Richmond Field Station

University of California, Berkeley

RICHMOND FIELD STATION
AIR QUALITY SAMPLING AND ANALYSIS PLAN

Prepared for:

RICHMOND FIELD STATION
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA

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DECEMBER 12, 2007

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1.0 INTRODUCTION

Tetra Tech EM Inc. (Tetra Tech) has prepared this air quality sampling and analysis plan (SAP) to describe the procedures that will be used to collect quality-assured data for an air quality study at the Richmond Field Station (RFS), in accordance with the statement of work (SOW) submitted to RFS by Tetra Tech on September 17, 2007. Data obtained from sampling and analysis will be used by RFS to evaluate the relative level of health risk present inside select buildings on the RFS campus. The sampling approach will be focused on collecting air samples to assess findings reported in the document titled *Evaluation of Exposure to Contaminants at the University of California, Berkeley, Richmond Field Station, 1301 South 46th Street*, prepared by California Department of Public Health (CDPH).

Tetra Tech will install 12 indoor and outdoor air sampling stations at the RFS and the University of California (UC) Berkeley main campus to evaluate airborne concentrations of volatile organic compounds (VOC), particulate metals, and carbonyl compounds. Locations were identified during a site walk conducted with UC Berkeley staff on October 24, 2007. Each sampling station will be configured to collect air samples for a continuous 24-hour sample period. The first sample event is scheduled for October 25 - 26, 2007, and subsequent samples will be collected twice per month until eight samples from each location have been collected. Additional quality assurance samples consisting of duplicate and field blank samples will also be collected.

Each set of samples will be analyzed for the following constituents of concern:

- Formaldehyde
- Trichloroethylene (TCE)
- Tetrachloroethylene (PCE)
- Dichloroethylene (DCE)
- Vinyl chloride
- Benzene
- Methylene chloride
- 1,2-Dichloroethane (1,2-DCA)
- Chloroform
- Arsenic

Each sample will be collected, handled, stored, and analyzed using the following U.S. Environmental Protection Agency (EPA) Compendium Methods:

- *EPA Compendium Methods TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) (Active Sampling Method)*

- *EPA Compendium Methods TO-15: Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed By Gas Chromatograph and Mass Spectrometry(GC/MS)*

- *EPA Compendium Methods IO-3.3: Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectroscopy (XRF)*

This SAP/QAP provides information on the installation, calibration, and operational procedures for the 12 air quality sampling stations, as well as expectations and recommendations for the collection of quality assured data. All sample collection and handling will be performed by qualified Tetra Tech air sampling personnel, and project oversight will be performed by a certified industrial hygienist (CIH).

Section 2.0 describes the proposed air sampling locations, site history and current uses, nearby populations, and air quality influences. Section 3.0 discusses the installation, calibration, and operational schedule of the air quality sampling stations. Section 4.0 discusses the sampling methodology and sampling equipment specifications. Section 5.0 presents the data and quality assurance (QA) objectives program for the air quality study. References cited in this document are listed in Section 6.0.

2.0 SITE DESCRIPTION

The RFS property is owned by the Regents of the University of California and is located at 1301 South 46th Street in Richmond, California, in western Contra Costa County. RFS is situated south and west of Highway 580, approximately 5 miles northwest of UC Berkeley's main campus. The property consists of teaching and research facilities in upland areas, a tidal salt marsh, and a transition zone between the upland areas and the marsh. The RFS property currently accommodates a range of UC research facilities, including the Earthquake Engineering Research Center of the College of Engineering, and the UC Northern Regional Library; and some non-University lessees, such as the U.S. EPA Region 9 Laboratory.

The RFS property is 152 acres, consisting of 100 acres of uplands, with the remainder of the property (offshore areas) consisting of tidal marsh or bay lands. The climate is characterized as Mediterranean. The average annual precipitation in the area is 22 inches. Precipitation occurs mostly in the winter, with January being the month that typically receives the most rain. Within a 1-mile radius of RFS are residences, public areas, and commercial and industrial facilities. The upland portion of the RFS property is adjacent to vulnerable or sensitive animal populations and habitats and natural resources, including a tidal salt marsh and coastal terrace prairie.

The adjacent property to the east of RFS is the location of a former chemical production facility previously owned by several entities, including Stauffer and Zeneca, and is currently owned by Cherokee Simeon Venture (CSV). The former Liquid Gold Corporation site is located east of the former Zeneca site. Hoffman Marsh and Point Isabel are slightly farther to the east, approximately 1.5 miles from RFS.

Richmond Inner Harbor, Stege Marsh, and the central San Francisco Bay border the RFS property to the south. Marina Bay, a mixed-use residential and commercial development, lies adjacent to the southwest border of RFS. Marina Bay consists of approximately 350 acres with 2,100 residential units. The Bay Trail, on the former Southern Pacific Railroad right-of-way, is near the property to the south. Tidal mudflats fronting the Richmond Inner Harbor are located further south of the RFS.

The City of Richmond, with an estimated population of 100,000, is beyond the adjacent property boundaries to the north, west, and east. The East shore neighborhood of Richmond is the closest residential community to the site, and is located approximately 1,000 feet to the north, on the north side of I-580.

3.0 INSTALLATION, CALIBRATION, AND OPERATIONAL SCHEDULE

Tetra Tech staff will be on site for 1 to 2 days to meet with RFS site personnel, locate and install the temporary sampling stations, and perform initial calibrations on the sampling devices. Each station will be configured to collect samples, and all samples will be started manually. After the initial sample collection, Tetra Tech staff will return to the site to remove the samples. This process will be repeated for all eight sample collection efforts over the duration of the 4-month sample period. At the completion of the project, Tetra Tech staff will disassemble and remove the stations and all sampling equipment.

The initial sample collection was scheduled to run continuously from approximately 12:00 noon October 25, 2007, to 12:00 noon October 26, 2007. The exact sample locations were determined during an on-site tour and evaluation on October 24, 2007. The sample locations, as shown on Figures 3 - 8, are as follows:

- Station 1 at Building 155: one interior office location
- Stations 2, 3, and 4 at Building 163: two indoor locations, an office and a hallway, and one outdoor location along the eastern side of the building
- Stations 5 and 6 at Building 175: one interior location in the main foyer, and one rooftop location
- Station 7 at Building 177: one interior office location
- Stations 8, 9, and 10 at Building 478: three interior locations (an office, foyer, and lunchroom)
- Station 11 (RFS background): one location along the RFS fence line in the upwind direction of the prevailing winds on the sample date
- Station 12 (regional reference): one location at the main campus located in Berkeley, California

Each sampling station will be outfitted with a platform for placement of the air samplers and the electrical connections to power instrumentation. All sampling stations will be set up temporarily, and equipment will be removed after completion of each sample event and stored in a secure location.

