing up to 61 preselected elements can be analyzed by ICP simultaneous analysis at a rate of 1 sample per minute. The ICP technique can analyze a large range of concentrations. A single calibration curve can accomodate changes in concentration of 5 orders of magnitude.

3.2 Sample Extraction

Two extraction procedures may be performed: hot acid extraction or microwave extraction, as documented in Inorganic Compendium Method IO-3.1. Extraction involving hot acids is hazardous and must be performed in a well-ventilated fume hood.

3.3 Sample Analysis

A technique for the simultaneous or sequential multi-element determination of trace elements in an acid solution is described in this Compendium method (see Figure 2). The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency ICP. The spectra are dispersed by a grating spectrometer, and the intensities of the line are monitored by photo multiplier tubes. The photo currents from the photo multiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Data is processed by computer and yields micrograms of metal of interest per cubic meter of air sampled ($\mu g/m^3$).

4. Significance

4.1 The area of toxic air pollutants has been the subject of interest and concern for many years. Recently, the use of receptor models has documented the need for elemental composition of atmospheric aerosol into components as a means of identifying their origins. The assessment of human health impacts, resulting in major control actions by federal, state, and local governments, is based on these data. Accurate measures of toxic air pollutants at trace levels are essential for proper assessments. The advent of inductively coupled plasma spectroscopy has improved the speed and performance of metals analysis in many applications.

4.2 ICP spectroscopy is capable of quantitatively determining most metals at levels that are required by federal, state, and local regulatory agencies. Sensitivity and detection limits may vary from instrument to instrument.

5. Definitions

[Note: Definitions used in this method are consistent with ASTM methods. All pertinent abbreviations and symbols are defined within this document at point of use.]

5.1 Autosampler. Device that automatically sequences injections of sample solutions into the ICP.

5.2 Background Correction. Removing a high or variable background signal, using only the peak height of intensity for calculating concentration. Instruments measure background at one or more points slightly off the emission wavelength and subtract the intensity from the total intensity measured at the analytical wavelength.

5.3 Channels. Simultaneous ICPs have an array of photo multiplier tubes positioned to look at a fixed set of elements (wavelengths); each wavelength is a "channel," which varies by instrument.

5.4 Detection Limits. Determined by calibrating the ICP and determining the standard deviation of apparent concentrations measured in pure water. The result (F) is multiplied by a factor from 2 to 10 (usually 3) to define a "detection limit." Complex sample matrices result in a higher background noise than pure water, so actual detection limits vary considerably with sample type. It is recommended that an instrument detection limit (IDL) be determined in a standard whose concentration is about three times the expected detection limit.

5.5 Detectors. Photomultiplier tubes (PMTs).

5.6 Fixed Optics. The most crucial element in the optical design. If the grating moves during measurement, uncertainties in the results are inevitable.

5.7 Grating. The optical element that disperses light.

5.8 Integration Time. The length of time the signal from the PMT is integrated for an intensity measurement. The most precise measurements are taken at the peak intensity.

5.9 Inter Element Intereference. When emission lines from two elements overlap at the exit slit, light measured by the PMT is no longer a simple measure of the concentration of one element. The second element interferes with the measurement of the first at that wavelength. If lines free of interference can't be found, approximate concentrations of the element of interest can be calculated by calibrating that element and the interferent (inter element correction).

5.10 Linear Dynamic Range. The light intensity in an ICP source varies linearly with the concentration of atoms over more than 6 orders of magnitude (the linear dynamic range). This variation allows for determination of trace and major elements in a single sample, without dilution. Fewer standards for calibration are needed, often a high standard and a blank suffice.

5.11 Limit of Quantitation. The lowest level at which reliable measurements can be made. Defined as ten times the standard deviation of a measurement made in a blank (pure water), which is 3.3 times the "3F" detection limit.

5.12 Monochromator. The spectrometer design on a sequential ICP.

5.13 Nebulizer. A device creating a fine spray of sample solution to be carried into the plasma for measurement. Its performance is critical for good analyses.

5.14 Photomultiplier Tubes (PMTs). Light detectors in ICP instruments. When struck by light, the PMT generates a current proportional to the intensity.

5.15 Polychromator. The spectrometer design of a simultaneous ICP.

6. Ranges, Sensitivities, and Detection Limits

6.1 Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on a particular instrument. All measurements must be within the instrument linear range where correction factors are valid. The analyst must verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data, i.e., confirming instrument performance and analytical results.

6.2 For comparison, Table 1 provides typical maximum element concentrations obtained on a Thermo Jarrell Ash Model 975 Plasma AtomComp ICP.

6.3 Calibration sensitivities are dependent upon spectral line intensities. For comparison, Table 1 provides typical sensitivities for the ICP mentioned in Section 6.2 for a Jarrell Ash Model 975 Plasma AtomComp ICP.

6.4 Detection limits vary for various makes and models. Typical detection limits achievable by the Thermo Jarrell Ash Model 975 ICP are given in Table 1. These are computed as 3.3 times the standard deviation of the distribution of outputs for the repeated measurement of a standard, which contains no metals and is used as the zero point for a two-point instrument standardization described in Section 11.3. The acid concentrations of this standard must match the acid concentrations of blanks and samples.

7. Precision and Accuracy

7.1 Accuracy for this procedure has not been determined. Spiked strips used for audits have been developed by the EPA. The main use of the audit results is to document chronologically the consistency of analytical performance. One multi-element audit sample should be extracted daily with normal ambient air samples. Audit samples can only approximate true atmospheric particulates, which contributes to the overall uncertainty. Attempts should be made to use National Institute of Standards and Technology (NIST) 1648 (urban particulate) to judge recovery. This material is not ideal because (1) there is no filter substrate; (2) relatively large amounts (100 mg) are required to overcome problems of apparent inhomogeneity, which in turn necessitates dilutions not required in normal application of this method; and (3) element ratios differ somewhat from those found in real samples. Typical recoveries experienced with the spiked strips and NIST 1648 are presented in Table 2.

7.2 Typical precision, bias, and correlation coefficients calculated from audit samples vs. blind replicate analyses are shown in Table 3. Treatment of the glass fibers during filter manufacture affects both recovery and precision of sample replicate pairs. This fact should be considered when studies are designed.

7.3 Good precision data does not imply accuracy; bias is still possible. Bias is nearly impossible to detect when a given type of sample is always analyzed by the same method using the same instrumentation. In this method, bias, if any, is most likely to arise during the sampling and sample preparation steps.

7.4 Quality assurance (QA) activities are discussed in Section 13 of this method. QA data for the method are composed of QA data for the instrument and for the sampling and sample preparation steps. The former are relatively easy to obtain by the analysis of known solutions and are usually quite good because of the inherent stability and linearity of the plasma and associated electronics. QA data for the sampling and sample preparation steps are nearly always poorer than for the instrument and thus dictate the QA data for the method as a whole. Consequently, a good instrumental calibration does not guarantee that the data produced are accurate. For instance, independent analysis (by neutron activation analysis) of real samples and of NIST SRM 1648 has revealed that Cr and Ti extractions are 25-75% efficient using the method described herein, yet both elements in solution are recovered very well by the plasma instrument.

8. Interferences

8.1 Spectral Interferences

Spectral interferences result when spectrally pure solutions of one element produce a finite output on channels assigned to other elements. Table 4 provides recommended wavelengths to monitor selected metals using ICP in order to minimize spectral interferences. When the quantitative correction is made, the order of correction is arranged so that only "true" (that is, interference-free or previously corrected) values are used in any quantitative correction of another element for comparison. The quantitative correction factors are listed in Table 10 in the order in which they are applied in the data-processing step for the analysis of ambient air using the Thermo Jarrell Ash Model 975 ICP. The correction relation for any affected element is:

$$\text{"true" concentration} = \frac{(\text{apparent conc.}) \& (\text{correction factor "true"})}{(\text{concentration of the affecting element})}$$

[Note: The information in Table 10 was generated using a specific instrument and is presented only to provide an indication of potential interferences. Specific correction factors must be generated for each instrument during each analysis.]

8.2 Matrix Interference

Matrix interferences do exist. This problem has been minimized by matrix matching of standards and samples. Matrix interferences depend on the types and quantities of acids used; element emission lines may be enhanced or depressed. These interferences may be circumvented by careful matrix matching of standards, QC solutions, and samples. Careful matches were made in the development of this procedure.

9. Apparatus

[Note: This method was developed using the Thermo Jarrell Ash Model 975 Plasma AtomComp, 27 Forge Parkway, Franklin, MA 02038, (508) 520-1880, as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

9.1 Desiccator. For cooling oven-dried chemicals.

9.2 Gravity Convection Type Drying Oven. Drying chemicals and glassware, Precision Scientific 31281 or equivalent.

9.3 Mechanical Convection Type Drying Oven. For drying plastic ware (Blue Island Electric OV 510A-2 or equivalent).

9.4 Inductively Coupled Plasma Emission Spectrometer. The ICP described in this method is the Thermo Jarrell Ash Model 975 Plasma AtomComp, 27 Forge Parkway, Franklin, MA 02038, (508) 520-1880. EPA has experience in use of this equipment during various field monitoring programs. Other manufacturers' equipment should work as well. The instrument uses a Plasma Therm HFS 2000D R.F. generator as the power supply for the plasma. The excitation source is a three-turn inductively coupled plasma torch with a cross-flow pneumatic nebulizer for sample introduction. Samples are pumped to the nebulizer with a Gilson Minipuls II single channel peristaltic pump. The instrument is equipped to read 48 elements as identified in Table 4. A dedicated PDP-8E (Digital Equipment Corporation) minicomputer controls the instrument and yields a concentration printout. To achieve data storage capability, the PDP-8E has been interfaced with a PDP11/34.

9.5 Bottles. Linear polyethylene or polypropylene with leakproof caps for storage of samples. (500 mL, 125 mL, and 30 mL). Teflon bottles for storing multi-element standards.

9.6 Pipettes. Volumetric 50 mL, 25 mL, 20 mL, 15 mL, 10 mL, 9 mL, 8 mL, 7 mL, 6 mL, 5 mL, 4 mL, 3 mL, 2 mL, Class A borosilicate glass.

9.7 Pipettes. Graduated 10 mL, Class A Borosilicate glass.

9.8 Pipette. Automatic dispensing with accuracy of 0.1 mL or better and repeatability of 20 FL (Grumman Automatic Dispensing Pipet, model ADP-30DT, or equivalent).

10. Reagents

10.1 Hydrochloric Acid. Ultrex grade, 12.3 M (Baker 1-4800) for preparing standards.

10.2 Nitric Acid. ACS reagent grade, concentrated (16 M) for preparing 10% v/v nitric acid, to clean labware only (Fisher A-200). Add 100 mL of concentrated HNO_3 to ~ 500 mL of ASTM Type II water and dilute to 1 L.

[Note: This acid is not for sample preparation; it contains excessive metals].

10.3 Nitric Acid. Ultrex grade, 16 M (Baker 1-4801) for preparing standards.

10.4 Stock Calibration Standards. Multi-element and single-element plasma-grade stocks are used for the analysis. The stocks are purchased from Spex Industries, Inc., Inorganic Ventures, Inc., or equivalent. Working calibration standards are prepared by dilution of the concentrated calibration stocks. The calibration standard stocks used for instrument calibration and initial calibration verification (ICV) are purchased from different suppliers. The source (manufacturer and lot), concentration, expiration date, and acid matrix are recorded for all calibration standards used for the analysis. Stock solutions should be stored in Teflon bottles. The final concentration of nitric and hydrochloric acid in the calibration standards should be the same as those in the prepared samples.

10.5 Compressed Argon in Cylinders and Liquid Argon in Tanks, Purity 99.95%. Best source.

10.6 ASTM Type I water (ASTM D1193). Best source. The Type I water should have a minimum resistance of 16.67 milli-ohms, as evidenced by the reading of the resistivity meter during water flow.

11. Analysis

11.1 Standard Stock Solutions

11.1.1 All labware should be scrupulously cleaned. The following procedure is recommended: Wash with laboratory detergent or ultrasonic for 30 min with laboratory detergent. Rinse and soak a minimum of 4 hr in 10% V/V nitric acid. Rinse 3 times with deionized, distilled water, and oven dry.

[Note: Nitric and hydrochloric acid fumes are toxic. Prepare in a well-ventilated fume hood. Mixing results in an exothermic reaction. Stir slowly.]

11.1.2 Preparing Calibration Curve Standards. Mixed calibration curve standards are prepared by diluting appropriate volumes of the stock calibration standards in Class A volumetric flasks. Table 1 provides examples of typical concentrations used for calibration for several elements. Each working standard solution should be labeled with a name, an expiration date, and the initials of the preparer.

11.1.3 Prepare Initial Calibration Verification Standard (ICV). The ICV standards are analyzed immediately following initial calibration. The ICV standards are prepared at the midpoints of the calibration curves. These standards are prepared from certified stocks having a different manufacturer than the calibration standards. The final concentration of the ICV should be in the range of 25 µg/mL for Al, Ca, Fe, Mg, K and Na. All other analytes should be in the range of 2 µg/mL.

11.1.4 Prepare Interference Check Standard (ICS). The interference check standards are analyzed at the beginning and end of the sample run and for every 8 hours of continuous operation. The ICS should contain approximately 200 µg/mL of Al, Ca, Fe, and Mg. In addition, the ICS should contain approximately 1 µg/mL of all other analytes, including Ag, Be, Ca, Cd, Co, Cr, Cu, Fe, Pb, Se T, Y, Zn, and Bi.

11.1.5 Laboratory Control Spike (LCS). An LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The LCS is prepared for all analytes at the 2 µg/mL level and when analyzed, should be within 80% to 120% of actual concentration. If the results are not within this criterion, then the results must be qualified.

11.1.6 Matrix Spike (MS). A MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The MS should be at the 25 µg/strip level. The percent recovery for the analyte as part of the MS should be between 75% and 125% for all analytes.

11.1.7 Prepare a Reagent Blank (RB). Prepare a reagent blank that contains all the reagents in the same volumes used in processing the routine samples. The reagent blank must be carried through the entire preparation procedure and analysis scheme. The final solution should contain the same acid concentration as sample solutions for analysis. The running frequency of analysis of a reagent blank is about 1 for every 40 real samples.

11.2 ICP Operating Parameters

A daily log of the operating parameters should be maintained for reference. Entries are made by the analyst of periodic intervals throughout the run. The following list of parameters are examples from the Thermo Jarrell Ash Model 975 Plasma AtomComp. Specific manufacturer's guidelines should be followed.

ICP HARDWARE	SPECIFICATIONS
• Plasma power	1.1 kW forward automatic control 11 W reflected (minimum possible)
• Argon coolant flow	18 1/min liquid argon source
• Argon nebulizer flow	16 psi (approx. 700 mL/min)
• Sample uptake	Avg. 1.85 mL/min
• Observation Zone	Centered 16 mm above the load coil
• Sample preflush time	45 s; preburn, 1 s
• Exposure	10 s
• H_2O Post Flush	10 s then proceed to next sample
• Slits	25-µm entrance slit; 75-µm exit slit
• Photomultiplier tube voltage	900 V

11.3 Instrumental Preparations

11.3.1 Calibration Curve Linearity. ICP spectrometers generally are considered to yield a linear response over wide concentration ranges; however, investigation for linearity for elements expected to exceed concentrations of about 25 µg/mL may be necessary. Linearity may vary among manufacturers and according to operating parameters. The method and conditions described in this procedure have imposed the following limitations:

- Ca response is linear to 40 µg/mL, becoming non-linear.
- Cr saturates the electronics at 50 µg/mL.
- Cu saturates the electronics at 40 µg/mL.
- Fe saturates the electronics at 230 µg/mL.

- Mg response is curvilinear to 40 µg/mL, becoming unuseable.
- Na response is curvilinear to 80 µg/mL, becoming unuseable.

The curvilinear nature of Mg and Na responses below the levels specified were made acceptable by programming the ICP computer with segmented calibration curves as described in the manufacturer's instructions.

11.3.2 Spectral Interferences. Section 8 described briefly spectral interferences. A thorough determination of spectral interferences is a lengthy, time-consuming study in itself. The following are some of the factors influencing the presence or absence and magnitude of interferences:

- Wavelength of lines being read;
- Expected concentrations of the elements involved;
- Quality and the stability of the system optics (i.e., minimal deterioration with time);
- Quality and stability of photo multiplier tubes and electronics; and
- Purity of chemicals in use.

A thorough study of interferences has been conducted by EPA in the development of this method and have been addressed in the data processing program listed in Table 5.

[Note: The spectral interference factors listed in Table 5 were determined by analyzing single element solutions of each interfering element. The concentration of each single element solution was within the linear dynamic range (LDR) of the analysis, usually 100 µg/mL. The criteria for listing a spectral interference was an apparent analyte concentration from the interfering single element solution that was outside the 95% confidence interval estimates for the determined method detection limit (MDL) of the analyte. The factors are presented as a guide for users of this method for determining interrelement interference effects. The user is cautioned that other analytical systems other than the Thermo Jarrell Ash Model 975 Plasma AtomComp described in this method may exhibit somewhat different levels of interference than those listed in Table 5 and that the interference effects must be evaluated for each individual system.]

11.3.3 Matrix Interferences. Matrix interferences depend on the types and quantities of acids used; element emission lines may be enhanced or depressed. These interferences may be circumvented by careful matrix matching of standards, QC solutions, and samples. Careful matches should be made in the use of this procedure.

11.4 Sample Receipt in the Laboratory

11.4.1 The sample should be received from the extraction laboratory in a centrifuge tube, as documented in Inorganic Compendium Method IO-3.1.

11.4.2 No additional preservation is needed at this time. Sample is ready for ICP analysis.

11.5 ICP Operation

[Note: This method was developed using the Thermo Jarrell Ash 975 Plasma AtomComp spectrometer. EPA has experience in the use of the Model 975 spectrometer associated with various field monitoring programs involving analysis of filterable particulate matter for metals using ICP over the last several years. The use of other manufacturers of ICP spectrometers should work as well as long as the quality assurance and quality control specifications identified in Sections 13, Quality Control, are met. However, modifications to Compendium Method 10-3.4 procedures may be necessary if another commercial ICP spectrometer is used.]

11.5.1 Start and allow the instrument at least 45 min for warmup.

11.5.2 Profile following manufacturer's directions. Run 12 warmup burns of old high QC solution to exercise the photomultiplier tubes.

11.5.3 Standardize by opening the standardization buffers with a J command on the CRT operating off-line from the PDP-11/34. Flush for 2 min with the first working standard. Make two exposures, print the average ratio on the teletype, and identify the standard when queried. Repeat for all five working standards. Complete with an S command and answer the query "Enter LCN" with a carriage return (RTN). Calibration data are not stored in the PDP-ll.

11.5.4 Go on-line to the PDP-ll by typing "RUN JA" and answer PDP-ll queries to identify the operator, data storage, and operating condition codes.

11.5.5 The PDP-ll will automatically acquire gains and offsets (slopes and X-intercepts of the calibration curve) determined by the ICP standardization. Values falling outside a previously determined bandwidth will be reported by the computer. When this occurs, corrective action must be taken. Gain and offset values are element-specific.

11.5.6 Measure the sample-pump uptake rate which should be approximately 1.8 mL/min.

11.5.7 Select a QC solution for analysis. On the CRT, enter RTN "QC" RTN "21", RTN for high QC, or "QC" RTN "22", RTN for low QC. When "DSC" appears on CRT, type "HIQC" or "LOQC", as applicable, followed by its prep date and RTN. The number "1.0" will appear twice, indicating the multiplication and dilution factors have been set to 1.0. This step is followed by the query "OK?"

11.5.8 Begin pumping the QC solution selected in Section 11.5.7 from an aliquot. Start the stopwatch when the leading edge of the solution has just entered the nebulizer. Time for 45 s and press RTN on the CRT to begin the exposure. The end is signaled by the CRT bell. Transfer the pickup tube to deionized distilled water.

11.5.9 When the PDP-ll has acquired the data, it will query "QC SMP:." Type RTN, "STD," RTN "21," RTN to identify the zero standard (Working Standard No. 1; see Section 11.1). After "DCS:" As in Section 11.5.7, the multiplication and dilution factors will default to 1.0, and the query "OK?" will appear.

11.5.10 Begin pumping from an aliquot of the zero standard and time for 45 s, as in Section 11.5.8. Start the exposure with RTN on the CRT. At the bell, return the pickup to deionized, distilled water.

11.5.11 When the PDP-ll has acquired the data, it will query "STD SMP:." Type "1," RTN, RTN, and it will query "OK?" Type "NO," RTN and the cursor will move to the left end of the line.

11.5.12 Select the first sample. On the CRT, enter the Project I.D. from the label. Press RTN. Type numerical sample number and RTN. After "DCS:," type the four letter I.D. code and RTN. The computer next queries "MLT:" (for multiplication factor); enter "360", RTN. After "DIL:" (for dilution factor), enter "1," RTN. The computer then asks "OK?"

11.5.13 Begin pumping the sample from the sample bottle and time for 45 s before pressing RTN. At the bell, return the pickup to deionized, distilled water and select the next sample.

11.5.14 Enter second sample by typing the sample number, RTN, 4-letter I.D., RTN, and another RTN to begin the exposure.

11.5.15 Present 8 samples to the instrument.

11.5.16 Challenge the instrument with the QC solution that was not selected in Section 11.3.7. Repeat CRT entries and procedure in Sections 11.5.7 and 11.5.8.

11.5.17 Resume sample analysis. Repeat Sections 11.5.11 through 11.5.13.

11.5.18 Analyze nine samples.

11.5.19 Return to Section 11.5.6 and repeat through Section 11.5.17.

11.5.20 End the analytical session after about 3 to 3.5 h. Type "-1," RTN. The computer will query "DO YOU WISH TO SAVE THIS SESSION'S DATA?" Type "YES," RTN. The computer will back up the data and issue instructions. This terminates the RUN JA program.

11.5.21 Usually two sessions per day are attempted. Repeat Sections 11.5.2 through 11.5.20 for the second session.

11.5.22 Instrument operating parameters are recorded before and after every 20 burns. A typical day's record is shown in Figure 3.

11.5.23 With minimal experience, the instrument operator will be able to compress the above steps (i.e., process more than one sample at a time by overlapping the steps required for the different samples).

12. Data Processing

12.1 Filter Blanks and Discrimination Limit

Since individual blanks are not available from each filter used for sampling, the mean unexposed filter value is subtracted from the result for each exposed sample to obtain the best estimate of each element in the filter particulate material. A discrimination limit must be defined so that possible contributions from an individual filter are not falsely reported as being from the particulate material. Calculate the filter batch mean, F_m (see

Method IO-3.2), and the standard deviation of the F_m values for each filter. If F_m is greater than the instrumental detection limit, then F_m must be subtracted from the total elemental content for each particulate bearing filter when the net metal in the particulate material is calculated. Determine the smallest atmospheric concentration of the element that can be reliably distinguished from the filter's contribution by multiplying the standard deviation for the filter batch by 3.3 and dividing by the average volume of air sampled, usually 1700 m^3. The resulting value will be the discrimination limit for that element.

12.2 Metal Concentration in Filter

12.2.1 Calculate the air volume sampled, corrected to EPA-reference conditions:

$$V_{std} = V_s \left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}}{P_{std}}\right)$$

where:

V_{std} = volume of ambient air sampled at EPA-reference conditions, m^3.
V_s = volume of ambient air pulled through the sampler, m^3.
T_{std} = absolute EPA-reference temperature, 298EK.
T_m = average ambient temperature, EK.
P_{bar} = barometric pressure during sampling measurement condition, mmHg.
P_{std} = EPA-reference barometric pressure, 760 mmHg.

12.2.2 Metal concentration in the air sample can then be calculated as follows:

$$C = [(\mu g \text{ metal/mL})(\text{final extraction volume (i.e., 20 mL)/strip})(9) - F_m]/V_{std}$$

where:

C = concentration, µg metal/std. m^3
µg metal/mL = metal concentration determined from Section 11.5.
Final extraction volume, mL/strip = total sample extraction volume, mL, from extraction procedure (i.e., 20 mL).

$$9 = \frac{\text{Useable filter area [20 cm x 23 cm (8" x 9")]}}{\text{Exposed area of one strip [2.5 cm x 20 cm (1" x 8")]}}$$

F_m = average concentration of blank filters, µg.
V_{std} = standard air volume pulled through filter, std m^3, (25EC and 760 mmHg).

13. Quality Assurance (QA)

13.1 Instrumental Tuning and Standardization

13.1.1 The instrument must be tuned by the manufacturer at installation. However, the element lines should be checked periodically to determine if they have maintained their positions relative to the mercury profile line. Follow the manufacturer's instructions.

13.1.2 The Thermo Jarrell Ash Company published directions for performing instrument diagnostic checks and pertinent acceptable data limits (Ward, 1978, 1979 a, b, 1980 a, b). Diagnostic checks should be run periodically at a frequency dictated by the "goodness" of instrumental QC checks.

13.2 Calibration For Quantitative Analysis

See Section 13.3.2.1.

13.3 Daily QA Check and Analytical Run Sequence

Data validation steps described in this section are primarily instrumental and do not guarantee extraction efficiency.

13.3.1 Real-Time Judgments: Standards, Gains, Offsets. This system requires virtually no data computations by the operator. However, the operator is required at several points to judge, based on historical experience, the validity of numbers generated and to decide whether to continue or stop. During the standardization, the operator must observe element response to determine if values are normal. The operator must watch for computer-generated messages reporting gains or offsets that exceed the tolerance limits. Proper corrective action is based on operator experience and is discussed in Section 14.5.

13.3.2 General Quality Control. The required general quality control requirements for ICP analysis are discussed below and summarized in Table 6.

13.3.2.1 Initial Calibration. At least two calibration standards and a calibration blank are analyzed at the beginning of an analysis run. The standards used to calibration are diluted from certified stock standards (see Section 11.1) and are used within the expiration dates. The calibration standards and blanks are prepared in the same nitric and hydrochloric acid matrix as the samples.

13.3.2.2 Initial Calibration Verification (ICV). The ICV standards are analyzed immediately following initial calibration. The ICV standards are prepared from certified stocks having a different manufacturer than the calibration standards. The measured concentration should be within 90% to 110% of the actual concentration.

13.3.2.3 Initial Calibration Blank (ICB). The ICB is analyzed immediately following ICV and prior to the high standard verification. The acceptance criteria for the ICB is the same as for continuing calibration blank (CCB) verification.

13.3.2.4 High Standard Verification (HSV). Immediately after the analysis of the ICB, and prior to the analysis of samples, the HSVs are reanalyzed. The measured concentration should be within 95% to 105% of actual concentration.

13.3.2.5 Interference Check Standards (ICSs). The ICSs are analyzed at the beginning and end of the run and for every 8 hours of continuous operation. The results for the analytes should be within 80% and 120% of the actual concentration. Samples containing levels of interferences above the levels in the ICS should be considered for dilution.

13.3.2.6 Continuing Calibration Verification (CCV). CCV standards are prepared from the calibration standard stocks at the midpoint of the calibration curve. The CCV standards are analyzed at the beginning of the run prior to samples, after every 10 samples, and at the end of the run prior to the last continuing calibration blank (CCB) analysis. The measured concentration should be within 90% and 110% of the actual concentration.

13.3.2.7 Continuing Calibration Blanks (CCBs). The CCBs are analyzed following each CCV. The results of the CCBs are evaluated as follows:

- The CCBs are compared to the method detection limits.
- The absolute value of the instrument response must be less than the method detection limits.-

- If not, then sample results for analytes < 5 times the amount in the blank must be flagged or analysis must be repeated.

13.3.2.8 Reagent Blank (RB). A RB sample is prepared and analyzed with each sample batch. This analysis is used to determine if concentrations reflect background levels from sample digestion. If the instrument measured response is greater than the method detection limits, then the sample results for the affected analyte(s) must be flagged. Samples may be considered candidates for redigestion and reanalysis for that analyte.

13.3.2.9 Laboratory Control Spike (LCS). An LCS is prepared and analyzed with each sample batch (or 1 per 20 samples). The results for the analytes should be within 80% to 120% of actual concentration. If the results are not within this criterion, then strips of the LCS and all samples should be redigested and reanalyzed.

13.3.2.10 Matrix Spike (MS). A MS sample is prepared and analyzed with each sample batch (or 1 per 20 samples). These samples are used to provide information about the effect of the sample matrix on the digestion and measurement methodology. The spike is added before the digestion, (i.e., prior to the addition of other reagents). The percent recovery for the analyte as part of the MS should be between 75% and 125% for all analytes.

13.3.2.11 Duplicate and/or Spike Duplicate. Duplicate samples and/or matrix spike duplicates are prepared and analyzed with each sample batch. These samples are used to estimate method precision, expressed as relative percent difference (RPD). The RPD between the duplicate and/or matrix spike duplicate final concentrations should be < 20%.

13.3.2.12 Serial Dilution. The ICP serial dilution analysis must be performed on one sample per batch. After a fivefold serial dilution, the analyte concentration must be within 90% and 110% of the undiluted sample results.

13.3.2.13 Sample Dilution. Dilute and reanalyze samples that are more concentrated than the linear calibration limit.

13.4 Corrective Actions

13.4.1 The plasma must operate in a stable mode with a uniform sample feed rate. Failure to reproduce standards' responses or QC values usually is caused by a partially or totally plugged nebulizer. This condition may be verified by observing a decrease in the pump rate or the absence of a fog in the nebulizer spray chamber. A similar effect will be observed if the argon supply pressure or the RF power should change. Experience with the sample pump and the RF power supply has been excellent, and both appear to be very stable electronically.

13.4.2 Intermittent failure of QC solutions to fall within the tolerance band may be due to an intermittent failure in a spectrometer circuit or to a broken nebulizer needle. Both are difficult to detect without extensive testing or dismantling of equipment. Leaks in the argon supply lines are also likely causes of such problems. Leaks in the ground-glass joints of the torch-spray chamber can be eliminated by the light use of a good grade stopcock grease (not silicone-base) (see Section 13.5).

13.4.3 One intended purpose of the repeated analysis of QC solutions was to detect and correct instrument drift occurring within any 1 day. Experience has shown that drift is not a problem when the instrument is standardized twice daily. When drift has been detected, it has been attributed to thermal drift and corrected by repro filing (i.e., adjusting the optical alignment). The instrument must be restandardized after profiling.

13.4.4 Long-term drift is more difficult to detect. A gradual increase in the gains of short-wavelength elements over a period of weeks or months is probably due to degradation of mirror coatings. Washing the mirrors may help in the short term, but usually they must be replaced. Mirrors may be ruined if washed

improperly; manufacturer-approved procedures should be followed. Gradual degradation of electronic circuits will also cause long-term drift.

13.5 Routine Maintenance

13.5.1 The torch and spray chambers occasionally must be cleaned. Frequency of cleaning must be determined through experience, as a schedule and criteria have not been established. Ultrasonic the chambers in a hot detergent for at least 30 min, soak in aqua regia overnight, and rinse in deionized, distilled water.

[Note: Aqua regia is a strong oxidizing agent. Wear protective clothing and a face shield.]

13.5.2 The ground-glass joints of the torch-spray chamber should be greased with a good grade of non-silicone base stopcock grease. After reassembly, the torch must be optimized for maximum flux throughput according to manufacturer's instructions.

13.5.3 Should the plasma be extinguished during an analysis session, the session must be ended. Restandardization is necessary after the plasma is reignited. Restandardization must be delayed until the reflected power has been at a minimum for approximately 10 min.

14. Method Safety

The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely; however, each chemical compound should be treated as a potential health hazard. 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 handling data sheets should be made available to all personnel involved in the chemical analysis.

15. References

1. "Standard Operating Procedures for the ICP-DES Determination of Trace Elements in Suspended Particulate Matter Collected on Glass-Fiber Filters," EMSL/RTP-SOP-EMO-002, Revision, October, 1983.

2. "Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," *Code of Federal Regulations*, Title 40, Part 50, Appendix B, pp. 12-16 (July 1, 1975).

3. "Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air.," *Federal Register* 43 (194): 46262-3, 1978.

4. Rhodes, R. C., 1981, "Special Extractability Study of Whatman and Schleicher and Schuell Hi-Vol Filters," Memo to file, August 5, 1981, Quality Assurance Division, Environmental Monitoring Systems Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, NC.

5. Ward, A. F., *The Jarrell-Ash Plasma Newsletter*, Volumes I, II, and III.

6. Nygaard, D., and Sot, J. J., "Determination Near the Detection Limit: A Comparison of Sequential and Simultaneous Plasma Emission Spectrometers," *Spectroscopy*, Vol. 3(4).

7. "Simplex Optimization of Multielement Ultrasonic Extraction of Atmospheric Particulates," Harper, et. al., *Analytical Chemistry*, Vol. 55(9), August 1983.

TABLE 1. TYPICAL CONCENTRATIONS OF THE MOST CONCENTRATED WORKING STANDARD,[1] TYPICAL ICP CALIBRATING SENSITIVITIES AND TYPICAL METHOD DETECTION LIMITS[2]

Element	Most Conc. Working Std., mg/L	Calibrating Sensitivity, counts/Fg metal	Detection[3] Limit	
			mg/L	ng/m^3
Al	50.0	4,887	0.061	13.5
As	5.0	5,063	0.025	5.5
Au	5.0	11,683	0.009	1.9
B	10.0	42,892	0.030	6.6
Ba	10.0	13,430	0.003	0.7
Be	2.0	57,457	0.002	0.4
Bi	10.0	467	1.030	226.6
Ca	40.0	52,787	0.103	22.7
Cd	4.0	37,438	0.005	1.1
Ce	5.0	13,859	0.048	10.6
Co	5.0	2,787	0.015	3.3
Cr	4.0	76,772	0.012	2.6
Cu	20.0	159,213	0.010	2.2
Fe	50.0	16,985	0.034	7.5
Ge	5.0	1,645	0.079	17.5
Hg	5.0	9,031	0.055	12.1
In	5.0	520	0.081	18.5
K	20.0	253	0.205	45.1
La	2.0	44,468	0.007	1.5
Li	2.0	12,500	0.003	0.7
Mg	40.0	70,951	0.024	5.3
Mn	10.0	108,751	0.004	0.9
Mo	5.0	5,266	0.009	1.9
Na	80.0	186	inoperative	inoperative
Nb	2.0	59,859	0.11	2.4
Ni	5.0	4,306	0.014	3.1
P	20.0	2,941	0.104	22.9
Pb	25.0	10,324	0.032	7.0
Pd	5.0	7,996	0.130	7.0
Pt	5.0	847	0.107	23.5
Re	10.0	288	0.150	33.0
Rh	5.0	32,421	2.000	440.0
Ru	10.0	5,227	0.187	41.1
Sb	5.0	4,246	0.025	5.5
Se	5.0	930	0.156	34.3
Si	50.0	9,152	0.172	37.8
Sm	5.0	52,532	0.024	5.4
Sn	5.0	469	0.042	9.2
Sr	5.0	55,091	0.001	0.2
Ta	5.0	21,030	0.145	52.1
Te	5.0	4,676	0.021	4.6
Ti	5.0	58,777	0.003	0.7
Tl	5.0	3,063	0.152	33.4
V	5.0	107,250	0.007	1.5
W	5.0	1,170	0.057	12.5
Y	5.0	35,800	0.004	0.9
Zn	20.0	478	0.120	26.4
Zr	5.0	18,010	0.008	1.8

[1]The least concentrated working standard contains no metals.
[2]Data source is 48 determinations of standard No.1 made from 01/26/83--03/22/83 during analysis of 1982 NAMS filters.
[3]Based upon sampling rate of 1.13 m^3/min for 24-hr for a total sample volume of 1627.2 m^3; factor of 9 for partial filter analysis; digestion of 0.020 L/filter.

TABLE 2. RECOVERIES FROM SPIKED STRIPS[1] AND FROM NIST SRM 1648

Element	% Recovery	%RSD
Spiked Strips[1]		
As	96.5	2.7
Co	95.5	3.4
Cu	76.1	4.3
Fe	98.3	3.7
Mn	96.9	4.0
Ni	96.4	3.9
Pb	99.1	1.9
Sr	96.4	4.4
V	94.0	2.1
Zn	89.4	6.2
NIST SRM 1648		
Ba	80	0.8
Be	not listed by NIST	
Cd	114	8.5
Cu	100	1.4
Fe	68	1.4
Mn	88	1.6
Mo	not listed by NIST	
Ni	90	9.0
Pb	95	1.1
V	79	1.9
Zn	97	3.8

[1]Recovery values based on X-ray fluorescence analytical values taken as "true".

TABLE 3. TYPICAL PRECISION, BIAS, AND CORRELATION COEFFICIENTS OBTAINED BY SAMPLE/REPLICATE PAIR ANALYSIS[1]

Element	Pairs Found	Coefficient Variation (%)	Coefficient Bias (%)	Coefficient
B	32	10	1.0	0.95
Ba	32	9	0	1.0
Cd	17	11	0	1.0
Cu	32	4	-1.0	1.0
Fe	32	8	1.0	0.99
Mn	32	21	5.0	0.99
Ni	14	10	-2.0	1.0
Pb	31	3	0.0	1.0
Sb	4	5	3.0	0.99
Sr	32	7	1.0	1.0
V	25	6	-1.0	1.0
Zn	31	16	-3.0	0.94

[1]Based on the analysis of 32 sample/replicate pairs of 1982 NAMS filters from 01/26/83 - 03/22/83. Because these data were obtained from real samples, there was no control over the actual concentrations. Elements displaying a large coefficient of variation tended to have mean concentrations in the lower end of the quantifiable range.

TABLE 4. ICP SPECTROMETER ELEMENTS WITH WAVELENGTHS

Element	Wavelength	Element	Wavelength
Al	308.22	Nb	316.34
As	193.76	Ni	231.60
Au	242.80	P	214.91
B	249.77	Pb	220.35
Ba	493.41	Pd	363.47
Be	313.04	Pt	265.95
Bi	195.33	Re	209.24
Ca	396.85	Rh	343.49
Cd	226.50	Ru	297.66
Ce	446.02	Sb	206.84
Co	228.62	Se	196.09
Cr	357.87	Si	288.16
Cu	324.75	Sm	442.43
Fe	259.94	Sn	189.99
Ge	199.82	Sr	407.77
Hg	253.65	Ta	240.06
In	230.69	Te	214.28
K	766.49	Ti	334.90
La	379.48	Tl	351.92
Li	670.78	V	292.40
Mg	279.55	W	202.99
Mn	257.61	Y	371.03
Mo	202.03	Zn	206.19
Na	589.00	Zr	339.20

TABLE 5. CORRECTION FACTORS FOR SPECTRAL INTERFERENCES

Affecting Element	Affecting Factor	Affected Element	Affecting Element	Affecting Factor	Affected Element
Ta	0.0166	Co	Bi	0.0268	Rh
Ta	0.0026	Fe	Bi	0.0116	Se
Al	0.0141	Ta	Bi	0.0041	Si
Al	0.0375	V	Bi	0.0125	Sr
B	0.0181	Zr	Ge	0.0071	Al
Be	0.0020	Nb	Ge	0.0015	Be
Be	0.0025	V	Ge	0.0085	Mo
Ce	0.2313	V	Ge	0.0293	Nb
Hg	0.0574	Co	Ge	0.1489	Ta
Hg	0.0151	Fe	P	0.0017	Al
La	0.0028	Fe	P	0.0265	Cu
La	0.0122	V	P	0.0016	Fe
Pb	0.1104	Nb	P	0.0032	Mg
Pd	0.0247	Nb	P	0.0100	Nb
Pd	0.1649	Sm	P	0.0017	Si
Pd	0.0125	Ti	P	0.0010	Zn
Pt	0.0600	Cr	Re	0.0240	Al
Pt	0.0175	Nb	Re	0.0110	B
Pt	0.1300	Ta	Re	0.1609	Mn
Pt	0.0210	V	Re	1.2400	Mo
Si	0.0281	Nb	Re	0.0556	Pd
Si	0.1300	Ta	Re	0.0044	Si
Si	0.2495	Zr	Re	0.2146	V
Te	0.0254	V	Ru	0.0141	Fe
Tl	0.0607	Ce	Ru	0.0843	Mn
Tl	0.0229	Zr	Ru	0.0233	Mo
Zn	0.0132	Ta	Ru	0.0827	Nb
As	0.0119	A1	Ru	0.2531	Ta
As	0.1736	Pt	Ru	0.0364	Ti
As	0.0125	V	Ru	5.5170	V
Bi	0.0083	A1	Ru	0.4996	Zr
Bi	0.0212	Cr	W	0.0021	Al
Bi	0.0065	Fe	W	0.0039	Mg
Bi	0.0326	La	W	0.0027	Zn
Bi	0.0155	Mg	As	0.0218	Ge
Bi	0.0312	Mn			

TABLE 6. EXAMPLE REQUIRED QUALITY CONTROL REQUIREMENTS FOR ICP ANALYSIS

QC procedure	Typical frequency	Criteria
Initial calibration (IC)	At the beginning of the analysis	None
Initial calibration verification (ICV)	Immediately after initial calibrations	90-110% of the actual concentration
Initial calibration blank (ICB)	Immediately after initial calibration verification	Must be less than project detection limits
High standard verification (HSV)	Following the initial calibration blank analysis	95-105% of the actual concentration
Interference check standard (ICS)	Following the high standard verification, every 8 hours, and at the end of a run	80-120% of the actual concentration
Continuing calibration verification (CCV)	Analyzed before the first sample, after every 10 samples, and at the end of the run	90-110% of the actual concentration
Continuing calibration blanks (CCBs)	Analyzed following each continuing calibration verification	Must be less than project detection limits (MDLs)
Reagent blank (RB)	1 per 40 samples, a minimum of 1 per batch	Must be less than project detection limits
Laboratory control spike (LCS)	1 per 20 samples, a minimum of 1 per batch	80-120% recovery, with the exception of Ag and Sb
Duplicate and/or spike duplicate	1 per sample batch	RPD # 20%
Matrix spike (MS)	1 per 20 samples per sample batch	Percent recovery of 75-125%
Serial dilution	1 per sample batch	90-110% of undiluted sample
Sample dilution	Dilute sample beneath the upper calibration limit and at least 5X the MDL	As needed

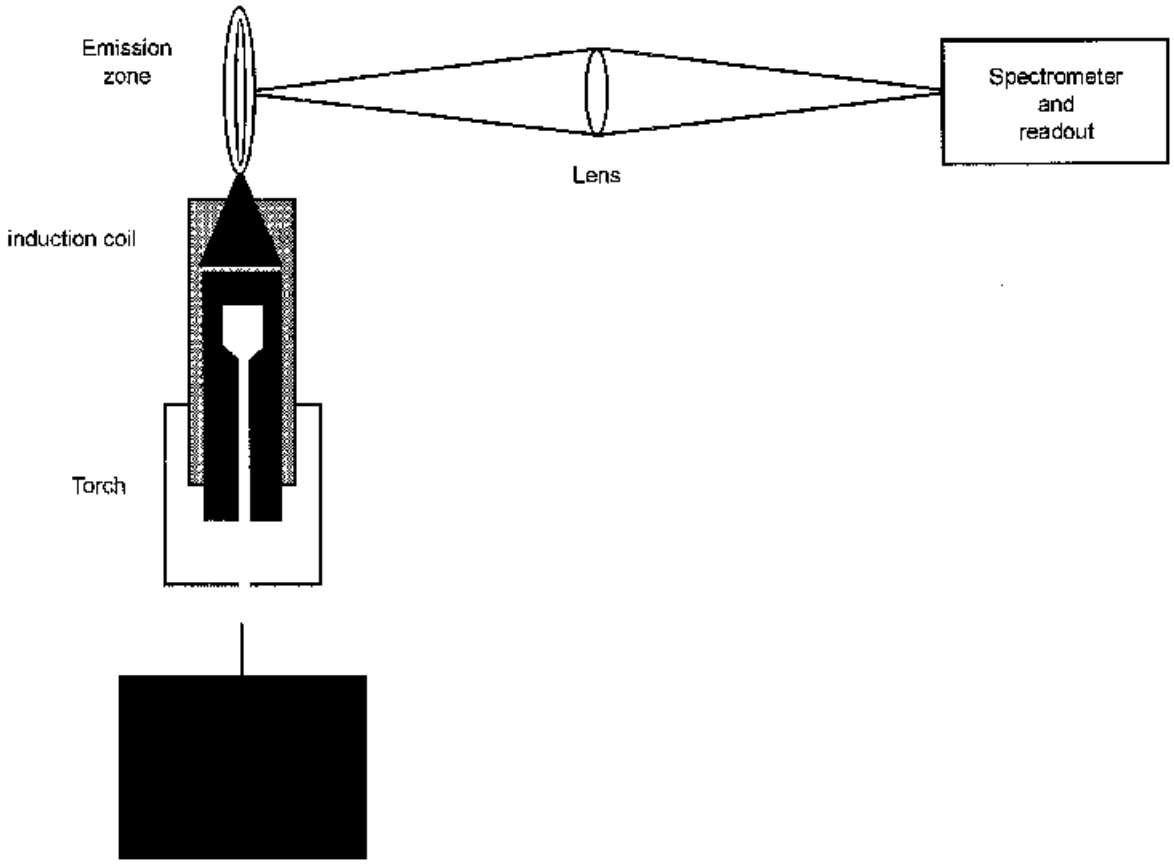

Figure 1. Schematic diagram of a typical inductively coupled plasma-optical emission spectroscopy instrument featuring parts of the instrument most important to the user.

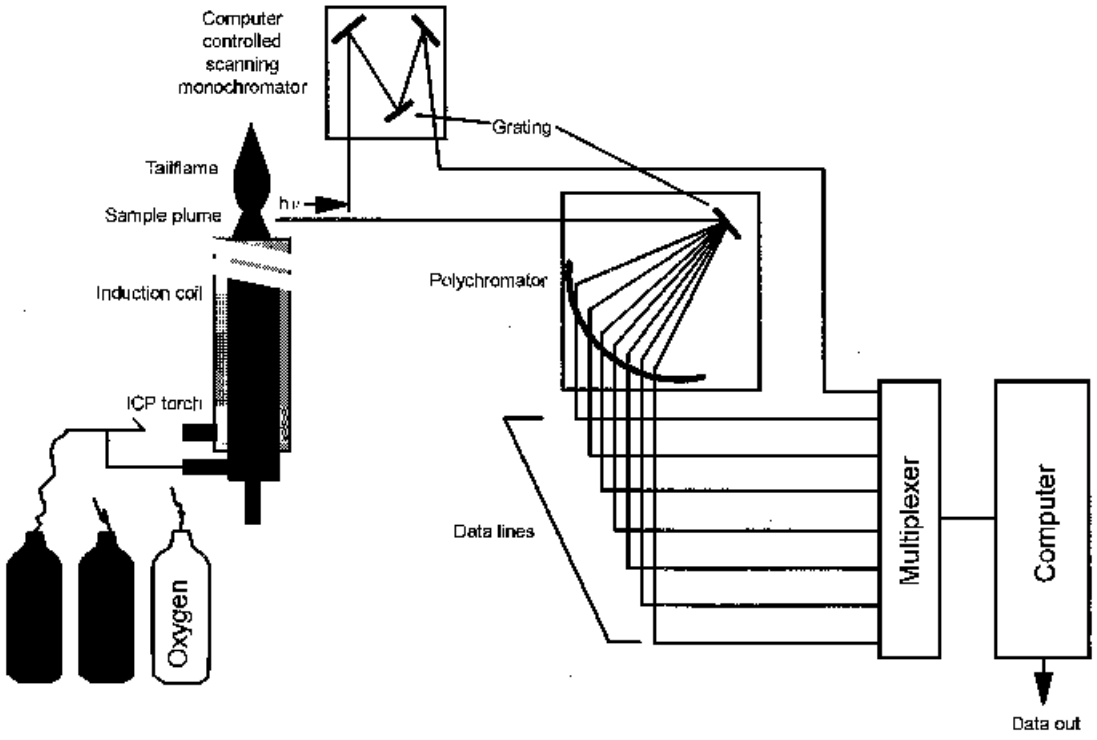

Figure 2. Simultaneous or sequential multi-element determination of trace elements by ICP.

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APPENDIX D

USEPA Compendium Method TO-9A

APPENDIX E

USEPA Compendium Method TO-11A

EPA/625/R-96/010b

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

Second Edition

Compendium Method TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]

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

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Method TO-11A
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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
- Silvestre Tejada, U.S. EPA, NERL, RTP, NC
- Bill Lonneman, U.S. EPA, NERL, RTP, NC
- Ted Kleindienst, ManTech, RTP, NC

Peer Reviewers

- Robert G. Lewis, U.S. EPA, NERL, RTP, NC
- Sucha S. Parmar, Atmospheric Analysis and Consulting, Ventura, CA
- Joette Steger, Eastern Research Group, Morrisville, NC
- Lauren Drees, U.S. EPA, NRMRL, Cincinnati, OH

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DISCLAIMER

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

Method TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

METHOD TO-11A

Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology]

1. Scope

1.1 This document describes a method for the determination of formaldehyde and other carbonyl compounds (aldehydes and ketones) in ambient air utilizing a coated-solid adsorbent followed by high performance liquid chromatographic detection. Formaldehyde has been found to be a major promoter in the formation of photochemical ozone. In particular, short term exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, crotonaldehyde) is known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract**.**

1.2 Over the last several years, numerous methods have been developed for the sampling and analysis of carbonyl compounds. Because of the role which formaldehyde plays in photochemistry, most of the more recent methods were designed to quantitate formaldehyde specifically. Early methods centered around wet chemical technology involving a bubbler or impinger containing a reactive reagent (1). In some cases the reactive reagent produced a color in the presence of formaldehyde. Examples of the more commonly used reagents were: 3-methyl-2-benzothiazolone hydrazone (MBTH), sodium sulfite, 4-hexylresorcinol, water, sodium tetrachloromercurate, and chromatropic acid. These reagents demonstrated high collection efficiency (>95%), provided fairly stable non-volatile products and minimized formation of undesirable by-products. Indeed, as part of U. S. Environmental Protection Agency's (EPA's) effort to quantitate atmospheric concentrations of formaldehyde, the National Air Sampling Network utilized the impinger technique for several years containing chromatrophic acid specifically for formaldehyde. However, impinger sampling had numerous weaknesses which eventually lead to its demise. They were**:**

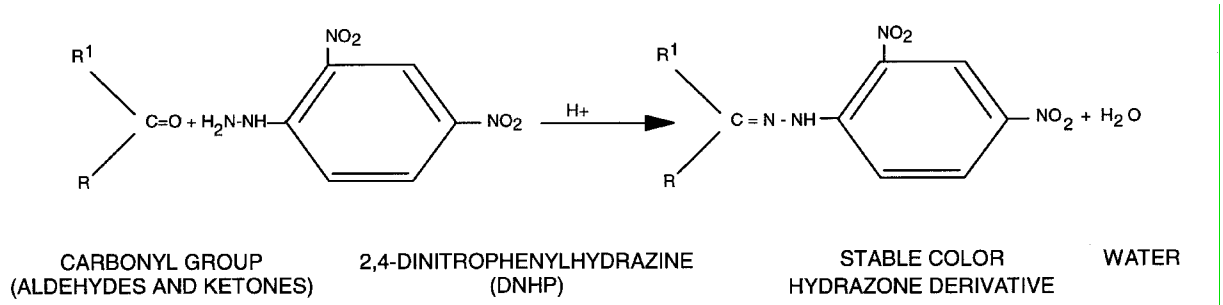
- Labor intense.
- Used acidic/hazardous reagents.
- Lacked sensitivity.
- Prone to interferences.
- Poor reproducibility at ambient concentration levels.

As EPA's interest focused upon formaldehyde and it's sources, the development of passive personal sampling devices (PSDs) developed (2). These devices were mainly used by industrial hygienists to assess the efforts of respiratory exposure for formaldehyde on workers. However, because of the design and flow rate limitation, they require long exposures (up to 7 days) to the atmosphere to meet traditional bubbler technique sensitivities. Consequently, the passive PSD had limited application to ambient monitoring.

To address the need for a monitoring method to sample carbonyl compounds in the air at sensitivities needed to reach health-base detection limits (10^{-6} risk level), a combination of wet chemistry and solid adsorbent methodology was developed (3-6). Activating or wetting the surface of an adsorbent with a chemical specific for reacting with carbonyl compounds allowed greater volumes of air to be sampled, thus enabling better sensitivity in the methodology. Various chemicals and adsorbents combinations have been utilized with various levels of success. The most commonly used technique is based on reacting airborne carbonyls with 2,4-dinitrophenylhydrazine (2,4-DNPH) coated on an adsorbent cartridge followed by separation and analysis of the hydrazone derivative by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection.

1.3 Historically, Compendium Method TO-5, "*Method For the Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC)*" was used to quantitate formaldehyde in ambient air. This method involved drawing ambient air through a midget impinger sampling train containing 10 mL of 2N HCl/0.05% 2,4-DNPH reagent. Formaldehyde (and other aldehydes and ketones) readily formed a stable derivative with the DNPH reagent, and the DNPH derivative is analyzed for aldehydes and ketones utilizing HPLC. Compendium Method T0-11 modifies the

sampling procedures outlined in Method TO-5 by introducing a coated adsorbent. Compendium Method TO-11 is based on the specific reaction of organic carbonyl compounds (aldehydes and ketones) with DNPH-coated silica gel cartridges in the presence of a strong acid, as a catalyst, to form a stable color hydrazone derivative according to the following reaction**:**



where R and R^1 are organic alkyl or aromatic group (ketones) or either substituent is a hydrogen (aldehydes). The reaction proceeds by nucleophilic addition to the carbonyl followed by 1,2-elimination of water to form the 2,4-diphenylhydrazone derivative. The determination of formaldehyde from the DNPH-formaldehyde derivative is similar to Method TO-5 in incorporating HPLC as the analytical methodology.

1.4 Due to recent requirements in atmospheric carbonyl monitoring, EPA has determined a need to update the present methodology found in Compendium Method TO-11. The revised Compendium Method TO-11A, as published here, incl

- Guidance on collocated sampling.
- Addition of ozone denuder or scrubber to reduce interferences.
- Sampler design update to allow heated-inlet and sequential sampling.
- Update HPLC procedure for column alternatives.
- Use of commercially prepared low pressure drop DNPH-coated cartridges.

The target compound for this method is formaldehyde; however, at least 14 other carbonyl compounds can be detected and quantified.

1.5 The sampling method gives a time-weighted average (TWA) sample. It can be used for long-term (1-24 hr) sampling of ambient air where the concentration of formaldehyde is generally in the low ppb (v/v) or for short-term (5-60 min) sampling of source-impacted atmospheres where the concentration of formaldehyde could reach the ppm (v/v) levels.

1.6 The method instructs the user to purchase commercially pre-coated DNPH cartridges. The method still includes the instructions of Compendium Method TO-11 for the preparation of DNPH-coated cartridges. However due to the tedious preparation and clean room requirements, the method recommends the purchase of pre-coated DNPH cartridges that are now commercially available from at least three major suppliers. Different from previous cartridges identified in Compendium Method TO-11, the pressure drop across the newer low-pressure drop cartridges are less than 37 inches of water at a sampling flow of up to 2.0 liters/minute, allowing compatibility with pumps used in personal sampling equipment. These pre-coated commercial cartridges have generally lower and more consistent background (7) concentration of carbonyls than cartridges prepared under normal chemical laboratory environment, as specified in the original Compendium Method TO-11.

1.7 The commercially-prepared pre-coated cartridges are used as received and are discarded after use. The collected and uncollected cartridges are stored in culture tubes with polypropylene caps and placed in cold storage when not in use.

1.8 This method may involve hazardous materials, operations, and equipments. This method does not purport to address all the safety problems associated with its use. It is the responsibility of whoever uses this method to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Applicable Documents

2.1 ASTM Standards

- D1193 *Specification for Reagent Water*
- D1356 *Terminology Relating to Atmospheric Sampling and Analysis*
- D3195 *Practice for Rotameter Calibration*
- D3631 *Method for Measuring Surface Atmospheric Pressure*
- D5197 *Determination of Formaldehyde and Other Carbonyl Compounds in Air (Active Sampler Methodology)*
- E177 *Practice for Use of the Terms Precision and Bias in ASTM Test Methods*
- E682 *Practice for Liquid Chromatography Terms and Relationships*

2.2 Other Documents

- *Technical Assistance Document for Sampling and Analysis 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-D38b, May 1994.
- *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air: Method TO-11, Second Supplement*, U. S. Environmental Protection Agency, EPA-600/4-89-018, March 1989.

2.3 Other Documents

- Existing Procedures (8-10).
- Ambient Air Studies (11-15).

3. Summary of Method

3.1 A known volume of ambient air is drawn through a prepacked cartridge coated with acidified DNPH at a sampling rate of 100-2000 mL/min for an appropriate period of time. Sampling rate and time are dependent upon carbonyl concentration in the test atmosphere.

3.2 After sampling, the sample cartridges and field blanks are individually capped and placed in shipping tubes with polypropylene caps. Sample identifying tags and labels are then attached to the capped tubes. The capped tubes are then placed in a polypropylene shipping container cooled to subambient temperature (~4°C), and returned to the laboratory for analysis. Alternatively, the sample vials can be placed in a thermally-insulated styrofoam box with appropriate padding for shipment to the laboratory. The cartridges may either be placed in cold storage until analysis or immediately washed by gravity feed elution with 5 mL of acetonitrile from a plastic syringe reservoir to a graduated test tube or a 5 mL volumetric flask.

3.3 The eluate is then diluted to a known volume and refrigerated until analysis.

3.4 For determining formaldehyde, the DNPH-formaldehyde derivative can be determined using isocratic reverse phase HPLC with an ultraviolet (UV) absorption detector operated at 360 nm. To determine formaldehyde and 14 other carbonyls, the HPLC system is operated in the linear gradient program mode.

3.5 For quantitative evaluation of formaldehyde and other carbonyl compounds, a cartridge blank is likewise desorbed and analyzed.

3.6 Formaldehyde and other carbonyl compounds in the sample are identified and quantified by comparison of their retention times and peak heights or peak areas with those of standard solutions. Typically, C_1-C_7 carbonyl compounds, including benzaldehyde, are measured effectively to less than 0.5 ppbv.

4. Significance

4.1 Formaldehyde is a major compound in the formation of photochemical ozone (16). Short term exposure to formaldehyde and other specific aldehydes (acetaldehyde, acrolein, crotonaldehyde) is known to cause irritation of the eyes, skin, and mucous membranes of the upper respiratory tract (19). Animal studies indicate that high concentrations can injure the lungs and other organs of the body (19). In polluted atmospheres, formaldehyde may contribute to eye irritation and unpleasant odors that are common annoyances.

4.2 Over the last several years, carbonyl compounds including low molecular weight aldehydes and ketones have received increased attention in the regulatory community. This is due in part to their effects on humans and animals as primary irritation of the mucous membranes of the eyes, the upper respiratory tract, and the skin. Animal studies indicate that high concentrations of carbonyl compounds, especially formaldehyde, can injure the lungs, may contribute to eye irritation and effect other organs of the body. Aldehydes, either directly of indirectly, may also cause injury to plants. Sources of carbonyl compounds into the atmosphere range from natural occurrences to secondary formation through atmospheric photochemical reactions. Consequently, carbonyl compounds are both primary (directly emitted) and secondary (formed in the atmosphere) air pollutants (19).

4.2.1 Natural Occurrence. Natural sources of carbonyls do not appear to be important contributors to air pollution. Acetaldehyde is found in apples and as a by-product of alcoholic fermentation process. Other lower molecular weight aliphatic aldehydes are not found in significant quantities in natural products. Olefinic and aromatic aldehydes are present in some of the essential oils in fruits and plants. These include citronella, in rose oil; citral, in oil of lemongrass; benzaldehyde, in oil of bitter almonds; and cinnamaldehyde, in oil of cinnamon.

4.2.2 Production Sources. Aldehydes are commercially manufactured by various processes, depending on the particular aldehyde. In general, they are prepared via oxidation reactions of hydrocarbons, hydroformulation of alkenes, dehydrogenation of alcohols, and addition reactions between aldehydes and other compounds. Formaldehyde is manufactured from the oxidation of methanol as illustrated in the following equation:

$$CH_3OH \xrightarrow{[cat.]} CH_2O + H_2$$

Formaldehyde and other aldehyde production in the United States has shown a substantial growth over the last several years. This is due, in part, to their use in a wide variety of industries, such as the chemical, rubber, tanning, paper, perfume, and food industries. The major use is as an intermediate in the synthesis of organic compounds, including, alcohols, carboxylic acids, dyes, and medicinals.

4.2.3 Mobile Combustion Sources. A major source of carbonyl compounds in the atmosphere may be attributed to motor vehicle emissions. In particular, formaldehyde is the major carbonyl in automobile exhaust, accounting for 50-70 percent of the total carbonyl burden to the atmosphere (19). Furthermore, motor vehicles emit reactive hydrocarbons that undergo photochemical oxidation to produce formaldehyde and other carbonyls in the atmosphere.

4.3 Secondary Pollutant. As a secondary pollutant (formed in the atmosphere), carbonyls are formed by very complex photo-oxidation mechanism involving volatile organic compounds (VOCs) with nitrogen oxide (20,21). Both anthropogenic and biogenic (e.g., isoprene) hydrocarbons leads to *in situ* formation of carbonyls, especially formaldehyde compounds. Aldehydes are both primary pollutants and secondary products of atmospheric photochemistry.

The complete photo-oxidation mechanism is indeed complex and not well understood. However, a brief discussion is warranted (22). When VOCs and oxides of nitrogen (NO_x) are in the atmosphere and are irradiated with sunlight, their equilibrium in the photostationary state is changed. The photostationary state is defined by the equilibrium between nitrogen dioxide (NO_2), nitrous oxide (NO) and ozone (O_3). This equilibrium is theoretically maintained until VOCs are introduced. Various reactions occur to produce OH radicals. The VOCs react with the OH radicals and produce RO_2 radicals that oxidizes NO to NO_2, destroying the photostationary state. Carbonyls react with OH to produce RO_2 radicals. Likewise carbonyls, particularly formaldehyde in sunlight, are sources of the OH radicals.

The results of these processes lead to the following:

- Accumulation of ozone.
- Oxidation of hydrocarbons (HCs) to aldehydes and ketones which lead to the continued production of $HO_2\cdot$ and $OH\cdot$ radicals, the real driving force in photochemistry smog.

Consequently, the determination of formaldehyde and other carbonyl compounds in the atmosphere is of interest because of their importance as precursors in the production of photochemical smog, as photochemical reaction products and as major source of free radicals in the atmosphere.

4.4 Historically, DNPH impinger techniques have been widely used to determine atmospheric carbonyls. However, due to the limitation of applying this technique to remote locations, the solid adsorbent methodology has become a convenient alternative to impinger sampling. A number of solid adsorbents have been used over the years to support the DNPH coating. They are: glass beads, glass fiber filters, silica gel, Chromosorb® P, Florisil®, Carbopack® B, XAD-2, and C18. Several of these adsorbents are available commercially as pre-packed cartridges. The commercially available cartridges provide convenience of use, reproducibility and low formaldehyde blanks. Two of the more widely used pre-packed adsorbents are silica gel and C18.

4.4.1 Silica Gel. Silica gel is a regenerative adsorbent, consisting of amorphous silica (SiO_2) with surface OH groups, making it a polar material and enhancing surface absorption. DNPH-coated silica gel cartridges have been used by numerous investigators since 1980 for sampling formaldehyde in ambient air. Tejada (3,4) evaluated several adsorbents, including C18, Florsil, silanized glass wool, and silica gel as possible supports for the DNPH coating. Results indicated that silica gel provided the best support with minimum interferences. The studies did document that olefinic aldehydes such as acrolein and crotonaldehyde degraded partially and formed unknown species. For stable carbonyls such as formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde, and acetone, correlation with an DNPH-impinger technique was excellent. However, further studies by Arnts and Tejada identified a severe loss of carbonyl-DNPH derivative due to the reaction of atmospheric ozone on DNPH-coated silica gel cartridges while sampling ambient air. This bias was eliminated when sampling continued with the application of an ozone scrubber system (KI denuder) preceding the cartridge.

4.4.2 C18 Cartridge. C18 is an octadecylsilane bonded silica substrate which is non-polar, hydrophobic, and relatively inert, whose surface has been passivated with non-polar paraffinic groups. Because of these qualities,

C18 has been used historically as an adsorbent trap for trace organics in environmental aqueous samples through hydrophobic interactions. The adsorbed trace organic molecules are then eluted from the adsorbent with various organic solvents. In early 1990, C18 was used in an ambient air study as the support for DNPH. While C18 showed promising results (23), it's use today as the support for DNPH is limited.

4.5 Both adsorbents have historically performed adequately as the support for the DNPH coating. The comparison between silica gel and C18 as the adsorbent for the DNPH is illustrated in Table 1. The user is encouraged to review the weaknesses and strengths outlined in Table 1 for using silica gel or C18 as the adsorbent for the DNPH coating.

5. Definitions

[Note: Definitions used in this document and any user-prepared Standard Operating Procedures (SOPs) should be consistent with those used in ASTM D1356. All abbreviations and symbols are defined within this document at the point of first use.]

5.1 C18— C18 is an octadecylsilane bonded silica substrate, which is non-polar, hydrophobic, and relatively inert.

5.2 HPLC— high performance liquid chromatography.

5.3 Method Detection Limit (MDL)— the minimum concentration of an analyte that can be reported with 95% confidence that the value is above zero, based on a standard deviation of at least seven repetitive measurements of the analyte in the matrix of concern at a concentration near the low standard.

5.4 Photochemical Reaction— any chemical reaction that is initiated as a result of absorption of light.

5.5 Photochemical Smog— air pollution resulting from photochemical reactions.

5.6 ppbv— a unit of measure of the concentration of gases in air expressed as parts of the gas per billion (10^9) parts of the air-gas mixture, normally both by volume.

5.7 ppmv— a unit of measure of the concentration of gases in air expressed as parts of the gas per million (10^6) parts of the air-gas mixture, normally both by volume.

5.8 Silica Gel—silica gel is a regenerative adsorbent consisting of amorphous silica (SiO_2) with OH surface groups making it a polar material and enhancing surface reactions.

5.9 Denuder— A device designed to remove gases from an air sampling stream by the process of molecular diffusion to a collecting surface.

5.10 Certification Blank— certification blank is defined as the mean value of the cartridge blank plus three standard deviations. For Compendium Method TO-11A, the Certification Blank should be less than 0.15 µg/cartridge for formaldehyde.

5.11 Cartridge Blank— cartridge blank is the measured value of the carbonyl compounds on an unsampled, DNPH-coated cartridge. This is the value used in the calculations delineated in section 12.

5.12 Scrubber— to remove a specific gas from the air stream by passing through a pack bed.

6. Extended Methodology and Common Interferences

6.1 This procedure has been written specifically for the sampling and analysis of formaldehyde. Other carbonyl compounds found in ambient air are also observed in the HPLC analysis. Resolution of these compounds depend upon column and mobile phase conditions during HPLC analysis. Organic compounds that have the same retention time and significant absorbance at 360 nm as the DNPH derivative of formaldehyde will interfere. Such interferences (24) can often be overcome by altering the separation conditions (e.g., using alternative HPLC columns or mobile phase compositions). In addition, other aldehydes and ketones can be detected with a modification of the basic procedure. In particular, chromatographic conditions can be optimized to separate acetone and propionaldehyde and 12 other higher molecular weight aldehydes and ketones (within an analysis time of about one hour), as identified below, by utilizing one or two Zorbax ODS columns in series under a linear gradient program:

Formaldehyde	Isovaleraldehyde	Propionaldehyde	p-Tolualdehyde
Acetaldehyde	Valeraldehyde	Crotonaldehyde	Hexanaldehyde
o-Tolualdehyde	Butyraldehyde	2,5-Dimethylbenzaldehyde	Methyl ethyl ketone
Acetone	m-Tolualdehyde	Benzaldehyde	

The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4, and benzaldehyde region of the chromatogram.

6.2 Formaldehyde may be a contamination of the DNPH reagent. If user- prepared cartridges are employed, the DNPH must be purified by multiple recrystallizations in UV grade carbonyl-free acetonitrile. Recrystallization is accomplished at 40-60°C by slow evaporation of the solvent to maximize crystal size. The purified DNPH crystals are stored under UV grade carbonyl-free acetonitrile until use. Impurity levels of carbonyl compounds in the DNPH are determined by HPLC prior to use and should be less than the Certification Blank value of 0.15 μg/cartridge**.**

6.3 The purity of acetonitrile is an important consideration in the determination of allowable formaldehyde blank concentration in the reagent. Background concentrations of formaldehyde in acetonitrile will be quantitatively converted to the hydrazone, adding a positive bias to the ambient air formaldehyde concentration. Within the project quality control procedures, the formaldehyde in the acetonitrile reagent should be checked on a regular basis (see Section 9.1).

6.4 Ozone at high concentrations has been shown to interfere negatively by reacting with both the DNPH and its carbonyl derivatives (hydrazones) on the cartridge (25,26). The extent of interference depends on the temporal variations of both the ozone and the carbonyl compounds and the duration of sampling. Significant negative interference from ozone was observed even at concentrations of formaldehyde and ozone typical of clean ambient air (i.e., 2 and 40 ppb, respectively).

6.5 Exposure of the DNPH-coated sampling cartridges to direct sunlight may produce artifacts and should be avoided.

6.6 The presence of ozone in the sample stream is readily inferred from the appearance of new compounds with retention times different from the other carbonyl hydrazone compounds.

6.7 The most direct solution to the ozone interference is to remove the ozone before the sample stream reaches the coated cartridge. This process entails constructing an ozone denuder (9) or scrubber and placing it in front of the cartridge. The denuder can be constructed of 1 m of 0.64-cm outside diameter (O.D.) by 0.46-cm inside diameter (I.D.) copper tubing, that is filled with a saturated solution of KI, allowed to stand for a few minutes, drained and dried

with a stream of clean air or nitrogen for about 1 h. The capacity of the ozone denuder as described is about 100,000 ppb-hour of ozone. Packed-bed granular potassium iodide (KI) scrubbers can also be used in place of the denuder and are commercially available. Very little work has been done on long term usage of a denuder or KI scrubber to remove ozone from the ambient air gas stream. The ozone removal devices should be replaced periodically (e.g., monthly) in the sample train to maintain the integrity of the data generated.

6.8 Test aldehydes or carbonyls (formaldehyde, acetaldehyde, acrolein, propionaldehyde, benzaldehyde, and p-tolualdehyde) that were dynamically spiked into an ambient sample air stream passed through the KI denuder with practically no losses (7). Similar tests were also performed for formaldehyde (26).

6.9 Ozone scrubbers (cartridge filled with granular KI) are also available from suppliers of pre-coated DNPH cartridges. These scrubbers are optimized when the ambient air contains a minimum of 15% relative humidity.

7. Apparatus

7.1 Isocratic HPLC. System consisting of a mobile phase reservoir a high pressure pump; an injection valve (automatic sampler with an optional 25-µL loop injector); a Zorbax ODS (DuPont Instruments, Wilmington, DE) reverse phase (RP) column, or equivalent (25-cm x 4.6-mm ID); a variable wavelength UV detector operating at 360 nm; and a data system, as illustrated in Figure 1.

[Note: Most commercial HPLC analytical systems will be adequate for this application.]

7.2 Cartridge sampler. Prepacked, pre-coated cartridge (see Figure 2), commercially available or coated *in situ* with DNPH according to Section 9.

[Note: This method was developed using the Waters Sep-Pak cartridge, coated in situ with DNPH on silica gel by the users, as delineated in the original Compendium Method TO-11 as a guideline. EPA has experience in use of this cartridge during various field monitoring programs over the last several years. Other manufacturer's cartridges should work as well. However, modifications to these procedures may be necessary if another commercially available cartridge is selected.]

Major suppliers of pre-coated cartridges are:

- Supelco, Supelco Park, Bellefonte, PA 16823-0048, (800) 247-6628.
- SKC Inc., 334 Valley View Road, Eighty Four, PA 15330-9614, (800) 752-8472.
- Millipore/Waters Chromatography, P.O. Box 9162, Marlborough, MA 01752-9748, (800) 252-4752.
- Atmospheric Analysis and Consulting (AAC) Inc., 4572 Telephone Rd., Suite 920, Ventura, CA 93003, (805) 650-1642.

[Note: The SKC cartridge (see Figure 2) is an example of a dual bed tube. The glass cartridge contains a front bed of 300 mg DNPH-coated silica gel with the back bed of 150 mg DNPH-coated silica gel. Air flow through the tube should be from front to back bed, as indicated by the arrows enscribed on the cartridge. The dual bed tube cartridge may be used in atmospheres containing carbonyl concentrations in excess of the American Conference of Government Industrial Hygienists (ACGIH) 8-hour exposure limit, where breakthrough of carbonyls on the adsorbent might occur. If used in routine ambient air monitoring applications, the tube is recovered as one unit, as specified in Section 11.2.]

If commercially prepared DNPH-coated cartridges are purchased, ensure that a *"Certification Blank for Formaldehyde"* is provided for the specific batch of which that cartridge is a member. For a commercial cartridge to be acceptable, the following criteria must be met:

- Formaldehyde concentration: <0.15 µg/cartridge.

If the enhanced carbonyl analysis is being performed, the following Certification Blank criteria must also be met:

- Speciated carbonyl concentration:
  - Acetaldehyde: <0.10 µg/cartridge
  - Acetone: <0.30 µg/cartridge
  - Other: <0.10 µg/cartridge

Typical physical and chemical characteristics of commercial cartridge adsorbents are listed in Table 2 and illustrated in Figure 2.

7.3 Sampling system. the DNPH-cartridge approach is capable of accurately and precisely sampling 100-2000 mL/min of ambient air. The monitoring of carbonyl compounds has recently been enhanced by the promulgation of new ambient air quality surveillance regulations outlined in Title 40, Part 58. These regulations require States to establish additional air monitoring stations as part of their existing State Implementation Plan (SIP) monitoring network as part of EPA's Photochemical Assessment Monitoring Stations (PAMS) to include provisions for enhanced (1) monitoring of ozone and oxides of nitrogen (NO_x), (2) monitoring of volatile organic compounds (VOCs), (3) monitoring of meteorological parameters, and (4) monitoring selected carbonyl compounds (formaldehyde, acetone, and acetaldehyde). Specifically, monitoring for carbonyl involves:

- 8, 3 h sequential samples starting at midnight.
- 1, 24 h time-integrated "reality check" sample.

Consequently, the sampler must be able to accommodate numerous regulatory and practical needs. Practical needs would include:

- Ability to sequence two cartridges in series for breakthrough volume confirmation for a 24-hour sampling event.
- Ability to collocate with any of the 8, 3 h samples.

Traditionally, three sampling approaches have been used to monitor carbonyl compounds in the ambient air. They are:

- Manual single-port carbonyl sampler.
- Programmable single-port carbonyl sampler.
- Automated multi-port sampler.

Components of the single-port carbonyl sampler, for both manual and semi-automatic, are illustrated in Figure 3. Components usually include a heated manifold/sample inlet, a denuder/cartridge assembly, a flow meter, a vacuum gauge/pump, a timer and a power supply. In operation, ambient air is drawn through the denuder/cartridge assembly with a vacuum pump at a fixed flow rate between 0.1 to 2 Lpm. The vacuum gauge is used to measure the net vacuum in the system for all flow-rate corrections. Controlling the system is usually a 7-day, 14-event timer to coordinate sampling events to allow a sample to be extracted continuously or intermittently over a period of time. Finally, an elapsed-time counter is employed to measure the actual time the sampling took place. This is particularly suitable for unattended sampling when power fails for short periods.

The automated multi-port sampler is especially designed to collect numerous short-term (2 to 3 hours) sample sequentially over a 24 hour, 7 day a week, nighttime and weekend monitoring period. This arrangement allows for the sampling of short periods where the objectives of the project are to identify progress of atmospheric reactions involving carbonyls. As illustrated in Figure 4, components of the fully automated multi-port carbonyl sampler

includes a heated inlet, ozone denuder (or scrubber) inlet manifold assembly, inlet check valves, DNPH multi-port cartridge assembly, exhaust manifold, mass flow controller and sample pump. The multi-port sampler automatically switches between sampling ports at preselected times, as programmed by the user. Typically, a sequential air sampler contains a microprocessor timer/controller that provides precise control over each sampling event. The microprocessor allows the user to program individual start date and time, sample duration, and delays between samples. The timer also allows activation of the flow system prior (approximately 10 min) to sequencing to allow purging of the sampler inlet with fresh sample. Finally, the automated sequential sampler can be operated from an external signal, such as an ozone monitor, so that sampling starts above certain preset ozone levels or via a modem. As a final option, various manufacturers provide wind sensor instrumentation (wind speed and direction) which is connected to the automated sequential sampler so that sampling begins when the wind is from a preset direction and speed.

Major suppliers of commercially available carbonyl samplers are:

- Supelco, Supelco Park, Bellefonte, PA 16823-0048, (800) 247-6628.
- SKC Inc., 334 Valley View Road, Eighty Four, PA 15330-9614, (800) 752-8472.
- Millipore/Waters Chromatography, P.O. Box 9162, Marlborough, MA 01752-9748, (800) 252-4752.
- XonTech, Inc. 6862 Hayvenhurst Avenue, Van Nuys, CA 91406, (818) 787-7380.
- ATEC Atmospheric Technology, P.O. Box 8062, Calabasas, CA 91372-8062, (310) 457-2671.
- Atmospheric Analysis and Consulting (AAC) Inc., 4572 Telephone Road, Suite 920, Ventura, CA 93003, (805) 650-1642.
- Scientific Instrumentation Specialists, P.O. Box 8941, Moscow, ID, (209) 882-3860.

7.4 Stopwatch.

7.5 Polypropylene shipping container (see Figure 5) with polyethylene-air bubble padding. To hold sample cartridges.

7.6 Thermometer. To record ambient temperature.

7.7 Barometer (optional).

7.8 Volumetric flasks. Various sizes, 5-2000 mL.

7.9 Pipets. Various sizes, 1-50 mL.

7.10 Erlenmeyer flask, 1 L. For preparing HPLC mobile phase.

7.11 Graduated cylinder, 1 L. For preparing HPLC mobile phase.

7.12 Syringe, 100-250 μL. For HPLC injection, with capacity at least four times the loop value.

7.13 Sample vials.

7.14 Melting point apparatus (optional).

7.15 Rotameters.

7.16 Calibrated syringes.

7.17 Soap bubble meter or wet test meter.

7.18 Mass flow meters and mass flow controllers. For metering/setting air flow rate through sample cartridge of 100-2000 mL/min.

[Note: The mass flow controllers are necessary because cartridges may develop a high pressure drop and at maximum flow rates, the cartridge behaves like a "critical orifice." Recent studies have shown that critical flow orifices may be used for 24-hour sampling periods at a maximum rate of 2 L/min for atmospheres not heavily loaded with particulates without any problems.]

7.19 Positive displacement. Repetitive dispensing pipets (Lab-Industries, or equivalent), 0-10 mL range.

7.20 Cartridge drying manifold. With multiple standard male Luer® connectors.

7.21 Liquid syringes. 10 mL (polypropylene syringes are adequate) for preparing DNPH-coated cartridges.

7.22 Syringe rack. Made of an aluminum plate (0.16 cm x 36 cm x 53 cm) with adjustable legs on four corners. A matrix (5 cm x 9 cm) of circular holes of diameter slightly larger than the diameter of the 10-mL syringes was symmetrically drilled from the center of the plate to enable batch processing of 45 cartridges for cleaning, coating, and/or sample elution.

7.23 Luer® fittings/plugs. To connect cartridges to sampling system and to cap prepared cartridges.

7.24 Hot plates, beakers, flasks, measuring and disposable pipets, volumetric flasks, etc. Used in the purification of DNPH.

7.25 Culture tubes (20 mm x 125 mm) with polypropylene screw caps. Used to transport coated cartridges for field applications (see Figure 5), Fisher Scientific, Pittsburgh, PA, or equivalent.

7.26 Polyethylene gloves. Used to handle cartridges, best source.

7.27 Dry test meter.

7.28 User-prepared copper tubing for ozone scrubber (see Figure 6a). A 36 inch length of ¼-inch O.D. copper tubing is used as the body of the ozone scrubber. The tubing should be coiled into a spiral approximately 2 inches in O.D. EPA has considerable field experience with the use of this denuder.

[Note: Ozone scrubbers (cartridge filled with granular KI) are also available from suppliers of pre-coated DNPH cartridges, as illustrated in Figure 6(b).]

7.29 Cord heater and Variac. A 24 inch long cord heater, rated at approximately 80 watts, wrapped around the outside of the copper coil denuder, controlled by a Variac, to provide heat (~50°C) to prevent condensation of water or organic compounds from occurring within the coil.

7.30 Fittings. Bulkhead unions are attached to the entrance and exit of the copper coil to allow attachment to other components of the sampling system.

8. Reagents and Materials

[Note: Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available; Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type II of ASTM Specifications D 1193.]

8.1 2,4-Dinitrophenylhydrazine (DNPH). Aldrich Chemical or J.T. Baker, reagent grade or equivalent. Recrystallize at least twice with UV grade acetonitrile before use.

8.2 DNPH coated cartridges. DNPH coated cartridge systems are available from several commercial suppliers.

8.3 High purity acetonitrile. UV grade, Burdick and Jackson "distilled-in-glass," or equivalent. The formaldehyde concentration in the acetonitrile should be <1.5 ng/mL. It is imperative (mandatory) that the user establish the purity of the acetonitrile before use (see Section 9.1).

8.4 Deionized-distilled water. Charcoal filtered**.**

8.5 Perchloric acid. Analytical grade, best source, 60%, specific gravity 1.51**.**

8.6 Ortho-phosphoric acid. Analytical grade, best source, 36.5-38%, specific gravity 1.19**.**

8.7 Formaldehyde. Analytical grade, best source, 37% solution (w/w).

8.8 Aldehydes and ketones, analytical grade, best source. Used for preparation of DNPH derivative standards (optional)**.**

8.9 Carbonyl hydrazones. Formaldehyde and other carbonyl hydrazones are available for use as standards from commercial sources at various levels of purity**.**

8.10 Ethanol or methanol. Analytical grade, best source**.**

8.11 Nitrogen. High purity grade, best source**.**

8.12 Charcoal. Granular, best source**.**

8.13 Helium. High purity grade, best source**.**

8.14 Potassium Iodide. Analytical grade, best source. Used for coating inside of copper tubing of denuder system to remove ozone interference.

9. Preparation of Reagents and Cartridges

9.1 Purity of the Acetonitrile

9.1.1 The purity of acetonitrile is an important consideration in the determination of the formaldehyde blank concentration. Formaldehyde in the reagent will be quantitatively converted to the hydrazone and measured as part of the blank. The contribution to the blank from the reagent is dependent on the formaldehyde concentration in the reagent and the amount of the reagent used for extraction. Some examples will illustrate these considerations.

Example A

- Silica gel DNPH cartridge has a blank level of 60 ng.
- Cartridge is eluted with 5-mL of acetonitrile reagent containing a formaldehyde of 3 ng/mL.
- Analyst measures a blank level of 75 ng of which 80% comes from the cartridge and 20% comes from the reagent.

Example B

- Silica gel DNPH cartridge has a blank level of 30 ng.
- Cartridge is eluted with 5 mL of acetonitrile reagent containing a formaldehyde of 6 ng/mL.
- Analyst measures a blank level of 60 ng of which 50% comes from the cartridge and 50% comes from the reagent.

9.1.2 As a quality control procedure, the formaldehyde in the acetonitrile reagent should be checked on a regular basis. This can be done by mixing known proportions of the acetonitrile reagent and a DNPH solution having a measured formaldehyde blank. (The extract from a blank cartridge can serve as the DNPH solution.) After analyzing the resultant solution, a mass balance is performed on the observed formaldehyde level and the contribution from the DNPH reagent as shown in the following example.

- 1 mL of a DNPH solution containing 2.1 ng/mL of formaldehyde (as carbonyl) is mixed with 9 mL of acetonitrile reagent containing as unknown formaldehyde blank. The analyst measures a resultant solution concentration of 1.55 ng of formaldehyde. This data can be used to calculate the formaldehyde in the reagent:

$$HCHO\ ng/mL = \frac{(1.55\ ng/mL \times 10\ mL - 2.1\ ng/mL \times 1\ mL)}{9\ mL} = 1.49\ ng/mL$$

The formaldehyde contribution to the cartridge blank should be as low as possible but certainly less than 20% of the total measured blank. Using a cartridge blank level of 30 ng/cartridge, the formaldehyde concentration in the reagent would have to be less than 1.5 ng/mL (i.e., 50 n*M*) to give a blank level less than 20% of the measured blank.

9.2 Purification of 2,4-Dinitrophenylhydrazine (DNPH)

[Note: This procedure should be performed under a properly ventilated hood, as inhalation of acetonitrile can result in nose and throat irritation. Various health effects are resultant from the inhalation of acetonitrile. At 500 ppm in air, brief inhalation has produced nose and throat irritation. At 160 ppm, inhalation for 4 hours has caused flushing of the face (2 hour delay after exposure) and bronchial tightness (5 hour delay). Heavier exposures have produced systemic effects with symptoms ranging from headache, nausea, and lassitude to vomiting, chest or abdominal pain, respiratory depression, extreme weakness, stupor, convulsions and death (dependent upon concentration and time).]

[Note: Purified DNPH, suitable for preparing cartridges, can be purchased commercially.]

9.2.1 Prepare a supersaturated solution of DNPH by boiling excess DNPH in 200 mL of acetonitrile for approximately one hour.

9.2.2 After one hour, remove and transfer the supernatant to a covered beaker on a hot plate and allow gradual cooling to 40-60°C.

9.2.3 Maintain the solution at this temperature (40-60°C) until 95% of solvent has evaporated.

9.2.4 Decant solution to waste, and rinse crystals twice with three times their apparent volume of acetonitrile.

9.2.5 Transfer crystals to another clean beaker, add 200 mL of acetonitrile, heat to boiling, and again let crystals grow slowly at 40-60°C until 95% of the solvent has evaporated.

9.2.6 Repeat rinsing process as described in Section 9.2.4.

9.2.7 Take an aliquot of the second rinse, dilute 10 times with acetonitrile, acidify with 1 mL of 3.8 M perchloric acid per 100 mL of DNPH solution, and analyze by HPLC.

[Note: An acid is necessary to catalyze the reaction of the carbonyls with DNPH. Most strong inorganic acids such as hydrochloric, sulfuric, phosphoric, or perchloric acids will do the job. Perchloric or phosphoric acids are the preferred catalyst for using acetonitrile solution of DNPH as the absorbing solution. The DNPH derivatives do not precipitate from solution as readily as when hydrochloric or phosphoric acids are used as the catalyst. This is an ideal situation for an HPLC analytical finish as this minimizes sample handling. For most ambient air sampling, precipitation is not a problem because the carbonyl concentration is generally in the ppb range.]

9.2.8 An impurity level of <0.15 μg/cartridge of formaldehyde in DNPH-coated cartridge is acceptable (based on the Certification Blank section 5.10). An acceptable impurity level for an intended sampling application may be defined as the mass of the analyte (e.g., DNPH-formaldehyde derivative) in a unit volume of the reagent solution equivalent to less than one tenth (0.1) the mass of the corresponding analyte from a volume of an air sample when the carbonyl (e.g., formaldehyde) is collected as DNPH derivative in an equal unit volume of the reagent solution. An impurity level unacceptable for a typical 10 L sample volume may be acceptable if sample volume is increased to 100 L. If the impurity level is not acceptable for intended sampling application, repeat recrystallization.

9.2.9 If the impurity level is not satisfactory, pipet off the solution to waste, then add 25 mL of acetonitrile to the purified crystals. Repeat rinsing with 20 mL portions of acetonitrile until a satisfactorily low impurity level in the supernatant is confirmed by HPLC analysis.

9.2.10 If the impurity level is satisfactory, add another 25 mL of acetonitrile, stopper and shake the reagent bottle, then set aside. The saturated solution above the purified crystals is the stock DNPH reagent.

9.2.11 Maintain only a minimum volume of saturated solution adequate for day to day operation. This will minimize wastage of purified reagent should it ever become necessary to re-rinse the crystals to decrease the level of impurity for applications requiring more stringent purity specifications.

9.2.12 Use clean pipets when removing saturated DNPH stock solution for any analytical applications. Do not pour the stock solution from the reagent bottle.

9.3 Preparation of DNPH-Formaldehyde Derivative

[Note: Purified crystals or solutions of DNPH-derivatives can be purchased commercially.]

9.3.1 To a portion of the recrystallized DNPH, add sufficient 2N HCl to obtain an approximately saturated solution. Add to this solution formaldehyde (other aldehydes or ketones may be used if their detection is desirable), in molar excess of the DNPH. Allow it to dry in air.

9.3.2 Filter the colored precipitate, wash with 2N HCl and water and let the precipitate air dry.

9.3.3 Check the purity of the DNPH-formaldehyde derivative by melting point determination or HPLC analysis. The DNPH-formaldehyde derivative should melt at 167°C ± 1°C. If the impurity level is not acceptable, recrystallize the

derivative in ethanol. Repeat purity check and recrystallization as necessary until acceptable level of purity (e.g., 99%) is achieved.

9.3.4 DNPH derivatives of formaldehyde and other carbonyls suitable for use as standards are commercially available both in the form of pure crystals and as individual or mixed stock solutions in acetonitrile.

9.4 Preparation of DNPH-Formaldehyde Standards

9.4.1 Prepare a standard stock solution of the DNPH-formaldehyde derivative by dissolving accurately weighed amounts in acetonitrile.

9.4.2 Prepare a working calibration standard mix from serial dilution of the standard stock solution. The concentration of the DNPH-formaldehyde compound in the standard mix solutions should be adjusted to reflect relative distribution in a real sample.

[Note: Individual stock solutions of approximately 100 mg/L are prepared by dissolving 10 mg of the solid derivative in 100 mL of acetonitrile. The individual solution is used to prepare calibration standards containing the derivative of interest at concentrations of 0.5-20 μg/mL, which spans the concentration of interest for most ambient air work.]

9.4.3 Store all standard solutions in a refrigerator. They should be stable at least one month.

9.4.4 DNPH-formaldehyde standards can also be purchased from various commercial suppliers. If purchased, ensure that a "*Certification of Concentration*" is provided.

9.5 Preparation of DNPH-Coated Cartridges

[Note: This procedure must be performed in an atmosphere with a very low aldehyde background. All glassware and plastic ware must be scrupulously cleaned and rinsed with deionized water and carbonyl free acetonitrile. Contact of reagents with laboratory air must be minimized. Polyethylene gloves must be worn when handling the cartridges. If the user wishes to purchase commercially prepared DNPH-coated cartridges, they are available from various vendors. If commercial prepared DNPH-coated cartridges are purchased, ensure that a "Certification Blank for Formaldehyde" is provided for the specific batch of which that cartridge is a member. For a commercial cartridge to be acceptable, the following criteria must be met:

- *Formaldehyde concentration: <0.15 μg/cartridge.*

If the enhanced carbonyl analysis is being performed, the following Certification Blank criteria must also be met:

- *Speciated carbonyl concentration:*
  - *Acetaldehyde: <0.10 μg/cartridge*
  - *Acetone: <0.30 μg/cartridge*
  - *Other: <0.10 μg/cartridge*

One who is not experienced in the preparation of DNPH-coated cartridge is strongly advised to use certified commercially available cartridges.]

9.5.1 DNPH Coating Solution

9.5.1.1 Pipet 30 mL of saturated DNPH stock solution to a 1000 mL volumetric flask, then add 500 mL acetonitrile.

9.5.1.2 Acidify with 1.0 mL of ortho-phosphoric acid (H_3PO_4).

[Note: The atmosphere above the acidified solution should preferably be filtered through a DNPH-coated cartridge to minimize contamination from laboratory air. Shake solution, then make up to volume with acetonitrile. Stopper the flask, invert and shake several times until the solution is homogeneous. Transfer the acidified solution to a reagent bottle with a 0-10 mL range positive displacement dispenser.]

9.5.1.3 Prime the dispenser and slowly dispense 10-20 mL to waste.

9.5.1.4 Dispense an aliquot solution to a sample vial, and check the impurity level of the acidified solution by HPLC according to Section 9.2.

9.5.1.5 The impurity level should be less than the Certification Blank of <0.15 μg/cartridge for formaldehyde, similar to that in the DNPH coating solution.

9.5.2 Coating of Cartridges

9.5.2.1 Open the pre-packed cartridge package, connect the short end to a 10-mL syringe, and place it in a syringe rack (see Figure 7).

[Note: Prepare as many cartridges (~100) and syringes as possible.]

9.5.2.2 Using a positive displacement repetitive pipet, add 10 mL of acetonitrile to each of the syringes (see Figure 7).

9.5.2.3 Let liquid drain to waste by gravity.

[Note: Remove any air bubbles that may be trapped between the syringe and the silica cartridge by displacing them with the acetonitrile in the syringe.]

9.5.2.4 Set the repetitive dispenser containing the acidified DNPH coating solution to dispense 7 mL into the cartridges.

9.5.2.5 Once the effluent flow at the outlet of the cartridge has stopped, dispense 7 mL of the DNPH coating reagent into each of the syringes (see Figure 7).

9.5.2.6 Let the coating reagent drain by gravity through the cartridge until flow at the other end of the cartridge stops.

9.5.2.7 Wipe the excess liquid at the outlet of each of the cartridges with clean tissue paper.

9.5.2.8 Assemble a drying manifold with a scrubber or "guard cartridge" connected to each of the ports (see Figure 7). These "guard cartridges" are DNPH-coated and serve to remove any trace of formaldehyde in the nitrogen gas supply.

9.5.2.9 Insert cartridge connectors (flared at both ends, 0.64 by 2.5-cm outside diameter TFE-fluorocarbon FEP tubing with inside diameter slightly smaller than the outside diameter of the cartridge port) onto the long end of the scrubber cartridges.

9.5.2.10 Remove the cartridges from the syringes and connect the short ends to the exit end of the scrubber cartridge.

9.5.2.11 Pass nitrogen through each of the cartridges at about 300-400 mL/min for 5-10 minutes.

9.5.2.12 Within 10 minutes of the drying process, rinse the exterior surfaces and outlet ends of the cartridges with acetonitrile using a Pasteur pipet.

9.5.2.13 Stop the flow of nitrogen after 15 minutes, wipe the cartridge exterior free of rinsed acetonitrile and remove the dried cartridge.

9.5.2.14 Plug both ends of the coated cartridge with standard polypropylene Luer® male plugs, place the plugged cartridge in a shipping tube with polypropylene screw caps.

9.5.2.15 Put a serial number and a lot number label on each of the individual shipping tubes.

9.5.2.16 Store shipping tubes containing the DNPH-coated cartridges in a refrigerator at 4°C until use.

[Note: Plugged cartridges may also be placed in screw-capped glass culture tubes and placed in a refrigerator until use. Cartridges will maintain their integrity for up to 90 days stored in refrigerated, capped shipping tubes.]

9.5.2.17 Take a minimum of 3 blank cartridges from the cartridge batch and analyze for formaldehyde, as delineated in Section 11. The batch of user-prepared DNPH-coated cartridges is acceptable if the following criteria are met:

- Formaldehyde Certification Blank: <0.15 µg/cartridge.

If the enhanced carbonyl analysis is being performed, the following certification criteria must also be met:

- Speciated carbonyl concentration:
  - Acetaldehyde: <0.10 µg/cartridge
  - Acetone: <0.30 µg/cartridge
  - Other: <0.10 µg/cartridge

9.5.2.18 If analysis meets the above criteria, provide documentation with all cartridges associated with

that batch involving *"Certification Blank for Formaldehyde."* This certificate must be part of the project records.

9.5.2.19 If the cartridge results are close to, but above the Certification Blank, run a few more blank cartridges to check background level.

9.5.2.20 If analysis indicates failure of the cartridge, then *all* cartridges in that batch are unacceptable. Prepare a new batch of cartridges according to Section 9.5 until certification is achieved.

9.5.2.21 Store all certified cartridges in a refrigerator at 4°C until use.

9.5.2.22 Before transport, remove the shipping container (or screw-capped glass culture tubes) containing the adsorbent tubes from the refrigerator and place culture tubes in a friction-top metal can containing 1-2 inches of charcoal for shipment to sampling location. Alternately, acidified DNPH-coated filters can be used in place of charcoal filters to remove impurity carbonyl compounds in the air.

9.5.2.23 As an alternative to friction-top cans for transporting sample cartridges, the coated cartridges could be shipped in their individual glass containers (see Figure 5a). A batch of coated cartridges may also be packed in a polypropylene shipping container for shipment to the field (see Figure 5b). The container should be padded with clean tissue paper or polyethylene-air bubble padding. Do not use polyurethane foam or newspaper as padding material.

9.5.2.24 The cartridges should be immediately stored in a refrigerator or freezer (<4°C) upon arrival in the field.

9.6 Equivalent Formaldehyde Cartridge Concentration

9.6.1 One can calculate the equivalent formaldehyde background concentration (ppbv) contributed from a commercial or user-prepared DNPH-coated cartridge following exposure to formaldehyde-free air.

9.6.2 The equivalent formaldehyde background concentration includes the contribution of formaldehyde from both the acetonitrile and the cartridge.

9.6.3 Knowing the equivalent background concentration, as determined by the user (see Section 9.5.2) or supplied by the commercial supplier (see *Note*, Section 9.5), of formaldehyde in the cartridge (ng/cartridge), the formaldehyde background concentration contributed by the DNPH-coated cartridge (thus the method minimum detection limits) can be related to the total sample volume, as identified in Table 3.

9.6.4 For example, if the averaged background formaldehyde concentration supplied by the manufacturer is 70 ng/cartridge, then that cartridge can add 0.95 ppbv of equivalent formaldehyde, to the final ambient air concentration value, as delineated in Table 3 for a total air volume of 60 L.

9.6.5 The user should use DNPH-coated cartridges with the lowest background concentration to improve accuracy and detection limits.

10. Sampling Procedure

10.1 The sampling system is assembled and should be similar to that shown in Figures 3 and 4.

[Note: Figures 3 and 4 illustrate different tube/pump configurations. The tester should ensure that the pump is capable of constant flow rate throughout the sampling period.]

It is recommended that the sampling system employ a heated inlet (~50°C) coupled to an ozone denuder or scrubber to minimize water and ozone interference associated with the DNPH-coated adsorbent tube. Historically, the coated cartridges have been used as direct probes and traps for sampling ambient air when the ambient temperature was above freezing.

[Note: As illustrated in Figure 8, the ozone denuder has been effective for up to 80 hours without

breakthrough at ozone levels of approximately 700 ppb. Other studies have evaluated both denuders and scrubbers at ozone concentrations between 125 and 200ppbv and found they have effectively removed ozone from the air stream for up to 100,000 ppb-hours; however, moisture was required (~10% RH) in the gas stream (26). The user should evaluate the length of time of the application of the denuder or scrubber to his field work. Caution should be utilized when using these devices for extensive periods of time at high humidity (>65%). Regarding the 24 hour samples, special caution shoud be taken while sampling nighttime periods when relative humidities approaching 100% are frequently encountered. It is recommended that routine schedule of ozone removal device replacement should be implemented as part of the sampling program.]

[Note: For sampling ambient air below freezing, a short length (30-60 cm) of heated (50-60°F) stainless steel tubing must be added to condition the air sample prior to collection on the DNPH-coated cartridges.]

10.2 Before sample collection, the system must be checked for leaks. Plug the inlet of the system so no flow is indicated at the output end of the pump. The mass flow meter should not indicate any air flow through the sampling apparatus.

10.3 Air flow through the DNPH-adsorbent cartridge may change during sampling as airborne particles deposit on the front of the cartridge. The flow change could be significant when sampling particulate-laden atmospheres. Particle concentrations greater than 50 ug/m^3 are likely to represent a problem. For unattended or extended sampling periods, a mass flow controller is highly recommended to maintain constant flow. The mass flow controller should be set at least 20% below the maximum air flow through the cartridge.

10.4 The entire assembly (including a "test" sampling cartridge) is installed and the flow rate checked at a value near the desired sampling rate. In general, flow rates of 1,000-2,000 mL/min should be employed. The total sample volume should be selected to ensure that the collected formaldehyde concentration exceeds the background formaldehyde DNPH-cartridge concentration, as illustrated in Table 3. The total moles of carbonyl in the volume of air sampled should

not exceed that of the DNPH concentration (i.e., 2 mg cartridge). In general, a safe estimate of the sample size should be 75% of the DNPH loading of the cartridge.

[Note: If the user suspects that there will be breakthrough of a DNPH-coated cartridge during the sampling event, a backup cartridge should be used during the first sampling event. One would analyze the back-up cartridge for formaldehyde. If the back-up cartridge concentration exceeds 10% of the formaldehyde concentration on the front cartridge, then continue to use back-up cartridges in the monitoring program. However, if formaldehyde is not detected above the average blank level in the back-up cartridge after the first sampling event, then one can continue to use only one cartridge under normal representative conditions.]

[Note: The SKC tube is a dual bed configuration, allowing one to analyze the back bed (see Figure 2) for quantifying breakthrough.]

Generally, calibration is accomplished using a soap bubble flow meter or calibrated wet test meter connected to the flow exit, assuming the system is sealed.

[Note: ASTM Method D3686 describes an appropriate calibration scheme that does not require a sealed flow system downstream of the pump.]

10.5 The operator must measure and record the sampling flow rate at the beginning and end of the sampling period to determine sample volume. A dry gas meter may be included in the system to measure total sample volume and to compare against the in-line mass flow controller. Some commerical systems use flow monitors with data loggers to make these measurements.

10.6 Before sampling, flush the inlet (denuder/manifold, etc.) for approximately 15 min at the established flow rate to condition the system. Remove the glass culture tube from the friction-top metal can or styrofoam box. Let the cartridge warm to ambient temperature in the glass tube before connecting it to the sample train.

10.7 Using polyethylene gloves, remove the DNPH-coated cartridge from the shipping container and connect it to the sampling system with a Luer® adapter fitting. Most commercially available cartridges are bidirectional. However, review manufacturer suggestions for orientation of the cartridge to the inlet of the sampler.

[Note: If using the SKC dual bed tube, ensure the ambient air is pulled through the tube in the direction enscribed on the tube by an arrow.]

Record the following parameters on Compendium Method TO-11A field test data sheet (FTDS), as illustrated in Figure 9: date, sampling location, time, ambient temperature, barometric pressure (if available), relative humidity (if available), dry gas meter reading (if appropriate), flow rate, rotameter setting, cartridge batch number, and dry gas meter pump identification numbers.

10.8 The sampler is turned on and the flow is adjusted to the desired rate. A typical flow rate through one cartridge is 1.0 L/min and 0.8 L/min for two tandem cartridges.

10.9 The sampler is operated for the desired period, with periodic recording of the variables listed in Figure 9.

10.10 If the ambient air temperature during sampling is below 15°C, a heated inlet probe is recommended. However, no pronounced effect of relative humidity (between 25% - 90%) has been observed for sampling under various weather

conditions--cold, wet, and dry winter months and hot and humid summer months. However, a negative bias has been observed when the relative humidity is <25%. At high humidity, the possibility of condensation must be guarded against, especially when sampling is an air conditioned trailer.

10.11 At the end of the sampling period, the parameters discussed in Section 10.7 are recorded and the sample flow is stopped. If a dry gas meter is not used, the flow rate must be checked at the end of the sampling interval. If the flow rates at the beginning and end of the sampling period differ by more than 10%, the sample should be marked as suspect.

10.12 Immediately after sampling, remove the cartridge (using polyethylene gloves) from the sampling system, cap with Luer® end plugs, and place it back in the original labeled glass shipping container or culture tube. Cap, seal with TFE-fluorocarbon tape, and place it in appropriate padding. Refrigerate at 4°C until analysis. Refrigeration period prior to analysis should not exceed 2 weeks. If a longer storage period is expected, the cartridge should be extracted with 5 mL of acetonitrile (see Section 11.2.4 and 11.2.5) and the eluant placed in a vial for long term storage.

[Note: If samples are to be shipped to a central laboratory for analysis, the duration of the non-refrigerated period should be kept to a minimum, preferably less than two days.]

10.13 If a dry gas meter or equivalent total flow indicator is not used, the average sample flow rate must be calculated according to the following equation:

$$Q_A = \frac{Q_1 + Q_2 + \ldots Q_N}{N}$$

where:

Q_A = average flow rate, L/min.
$Q_1, Q_2 \ldots Q_N$ = flow rates determined at beginning, end, and intermediate points during sampling, L/min.
N = number of points averaged.

10.14 The total flow rate is then calculated using the following equation:

$$V_m = (T_2 - T_1) \times Q_A$$

where:

V_m = total volume sampled at measured temperature and pressure, L.
T_2 = stop time, minutes.
T_1 = start time, minutes.
$T_2 - T_1$ = total sampling time, minutes.
Q_A = average flow rate, L/min.

10.15 The total volume (V_s) at EPA standard conditions, 25°C and 760 mm Hg, is calculated from the following equation:

$$V_s = V_m \times \frac{\overline{P_A}}{760} \times \frac{298}{273 + \overline{T_A}}$$

where:

V_s = total sample volume at 25°C and 760 mm Hg pressure, L.
V_m = total sample volume at measured temperature and pressure, L.
$\overline{P_A}$ = average ambient pressure, mm Hg.
$\overline{T_A}$ = average ambient temperature, °C.

11. Sample Analysis

11.1 Sample Preparation

11.1.1 The samples (trip blank, field blank and field samples) are returned to the laboratory in a shipping container and stored in a refrigerator at (<4°C) until analysis. Alternatively, the samples may also be stored alone in their individual containers.

11.1.2 The time between sampling and extraction should not exceed 2 weeks. Since background levels in the cartridges may change due to adsorption during storage, always compare field samples to their associated field and trip blank samples, stored under the same conditions.

11.2 Sample Extraction

[Note: Beware of unintentional exposure of samplers and eluted samples to aldehyde and ketone sources. Laboratory air often holds high concentrations of acetone. Labeling inks, adhesives, and packaging containers (including vials with plastic caps) are all possible sources on contamination.]

[Note: Contamination is most likely to occur during sample extraction. Before eluting derivatives, clean all glassware by rinsing with acetonitrile, then heating in a 60°C vacuum oven for at least 30 minutes. Eluting the samples in a nitrogen-purged glove bag further reduces the risk of contamination.

The acetonitrile used to elute the DNPH derivatives is a typical source of contamination. Formaldehyde-free acetonitrile used to elute samples should be used only for this purpose, and stored in a carbonyl free environment. A concentration of 10 µg/L of any aldehyde or ketone in the acetonitrile adds 0.05 µg of that carbonyl to sample blank values if using 5 mL extraction volumes.]

11.2.1 Remove the sample cartridge from the labeled shipping tube or container. Connect the sample cartridge to a clean syringe.(Some commerical cartridges do not require the addition of a syringe for elution.)

[Note: The liquid flow during desorption should be in the reverse direction of air flow during sample collection.]

11.2.2 Place the sample cartridge syringe in the syringe rack (see Figure 7).

[Note: If the two beds in the SKC tube are being recovered separately for breakthrough studies, break the tube and place the beds in separate vials. Add exactly 5 mL of acetonitrile to each vial. Proceed with recovery, as specified in Section 11.2.4 through Section 11.2.5. Particulate in the relatively small number of samples used in the breakthrough studies should not adversely impact the sample valve or back pressure.]

11.2.3 Backflush the cartridge (gravity feed) by passing 5 mL of acetonitrile from the syringe through the cartridge to a 5-mL volumetric flask. The backflush elution approach may add particulate particles also collected on the cartridge to the acetonitrile solution which can cause sample valve failure and increase column back pressure. To minimize this, frontflush the cartridge contents with the acetonitrile reagent rather than blackflush. The use of 5mL of acetonitrile is sufficient for quantitative cartridge sample elution in either mode.

[Note: A dry cartridge has an acetonitrile holdup volume of about 0.3 mL. The eluant flow may stop before the acetonitrile in the syringe is completely drained into the cartridge because of air trapped between the cartridge filter and the syringe Luer® tip. If this happens, displace the trapped air with the acetonitrile in the syringe using a long-tip disposable Pasteur pipet.]

11.2.4 Dilute to the 5-mL mark with acetonitrile. Label the flask with sample identification. Store in refrigerated conditions until the sample is analyzed by HPLC. Pipet two aliquots into sample vials with TFE-fluorocarbon-lined septa. Analyze the first aliquot for the derivative carbonyls by HPLC. Store the second aliquot in the refrigerator until the results of the analysis of the first aliquot are complete and validated. The second aliquot can be used for confirmatory analysis, if necessary.

11.2.5 Sample eluates are stable at 4°C for up to one month.

11.3 HPLC Analysis

11.3.1 The HPLC system is assembled and calibrated as described in Section 11.4. The operating

parameters are as follows when formaldehyde is the only carbonyl of interest:

Column:	Zorbax ODS (4.6-mm ID x 25-cm), or equivalent.
Mobile Phase:	60% acetonitrile/40% water, isocratic.
Detector:	ultraviolet, operating at 360 nm.
Flow Rate:	1.0 mL/min.
Retention Time:	7 minutes for formaldehyde with one Zorbax ODS column. Thirteen minutes for formaldehyde with two Zorbax ODS columns.
Sample Injection Volume:	25 µL.

Before each analysis, the detector baseline is checked to ensure stable conditions.

11.3.2 The HPLC mobile phase is prepared by mixing 600 mL of acetonitrile and 400 mL of water. This mixture is filtered through a 0.22-μm polyester membrane filter in an all-glass and Teflon® suction filtration apparatus. The filtered mobile phase is degassed by purging with helium for 10-15 minutes (100 mL/min) or by heating to 60°C for 5-10 minutes in an Erlenmeyer flask covered with a watch glass. A constant back pressure restrictor (350 kPa) or short length (15-30 cm) of 0.25-mm (0.01 inch) ID Teflon® tubing should be placed after the detector to eliminate further mobile phase outgassing.

11.3.3 The mobile phase is placed in the HPLC solvent reservoir and the pump is set at a flow rate of 1.0 mL/min and allowed to pump for 20-30 minutes before the first analysis. The detector is switched on at least 30 minutes before the first analysis, and the detector output is displayed on a strip chart recorder or similar output device. The isocratic flow of 60% acetonitrile/40% water is adequate for the analysis of formaldehyde; however, sufficient time between air sample analyses is required to assure that all other carbonyl compounds are eluted from the HPLC column prior to the next sample. The gradient flow approach ,mentioned later (see Section 14.3) is properly programmed to elute other carbonyl compounds.

11.3.4 A 100-µL aliquot of the sample is drawn into a clean HPLC injection syringe. The sample injection loop (25-µL) is loaded and an injection is made. The data system, if available, is activated simultaneously with the injection. If a strip chart recorder is used, mark the point of injection on the chart paper.

11.3.5 After approximately one minute, the injection valve is returned to the "load" position and the syringe and valve are rinsed or flushed with acetonitrile/water mixture in preparation for the next sample analysis.

[Note: The flush/rinse solvent should not pass through the sample loop during flushing.]

The loop is cleaned while the valve is in the "load" mode.

11.3.6 After elution of the DNPH-formaldehyde derivative (see Figure 10), data acquisition is terminated and the component concentrations are calculated as described in Section 12.

11.3.7 After a stable baseline is achieved, the system can be used for further sample analyses as described above. Be sure to examine the chromatogram closely to ensure that background DNPH-formaldehyde derivative peaks are not on the solvent slope of the DNPH peak.

[Note: After several cartridge analyses, background buildup on the column may be removed by flushing with several column volumes of 100% acetonitrile.]

11.3.8 If the concentration of analyte exceeds the linear range of the instrument, the sample should be diluted with mobile phase, or a smaller volume can be injected into the HPLC.

11.3.9 If the retention time is not duplicated ($\pm$10%), the acetonitrile/water ratio may be increased or decreased to obtain the correct elution time. If the elution time is too long, increase the ratio; if it is too short, decrease the ratio. If retention time is not reproducing, the problem may be associated with the HPLC flow system. A control chart is recommended to evaluate retention time changes.

[Note: The chromatographic conditions described here have been optimized for the detection of formaldehyde. Analysts are advised to experiment with their HPLC system to optimize chromatographic conditions for their particular analytical needs. If a solvent change is necessary, always recalibrate before running samples.]

11.4 HPLC Calibration

11.4.1 Calibration standards can be prepared by the user in acetonitrile from the solid DNPH-formaldehyde derivative or liquid standards can be purchased from various manufacturers. From the solid compound, individual stock solutions of 100 ug/mL are prepared by dissolving 10 mg of solid derivative in 100 mL of acetronitrile. Since the MW of HCHO-hydrazone is 210 g/mol, and the MW of HCHO is 30 g/mol, the stock solution concentration converts to 14.3 ug/mL as formaldehyde (30/210 x 100mg/mL). The solid compound is weighed using a 5-place analytical balance and liquid dilutions are made with volumetric glassware. Stock solutions obtained from commercial suppliers generally range from 1 to 50 ug/mL as the carbonyl compound. These stock solutions are typically provided in 1 mL ampules.

11.4.2 Using the stock solution, working calibration standards are produced. To generate the highest concentration working standard, use a pipette to quantitatively transfer 1.00 ml of the stock solution to a 25 mL volumetric flask. For example, using a 14.3 ug/mL stock solution produces a working standard solution of 570 ng/mL

(14300 ng/mL x 1/25). The high concentration working standard diluted serially, using 1 to 5 mL pipettes and volumetric flasks, can produce working standards ranging between 28.5 and 570 ng/mL.

11.4.3 Each calibration standard (at least five levels) is analyzed three times and area response is tabulated against mass concentration injected (see Figure 11). All calibration runs are performed as described for sample analyses in Section 11.3. The results are used to prepare a calibration curve, as illustrated in Figure 12. The slope of the calibration curve gives the response factor, RF. Linear response is indicated where a correlation coefficient of at least 0.999 for a linear least-squares fit of the data (mass concentration versus area response) is obtained. The intercept of the calibration curve should pass through the origin. If it does not, check your reagents and standard solutions preparation procedure for possible contamination. If the calibration curve does not pass through the origin, the equation for the calibration curve should include the intercept.

11.4.4 Each new calibration curve should be verified by analyzing a standard prepared from material obtained from a second source. This standard should show a recovery of 85 to 115%. If not, corrective action is required to eliminate the discrepancy between the two sources of the standard material.

11.4.5 Once linear response has been documented, a concentration standard near the anticipated levels of each carbonyl component, but at least 10 times the detection limit, should be chosen for daily calibration. The day to day response for the various components should be within 10% of the calibration value. If greater variability is observed, prepare a fresh calibration check standard. If the variability using a freshly prepared calibration check standard is greater than 15% , a new calibration curve must be developed from fresh standards. A plot of the daily values on a Quality Control Chart (day versus concentration) is helpful to check for long term drift of the concentration value.

11.4.6 The response for each component in the daily calibration standard is used to calculate a response factor according to the following equation shown for formaldehyde:

$$RF_{HCHO} = \frac{(P - P_o)}{C_{HCHO}}$$

where:

RF_{HCHO} = response factor for formaldehyde given as area counts per ng/mL.
C_{HCHO} = concentration of analyte in the calibration standard in units of ng/mL.
P = peak area counts for the formaldehyde standard.
P_o = calibration curve intercept; in most cases this is zero.

11.4.7 The RF for each carbonyl compound is determined in the same way as that given for formaldehyde. The concentration of HCHO and other carbonyl compounds is determined with the calibration curves for each component in the analyzed sample. Example calculation for HCHO is given in section 12.

12. Calculations

Determination of the carbonyl compound air concentration requires three steps: (1) determination of the average blank and the standard deviation of the blank; (2) determination of the collected carbonyl compound mass of the cartridge; (3) calculation of the carbonyl compound air concentration. The following discusion provides these steps for formaldehyde.

12.1 Blank Determination

Since the blank level for any arbitary cartridge is unknown, an average value for the blank is used in the calculation. As noted earlier, the average blank value is determined for each lot of cartridges. For a given lot size, N, a minimum of $\sqrt{N}$ cartridge blanks (rounded to the next whole number) should be analyzed; i.e., for a lot size of

200, a minimum of $\sqrt{200}$ or 14 cartridge blanks should be analyzed. A minimum of 3 of these blanks are used for the Certification Blank, and the remaining 11 are used for field blanks. The mass of HCHO on each cartridge is determined by multiplying the observed peak area for blank cartridge solution by the acetonitrile extract volume (typically 5 mL) and dividing by the response factor as provided in the following equation:

$$M_{BL\text{-}HCHO_i} = \frac{P_{BL\text{-}HCHO_i} \times V_E}{RF_{HCHO}}$$

where:

$M_{BL\text{-}HCHOi}$ = the blank HCHO mass for cartridge , i.
RF_{HCHO} = HCHO response factor calculated in Section 11.4.5.
$P_{BL\text{-}HCHOi}$ = area counts for HCHO in blank sample extract.
V_E =extract volume in mL (usually 5 mL).

Once all blank cartridges have been measured, the average blank value is determined by the following equation:

$$\bar{M}_{BL\text{-}HCHO} = \frac{1}{N} \times \sum_{N}^{i=1} M_{BL\text{-}HCHO_i}$$

where:

$\bar{M}_{BL\text{-}HCHO}$ = the average HCHO mass for all cartridges.
$M_{BL\text{-}HCHOi}$ = blank HCHO mass for cartridge, i.
N = the number of blank cartridges.

[Note: Measurement of cartridge blanks should be distributed over the period that this particular cartridge lot is used for ambient air sampling. It is recommended that a trend plot of blank results be constructed to evaluate background carbonyl results over the period of cartridge lot utilization in the sampling program. If significant drifting is observed, blank average values should be segmented to be more representative of carbonyl background.]

12.2 Carbonyl Analyte Mass

The calculation equation for the mass of the collected carbonyl compounds on an individual cartridge is the same as that for the cartridge blanks. The gross measured carbonyl mass is determined with an equation analogous to that given in section 12.1. The equation for formaldehyde is given as**:**

$$M_{SA_i} = \frac{P_{SA_i} \times V_E}{RF_{HCHO}}$$

where:

M_{SAi} = gross HCHO mass for cartridge, i.
P_{SAi} = HCHO peak area counts for cartridge, I.

RF_{HCHO} = the response factor for HCHO.
V_E = acetonitrile extract volume in mL (typically 5 mL).

The net HCHO mass for an individual cartridge is determined by substracting the average blank value from the gross HCHO mass obtained for sample i, and is given as:

$$M_{HCHO_i} = M_{SA_i} - \bar{M}_{BL\text{-}HCHO}$$

12.3 Carbonyl Compound Concentration

The sample air concentration for carbonyl compounds cannot be determined directly from the mass measurement and requires conversion to units of volume. The conversion calculation for HCHO is determined using the ideal gas law and is given by the following equation:

$$V_{HCHO_i} = \frac{M_{HCHO_i}}{MW} \times (R \times T_{AMB}) \times \frac{760}{P_{AMB}}$$

where:

V_{HCHOi} = gas volume of HCHO on cartridge, i.
M_{HCHOi} = mass of HCHO on cartridge, i.
MW = molecular weight of HCHO, 30.03 g/mole.
R = gas constant, 0.082 L-atm/mol-deg.
T_{AMB} = ambient air temperature in degrees Kelvin, 273 + T (C^o).
P_{AMB} = ambient air pressure in torr.

For an ambient air temperature of 25°C and a pressure of 760 torr, the ideal law equation reduces to:

$$V_{HCHO_i} = 1.2276 \times M_{HCHO_i}$$

In this equation, the HCHO mass in ng is converted to a volume in nL. The volume of air that was passed through the cartridge was measured by either a mass flow controller or dry test meter calibrated at a known temperature and pressure. To determine HCHO concentration in the units of ppbv, apply the following equation:

$$C_{HCHO\ ppbv} = \frac{V_{HCHO_i}}{V_{AIR}}$$

where:

V_{HCHOi} = volume of formaldehyde in nL
V_{AIR} = volume of sample air through the cartridge

13. Performance Criterial and Quality Assurance

This section summarizes required quality assurance measures and provides guidance concerning performance criteria that should be achieved within each laboratory.

13.1 Standard Operating Procedures (SOPs).

13.1.1 Users should generate SOPs describing the following activities in their laboratory: (1) assembly, calibration, and operation of the sampling system, with make and model of equipment used; (2) preparation, purification, storage, and handling of sampling reagent and samples; (3) assembly, calibration, and operation of the HPLC system, with make and model of equipment used; and (4) all aspects of data recording and processing including lists of computer hardware and software used.

13.1.2 SOPs should provide specific stepwise instructions and should be readily available to and understood by the laboratory personnel conducting the work.

13.2 HPLC System Performance

13.2.1 The general appearance of the HPLC system should be similar to that illustrated in Figure 1.

13.2.2 HPLC system efficiency is calculated according to the following equation:

$$N = 5.54 \left(\frac{t_r}{W_{1/2}} \right)^2$$

where:

N = column efficiency, theoretical plates.
t_r = retention time of analyte, seconds.
$W_{1/2}$ = width of component peak at half height, seconds.

A column efficiency of >5,000 theoretical plates should be utilized.

13.2.3 Precision of response for replicate HPLC injections should be ±10% or less, day to day, for analyte calibration standards at 150 ng/mL or greater levels (as the carbonyl compound). At 75 ng/mL levels and below, precision of replicate analyses could vary up to 25%. Precision of retention times should be ±7% on a given day.

13.3 Process Blanks

13.3.1 At least one field blank should be used for each day of field sampling, shipped and analyzed with each group of samples. The number of samples within a group and/or time frame should be recorded so that a specified minimum number of blanks is obtained for a given cartridge lot used for field samples. The field blank is treated identically to the samples except that no air is drawn through the cartridge. The performance criteria described in Section 9.2 should be met for field blanks. It is also desirable to analyze trip and laboratory blank cartridges as well, to distinguish between possible field and lab contamination.