The initial site visit and first sample event were scheduled for October 24 to 26, 2007, and subsequent sample events will be completed approximately twice per month thereafter until eight sample events have

been completed. A contingency plan has been developed to address possible equipment failures: If a sample fails to complete 75 percent of the 24-hour sample period, the sample will be voided. A makeup or replacement sample will be collected prior to the next scheduled sample event. Table 4 outlines the proposed project schedule.

After receipt of laboratory results, Tetra Tech will prepare a summary report of results and findings. The report will be submitted to UC Berkeley within 2 weeks of the date when Tetra Tech receives the final laboratory results. All samples will be submitted to laboratories with the standard turn-around time (TAT) of 10 days. Once received from the laboratory, all data results will be reviewed by the Tetra Tech Task Manager and CIH. If any anomalies are identified in the laboratory results, the Tetra Tech Project Manager will be contacted, and the results will be further investigated. After completion of laboratory review, the laboratory reports will be provided electronically to UC Berkeley via email, and hard copies will be provided with the summary report.

TABLE 1

PROPOSED PROJECT SCHEDULE

Date	Task Deadline
October 24-26, 2007	Site visit by Tetra Tech with RFS personnel, selection of air sample stations, and completion of first sampling event
November 5-6, 2007	Completion of second sampling event
November 28-29, 2007	Completion of third sampling event
December 11-12, 2007	Completion of fourth sampling event
December 18-19, 2007	Completion of fifth sampling event
January 8-9, 2008	Completion of sixth sampling event
January 22-23, 2008	Completion of seventh sampling event
February 5-6, 2008	Completion of final sampling event
March 31, 2008 (tentative)	Air sampling summary report submitted to RFS

4.0 METHODOLOGY AND EQUIPMENT SPECIFICATIONS

Tetra Tech will install 12 indoor and outdoor air sampling stations at RFS and the UC Berkeley main campus to evaluate airborne concentrations of VOCs, particulate metals, and carbonyl compounds. Exact locations were determined during a site-walk evaluation on October 24, 2007. Each sampling station will be configured to collect air samples for a continuous 24-hour sample period. The first sampling event was scheduled for October 25 - 26, 2007, and subsequent samples will be collected twice per month until eight samples from each location have been collected (Table 1). Additional quality assurance samples will also be collected and consist of duplicate and trip blank samples. Duplicate (or co-located) and field blank samples will be collected at Building 163, location 2, for each of the eight sample events. The duplicate sample will consist of collecting two samples at the same location using duplicate samplers or collocated sample media using one sample pump or orifice. One sample will serve as the primary sample and one will serve as the duplicate. Field blank samples will also be collected at a rate of one per sample event and consist of transporting sampling media or apparatus to a designated location, opening the media, placing in the sampler and removing (where applicable). The blank sample is then removed, stored, and shipped with samples to respective laboratories.

Each set of samples will be analyzed for following constituents of concern:

- Formaldehyde
- Trichloroethylene (TCE)
- Tetrachloroethylene (PCE)
- Dichloroethylene (DCE)
- Vinyl chloride
- Benzene
- Methylene chloride
- 1,2-Dichloroethane (1,2-DCA)
- Chloroform
- Arsenic

Each sampling station will be configured with the following air sampling equipment and sample media:

- One Airmetrics Inc. Mini-Vol air sampler configured with omni-directional inlet, particulate matter less than 10 microns (PM_{10}) impactor, and 47-millimeter (mm) Teflon filter media for metals analysis

- One selective ion monitoring (SIM)-certified Summa canister VOC sampler and SIM-certified 24-hour flow controller

- One SKC Inc. low-volume pump with 2,4-dinitrophenylhydrazine (DNPH)-coated silica gel adsorbent (formaldehyde) cartridge

All samplers will be operated according to EPA guidance, National Institute of Occupational Safety and Health (NIOSH) standards, or Occupational Safety and Health (OSHA) methods. All sampling devices are equipped with timers, flow controllers, and pressure gauges to document sample time, as well as flow and vacuum pressure during sample collection.

Each sample will be collected, handled, stored, and analyzed using the following EPA Compendium Methods:

- *EPA Compendium Methods TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) (Active Sampling Method)*
- *EPA Compendium Methods TO-15: Determination of Volatile Organic Compounds in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatograph and Mass Spectrometry(GC/MS)*
- *EPA Compendium Methods IO-3.3: Determination of Metals in Ambient Particulate Matter Using X-Ray Fluorescence Spectroscopy (XRF)*

Typically, indoor air samples are collected using NIOSH or OSHA-approved sampling methods; however, this air quality study requires lower detection limits and more accurate results. The following NIOSH methods have been cross-referenced to ensure sample collection methods proposed in this SAP/QAP will meet or exceed the corresponding NIOSH sample requirements:

- *NIOSH Method 7900 – Arsenic and compounds, as arsenic (As)*
- *NIOSH Method 2016 – Formaldehyde*
- *NIOSH Method 1501 – Aromatic Hydrocarbons*

Each air sampling station will be outfitted with a sample platform, and samplers will be secured on the platform. Sampler inlets will be positioned at breathing height, approximately 5 feet above ground or floor surface. Samplers will be started and stopped manually, and the start-stop times and timer readings will be recorded on field data summary sheets. Sample start times will vary based on sample location. In general, sample events will be started between 10:00 AM and 2:00 PM, and will sample continuously for

a minimum of 24 hours. Samplers will be stopped and samples retrieved after the 24-hour sample period. All sample data will be recorded on field data sheets. Sampling equipment will then be returned to a temporary storage location, and samples will be prepared for shipment to respective laboratories.

Chain-of-custody (COC) forms and Federal Express labels will be completed and copies of all documents will be made and kept on site. Summa canisters and formaldehyde samples will be shipped to Air Toxics Ltd. Arsenic samples will be shipped to Desert Research Institute. Analytical results from the respective laboratories will be sent to Tetra Tech electronically, via pdf, and in hard copy. Sampling parameters are summarized in Table 2. Upon the completion of all eight rounds of sampling, the analytical results will be compiled into a report, along with a summary overview of the field efforts. The sampling data will be evaluated against occupational screening values, as well as compared to other previously identified values (California Department of Public Health). Occupational health, and other comparison values are presented in Table 3.