[Note: Remember to use the field blank value for each cartridge lot when calculating concentration. Do not mix cartridge lots in the blank value determinations]

13.4 Method Precision and Accuracy

13.4.1 At least 50% of the sampling events should include a collocated sample. A collocated sample is defined as a second sampling port off the common sampling manifold. If more than five samples are collected per sampling event, a collocated sample should be collected for each sampling event. Precision for the collocated samples should be ±20% or better. EPA historical data has demonstrated effectiveness in reaching ±20%, as illustrated in Figure 13.

13.4.2 Precision for replicate HPLC injections should be ±10% or better, day to day, for calibration standards.

13.4.3 Cartridges spiked with analytes of interest can be used in round-robin studies to intercompare several laboratories performing carbonyl analyses. The spiked samples are prepared in the laboratory by spiking a blank cartridge with a solution of derivatized carbonyls in acetonitrile. The laboratory preparing the spike samples should analyze at a minimum 3 of the prepared spiked samples to evaluate the consistency of prepared samples.

13.4.4 Before initial use of the method, each laboratory should generate triplicate spiked samples at a minimum of three concentration levels, bracketing the range of interest for each compound. Triplicate nonspiked samples must also be processed. Spike recoveries of >80 ±10% and blank levels should be achieved.

13.4.5 For ambient air sampling, an ozone denuder must be used as part of the sampling system. As discussed in Section 6.4, ozone effects the ultimate method precision and accuracy by reacting with its carbonyl derivative (hydrazones) on the cartridge. To illustrate this point, Figure 14 documents the concentration of formaldehyde captured on collocated DNPH-cartridges, one with a denuder (see Figure 14a) and the other without a denuder (see Figure 14b). The formaldehyde peak is considerably higher with use of an ozone denuder.

13.5 Method Detection Limits

13.5.1 Determine method detection limits using the procedures in 40 CFR Part 136B. Prepare a low level standard of the carbonyl derivatives at a concentration within two to five times the estimated method detection limit. Inject the standard into the analytical system seven times.

13.5.2 Calculate the measured concentration using the calibration curve.

13.5.3 Determine the standard deviation for the seven analyses and use the standard deviation to calculate the detection limit as described in 40 CFR Part 136B.

13.6 General QA/QC Requirements

13.6.1 General QA/QC requirements associated with the performance of Compendium Method TO-11A include:

Sampling

- Each sampling event, flow calibration with bubble meter, both pre- and post-checks.
- Mass flow meter calibration factor determined every quarter.
- Each sampling event, leak check, both pre- and post-checks.
- 10 percent of field samples collocated to help calculate method precision and evaluate biases.
- 10 percent of field samples operated with back-up cartridge to evaluate analyte breakthrough.
- Field and trip (optional) blank cartridges are included with each field sample collection program.
- Sample volumes calculated and reviewed project QA officer.

Reagents

- Coating solution prepared from concentrated stock solution immediately before each coating.

- Solution analyzed before each coating to determine acceptability (less than 0.15 µg/cartridge for each aldehyde), control chart of contaminant concentration maintained.
- Three blank cartridges per lot for immediate elution/analysis to determine Certification Blank for the carbonyl compounds.

Analysis

- Multi point calibration curve performed each six months.
- Each initial calibration verified with a standard from a second source.
- Continuing calibration standard (mid-level) analyses every analytical run to evaluate precision, peak resolution and retention time drift.
- Method detection limits (MDLs) verified annually or after each instrument change.
- Replicate analysis of approximately 10 percent of sample eluents to evaluate precision.
- Samples quantitated against least squares calibration line.
- Performance evaluation (PE) sample acquired from independent sources analyzed prior to and after field samples.
- Random collocated samples shipped to independent laboratory for analysis and compared to in-house collocated sample.
- Testing of acetonitrile used for sample extraction for background carbonyl evaluation.

Data Acquisition

- Sample chromatograms and standards checked daily for peak shape and integration quality, resolution of carbonyls, overall sensitivity and retention time drift.
- Separate tape backups made of raw data immediately after completion of each analysis.
- Peaks in each sample checked for correct ID and integration using system software before export to ASCII file.
- Final results checked and edited by project QA officer before producing final report.
- Tape backups of final data files produced.

13.6.2 All results should be reviewed by the project QA officer, independent of the field and laboratory operations, to evaluate the overall adherence to the methodology in meeting the program data quality objectives (DQOs).

14. Detection of Other Aldehydes and Ketones

14.1 Introduction

14.1.1 The procedure outlined above has been written specifically for the sampling and analysis of formaldehyde in ambient air using an adsorbent cartridge and HPLC. Ambient air contains other aldehydes and ketones. Optimizing chromatographic conditions by using two Zorbax ODS columns in series and varying the mobile phase composition through a gradient program will enable the analysis of other aldehydes and ketones. Alternatively, other aldehydes and ketones may also be analyzed using a single C-18, reverse phase column and a ternary gradient as described by Waters or Smith, et al. (*J. Chromatography*, 483, 1989, 431-436). Thus, other aldehydes and ketones can be detected with a modification of the basic procedure.

14.1.2 In particular, chromatographic conditions can be optimized to separate acetaldehyde, acetone, propionaldehyde, and some higher molecular weight carbonyls within an analysis time of about 1 h by utilizing two Zorbax ODS columns in series, and a linear mobile phase program. Operating the HPLC in a gradient mode with one Zorbax ODS column may also provide adequate resolution and separation. Carbonyl compounds covered within the scope of this modification include:

Formaldehyde	Crotonaldehyde	
o-Tolualdehyde		
Aceteldehyde	Butyraldehyde	
m-Tolualdehyde		
Acetone	Benzaldehyde	
p-Tolualdehyde		
Propionaldehdye	Isovaleraldehyde	
Hexanaldehyde		
Valeraldehyde	2,5-Dimethylbenzaldehyde	Methyl ethyl ketone

14.1.3 The linear gradient program varies the mobile phase composition periodically to achieve maximum resolution of the C-3, C-4 and benzaldehyde region of the chromatogram. The following gradient program was found to be adequate to achieve this goal: Upon sample injection, linear gradient from 65% acetonitrile (ACN)/35% water to 55% ACN/45% water in 36 min; to 100% ACN in 20 min; 100% ACN for 5 min; reverse linear gradient from 100% ACN to 60% ACN/40% water in 1 min; maintain at 60% ACN/40% water for 15 min.

14.2 Sampling Procedures

Same as Section 10.

14.3 HPLC Analysis

14.3.1 The HPLC system is assembled and calibrated as described in Section 11. The operating parameters are as follows:

Column:	Zorbax ODS, two columns in series
Mobile Phase:	Acetonitrile/water, linear gradient
Step 1.	60-75% acetonitrile/40-25% water in 30 minutes.
Step 2.	75-100% acetonitrile/25-0% water in 20 minutes.
Step 3.	100% acetonitrile for 5 minutes.
Step 4.	60% acetonitrile/40% water reverse gradient in 1 minute.
Step 5.	60% acetonitrile/40% water, isocratic, for 15 minutes.
Detector:	Ultraviolet, operating at 360 nm
Flow Rate:	1.0 mL/min
Sample Injection Volume:	25 µL

14.3.2 The gradient program allows for optimization of chromatographic conditions to separate acetaldehyde, acetone, propionaldehyde, and other higher molecular weight aldehydes and ketones in an analysis time of about one hour.

14.3.3 The chromatographic conditions described here have been optimized for a gradient HPLC system equipped with a UV detector (variable wavelength), an automatic sampler with a 25-µL loop injector and two DuPont Zorbax ODS columns (4.6 x 250-mm), a recorder, and an electronic integrator. Analysts are advised to experiment with their HPLC systems to optimize chromatographic conditions for their particular analytical needs. Highest chromatographic resolution and sensitivity are desirable but may not be achieved. The separation of acetaldehyde, acetone, and propionaldehyde should be a minimum goal of the optimization.

14.3.4 The carbonyl compounds in the sample are identified and quantified by comparing their retention times and area counts with those of standard DNPH derivatives. Formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde, benzaldehyde, and o-, m-, p-tolualdehydes can be identified with a high degree of confidence. The

identification of butyraldehyde is less certain because it coelutes with isobutyraldehyde and is only partially resolved from methyl ethyl ketone under the stated chromatographic conditions. A typical chromatogram obtained with the gradient HPLC system for detection of other aldehydes and ketones is illustrated in Figure 15.

14.3.5 The concentrations of individual carbonyl compounds are determined as outlined in Section 12.

14.3.6 Performance criteria and quality assurance activities should meet those requirements outlined in Section 13.

15. Precision and Bias

15.1 This test method has been evaluated by round robin testing. It has also been used by two different laboratories for analysis of over 1,500 measurements of formaldehyde and other aldehydes in ambient air for EPA's Urban Air Toxics Program (UATP), conducted in 14 cities throughout the United States.

15.2 The precision of 45 replicate HPLC injections of a stock solution of formaldehyde-DNPH derivative over a 2-month period has been shown to be 0.85% relative standard deviation (RSD).

15.3 Triplicate analyses of each of twelve identical samples of exposed DNPH cartridges provided formaldehyde measurements that agreed within 10.9% RSD.

15.4 A total of 16 laboratories in the U.S., Canada, and Europe participated in a round robin test that included 250 blank DNPH-cartridges, three sets of 30 cartridges spiked at three levels with DNPH derivatives, and 13 sets of cartridges exposed to diluted automobile exhaust gas. All round robin samples were randomly distributed to the participating laboratories. A summary of the round robin results is shown in Table 4.

15.5 The absolute percent differences between collocated duplicate sample sets from the 1988 UATP program were 11.8% for formaldehyde (n=405), 14.5% for acetaldehyde (n=386), and 16.7% for acetone (n=346).

15.6 Collocated duplicate samples collected in the 1989 UATP program and analyzed by a different laboratory showed a mean RSD of 0.07, correlation coefficient of 0.98, and bias of -0.05 for formaldehyde. Corresponding values for acetaldehyde were 0.12, 0.95 and -0.54, respectively. In the 1988 UATP program, single laboratory analyses of spiked DNPH cartridges provided over the year showed an average bias of +6.2% for formaldehyde (n=14) and +13.8% for acetaldehyde (n=13).

15.7 Single laboratory analyses of 30 spiked DNPH cartridges during the 1989 UATP program showed an average bias of +1.0% (range -49 to +28%) for formaldehyde and 5.1% (range -38% to +39%) for acetaldehyde.

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TABLE 1. COMPARISON OF DNPH COATED CARTRIDGES: SILICA GEL VS. C18

Topic	Comparison	Discussion
Background	Silica gel < C18	Silica gel is purer, therefore less background contamination from acetone and formaldehyde as compared to C18.
Breakthrough	Silica gel < C18	C18 allows carbonyl compounds to breakthrough easier with longer sampling periods, thus causing bias results. C18 has a lower capacity for carbonyls in general. Loading of DNPH on C18 plays an important role in breakthrough for carbonyls.
Ozone interference	Silica gel C18	Ozone interference with silica gel is documented. Ozone interference with C18 is not clear at this time. Therefore, must use denuder with both systems.
Extraneous chromato-graphic peaks	Silica gel C18	Researchers have detected extraneous peaks in the chromatography of both C18 and silica gel when ozone is present.

TABLE 2. TYPICAL DNPH-CARTRIDGE SPECIFICATIONS

Category	Typical Specifications
Adsorbent	chromatographic grade silica or C18 coated with 2,4-dinitrophenylhydrazine (DNPH)
Particle size	150-1000 µm (60/100 mesh to 18/35 mesh)
DNPH loading[1]	0.3-0.9% (~1-3 mg/cartridge)
Bed weight[2]	approx. 350 mg
Capacity	approx. 75 µg formaldehyde, assuming a 50% consumption of DNPH
Background (per cartridge)	<0.15 µg formaldehyde <0.10 µg acetaldehyde <0.10 µg other carbonyls <0.30 µg acetone
Pressure drop	7 inches of water @ 0.5 L/min 15 inches of water @ 1.0 L/min 37 inches of water @ 2.0 L/min
Sampling temperature	10°C to 100°C
Collection efficiency	>95% for formaldehyde for sampling rates up to 2.0 L/min
Solvent hold-up volume	~1.0 mL
Tube dimensions	From ~2 inches to ~5 inches in length ~1 inch O.D. at widest point

[1]Loading is variable among commercial suppliers.
[2]The SKC tube is a dual bed cartridge with 300 mg of DNPH-coated silica gel in the front bed and 150 mg of DNPH-coated silica gel in the back bed.

TABLE 3. EQUIVALENT FORMALDEHYDE CONCENTRATION (ppbv) RELATED TO BACKGROUND FORMALDEHYDE CONCENTRATION (ng/cartridge)

Equivalent formaldehyde concentration (ppbv)		Sample volume, L			
		60	120	180	1440
formaldehyde cartridge concentration ng/cartridge	70	0.950	0.475	0.317	0.040
	100	1.358	0.679	0.453	0.057
	150	2.037	1.018	0.679	0.085

TABLE 4. ROUND ROBIN TEST RESULTS[a]

Sample Type	Formaldehyde	Acetaldehyde	Propionaldehyde	Benzaldehyde
Blank cartridges:				
µg aldehyde	0.13	0.18	0.12	0.06
(% RSD)	46	70	47	44
n	33	33	23	8
Spiked[b] cartridges:				
% recovery (% RSD)				
low				
medium	89.0 (6.02)	92.6 (13.8)	108.7 (32.6)	114.7 (36.1)
high	97.2 (3.56)	97.8 (7.98)	100.9 (13.2)	123.5 (10.4)
n	97.5 (2.15)	102.2 (6.93)	100.1 (6.77)	120.0 (8.21)
	12	13	12	14
Exhaust samples:				
µg aldehyde	5.926	7.990	0.522	0.288
% RSD	12.6	16.54	26.4	19.4
n	31	32	32	17

[a]Sixteen participating laboratories. Statistics shown after removal of outliers.
[b]Normal spiking levels were approximately 0.5, 5 and 10 µg of aldehyde, designated as low, medium, and high in this table.

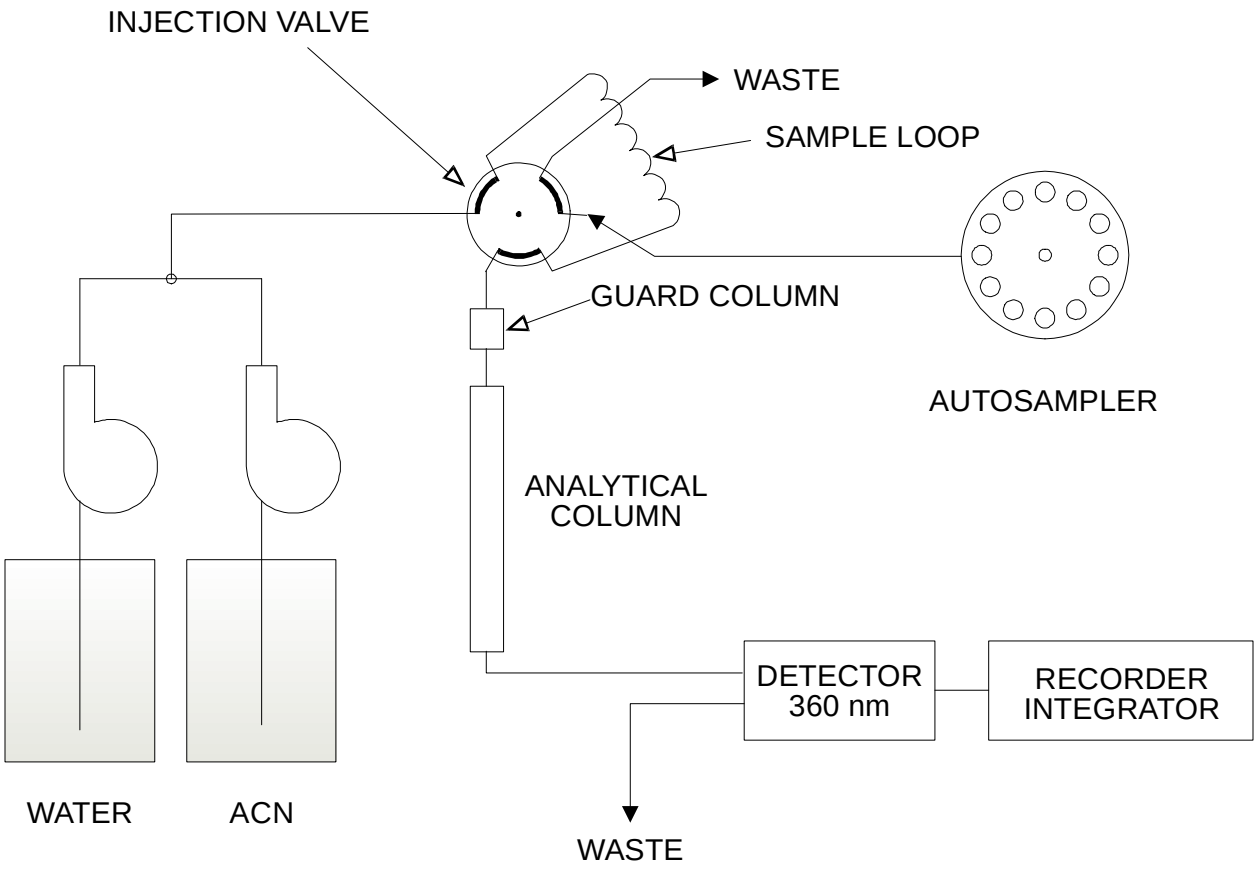


Figure 1. Basic high-performance liquid chromatographic (HPLC) system used for carbonyl analysis.

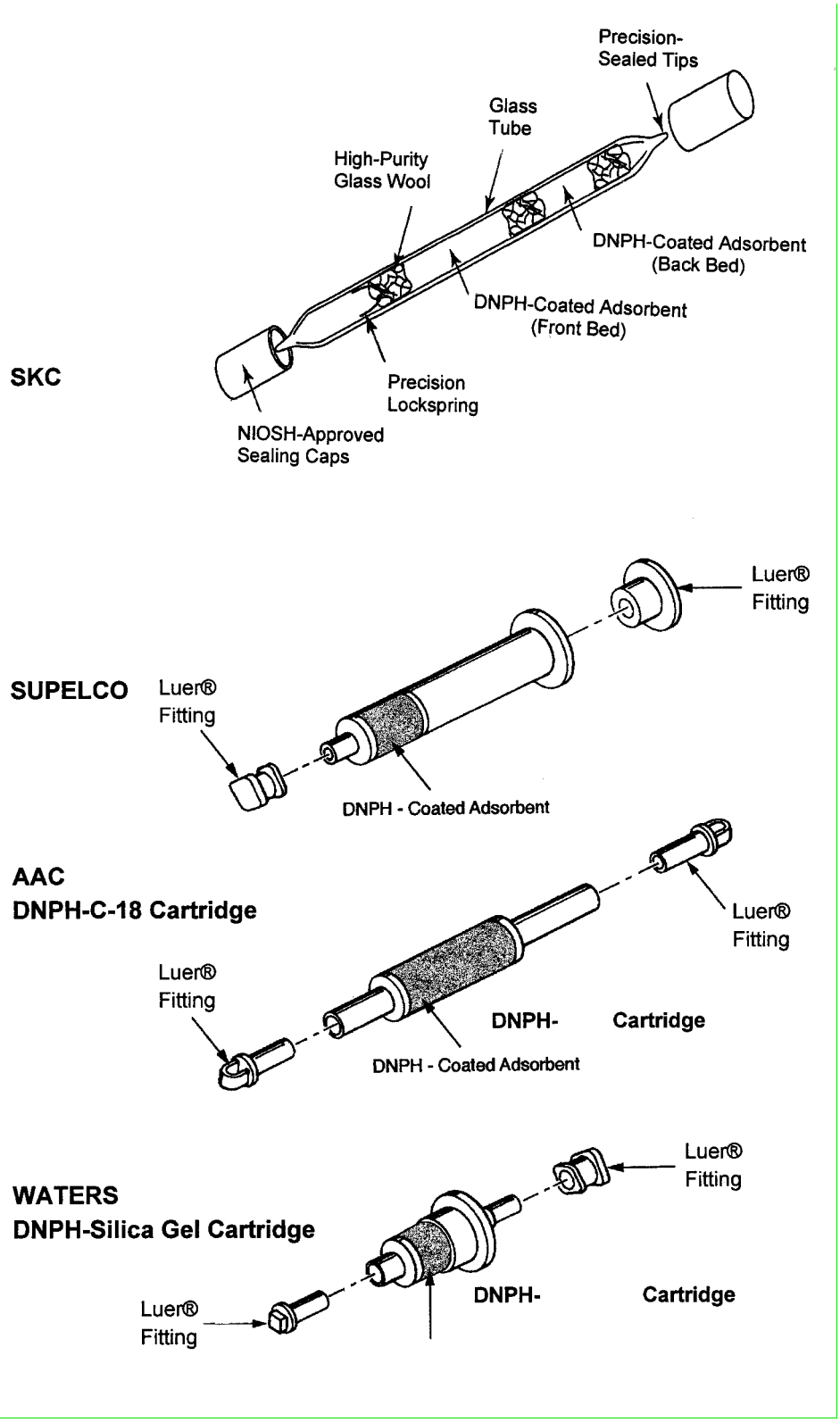


Figure 2. Example of commercially available DNPH-cartridges.

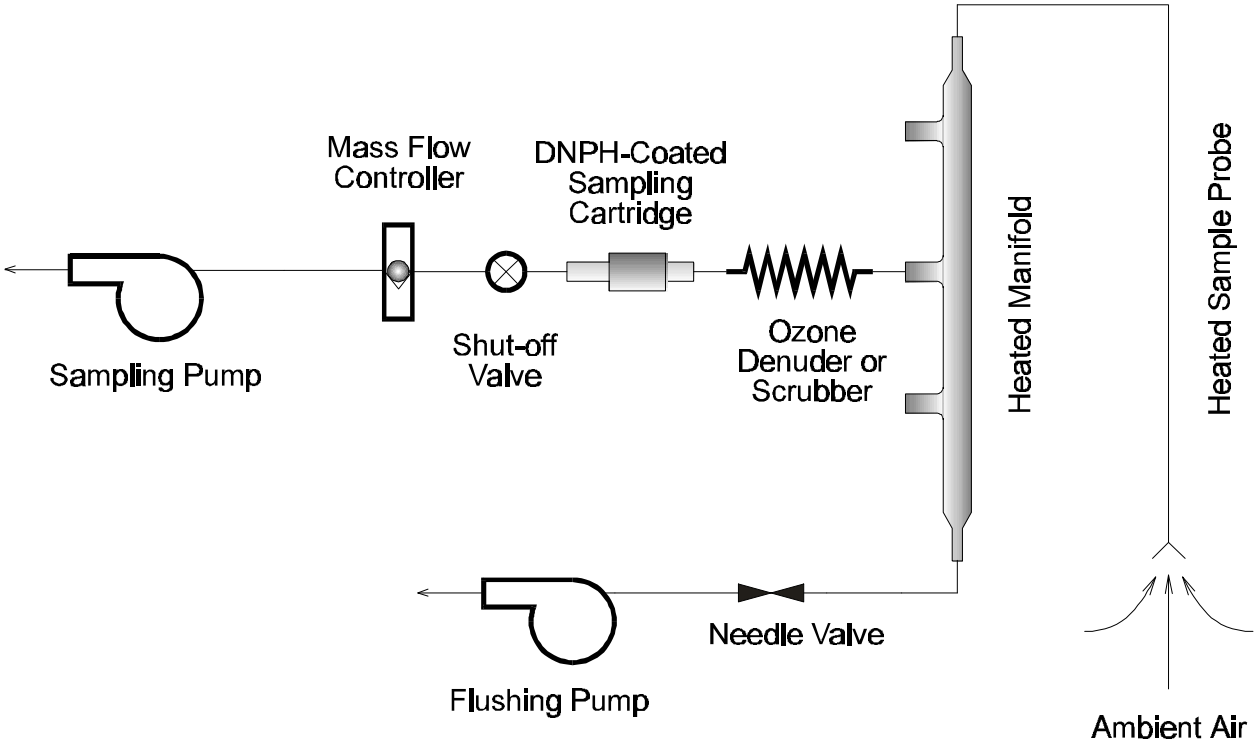


Figure 3. Example of configuration of a single-port carbonyl sampler using DNPH-coated cartridges.

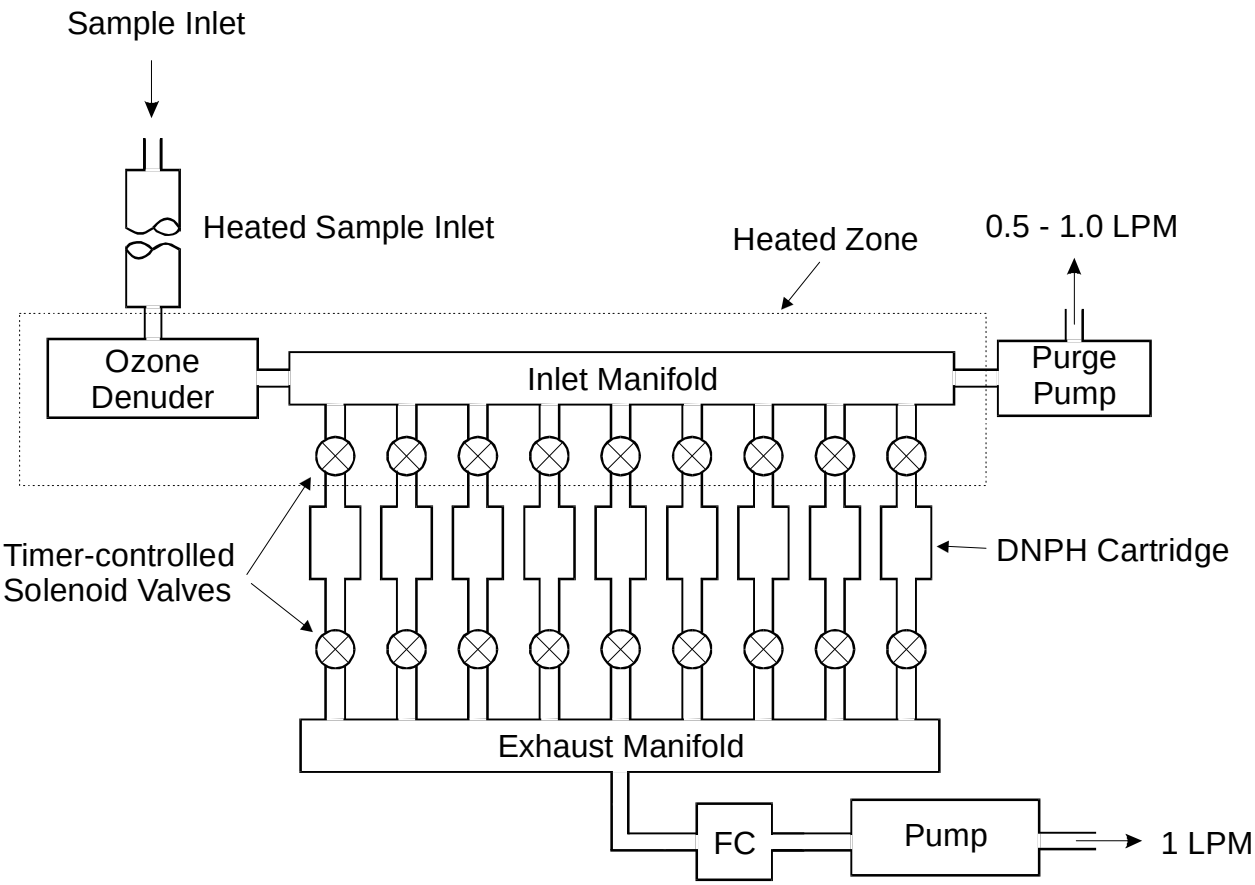


Figure 4. Example of components of an automated multi-port sampler for carbonyls monitoring using DNPH-coated cartridges.

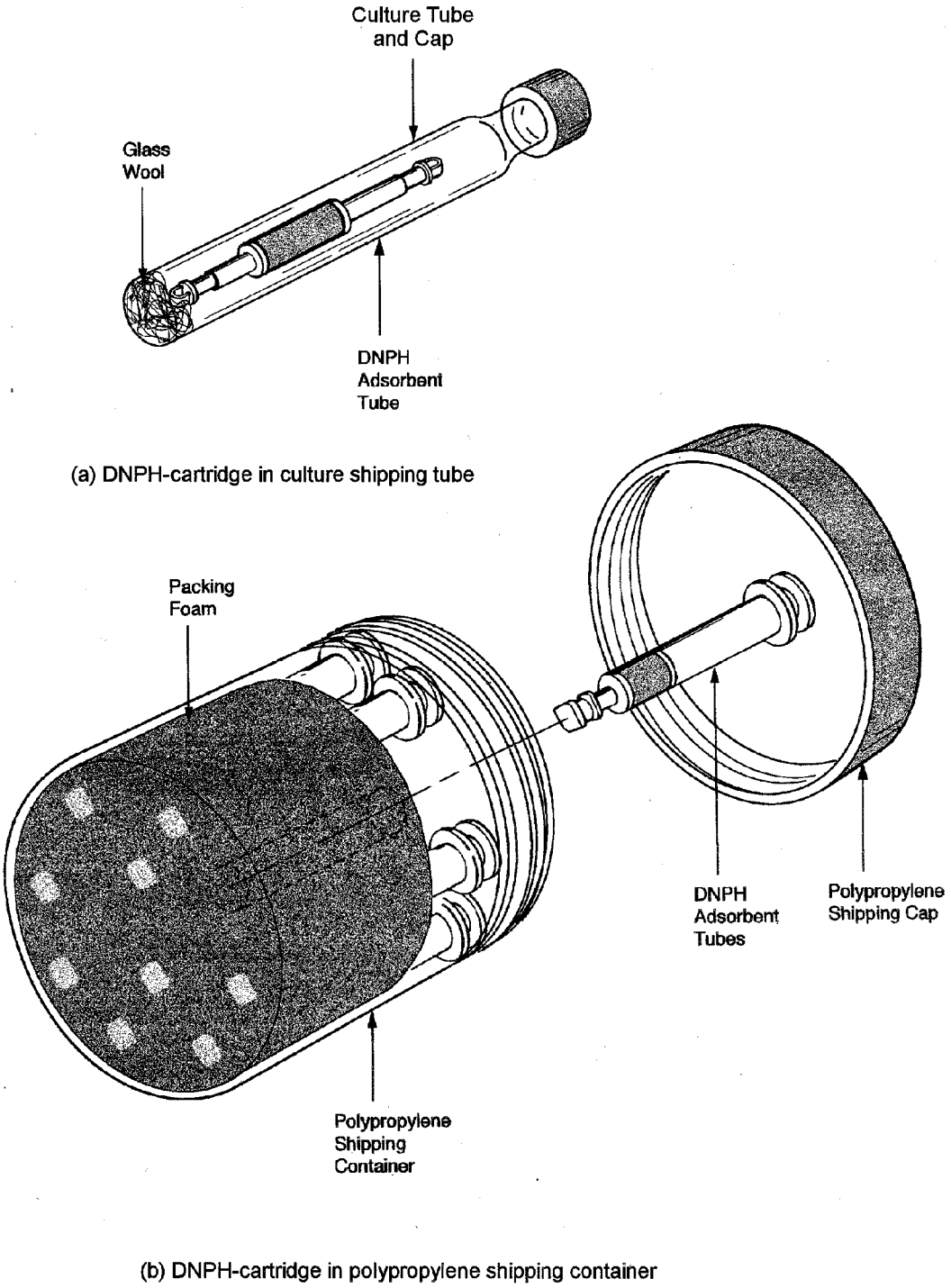
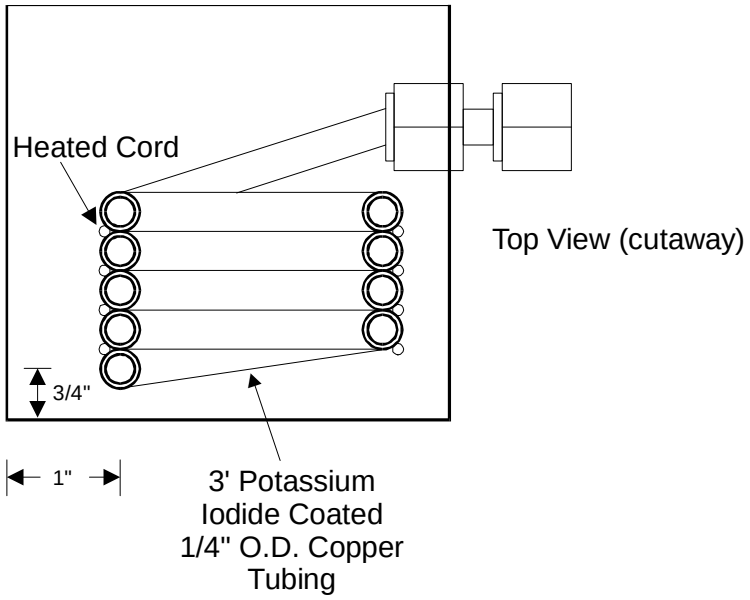
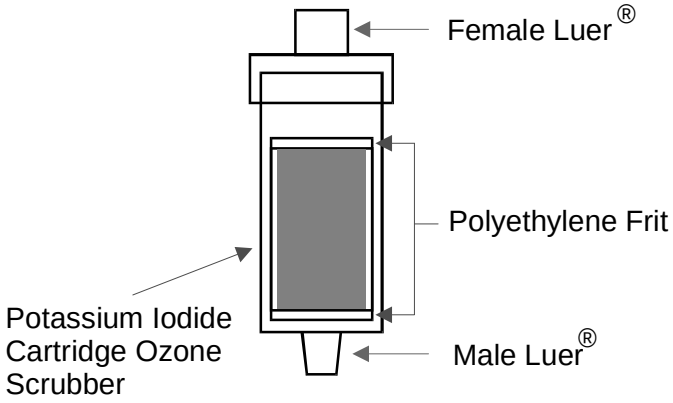


Figure 5. Example of commercially available shipping containers for DNPH cartridges.



(a) Cross-sectional view of EPA's ozone denuder assembly



(b) Commercially available packed granular potassium iodide (KI) ozone scrubber

Figure 6. Example of (a) cross-sectional view of EPA's ozone denuder assembly, and (b) commercially available packed granular potassium iodide (KI) ozone scrubber.

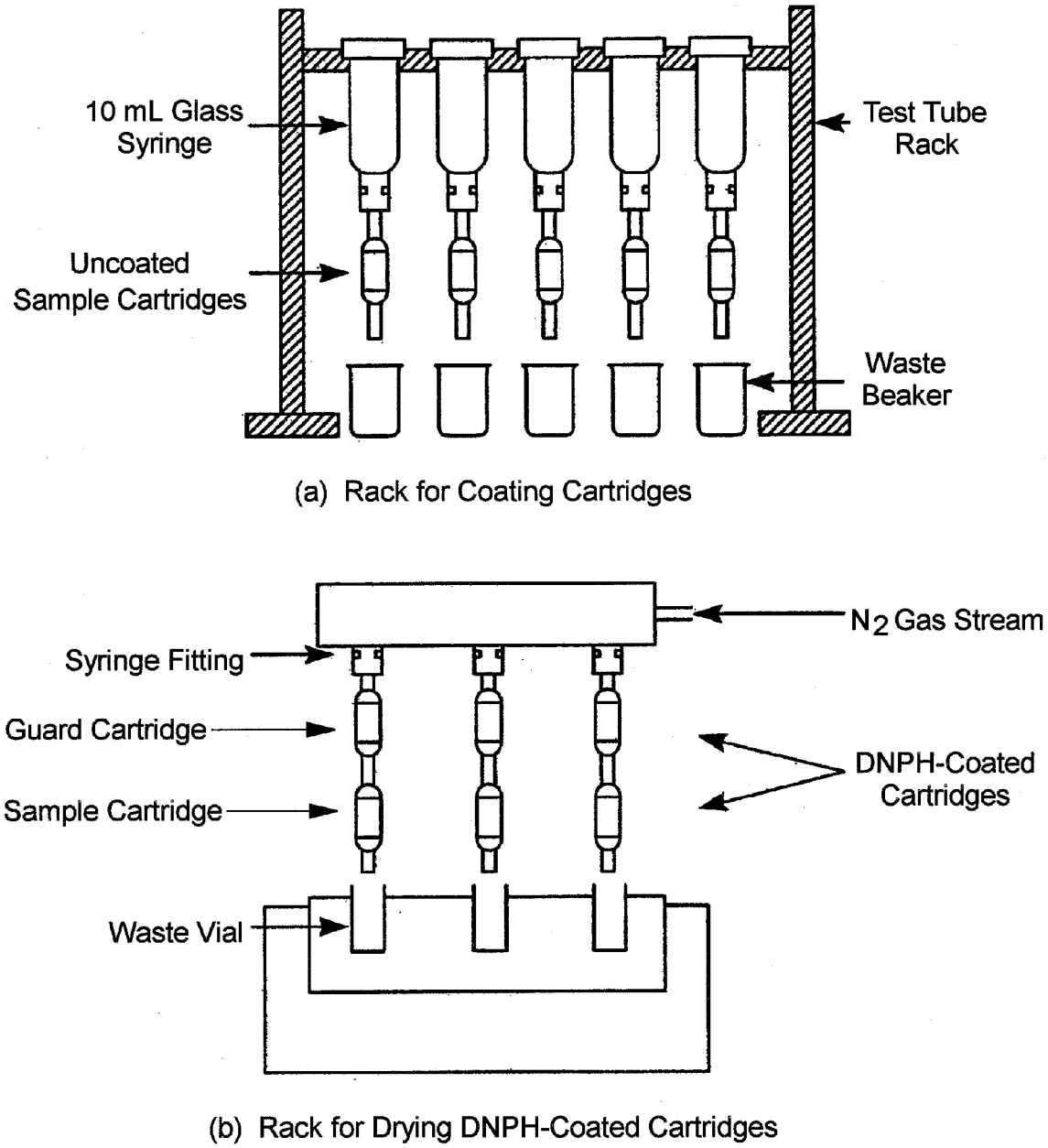


Figure 7. Example of a typical syringe rack for coating (a) and drying (b) sample cartridges.

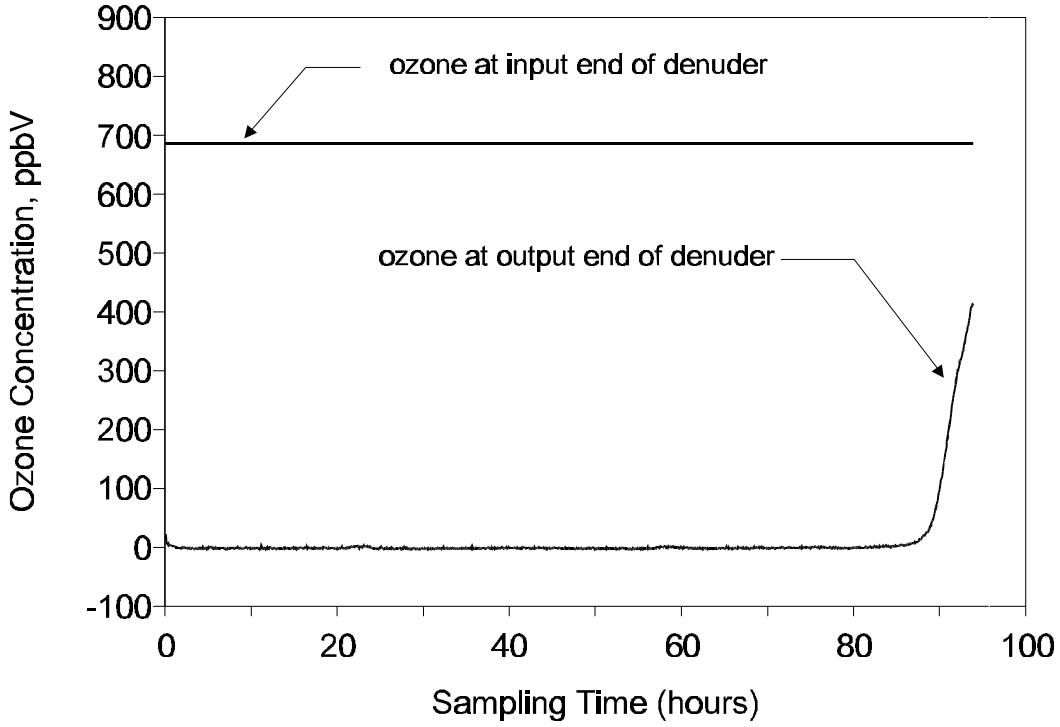


Figure 8. Example of capacity of 3' x 0.25" O.D. x 4.6-mm I.D. copper KI ozone denuder at 2 L/min flow.

COMPENDIUM METHOD TO-11A
CARBONYL SAMPLING FIELD TEST DATA SHEET
(One Sample per Data Sheet)

I. GENERAL INFORMATION

PROJECT: _____
SITE: _____
LOCATION: _____
INSTRUMENT MODEL NO.: _____
PUMP SERIAL NO.: _____
ADSORBENT CARTRIDGE INFORMATION:
Type: _____
Adsorbent: _____
Serial Number: _____
Sample Number: _____

DATES(S) SAMPLED: _____
TIME PERIOD SAMPLED: _____
OPERATOR: _____
CALIBRATED BY: _____
OZONE DENUDER USE TIME (Hr): _____
HEATED INLET: _____ YES _____ NO

II. SAMPLING DATA INFORMATION

Start Time: _____ Stop Time: _____

Time	Dry Gas Meter Reading	Rotameter Reading	Flow Rate, *QmL/min	Ambient Temperature, °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments
Avg.							

* Flow rate from rotameter or soap bubble calibrator (specify which).
Total Volume Data (V_m) (use data from dry gras meter, if available)

V_m = (Final - Initial) Dry Gas Meter Reading, or = _____ L
or

$$V_m = \frac{Q_1 + Q_2 + Q_3 \ldots Q_N}{N} \times \frac{1}{1000 \times (Sampling\ Time\ in\ Minutes)}$$ = ___ L

III. COMMENTS

_____
_____
_____

Figure 9. Example of Compendium Method TO-11A field test data sheet (FTDS).

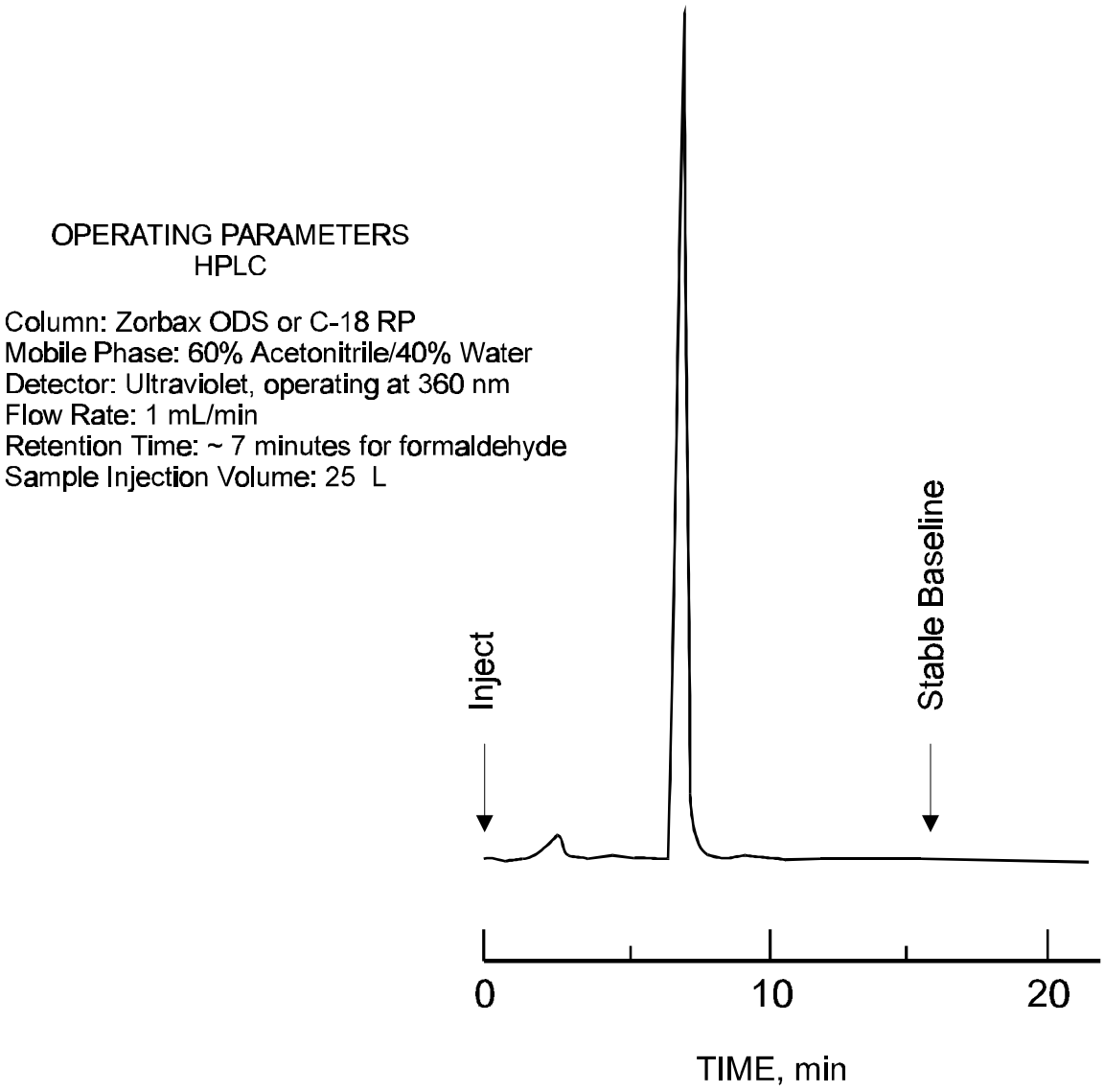


Figure 10. Example of chromatogram of DNPH-formaldehyde derivative.

OPERATING PARAMETERS HPLC

Column: Zorbax ODS or C-18 RP
Mobile Phase: 60% Acetontrile/40% Water
Detector: Ultraviolet, operating at 360 nm
Flow Rate: 1 mL/min
Retention Time: ~ 7 minutes for formaldehyde
Sample Injection Volume: 25 μL

Peak	Conc. μg/mL	Area Counts
a	0.61	226541
b	1.23	452186
c	6.16	2257271
d	12.32	4711408
e	18.48	6053812

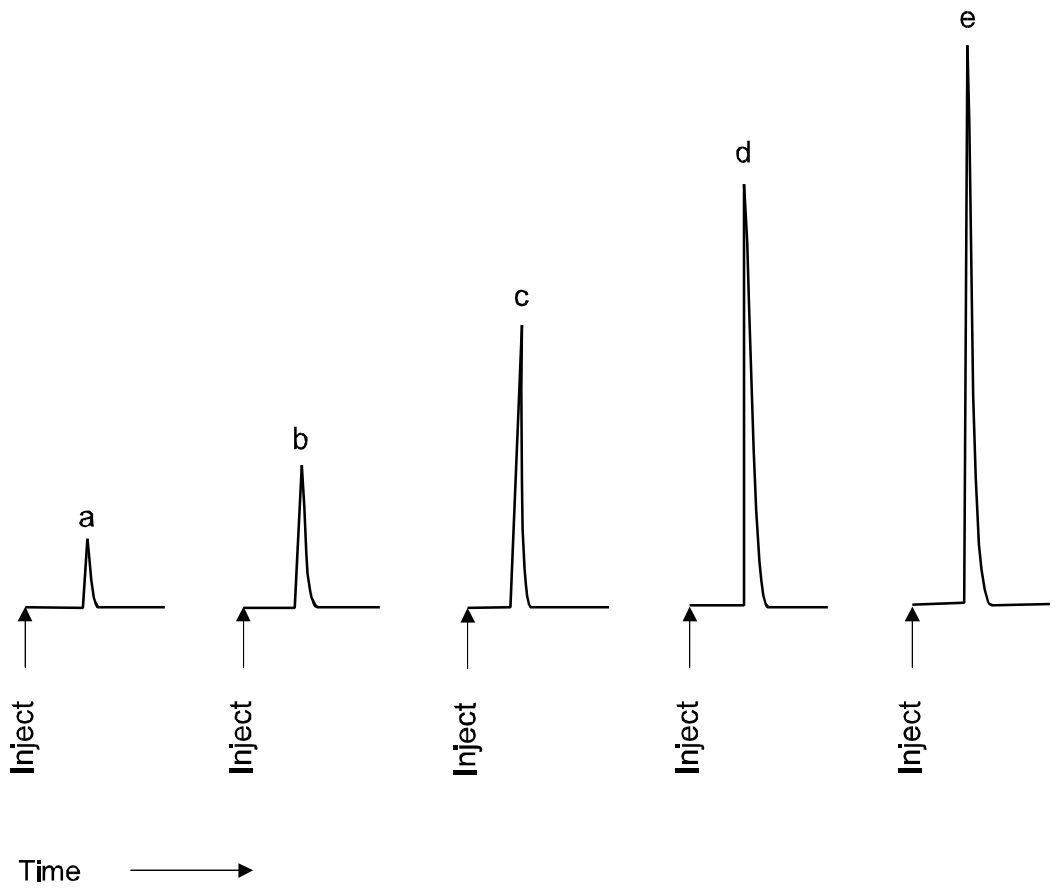


Figure 11. Example of HPLC chromatogram of varying concentration of DNPH-formaldehyde derivative.

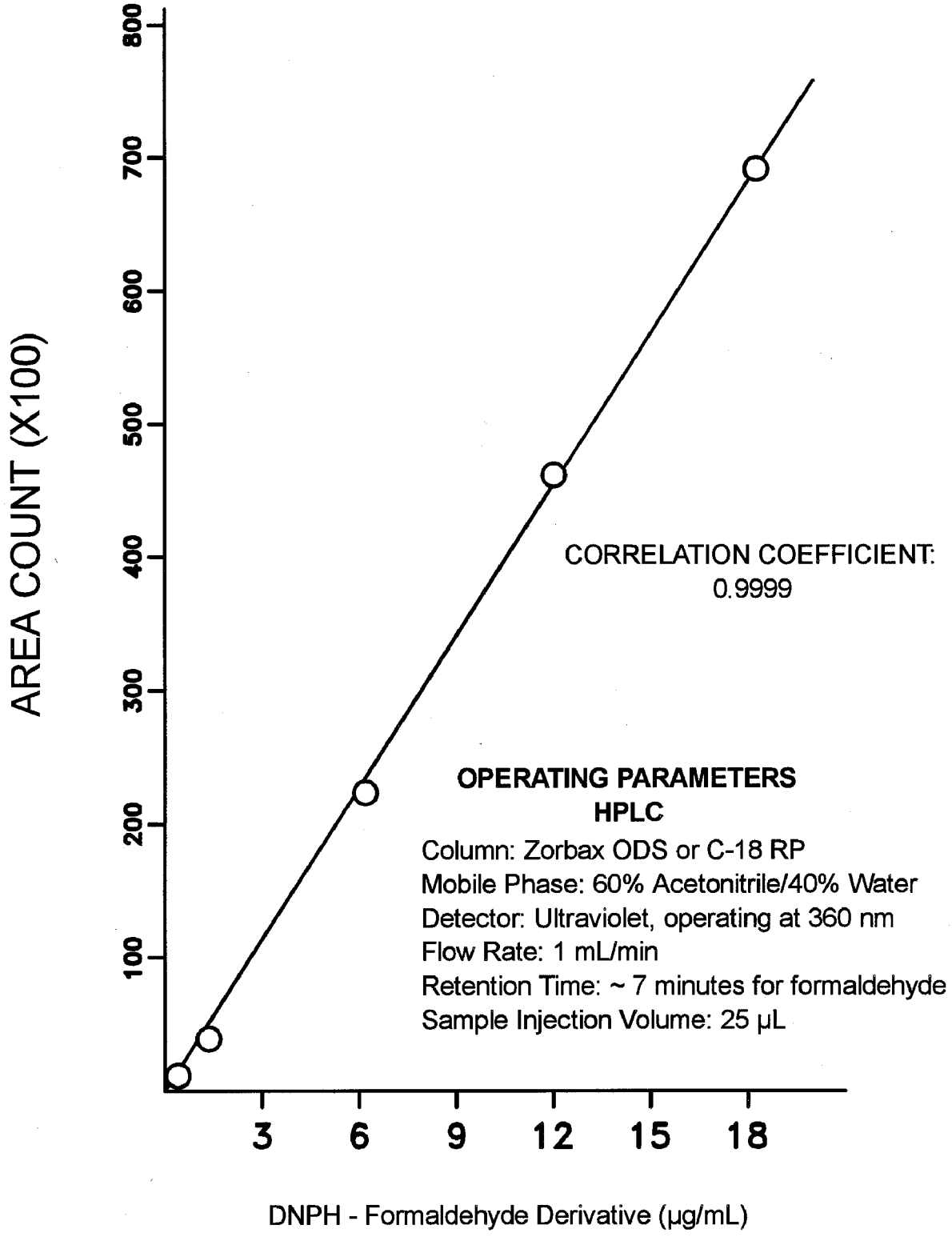


Figure 12. Example of calibration curve for formaldehyde.

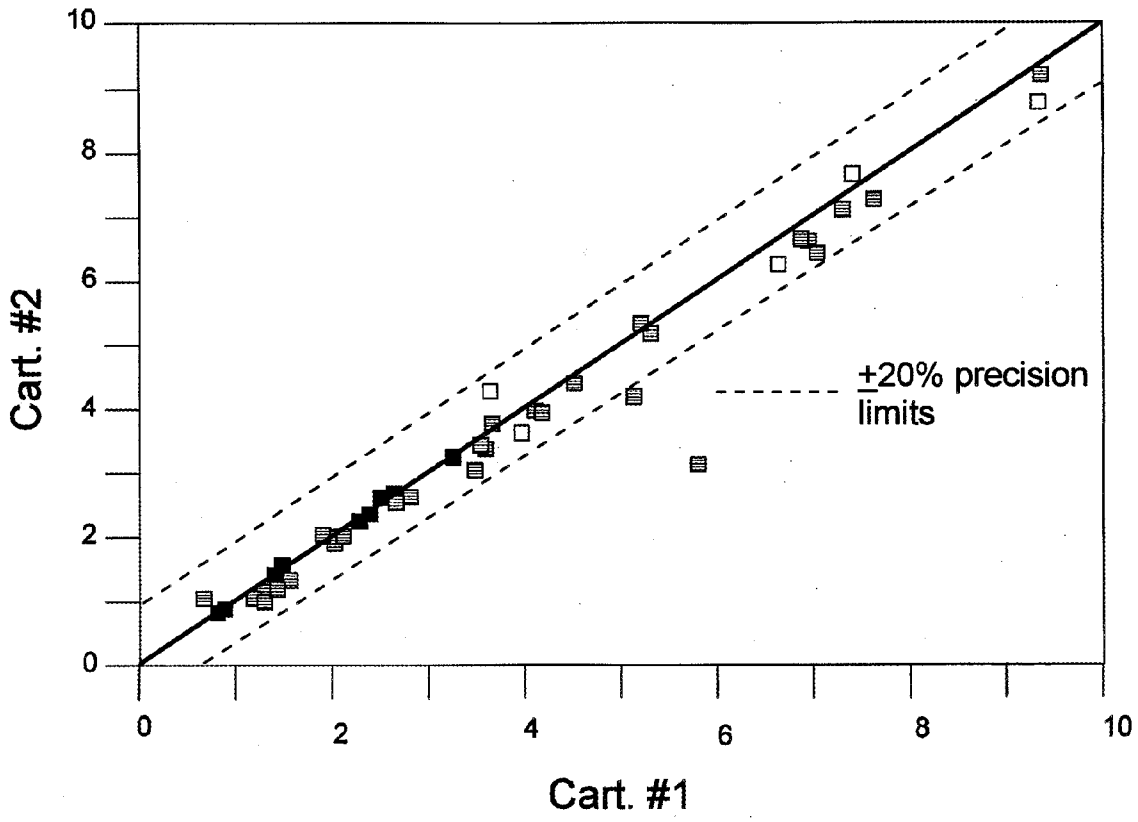


Figure 13. Historical data associated with collocated samples for formaldehyde (ppbv) in establishing 20% precision.

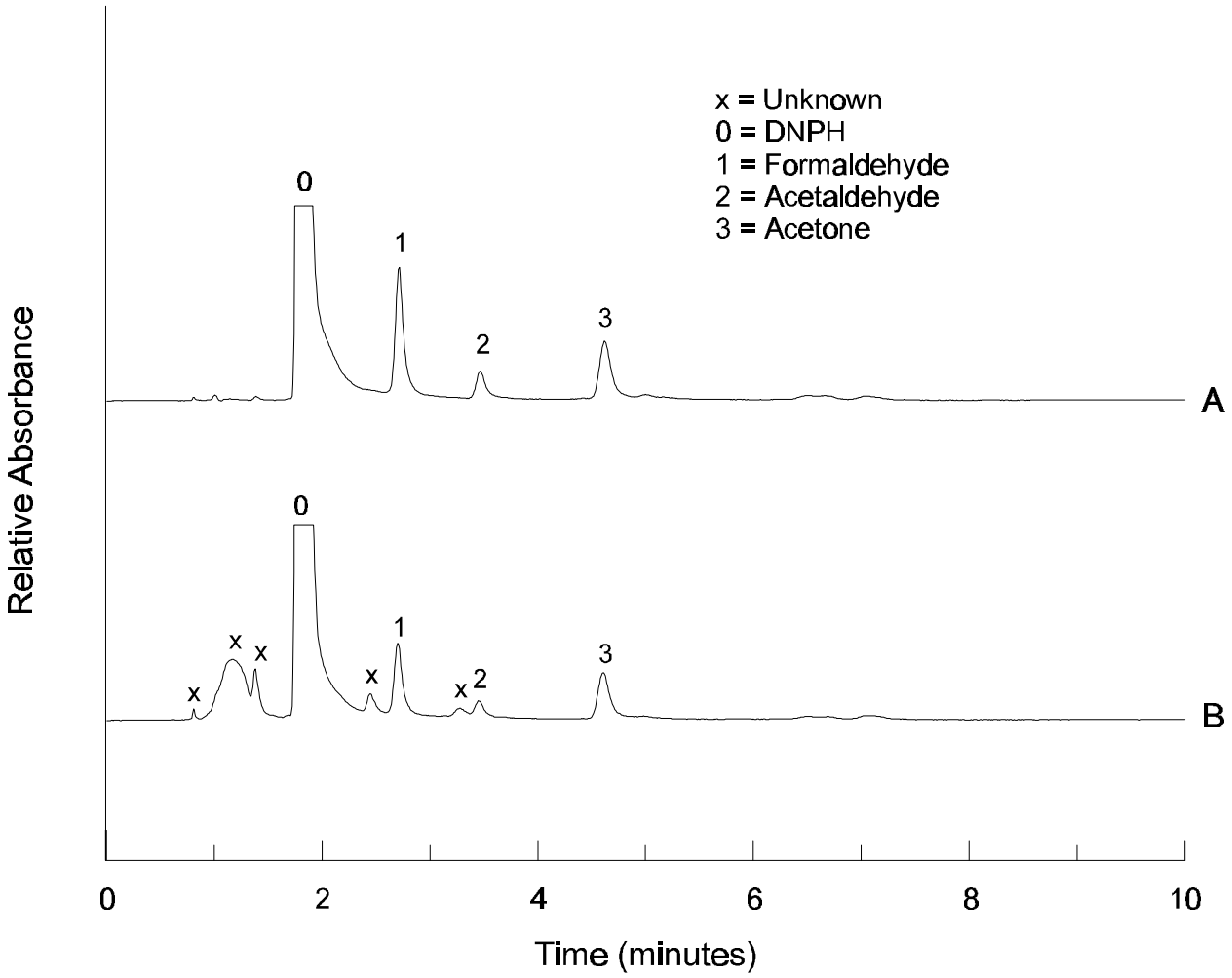


Figure 14. Example of analysis demonstrating DNPH-coated cartridges sampling air with (A) and without (B) ozone denuders, in the determination of formaldehyde.

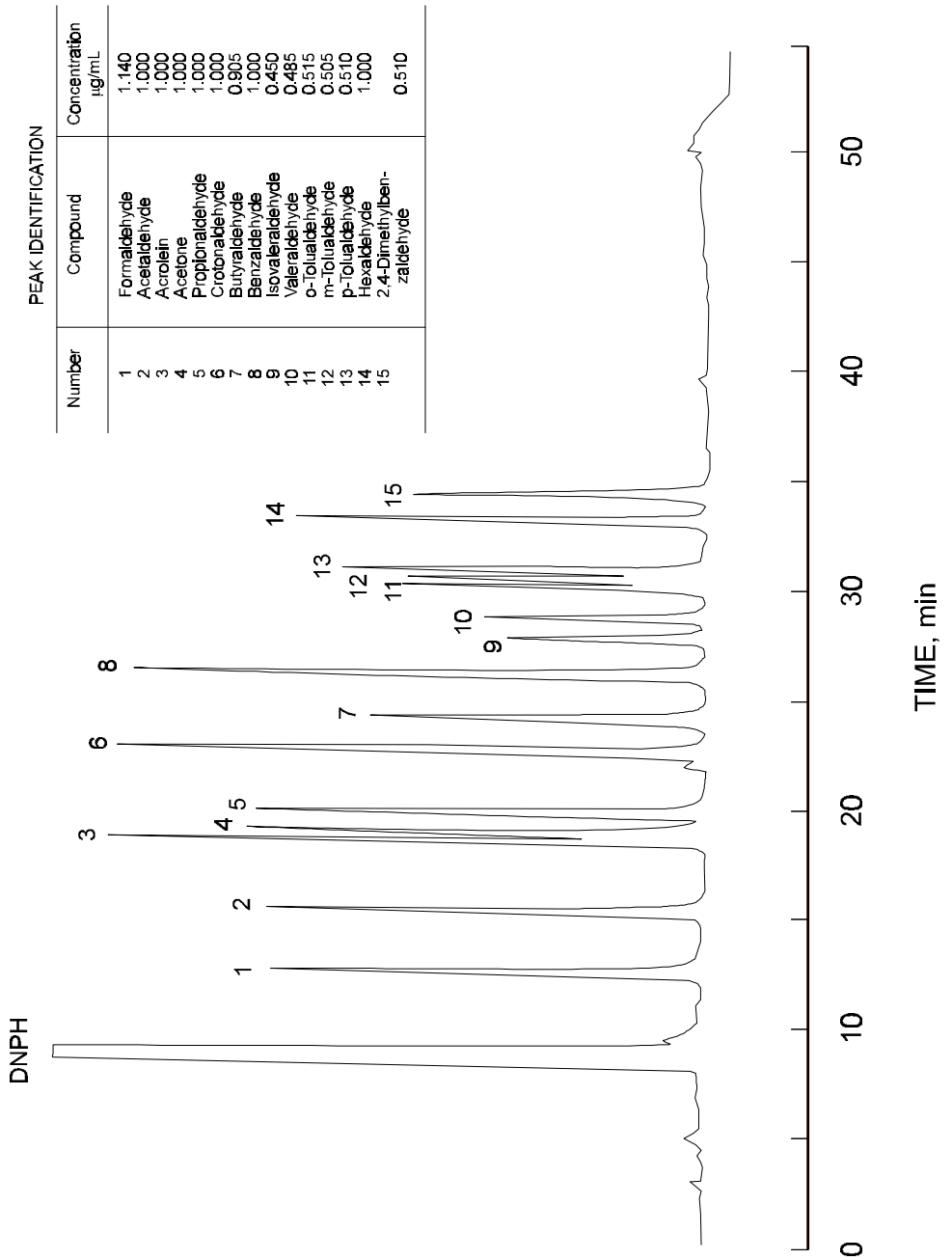


Figure 15. Typical chromatogram of a linear gradient program for analyzing other aldehydes/ketones from a DNPH-coated cartridge.

APPENDIX F

USEPA Compendium Method TO-13A

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
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- 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
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DISCLAIMER

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

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METHOD TO-13A

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

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.

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TABLE 1. FORMULAE AND PHYSICAL PROPERTIES OF SELECTED PAHs

Compound	Formula	Molecular Weight	Melting Point, °C	Boiling Point, °C	Vapor Pressure, kPa	CAS RN #
Naphthalene	$C_{10}H_8$	128.18	80,2	218	1.1x10	91-20-3
Acenaphthylene	$C_{12}H_8$	152.20	92-93	265-280	3.9x10	208-96-8
Acenaphthene	$C_{12}H_{10}$	154.20	90-96	278-279	2.1x10	83-32-9
Fluorene	$C_{13}H_{10}$	166.23	116-118	293-295	8.7x10	86-73-7
Anthracene	$C_{14}H_{10}$	178.24	216-219	340	36x10	120-12-7
Phenanthrene	$C_{14}H_{10}$	178.24	96-101	339-340	2.3x10	85-01-8
Fluoranthene	$C_{16}H_{10}$	202.26	107-111	375-393	6.5x10	206-44-0
Pyrene	$C_{16}H_{10}$	202.26	150-156	360-404	3.1x10	129-00-0
Benz(a)anthracene	$C_{18}H_{12}$	228.30	157-167	435	1.5x10	56-55-3
Chrysene	$C_{18}H_{12}$	228.30	252-256	441-448	5.7x10	218-01-9
Benzo(b)fluoranthene	$C_{20}H_{12}$	252.32	167-168	481	6.7x10	205-99-2
Benzo(k)fluoranthene	$C_{20}H_{12}$	252.32	198-217	480-471	2.1x10	207-08-9
Perylene	$C_{20}H_{12}$	252.32	273-278	500-503	7.0x10	198-55-8
Benzo(a)pyrene	$C_{20}H_{12}$	252.32	177-179	493-496	7.3x10	50-32-8
Benzo(e)pyrene	$C_{20}H_{12}$	252.32	178-179	493	7.4x10	192-92-2
Benzo(g,h,i)perylene	$C_{22}H_{12}$	276.34	275-278	525	1.3x10	191-24-2
Indeno(1,2,3-cd)pyrene	$C_{22}H_{12}$	276.34	162-163	--	ca.10	193-39-5
Dibenz(a,h)anthracene	$C_{22}H_{14}$	278.35	266-270	524	1.3x10	53-70-3
Coronene	$C_{24}H_{12}$	300.36	438-440	525	2.0x10	191-07-1

Many of these compounds sublime.

TABLE 2. GC-MS OPERATING CONDITIONS

Activity	Conditions
Gas Chromatography	
Column	J&W Scientific, DB-5 crosslinked 5% phenylmethyl silicone (30 m x 0.32 mm, 1.0 µm film thickness) or equivalent
Carrier Gas	Helium, velocity between 28-30 cm^3/sec at 250°C
Injection Volume	2 µL, Grob-type, splitless
Injector Temperature	290°C
Temperature Program	
Initial Column Temperature	70°C
Initial Hold Time	4 ± 0.1 min.
Program	10°C/min to 300°C and hold 10 min.
Final Temperature	300°C
Final Hold Time	10 min. or until all compounds of interest have eluted
Mass Spectrometer	
Transfer Line Temperature	290°C or According to Manufacturer's Specification
Source Temperature	According to Manufacturer's Specifications
Electron Energy	70 volts (nominal)
Ionization Mode	EI
Mass Range	35 to 500 amu, full range data acquisition (SCAN) mode
Scan Time	At least 5 scans per peak, not to exceed 1 second per scan.

TABLE 3. DFTPP KEY IONS & ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
51	30 to 60% of mass 198
68 70	Less than 2% of mass 69 Less than 2% of mass 69
127	40 to 60% of mass 198
197 198 199	Less than 2% of mass 198 Base peak, 100% relative abundance 5 to 9% of mass 198
275	10 to 30% of mass 198
365	Greater than 1.0% of mass 198
441 442 443	Present but less than mass 443 40% of mass 198 17 to 23% of mass 442

TABLE 4. COMPOSITION AND APPROXIMATE CONCENTRATION OF CALIBRATION SOLUTIONS

Target Compound	Concentration, ng/µL				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
PAHs	0.10	0.25	0.50	1.25	2.50
Acenaphthene	0.10	0.25	0.50	1.25	2.50
Acenaphthylene	0.10	0.25	0.50	1.25	2.50
Anthracene	0.10	0.25	0.50	1.25	2.50
Benz(a)anthracene	0.10	0.25	0.50	1.25	2.50
Benzo(a)pyrene	0.10	0.25	0.50	1.25	2.50
Benzo(b)fluoranthene	0.10	0.25	0.50	1.25	2.50
Benzo(e)pyrene	0.10	0.25	0.50	1.25	2.50
Benzo(g,h,i)perylene	0.10	0.25	0.50	1.25	2.50
Benzo(k)fluoranthene	0.10	0.25	0.50	1.25	2.50
Chrysene	0.10	0.25	0.50	1.25	2.50
Perylene	0.10	0.25	0.50	1.25	2.50
Dibenz(a,h)anthracene	0.10	0.25	0.50	1.25	2.50
Fluoranthene	0.10	0.25	0.50	1.25	2.50
Fluorene	0.10	0.25	0.50	1.25	2.50
Indeno(1,2,3-c,d)pyrene	0.10	0.25	0.50	1.25	2.50
Naphthalene	0.10	0.25	0.50	1.25	2.50
Coronene	0.10	0.25	0.50	1.25	2.50
Phenanthrene	0.10	0.25	0.50	1.25	2.50
Pyrene	0.10	0.25	0.50	1.25	2.50

TABLE 4. (Continued)

Target Compound	Concentration, ng/µL				
	CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
SUGGESTED INTERNAL STANDARDS					
D_8-Naphthalene	0.5	0.5	0.5	0.5	0.5
D_{10}-Acenaphthene	0.5	0.5	0.5	0.5	0.5
D_{10}-Phenanthrene	0.5	0.5	0.5	0.5	0.5
D_{12}-Chrysene	0.5	0.5	0.5	0.5	0.5
D_{12}-Perylene	0.5	0.5	0.5	0.5	0.5
SUGGESTED SURROGATE COMPOUNDS					
D_{10}-Fluoranthene (field)	0.10	0.25	0.50	1.25	2.50
D_{12}-Benzo[a]pyrene (field)	0.10	0.25	0.50	1.25	2.50
D_{10}-Fluorene (lab)	0.10	0.25	0.50	1.25	2.50
D_{10}-Pyrene (lab)	0.10	0.25	0.50	1.25	2.50

TABLE 5. CHARACTERISTIC IONS FOR SURROGATE SUGGESTED STANDARDS

Classification	Primary Ion	Secondary Ion
Internal Standards		
D_8-Naphthalene	136	68,137
D_{10}-Acenaphthene	164	162,165
D_{10}-Phenanthrene	188	94,189
D_{12}-Chrysene	240	120,241
D_{12}-Perylene	264	260,265
Laboratory Surrogates		
D_{10}-Fluorene	176	88,177
D_{10}-Pyrene	212	106,213
Field Surrogates		
D_{10}-Fluoranthene	212	106,213
D_{12}-Benzo(a)pyrene	264	132,265

TABLE 6. EXAMPLE OF CHARACTERISTIC IONS FOR COMMON PAHs

Analyte	Primary Ion	Secondary Ion(s)
Pyrene	202	101,203
Benz(a)anthracene	228	229,226
Chrysene	228	226,229
Benzo(a)pyrene	252	253,126
Benzo(b)fluoranthene	252	253,126
Benzo(k)fluoranthene	252	253,126
Benzo(g,h,i)perylene	276	138,277
Dibenz(a,h)anthracene	278	139,279
Anthracene	178	179,176
Phenanthrene	178	179,176
Acenaphthene	154	153,152
Acenaphthylene	152	151,153
Benzo(e)pyrene	252	253,126
Fluoranthene	202	101,203
Fluorene	166	165,167
Ideno(1,2,3-cd)pyrene	276	138,227
Naphthalene	128	129,127
Perylene	252	253,126
Coronene	300	150,301

TABLE 7. EXAMPLE OF RELATIVE RESPONSE FACTOR CRITERIA FOR INITIAL AND CONTINUING CALIBRATION OF COMMON SEMI-VOLATILE COMPOUNDS

Semi-volatile Compounds	Minimum RRF	Maximum %RSD	Maximum %Difference
Naphthalene	0.700	30	30
Acenaphthylene	1.300	30	30
Acenaphthene	0.800	30	30
Fluorene	0.900	30	30
Phenanthrene	0.700	30	30
Anthracene	0.700	30	30
Fluoranthene	0.600	30	30
Pyrene	0.600	30	30
Benz(a)anthracene	0.800	30	30
Chrysene	0.700	30	30
Benzo(b)fluoranthene	0.700	30	30
Benzo(k)fluoranthene	0.700	30	30
Benzo(a)pyrene	0.700	30	30
Indeno(1,2,3-cd)pyrene	0.500	30	30
Dibenz(a,h)anthracene	0.400	30	30
Benzo(g,h,i)perylene	0.500	30	30
Perylene	0.500	30	30
Coronene	0.700	30	30

TABLE 8. MINIMUM SAMPLING EQUIPMENT CALIBRATION AND ACCURACY REQUIREMENTS

Equipment	Acceptance limits	Frequency and method of measurement	Action if require-ments are not met
Sampler	Indicated flow rate = true flow rate, ±10%.	Calibrate with certified transfer standard on receipt, after maintenance on sampler, and any time audits or flow checks deviate more than ±10% from the indicated flow rate or ±10% from the design flow rate.	Recalibrate
Associated equipment			
Sampler on/off timer	±30 min/24 hour	Check at purchase and routinely on sample-recovery days	Adjust or replace
Elapsed-time meter	±30 min/24 hour	Compare with a standard time-piece of known accuracy at receipt and at 6-month intervals	Adjust or replace
Flowrate transfer standard (orifice device)	Check at receipt for visual damage	Recalibrate annually against positive displacement standard volume meter	Adopt new calibration curve

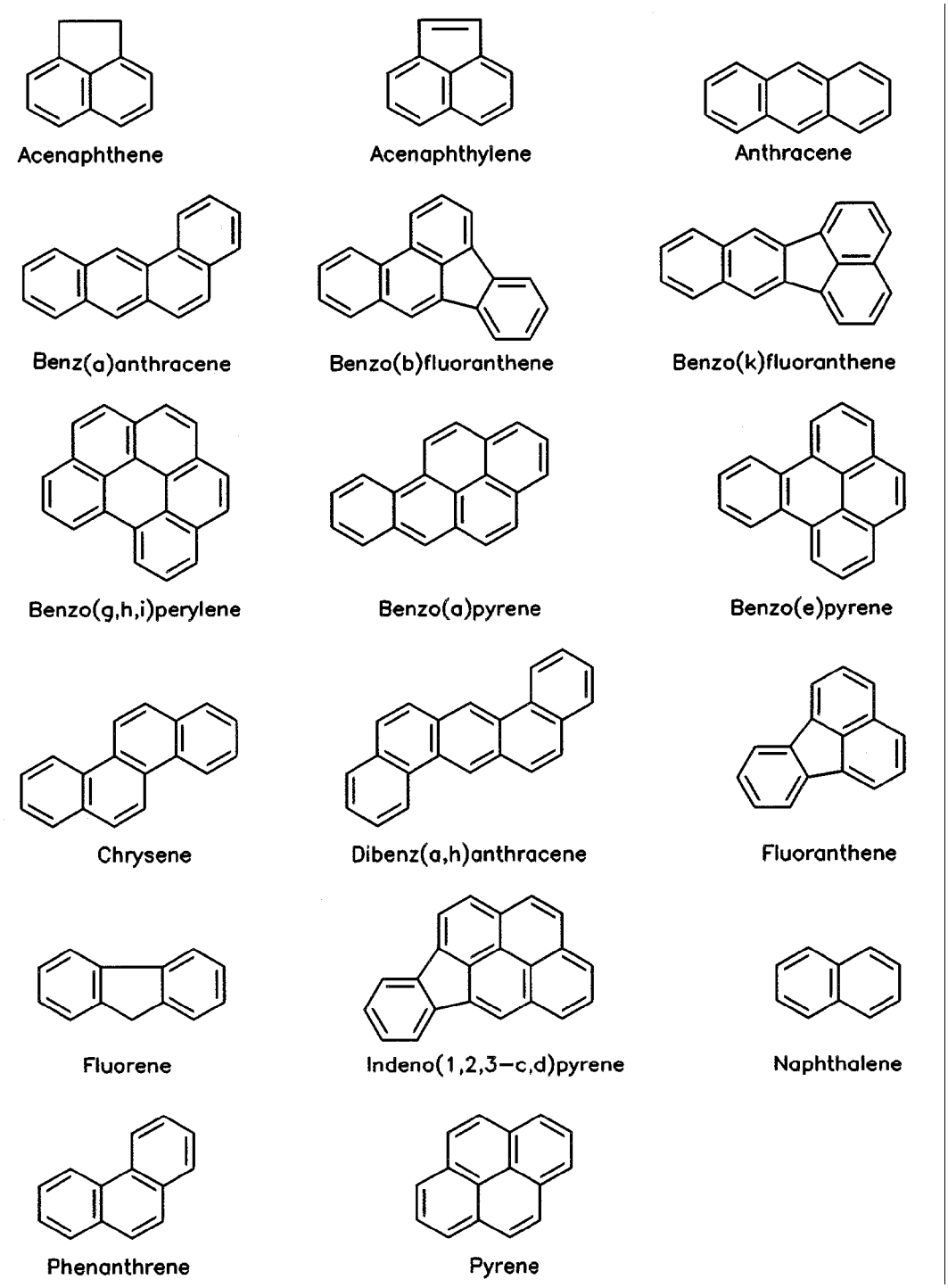


Figure 1. Ring structure of common PAHs.

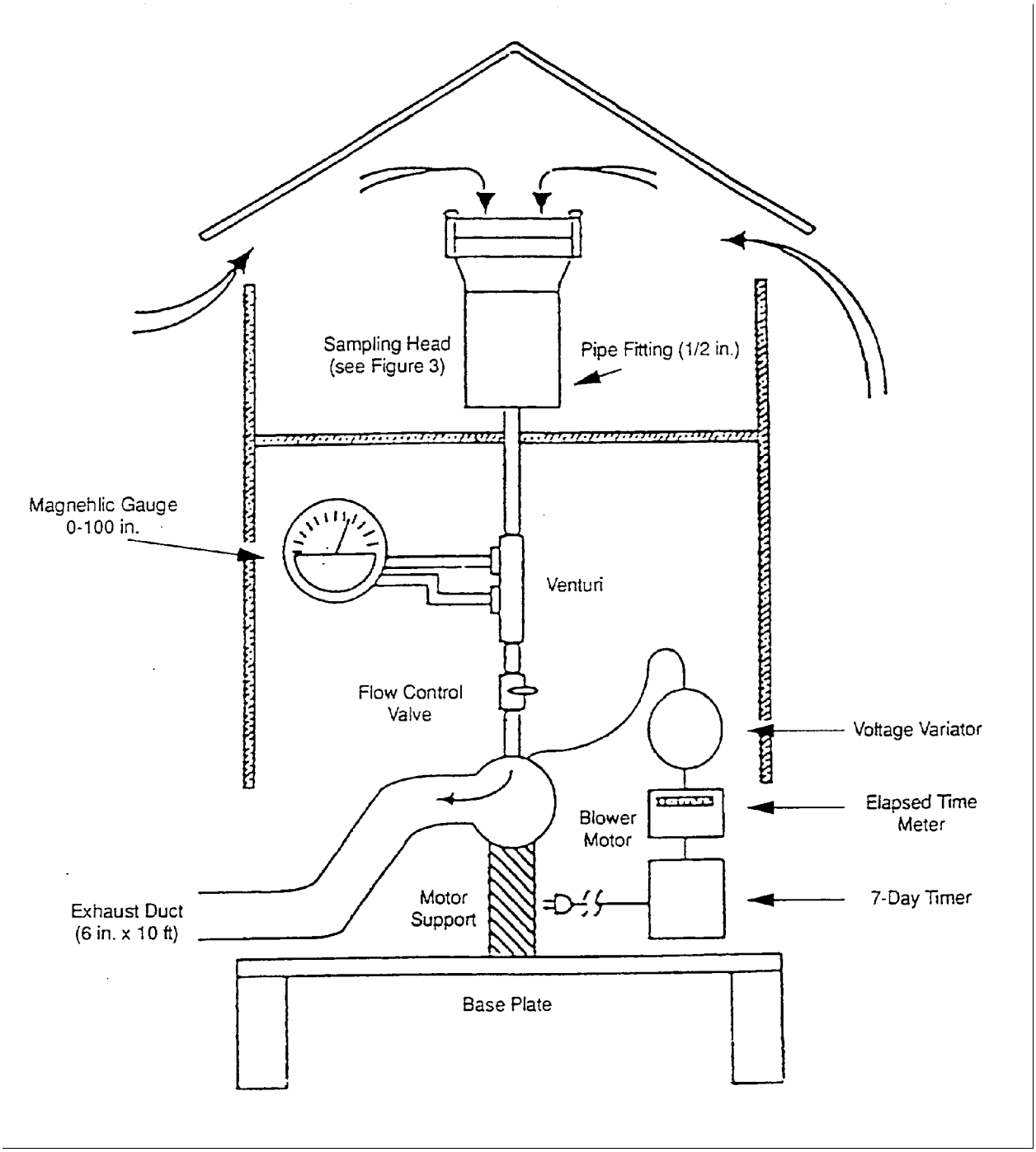


Figure 2. Typical high volume air sampler for PAHs.

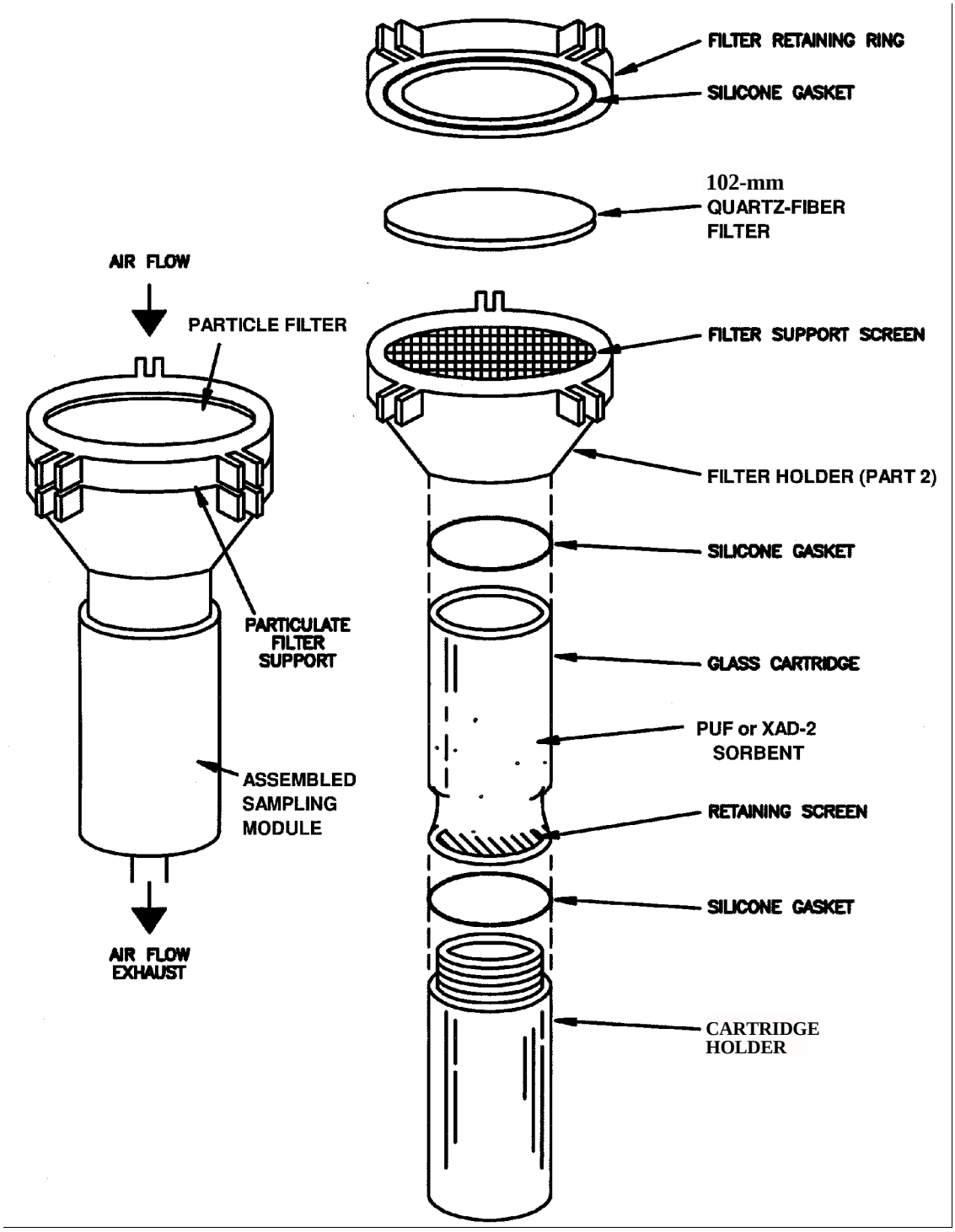


Figure 3. Typical absorbent cartridge assembly for sampling PAHs.

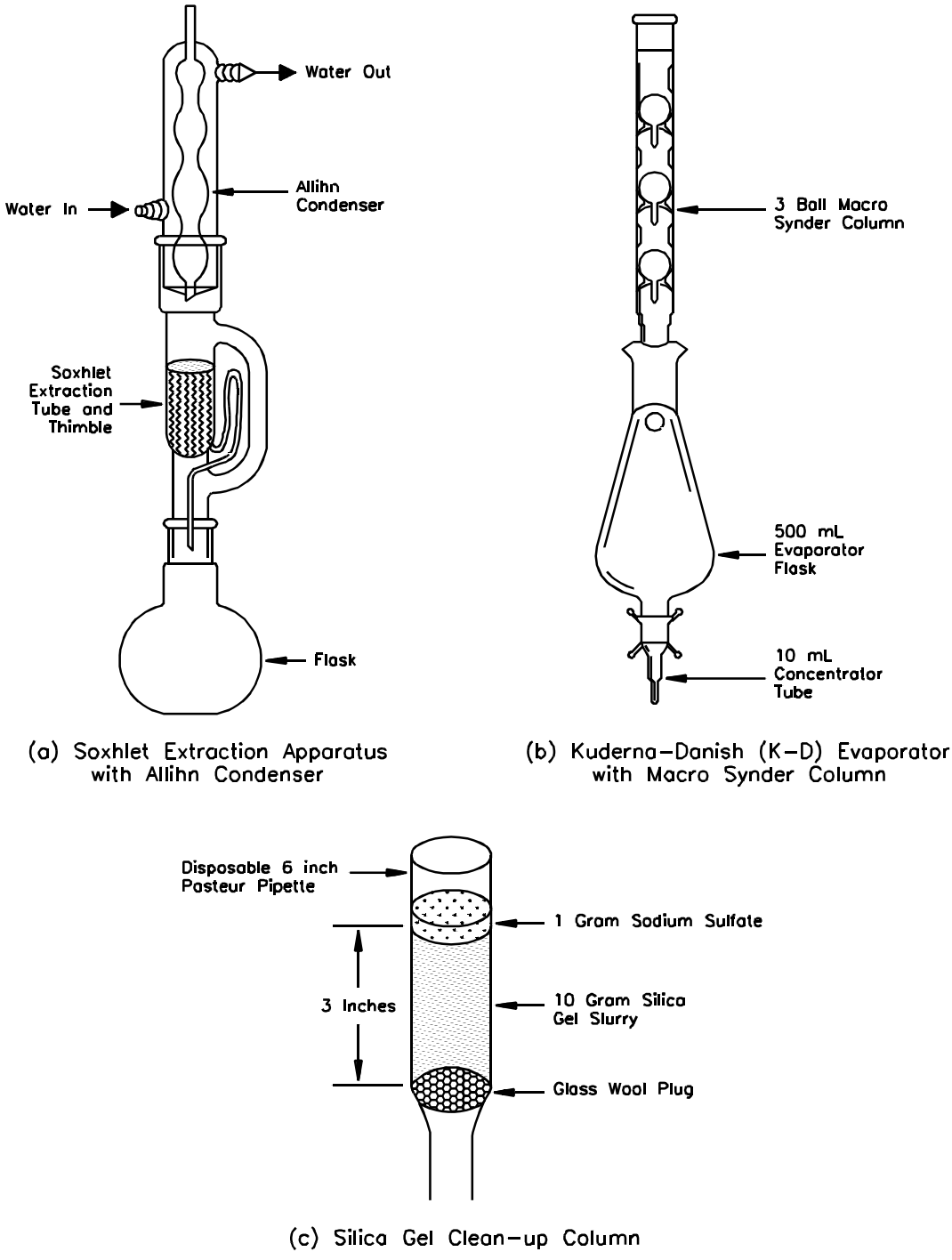
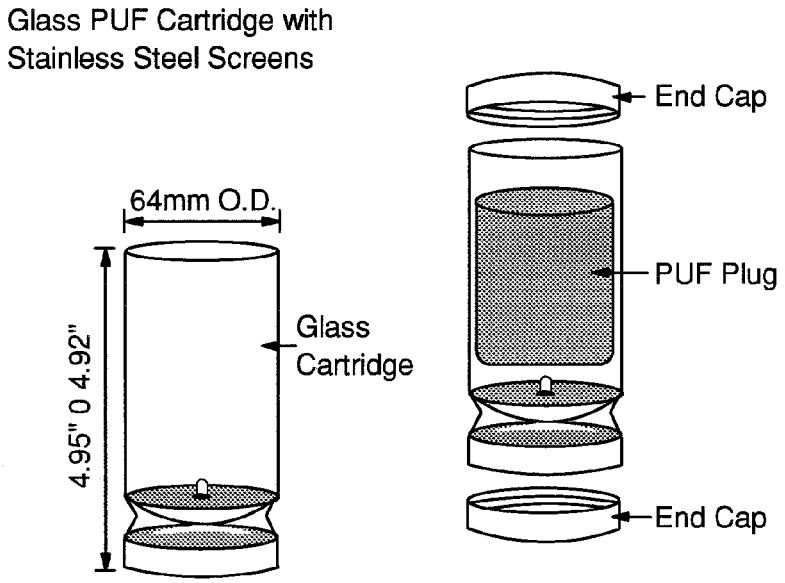
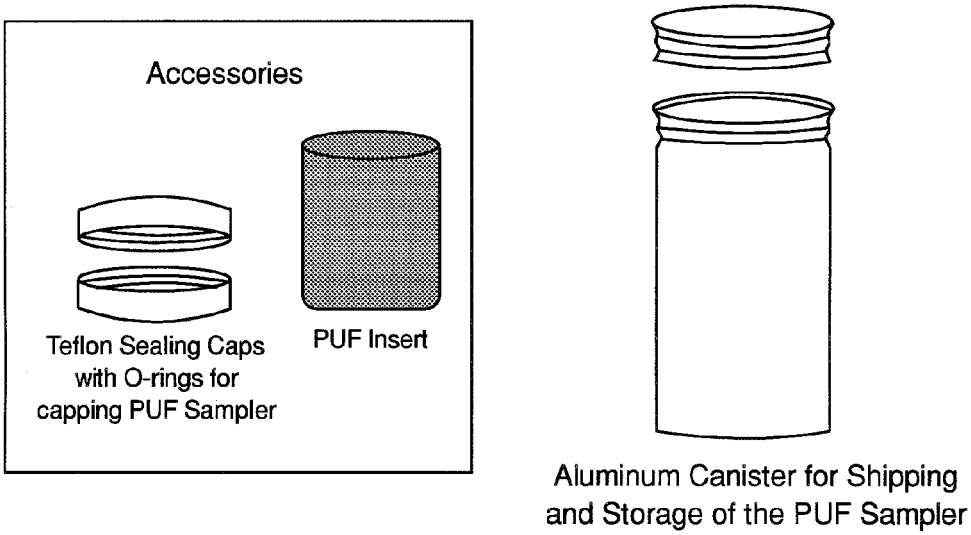


Figure 4. Apparatus used for sample clean-up and extraction.



5a. Glass PUF cartridge, plug, and end caps.



5b. PUF shipping container.

Figure 5. Glass PUF cartridge (5a) and shipping container (5b) for use with Compendium Method TO-13A.

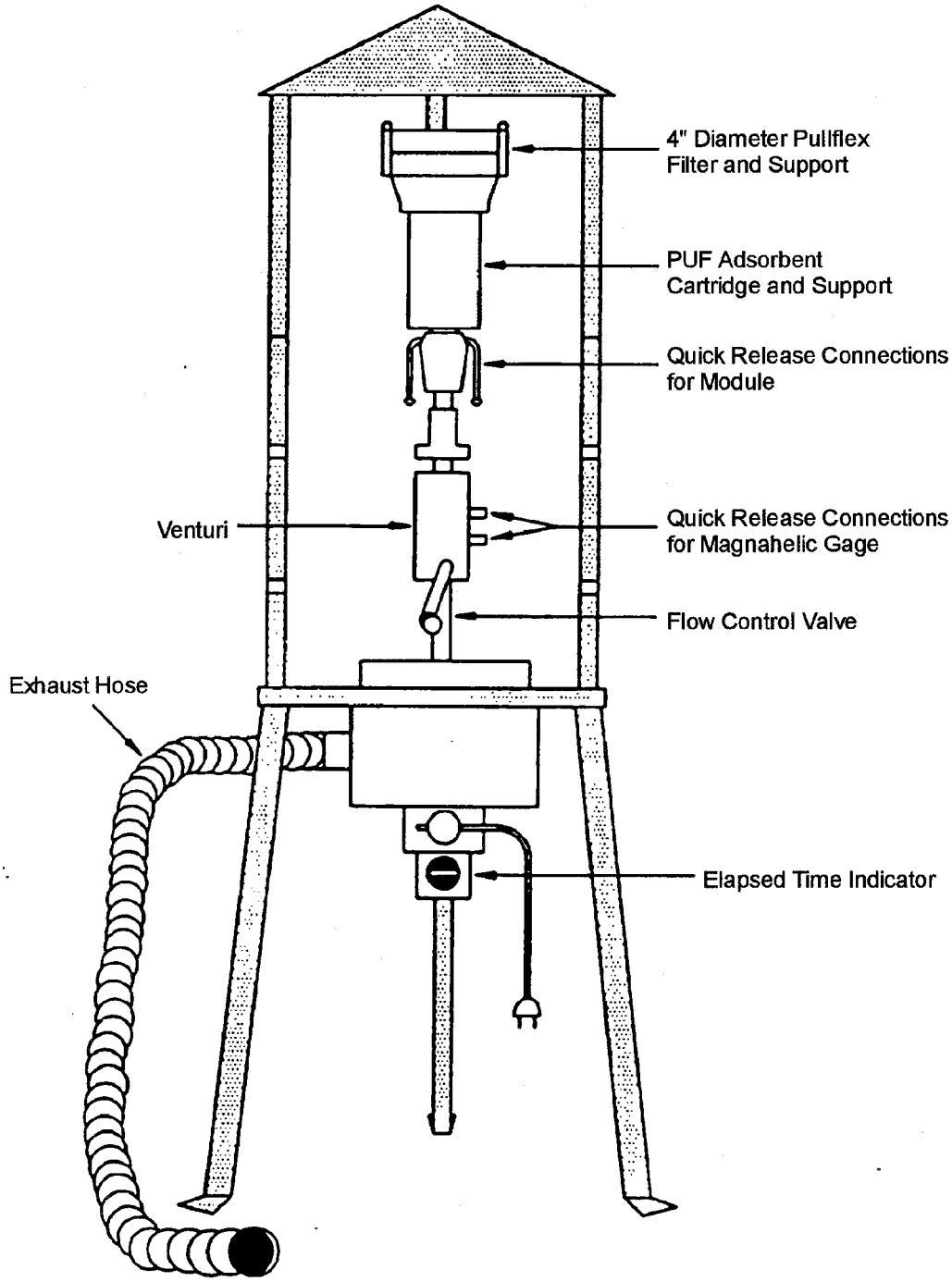


Figure 6. Example of a field portable high volume air sampler for sampling PAHs developed by EPA.

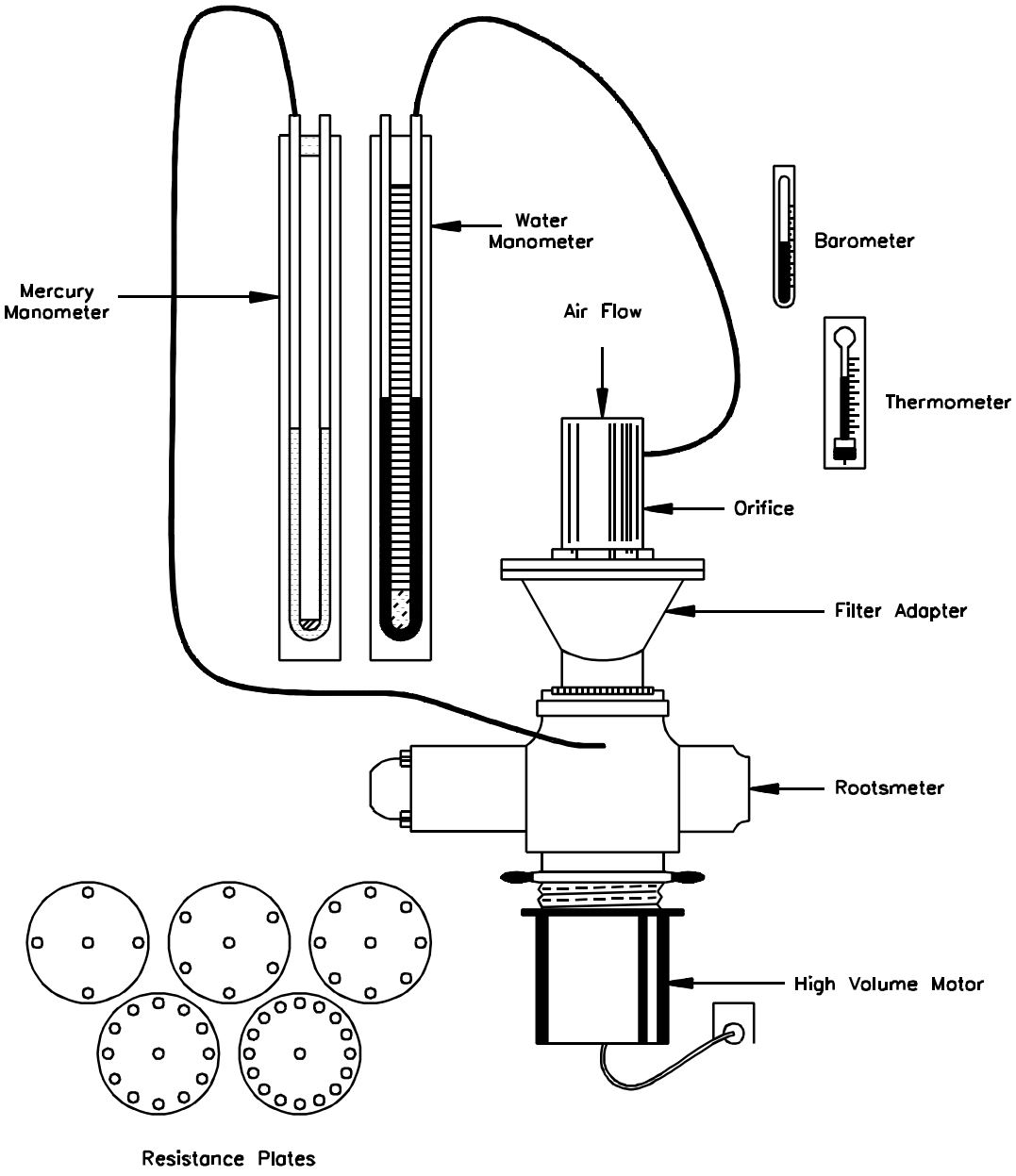


Figure 7. Positive displacement rootsmeter used to calibrate orifice transfer standard used in Compendium Method TO-13A.

COMPENDIUM METHOD TO-13A
ORIFICE CALIBRATION DATA SHEET

T_1 _____ Name _____

P_1 _____ mmHg Date _____

Orifice No. _____

Rootsmeter No. _____

Resistance Plants (No. of holes)	Air Volume Measured by Rootsmeter V_m		Standard Volume, V_{std} (std m^3)	Time for Air Volume to Pass Through Rootsmeter, θ (min)	Rootsmeter Pressure Differential, ΔP (mm Hg)	Pressure Drop Across Orifice, ΔH (in. H_2O)	x-Axis Standard Flowrate, Q_{std} (std m^3/min)	
	(R^3)	(m^3)						
5	200	5.66						
7	200	5.66						
10	300	8.50						
13	300	8.50						
18	300	8.50						

Factors: $(R^3)(0.02832\ \frac{m^3}{R^3}) = m^3$ and (in. Hg) $25.4\ (\frac{mm\ Hg}{in.\ Hg}) = mm\ Hg$

Calculation Equations:

1. $V_{std} = V_m\ (\frac{P_1 - \Delta P}{P_{std}})(\frac{T_{std}}{T_1})$

where:

$T_{std} = 296°K$

$P_{std} = 760.0$ mm Hg

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

Figure 8. Example of a high-volume orifice calibration data sheet for Compendium Method TO-13A.

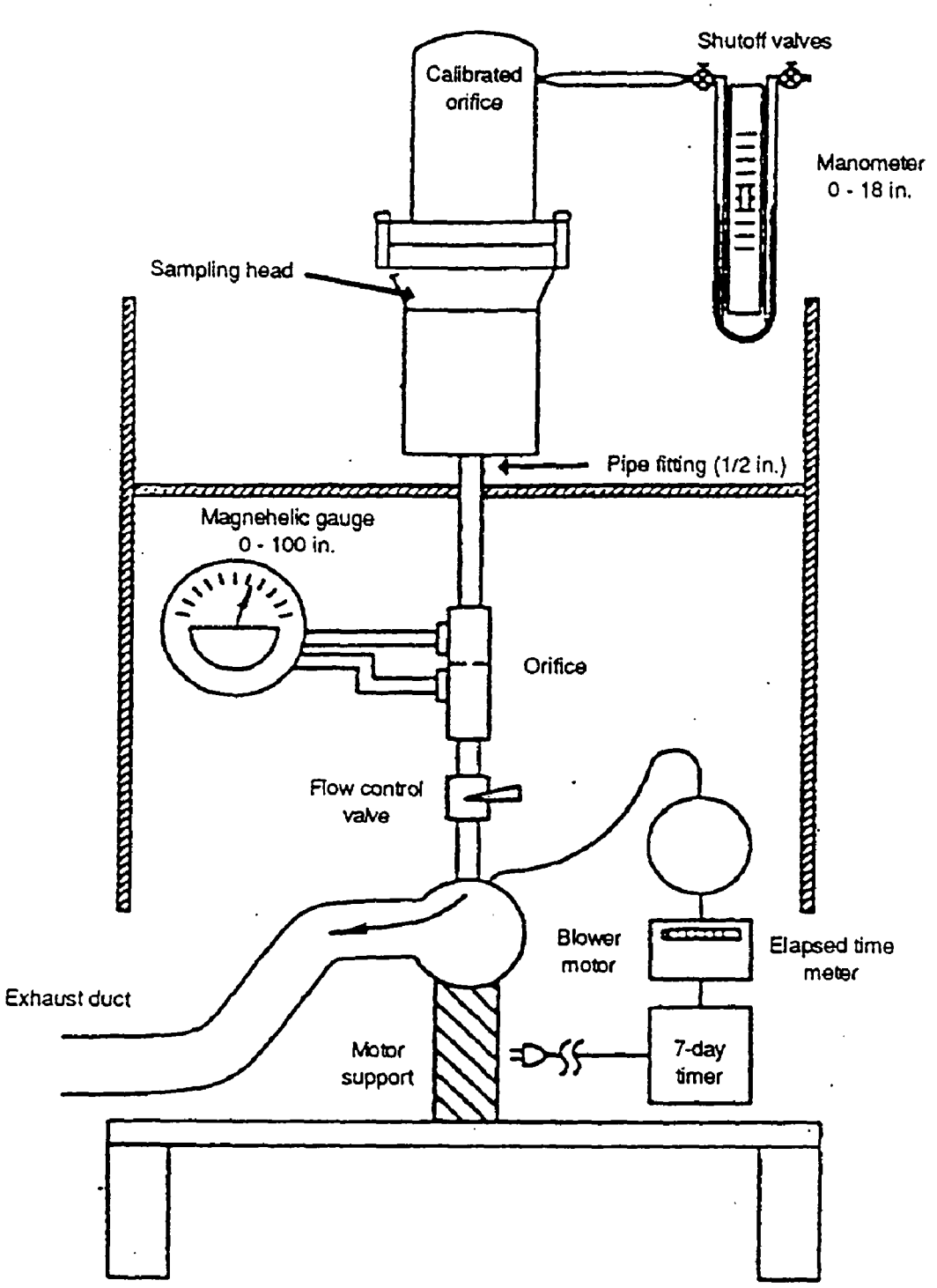


Figure 9. Typical field calibration configuration for Compendium Method TO-13A sampler.

FIELD CALIBRATION DATA SHEET FOR COMPENDIUM METHOD TO-13A PAH
SAMPLER CALIBRATION

Sampler ID: _____

Sampler Location: _____

Calibration Orifice ID: _____

Job No.: _____

High Volume Transfer Orifice Data:

Correlation Coefficient (CC1): _____ Slope (M1): _____

(CC2): _____ (M2): _____

Intercept (B1): _____

(B2): _____

Calibration Date: ___ Time: _____

Calibration Ambient Temperature: ___°F ___°C CALIBRATOR'S SIGNATURE

Calibration Ambient Barometric Pressure: ___ "Hg ___ mm Hg _____

Calibration set point (SP): _____

SAMPLER CALIBRATION

Actual values from calibration		Calibrated values		
Orifice manometer, inches (Y1)	Monitor magnehelic, inches (Y2)	Orifice manometer (Y3)	Monitor magnehelic (Y4)	Calculated value orifice flow, scm (X1)
	70			
	60			
	50			
	40			
	30			
	20			
	10			

Definitions

Y1 = Calibration orifice reading, in. H_2O

Y2 = Monitor magnehelic reading, in. H_2O

P_a = Barometric pressure actual, mm Hg

B1 = Manufacturer's Calibration orifice Intercept

M1 = Manufacturer's Calibration orifice manometer slope

Y3 = Calculated value for orifice manometer
= $\{Y1(Pa/760)[298/(Ta + 273)]\}^{½}$

Y4 = Calculated value for magnehelic
= $\{Y2(Pa/760)[298/(Ta + 273)]\}^{½}$

X1 = Calculated value orifice flow, scm
= (Y3 - B1)/M1

P_{std} = Barometric pressure standard, 760 mm Hg

T_a = Temperature actual, °C

T_{std} = Temperature standard, 25°C

Figure 10. Typical orifice transfer field calibration data sheet for Compendium Method TO-13A.

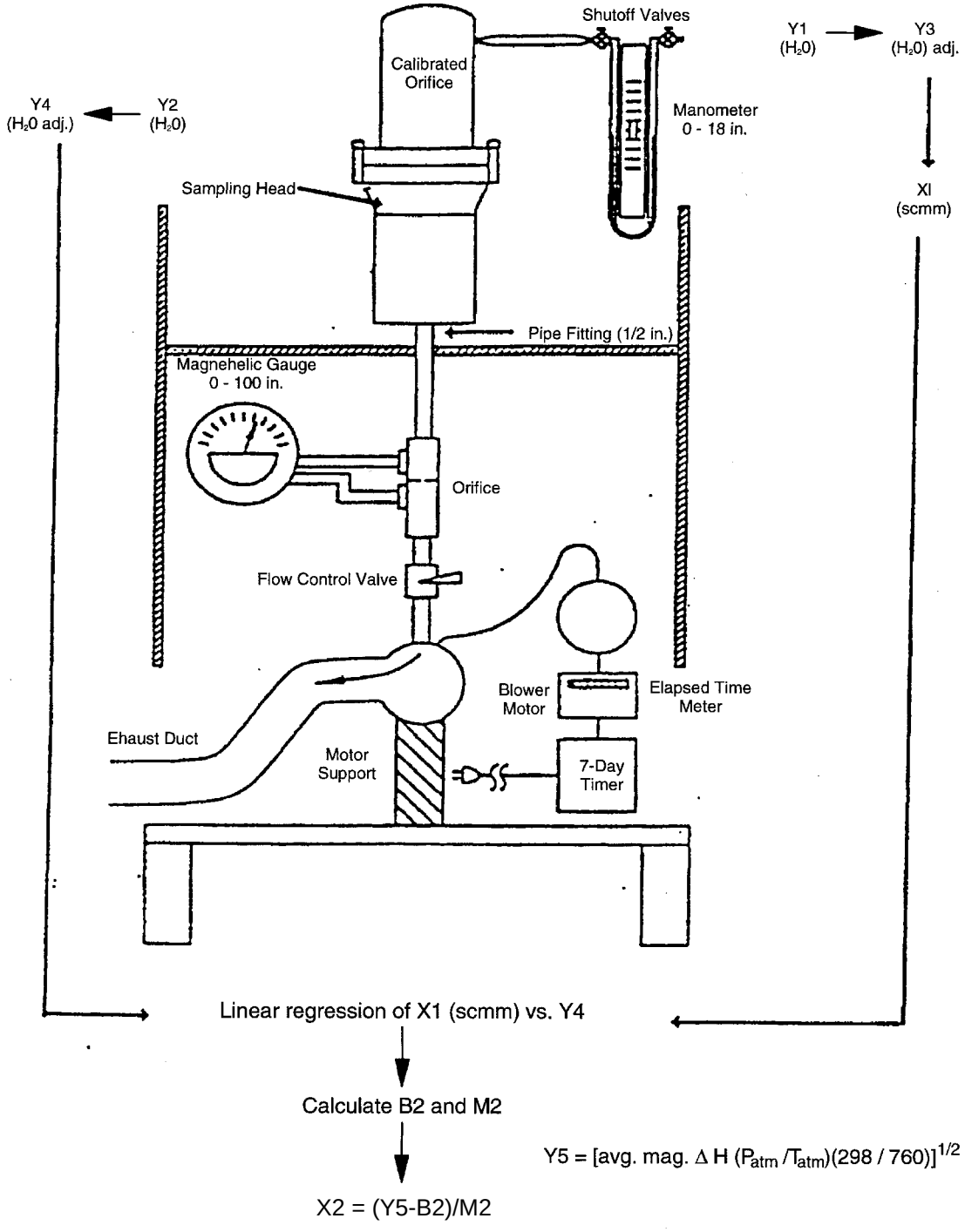


Figure 11. Example of relationship between orifice transfer standard and flow rate through Compendium Method TO-13A sampler.

COMPENDIUM METHOD TO-13A
FIELD TEST DATA SHEET
GENERAL INFORMATION

Sampler I.D. No.: _____
Lab PUF Sample No.: _____
Sample location: _____
_____
_____

Operator: _____
Other: _____
_____
_____

PUF Cartridge Certification Date: _____
Date/Time PUF Cartridge Installed: _____
Elapsed Timer: _____
Start _____
Stop _____
Diff. _____

Sampling

M1 _____ **B1** _____
M2 _____ **B2** _____

	Start	Stop
Barometric pressure ("Hg)	_____	_____
Ambient Temperature (°F)	_____	_____
Rain	**Yes** _____	**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).

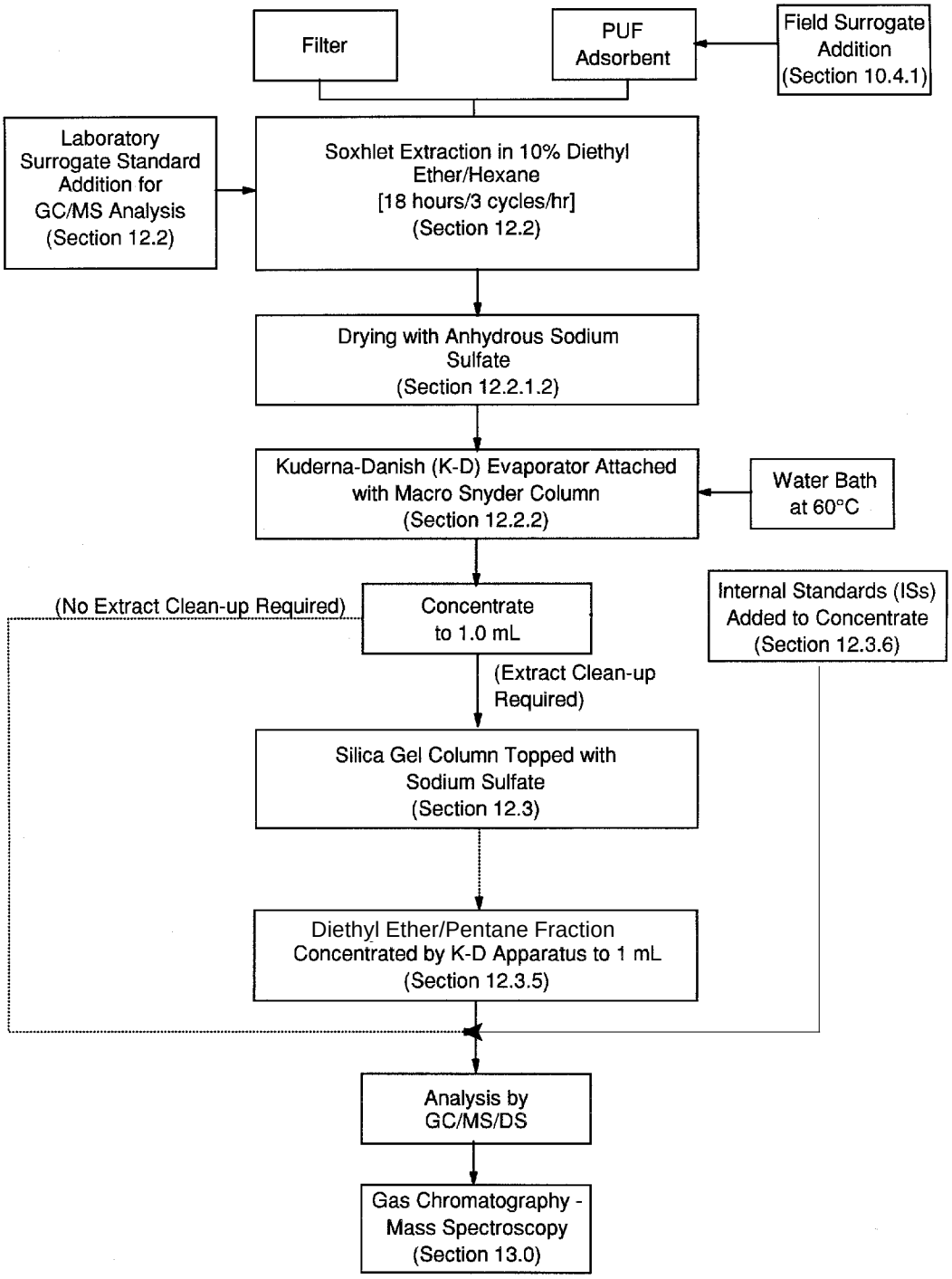


Figure 13. Sample clean-up, concentration, separation and analysis sequence for common PAHs.
[Note: XAD-2 sequence is similar to PUF except methylene chloride is the solvent.]

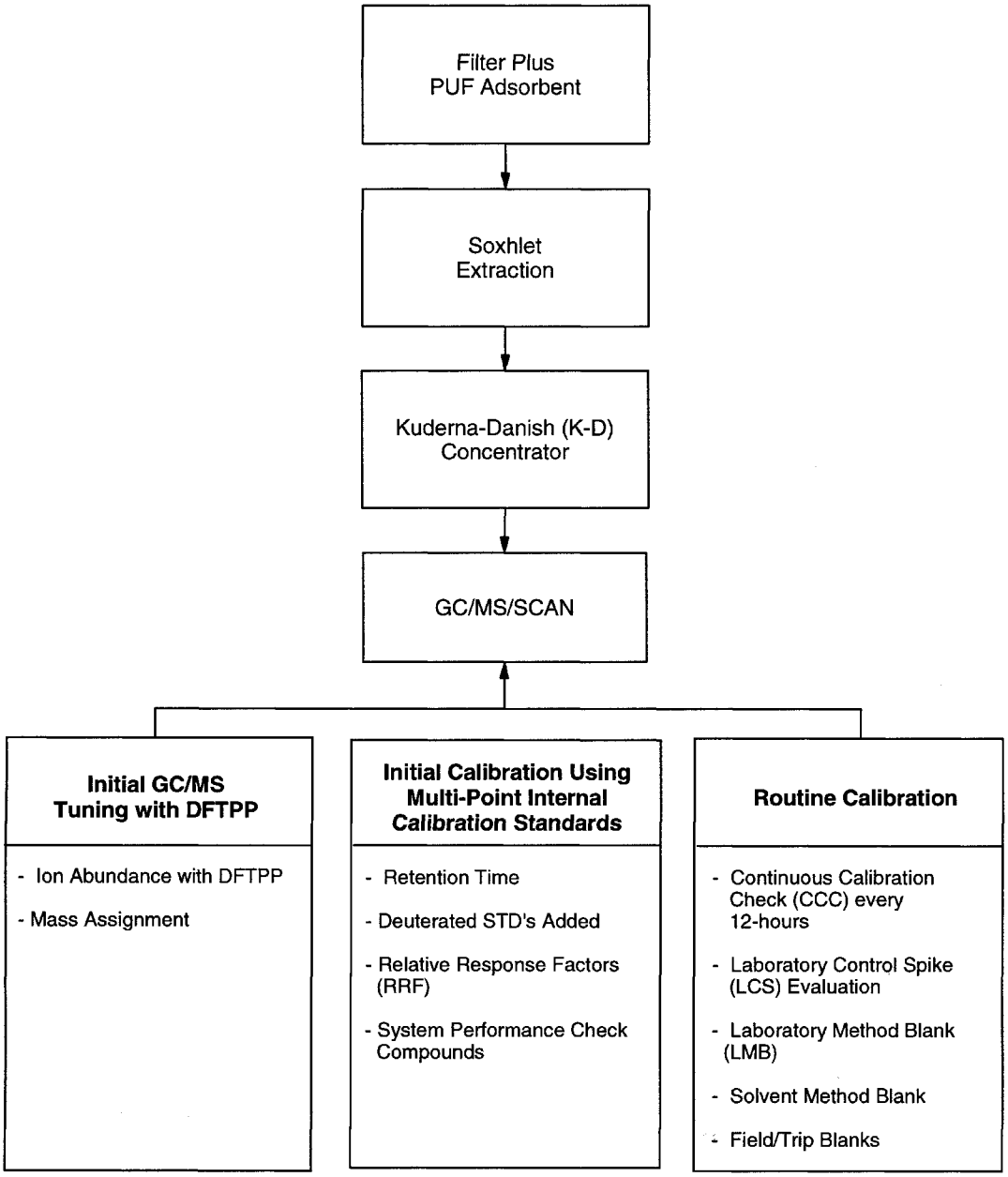


Figure 14. Typical quality assurance specifications for GC/MS/DS operation.