Table 2
Air Sampling Parameters
Richmond Field Station Air Quality Study

Chemicals of Concern	Sample Equipment Specifications	Sample Media	Duration of Sample Collection	Sample Holding Time	Method of Sample Analysis	Target Detection Limit
Formaldehyde	SKC sampler @ 1 liter/min. flow rate	Adsorbent cartridge (coated with DNPH)	24 hours	7 days	EPA TO-11A SIM	0.03 µg/m^{3a}
Benzene	Summa Canister with 24-hr. flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO - 15A SIM	0.05 ppbv
Chloroform	Summa Canister with 24-hr flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO - 15A SIM	0.02 ppbv
Dichloroethylene (DCE)	Summa Canister with 24-hr flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO - 15A SIM	0.01 ppbv
1,2 dichloroethane (1,2 DCA)	Summa Canister with 24-hr flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO - 15A SIM	0.02 ppbv
Methylene Chloride	Summa Canister with 24-hr flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO - 15A SIM	0.2 ppbv
Tetrachloroethylene (PCE)	Summa Canister with 24-hr flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO - 15A SIM	0.003 ppbv
Trichloroethylene (TCE)	Summa Canister with 24-hr flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO-15A SIM	0.003 ppbv
Vinyl Chloride	Summa Canister with 24-hr flow regulator	6-Liter Summa Canister	24 hours	14 days	EPA TO - 15A SIM	0.01 ppbv
Arsenic	Airmetrics Mini-Vol Sampler @ 5 liters/min. flow rate	47-mm Teflon filter	24 hours	14 days	EPA IO 3.3 (XRF)	1.7 e-4 µg/m^{3b}

Notes:

[a] Assumes sample flow rate of 1 liter per minute and 24-hour sample. Actual volume and detection limit may vary slightly.

[b] Assumes sample flow rate of 5 liters per minute and 24-hour sample. Actual volume and detection limit may vary slightly.

Table 3

Occupational Health and Other Comparison Values

Chemicals of Concern	OSHA PEL ($\mu g/m^3$)	CAL-OSHA PEL ($\mu g/m^3$)	NIOSH REL ($\mu g/m^3$)	ACGIH TVL ($\mu g/m^3$)	OEHHA REL ($\mu g/m^3$)	ATSDR CREG ($\mu g/m^3$)	EPA, Region 9 PRG ($\mu g/m^3$)	ATSDR MRL ($\mu g/m^3$)
Formaldehyde	920.6	920.6	19.68	368.2	94 (acute) 3 (chronic)	0.08	--	40
Benzene	3.19e4	3190	319	1590	60	0.10	--	160
Chloroform	2.43e5	9700	9780 (60 min.STEL)	4.87e4	300	0.04	--	--
Dichloroethylene (DCE)	3.96e5	3.96e3	--	--	--	--	--	--
1,2 Dichloroethane (1,2 DCA)	2.02e5	4040	4000	--	--	--	--	--
Methylene Chloride	8.67e4	8.67e4	--	1.73e5	--	3.0	4.1	--
Tetrachloroethylene (PCE)	6.77e5	1.69e5	--	1.69e5	35	--	270	0.32
Trichloroethylene (TCE)	5.37e5	1.34e5	1.34e5	5.37e4	540	--	0.017	--
Vinyl Chloride	2600	2600	--	2550	--	--	--	--
Arsenic	500	10	--	10	0.19 (acute) 0.03 chronic)	0.0002	--	--

-- None available.
OSHA PEL: Occupational Safety and Health Administration, Permissible Exposure Level
CAL-OSHA PEL: California Occupational Safety and Health Administration, Permissible Exposure Level
NIOSH REL: National Institute for Occupational Safety and Health, Recommended Exposure Level
ACGIH TVL: American Conference of Governmental Industrial Hygienists, Threshold Limit Values
OEHHA REL: Office of Environmental Health Hazard Assessment, Reference Exposure Level
ATSDR CREG: Agency for Toxic Substances and Disease Registry, Cancer Risk Evaluation Guide for 1 in 1,000,000 increased cancer risk
EPA, Region 9 PRG: U.S. Environmental Protection Agency Region 9, Preliminary Remediation Goal, based upon cancer endpoint (levels reflect 1 in 1,000,000 increased cancer risk, considered no apparent risk)
ATSRD MRL: Agency for Toxic Substances and Disease Registry, Chronic Minimal Risk Level

5.0 QUALITY ASSURANCE PROGRAM

A quality assurance (QA) program ensures that all installation, setup, and calibration procedures are followed to collect data of the highest quality. The following sections discuss the project data quality objectives, equipment calibration and data validation procedures, and identification of responsibilities.

5.1 DATA QUALITY OBJECTIVES

Air quality data obtained from this sampling effort will be used to address data inconsistencies identified in the CDPH document, *Evaluation of Exposure to Contaminants at the University of California, Berkeley, Richmond Field Station, 1301 South 46th Street*. The QA objective of this sampling project is to collect quality-assured data that can be used to make informed decisions regarding air quality in and around the RFS.

The following tasks will be performed to achieve project data quality objectives:

- Initial equipment installation and calibration
- Pre-sampling and post-sampling calibration of all sampling equipment
- Review of equipment-specific standard operating procedures (SOP)
- Completion of all field sample documentation sheets
- Completion of laboratory COC forms
- On-site storage of copies of all documentation

5.2 EQUIPMENT CALIBRATION

Calibration and equipment checks will be performed according to manufacturers' specifications and recommendations to ensure data quality and minimize the occurrence of invalid data due to equipment malfunction or error. Where applicable, air sampling equipment will be calibrated at the beginning and end of each sample period. Any required adjustments or discrepancies will be noted.

Records of all site maintenance, operational, and calibration activities will be maintained in a site logbook or field log sheets. At a minimum, the following information will be recorded:

- Date and time of the sample start and sample stop
- Sample location

- Sampler serial number
- Filter media identification number
- Summa canister and flow controller serial numbers
- Documentation for duplicate and field blank samples
- Name of calibration person or team members
- Calibration method used
- Action taken and/or recommended

5.3 DUPLICATE SAMPLES AND FIELD BLANK SAMPLES

Duplicate (co-located) and field blank samples will be collected at Building 163, location 2, for each of the eight sample events. For the duplicate sample, two samples will be collected at the same location, either using duplicate samplers or co-located sample media using one sample pump or orifice. One sample will serve as the primary sample, and one will serve as the duplicate. Field blank samples will be collected at a rate of one per sample event and consist of transporting sampling media or apparatus to a designated location, opening the media, then immediately closing and removing. The blank sample is then removed, preserved, and shipped with routine samples to respective laboratories.