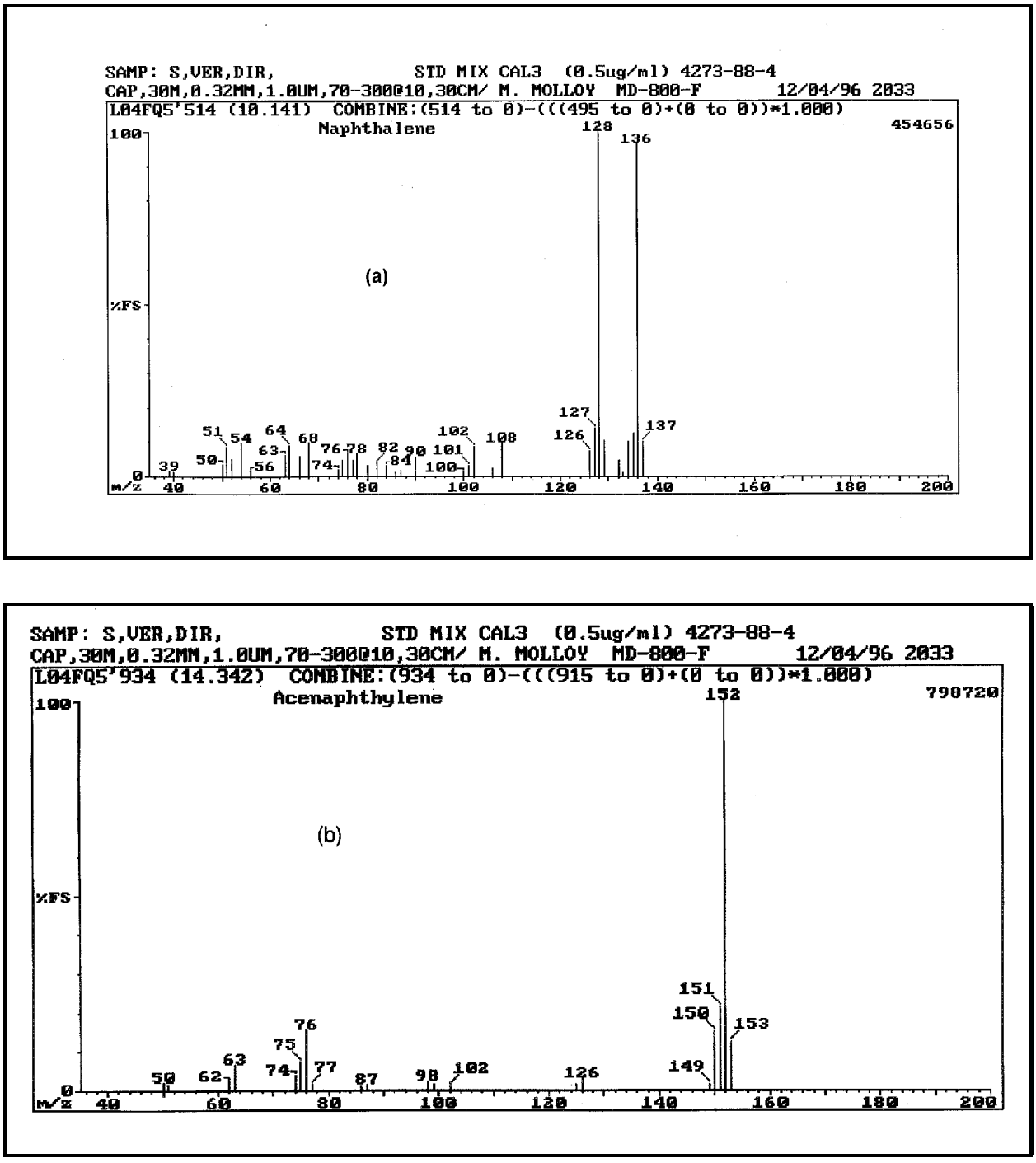
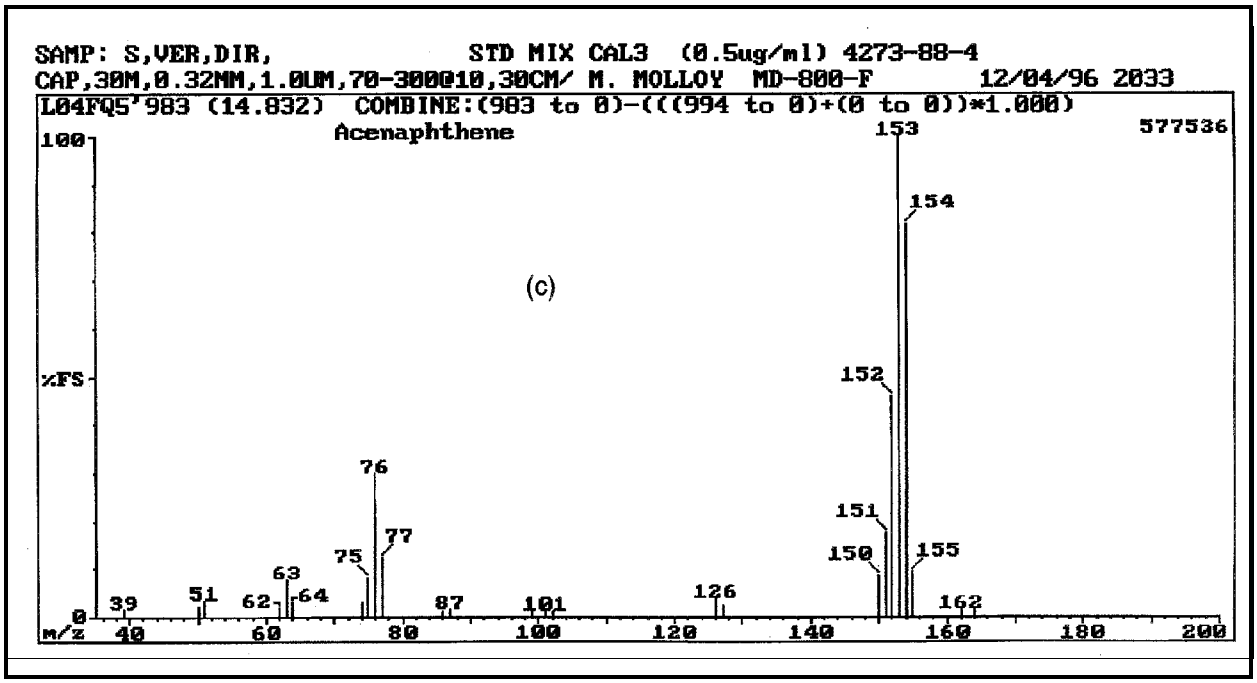


Figure 15. Mass spectra of Compendium Method TO-13A compounds for (a) naphthalene and (b) acenaphthylene.



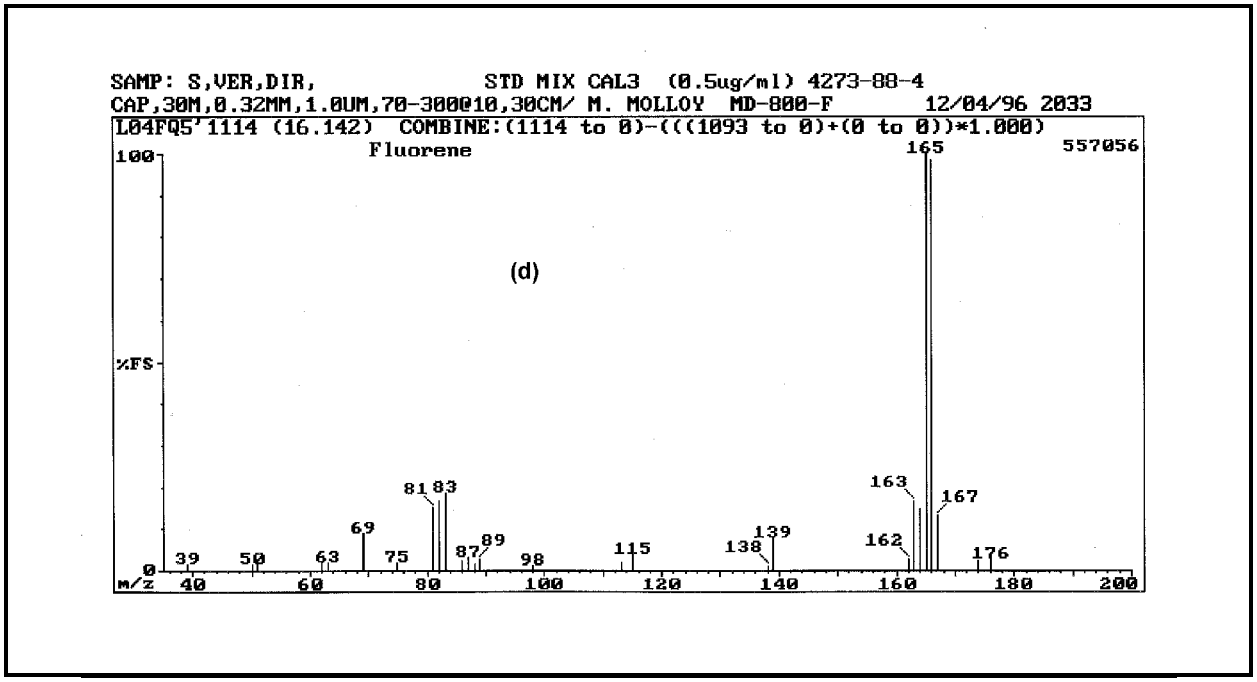
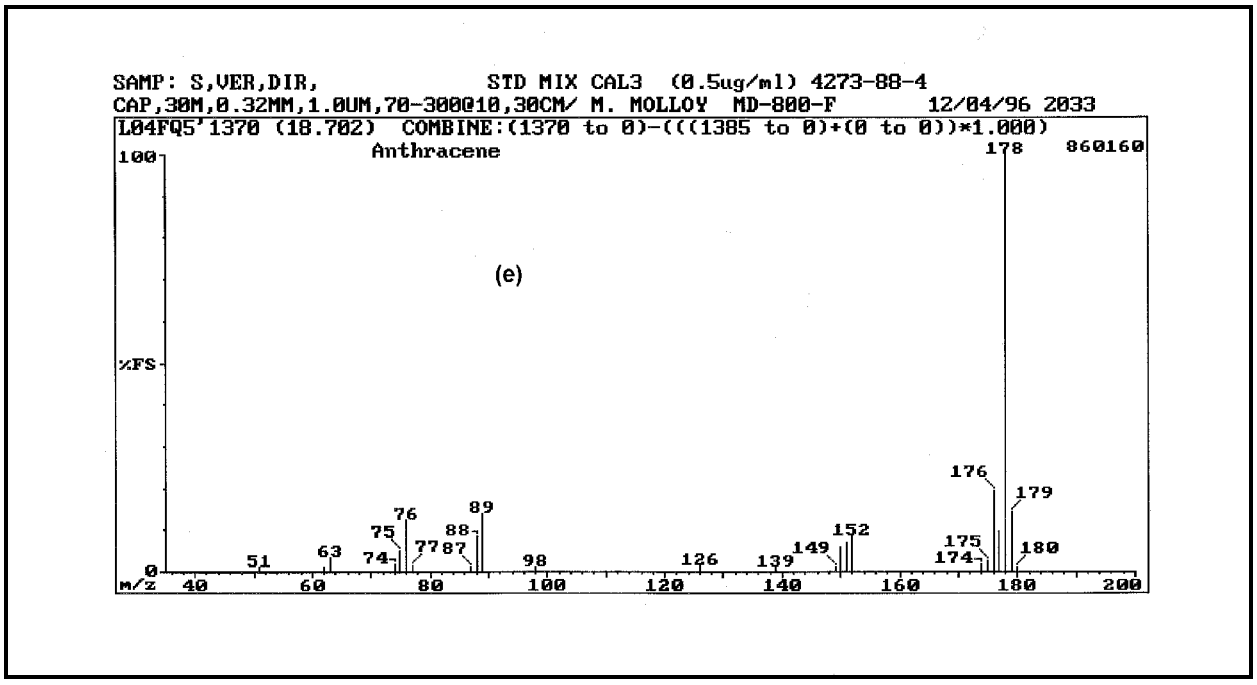


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (c) acenaphthene and (d) fluorene.



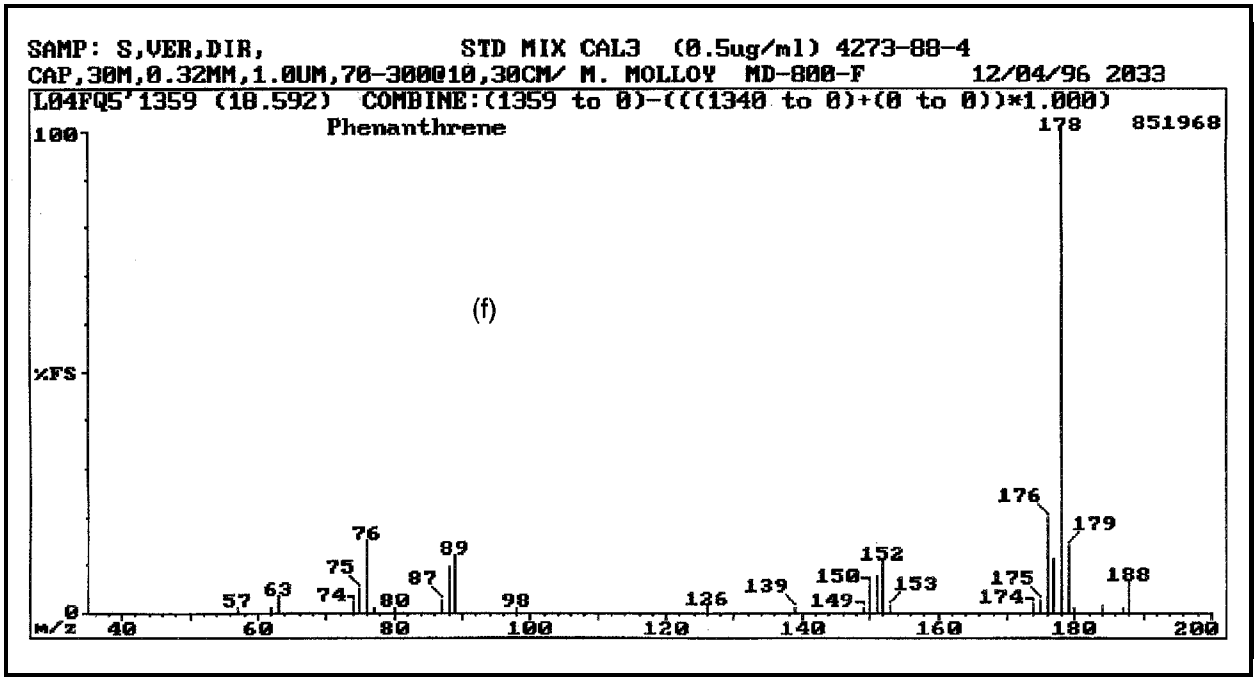
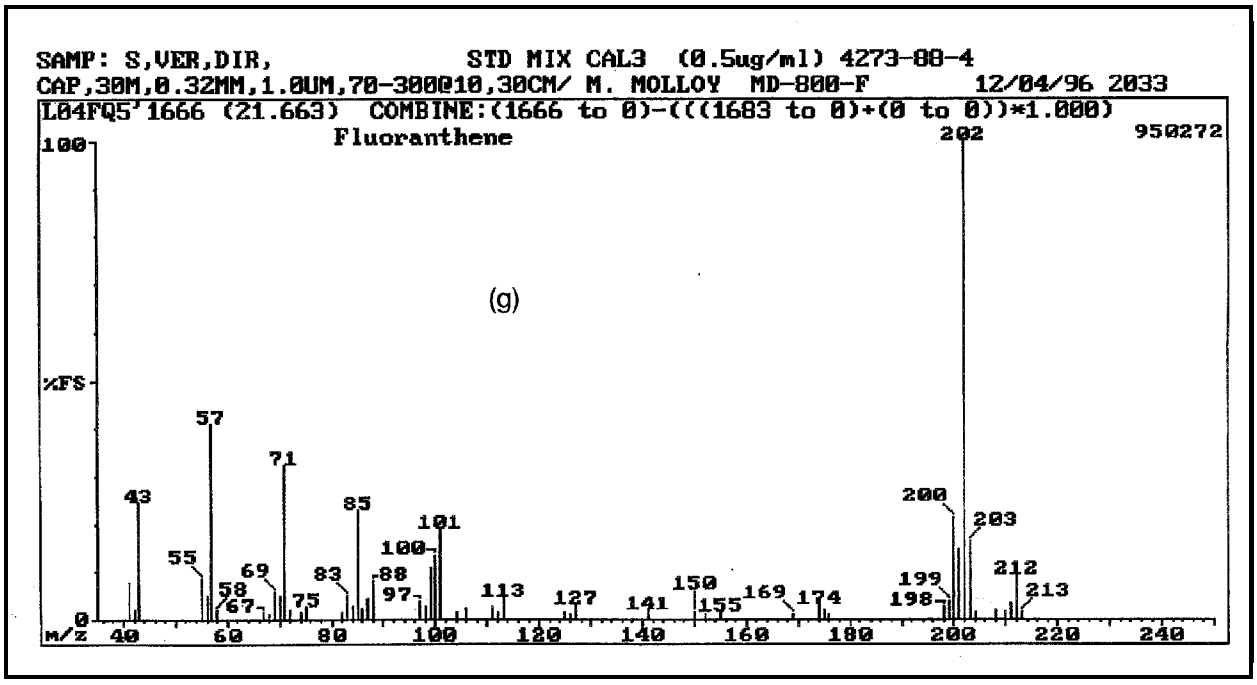


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (e) anthracene and (f) phenanthrene.



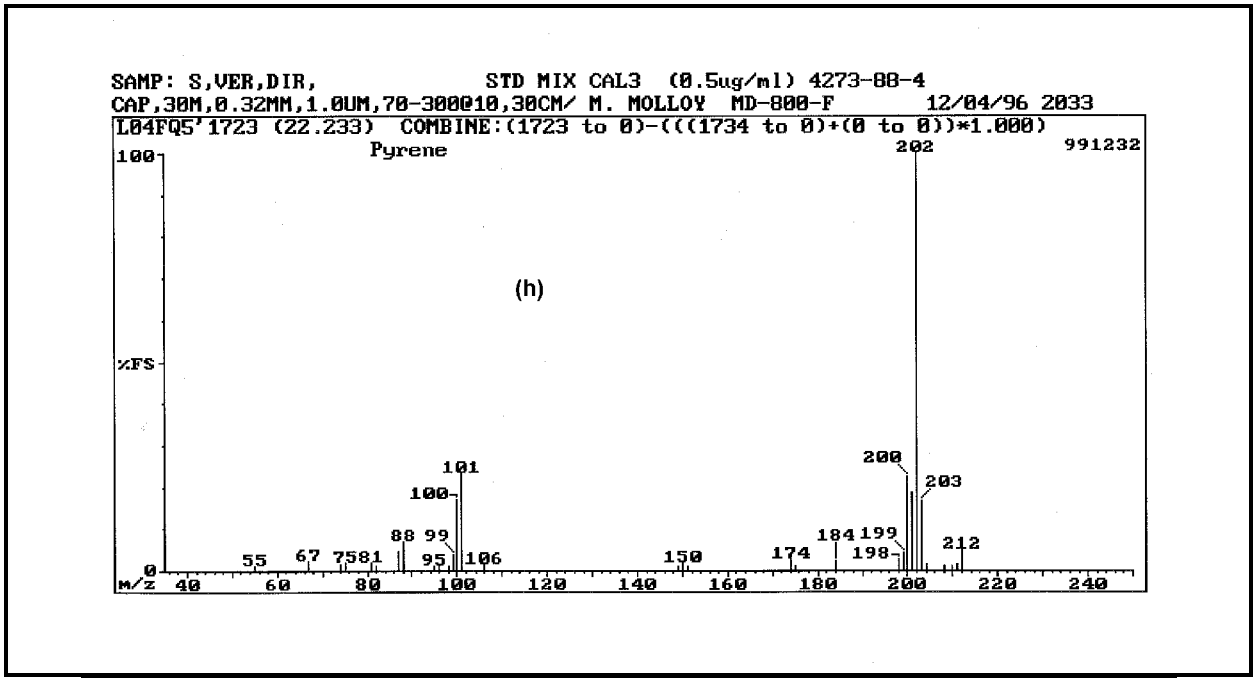


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (g) fluoranthene and (h) pyrene.

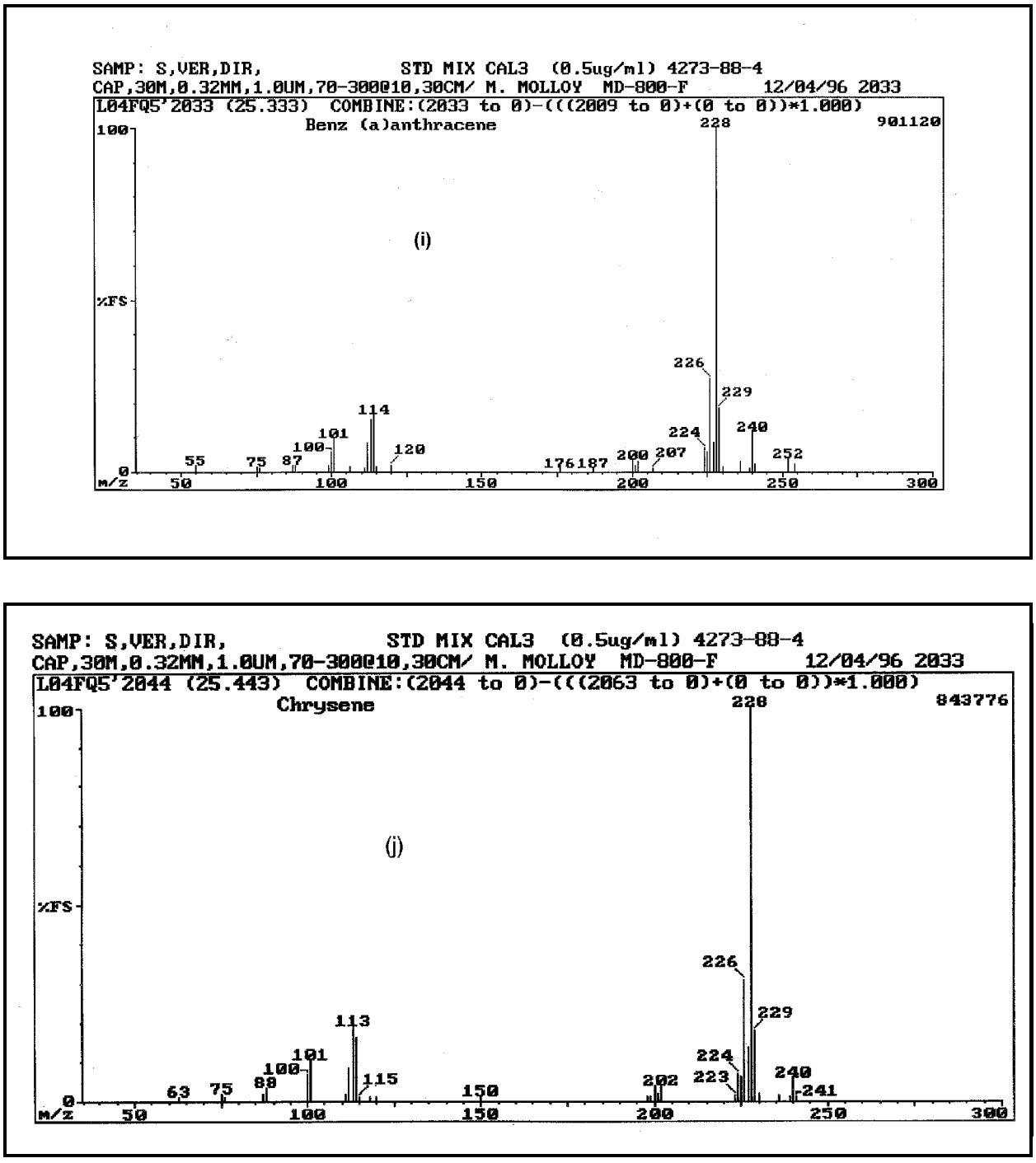
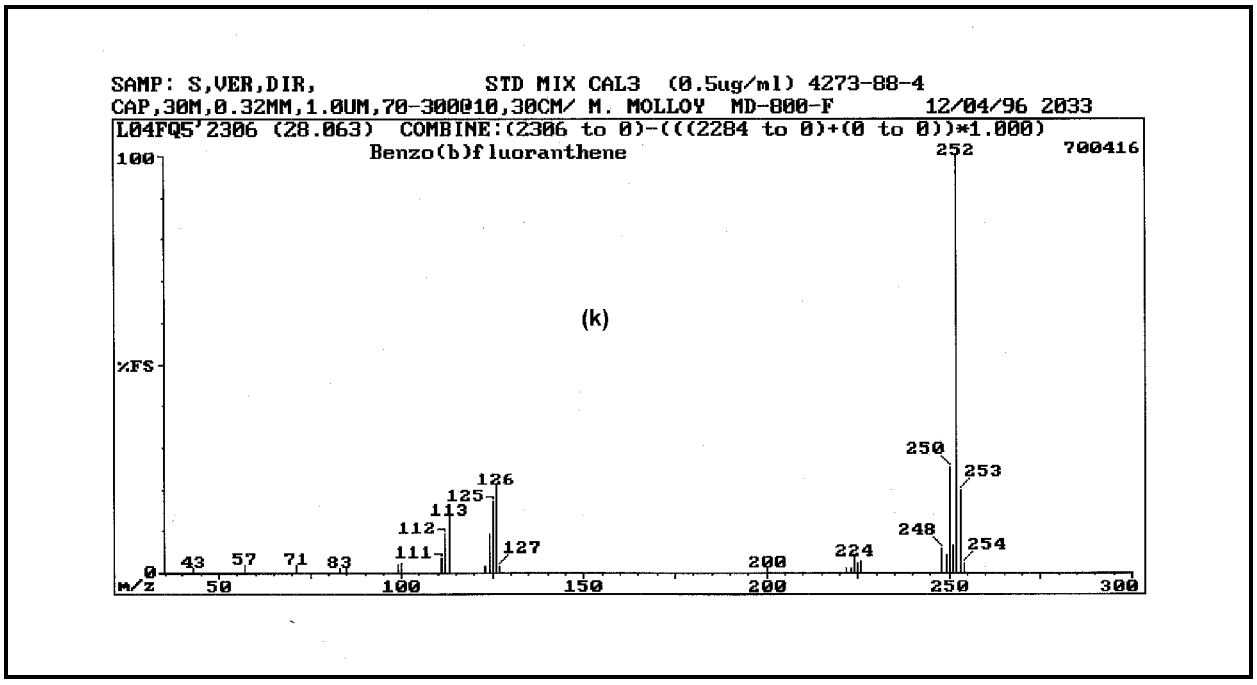


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (i) benz(a)anthracene and (j) chrysene.



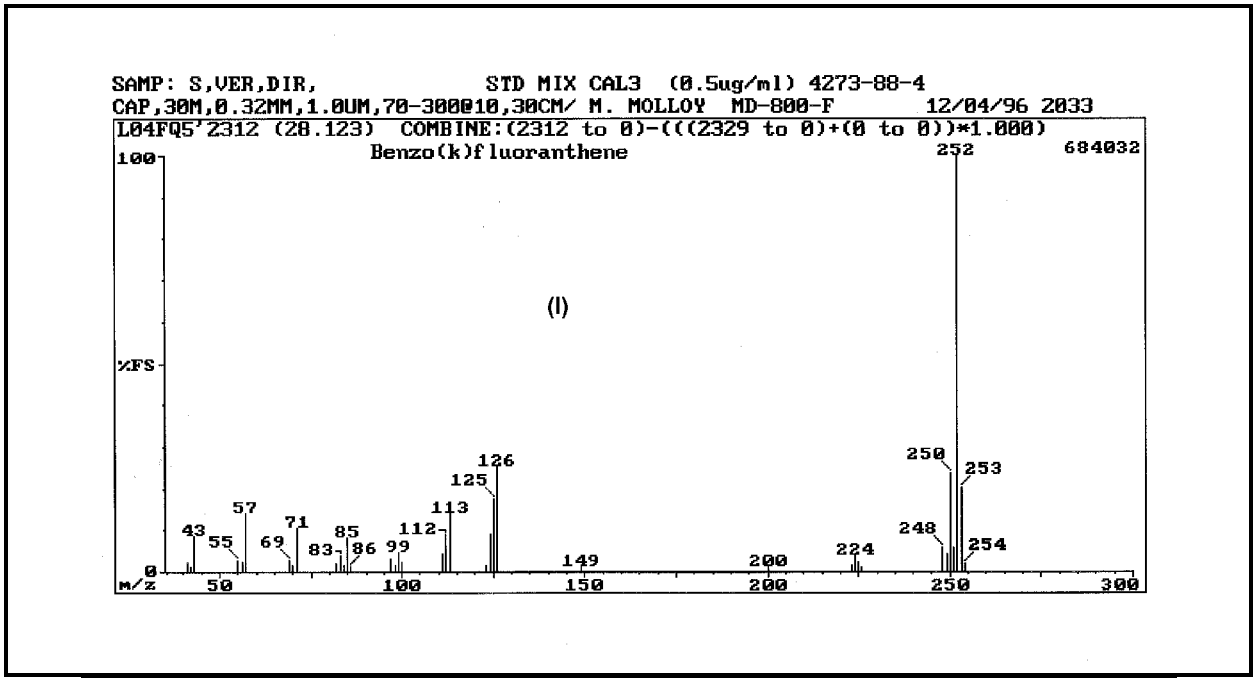
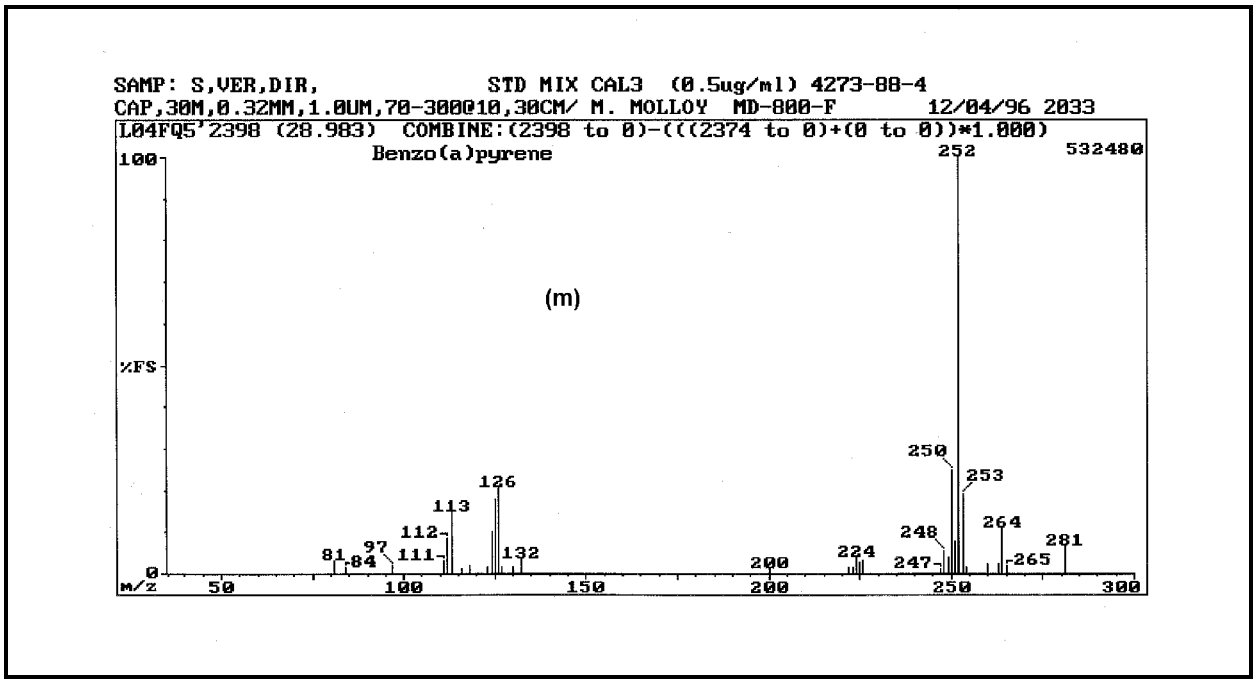


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (k) benzo(b)fluoranthene and (l) benzo(k)fluoranthene.



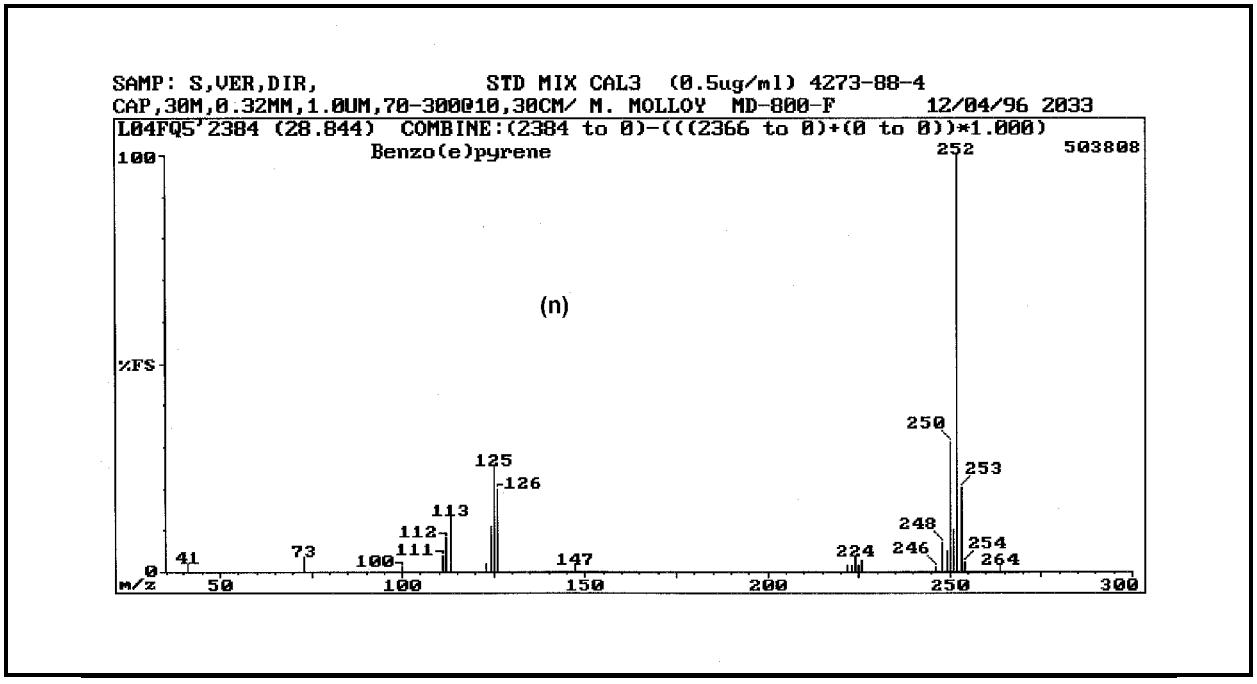
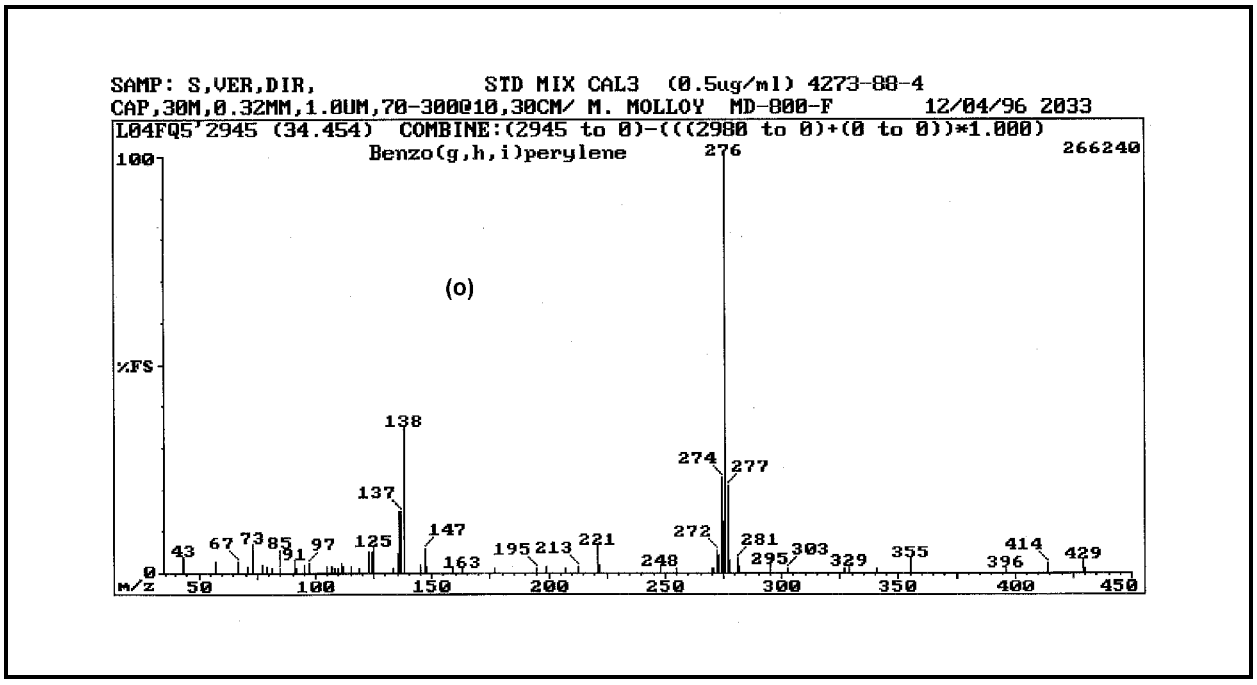


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (m) benzo(a)pyrene and (n) benzo(e)pyrene.



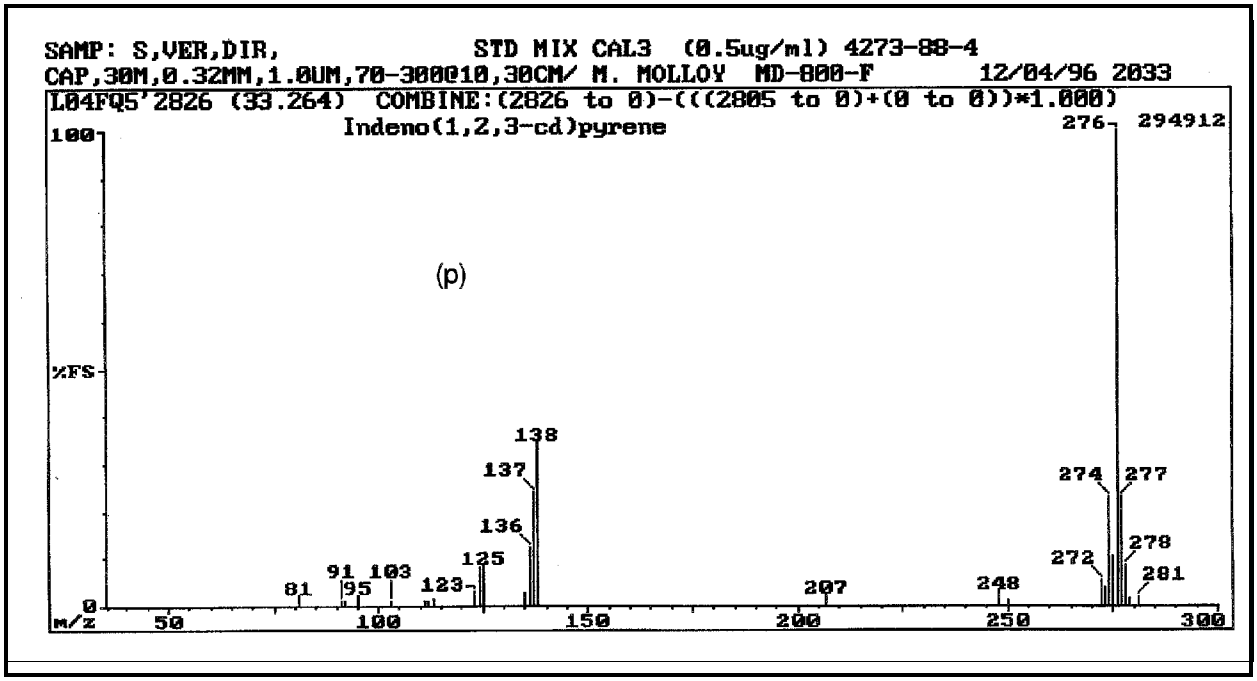


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (o) benzo(g,h,i)perylene and (p) indeno(1,2,3-cd)pyrene.

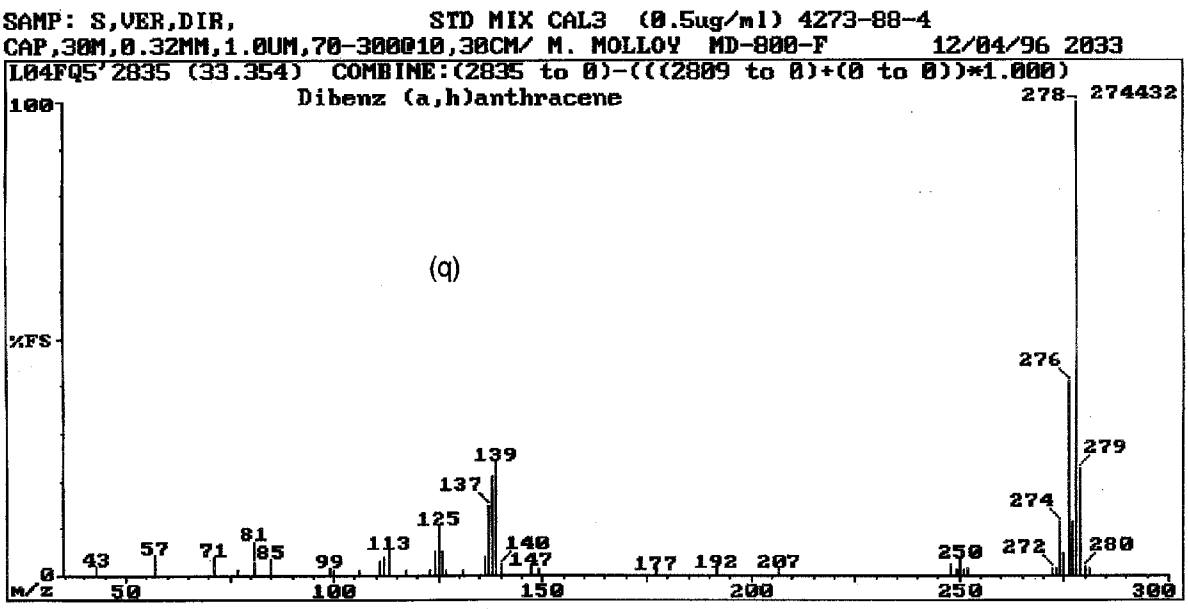


Figure 15 (Cont). Mass spectra of Compendium Method TO-13A compounds for (q) dibenz(a,h)anthracene.

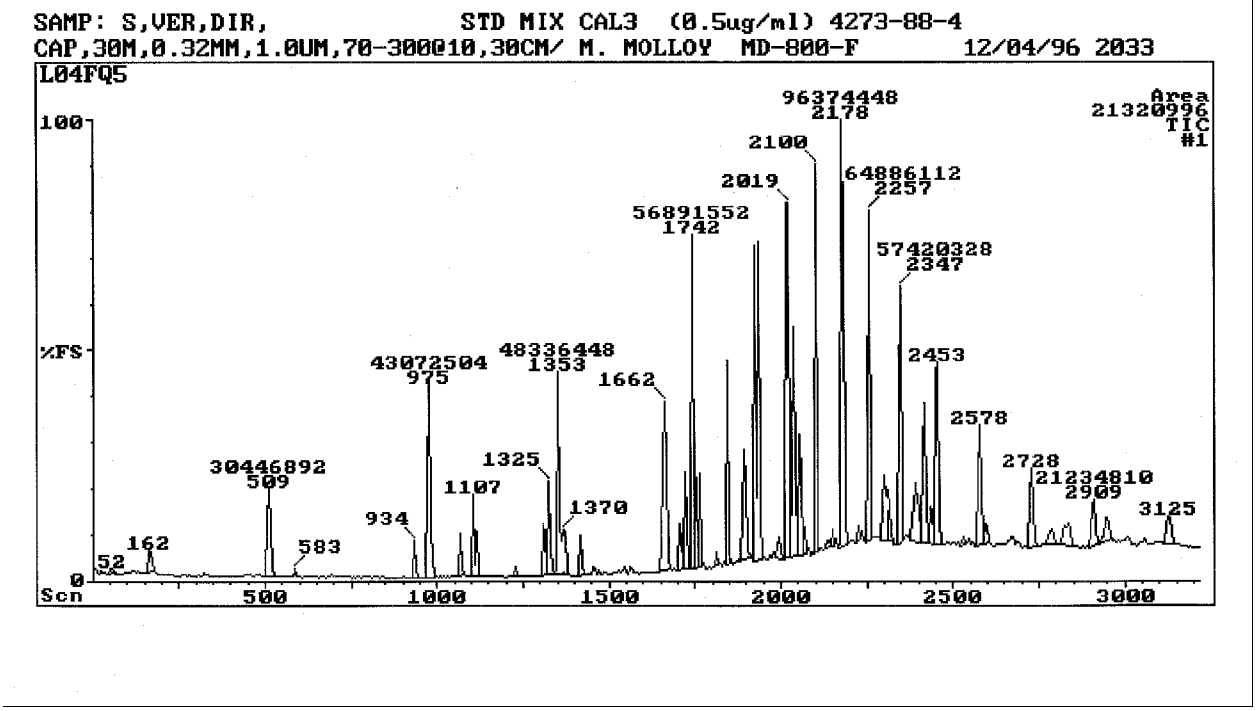


Figure 16. Total ion chromatogram (TIC) of Compendium Method TO-13A target PAHs.

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APPENDIX G

USEPA Compendium Method TO-15

EPA/625/R-96/010b

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

Second Edition

Compendium Method TO-15

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

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

January 1999

Method TO-15
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Author(s)
- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Michael W. Holdren, Battelle, Columbus, OH

Peer Reviewers
- Karen Oliver, ManTech, RTP, NC
- Jim Cheney, Corps of Engineers, Omaha, NB
- Elizabeth Almasi, Varian Chromatography Systems, Walnut Creek, CA
- Norm Kirshen, Varian Chromatography Systems, Walnut Creek, CA
- Richard Jesser, Graseby, Smyrna, GA
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DISCLAIMER

METHOD TO-15

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

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

METHOD TO-15

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

1. Scope

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

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

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

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

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

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

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

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

2. Summary of Method

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

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

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

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

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

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

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

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

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

3. Significance

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

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

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

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

4. Applicable Documents

4.1 ASTM Standards

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

4.2 EPA Documents

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

5. Definitions

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

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

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

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

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

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

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

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

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

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

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

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

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

6. Interferences and Contamination

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

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

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

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

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

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

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

7. Apparatus and Reagents

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

7.1 Sampling Apparatus

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

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

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

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

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

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

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

7.1.1.6 Electronic Timer. For unattended sample collection.

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

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

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

7.1.1.10 Heater Thermostat. Automatically regulates heater temperature.

7.1.1.11 Fan. For cooling sampling system.

7.1.1.12 Fan Thermostat. Automatically regulates fan operation.

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

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

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

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

7.1.1.16 Elapsed Time Meter. Measures duration of sampling.

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

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

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

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

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

7.2 Analytical Apparatus

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

7.3 Calibration System and Manifold Apparatus (see Figure 8)

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

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

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

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

7.4 Reagents

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

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

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

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

8. Collection of Samples in Canisters

8.1 Introduction

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

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

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

8.2 Sampling System Description

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

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

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

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

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

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

8.2.3 All Samplers.

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

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

where:

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

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

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

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

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

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

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

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

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

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

8.3 Sampling Procedure

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The sampler is turned off.

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

8.4 Cleaning and Certification Program

8.4.1 Canister Cleaning and Certification.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

8.4.2 Cleaning Sampling System Components.

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

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

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

8.4.3 Zero Air Certification.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

8.4.5 Sampler System Certification without Compressed Gas Cylinder Standards.

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

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

9. GC/MS Analysis of Volatiles from Canisters

9.1 Introduction

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

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

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

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

9.2 Preparation of Standards

9.2.1 Introduction.

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

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

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

9.2.2 Preparing Working Standards.

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

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

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

9.2.3 Standard Preparation by Dynamic Dilution Technique.

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

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

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

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

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

9.2.4 Standard Preparation by Static Dilution Bottle Technique

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

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

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

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

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

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

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

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

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

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

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

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

9.2.5 Standard Preparation Procedure in High Pressure Cylinders

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

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

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

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

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

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

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

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

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

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

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

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

and:

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

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

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

9.2.6 Standard Preparation by Water Methods.

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

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

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

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

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

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

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

9.2.6.6 The canister is allowed to equilibrate overnight before use.

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

9.2.7 Preparation of Standards by Permeation Tubes.

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

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

9.2.8 Storage of Standards.

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

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

10. GC/MS Operating Conditions

10.1 Preconcentrator

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

10.1.1 Sample Collection Conditions

Cryogenic Trap	**Adsorbent Trap**

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

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

10.1.2 Desorption Conditions

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

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

10.1.3 Trap Reconditioning Conditions.

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

10.2 GC/MS System

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

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

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

10.2.3 The following are the recommended mass spectrometer conditions:

Item	**Condition**

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

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

10.3 Analytical Sequence

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

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

10.4 Instrument Performance Check

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

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

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

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

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

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

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

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

10.5 Initial Calibration

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

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

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

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

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

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

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

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

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

10.5.4 Calculations.

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

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

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

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

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

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

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

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

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

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

and

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

10.5.5 Technical Acceptance Criteria for the Initial Calibration.

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

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

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

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

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

10.5.6 Corrective Action.

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

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

10.6 Daily Calibration

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

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

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

10.6.4 Calculations. Perform the following calculations.

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

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

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

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

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

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

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

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

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

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

10.7 Blank Analyses

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

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

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

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

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

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

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

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

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

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

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

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

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

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

10.8 Sample Analysis

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

where: C_x = Compound concentration, ppbv.

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

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

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

.

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

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

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

10.8.5 Technical Acceptance Criteria.

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

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

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

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

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

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

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

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

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

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

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

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

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

11.1 Introduction

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

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

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

11.2 Method Detection Limit

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

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

11.3 Replicate Precision

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

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

where: x_1 = First measurement value.

x_2 = Second measurement value.

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

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

11.4 Audit Accuracy

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

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

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

12. References

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APPENDIX A.

LISTING OF SOME COMMERCIAL WATER MANAGEMENT SYSTEMS USED WITH AUTOGC SYSTEMS

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

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

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

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

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

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

APPENDIX B.

COMMENT ON CANISTER CLEANING PROCEDURES

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

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

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

APPENDIX C.

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

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

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

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

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

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

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

APPENDIX D.

LISTING OF COMMERCIAL SUPPLIERS OF PERMEATION TUBES AND SYSTEMS

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

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

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

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

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

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

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

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

TABLE 1. (continued)

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

TABLE 1. (continued)

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

TABLE 1. (continued)

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

TABLE 1. (continued)

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

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

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

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

TABLE 2. (continued)

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

TABLE 2. (continued)

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

TABLE 3. REQUIRED BFB KEY IONS AND ION ABUNDANCE CRITERIA

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

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

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

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

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

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

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

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

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

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

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

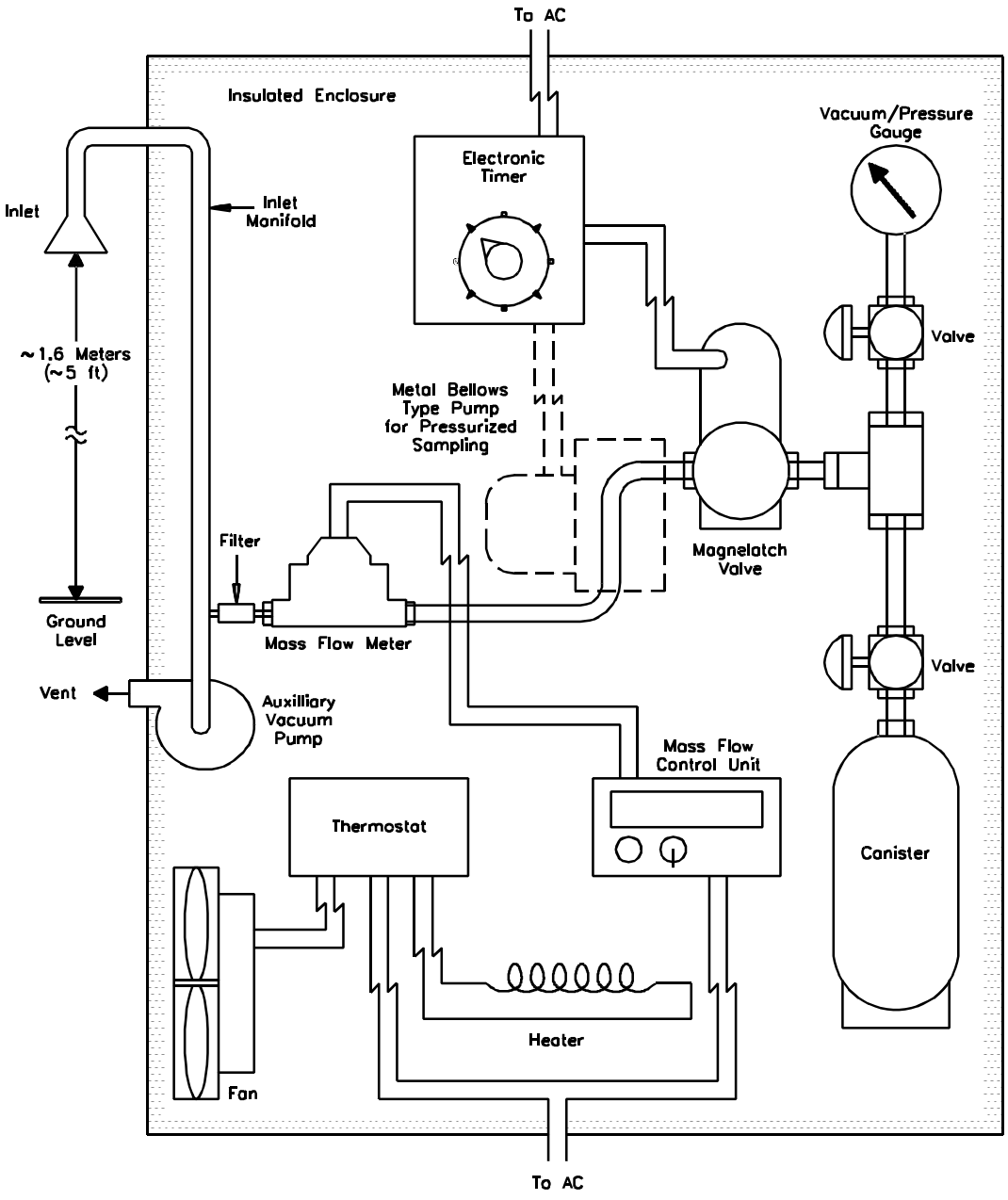
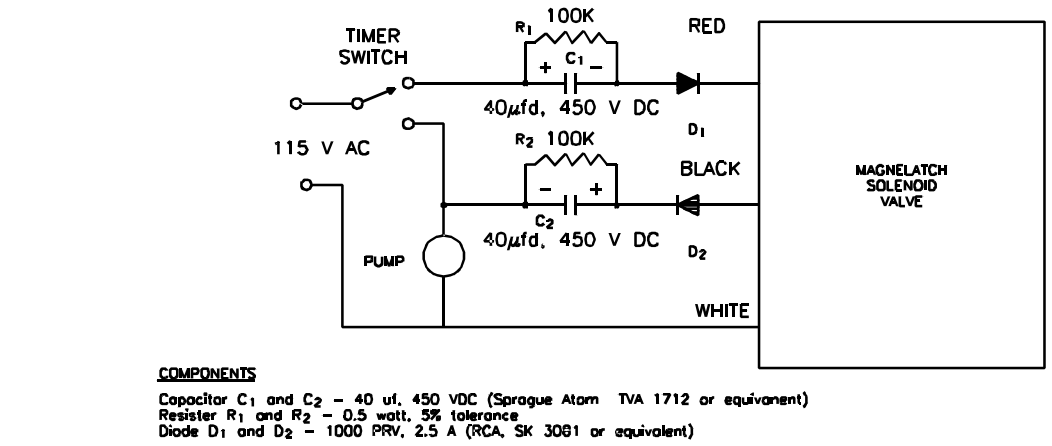
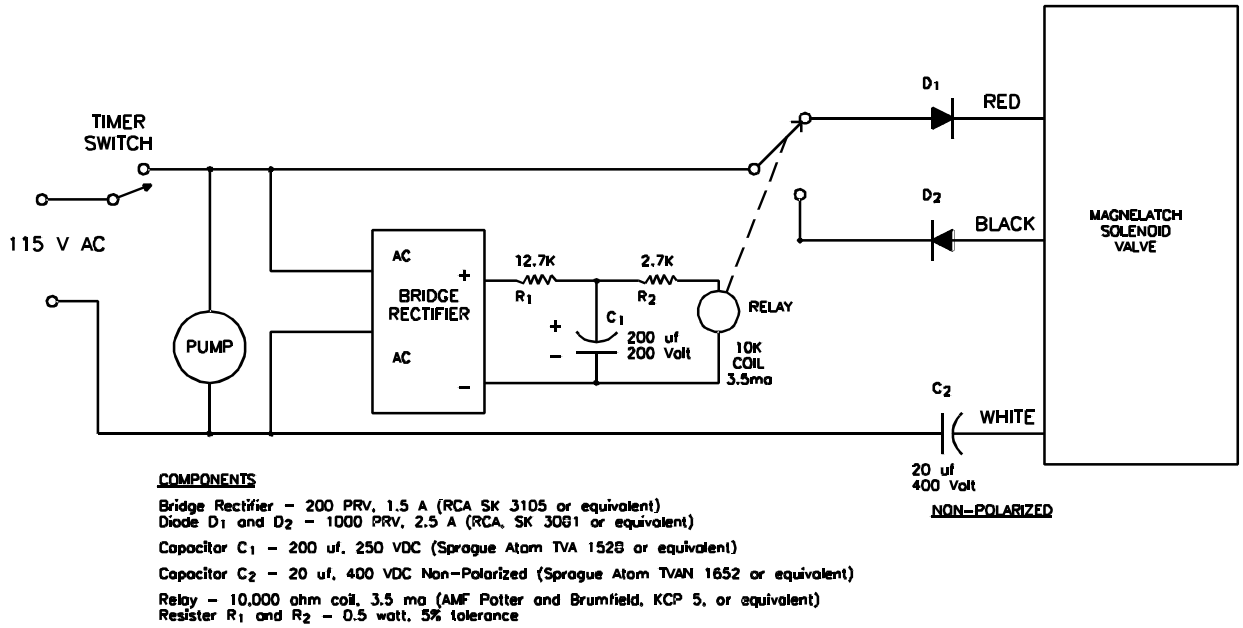


Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.



(a). Simple Circuit for Operating Magnelatch Valve



(b). Improved Circuit Designed to Handle Power Interruptions

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

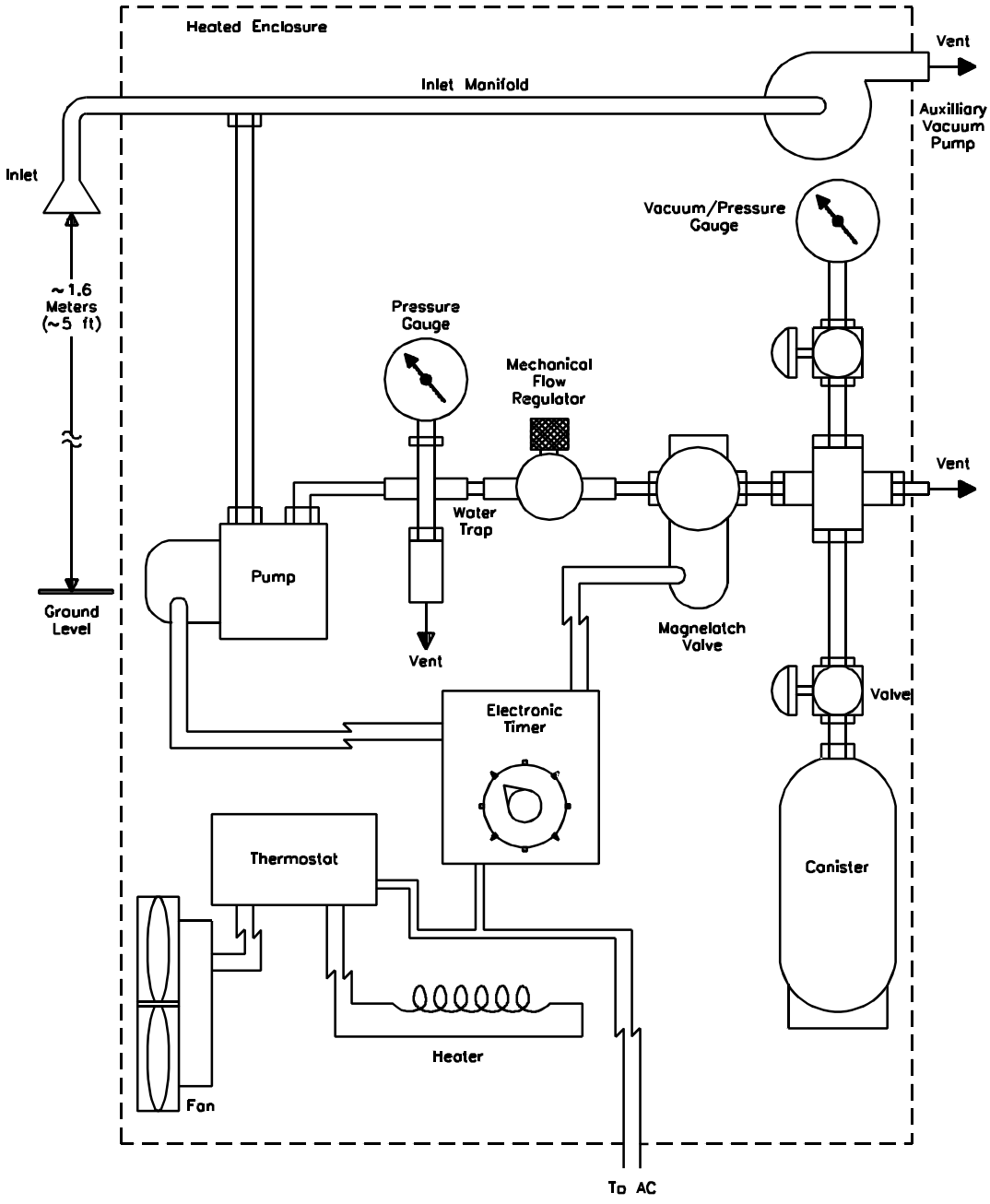


Figure 3. Alternative sampler configuration for pressurized canister sampling.

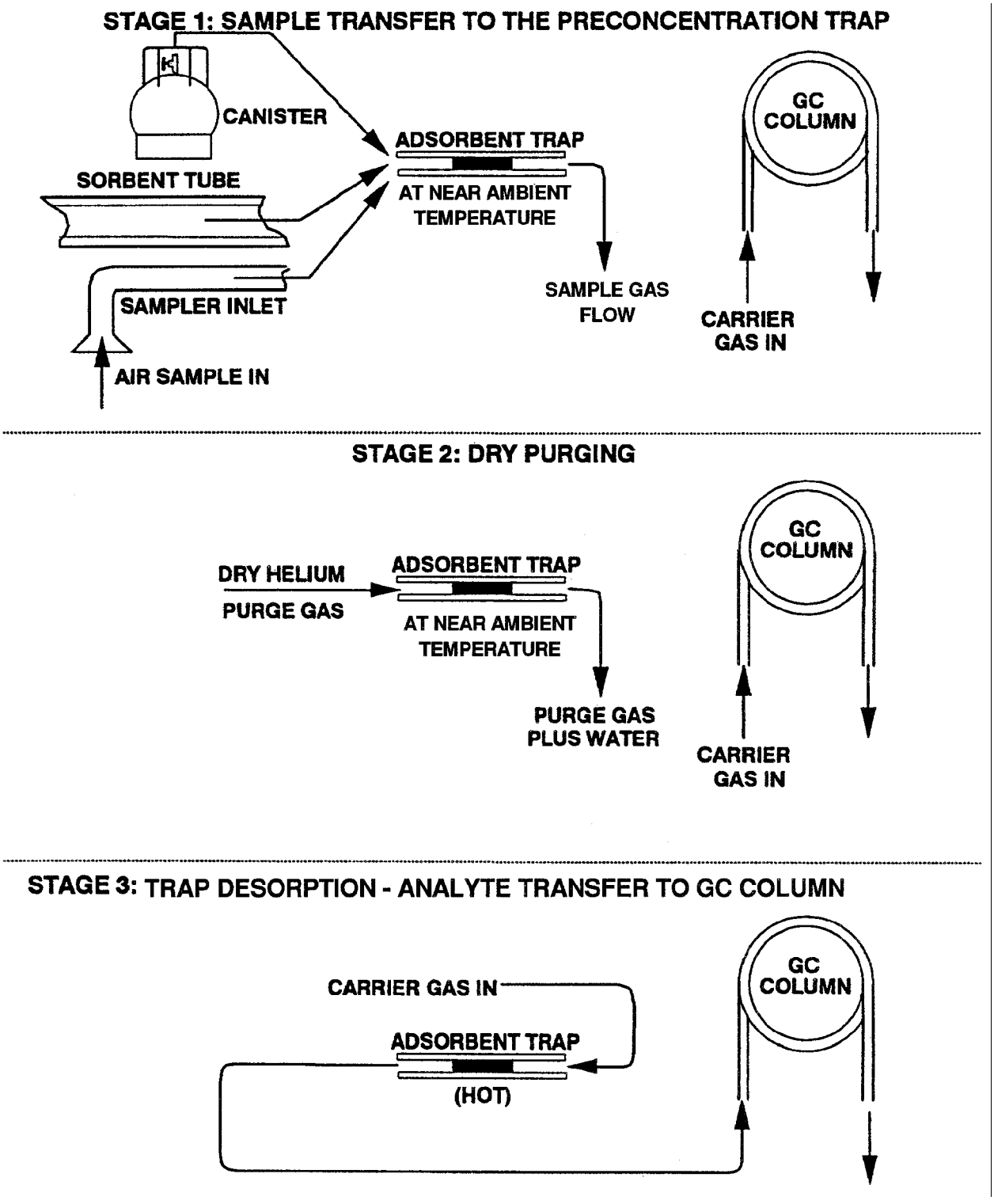


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

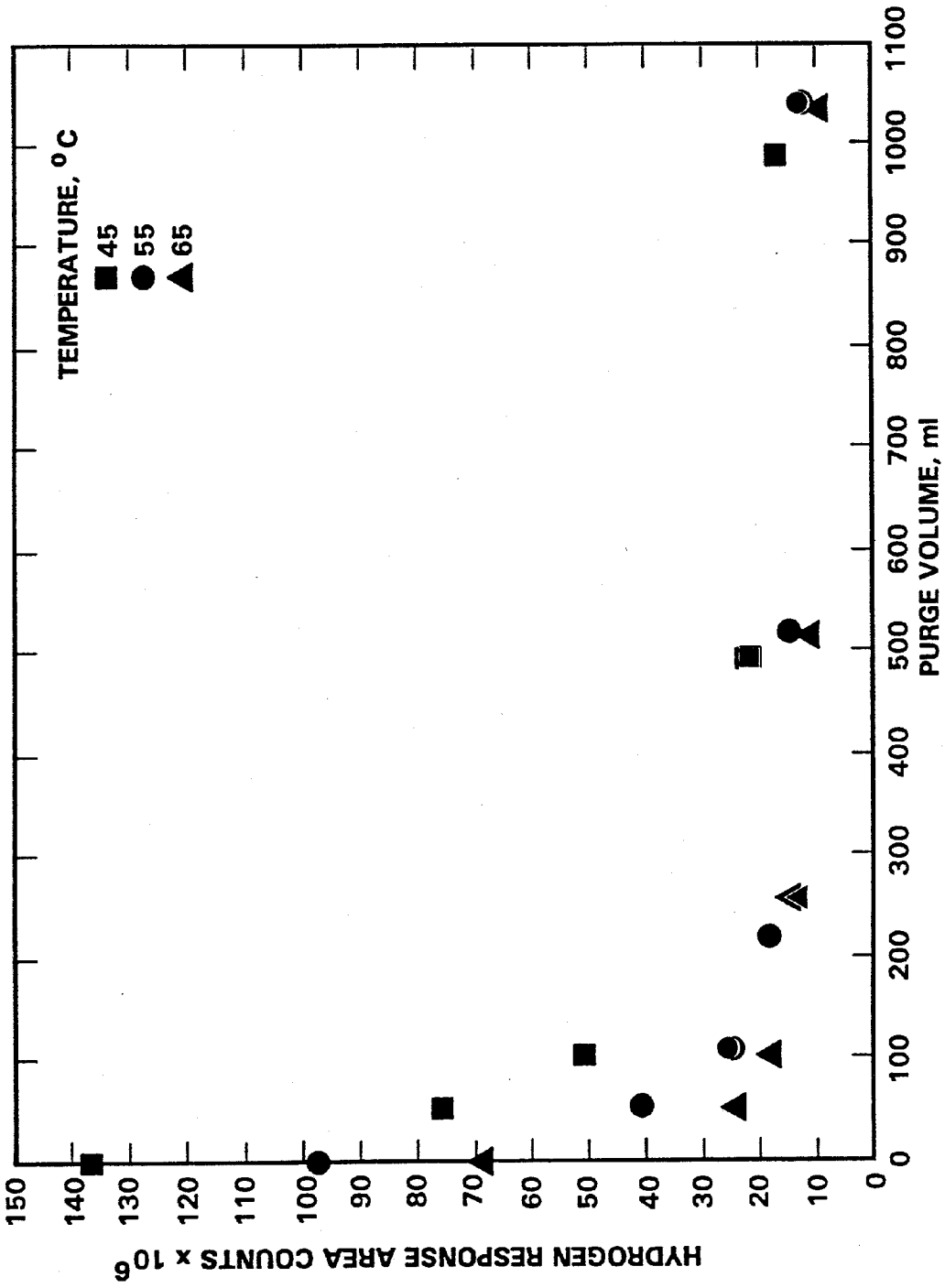


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

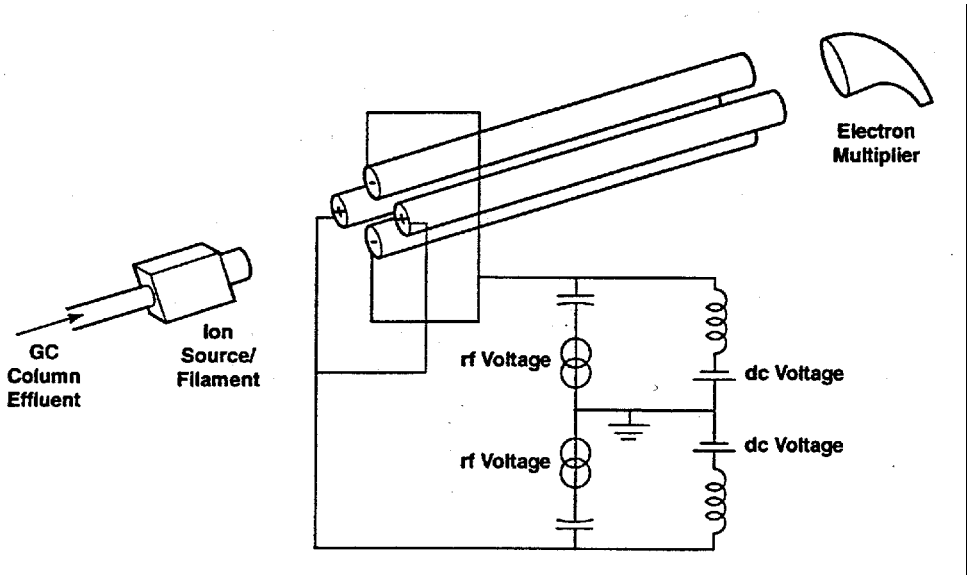


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

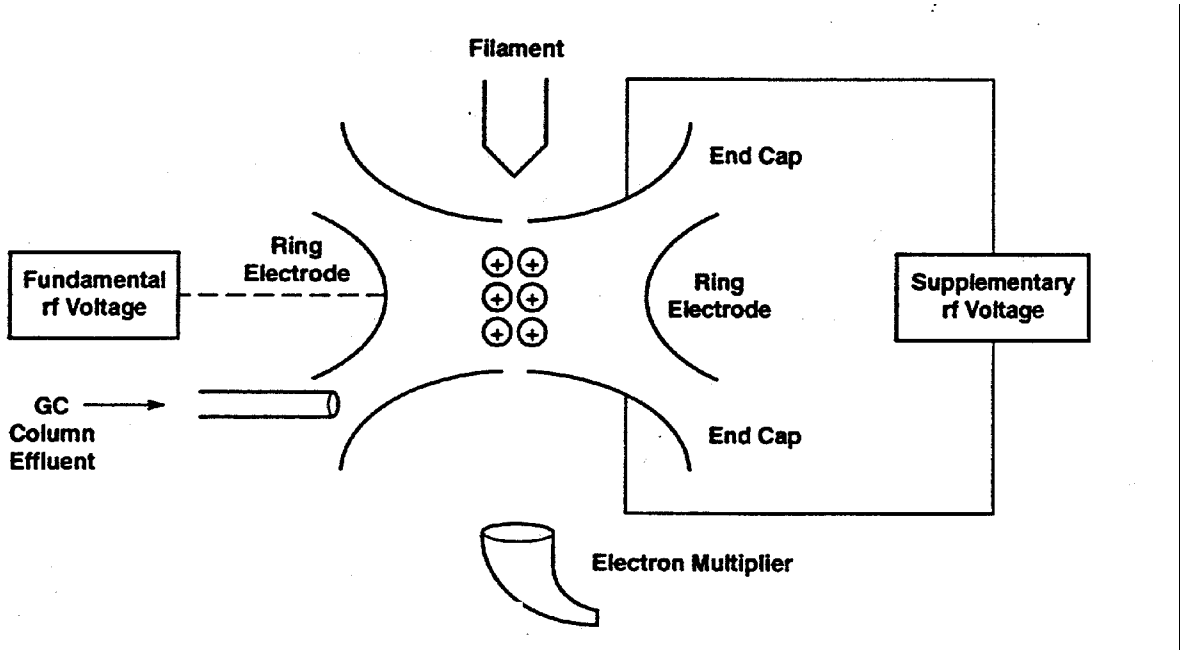


Figure 7. Simplified diagram of an ion trap mass spectrometer.

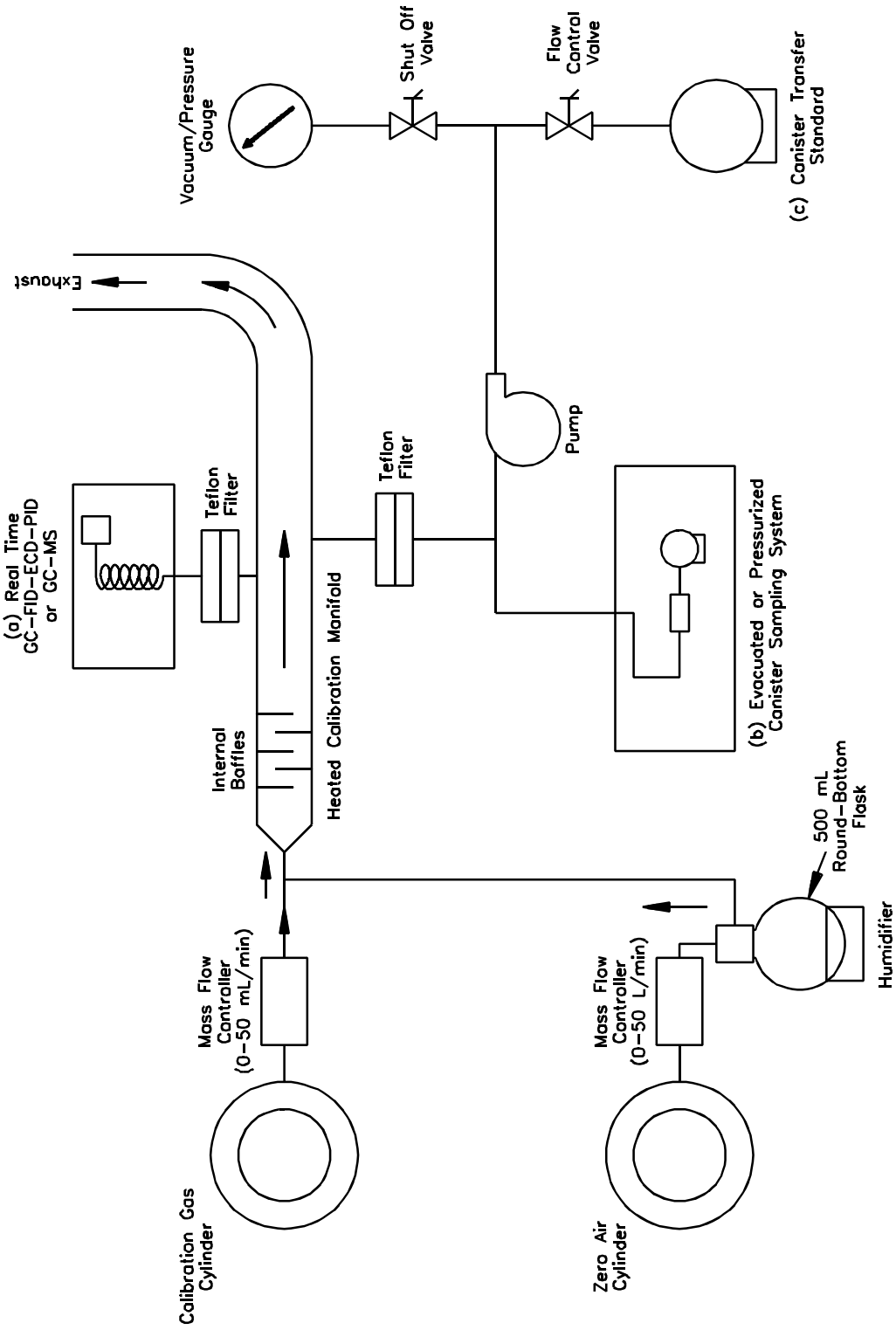


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET

A.GENERAL INFORMATION

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

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

B. SAMPLING INFORMATION

	TEMPERATURE				PRESSURE	
	INTERIOR	AMBIENT	MAXIMUM	MINIMUM	CANISTER PRESSURE	
START						
STOP						

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

SAMPLING SYSTEM CERTIFICATION DATE: _____
QUARTERLY RECERTIFICATION DATE: _____

C. LABORATORY INFORMATION

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

_____
SIGNATURE/TITLE

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

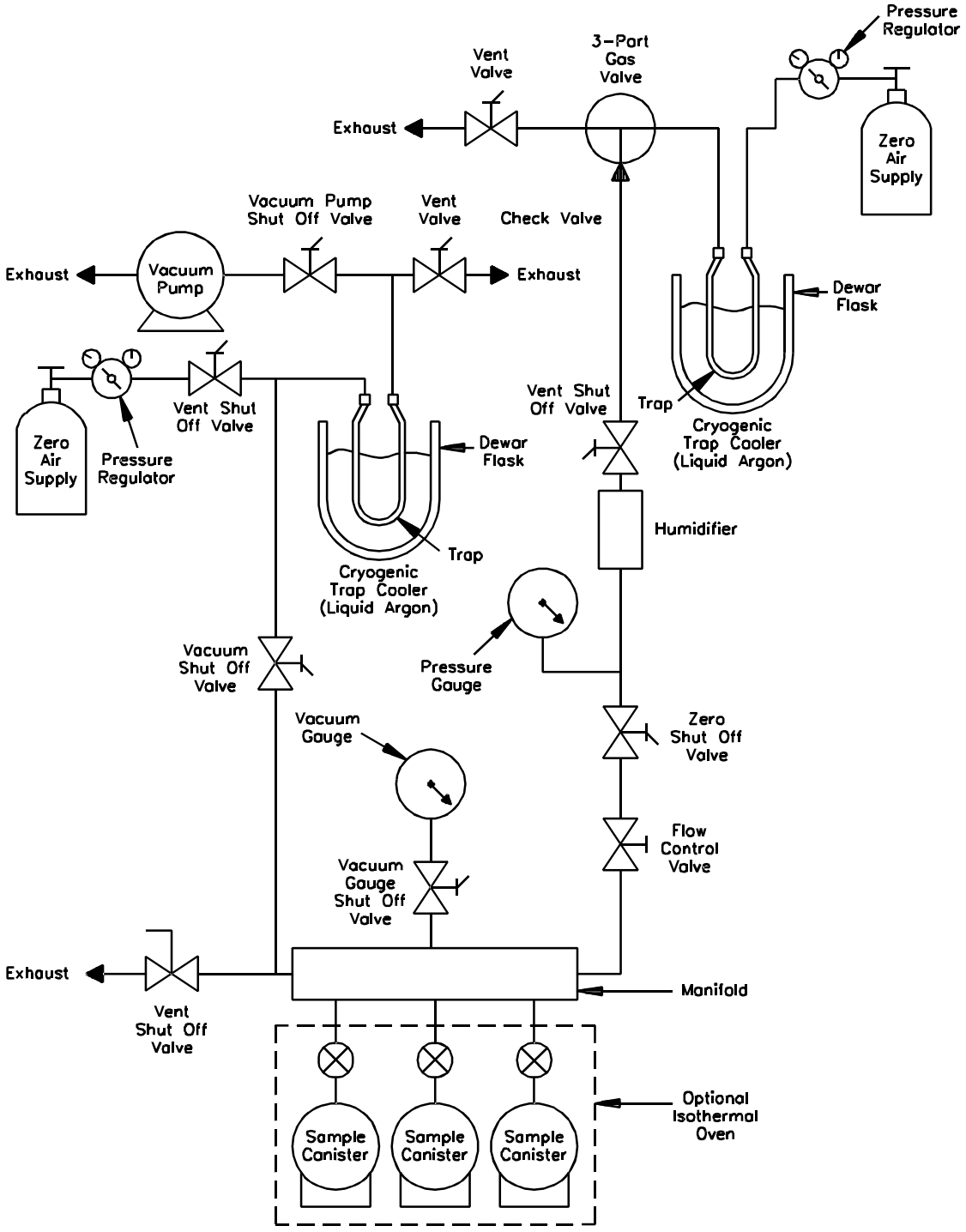


Figure 10. Canister cleaning system.

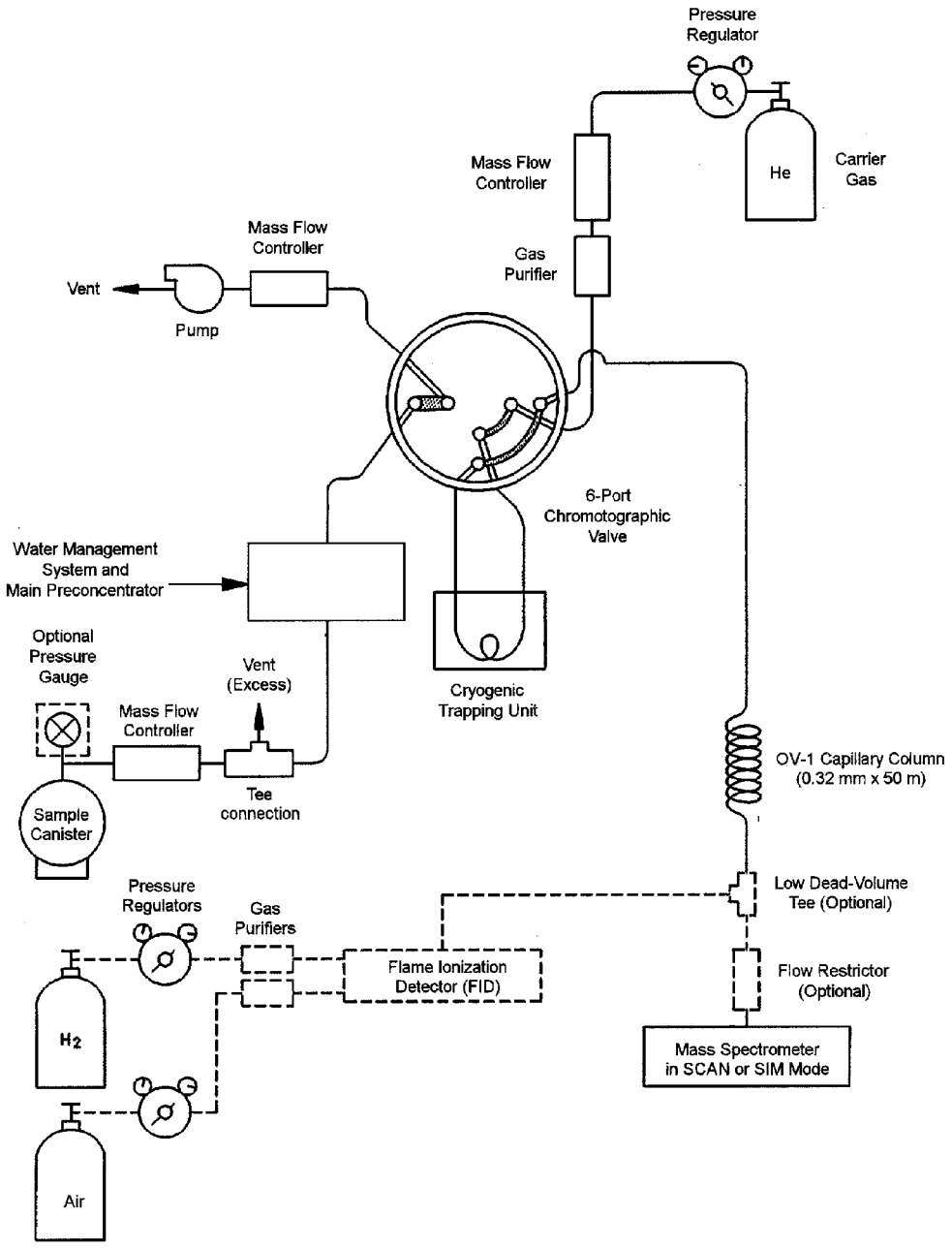
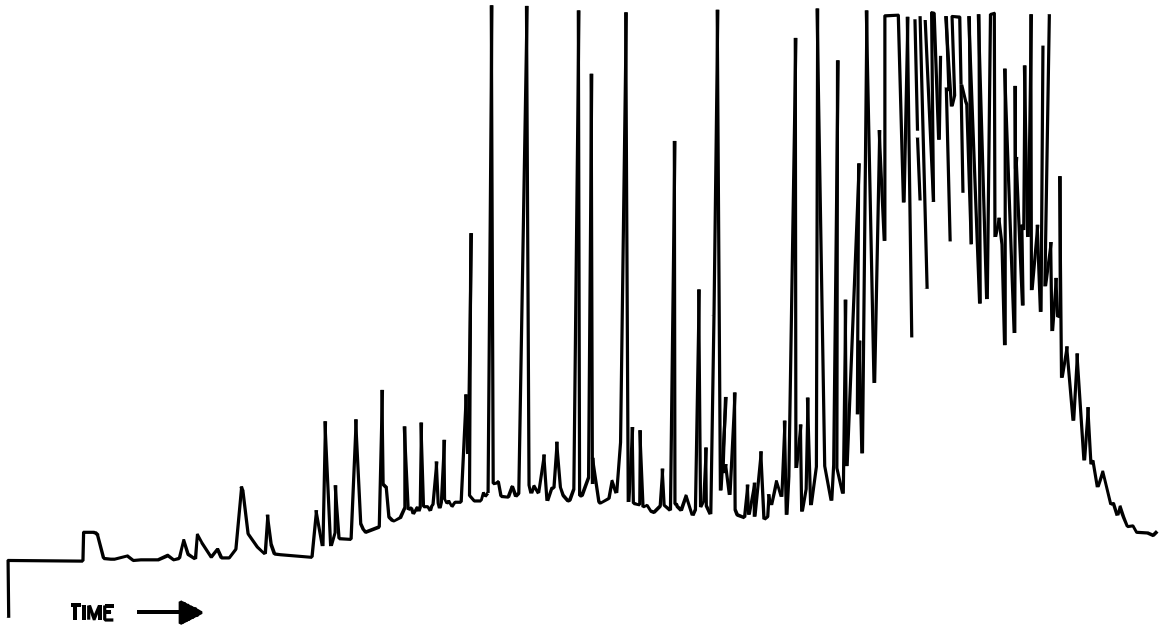


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]

(a). Certified Sampler



(b). Contaminated Sampler

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

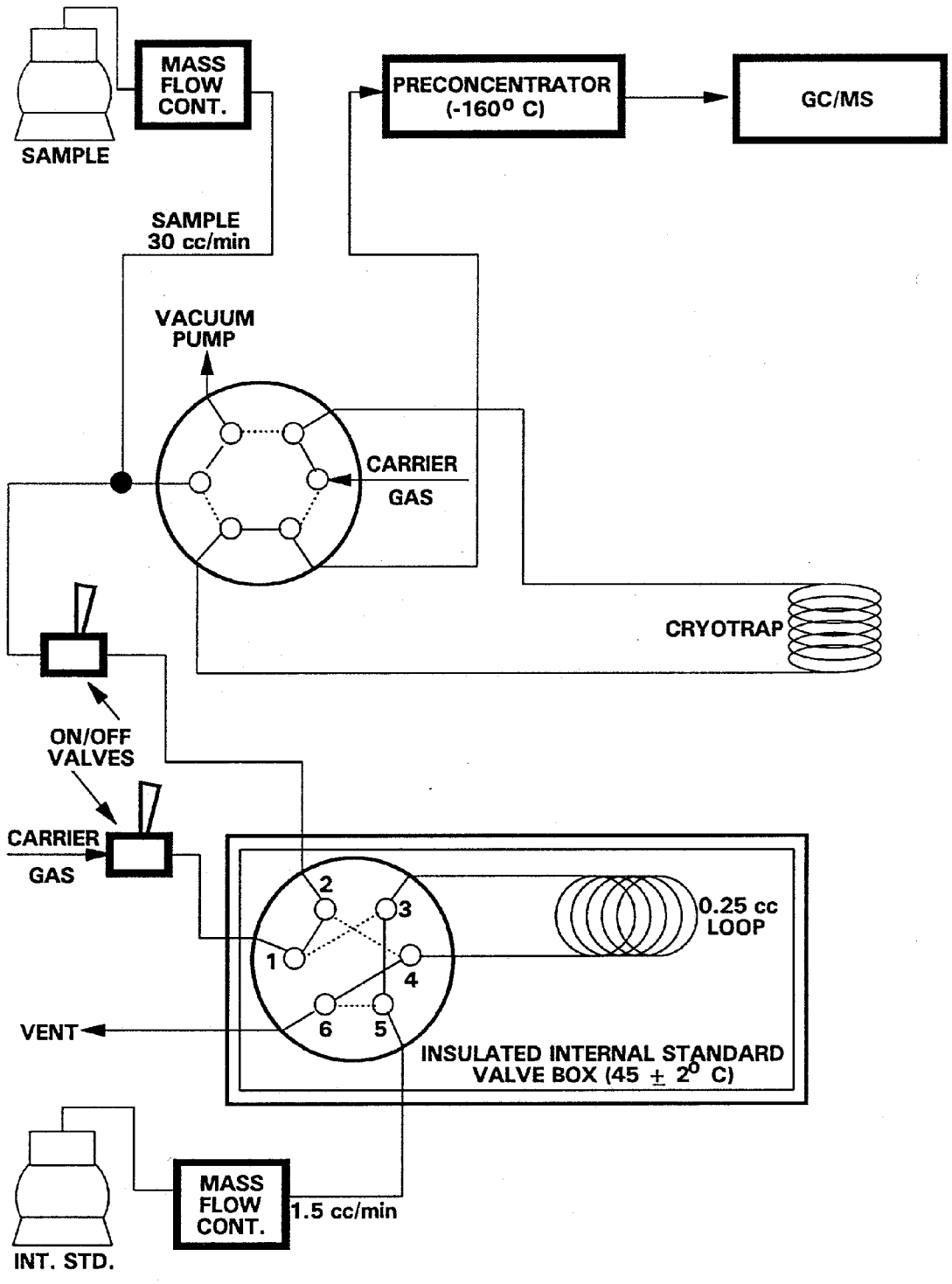


Figure 13. Diagram of design for internal standard addition.

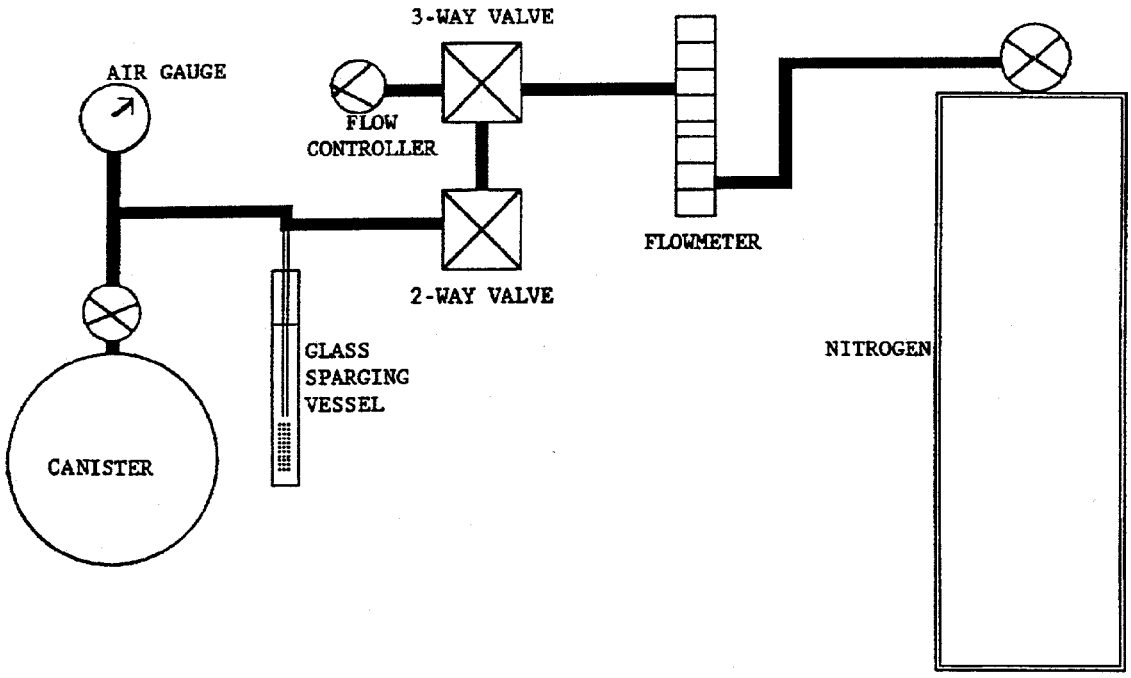


Figure 14. Water method of standard preparation in canisters.

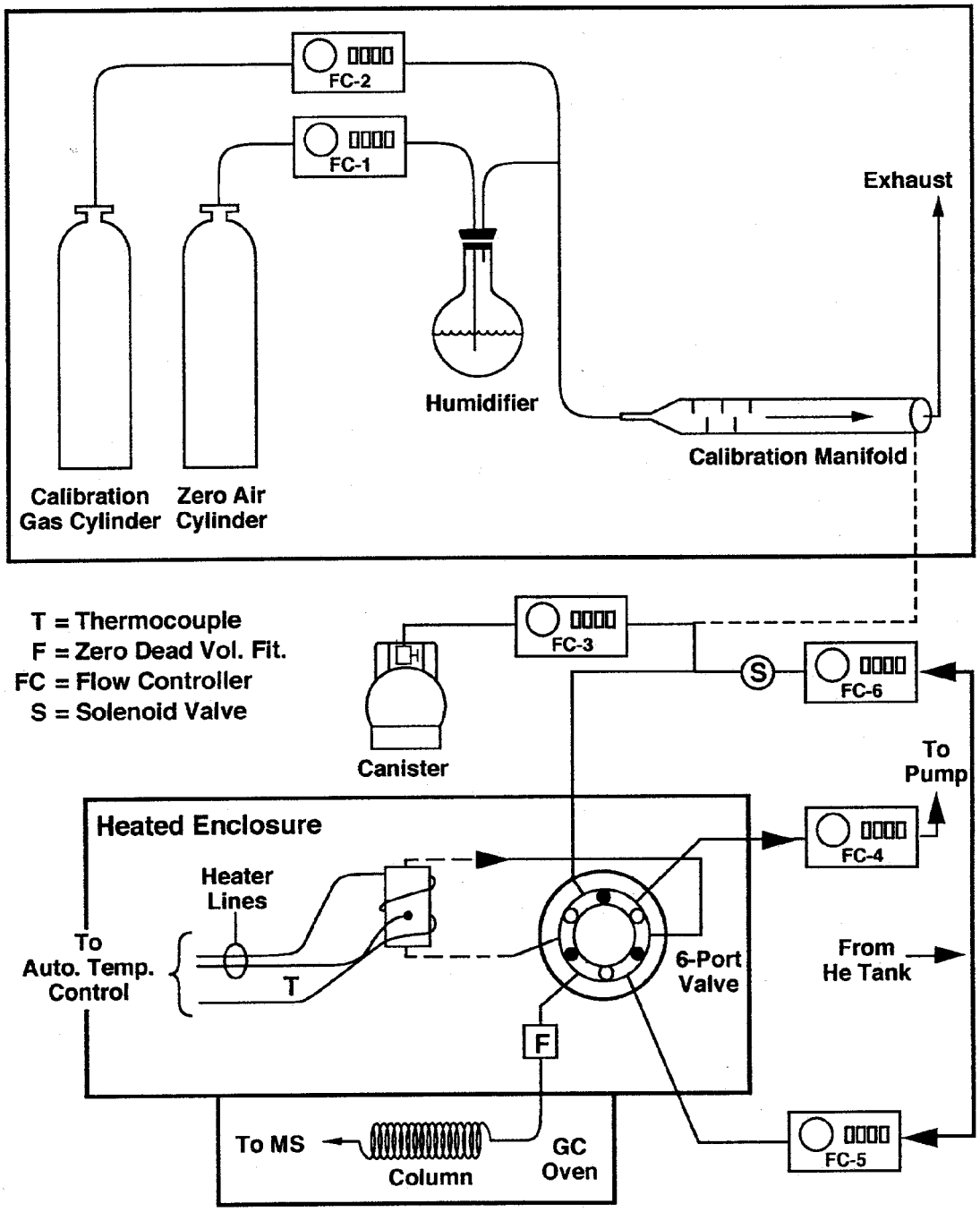


Figure 15. Diagram of the GC/MS analytical system.

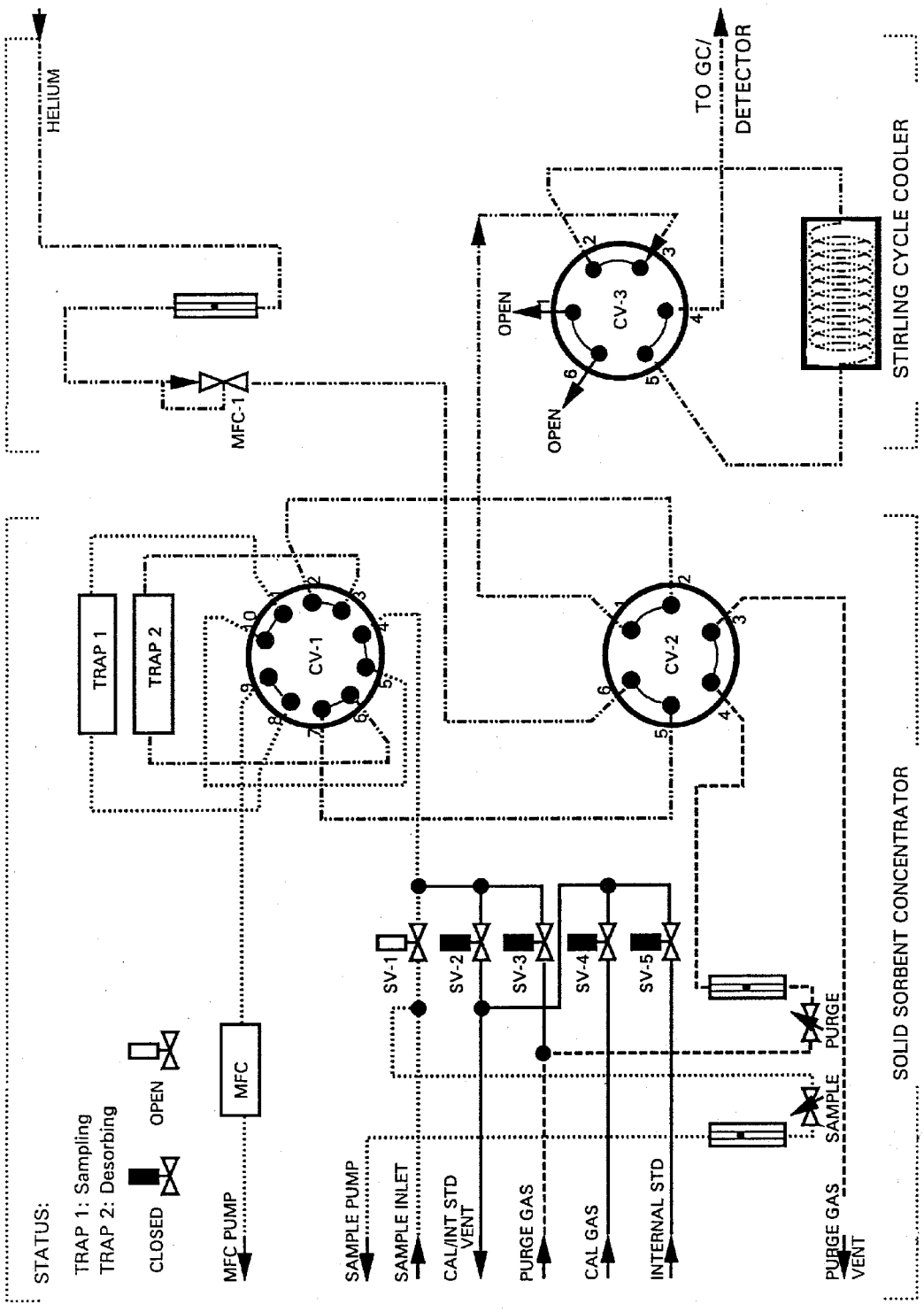


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).

APPENDIX H

USACHPPM Laboratory SOP CAD 26.3

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SOP NO: CAD 26.3
EFFECTIVE DATE: SEPTEMBER 2002

STANDING OPERATING PROCEDURE
DIRECTORATE OF LABORATORY SCIENCES
CHROMATOGRAPHIC ANALYSIS DIVISION

PROCEDURE FOR ANALYSIS OF EXPLOSIVES IN AMBIENT AIR

SOP NO: CAD 26.3
EFFECTIVE DATE: SEPTEMBER 2002
PAGE 1 OF 14
REMOVAL DATE:

STANDING OPERATING PROCEDURE

Procedure for Analysis of Explosives in Ambient Air

Curtis Oliver — Preparer — 12Sept02 — Date

Chief, Chromatographic Analysis Division — 12 Sept 2002 — Date

Rosemary Gaffney — DLS Quality Compliance Manager — 13Sep02 — Date

Annual Review

Reviewed	Date Reviewed
Approved	Date Approved
Reviewed	Date Reviewed
Approved	Date Approved
Reviewed	Date Reviewed
Approved	Date Approved
Reviewed	Date Reviewed
Approved	Date Approved
Reviewed	Date Reviewed
Approved	Date Approved

U.S. ARMY CENTER FOR HEALTH PROMOTION AND PREVENTIVE MEDICINE
DIRECTORATE OF LABORATORY SCIENCES
CHROMATOGRAPHIC ANALYSIS DIVISION
ABERDEEN PROVING GROUND, MD 21010-5403

MCHB-TS-LCD

PROCEDURE FOR ANALYSIS OF EXPLOSIVES IN AMBIENT AIR

Use of company names does not imply endorsement by the U.S. Army but is intended only to assist in identification of a specific product.

1.0 PURPOSE. This standing operating procedure (SOP) describes a method for the extraction and analysis of energetic compounds from ambient air samples. The procedure has application toward monitoring operations involving weapons testing and open burning/ detonations of munitions. The method employs a glass cartridge assembly containing XAD-2 resin to trap the compounds from the air, desorption of the compounds from the resin using a suitable organic solvent, and analysis of the extract using gas chromatography with electron capture detection (GC-ECD) or other suitable detector.

2.0 SCOPE. This SOP describes the process used for the extraction and analysis of XAD-2 resin used to sample explosives and related compounds from air. Compounds validated for testing include:

- 2,6-Dinitrotoluene (2,6-DNT)
- 2,4-Dinitrotoluene (2,4-DNT)
- 2,4,6-Trinitrotoluene (2,4,6-TNT)
- Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
- Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
- 2-Nitrotoluene (2-NT)
- 3-Nitrotoluene (3-NT)
- 4-Nitrotoluene (4-NT)
- 1,3-Dinitrobenzene (1,3-DNB)
- 1,3,5-Trinitrobenzene (1,3,5-TNB)
- 4-Amino-2,6-Dinitrotoluene (4A26DNT)
- 2-Amino-4,6-Dinitrotoluene (2A46DNT)
- Nitrobenzene (NB)
- Methyl-2,4,6-trinitrophenylnitramine (Tetryl)
- Nitroglycerin (NG)
- 3,4-Dinitrotoluene (3,4-DNT), a surrogate compound

Additional compounds which have been tested and for which partial validation data exists include the following:

- Pentaerythritol Tetranitrate (PETN)
- Diphenylamine (DPA)
- Dibutylphthalate (DBP)
- Dioctylphthalate (DOP)

Other related compounds may potentially be done using this procedure if they can be demonstrated to be collectable and retained by XAD-2 resin and can be efficiently desorbed from the resin by the solvent employed.

3.0 DEFINITIONS.

3.1 POHC. Principal Organic Hazardous Constituents. Term used in conjunction with stack emission sampling.

3.2 EPA Method 5 Train. A sampling train used to monitor stack emissions for POHCs.

3.3 USACHPPM STEM (Sampling Train for Energetic Materials) Train. A modification of the EPA Method 5 Train which employs a four stage (5 g each) XAD-2 resin cartridge located after the impingers in the train.

4.0 DISCUSSION. This procedure is a modification of methods used to monitor explosives residues produced during the incineration of obsolete or off-specification munitions, propellants and explosives. The USACHPPM STEM train has been routinely used to evaluate the destruction and removal efficiency (DRE) of POHCs such as the compounds listed above. XAD-2 resin is used for the sample collection of all listed compounds. The two possible sampling cartridges used in this ambient air procedure also employ XAD-2 resin. One is in the configuration and amount (50 g) similar to that used with USEPA Toxic Organics methods such as TO 13 and the other uses a smaller amount of XAD-2 (two 10 g sections). The larger cartridge is generally used for high-volume sampling and the smaller cartridge for shorter test intervals. The target analyte compounds are desorbed from the resin using a shake-out with isoamyl acetate, and the analysis of the extract for the energetics is done by GC-ECD. Phthalates and diphenylamine require a different GC detector; their analysis is addressed in Section 7.8 of this SOP. These analytes can also be analyzed using GC-MSD as described in CAD SOP 69, current version. A surrogate compound (3,4-Dinitrotoluene) is spiked on the sampling cartridges prior to sampling and is used to monitor sampling/analysis recoveries. The GC-ECD procedure is similar to that used within USACHPPM for analysis of nitroaromatics and nitramines in water samples and for STEM Train analyses.

5.0 RESPONSIBILITIES. Personnel using this SOP for sample analysis must follow the guidance set by this SOP and must be skilled with, and authorized to use GC-ECD.

6.0 REQUIREMENTS.

6.1 Chemical Reagents:

6.1.1 Analytical standards: These compounds are Standard Analytical Reference Materials (SARMs) obtained as neat compounds or as solutions from commercial vendors (such as AccuStandard or Supelco). Diphenylamine and phthalate esters are available commercially as neat chemicals.

6.1.2 Isoamyl acetate, Anhydrous. Aldrich, 30696-7.

6.1.3 Acetonitrile. Omnisolve, EM Science, DX0831-1.

6.1.4 XAD-2 Resin, Ultra-Clean from Restek Corporation, Cat. No 24230

6.2 Equipment.

6.2.1 Analytical Balance, capable of weighing to 0.0001 grams.

6.2.2 Volumetric flasks - 1.0 to 100 mL.

6.2.3 Volumetric pipets - 0.5 to 100 mL.

6.2.4 Graduated syringes - 10 to 250 uL.

6.2.5 Appropriate size glass containers with PTFE seal lids.

6.2.6 Disposable Pasteur pipets for sample transfer.

6.2.7 Gas chromatographic system, as listed in Table 1, or an equivalent system.

6.2.8 Autosampler vials, 2 mL capacity or limited insert.

6.2.9 TotalChrom data collection system, or equivalent.

6.3 Interferences. Any organic compound which elutes from the chromatographic system in the region where the analytes elute can cause positive interferences. In this instance, alternate chromatographic columns or operating conditions should be investigated.

6.4 Precision and Accuracy. Available recovery and statistical data for the analytical

procedure are provided in Appendix B.

7.0 PROCEDURE.

7.1 Air Sampling. Details on the assembly and use of the glass cartridge sampling traps are beyond the scope of this SOP. USEPA protocols, such as TO 13 should be used as guidance for sample collection. The air volume to sample should not exceed 350 m^3 for the larger cartridge or 35 m^3 for the smaller cartridge unless it can be demonstrated that breakthrough does not occur with larger air volumes.

7.2 Filters. Some project requirements specify that a filter be used to collect particulate matter. During sampling these filters are placed before the XAD-2 cartridges. The filters that have been used for several projects are 102mm quartz filters.

7.3 Surrogate Preparation. Spike 75 µL of a 1.0 mg/mL 3,4-DNT solution onto each large XAD-2 cartridge or 15 µL of a 1.0 mg/mL 3,4-DNT solution onto each smaller XAD-2 cartridge that is to be sampled. This should be done as near to the sampling date as possible. The theoretical surrogate value is 75 µg 3,4-DNT or 15 µg 3,4-DNT respectively.

7.4 Standards Preparation.

7.4.1 Preparation of individual stock solutions. Stock solutions of each compound are made at a 1 mg/mL level by placing 50 mg of a SARM in 50 mL of residue grade acetonitrile in a volumetric flask. Alternately, commercial standards for the energetics (nitroaromatics and nitramines) may be procured (these are often available at a 1 mg/mL level, but concentrations may vary for some compounds). Note: This does not include PETN, DPA or the phthalates; they are discussed in Section 7.8.

7.4.2 Prepare working standards within the working range of the ECD detector through serial dilutions of the stock solution using isoamyl acetate. The recommended range is between 0.01 µg/mL and 2.00 µg/mL for all compounds except HMX, which should be prepared at twice this range.

7.4.3 Store standards in a freezer at -4 to -10 degrees Celsius until analysis. Stock standards are good for six months from preparation.

7.5 Sample Preparation. Note: Samples must be extracted within fourteen days of collection.

7.5.1 After sample collection, remove the XAD-2 from the sampling cartridge and place in an appropriate size glass container with a PTFE seal. Note that the XAD-2 front and back sections from the smaller cartridges should be placed in separate containers. Also note that if quartz filters are used, depending on project requirements, they are either extracted with the XAD-2 or extracted separately in the field (using 20mL of isoamyl acetate).

7.5.2 Add an adequate volume of isoamyl acetate to cover the XAD-2 in the container (a typical volume would be 120mL for the XAD-2 from the large cartridges and 25mL for each XAD-2 section from the small cartridges) to desorb the analytes from the resin. Seal the container and agitate it on a rotary or flat bed shaker for two hours and then allow to stand overnight in a refrigerator at 2 - 8 degrees Celsius.

7.5.3 Withdraw a portion of the solvent using a Pasteur pipet and place it in a 2 mL or a limited insert autosampler vial.

7.5.4 Store extracts in a freezer at -4 to -10 degrees Celsius until it can be analyzed (40 day holding time).

NOTE: Both toluene and isoamyl acetate have been used for the extraction of nitroaromatics and nitramines from XAD-2 resin in the UASCHPPM Stem Train method for many **years. However, isoamyl acetate is the solvent of choice for this method because of its superior extraction efficiency for both nitroaromatics and nitramines from XAD-2 resin.**

7.6 Instrument Set-up. Set up the chromatographic system for energetics analysis using the conditions listed in Table 1 as a guide. Set up a TotalChrom method and sequence to run the sample extracts, standards, laboratory reagent blank, and any quality controls together.

7.7 Analysis for Energetics.

7.7.1 The analysis is conducted using two chromatographic columns with dissimilar stationary phases. The “primary” column is used to quantitate all standards and samples. A “confirmation” column is used to confirm or quantitate those samples that have positive results on the primary column and/or where interfering compounds co-elute with analytes on the primary column. Recommendation for the “primary” column is one containing a non-polar phase such as DB-1, or equivalent. Recommendations for “confirmation” columns are

mid-polar and polar columns such as DB-17 and DB-210, or phase equivalents. The choice of which secondary column(s) to use depend on the compounds to be confirmed and the sample matrix; the mid-polar column is preferable for the nitramines and the polar column for the nitroaromatics. When significant differences exist in quantitative values between the primary and the confirmation columns, a third column or a different detector (i.e. mass selective) may be used to resolve the differences.

7.7.2 Injection Port Selection. Injections into the gas chromatograph are made in the splitless mode. Splitless injections will provide excellent chromatography **where an inert injection port liner and seal are used.** A Silcosleeve™ (Restek) liner and Silcosteel® (Restek) seal are recommended.

.

7.8 Analysis for Additional Compounds

7.8.1 Prepare independent standards for PETN as described above for the other compounds. Prepare combined standards for the phthalates and DPA in the range 0.5 to 5.0 ug/mL in isoamyl acetate.

7.8.2 PETN is analyzed the same as the other energetics, but must be run separately from them because it co-elutes with other compounds (e.g. RDX on the DB-1 column).

7.8.3 Phthalate esters may be analyzed using GC with a flame ionization detector; Diphenylamine may be analyzed using GC with a nitrogen-phosphorus detector. Alternatively, they may all be analyzed together using a mass selective detector (MSD). This is the preferred procedure and is described in CAD SOP 69, current version. Chromatographic details are provided in Table 2.

™ Silcosleeve is a trademark of Restek, Corporation, Bellefonte, Pennsylvania

® Silcosteel is a registered trademark of Restek, Corporation, Bellefonte, Pennsylvania

7.9 Instrument Shutdown. The gas chromatograph is shutdown by turning off the detector, column oven, injection port heater, and detector heater. The gases (both carrier and makeup gases) are also turned off. Remove the autosampler vials from the autosampler and dispose of contents in accordance with appropriate waste disposal regulations.

8.0 Quality Control.

8.1 Controls. Blind controls are independently submitted to be analyzed along with the actual samples at a minimum of 5 percent frequency or one per sample extraction batch. Acceptance criteria for the individual analytes in the control are generated by the laboratory quality control coordinator using historical data.

8.2 Check standards. During sample analysis one of the standards is analyzed after every fifth sample to monitor for shifts in the calibration. Acceptance criteria for these check standards is ± 20 percent of the theoretical value.

8.3 Blanks. A solvent blank is analyzed to determine if there are any spurious chromatographic peaks due to impurities in the reagents and/or carrier gas, etc.

8.4 Acceptance Criteria.

8.4.1 Retention time criteria for the primary and confirmation columns are normally set at a 1 sec. absolute window and a 5 percent relative window. Some compounds that elute at the beginning of the run or elute close to each other may have smaller retention time windows

8.4.2 The peak height or area is measured and recorded for each analyte peak. If there is a positive peak on the GC system, confirm the analyte on a column of dissimilar polarity. If there is a match, then report the analyte as a positive result. If any of the peak heights/areas of the peaks of interest are above the range of standards or an interference exists, dilute that sample with isoamyl acetate and rerun. Sample results below the method reporting limit, but above what the method can detect, can be qualified as an estimated value in the report.

9.0 CALCULATIONS.

$$C_W = C * D * V_I$$

where: C_W = Concentration of explosives (µg/sample) in air

C = Concentration of explosives from linear regression curve (µg/mL)

D = Dilution factor (if required)

V_I = Volume of isoamyl acetate used (mL)

10.0 RECORDKEEPING. Record keeping consists of chain-of-custody paperwork where applicable, and recording the analysis in the analyst's notebook. See the latest revision of the DLS SOP on notebook control and use for specifics.

11.0 SAFETY CONSIDERATIONS. Safety glasses should be worn during all phases of this method. Care should be taken when weighing all explosives. Follow guidelines in CAD SOPs for Safety Precautions and Procedures for the Analyses of Energetic Material. Solvents used or consumed in this procedure are hazardous wastes which must be properly disposed of in accordance with division SOPs and APG Reg 200-60.

12.0 REFERENCES.

12.1 *Safety Precautions and Procedures During Operations involving Handling of Neat Energetic Materials in CAD*. DLS CAD SOP 3.1, Aberdeen Proving Ground, Maryland, 1997.

12.2 M. Hable, C. Stern, CPT C. Asowata, and K. Williams. *The Determination of Nitroaromatics and Nitramines in Ground and Drinking Water by Wide-Bore Capillary Gas Chromatography*. J. Chrom. Sci., Vol 29, pp 131-135. 1991.

12.3 TO 13. Determination of Polyaromatic Hydrocarbons (PAHs) in Ambient Air using High Volume Sampling with GC-MS and High Resolution Liquid Chromatography Analysis. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*. EPA, June 1988. (NTIS PB90-127374).

12.4 F. Belkin, R. Bishop, and M. Sheely. Analysis of Explosives in Water by *Capillary Gas Chromatography*. J. Chrom. Sci., Vol 24, pp 532-534. 1985.

APPENDIX A

TABLE 1. GAS CHROMATOGRAPHIC CONDITIONS FOR ENERGETICS ANALYSIS

A. Gas Chromatograph

Hewlett Packard model 5890 or 6890 equipped with a ^{63}Ni ECD and a HP model 7673 Autosampler or equivalent.

B. Temperatures

Injection Port (splitless, 1 µL inj.)	225 °C
Detector Block	250 °C
Oven Temperature Program	
Initial 1 Temp.	80 °C
Rate 1	15 °C/min.
Final 1 Temp.	140 °C for 0 min.
Rate 2	3.0 °C/min.
Final 2 Temp.	170 °C for 0 min
Rate 3	5.0 °C/min.
Final 3 Temp.	200 °C for 2 min.
Equilibration Time	0.50 min

C. Columns

DB-1 fused silica capillary column (J & W Scientific),7 m * 0.53 mm i.d., 1.0 u film thickness. Confirmation is done on a DB-210 or DB-17 Megabore column of the same length.

D. Flow/Pressure

Carrier –Helium @ 2.0 PSIG, ramped to 4.0 PSIG at 14.5 min.
Makeup – Nitrogen @ 40mL/min.

E. Data Collection

Perkin Elmer TotalChrom (current version)

TABLE 2. GAS CHROMATOGRAPHIC CONDITIONS FOR MSD ANALYSIS OF PHTHALATE ESTERS AND DIPHENYLAMINE

A. Gas Chromatograph

Hewlett Packard model 5890 equipped with a HP 5972 Mass Selective Detector and a HP model 7673 Autosampler or equivalent.

B. Temperatures

Injection Port (splitless, 2 µL injection)	275 °C
Transfer Line Interface	250 °C
Oven Temperature Program	
Initial Temp.	40 °C
Rate	30 °C/min.
Final Temp.	250 °C for 3 min.
Equilibration Time	0.50 min

C. Column

RTX-5MS fused silica capillary column (Restek),10 m * 0.25 mm i.d., 0.25 u film thickness.

D. Flow/Pressure

Carrier - Helium with pressure program from 3.0 psi (1 minute) to 7 psi @ 2 psi/minute and hold.

E. Data Collection

Hewlett Packard Enviroquant
Scan from m/z 45 to 300
Quantitate on mass 169 for DPA, mass 149 for the phthalate esters.
Solvent delay time 4.0 minutes

APPENDIX B

STATISTICAL DATA FOR PROCEDURE

(A) Precision & Accuracy Study for the cartridge containing 50g XAD-2 section*:

Compound	% Recovery	Precision (%RSD)
2,6-DNT	88	8.1
2,4-DNT	89	7.2
3,4-DNT**	87	6.2
2,4,6-TNT	91	6.9
RDX	101	5.2
HMX	107	17.7
2-NT	99	13.9
3-NT	103	18.8
4-NT	114	17.2
NB	89	9.1
1,3-DNB	87	7.4
1,3,5-TNB	85	7.9
4A26DNT	93	6.6
2A46DNT	103	5.1
Tetryl	96	11.2
NG	104	16.0

* 130 m^3 volume sampled. Seven spikes at 100ug.
** Surrogate compound. Six spikes were done for this compound.

STATISTICAL DATA FOR PROCEDURE

(B) Precision & Accuracy Study for the cartridge containing two 10g XAD-2 sections*:

Compound	% Recovery	Precision (%RSD)
2,6-DNT	95	18.8
2,4-DNT	93	18.1
3,4-DNT**	100	21.9
2,4,6-TNT	101	14.5
RDX	125	17.3
HMX	118	14.3
2-NT	77	16.9
3-NT	94	5.0
4-NT	95	19.3
NB	85	15.6
1,3-DNB	93	17.7
1,3,5-TNB	94	16.5
4A26DNT	102	15.5
2A46DNT	109	14.3
Tetryl	100	18.3
NG	125	17.8

* 2.6-2.7 m^3 volume sampled. Seven spikes at 15ug.
** Surrogate compound. Four spikes were done for this compound.

APPENDIX I

Harding ESE, Inc. Standard Operating Procedure for MIE DataRAM Real-time PM_{10} Monitor HESE SOP-101

Harding ESE, Inc.
Standard Operating Procedure

90 Digital Dr. **Novato, CA 94949**	**Original Date Issued:** **Type:** **Revision Date:** **Procedure #:** **Total Pages:**	**August 2002** **Revision 0** **HESE SOP-101** **6**

NAME **Standard Operating Procedure for Using Real-time PM_{10} Monitor**

SCOPE The scope of the SOP will detail the operating procedures and the procedures used to perform calibrations on the DataRam Monitor.

REFERENCE MIE Personal DataRam User's Manual

EQUIPMENT MIE DataRam Direct Reading Aerosol Monitor

PROCEDURES

The operating and calibration procedures for the MIE DataRam Direct Reading Aerosol Monitor sampler are as follows.

1. SETUP

It is recommended that each personal DataRAM (RAM) be tested and configured prior to beginning any fieldwork operations. By setting all of the RAMs to the same computer, the internal date, time and logging parameters between the different RAMs will be consistent and the datasets may be compared directly.

1. Load the program onto the computer (current version may be found at: http://www.a-i-i.com/MIE/new_page_4.htm select: *personal* DataRAM *version 1.62 (self-extracting zip file, 585 KB)*).

2. Connect serial cable to available port on computer (note the port # if possible).

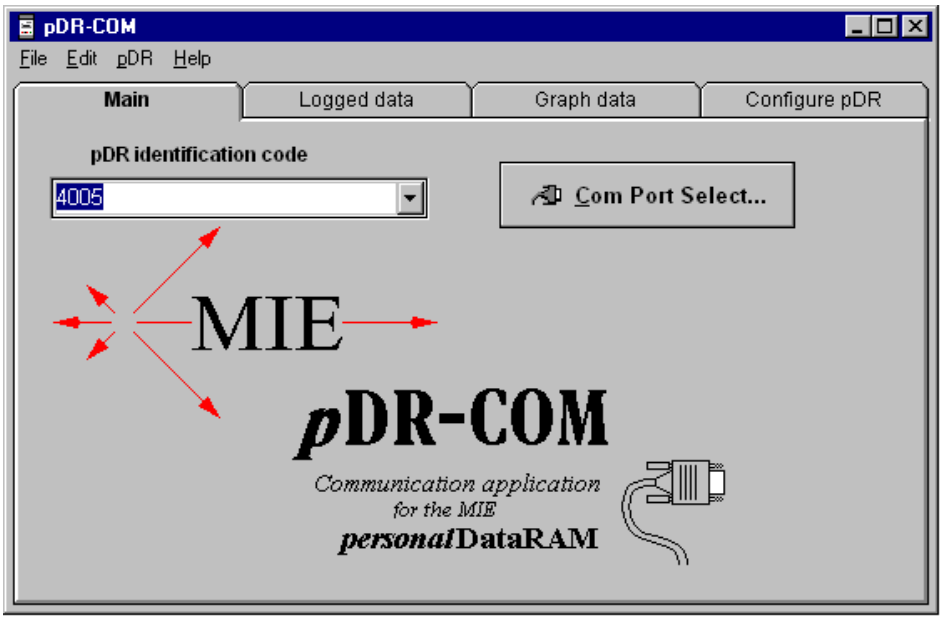
3. Start pDR-COM program.