5.4 IDENTIFICATION OF RESPONSIBILITIES

Tetra Tech personnel are responsible for all aspects of this SAP/QAP. In the event of any equipment malfunction or breakdown during the operational period, Tetra Tech will take corrective actions to prevent additional breakdowns and loss of data.

Comments or issues regarding this SAP/QAP can be directed to the following personnel:

1) Douglas Herlocker (primary contact)
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3) Rick Ecord (secondary contact)
Certified Industrial Hygienist
Centennial Tower
101 Marietta Street, NW STE 2400
Atlanta, GA 30303
(404) 225-5527

6.0 REFERENCES

Air Toxics Ltd. Date unknown. "Guide to Canister Air Sampling and Analysis."

California Department of Public Health. Date Unknown. 2007. "Evaluation of Exposure to Contaminates at the University of California, Berkeley, Richmond Field Station, 1301 South 46th Street."

SKC Inc. Date Unknown. "Operating Instructions Universal Sample Pump Catalog No. 224-PCXR8."

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U.S. Environmental Protection Agency (EPA). 1999. "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 Spectroscopy (GC/MS)." Center for Environmental Research Information. Office of Research and Development. U.S. EPA. January.

U.S. Environmental Protection Agency (EPA). 1999. "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)." Center for Environmental Research Information. Office of Research and Development. U.S. EPA. January.

U.S. Environmental Protection Agency (EPA). 1999. "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Second Edition. Compendium Method IO-3.3. Determination of Metals In Ambient Particulate Matter Using X-Ray Fluorescence (XRF) Spectroscopy." Center for Environmental Research Information. Office of Research and Development. U.S. EPA. June.

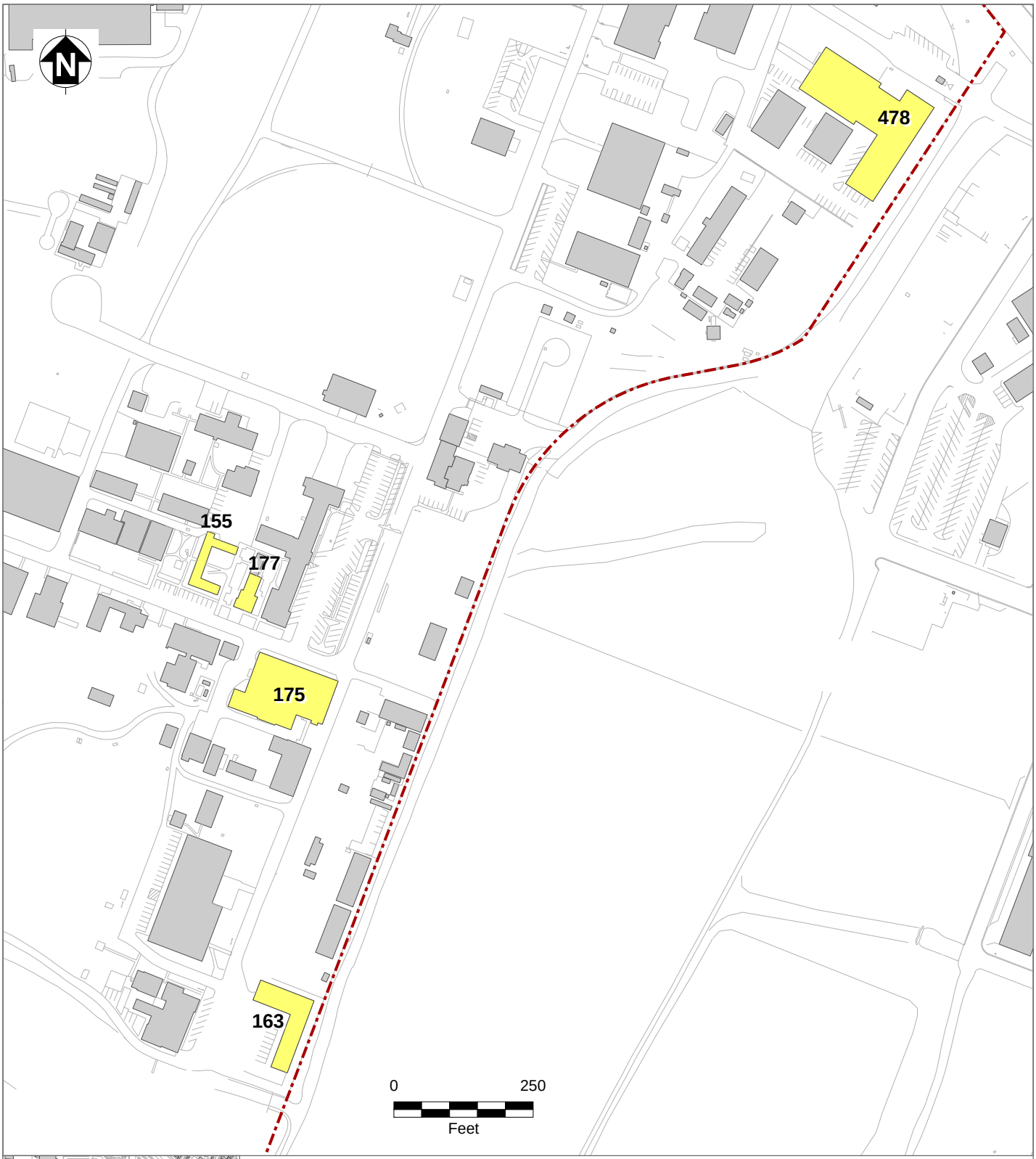
FIGURES

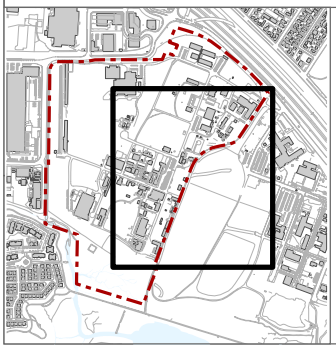
TETRA TECH EM INC.