4. Connect serial cable to port on RAM.

5. Turn on RAM.

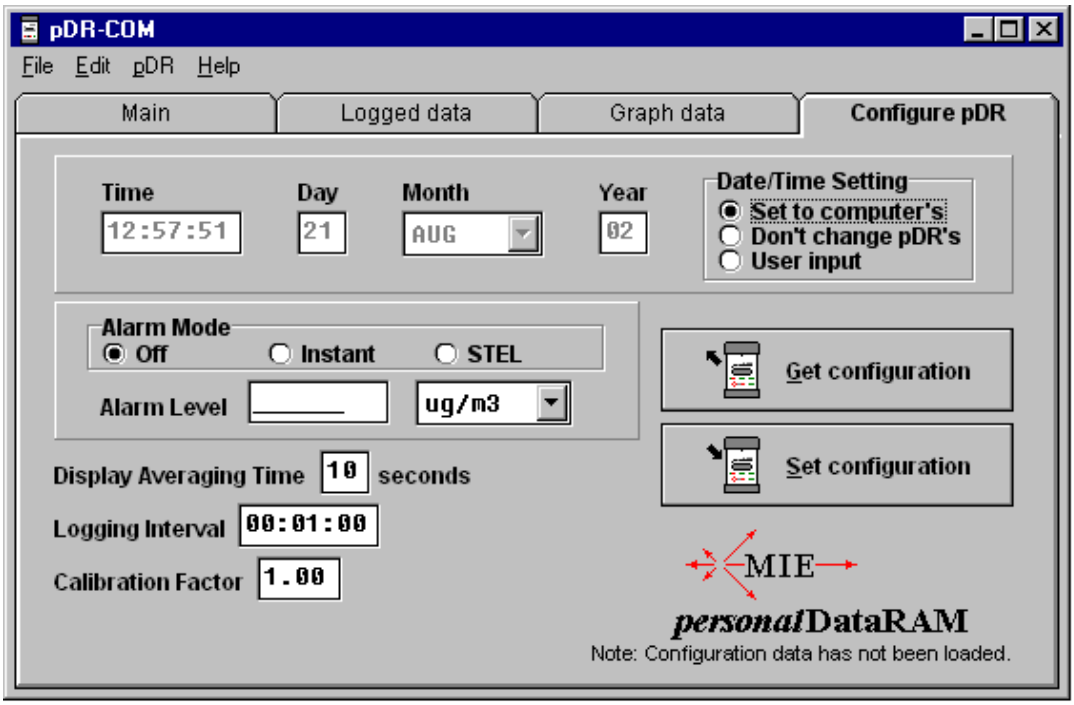
6. Select "NEXT" (button on RAM) repeatedly until the "CONNECT TO PC" screen appears.

The starting screen is shown below:



7. Click on "Com Port Select…" button and select proper serial port (from above). The computer should now be able to find the RAM and will display the pDR (RAM) identification code for that instrument (same as the serial number on the back of the RAM).

8. Once communication is established, select the "Configure pDR" tab. The following screen will be presented.



9. Select “Date/Time Setting” … “Set to computer’s”
   Verify Date and Time shown.
   Verify that all other parameters are as shown.

10. Click on “Set configuration”

11. Return to “Main” tab and go to # 4) above for each subsequent RAM.

2. CALIBRATION

Calibration (zeroing) of the RAMs will be performed daily. This assures that any particulate accumulation on the sensor is eliminated from the reported values. The procedure requires a “Z-Bag”, essentially a zip-lock bag and a hand-pump fitted with a HEPA filter. The RAM is wiped clean, sealed in the bag, calibration is initiated and the bag is kept inflated with 99.9% particulate free air.

1. Wipe RAM to remove any loose particulate.

2. Turn on RAM.

3. Place inside Z-Bag and press “ENTER” to start zeroing.

4. Seal Z-Bag and gently inflate the bag with the hand pump.

5. Maintain inflation until “CALIBRATION: OK” appears on the screen.

6. Remove from Z-Bag. The calibration is now complete.

7. Press the “NEXT” key to initiate logging, BEFORE starting the monitoring run.

3. DAILY AIR MONITORING

Air monitoring with the RAM may be performed either with or without data-logging. The purpose of this testing is to collect as much data as possible; therefore, data-logging is essential to this work. Please note! The default RAM setting is “LOGGING DISABLED”. Logging must be selected every time the RAM is shut off, batteries changed or any time the display goes blank for any reason. The following keystrokes should be followed carefully to assure that data is correctly collected.

Actual keystrokes for daily sampling are as follow:

1.	ON/OFF	"START ZERO: ENTER"
		"GO TO RUN: NEXT"
2.	ENTER	"ZEROING V2.00"
		"CALIBRATION: OK"
3.	NEXT	"START RUN: ENTER"
		"READY: NEXT"
4.	NEXT	"LOGGING DISABLED"

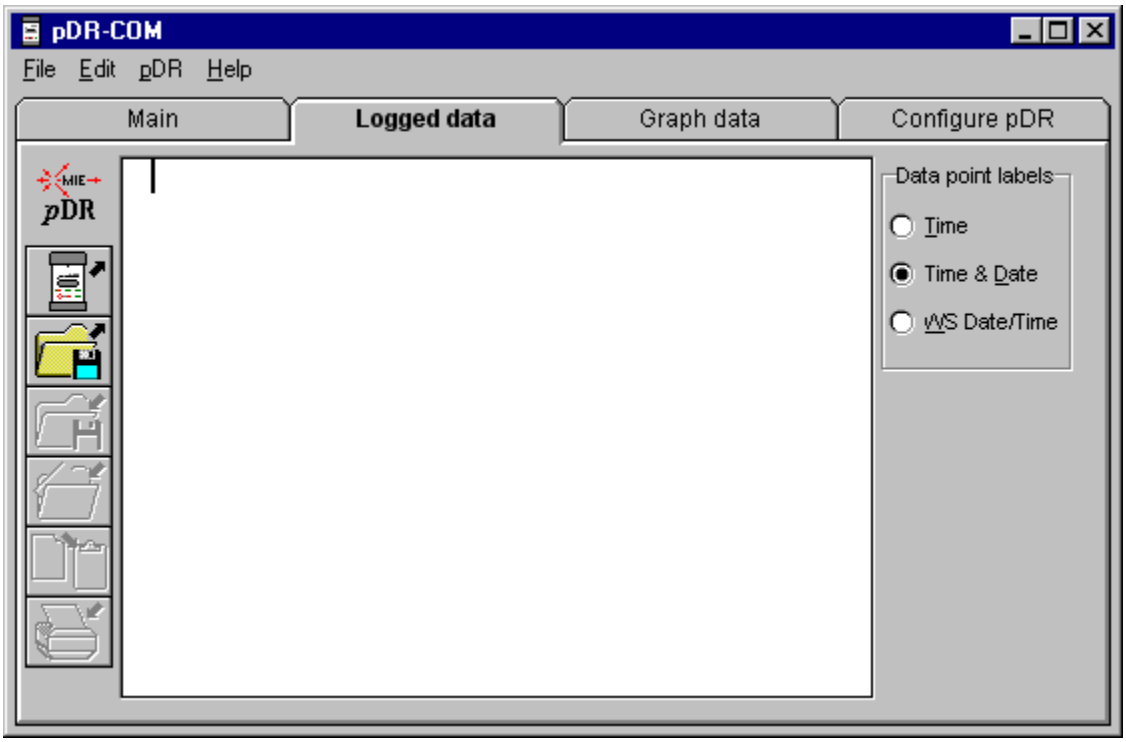
5.	ENTER	"LOG INTRVL ___s" "TAG#: X"
6.	NEXT	"ALARM: OFF
7.	NEXT	"ANALOG OUTPUT:" "DISABLED"
8.	NEXT	"CAL FACTOR: 1.00" "DIS AVG TIME 10s"
9.	NEXT	"BATTERY LEFT 83%" "MEMORY LEFT 98%"
10.	NEXT	"CONNECT TO PC"
11.	NEXT	"START RUN: ENTER" "READY: NEXT"
12.	ENTER	"LOG INTRVL ___s' " TAG#: X" "CONC*0.047 mg/m3" "TWA 0.039 mg/m3"

<u>After sampling is concluded:</u>

13.	EXIT	"TERMINATE RUN?" "Y:ENTER N:EXIT"
14.	ENTER	

4. DOWNLOADING DATA

Downloading should be performed after each day's sampling is completed. The principal steps are the same as the SETUP above. Establish communication with the computer and select the "Logged Data" tab. You should see the following screen.



Click on the  pDR icon and the data will be extracted form the RAM.

Save the file in the default format with an easily identified file name (specific location ID's work well). Do not delete the data tag. Errors downloading have been known to occur. The files will be checked at the conclusion of the project and any missing files will be re-downloaded.

Notes:

Use the plug-in electrical adapter when setting up and downloading the RAMs. This will conserve the battery life considerably and will prevent irretrievable data losses.
Check battery charge after enabling the logging function (during start-up). If the battery shows 50% or less, CHANGE BATTERY! Below 40% the RAM will shut off and stop logging. I use the remaining battery life to preserve the logging memory. Batteries will generally last 16-20 hours (two work shifts) before they are too low. It's easier to change the battery when attached to the power supply and computer than when the RAM is in the field.
When collecting readings (15-minute intervals), record the first value that you see displayed. This will produce more consistent values. Do not try to average several values "mentally". Also, please note the starting and stopping times accurately. There is frequently a "spike" when setting and picking up the instrument.

CADA AIR MONITORING PROGRAM
MINIRAM SAMPLING FIELD DATA FORM

TECHNICIAN:	PROJ #:	DATE: / / 2002	
LOCATION:			
DataRAM #:	Pre Calibration Time:	Post Calibration Time:	
TIME	READING (mg/m^3)	WIND: DIR/SPEED	COMMENTS

❑ Data downloaded to file:_____

APPENDIX J

Harding ESE, Inc. Standard Operating Procedure for GMW Model PS-1 PUF Sampler HESE SOP-102

Harding ESE, Inc.
Standard Operating Procedure

90 Digital Dr.	**Original Date Issued:**	**August 2002**
Novato, CA 94949	**Type:**	**Revision 0**
	Revision Date:	
	Procedure #:	**HESE SOP-102**
	Total Pages:	**9**

NAME **Standard Operating Procedure for Sampling Semi-volatile with GMW Model PS-1 PUF Sampler**

SCOPE The scope of the SOP will detail the sample collection procedures and the procedures used to perform calibrations on the PUF sampler.

REFERENCE EPA Compendium Method TO-13A
EPA Compendium Method TO-9A
GMW Model PS-1 PUF Sampler User's Manual

EQUIPMENT GMW Model PS-1 PUF Sampler

PROCEDURES

The operating and calibration procedures for the GMW Model PS-1 PUF sampler are as follows.

1. CALIBRATION PROCEDURES

The modified high-volume PUF sampler is calibrated using a GMW-40 Calibration: certified against a Roots meter by BGI, Inc. The data contained on the orifice: calibration certificate are used to correlate the PUF sampler flow rates to the: certified transfer standard. The calibration procedures are as follows:

1. The PUF sampler is calibrated with no foam slug or filter in place. The empty glass cartridge must remain in the lower canister to insure a good seal through the sampling module.

2. Install the GMW-40 Calibrator on top of the 4" filter holder by removing the filter retaining ring and the two Teflon gaskets. Fasten the calibrator to the filter holder with the 3 wing nuts.

3. Connect an 8" water manometer to the calibrator using Tygon tubing. Open both ports of the manometer and zero the meniscus of the manometer.

4. Record the ambient temperature (°C) and barometric pressure (mm Hg) on the PUF Calibration Worksheet (Figure 1).

5. Open the ball valve fully on the flow venturi.

6. Zero the magnehelic gauge (if needed) using the zero adjust screw on the face of the gauge.

7. Turn the motor on by tripping the manual switch on the timer. Allow 3 - 5 minutes to warm up the sampler before proceeding.

8. Adjust the voltage variator to obtain a magnehelic gauge reading of 70".

9. Record the 70" reading and the corresponding manometer reading as the first set of calibration data on the PUF Calibration Worksheet (Figure 1).

10. Close the ball valve on the flow venturi slightly to obtain a 60" reading on the magnehelic gauge. Record the gauge reading and the manometer reading on the PUF Calibration Worksheet.

11. Repeat Step 10 for gauge readings of 50", 40", and 30".

12. Readjust the ball valve on the flow venturi and the voltage variator to the fully open position.

13. Turn off the sampler.

14. Correct the orifice manometer reading for standard temperature and pressure using the following equation:

$$X = \sqrt{\Delta H \left(\frac{P_2}{P_{std}}\right)\left(\frac{T_{std}}{T_2}\right)}$$

where:
X = adjusted manometer reading to standard temperature and pressure (inches of water).
ΔH = observed manometer reading (inches of water).
P_2 = ambient atmospheric pressure (mm Hg).
P_{std} = standard pressure (760 mm Hg).
T_2 = ambient temperature (°K), (K = °C + 273).
T_{std} = standard temperature (298°K).

Example: $X = \sqrt{8.05\left(\frac{761.49}{760}\right)\left(\frac{298}{296}\right)}$

15. Calculate the standard flow rate for each corrected manometer reading by the following equation:

$$Q_{std} = \frac{x - b}{M}$$

where: Q_{std} = standard flow rate (ft^3/min), (ft^3/niin = m^3/min x 35.31)
M = slope of flow rate transfer standard calibration curve.
X = corrected manometer reading from Step 14.

B = intercept of flow rate transfer standard calibration curve.

Example: $Q_{std} = \frac{2.85 - (-0.017775)}{9.84}$

= 0.2914 x 35.31

= 10.290 ft^3/min

16. Correct the magnehelic gauge readings to standard temperature and pressure using the following equation:

$$M_{std} = \sqrt{M\left(\frac{P_a}{P_{std}}\right)\left(\frac{T_{std}}{T_a}\right)}$$

where:

M_{std} = adjusted magnehelic reading to standard temperature and pressure (inches of water).

M = observed magnehelic reading (inches of water). ambient atmospheric pressure (mm Hg).

P_a = standard pressure (760 mm Hg).

T_a = ambient temperature (°K),

T_{std} = standard temperature (298°K).

Example: $M_{std} = \sqrt{70\left(\frac{761.49}{760}\right)\left(\frac{298}{296}\right)} = 8.404$

17. Repeat Steps 15 and 16 for each of the 5 calibration points.

18. Calculate a linear regression Q_{std} value (x-axis) versus M_{std} value (y-axis). Retain this regression to calculate the standard flow rate for the field samples.

2. SAMPLE COLLECTION

The PUF samples will be collected using a dual chambered aluminum sampling module consisting of a filter holder support, filter holder, and filter retaining ring to support the 4" diameter filter media. The PUP and XAD-2 media are housed in a glass cartridge, which is placed in the lower canister of the sampling module. Each sample period assembly and disassembly of the 4" filter media and the PUF/XAD-2 media are performed using the following procedure.

1. The samples will be assembled and disassembled inside the air monitoring shelter by air quality personnel wearing clean latex gloves.

2. Place an adequate sheet of aluminum foil on the counter such that the sampling module can be disassembled, the lower canister and filter holder support can be rinsed with reagent grade hexane, and placed on the foil to dry.

3. Attach the filter holder support to the filter holder and place on the foil with the filter holder facing upward. Turn the Petri dish, housing the 4" filter, upside down such that the filter's

nontextured side is facing upward in the cover of the Petri dish. Open the Petri dish keeping the filter in the same upside down position. Carefully place the filter (textured side up) on the top of the Teflon filter gasket on the faceplate of the filter holder by turning the cover of the Petri dish right side up. Use the top Teflon filter gasket to center the filter on the filter holder. (This technique will be used instead of using forceps because the filter media is very soft and easily torn by its own weight against the forceps tips). Place the top Teflon filter gasket on the filter and place the retaining ring on top of the filter. Place the triangular shaped sample saver on the retainer ring and clamp the filter assembly together with the three wing nuts.

4. Place the filter holder assembly upside down on the foil such that the filter holder support is facing upward. Remove the glass cartridge containing the PUF/XAD-2 media from the shipping container and place the open end of the glass cartridge inside the filter holder support. Place the lower canister over the glass cartridge and attach the lower canister to the filter holder. Place a small piece of aluminum foil over the opening of the canister to prevent foreign matter from entering the sample module.

5. Insure that all module connections are tightly assembled.

6. With the sampler off, attach the sample module to the flow venturi on the PS-I sampler by removing the aluminum foil cap on the module and inserting the male connector into the compression fitting on the sampler.

7. Remove the sample saver from the 4” filter holder. Adjust the magnehelic zero reading (if needed) by adjusting the screw on the face of e gauge. Fully open the flow control valve and turn the voltage variator adjustment screw fully counterclockwise. Turn on the sampler, allow 2 - 3 minutes for the sampler to stabilize and record the magnehelic reading and the initial elapsed timer reading on the PUP Data Sheet. Allow the sampler to run 10 hours.

8. At the end of the sample run (10 hours) and before the sampler is turned off, record the magnehelic gauge reading.

9. Turn off the sampler. Record the final elapsed time on the PUP Data Sheet. Obtain the average ambient temperature and barometric pressure readings for the 10-hour sample time from the onsite meteorological station and record on the PUF Data Sheet.

10. Remove the sampling module from the PS-i sampler using the following procedure. Place the sample saver on the 4” filter holder. Remove the sampling module from the flow venturi and cap the end with aluminum foil. Return the sampling module to the air quality shelter for retrieval of the 4” filter and PUF/XAD-2 cartridge.

11. The sample retrieval procedure is the reverse of the assembly. Place a clean sheet of aluminum foil on the counter. Detach the lower canister from the filter holder support, remove the glass cartridge and prepare for shipment the same way the cartridge was received from the laboratory. Place the glass cartridge assembly in the refrigerator until packaged for shipping to the laboratory. Place the filter holder support on the aluminum foil with the 4” filter facing upward. Remove the sample saver from the top of the filter-retaining ring. Remove the filter retaining ring and the top Teflon gasket from the 4” filter. Using the Teflon gasket, carefully slide the filter into the Petri dish and package the Petri dish for return to the laboratory the same way the sample was received.

12. All samples will be packaged in an ice chest with blue ice for return shipment to the laboratory. Complete the Chain-of-Custody form, include a copy with the samples and ship to the laboratory via express carrier the next business day.

13. Calculate the average sample flow rate using the equations and examples provided on the PUF Sampler Data Form as follows:

    a. Magnehelic Start = magnehelic gauge reading at the start of sampling
       = 55.0 inches H_2O

    b. Magnehelic Stop = magnehelic gauge reading at the end of sampling
       = 53.0 inches H_2O

    c. Magnehelic Average = average magnehelic gauge reading for the sampling period.
       = 55.0 **+** 53.0/2
       = 54.0 inches H_20

    d. Standard Flowrate = $$\sqrt{\frac{M_g\, avg\left(\frac{P_{act}}{P_{std}}\right)\left(\frac{T_{std}}{T_{ac}}\right) - B}{M}}$$

    where:
    $M_g\ avg.$ = magnehelic average
    P_{act} = actual pressure during sample period
    T_{act} = actual temperature during sample period
    M = slope of the orifice standard versus magnehelic standard flow from the Calibration data sheet
    B = y-intercept of the orifice standard versus magnehelic standard flow from the calibration data sheet

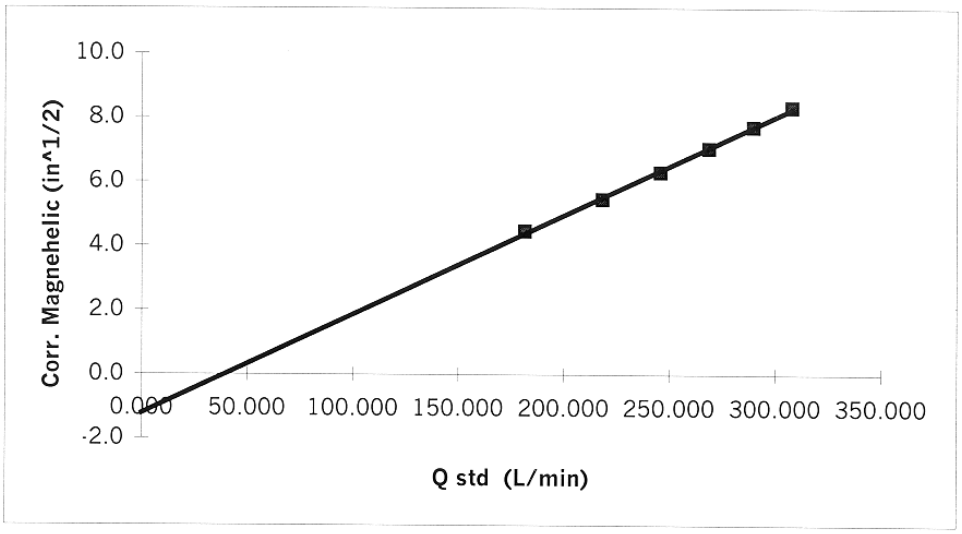
Figure 1: PUF Calibration Worksheet

PUF SAMPLER CALIBRATION WORKSHEET

Date:	3/22/2001	Orifice S/N:	2C
Location:	Brunswick	Orifice Slope:	10.02
Site:	Georgia Coastal College	Orifice Intercept:	0.015
Sampler #:	114396 / Motor 1741	Last Calibrated:	3/2/2001
Operator:	C.Nagle	Orifice Calibrated by:	BGI
Ambient Pres. (mmHg):	768.00	Std. Pres. (mmHg):	760.00
Ambient Temp. (K):	304.18	Std. Temp. (K):	298.15

Valve Position	Manometer Pressure Drop in	Corrected Pressure in^1/2	Magnehelic in	Flow Rate Q std L/min	Corrected Magnehelic in ^1/2
1	9.70	3.10	70.0	307.875	8.3
2	8.60	2.92	60.0	289.807	7.7
3	7.40	2.71	50.0	268.723	7.0
4	6.20	2.48	40.0	245.847	6.3
5	4.90	2.20	30.0	218.395	5.5
6	3.40	1.84	20.0	181.676	4.5

SLOPE:	**0.0308**
INTERCEPT:	**-1.225**
CORRELATION:	**0.998**



Comments: New Motor# 1741

Figure 2: PE Photovac Voyager Portable Gas Chromatograph Field Calibration Sheet

PE PHOTOVAC VOYAGER PORTABLE GAS CHROMATOGRAPH
FIELD CALIBRATION SHEET

LOG FOR WEEK OF: _____ VOYAGER SERIAL NUMBER: _____ PROJECT LOCATION: _____

Multi-Point Calibration Date: _____ *Successful Cal (Y/N)? ____ Standards Used:_____ Initial:_____

Daily Recalibrations

Date	Std. Concentration	*Update Successful?	Observed Blank Value	Comments

Continuing Calibration Checks

Date	Expected Value	Observed Value	Percent Difference	Comments

*A successful calibration means that no fault conditions were displayed by Voyager upon completion of the calibration.

Figure 3: PE Photovac Voyager Portable Gas Chromatograph Field Maintenance Log

PE PHOTOVAC VOYAGER PORTABLE GAS CHROMATOGRAPH
FIELD MAINTENANCE LOG

Voyager Serial Number: _____

	Maintenance Activity Performed								
Date	Refill Internal Cylinder	Replace Inlet Filter	Replace UV Lamp	Clean UV Lamp (Window)	Replace Injection Port Septum	Recharge/Replace Battery Pack	Flush Column	Comments/Other Maintenance	Analyst

Figure 4: PE Photovac Voyager Portable Gas Chromatograph
Field Sampling and Analytical Log

PE PHOTOVAC VOYAGER PORTABLE GAS CHROMATOGRAPH
FIELD SAMPLING AND ANALYTICAL LOG

Voyager Serial Number:_____ Site Name: _____ Analyst: _____

Meteorological Conditions Including Wind Direction: _____

Date	Time	TAG Identifier Used and Specific Location Sampled	Benzene Result

APPENDIX K

Harding ESE, Inc. Standard Operating Procedure for GMW Model 2000H High-Volume Sampler HESE SOP-103

Harding ESE, Inc.
Standard Operating Procedure

90 Digital Dr.	**Original Date Issued:**	**August 2002**
Novato, CA 94949	**Type:**	**Revision 0**
	Revision Date:	
	Procedure #:	**HESE SOP-103**
	Total Pages:	**10**

NAME **Standard Operating Procedure for Sampling Total Suspended Particulate with GMW Model 2000H High-Volume Sampler**

SCOPE The scope of the SOP will detail the operating procedures and the procedures used to perform calibrations on GMW Model 2000H High-Volume Sampler.

REFERENCE EPA Compendium Method IO-2.1
GMW Model 2000H High-Volume Sampler User's Manual
Anderson Model GFH360 Volumetric Flow Controller User's Manual

EQUIPMENT GMW Model 2000H High-Volume Sampler.
Anderson Model GFH360 Volumetric Flow Controller

PROCEDURES

The operating and calibration procedures for the GMW Model 2000H High-Volume Sampler are as follows.

1. EQUIPMENT CALIBRATION

Before the TSP sampling can be initiated, the majority of its components must be calibrated. Routine equipment calibrations are necessary, as well as some unscheduled calibrations (e.g., after equipment failure or when audit values are not within limits. The following subsections detail calibration procedures to be followed by field and/or laboratory technicians, indicate calibrations to be performed by manufacturers or other sources, and specify the frequency of calibrations.

1.1 Analytical Balance

The analytical balance is calibrated daily or each time the balance is moved or subjected to rough handling, or during routine operations when a standard weight cannot be weighed within ±0.5 milligram (mg) of its stated weight. Using Class "S" weights, select three to five weights covering the normal weight range for filters. Weigh the selected weights. If at any time one or more of the weights cannot be measured within ±0.5 mg of its stated value, have the balance recalibrated. Record weight check results in the weight room logbook.

1.2 Relative Humidity Indicator

The hygrothermograph is used to continuously record relative humidity (RH) in the weight room. The hygrothermograph is checked every 6 months against a Rotronics Hygroskop RH transfer standard. If the difference between the RH indicator and the corresponding psychrometer readings is within ±6 percent, continue to use the RH indicator. If the readings disagree by more than ±6 percent, calibrate or replace the indicator. Record RH indicator check results in the weight room logbook.

1.3 Elapsed Time Meters

Elapsed time meters will be calibrated by Harding ESE technicians before and after sampling to an accurate chronometer.

Record results of these checks on the Elapsed Time Indicator Calibration Sheet (Figure 1). If there is a gain or loss of more than 2 minutes in a 24-hour period, replace the meter.

1.4 Variable Resistance Calibrator

A variable resistance orifice calibrator (VRC) will be calibrated against a National Institute of Standards and Technology (NIST) traceable standard upon receipt and at 1-year intervals thereafter.

1.5 TSP Sampler Motors

Sampler motors will be calibrated before initial use, before and after replacement of motor brushes, any time the flow-rate measuring device has to be replaced or repaired, and/or any time the 1-point audit check deviates more than ± 7 percent from the calibration curve.

When the orifice calibration unit is used to calibrate a sampler, a relationship is determined between the sampler volumetric flow rate (Q_a) the actual temperature (T_a), and the ratio of the sampler stagnation pressure (P_1) downstream of the filter to the actual pressure (P_a) and the variable resistance orifice flow rate (Q_{act}) corrected to actual P_a and T_a.

The following steps will be followed in the calibration of the sampler motors:

1. Assemble the STP sampler with a clean quartz filter and leave in place throughout the calibration procedure.

2. Install the top-loading adapter and variable resistance orifice calibrator on the respective sampler. Attach a 24-inch water manometer to the pressure tap port of the orifice calibrator to monitor ΔH total to determine Q_{act} from the orifice calibration worksheet. The same 24-inch water manometer will be used to determine the stagnation pressure (ΔP_f) from the tap on the respective sampler.

3. Adjust the orifice fully counterclockwise to allow maximum flow through the orifice.

4. Turn the motor on and allow at least 5 minutes for the motor to stabilize. Record the orifice ΔH total then attach the manometer to the samplers stagnation tap and record ΔP_f. Document both manometer readings on the VFC Sampler Calibration Data Sheet (Figure 2).

5. Record on the calibration data worksheet (Figure 2) the actual barometric pressure in [millimeters of mercury (mm Hg)] and actual temperature in °C.

6. Adjust the orifice to obtain two additional flow rates between 1.02 and 1.13 m^3/min. Record the orifice ΔH total and the sampler's stagnation tap ΔP_f for each flow rate.

7. Determine the critical orifice actual flow rates corrected to the barometric pressure and temperature recorded in Step 5. The critical orifice flow rates are determined using the following equation:

$$Q_{act}\ (orifice) = \left\{\left[\Delta H\left(T_a / P_a\right)\right]^{1/2} - b\right\}\left(\frac{1}{m}\right) \quad (1)$$

where: Q_{act} *(orifice)* = actual volumetric flow rate as indicated by the critical orifice, m^3/min;
ΔH = pressure drop across the orifice in inches of water;
T_a = ambient temperature determined from Step 5, K (K = °C + 273);
P_a = ambient barometric pressure recorded in Step 5 mm Hg;
b = intercept of the critical orifice calibration relationship; and
m = slope of the critical orifice calibration relationship.

8. When calibrating the Andersen STP sampler, the terminology is as follows:

where: P_a = actual pressure,
T_a = actual temperature,
P_f = pressure differential across the filter (taken from stagnation tap),
ΔH *orifice* = total pressure differential from the orifice calibrator, and $P_o/P_s = (P_a - P_f)/P_a = P_o/P_a$

The ratio P_o/P_a with the T_a values is used to determine the sampler flow rate taken from the look-up table for the Andersen VFC sampler.

If any of the three lookup points of the calibration do not fall within ±4 percent of the known flow rate from the VRC or if at least two of the three points are not between 39 and 60 cmf, check for leaks, perform any required maintenance and repeat the calibration until these conditions are met. The percent deviation is calculated by taking the sampler's flow rate (X_i) and the orifice calibration curve flow rate (Y_i) for the same flow reading.

$$Percent\ deviation = \frac{X_i - Y_i}{Y_i} \quad x \quad 100 \quad (2)$$

9. Remove the variable resistance orifice and restore the equipment to sampling readiness.

2. FILTER SELECTION AND PREPARATION

Gelman Type A/E glass fiber filters will be used for the TSP samplers. The following subsections detail filter selection and preparation procedures to be followed throughout the monitoring period.

2.1 Filter Selection

Use only filters having a collection efficiency of at least 99 percent for particles of 0.3-µm diameter, as measured by the DOP test [American Society for Testing and Materials (ASTM-D2986-71)]. The manufacturer is required to furnish proof of the collection efficiency of a batch of new filters when purchased. Inspect each filter with the aid of a light table. Discard filters with pinholes and other defects such as tears, creases, or lumps. Remove loose particles with a soft brush.

2.2 Filter Identification and Equilibration

Assign a serial number to each filter. Stamp this number on two diagonally opposite corners, one stamp on each side of the filter. To minimize errors in measuring for weight, allow the filters to equilibrate in the weight room for 24 hours prior to weighing. The weight room must have an average temperature between 20 and 25□C (varying not more than ±3°C) and an RH of less than 50 percent (varying not more than ±5 percent). If the temperature and RH conditions are not within limits, DO NOT WEIGH FILTERS.

2.3 Filter Weighting

Process clean filters in lots. Before weighing the first filter, perform a balance check by weighing a standard Class "S" weight of between 3 and 5 grams (g). Record actual and measured weights and the date in the weight room logbook and initial the record. If the actual and measured values differ by more than ±0.5 mg (0.0005 g), report the discrepancy to the laboratory supervisor before proceeding.

If the actual and measured values agree to within ±0.5 mg, record the weight of each filter to the nearest milligram. Record the tare weight and serial number of each filter in the filter logbook. Do not fold or crease clean filters prior to weighing or use.

2.4 Filter Handling

A quantity of filters sufficient for at least a 3-month period for each sampler will be numbered and weighed at one time. Pack the filters in their original container or a box of similar size such that each filter is separated by a sheet of 8 1/2- x 11-inch tracing paper. Stack the filters in the

box in numerical order so that the QST field engineer will use the proper filter first. The technician must account for every filter issued. This is a vital part of the chain of custody of data. In addition to filters, field engineers will be supplied with filter holders to protect the filters during transport and subsequent analysis.

3. SAMPLING PROCEDURES

The GMW Model 2000H STP high-volume sampler equipped with an Andersen Model GFH360 Volumetric Flow Controller (VFC) will be used to collect STP samples at all the integrated sampling sites. Installation of the samplers will be in accordance with the manufacturers instrument manual.

The sample flow rate in the Andersen Model GUV360 VFC is controlled and maintained by a VFC. The VFC system consists of three distinct portions: the filter holder with stagnation tap, VFC, and a blower/motor. The VFC is a dimensional venturi device used to control gas flow. Plow control is accomplished by accelerating the airflow through the venturi. At some point in the flow stream, the air velocity will equal the acoustic velocity, achieving critical flow. This choking condition is a distinctive characteristic of the VFC. The VFC uses this principle of choked flow to maintain a constant actual flow rate of 40 cfm over a sample period.

Before installing a new filter, clean the rubber gasket on the filter holder to remove any filter fibers or dust. Use a clean, dry cloth or paint brush to clean the area surrounding the filter holder.

The following instrumentation and time-integrated air monitoring techniques will be used to collect air samples for analysis of STP.

1. Record the project number, motor number, filter number, station number, date of sample collection, and time started [use military time (e.g., 2400 hours or 0001 hours)] on the TSP Field Envelope (Figure 3).

2. Carefully remove clean filter from box and place in filter holder. If the filter is torn or broken, discard it, record disposition, and use the next filter in the box.

3. Center the holder on the screen so that when the faceplate is in position, the gasket will form an airtight seal on the outer edge of the holder. When aligned correctly, the edges of the filter should be parallel both to the edges of the screen below it and to the faceplate gasket above it.

4. Once the filter holder is in place, tighten the four wing nuts so that the gasket is airtight against the filter holder. Tighten the wing nuts evenly at diagonals, avoiding excessive tightening to minimize the filter's tendency to stick to the gasket and to guard against damage to the gasket.

5. Turn the motor on and allow it to warm up for approximately 5 minutes. Attach a 24-inch water manometer to the stagnation pressure tap.

6. After warm-up, record the total manometer reading (Pf1) on the TSP Field Envelope.

7. Turn the motor off and set the timer so that the sampler will begin sampling at the appropriate time of the day.

8. Enter the initial elapsed time reading on the TSP Field Envelope.

9. Close the sampler inlet and complete the seasonal operating conditions data on the TSP Field Envelope.

10. Note on the envelope any anomalies in ambient conditions (e.g., high winds, construction activity, dust storms, forest fires).

Use the following procedures to remove a collected sample:

1. Turn the sampler motor on and allow the motor to stabilize for approximately 5 minutes.

2. Attach the 24-inch manometer to the sampler stagnation pressure tap and record the Pf2 differential pressure.

3. Turn the sampler motor off.

4. Record the final elapsed time on the TSP Field Envelope.

5. Without touching the exposed area, gently remove the exposed filter and filter holder.

6. Remove the filter from the filter holder and fold the exposed area together lengthwise.

7. Calculate the average sample flow rate using the equations and examples provided on the TSP Field Envelope as follows:

    a. PP_1 = manometer right side reading + left side reading at filter installation
    = 14.50 + 15.0 = 29.50 inches H_20.
    b. PF_2 = manometer right side reading + left side reading = 14.50 + 14.50
    = 29.0 inches H_20.
    c. PFa = average flow for the respective sampling period (mm Hg)
    = [PF_1 + PF_2/2] x 1.8663 = [29.50 + 29.0/2] x 1.8663
    = [58.5/2] x 1.8663 = [29.25] x 1.8663 = 54.59 mm Hg.
    where: 1.8663 = conversion factor for inches of H_20 to mm Hg.
    d. Po/Ps = pressure ratio across the filter based on seasonal barometric pressure
    = 1 - (Pfa-Ps) = 1 - (54.59-751.65) = 1 - 0.073 = 0.927.
    e. SQa = seasonal flow rate derived from the look-up table for the specific VFC based on the P0/Ps ratio and seasonal temperature
    = Po/Ps = 0.927 = Ts = 41.6°F or 6.33°C = 41.6 cfm or 1.178.

8. Place the respective filter in the envelope for shipment to the laboratory.

4.0 ROUTINE CHECKS

The following checks should be made when removing an exposed filter.

1 Check the filter for signs of air leakage. Leakage may result from (1) a worn faceplate

gasket, (2) an improperly installed gasket, or (3) over tightening of the faceplate gasket, which can cut the filter along the gasket interface.

2 Any time a leak is observed, indicate the problem on the envelope and take corrective action before starting another sampling period. Corrective action would be to replace the gasket, take more care in installing the filter, or apply more caution in tightening the gasket. Generally, a gasket deteriorates slowly (faster in summer months), and the operator can determine well in advance (by an increasing fuzziness of the sample outline) when to change the gasket before a total failure.

3 Visually inspect the gasket for glass fibers from the previous filter. The presence of glass fibers is a sign of over tightening the gasket. Tighten the gasket just enough to prevent leakage.

4 Check the exposed filter for physical damage that may have occurred during or after sampling. Physical damage to the filter after sample collection does not always invalidate the sample. For example, accidentally tearing off a corner while removing the filter does not invalidate the sample if all pieces of the filter are included in the folder. However, any loss of sample due to leakages during the sampling period or to the loss of loose particulates from the filter after sampling (e.g., loss of particulates when folding the filter) may invalidate the sample. Therefore, care should be taken to prevent these occurrences. Mark all suspect samples on the envelope and forward to the laboratory. Insects (such as gnats) loosely attached to the filter should be removed by the laboratory technician with a pin or with Teflon□-tipped tweezers. If insects are embedded in the particulates, note on the folder, but do not try to remove them.

5 The appearance of the particulates should be checked. Any changes from the normal color may indicate new emission sources, forest fires, or construction activity, etc. in the area. The change should be noted on the filter folder along with any other obvious reasons for the change.

Figure 1: Elapsed Time Indicator Calibration Sheet

ELAPSED TIME INDICATOR CALIBRATION SHEET

(NATIONAL BUREAU OF STANDARDS TIME-- TEL. 1/303/499-7111)

Elapsed Time Indicator Number	Calibration Started		Calibration Stopped		E.T.I. Initial Reading	E.T.I. Final Reading	Percent Accuracy	Calibrated by (Signature)
	Date	Time	Date	Time				

Figure 2: VFC Sampler Calibration Data Sheet

VFC SAMPLER CALIBRATION DATA SHEET

Station location_____ Date_____ Time_____

Sampler Model_____ S/N_____ Operator_____

Pa_____mmHg. Ta_____ C _____K Unusual Conditions_____

Orifice S/N_____ Orifice Calibration Date_____

Orifice Calibration Relationship: m =_____ b =_____ r =_____

Plate No.	Orifice H20 (in.)	Sidetap Pstg [H20(L+R) x 1.8663] (mmHg.)	Po [Pa-Pstg] (mmHg.)	Po/Pa	$[(Po/Pa)Ta]^{1/2}$	Qa (orifice) flow rate (m3/min)
Operational Conditions					Flow rate = _____	

$Qa(Orif) = 1/m\{[(\Delta H20)(Ta/Pa)]^{1/2}-b\}$

$$\% \text{ Difference} = \frac{Qa(samp)-Qa(Orif)}{Qa(Orif)} \times 100$$

[] Lookup table Validated
% Difference < 4

[] New calibration relationship
$x = Qa(Orif)$; $y = \{(Po/Pa)Ta\}^{1/2}$

Qa (Orifice)	Qa (Sampler) (Lookup Table)	% Difference

m = _____ b = _____ r = _____

For sampler flow rate: $Qa = \{[(Po/Pa)Ta]^{1/2}-b\}/m$

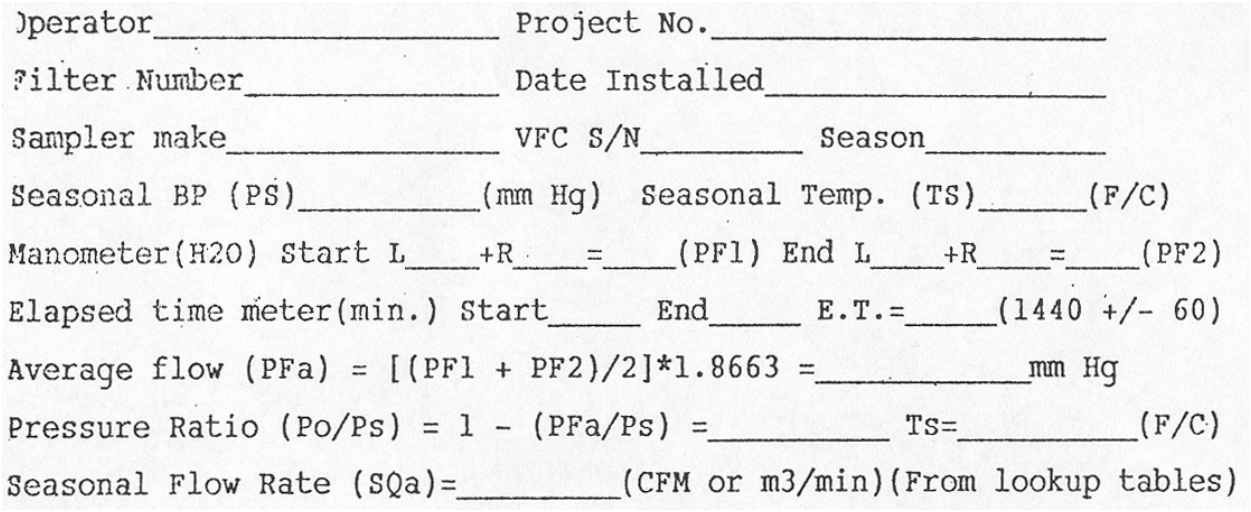
Operational flow rate _____ m3/min

NOTES:_____

_____

_____

Figure 3. STP Field Envelope



)perator_____ Project No._____

Filter Number_____ Date Installed_____

Sampler make_____ VFC S/N_____ Season_____

Seasonal BP (PS)_____(mm Hg) Seasonal Temp. (TS)_____(F/C)

Manometer(H20) Start L____+R____=____(PF1) End L____+R____=____(PF2)

Elapsed time meter(min.) Start_____ End_____ E.T.=_____(1440 +/- 60)

Average flow (PFa) = [(PF1 + PF2)/2]*1.8663 =_____mm Hg

Pressure Ratio (Po/Ps) = 1 - (PFa/Ps) =_____ Ts=_____(F/C)

Seasonal Flow Rate (SQa)=_____(CFM or m3/min)(From lookup tables)

APPENDIX L

Harding ESE, Inc. Standard Operating Procedure for AirMetrics MiniVol Portable Air Sampler HESE SOP-104

Harding ESE, Inc.
Standard Operating Procedure

90 Digital Dr.	**Original Date Issued:**	**August 2002**
Novato, CA 94949	**Type:**	**Revision 0**
	Revision Date:	
	Procedure #:	**HESE SOP-104**
	Total Pages:	**7**

NAME **Standard Operating Procedure for AirMetrics MiniVol Portable Sampler**

SCOPE The scope of the SOP will detail the operating procedures and the procedures used to perform calibrations on AirMetrics MiniVol Portable Air Sampler

REFERENCE EPA Compendium Method IO-2.1
AirMetrics MiniVol Portable Air Sampler User's Manual

EQUIPMENT AirMetrics MiniVol Portable Air Sampler

INTRODUCTION MiniVol

Although accurate and precise, the monitors are bulky and immobile, causing difficulty in studying remote sites without a power source. The EPA and the Lane Regional Air Pollution Authority addressed the need for portable sampling devices with the production of the AirMetrics MiniVol Portable Air Samplers. These ambient air sampling machines are designed to collect either PM_{10} or $PM_{2.5}$, depending on the attached impactor and filter head, and can also be used to measure non-reactive gases (CO & NO_X).

The MiniVols are not federal reference method (FRM) samplers, though their results closely approximate FRM air quality data. The MiniVol is a lightweight battery-operated sampler, which allows it to be used in remote areas. The low cost of the sampler allows for a network of MiniVols to be easily set up at a lower cost than a large machine network. Other features include a 7-day programmable timer, an elapsed time totalizer, rechargeable battery packs, and all-weather PVC construction.

The procedures that lie herein are to be used by the operator responsible for the collection of the PM10 and PM2.5 filters. Refer to the manufacturer's operation manual for integrated gas sampling, hardware descriptions, and maintenance details.

2. FILTER HANDLING AND PRESAMPLING PREPARATION

2.1 Filter Handling

The current filter media approved by the U.S. EPA for sampling particulate matter is a 2µm pore-size Teflon material in a white 47mm diameter casing. Filters will be provided by the processing laboratory, and should be returned there for analysis with a copy of the filter's data

form. Touching the individual filters could void the sample and physically handling should be avoided. Storage of the filters should be in a dry, controlled environment. There are no control limits on humidity and temperature for unexposed filters, but exposed filters should be kept below ambient temperature. A cooler type container loaded with “blue ice” and transported in an air-conditioned vehicle is recommended.

2.2 Connecting the Sampler Body and the Battery Pack

When connecting the sampler body and battery pack, note that the body’s pins are unevenly spaced and can only fit onto the battery pack in one way. The pin closest to a latch on the sampler body inserts into the odd-colored receptacle on the battery pack.

2.3 Sample Date and Time Programming

The Programmable Timer can be set to run for up to six cycles within 24 hours, in addition to separate time periods on different days within one week. The real-time clock must first be set to the correct day and time in order for sampling programming to be set. To set the day, hold down the “Clock” button until the correct day appears on the display. The time can be set by holding down the “Clock” button while depressing the “Hour” and “Min” buttons until the correct time is set.

To set the timer to sample, press the “Prog” button once to display the “Prog 1_{ON}” setting. Use the “Hour” and “Min” buttons to set the time of day for sampling to begin. Press the “Week” button until the correct sampling day appears on the display. Pressing the “Prog” button again will show the “Prog 1_{OFF}” setting. In this setting, program the monitor to stop sampling in the same manner as programming the monitor to turn on. Set the monitor to automatically run by pressing the “ON/AUTO/OFF” button until “AUTO” is selected.

2.3 Equipment Calibration

Calibration Apparatus A MiniFlo flow rate transfer standard device is used as the flow rate reference to calibrate the sampler's rotameter-. To be valid, the MiniFlo transfer standard must have been calibrated against a primary standard traceable to the NIST within the last year. A calibrated digital manometer, Magnehelic® gage, or water manometer is required to measure the pressure drop across the MiniFlo orifice element. The actual ambient temperature and barometric pressure must also be measured or obtained locally.

Precalibration System Check Procedures for the precalibration system check are as follows:

1. Place a filter into the MiniVol sampler filter holder and attach the filter holder assembly to the sampler. (Filters used for flow rate calibrations should not be used for subsequent sampling.)

2. Turn on the sampler and allow it to warm up to full operating temperature (at least 2 minutes).

3. While the sampler is running, depress and hold the reset button. (This allows the sampler to continue to run without tripping the low flow shut-off circuit.) Close off the inlet using the palm of your hand. Observe the rotameter, if there are no leaks the rotameter should drop to zero and remain there.

4. Verify that the transfer standard calibration equation is current and traceable to an acceptable primary standard.

5. Adjust manometer or Magnehelic® gage to read zero, and connect to the pressure tap on MiniFlo transfer standard. Note: Magnehelic® gage is sensitive to the position it is in when zeroed (vertical or horizontal). Maintain this position when taking readings.

Rotameter Calibration. Procedures for calibrating the sampler rotameter are as follows:

1. Install the MiniFlo transfer standard on the inlet tube of the MinVol sampler filter holder.

2. Turn on the sampler and allow it to warm up to normal operating temperature (at least 2 minutes). The transfer standard must also equilibrate before proceeding with the calibration.
6. Read and record the following parameters:
   - Ambient temperature (T_{act}), °K
   - Barometric pressure (P_{act}), mm Hg

4. Adjust the flow control until the rotameter displays 6.5 L/min.

5. Read and record the following parameters:
   - Transfer standard pressure drop (H), inches of water
   - Sampler rotameter indication (Qind), liters per minute

6. Repeat steps 4 and 5 for rotameter settings representing flow rates of 6.0, 5.5, 5.0, 4.5, and 4.0 L/min.

Calibration Calculations. Gather together all the calibration data, including the transfer standard calibration information and the MiniVol sampler calibration data sheet. The following calibration calculation procedures are recommended.

Note: These calculations should be done at the time of the calibration, rather than later. This approach will allow additional calibration points to be taken if questions arise about the data that has already been obtained.

Calculate Qact for each calibration point as determined by the transfer standard calibration equation (**Eq.A** from MiniFlo calibration certificate).

Calculate and record the standard corrections ($Q_{@std}$) for each calibration point as:

Eq. 1

$$Q_{@std} = Q_{act} \times \sqrt{\frac{T_{std}}{T_{act}} \frac{P_{act}}{P_{std}}}$$

where:
$Q_{@std}$ = standard correction flow rate, L/min
Q_{act} = flow rate at ambient conditions (transfer standard), L/min

T_{act} = ambient temperature, °K
P_{act} = ambient barometric pressure, mm Hg
T_{std} = standard temperature, 298 °K
P_{std} = standard pressure, 760 mm Hg.

On a sheet of graph paper or computer spreadsheet plot the calculated standard correction flow rates, $Q_{@std}$ (y-axis) versus the corresponding rotameter indicated flow rate, Q_{ind} (x-axis). Using a programmable calculator or a spreadsheet and the following model, calculate the linear regression slope (m_{vol}), intercept (b_{vol}), and correlation coefficient (r) to obtain the MiniVol™ sampler flow rate calibration relationship.

For the regression model y=mx+b

Eq. 3

$$let\ y = Q_{@std} = Q_{act}\sqrt{\frac{T_{std}}{T_{act}}\frac{P_{act}}{P_{std}}}\ \ and\ x = Q_{ind}$$

So that the model is given by:

Eq. 4

$$Q_{@std} = m_{vol}\,Q_{ind} + b_{vol}$$

A six-point calibration should yield a regression equation with a correlation coefficient of r > 0.990, with no point deviating more than 2% from the value predicted by the regression equation.

Note: For actual sample periods, the sampler's average actual operational flow rate Qact is calculated from the calibration slope and intercept using

Eq. 5

$$Q_{act} = \left(m_{vol}\,Q_{ind} + b_{vol}\right) \times \sqrt{\frac{T_{act}}{T_{std}}\frac{P_{std}}{P_{act}}}$$

where
Q_{act} = sampler flow rate at ambient conditions, actual L/min
Q_{ind} = rotameter response, L/min
T_{act} = ambient temperature, °K
P_{act} = ambient barometric pressure, mm Hg
T_{std} = standard temperature, 298 °K
P_{std} = standard pressure, 760 mm Hg
m_{vol} = slope of the MiniVol™ flow rate calibration relationship
b_{vol} = intercept of the MiniVol™ flow rate calibration relationship.

T_{act} and P_{act} readings may be measured on-site or obtained from a nearby U.S. National Weather Service or airport weather station. Barometric pressure readings obtained from remote stations must be at station pressure (not corrected to sea level), and they may have to be corrected for differences between the elevation of the monitoring site and that of the remote station. If ambient temperature and pressure readings are not available, a seasonal average temperature and barometric pressure can also be used. Care must be taken, however, that the actual conditions at the site can be reasonably represented by such averages. It is therefore recommended that seasonal values represent actual values within 20 EC and 40 mm Hg.

Rotameter Set Point Adjustment Procedure. Calculate and record the rotameter set point using temperatures and pressures expected on the day(s) sampling is conducted. These values can be seasonal set points or daily settings.

Eq. 6

$$I_{sp} = \frac{5.0 \times \sqrt{\frac{T_{std}}{T_{act}} \frac{P_{act}}{P_{std}}} - b_{vol}}{m_{vol}}$$

where:
I_{sp} = sampler rotameter set point flow rate adjustment
5.0 = MiniVol design flow rate, L/min
P_{act} = ambient barometric pressure, mm Hg
T_{act}= ambient temperature, EK.
T_{std} = standard temperature, 298 EK
P_{std} = standard pressure, 760 mm Hg
m_{vol} = slope of the MiniVol flow rate calibration relationship
b_{vol} = intercept of the MiniVol flow rate calibration relationship.

Adjusting the sampler rotameter to seasonal average conditions will help minimize data loss caused by exceeding the MiniVol's design condition specifications.

Sampler Calibration Frequency

To ensure accurate measurement of the PM10/PM2.5 concentrations, calibrate the sampler upon installation and then recalibrate it as follows:

1. At least annually.

2. After any repairs that might affect sampler calibration.

3. If the field calibration flow check results exceed QC limits (±7% from the sampler's indicated flow rate).

3. FIELD SAMPLING PROCEDURES

3.1 Sample Filter Cassette Recovery

1. Disconnect the AC cord from the battery pack and remove the MiniVol from its hanger. If possible, move indoors or under cover. Remove the handle by unscrewing a side cap, and removing the o-rings from the bar.

2. Lift the sampler out of the housing by holding the top 6" cap and lifting up gently. Support the sampler by either holding it above its housing or using the triangular mount stand on the bottom of the sampler. Use of the triangular stand should only be done when the battery pack is attached to the sampler. Do not pull the sampler completely out of the housing; the power cord will be torn.

3. Check for any light on the display board, such as "Low Flow" or "Low Battery" and record the findings in the Notes section of the data sheet.

4. Do a post flow check by turning on the pump and ensuring the Rotameter reads 5.0 LPM. Record this on the data sheet. If the pump does not start, press the reset button on the right side of the display board.

5. Record the hour meter value in the Hour Meter Stop field on the data sheet. Lower the sampler back into the housing.

6. Remove the filter head by pressing down on the quick-disconnect while pulling up on the filter assembly. Unscrew the base of the filter assembly and remove the filter with a gloved hand. Secure the filter cassette in the petri dish labeled with the correct filter number.

7. Return a copy of the data sheet with the exposed filter to the processing laboratory. If the PM_{10} monitor is not to be used until the next sampling run, it should be disconnected from the battery pack and properly stored indoors.

3.2 Sample Filter Cassette Installation

1. The operator is to record the following information for the new filter on the AirMetrics MiniVol $PM_{2.5}$ or PM_{10} Field Data Form:

    - Filter Run Date
    - Site ID
    - Type of Impactor ($PM_{2.5}$ or PM_{10})
    - Model Number
    - Sample ID
    - Filter Number
    - Filter Date In
    - Start Date/Time
    - Stop Date/Time
    - Hour Meter Start
    - Start Flow
    - Impactor Run

2. Place a new filter in the opened (from directions above) filter assembly with a gloved hand and re-assemble the unit. Place filter assembly on the quick-disconnect and press firmly down to snap it in place. Pull up to insure connection. Do not pull up on the small rain hood cap.

3. Remove the sampler body from its housing and support it as defined above. On the Programmable Timer, check the current standard time. The reading should be correct during the fall and one hour ahead during the spring. To adjust the time, hold the clock button down while depressing the "Min" or "Hour" keys.

4. Press the "Prog" key to access the 6 available programmable times to turn the sampler on and off. Scroll through each program (1-6) by pressing "Prog" and reset any existing programmed times by using the "RST/RCL" button.

5. At "Prog 1_{ON}", set the time for the beginning of the sample run, which will be 12am of the sampling day on the calendar. At "Prog 1," set the day of the week using the "Week" key. The days will scroll through 10 different choices for day runs. Set the day according to the calendar date. At "Prog 1_{OFF}", set the time for the end of the sample run, which will be 12am the next day. Set the day of the week (same as above). Press the "Clock" key to exit the Program menus.

6. Select the Automatic mode by depressing the "ON/AUTO/OFF" button. The sampler will now start sampling at the programmed time automatically.

7. Reassemble the sampler's handle and place it on the hanger with the impactor away from the hanger stand. Plug in the AC power cord if applicable.

* After every five sampling runs, return the impactor assembly to the processing laboratory. A clean assembly will be supplied for the next run. Only impactors designed for the collection of $PM_{2.5}$ will be supplied, so it is necessary to change the assembly if a new PM_{10} impactor is needed. Disassemble the entire unit, and switch the $PM_{2.5}$ impactor (with the small opening at its base) with the PM_{10} impactor (with the larger opening at its base). The PM_{10} impactor will be the only one present, and the entire unit will be half the size of the $PM_{2.5}$. Return the extra parts with the assembly after five runs.

3.3 Integrated Gas Sampling

For PM_{10} Sampling, Follow the steps below:

1. Ensure that the PM_{10} Impactor (silver) is installed in the preseparator assembly. The multiple impactor adapter is not needed, nor the $PM_{2.5}$ Impactor (gold)

2. Clean and ulbricate the target disk at least every 2-4 sampling periods, or more frequently depending on the degree of impaction stage soiling.

3. After the sampler has been assembled, After the sampler has been assembled, calibrated, verified to be in proper working order, and a filter loaded in the filter holder assembly, set flow rate adjustment in accordance with procedures as shown in the Operation Manual.

4. Follow all other procedures in the Operation Manual, noting that PM10 is being sampled.

APPENDIX M

Harding ESE, Inc. Standard Operating Procedure for Anderson Model GUV-16H High-Volume Sampler HESE SOP-105

Harding ESE, Inc.
Standard Operating Procedure

90 Digital Dr.	**Original Date Issued:**	**August 2002**
Novato, CA 94949	**Type:**	**Revision 0**
	Revision Date:	
	Procedure #:	**HESE SOP-105**
	Total Pages:	**9**

NAME **Standard Operating Procedure for Anderson Model GUV-16H PM_{10} High-Volume Sampler**

SCOPE The scope of the SOP will detail the operating procedures and the procedures used to perform calibrations on Anderson Model GUV-16H PM_{10} High-Volume Sampler.

REFERENCE EPA Compendium Method IO-2.1
Anderson Model GUV-16H PM_{10} High-Volume Sampler User's Manual

EQUIPMENT Anderson Model GUV-16H PM_{10} High-Volume Sampler
Anderson Model GFH360 Volumetric Flow Controller

PROCEDURES

The operating and calibration procedures for the Anderson Model GUV-16H PM_{10} High-Volume Sampler are as follows.

1. EQUIPMENT CALIBRATION

Before the PM_{10} sampling can be initiated, the majority of its components must be calibrated. Routine equipment calibrations are necessary, as well as some unscheduled calibrations (e.g., after equipment failure or when audit values are not within limits. The following subsections detail calibration procedures to be followed by field and/or laboratory technicians, indicate calibrations to be performed by manufacturers or other sources, and specify the frequency of calibrations.

1.1 Analytical Balance

The analytical balance is calibrated daily or each time the balance is moved or subjected to rough handling, or during routine operations when a standard weight cannot be weighed within ±0.5 milligram (mg) of its stated weight. Using Class "S" weights, select three to five weights covering the normal weight range for filters. Weigh the selected weights. If at any time one or more of the weights cannot be measured within ±0.5 mg of its stated value, have the balance recalibrated. Record weight check results in the weight room logbook.

1.2 Relative Humidity Indicator

The hygrothermograph is used to continuously record relative humidity (RH) in the weight room. The hygrothermograph is checked every 6 months against a Rotronics Hygroskop RH transfer standard. If the difference between the RH indicator and the corresponding psychrometer readings is within ±6 percent, continue to use the RH indicator. If the readings disagree by more than ±6 percent, calibrate or replace the indicator. Record RH indicator check results in the weight room logbook.

1.3 Elapsed Time Meters

Elapsed time meters will be calibrated by Harding ESE technicians before and after sampling to an accurate chronometer.

Record results of these checks on the Elapsed Time Indicator Calibration Sheet (Figure 1). If there is a gain or loss of more than 2 minutes in a 24-hour period, replace the meter.

1.4 Variable Resistance Calibrator

A variable resistance orifice calibrator (VRC) will be calibrated against a National Institute of Standards and Technology (NIST) traceable standard upon receipt and at 1-year intervals thereafter.

1.5 PM_{10} Sampler Motors

Sampler motors will be calibrated before initial use, before and after replacement of motor brushes, any time the flow-rate measuring device has to be replaced or repaired, and/or any time the 1-point audit check deviates more than ± 7 percent from the calibration curve.