Richmond Field Station
University of California, Berkeley

FIGURE 1
SITE LOCATION MAP

2007-10-17 V:\Misc_GIS\Richmond_Field_Station\Projects\Air_Sampling\Site_Location_Map_szA.mxd TtEMI-SF Kevin Ernst





Legend

- Buildings of Interest
- Other Buildings
- RFS Boundary
- Basemap

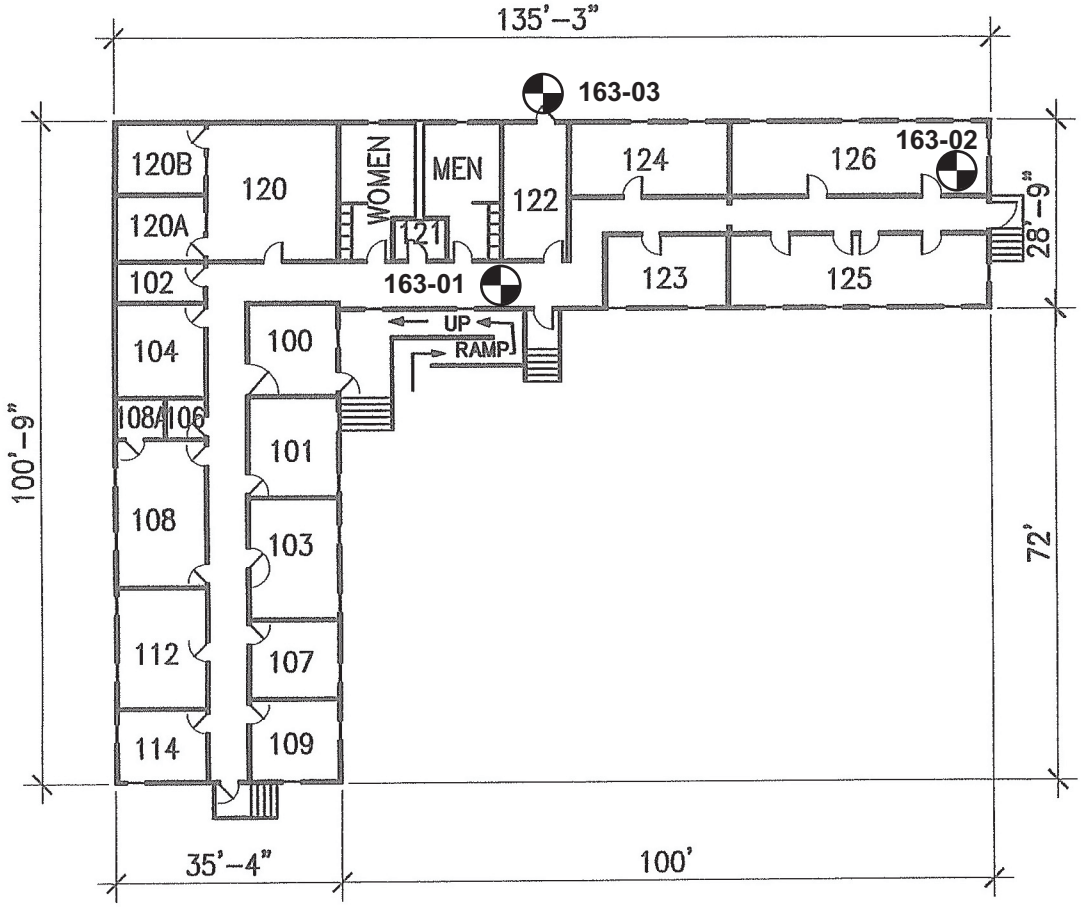
TETRA TECH EM INC.

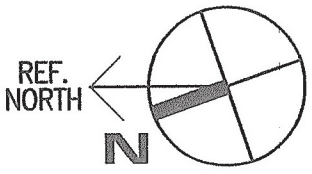
Richmond Field Station
University of California, Berkeley

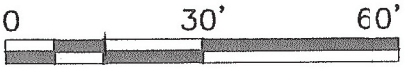
FIGURE 2

BUILDINGS 155, 163, 175, and 478

2007-10-17 V:\Misc_GIS\Richmond_Field_Station\Projects\Air_Sampling\Bldgs_air sampling_task08.mxd TtEMI-SF Kevin Ernst







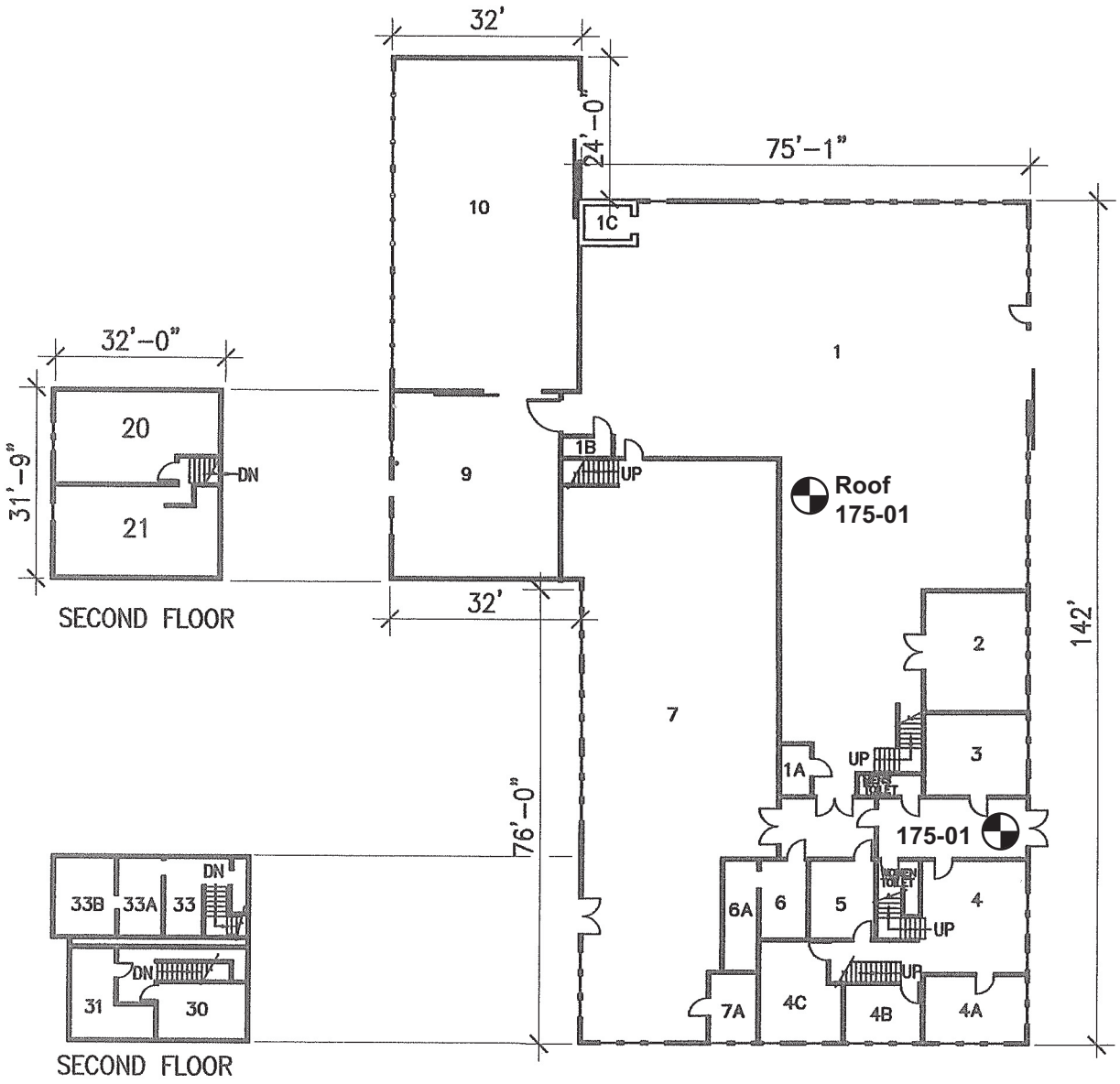
Air sampling location

TETRA TECH EM INC.

Richmond Field Station
University of California, Berkeley

FIGURE 3
BUILDING 163

Source: UC Berkeley Engineering Office, Revised October 17, 2000



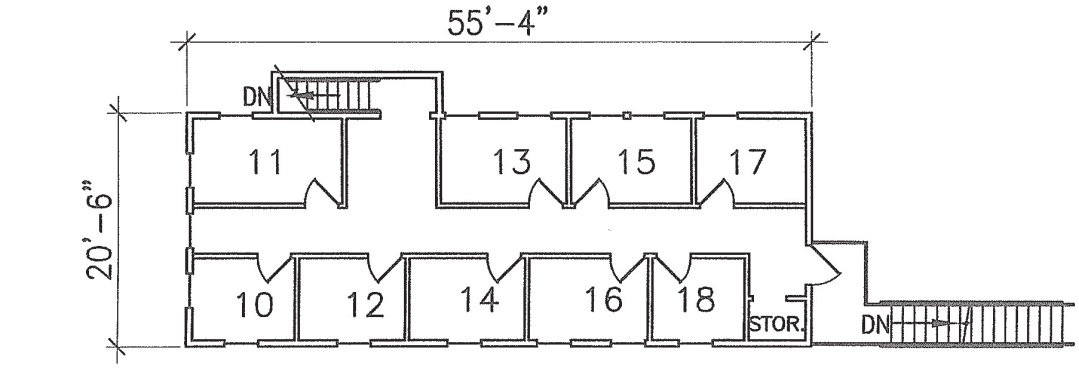
Air sampling location

TETRA TECH EM INC.

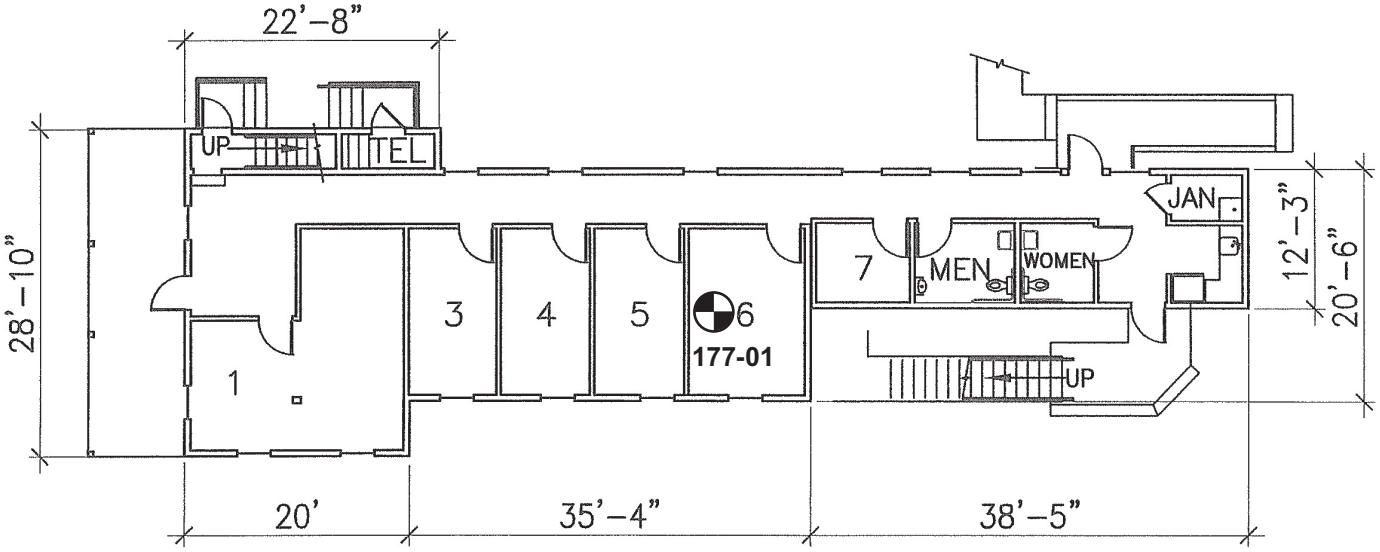
Richmond Field Station
University of California, Berkeley

FIGURE 4
BUILDING 175

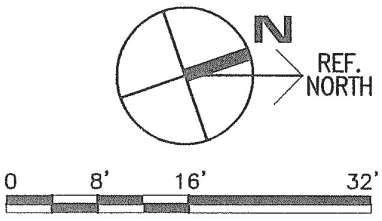
Source: UC Berkeley Engineering Office, Revised October 17, 2000