When the orifice calibration unit is used to calibrate a sampler, a relationship is determined between the sampler volumetric flow rate (Q_a) the actual temperature (T_a), and the ratio of the sampler stagnation pressure (P_1) downstream of the filter to the actual pressure (P_a) and the variable resistance orifice flow rate (Q_{act}) corrected to actual P_a and T_a.

The following steps will be followed in the calibration of the sampler motors:

1. Assemble the PM_{10} sampler with a clean quartz filter and leave in place throughout the calibration procedure.

2. Install the top-loading adapter and variable resistance orifice calibrator on the PM_{10} sampler. Attach a 24-inch water manometer to the pressure tap port of the orifice calibrator to monitor ΔH total to determine Q_{act} from the orifice calibration worksheet. The same 24-inch water manometer will be used to determine the stagnation pressure (ΔP_f) from the tap on the PM_{10} sampler.

3. Adjust the orifice fully counterclockwise to allow maximum flow through the orifice.

4. Turn the motor on and allow at least 5 minutes for the motor to stabilize. Record the orifice ΔH total then attach the manometer to the samplers stagnation tap and record ΔP_f. Document both manometer readings on the VFC Sampler Calibration Data Sheet (Figure 2).

5. Record on the calibration data worksheet (Figure 2) the actual barometric pressure in [millimeters of mercury (mm Hg)] and actual temperature in °C.

6. Adjust the orifice to obtain two additional flow rates between 1.02 and 1.13 m^3/min. Record the orifice ΔH total and the sampler's stagnation tap ΔP_f for each flow rate.

7. Determine the critical orifice actual flow rates corrected to the barometric pressure and temperature recorded in Step 5. The critical orifice flow rates are determined using the following equation:

$$Q_{act}\ (orifice) = \left\{\left[\Delta H\left(T_a / P_a\right)\right]^{1/2} - b\right\}\left(\frac{1}{m}\right) \quad (1)$$

where: Q_{act} *(orifice)* = actual volumetric flow rate as indicated by the critical orifice, m^3/min;
ΔH = pressure drop across the orifice in inches of water;
T_a = ambient temperature determined from Step 5, K (K = °C + 273);
P_a = ambient barometric pressure recorded in Step 5 mm Hg;
b = intercept of the critical orifice calibration relationship; and
m = slope of the critical orifice calibration relationship.

8. When calibrating the Andersen PM_{10} sampler, the terminology is as follows:

where: P_a = actual pressure,
T_a = actual temperature,
P_f = pressure differential across the filter (taken from stagnation tap),
ΔH *orifice* = total pressure differential from the orifice calibrator, and
$P_o/P_s = (P_a - P_f)/P_a = P_o/P_a$

The ratio P_o/P_a with the T_a values is used to determine the sampler flow rate taken from the look-up table for the Andersen VFC sampler.

If any of the three lookup points of the calibration do not fall within ±4 percent of the known flow rate from the VRC or if at least two of the three points are not between 39 and 60 cmf, check for leaks, perform any required maintenance and repeat the calibration until these conditions are met. The percent deviation is calculated by taking the sampler's flow rate (X_i) and the orifice calibration curve flow rate (Y_i) for the same flow reading.

$$Percent\ deviation = \frac{X_i - Y_i}{Y_i} \quad x \quad 100 \quad (2)$$

9. Remove the variable resistance orifice and restore the equipment to sampling readiness.

2. TIME-INTEGRATED AIR MONITORING TECHNIQUES

The Andersen Model GUV-16H PM_{10} high-volume sampler equipped with an Andersen Model GFH360 VFC will be used to collect PM_{10} samples at all the integrated sampling sites. Installation of the samplers will be in accordance with the manufacturers instrument manual.

The sample flow rate in the Andersen Model GUV360 VFC is controlled and maintained by a VFC. The VFC system consists of three distinct portions: the filter holder with stagnation tap, VFC, and a blower/motor. The VFC is a dimensional venturi device used to control gas flow. Plow control is accomplished by accelerating the airflow through the venturi. At some point in the flow stream, the air velocity will equal the acoustic velocity, achieving critical flow. This choking condition is a distinctive characteristic of the VFC. The VFC uses this principle of choked flow to maintain a constant actual flow rate of 40 cfm over a sample period.

Before installing a new filter, clean the rubber gasket on the filter holder to remove any filter fibers or dust. Use a clean, dry cloth or paint brush to clean the area surrounding the filter holder.

The following instrumentation and time-integrated air monitoring techniques will be used to collect air samples for analysis of PM_{10}.

1. Record the project number, motor number, filter number, station number, date of sample collection, and time started [use military time (e.g., 2400 hours or 0001 hours)] on the PM_{10} Field Envelope (Figure 4-3).

2. Carefully remove clean filter from box and place in filter holder. If the filter is torn or broken, discard it, record disposition, and use the next filter in the box.

3. Center the holder on the screen so that when the faceplate is in position, the gasket will form an airtight seal on the outer edge of the holder. When aligned correctly, the edges of the filter should be parallel both to the edges of the screen below it and to the faceplate gasket above it.

4. Once the filter holder is in place, tighten the four wing nuts so that the gasket is airtight against the filter holder. Tighten the wing nuts evenly at diagonals, avoiding excessive tightening to minimize the filter's tendency to stick to the gasket and to guard against damage to the gasket.

5. Turn the motor on and allow it to warm up for approximately 5 minutes. Attach a 24-inch water manometer to the stagnation pressure tap.

6. After warm-up, record the total manometer reading (Pf1) on the PM_{10} Field Envelope.

7. Turn the motor off and set the timer so that the sampler will begin sampling at the appropriate time of the day.

8. Enter the initial elapsed time reading on the PM_{10} Field Envelope.

9. Close the sampler inlet and complete the seasonal operating conditions data on the PM_{10} Field Envelope.

10. Note on the envelope any anomalies in ambient conditions (e.g., high winds, construction activity, dust storms, forest fires).

Use the following procedures to remove a collected sample:

1. Turn the sampler motor on and allow the motor to stabilize for approximately 5 minutes.

2. Attach the 24-inch manometer to the sampler stagnation pressure tap and record the Pf2 differential pressure.

3. Turn the sampler motor off.

4. Record the final elapsed time on the PM_{10} Field Envelope.

5. Without touching the exposed area, gently remove the exposed filter and filter holder.

6. Remove the filter from the filter holder and fold the exposed area together lengthwise.

7. Calculate the average sample flow rate using the equations and examples provided on the PM_{10} Field Envelope as follows:

   a. PP_1 = manometer right side reading + left side reading at filter installation
      = 14.50 + 15.0 = 29.50 inches H_20.
   b. PF_2 = manometer right side reading + left side reading = 14.50 + 14.50
      = 29.0 inches H_20.
   c. PFa = average flow for the respective sampling period (mm Hg)
      = [PF_1 + PF_2/2] x 1.8663 = [29.50 + 29.0/2] x 1.8663
      = [58.5/2] x 1.8663 = [29.25] x 1.8663 = 54.59 mm Hg.
      where: 1.8663 = conversion factor for inches of H_20 to mm Hg.
   d. Po/Ps = pressure ratio across the filter based on seasonal barometric pressure
      = 1 - (Pfa-Ps)
      = 1 - (54.59-751.65)
      = 1 - 0.073
      = 0.927.
   e. SQa = seasonal flow rate derived from the look-up table for the specific VFC based on the P0/Ps ratio and seasonal temperature
      = Po/Ps = 0.927
      = Ts = 41.6°F or 6.33°C
      = 41.6 cfm or 1.178.

8. Place the respective filter in the envelope for shipment to the laboratory.

3. ROUTINE CHECKS

The following checks should be made when removing an exposed filter.

1 Check the filter for signs of air leakage. Leakage may result from (1) a worn faceplate gasket, (2) an improperly installed gasket, or (3) over tightening of the faceplate gasket, which can cut the filter along the gasket interface.

2 Any time a leak is observed, indicate the problem on the envelope and take corrective action before starting another sampling period. Corrective action would be to replace the gasket, take more care in installing the filter, or apply more caution in tightening the gasket. Generally, a gasket deteriorates slowly (faster in summer months), and the operator can determine well in advance (by an increasing fuzziness of the sample outline) when to change the gasket before a total failure.

3 Visually inspect the gasket for glass fibers from the previous filter. The presence of glass fibers is a sign of over tightening the gasket. Tighten the gasket just enough to prevent leakage.

4 Check the exposed filter for physical damage that may have occurred during or after sampling. Physical damage to the filter after sample collection does not always invalidate the sample. For example, accidentally tearing off a corner while removing the filter does not invalidate the sample if all pieces of the filter are included in the folder. However, any loss of sample due to leakages during the sampling period or to the loss of loose particulates from the filter after sampling (e.g., loss of particulates when folding the filter) may invalidate the sample. Therefore, care should be taken to prevent these occurrences. Mark all suspect samples on the envelope and forward to the laboratory. Insects (such as gnats) loosely attached to the filter should be removed by the laboratory technician with a pin or with Teflon□-tipped tweezers. If insects are embedded in the particulates, note on the folder, but do not try to remove them.

5 The appearance of the particulates should be checked. Any changes from the normal color may indicate new emission sources, forest fires, or construction activity, etc. in the area. The change should be noted on the filter folder along with any other obvious reasons for the change.

Figure 1: Elapsed Time Indicator Calibration Sheet

ELAPSED TIME INDICATOR CALIBRATION SHEET

(NATIONAL BUREAU OF STANDARDS TIME-- TEL. 1/303/499-7111)

Elapsed Time Indicator Number	Calibration Started		Calibration Stopped		E.T.I. Initial Reading	E.T.I. Final Reading	Percent Accuracy	Calibrated by (Signature)
	Date	Time	Date	Time				

Figure 2: VFC Sampler Calibration Data Sheet

VFC SAMPLER CALIBRATION DATA SHEET

Station location_____ Date_____ Time_____

Sampler Model_____ S/N_____ Operator_____

Pa_____mmHg. Ta_____ C _____K Unusual Conditions_____

Orifice S/N_____ Orifice Calibration Date_____

Orifice Calibration Relationship: m =_____ b =_____ r =_____

Plate No.	Orifice H20 (in.)	Sidetap Pstg [H20(L+R) x 1.8663] (mmHg.)	Po [Pa-Pstg] (mmHg.)	Po/Pa	$[(Po/Pa)Ta]^{1/2}$	Qa (orifice) flow rate (m3/min)
Operational Conditions					Flow rate = _____	

$Qa(Orif) = 1/m(\{[(\Delta H20)(Ta/Pa)]^{1/2}-b\})$

$$\% \text{ Difference} = \frac{Qa(samp)-Qa(Orif)}{Qa(Orif)} \times 100$$

[ ] Lookup table Validated
% Difference < 4

[ ] New calibration relationship
$x = Qa(Orif)$; $y = \{(Po/Pa)Ta\}^{1/2}$

Qa (Orifice)	Qa (Sampler) (Lookup Table)	% Difference

m = _____ b = _____ r = _____

For sampler flow rate: $Qa = \{[(Po/Pa)Ta]^{1/2}-b\}/m$

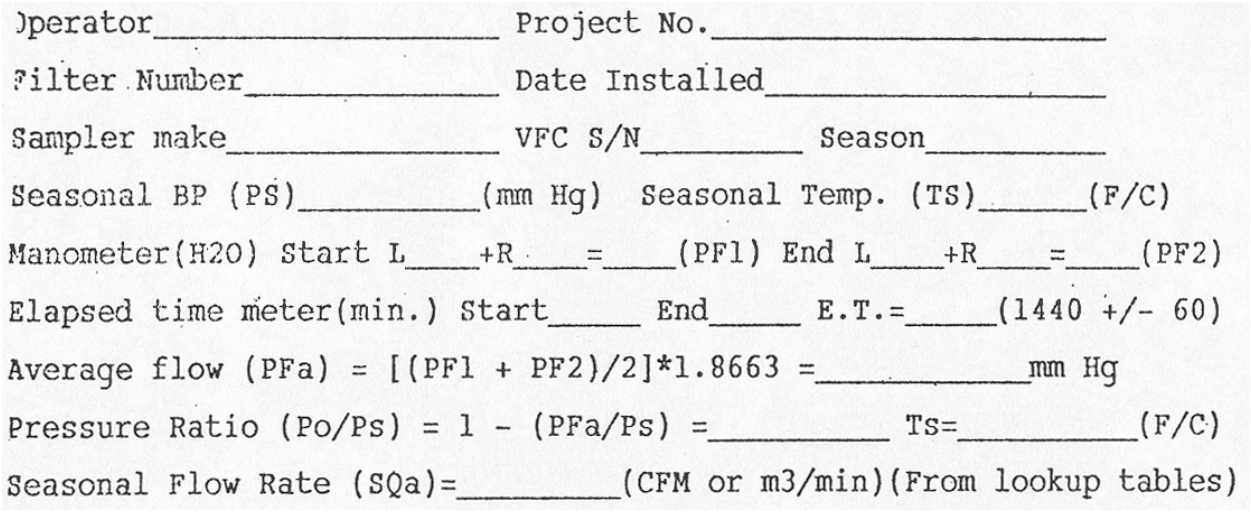
Operational flow rate _____ m3/min

NOTES:_____

_____

_____

Figure 3. PM_{10} Field Envelope



)perator_____ Project No._____

Filter Number_____ Date Installed_____

Sampler make_____ VFC S/N_____ Season_____

Seasonal BP (PS)_____(mm Hg) Seasonal Temp. (TS)_____(F/C)

Manometer(H20) Start L____+R____=____(PF1) End L____+R____=____(PF2)

Elapsed time meter(min.) Start_____ End_____ E.T.=_____(1440 +/- 60)

Average flow (PFa) = [(PF1 + PF2)/2]*1.8663 =_____mm Hg

Pressure Ratio (Po/Ps) = 1 - (PFa/Ps) =_____ Ts=_____(F/C)

Seasonal Flow Rate (SQa)=_____(CFM or m3/min)(From lookup tables)

APPENDIX N

Harding ESE, Inc. Standard Operating Procedure for
KSC PCXR4 Air Sampling Pump
HESE SOP-106

Harding ESE, Inc.
Standard Operating Procedure

90 Digital Dr.	**Original Date Issued:**	**August 2002**
Novato, CA 94949	**Type:**	**Revision 0**
	Revision Date:	
	Procedure #:	**HESE SOP-106**
	Total Pages:	**7**

NAME **Standard Operating Procedure for SKC Model PCXR4 Personal Air Sampling Pump**

SCOPE The scope of the SOP will detail the operating procedures and the procedures used to perform calibrations on SKC Model PCXR4 Personal Air Sampling Pump

REFERENCE EPA Compendium Method TO-11A
SKC Model PCXR4 Personal Air Sampling Pump User's Manual

EQUIPMENT SKC Model PCXR4 Personal Air Sampling Pump

PROCEDURES

Aldehyde samples will be collected using a personal air sampling pump set in a low flow configuration to achieve a flow rate of 10 ml/min. The maximum recommended volume is 5-liters for a total collection time of 500 minutes, 480 minutes (8-hrs) will produce a valid sample. The samples will be collected on glass sorbent tubes filled with treated XAD-2.

The pump is turned on and may be set to 2 l/min by the built in rotameter. The sorbent tubes (media) are broken open and inserted into the sampling train. The calibrator is attached to the end of the sampling train. The true flow rate is set by turning the Adjustable Low Flow Holder (ALFH) control screw to approximately 10 ml/min using a BIOS Dry-Cal as the primary standard. The starting rate average is accurately recorded, the pump may be shut off and the calibrator is removed. The sampling train is now ready for sample collection. Carefully record both the starting time and ending time. The pumps have internal timers; however, they are not always precise. Near the end of the sampling period, the samples will post-calibrated. The Dry-Cal will be attached

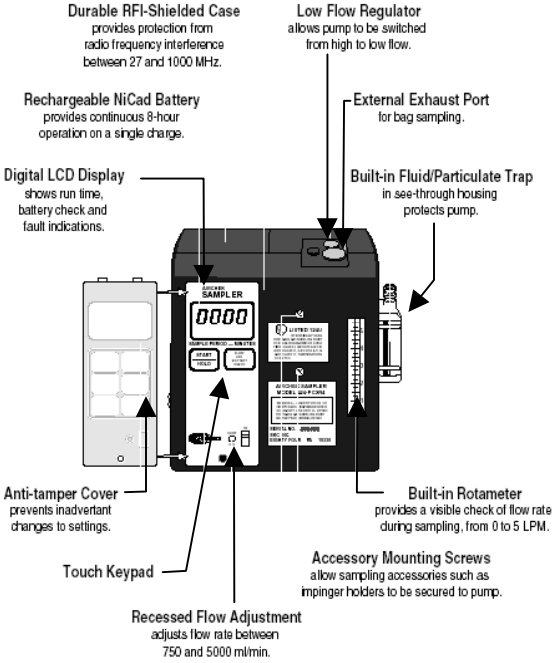
1. SAMPLE HANDLING

The sorbent tubes are chemically treated and therefor have a limited shelf life. Use only sorbent tubes procured for this task. Ideally the tubes should be stored in a cool, dark place – a refrigerator is ideal. The tubes have sealed ends, which will need to be broken off prior to sampling. The tubes are also marked with arrows indicating the direction of air flow. The tip of the arrow should point towards the sampling pump. The end of the arrow will be open to the air.

PUMP ← AIR

Use safety glasses and a tubing breaker to remove the ends. The ends are generally jagged and very sharp – use great care when inserting them into the sample train tubing, when removing them form the sample train tubing and especially when sealing them with end-caps.

2. PUMP SETUP



The illustration shows an SKC PCXR4 personal air-sampling pump. Note the location of the Low Flow Regulator (LFR) and the Recessed Flow Adjustment (RFA) control. To the right of the RFA control is a sliding ON/OFF switch. For low flow conditions (1-750 ml/min), the RFA is set to 2 liter/min and the LFR is rotated counterclockwise from the fully seated position 4-5 complete turns. Failing to open the LFR will cause the pump to FAULT.

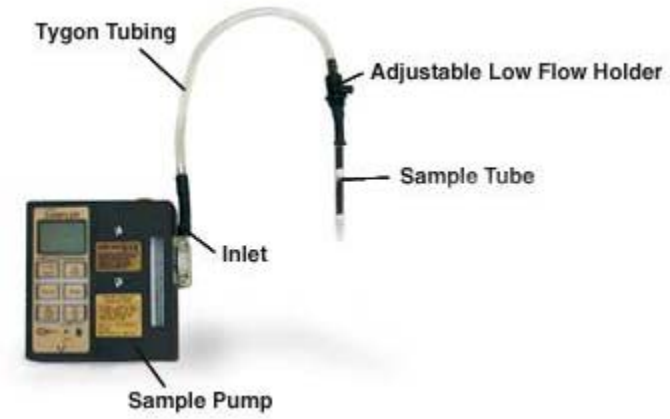
3. SAMPLING TRAIN

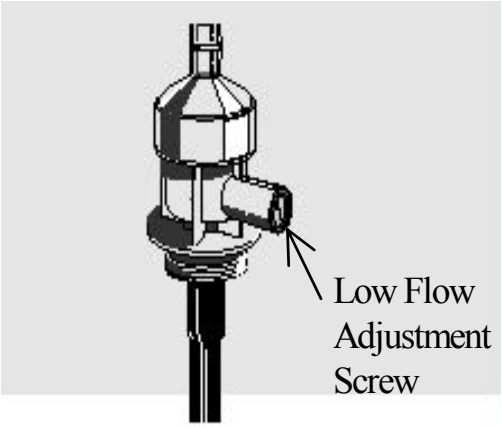
With the pump off, select a clean piece of tubing and attach it to the Fluid/Particulate Trap.

The ALFH should be attached to the other end of the tubing, if a cover is present on the ALFH is should be removed.

Break the sorbent tube and insert the end with the arrow point into the black rubber tubing on the end (under cover) of the ALFH. If there is no arrow on the sorbent tube, insert the end of the tube with the smallest sorbent section into the holder. See example shown below.

Following calibration of the sample, the cover may be replaced on the ALFH to prevent personal injury from the sharp tube ends.





Single Adjustable Low Flow Holder

4. CALIBRATION

Calibration will be performed before the sample is collected (pre-calibration) and at the end of the sampling shift (post-calibration). Allow the pump to run approximately 3-5 minutes (without the sample sorbent tube). This allows the pump to "warm up" to a steady operating state.

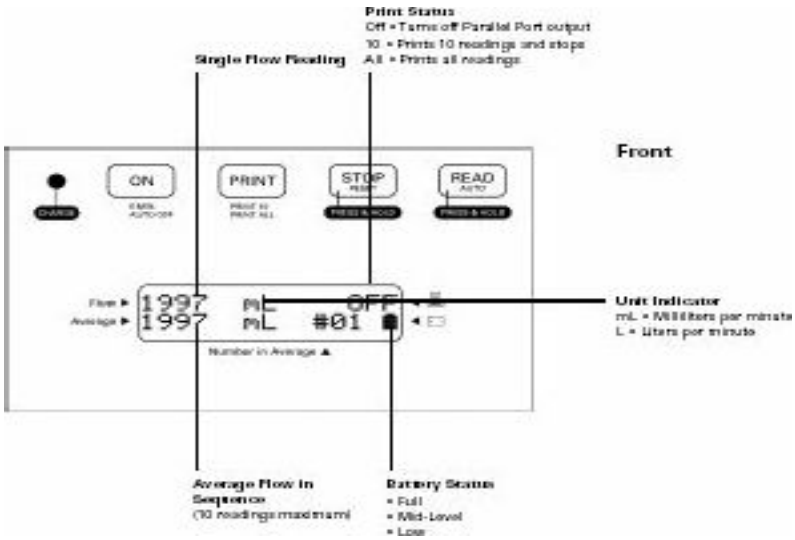
1. Connect the tube to the ALFH and connect the DryCal OUTLET port (see below) to the open end of the sample tube with a piece of clean tubing.

2. Turn on the sample pump.

3. Turn on the DryCal.

4. Press and release the “READ” button to obtain a single flow measurement. The flow measurement will appear on the LCD.

Note: Readings can be taken continuously in the auto-repeat mode for hands-free operation. The unit will automatically clear the average after ten readings and begin averaging a new sequence. Press and hold the “READ” button until a reading starts, then release.



5. Adjust the ALFH screw until the single flow reading approches 10 mL on the screen.

6. Continue to collect from 3-10 readings and record the average on the dataform.

7. The DryCal display and average may be cleared at any time by pressing and holding the “STOP” button.

8. Remove the tubing and DryCal from the sampling train.

9. The sampler is now ready for sampling.

Post-calibration is performed in the same way as pre-calibration; however, it is preferrable to measure the flowrate while the sample is being collected and before the pump is shut off.

The calibration setup is illustrated below (a different type of calibrator is shown).

At the conclusion of sampling, record the stop time (compare this to the internal clock on the sampling pump).

Carefully remove the sample tube.

Place end-caps firmly on the sample tube (this is when fingers get cut).

Label the sample and record the information on the Chain of Custody.

Record the sample volume on the Chain of Custody and in your notes.

Time x rate = volume. ∴ (minutes)(ml/min) = milliters

Aldehydes Screening NIOSH Method 2539 CG-FID

SAMPLER: SOLID SORBENT TUBE (10% 2-(hydroxymethyl) piperidine on XAD-2, 120 mg/60 mg) – limited shelf life.

FLOW RATE: 0.01 L/min (10 ml/min)

SAMPLE TIME: 8-hours (480-500 min)

VOLUME: 5 liters, maximum

SHIPMENT: @ 25 °C or lower

SAMPLE STABILITY: at least 1 week @ 25 °C (77 °F)

FIELD BLANKS: 2 to 10 field blanks per set

MEDIA BLANKS: 6 per set

TECHNIQUE: Gas Chromatography, FID & GC/MS

AIR SAMPLING DATA LOG

Client: _____ **Job Number** _____ **Rotometer Number** _____ **Date** _____

Name or Location	SS# or ID# or Description	Sample Type or Analyte	Sample #	Start Time	Stop Time	Total Time (minutes)	Start Rate	Stop Rate	Average Rate (l/min)	Volume (liters)	Turn Around Time

Collected By: _____

APPENDIX O

TSI Q-Trak Plus IAQ Monitor Operation and Service Manual

APPENDIX P

Response to Comments

RESPONSE TO COMMENTS ON THE DRAFT PRESCRIBED BURN AIR SAMPLING AND ANALYSIS PLAN RANGES 43-48, FORMER FORT ORD, CALIFORNIA, DATED JULY 2, 2002

I. DOUGLAS QUETIN, AIR POLLUTION CONTROL OFFICER, MONTEREY BAY UNIFIED AIR POLLUTION CONTROL DISTRICT COMMENTS DATED JULY 30, 2002

The purpose of this letter is to provide our District's comments on the *Draft Prescribed Burn Air Sampling and Analysis Plan, Ranges 43-48, Former Fort Ord, July 2, 2002*, called hereafter the Draft Air SAP.

General Comment:

In making these comments, it is important to note that it has been this agency's long-standing position that the Army:

- **must treat the community's concern regarding health issues as a top priority;**
- **conduct a complete and thorough analysis of the potential health impacts from the predicted air emissions from burning vegetation and ordnance; and**
- **complete a comprehensive review, including a comparison of risk, of alternatives for clearing vegetation.**

While the District realizes these actions may be covered by one or several of the other documents that are being prepared for this project, these elements are necessary to assure that the Army makes its selection of vegetation clearance methods upon a sound and informed basis. As the emissions data that will be collected under this SAP are crucial to the successful completion of these tasks, the District is very concerned that the air emissions from burning vegetation are essentially ignored in this SAP and that emissions from unexploded ordnance and explosives, which are widely expected to be inconsequential, constitute the entire focus of this document.

Response: A combined agency comment resolution meeting was held at Fort Ord on August 8, 2002, to discuss the overall goals and objectives of the air sampling program. The Draft Final SAP has been revised to reflect the consensus opinion regarding modifications to the sampling scope, including sampling for specific vegetation-related compounds.

Specific Comments:

Unless otherwise specified, the section and page numbers refer to the Draft Ranges 43-48 Air SAP.

Comment 1: **Pp. v - vii: Either here or elsewhere in this document, the Army must clarify the role, if any, the following organizations will have in this project: the United States Environmental Protection Agency, the Agency for Toxic Substances and Disease Registry, the California Department of Toxic Substance Control, the California Air Resources Board, and the Monterey Bay Unified Air Pollution Control District.**

Response 1: The roles of these agencies are now described in Section 5.1 of the Draft Final SAP.

Comment 2: **Pp. v - vii: Either here or elsewhere in this document, including a list of acronyms would be helpful.**

Response 2: A list of acronyms has been added.

Comment 3: **P. vi, para. 3: The Army recognizes here that smoke impacts from prescribed burning can adversely affect downwind populations, yet does not plan to assess the concentrations of vegetation-related combustion emissions. The Fort Ord Health Consultation completed by the Agency for Toxic Substances and Disease Registry in October 2001 concluded that sufficient data were not available to evaluate public health exposure during past fire events and provided suggestions for future sampling.**

Response 3: A combined agency comment resolution meeting was held at Fort Ord on August 8, 2002, to discuss the overall goals and objectives of the air sampling program. The Draft Final SAP has been revised to reflect the consensus opinion regarding modifications to the sampling scope, including sampling for specific vegetation-related compounds.

Comment 4: **P. 1, §1.0: Who will be responsible for preparing and implementing the QAPP for the air sampling activities? There have been no details provided on sampling equipment specifications, the standard operating procedures or protocols that will be used for site selection, sample collection, sample preservation, chain of custody, and collocated sampling. If this information is (will be) available in other documents, they should be referenced somewhere in the Draft Ranges 43-48 Air SAP.**

Response 4: A separate QAPP is not necessary for this program. Overall QA/QC objectives are outlined in the referenced CDQMP. The Draft Final SAP has been expanded to include SOPs and sampling and analysis methods and protocols.

Comment 5: **P. 5, §2.2.1: The *Draft Prescribed Burn Plan for Ranges 43-48, Former Fort Ord, June 19, 2002* lists the area to be burned as approximately 560 acres. The discrepancy should be corrected.**

Response 5: The Ranges 43-48 Interim Action site was initially identified as 555 acres including Site OE-15MOCO.2 (coincident with transfer parcel E21b.3) and the eastern portion of Site OE-15SEA.4 (portion of transfer parcel E23.2). In response to comments received on the Draft IA OE RI/FS, the Army reduced the Ranges 43-48 Interim Action site by approximately 82 acres within these two sites that are designated for future development. In addition, minor adjustments to the boundaries of the habitat reserve and future development areas within the site resulted in adjustment of the boundary for the Ranges 43-48 Interim Action site to include 473 acres of habitat reserve area and 25 acres of development area, for a total of 498 acres. Additional minor boundary changes may be necessary in order to conduct the prescribed burn in a safe manner. The approximate boundary for the Ranges 43-48 Interim Action site is shown on Plate 3 of the Draft Final Air SAP.

Comment 6: **P. 7, §2.4.1: The Fort Ord Health Consultation completed by the Agency for Toxic Substances and Disease Registry in October 2001 concluded that sufficient data were not available to evaluate public health exposure.**

Response 6: The Air Emissions Technical Memorandum was prepared subsequent to the ATSDR health consultation, and specifically examined the exposure levels of OE-related emissions from the proposed burn on Ranges 43-48. No conclusions were stated or implied regarding public health exposure to vegetation-related components of the smoke.

Comment 7: **P. 8, para. 3, §2.4.1.1: According to other documents, the Army has claimed that the density of OE for Ranges 43-48 is extremely high. Is the density from the 1998 study high enough to reflect the field situation for Ranges 43-48?**

Response 7: Yes. Subsequent surface sampling activities have confirmed the high density of OE in Ranges 43-48.

Comment 8: **P. 9, §2.4.1.2: The basic experimental design of the BangBox study was detonation or burning in a closed chamber, not open detonation. The species generated would be expected to be very different under field conditions. The TAG consultant, who was an author of the study, has questioned its use for this project.**

Response 8: Data from the BangBox study were used in conjunction with health-protective, reasonable upper bound assumptions to estimate emissions from incidental detonation of OE. This approach provided a high degree of confidence that the emission estimates are not likely to be exceeded in the actual prescribed burn at Ranges 43-48. This air sampling program has been proposed to test the conclusions of the air emission estimates.

Comment 9: **P. 11, para. 4, §2.4.1.2: Also see comment 8. Also, during prescribed burning with incidental OE detonations, conditions would exist that would favor the formation of dioxins and furans, i.e., the presence of sources of hydrocarbons, oxygen, and chlorine.**

Response 9: At the combined agency comment resolution meeting on August 8, 2002, it was agreed that sampling for polychlorinated dioxins and furans was warranted and would be added to the scope of the sampling program.

Comment 10: **P. 13, §2.4.1.3: The results of the Air Emissions Technical Memorandum do not justify that the emissions from the burning biomass will be below regulatory screening levels.**

Response 10: The Air Emissions Technical Memorandum specifically examined the exposure levels of OE-related emissions from the proposed burn on Ranges 43-48. No conclusions were stated or implied regarding public health exposure to vegetation-related components of the smoke.

Comment 11: **P. 14, last paragraph, §2.4.2: The District does not agree that nitrogen oxides are insignificant in the emissions from prescribed burning.**

Response 11: This statement is from the document referenced within the paragraph.

Comment 12: **P. 15, para. 2, §2.4.2: The high fuel loading for Ranges 43-48 is not considered.**

Response 12: The emissions data shown in this section are specific to the fuel loading in Ranges 43-48.

Comment 13: **P. 15, §2.4.2: The key to whether emissions are significant is not whether the amount is large in mass, but whether the potential health impact is large. Compounds which should be incorporated into the list of COPCs and Table 3 include: NOx, PAHs, dioxins, furans, acrolein, formaldehyde, and vinyl acetate.**

Response 13: A combined agency comment resolution meeting was held at Fort Ord on August 8, 2002, to discuss the overall goals and objectives of the air sampling program. The Draft Final SAP has been revised to reflect the consensus opinion regarding modifications to the sampling scope. The list of analytes has been expanded to include aldehydes and polychlorinated dioxons/furans.

Comment 14: **P. 16, §3.1: All air emissions, whether from the burning of vegetation or detonation of OE, that can impact the public must be monitored.**

Response 14: This section has been revised to reflect the new scope of the air sampling program.

Comment 15: **P. 18, §4.2: All air emissions, whether from the burning of vegetation or detonation of OE, that can impact the public must be considered.**

Response 15: This section has been revised to reflect the new scope of the air sampling program.

Comment 16: **P. 19, para. 3, §4.5: If measured concentrations of COPCs are less than established screening levels, but the public is impacted by smoke from the burns, will no modifications be made to future prescribed burn operations?**

Response 16: This section has been revised to reflect the new scope of the air sampling program. A post burn evaluation will be performed to evaluate the need for modifications to the prescribed burn operation.

Comment 17: **P. 19, para. 3, §4.5: If data for emissions from burning vegetation are not collected, it will not be possible to perform a valid human health risk assessment.**

Response 17: This section has been revised to reflect the new scope of the air sampling program.

Comment 18: **P. 21, bullet 5, §4.7: Collection sites based on locations where smoke impacts were observed during previous burns would not be productive, since different meteorological conditions will presumably be chosen for future burn prescriptions.**

Response 18: This section has been revised to reflect the new scope of the air sampling program.

Comment 19: **P. 21, bullet 8, §4.7: Two different kinds of sampling periods should be used to collect air samples: one, during the peak burn event to determine the maximum impacts; and the other which covers the entire event, including the smoldering phase.**

Response 19: This section has been revised to reflect the new scope of the air sampling program.

Comment 20: **P. 21, last bullet, §4.7: Revise the list of the COPCs in Table 3 to address comment 13.**

Response 20: Table 3 has been revised to reflect the new scope of the air sampling program.

Comment 21: **P. 22, bullet two, §5.1: To minimize adverse impacts upon the community, why not burn one of the other smaller high priority areas covered by the IA first?**

Response 21: The selection of Range 43-48 as the highest priority site is discussed in the Interim Action RI/FS.

Comment 22: **P. 24, last paragraph, §5.2: It is extremely important for the post-burn analysis that accurate records of the sampling locations are maintained.**

Response 22: Accurate coordinates of the sampling locations will be obtained by GPS and will be recorded and maintained.

Comment 23: **P. 25, §6.0: Other requirements that need to be included are: site selection requirements; sample collection/control/preservation SOPs; use of standard methods (EPA reference or CARB equivalent methods) for sample collection; quality assurance/quality control procedures; use of the standard recognized height for collecting air samples of 2 meters; and procedures for pre-conditioning filters.**

Response 23: A complete set of sampling and analytical methods are included in the Draft Final SAP.

Comment 24: **P. 26, para. 1, §6.1: How will it be assured that sample collection remains upwind of the propane-powered generators?**

Response 24: Generators will be used only where AC power is not available. Activities to minimize any cross-contamination from generator exhaust are discussed in Section 6 of the Draft Final SAP.

Comment 25: **P. 26, para. 2, §6.2: The District is not aware of the availability of Teflon filters of the size specified.**

Response 25: This sampling method has been changed.

Comment 26: **P. 26, para. 3, §6.2: It will be not possible to directly compare the samples collected by the two different sampling methods, since part of the smoke components will be missed due to differences in size distributions collected.**

Response 26: These sampling methods have been changed.

Comment 27: **Table 3: Compounds which should be incorporated into Table 3 include: NOx, PAHs, dioxins, furans, acrolein, formaldehyde, and vinyl acetate. In addition, the Table must also include the predicted emissions from ignition equipment, such as drip torches or Helitorch. From previous burns, we know that significant quantities of Alumagel Gasoline are used.**

Response 27: Acrolein, formaldehyde, acetaldehyde, and dioxins/furans have been added to the list of COPCs in Table 3. Combustion products from the fire ignition materials would be

indistinguishable from ubiquitous sources (e.g., motor vehicles) operating in and around the sampling locations, so sampling for those combustion products would not provide meaningful data for this program.

RESPONSE TO COMMENTS ON THE DRAFT PRESCRIBED BURN AIR SAMPLING AND ANALYSIS PLAN RANGES 43-48, FORMER FORT ORD, CALIFORNIA, DATED JULY 2, 2002

II. DEPARTMENT OF TOXIC SUBSTANCES CONTROL, JOHN P. CHRISTOPHER, Ph.D., D.A.B.T., STAFF TOXICOLOGIST, HUMAN AND ECOLOGICAL RISK DIVISION (HERD), COMMENTS DATED AUGUST 2, 2002

Background

Fort Ord is a closed military facility in Monterey County where the US Army Corps of Engineers is managing cleanup operations. Ranges 43-48 were used for several decades for training with weapons such as small arms, mortars, and anti-tank ordnance. The Army wants to remove exploded and unexploded ordnance (UXO), but vegetation must first be burned off to allow visualization of obscured objects on the ground. The current document describes air monitoring to be conducted during the prescribed burn.

Document Reviewed

We reviewed "Draft Prescribed Burn Air Sampling and Analysis Plan, Ranges 43048, Former Fort Ord, California", dated 2 July 2002 and prepared by Harding ESE, contractors to the Army.

General Comments:

Comment 1: **Overall: The sampling and analysis plan is clearly written. We believe the goals of the sampling must be given another examination by the project team to include the general and specific items listed below.**

Response 1: A combined agency comment resolution meeting was held at Fort Ord on August 8, 2002, to discuss the overall goals and objectives of the air sampling program. The Draft Final SAP has been revised to reflect the consensus opinion regarding modifications to the sampling scope.

Comment 2: **Principal Focus: From the perspective of risk assessment, two are goals are most important from this sampling plan. First, we want to see as many measurements as feasible to verify that the screening measurements made in the earlier technical memorandum were adequately health-protective. Second, we believe that Army should provide the impacted public with analytical information on the important contaminants generated in this burn. The list of analytes should be expanded to include irritant aldehydes and polychlorinated dioxins and furans.**

Response 2: The list of analytes has been expanded to include aldehydes and polychlorinated dioxons/furans.

Comment 3: **Glossary: This sampling plan and all documents related to ordnance removal must include a glossary for the many acronyms employed.**

Response 3: A list of acronyms has been added.

Specific Comments:

Comment 1: **Phthalates, Sec. 2.4.1.2, p. 11: Diethylphthalate was added to the list of analytes because of its regulatory status as a toxic air contaminant. Energetic chemicals were added to the target list because toxicity values are available. Other phthalates with available toxicity values are also commonly encountered and these should be added as analytes, including di-*n*-butylphthalate, dioctylphthalate, *bis*(2-ethylhexyl)phthalate, and *bis*(2-ethyl-hexyl)adipate. Toxicity values and candidate reference levels for these chemicals are published by the Office of Environmental Health Hazard Assessment (OEHHA) of Cal/EPA (http://www.oehha.ca.gov/risk/chemicalDB/index.asp) and in the Preliminary Remediation Goals from USEPA Region 9 (http://www.epa.gov/region09/waste/sfund/ prg/files/PRG2000.xlw).**

Response 1: At the combined agency comment resolution meeting on August 8, 2002, it was agreed that sampling for phthalates was not warranted.

Comment 2: **Dioxins and Furans, Sec. 2.4.1.2, p. 11: Although the Army does not expect to encounter significant concentrations of chlorinated dioxins or furans, we strongly urge them to analyze the smoke for these compounds. Bang-box studies found dioxins in only a few items of ordnance, but burning together with vegetation could provide a large source of chlorine and foster formation of these substances.**

Response 2: At the combined agency comment resolution meeting on August 8, 2002, it was agreed that sampling for polychlorinated dioxins and furans was warranted and would be added to the scope of the sampling program.

Comment 3: **Contaminants of Potential Concern (COPC), Sec. 2.4.1.4, p. 13: The Army identified COPC for this sampling program by focusing on those combustion products unique to detonation of ordnance and explosives. We believe that a separate and equally important focus is verifying the estimates made using the screening models in previous technical memoranda. Earlier modeling went through several iterations of refinement, each of which showed that rougher estimates in fact had been adequately health-protective. However, these estimates borrowed data of varying applicability. Now that the burn is going forward, the Army should collect identify and analyze COPC to allow verification of earlier estimates of concentrations of contaminants in air. We agree that the Army should try to identify items uniquely traceable to explosives, such as energetic materials. However, we are also concerned with the amounts arising from burned vegetation. In this regard, data on PM_{10} and metals will probably be the most useful for quantitative estimates of the mass of material arising from burning vegetation.**

Response 3: The sampling program has been expanded to include sampling for PM_{10} and metals at a greater number of locations in the surrounding communities.

Comment 4: **Irritant Aldehydes, Section 2.4.2, p. 15: Nearby residents and regional regulatory agencies have expressed strong interest in gathering information on toxic materials from the smoke in this burn. We believe the Army can help here**

by analyzing for the principal irritant aldehydes of smoke, including formaldehyde, acetaldehyde, and acrolein. For reference, Acute Reference Exposure Levels (REL) for these substances have been developed by OEHHA (httpp://www.oehha.ca.gov/air/acute_rels/allAcRELs.html).

Response 4: At the combined agency comment resolution meeting on August 8, 2002, it was agreed that sampling for aldehydes (including formaldehyde, acetaldehyde, and acrolein) was warranted and would be added to the scope of the sampling program.

Comment 5: **Location of Sampling Devices, Sec. 5.2, p. 24: As the Army considers where to place their sampling devices, we recommend that the age of the chaparral being burned and the number of known targets be added to the bulleted criteria shown on page 24. Areas with the heaviest concentrations of targets can be expected to produce the most material attributable to UXO, while the oldest stands of vegetation may be expected to produce the greatest mass of particulates in smoke.**

Response 5: It is not possible to place sampling equipment inside the burn area because of the substantial hazard from detonation of OE and from the fire itself. Sampling locations have been identified as close as possible to the burn area, and at other locations that may experience smoke impacts.

RESPONSE TO COMMENTS ON THE DRAFT PRESCRIBED BURN AIR SAMPLING AND ANALYSIS PLAN RANGES 43-48, FORMER FORT ORD, CALIFORNIA, DATED JULY 2, 2002

III. UNITED STATES ENVIRONMENTAL PROTECTION AGENCY, REGION IX JOHN D. CHESNUTT, REMEDIAL PROJECT MANAGER COMMENTS DATED AUGUST 2, 2002

The U.S. Environmental Protection Agency (EPA) has completed its review of the subject document and submits the following comments:

General Comments:

Comment 1: **Sampling locations: The draft plan includes provisions for air sampling at four fixed (one upwind and three downwind) and one mobile locations. EPA's concerned that if the smoke plume partially or altogether misses the three downwind fixed locations, the Army could obtain only one significant sample (the mobile location) from impacted areas and would therefore fail to meet plan objectives. The number and type (fixed vs mobile) of sampling locations should be reassessed.**

In addition, the text is somewhat inconsistent about how the locations likely to experience smoke impacts will be selected. In Section 4.7, page 21, it states that the locations will be based on observations from previous prescribed burn events. Section 5.2 describes how the locations will be installed in areas expected to be downwind of the burn based on a 48-hour meteorological forecast, as well as how the smoke dispersion modeling currently being conducted by the Monterey Bay Unified Air Pollution Control District may be used to help identify sampling locations. If the Army's burn prescription is designed to avoid the impacts of previous burns, then please explain how observations from the previous burn events will be useful in selecting sampling locations. The rationale for identifying downwind sampling locations needs to be clarified.

Response 1: The air sampling program has been expanded to include many more sampling locations than were proposed in the Draft SAP. Additional on-base locations and many more public (community) locations are now included in the program. With the additional spatial coverage, we expect that there will be more than adequate sampling representation under virtually any smoke dispersion pattern.

Comment 2: **Sampling frequency/duration: The 8-10 hour time weighted average (TWA) samples need to be clarified, especially in light of the projected 1 to 2 days fire duration (Draft Burn Plan, page 16). Are the fixed locations going to sample over the entire 1-2 day period with discreet 8-10 hour samples? Would it be better to do a 24 hour TWA sample at each location? Also, for the mobile sites, if the objective is to attempt to capture the heaviest smoke impacted areas, will they be readjusted each time period to capture the suspected highest smoke areas as the burn proceeds and smoke conditions change?**

Response 2: The TWA sampling is proposed for the period corresponding to the active burn period. If the burn cannot be completed in one day, then active ignition will stop until the next day. If the burn carries over into a second or third day, then air sampling will be repeated on each day of active ignition. The mobile station will be deployed to a location that will supplement the fixed sampling locations after smoke dispersion is observed on the day of the burn; the mobile station will not be moved once it is set up.

Comment 3: **Sampling instruments, methods, and analytes: The air sampling instrument procedures, analytical methods, and analyte summary discussions of Sections 6 and 7 lack the level of detail typically found in a Superfund Sampling and Analysis Plan/Quality Assurance Project Plan. Please provide full instrument and method quality assurance/control details for EPA review.**

Consideration should be made for including additional vegetation-related combustion compounds in the list of sampling analytes -- in particular certain smoke irritants for which the public and local agencies have voiced concern. In addition, consideration should be made for including dioxins/furans in the list of ordnance-related combustion analytes?

Response 3: A complete set of sampling and analytical methods, including associated QA/QC requirements, has been included in the Draft Final SAP. At the combined agency comment resolution meeting on August 8, 2002, it was agreed that sampling for aldehydes (including formaldehyde, acetaldehyde, and acrolein) and dioxins/furans was warranted and would be added to the scope of the sampling program.

Comment 4: **Coordinated sampling: EPA understands the Air District is also planning to collect air samples if a prescribed burn occurs at Ranges 43-48. EPA suggests the Army coordinate with the District and any other parties planning on sampling so as to maximize available resources and sampling locations/data.**

Response 4: Efforts are now underway to coordinate with the Monterey Bay Unified Air Pollution Control District to incorporate their available staff and equipment into the air sampling program.

<u>Specific Comments</u>:

Comment 1: **Sections 6.1, 6.2, 7.1, and 7.2: Please indicate the specific target analytes to be analyzed, and/or provide reference to Table 3.**

Response 1: This section has been completely revised and now references Table 3.

Comment 2: **Section 4.0: The Data Quality Objectives appear to be objectives more for monitoring than data quality. Please include more specific objectives for data quality.**

Response 2: Specific data quality objectives are included in the specific sampling and analytical methods which are now provided as Appendixes to the Draft Final SAP.

Comment 3: **Section 5.2, page 24: Assuming the Air District's modeling effort is completed in a timely manner, the text should state that the Army will, rather than may, work with the District to evaluate how the modeling could aid in the identification of**

potential sampling locations.

Response 3: "May" has been changed to "will."

Comment 4: **Section 6.1, page 26: The specific sorbent sampling media to be used should be identified in the plan. The example described, the OVS tubes, is understood to be used for indoor sampling. Are OVS tubes adequate for outdoor use?**

Response 4: This method is no longer proposed.

Comment 5: **Section 6.2, page 26: The section should describe provisions to seal off or isolate exhaust fumes of the propane-fueled generators from the samplers to avoid cross-contamination.**

Response 5: Actions to minimize possible cross-contamination from generator exhaust are now discussed.

Comment 6: **Section 6.3, page 26: The section should describe how the MIE DataRAM monitor will be calibrated to local conditions.**

Response 6: A Standard Operating Procedure (SOP) is now included for the MIE DataRAM.

RESPONSE TO COMMENTS ON THE DRAFT PRESCRIBED BURN AIR SAMPLING AND ANALYSIS PLAN RANGES 43-48, FORMER FORT ORD, CALIFORNIA, DATED JULY 2, 2002

IV. MIKE WHITE, USACHPPM COMMENTS DATED JULY 31, 2002

The U.S. Army Center for Health Promotion and Preventive Medicine reviewed the subject document on behalf of the Office of The Surgeon General and in accordance with the Memorandum Of Understanding between the U.S. Department of Defense and The Agency for Toxic substances and Disease Registry, U.S. Public Health Service. General and specific comments follow:

General Comments:

Comment 1: **The Burn Plan itself contains no reference to air sampling, other than on pp. 18-19 where it is mentioned that a comprehensive air monitoring program is planned. The details of this plan had yet to be worked out.**

Response 1: This comment is regarding the Burn Plan, not the Draft Air SAP.

Comment 2: **The air sampling and analysis plan contained a fine overall concept regarding the pollutant prediction models and objectives. However, the details for the actual sampling plan were vague. The main comment is that the overall sampling plan did not have very much information. Many more details (like a detailed protocol) should be prepared, including methods, meteorological data collection, number of samples, data analysis, etc.**

Response 2: The details regarding the sampling and analytical methods, number and location of samples, and QA/QC have now been included in the Draft Final SAP.

a. Energetics are typically analyzed with high-volume air samplers using polyurethane foam (PUF) as stated in the plan. However, the actual sampler stated to then be used was low-volume OSHA versatile sampler tubes. Which method will be used and must it meet EPA method requirements?

Response a: All sampling for energetics will be made using high-volume air samplers and PUF cartridges. The OSHA versatile sampler tubes will not be used.

b. PM_{10} and CO/CO_2 readings will be with direct reading instrumentation to determine if there were smoke-impacts. EPA methodology may be considered for PM_{10} measurements, also.

Response b: EPA methodology for PM_{10} sampling has been added to the air sampling program.

c. The description of sites, methods, QA, lab analysis needs much more information to describe what actually will be occurring.

Response c: The details regarding the sampling and analytical methods, number and location of samples, and QA/QC have now been included in the Draft Final SAP.

d. The number of samples (one upwind, one downwind at fuel break, three offsite downwind, one "mobile", and one duplicate) is very limited to allow much of any type of analysis. Ideally, enough data to be statistically significant should be collected. This probably not being feasible, I would think that a minimum of 5-10 samples per location would be better than only one burn with one sample....meaning that the data could be evaluated from 5 different burns on 5 different days to see if there is a trend or correlation with wind, etc. The results of the first burn could help determine what to do for the second burn, if more samples should be taken, etc. As far as each burn goes, the number of samples for each burn may be fine, however, the plan should detail the number of lab blanks, trip blanks, etc. and there should be collocated sampling performed at, at least a downwind site.

Response d: The number of sampling locations has been expanded considerably. Sampling will also be done on each day of the burn if more than one day is required to complete the burn. Details are now provided for lab QA/QC, trip blanks, and collocated sampling.

e. Recommend adding a section on the preliminary health risk assessment that will be conducted as part of the analysis plan. Pages 18-19 indicate that screening levels will be used for comparison to determine if further evaluation is necessary. However, even though this comparison is the stated purpose of the entire plan, little information is provided on exactly how this will be conducted. Recommend the section include the hierarchy of comparison values to be used to include reasons for selection above others (exposure duration, population, regulations, etc.).

Response e: Air screening levels are now included in the Draft Final SAP. If a health risk assessment is warranted based on the results of the air sampling program, then a separate work plan will be prepared for that effort and distributed for agency and public comment.

<u>Specific Comments</u>:

Comment 1: **Page v, Executive Summary. Recommend stating the purpose of the plan in the first paragraph. This is currently tucked into the last section.**

Response 1: Without the foregoing background and regulatory context, the purpose and scope of the air sampling plan would lack context.

Comment 2: **Page 4, 2.1.3, History of OE Use. The distinction between the use of the terms OE and UXO are unclear. The last two sentences of this section seem repetitive. Recommend defining usage to avoid confusion.**

Response 2: This language has been clarified.

Comment 3: **Page 6, 2.2.3, Risks from OE at Ranges 43-48. Isn't this section referring to UXO? Recommend clarifying that these hazards are physical, rather than chemical in nature.**

Response 3: This language has been clarified.

Comment 4: **Page 9, 2.4.1.2, Bang Box Studies. Were the emissions studies conducted at the Aberdeen Test Center considered for this plan? These studies, funded through the Army Environmental Center, sampled emissions specifically from some of the items listed in Section 2.2.2 and may be applicable here. They may be able to help address some of the limitations listed in section 2.4.1.4. Recommend contacting Ms. Tamera Rush at 410-436-6849 for additional information.**

Response 4: Yes, the Aberdeen Test Center data were reviewed. These data were very specific to the items being tested so it did not resolve the broader limitations as they applied to the wide variety of OE expected in Ranges 43-48.

Comments 5: **Page 11, Volatile Organic Compounds. What is MBUAPCD Rule 1000? Didn't see this spelled out. Recommend doing so for all acronyms.**

Response 5: The name of this rule has been added to the text where it is first called out. A list of acronyms has also been added to the Draft Final SAP.

Comment 6: **Table 3, Target Analytes. Recommend that chromium VI versus III be determined in the sample analysis. Screening values for CrVI are much more conservative and it will help in the screening analysis if these metals are speciated. Note: Per our air samplers Cr VI is probably not stable enough to analyze for as it reduces to Cr III almost immediately.**

Response 6: Per the note at the end of this comment, analyzing for Cr VI would not provide meaningful data. Analysis will be for total Cr.

RESPONSE TO COMMENTS ON THE DRAFT PRESCRIBED BURN AIR SAMPLING AND ANALYSIS PLAN RANGES 43-48, FORMER FORT ORD, CALIFORNIA, DATED JULY 2, 2002

V. MARK EVANS FEDERAL FACILITIES ASSESSMENT BRANCH, AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY (ATSDR) COMMENTS DATED JULY 31, 2002

The consultants are proposing a deterministic sampling plan, which implies that they know where they want to sample. As they are focusing on several adjacent neighborhoods, this seems like a reasonable assumption. However, the DQOs (section 4.0) present some potential issues that should be resolved.

Comment 1: **First, in sections 4.2 and 4.3, they have not identified the specific human health-based screening values that they propose as the basis for all subsequent decisions. These must be identified a priori. The sample design is only set up to assess time-weighted concentrations over the duration of the burn. As all health-based screening values will have a time component, they must ensure that they collect data over time periods compatible with the health standards. As designed, the sample plan does not allow for evaluation of acute exposures.**

Response 1: The proposed screening values are included in the Draft Final SAP. Short duration (e.g., 1-hour) samples are not practical for this program because of the expected low mass of many of the COPCs; a TWA sampling approach over the duration of the burn will be necessary to get laboratory reporting limits of the same order as the screening levels for these compounds. However, real-time monitoring of smoke signature compounds (PM_{10} and CO/CO_2) will support development of peak-to-mean ratios which can be used to estimate peak concentrations for those compounds sampled using a TWA method.

Comment 2: **Section 4.4, Identification of study boundary is based on visible smoke impacts. This assumes that all concentrations of the COPCs that may be of health concern will only be present in visible smoke. I am not sure this is a valid assumption.**

Response 2: "Visible" has been deleted to allow for other indicators of smoke impacts to be considered.

Comment 3: **Section 4.6, Specification of Limits on Decision Errors indicates that "confidence limits on decision errors are not applicable to this investigation." While, as stated, the overall sampling design is not random, there are still random aspects within the problem. Because the overall sampling design is not randomized, there is still sampling error which must be accounted for in the establishment of confidence limits. Ignoring such sampling error is simply assuming that all sample results are 100% accurate.**

Response 3: It is not expected that all sample results will be 100% accurate. The QA/QC requirements for each sampling and analytical method are included in the Draft Final SAP.

Comment 4: **Section 4.7, Optimization of Investigation Design for Obtaining Data states that "Also, because decisions will not be made using mean concentrations compared to the screening level...." is in fact false. The results will be made using time-weighted average values which are mean concentrations. Ultimately, health decisions will be made using this data and there needs to be some accounting for potential random and sampling errors. The sampling design, as established, is attempting to prove that the prescribed burns will not result in any adverse health effects to adjacent neighborhoods. Based on probable health-based screening values and distances to those neighborhoods, adverse health effects are unlikely. However, sampling never does a good job trying to prove a negative. A better approach to the sampling may be to determine the distance from the burns that plume concentrations will be above health comparison values.**

Response 4: TWA concentrations are not mean concentrations in the context of of this DQO requirement. This program does not rely on mean concentrations (the mathematical mean of multiple individual samples) for decisions. The sampling program is biased toward finding maximum values relative to the appropriate screening levels for the COPCs. There are specific QA/QC criteria for each sampling and analytical method. The proposed sampling approach is intended to test the conclusion that OE-related emissions will be inconsequential downwind of the burn; it is not intended to prove that prescribed burns will not result in any health effects to adjacent neighborhoods. Vegetation-related smoke compounds will be sampled to assess the adequacy of the burn prescription in minimizing downwind smoke impacts.

Comment 5: **Specifically, the sampling data should focus on calibrating an air dispersion model which could be used for subsequent predictions. Towards that end, I would like to highlight the recommendations contained within the ATSDR Health Consultation on the Former Fort Ord Site (August 24, 2001) which are as follows:**

1) **Acquire adequate source and sampling location information to better compare the sampling results with the model output.**

2) **Acquire better source description to determine the maximum downwind impact zones of such fires; this includes areas burned per hour and temperature of fire.**

3) **Plan to locate the samplers 200-300 meters downwind and move them in accordance with model predictions for each day.**

4) **Consider sampling equipment that collects sector-specific data, eliminating samples taken when the wind is blowing toward the fire (and keeping samples when the wind is blowing from the fire).**

Response 5: Calibrating an air dispersion model is not one of the stated goals of the air sampling program. Nonetheless, the collected data will provide a substantial data set for such a model calibration effort.

RESPONSE TO COMMENTS ON THE DRAFT PRESCRIBED BURN AIR SAMPLING AND ANALYSIS PLAN RANGES 43-48, FORMER FORT ORD, CALIFORNIA, DATED JULY 2, 2002

VI. ROBERT D. FLETCHER, CHIEF PLANNING AND TECHNICAL SUPPORT DIVISION AIR RESOURCES BOARD COMMENTS DATED AUGUST 7, 2002

ARB staff has reviewed the Draft Sampling Plan and finds that it lacks the detail of a comprehensive sampling plan. We believe the Draft Sampling Plan should be strengthened to provide greater assurance of the accuracy and validity of the resulting sampling data. The following are our recommendations for improvement.

Comment 1: **State clearly the specific objectives of the sampling plan, and the roles and responsibility of all sampling personnel and agencies.**

Response 1: This has been added in Section 5.1 of the Draft Final SAP.

Comment 2: **Provide the specific sampling locations, the basis for selecting each site, stated sampling objectives, and detailed site maps; also specify the locations for collocated sampling and the siting criteria.**

Response 2: This has been added to the Draft Final SAP.

Comment 3: **Address specific data quality parameters, including a description of the expected level of completeness, level of accuracy expected for sampling and analysis, and the spatial scale of representativeness for upwind and downwind monitoring locations.**

Response 3: Detailed sampling and analytical methods have been included in the Draft Final SAP. Because this sampling program is biased to characterize maximum downwind concentrations, spatial representativeness is not applicable.

Comment 4: **Describe equipment management, including flow verification, calibration, analytical quality control, and the specific equipment to be used, including model number; indicate whether flow audits will be conducted on the samplers before, during, or after sampling using traceable flow standards.**

Response 4: Detailed sampling and analytical methods have been included in the Draft Final SAP. Specific equipment is listed as a manufacturer and model number "or equivalent."

Comment 5: **Describe the sampling methods and how they compare with federal reference methods.**

Response 5: The sampling methods are included as Appendixes in the Draft Final SAP, and include references to specific EPA methods where applicable.

Comment 6: **Discuss sampling duration and interval with consideration for local meteorological conditions.**

Response 6: This has been added to the Draft Final SAP.

Comment 7: **Include details on the sample media preparation, field and trip blanks, and chain of custody considerations.**

Response 7: This has been added to the Draft Final SAP.

Comment 8: **Include a complete set of sampling, equipment, and data transfer forms and procedures.**

Response 8: This has been added to the Draft Final SAP.

Comment 9: **Include or reference a laboratory Standard Operating Procedure to support evaluation of what Quality Control will be used.**

Response 9: This has been added to the Draft Final SAP.

Comment 10: **Discuss how deviations from the stated sampling protocol will be managed and decided.**

Response 10: This has been added to the Draft Final SAP.

We also reviewed the list of proposed sampling devices and sample analysis methods and have some questions about some of the proposed sampling instruments and analytical methods. We would appreciate an opportunity to discuss these with you to understand better their appropriateness for achieving the stated objectives.

Response: A combined agency comment resolution meeting was held at Fort Ord on August 8, 2002, to discuss the overall goals and objectives of the air sampling program. The Draft Final SAP has been revised to reflect the consensus opinion regarding modifications to the sampling scope, including sampling for specific vegetation-related compounds.

We also suggest that you consider incorporating toxic air contaminant (TAC) monitoring and analysis in the Draft Sampling Plan since the greatest health risks are associated with TACs. Although other information (POLU13 model run and BangBox studies) indicates that TAC levels would be de minimus, TAC monitoring would document actual TAC levels and address any concerns from nearby receptors.

Response: OE-specific TACs are included in the air sampling program. Selected vegetation-related TACs are now included as well. Sampling for other TACs would not support the specific goals of the study as agreed during the combined agency meeting on August 8, 2002.

DISTRIBUTION

Final
Prescribed Burn Air Sampling
and Analysis Plan
Ranges 43-48
Former Fort Ord, California

July 8, 2003

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Sacramento District Corps of Engineers
1325 J Street
Sacramento, California 95814-2922

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Quality Control Reviewer

Donald R. Smallbeck
Senior Principal

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