SECOND FLOOR



FIRST FLOOR



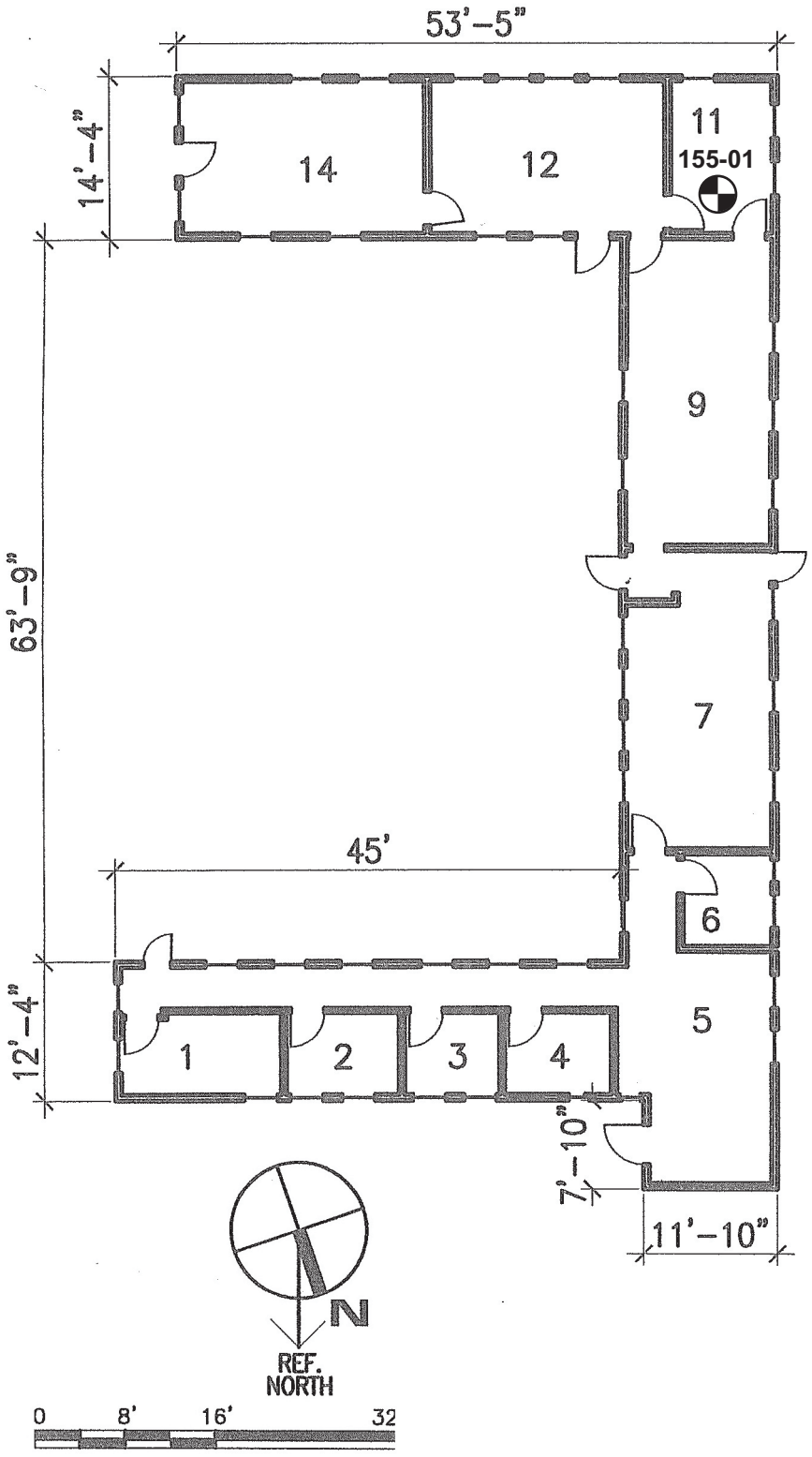
Air sampling location

TETRA TECH EM INC.

Richmond Field Station
University of California, Berkeley

FIGURE 5
BUILDING 177

Source: UC Berkeley Engineering Office, Revised November 9, 2000



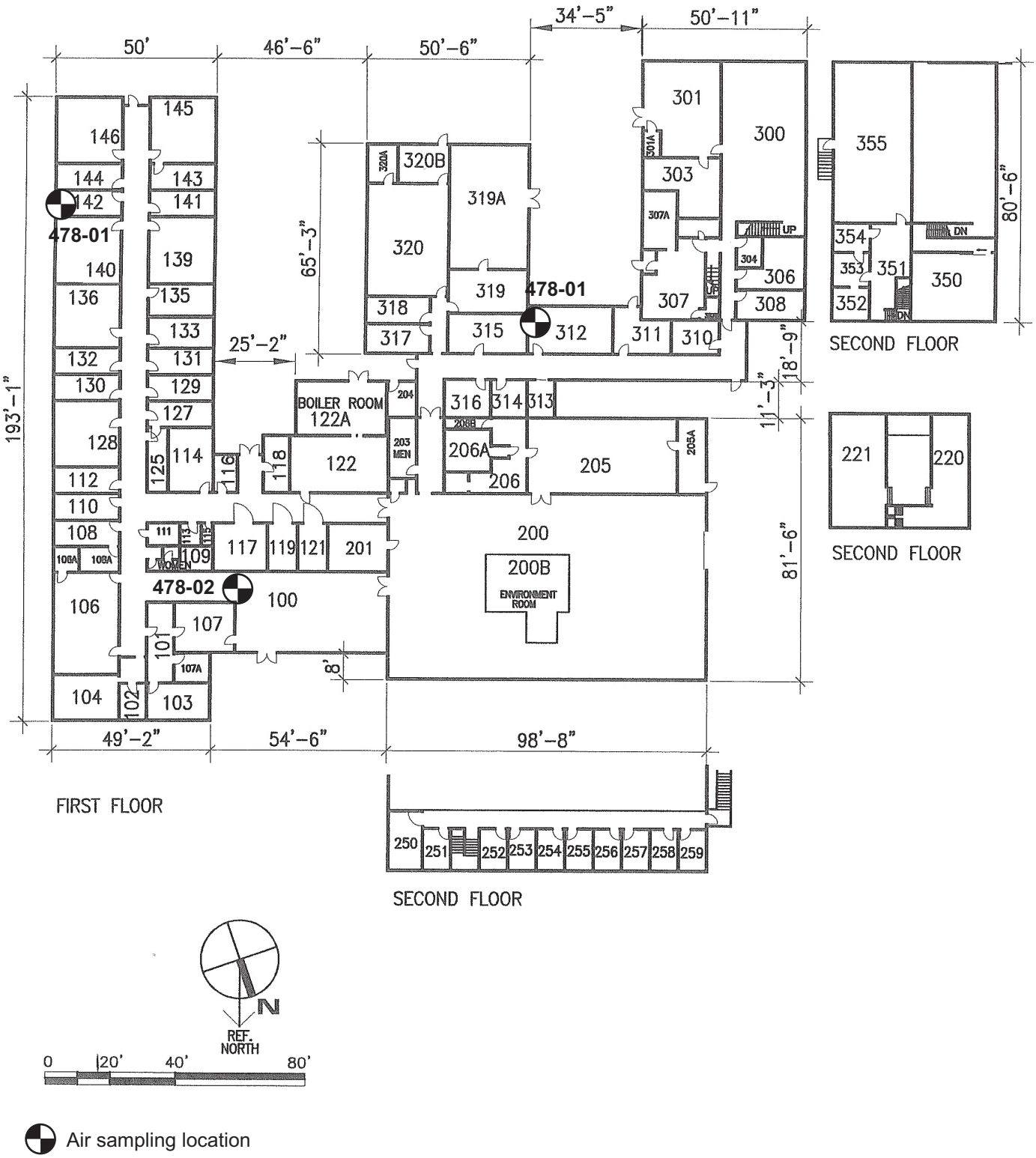
Air sampling location

TETRA TECH EM INC.

Richmond Field Station
University of California, Berkeley

FIGURE 6
BUILDING 155

Source: UC Berkeley Engineering Office, Revised September 24, 2002

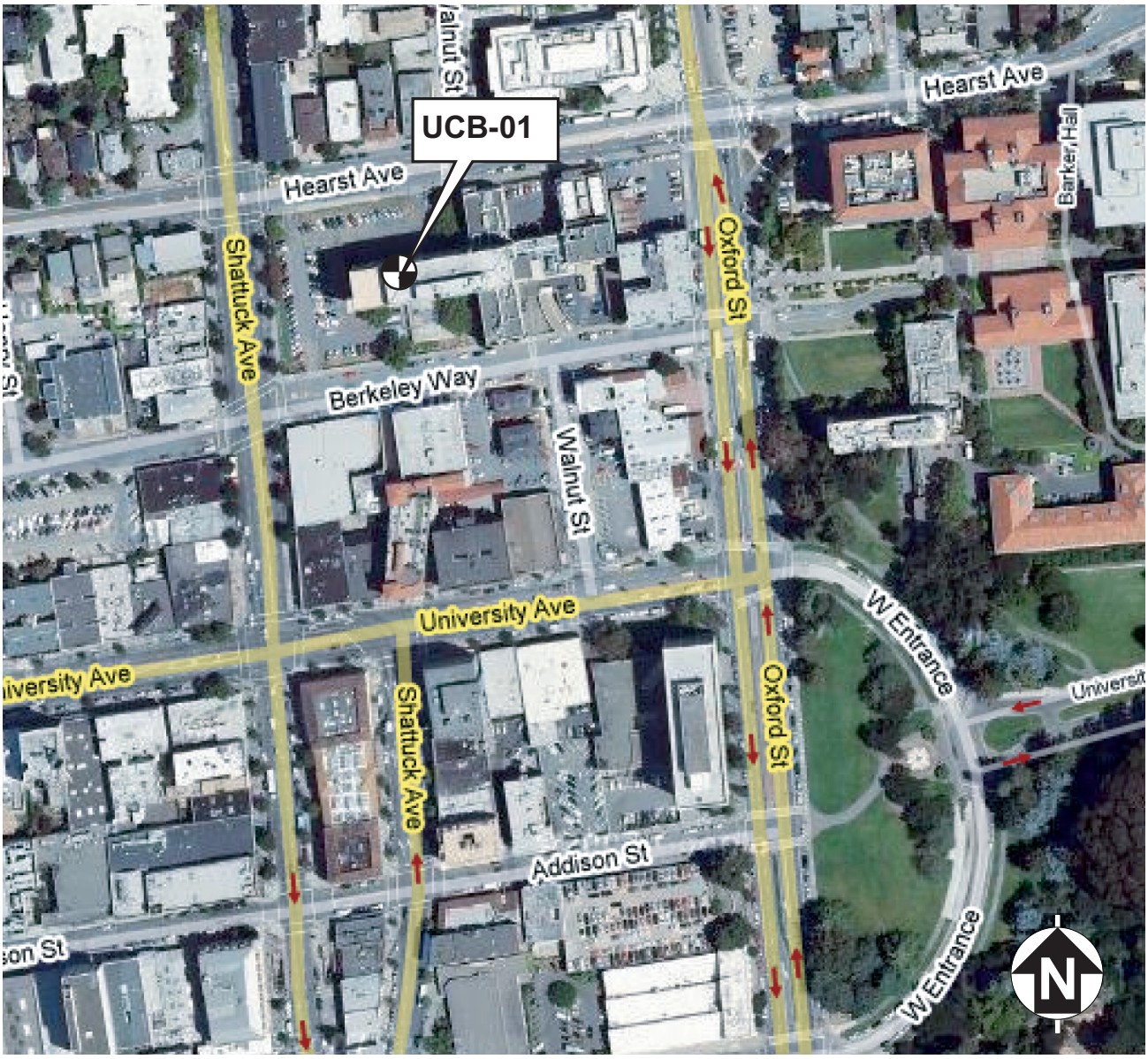


Source: UC Berkeley Engineering Office, Revised March 2, 2000

TETRA TECH EM INC.

Richmond Field Station
University of California, Berkeley

FIGURE 7
BUILDING 478



Source: Google Maps, 2007

Air sampling location

TETRA TECH EM INC.

Richmond Field Station
University of California, Berkeley

FIGURE 8
UCB MAIN CAMPUS
DHS BUILDING

APPENDIX A

EPA COMPENDIUM METHODS TO 11-A, TO-15, AND IO-3.3

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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Method TO-11 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-11 has been revised and updated as Method TO-11A in this Compendium to incorporate new or improved sampling and analytical technologies.

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

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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]

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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**:**

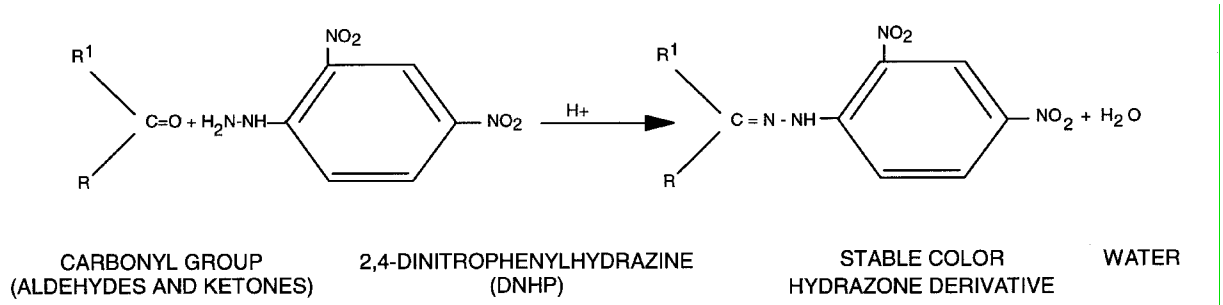
- Labor intense.
- Used acidic/hazardous reagents.
- Lacked sensitivity.
- Prone to interferences.
- Poor reproducibility at ambient concentration levels.

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.

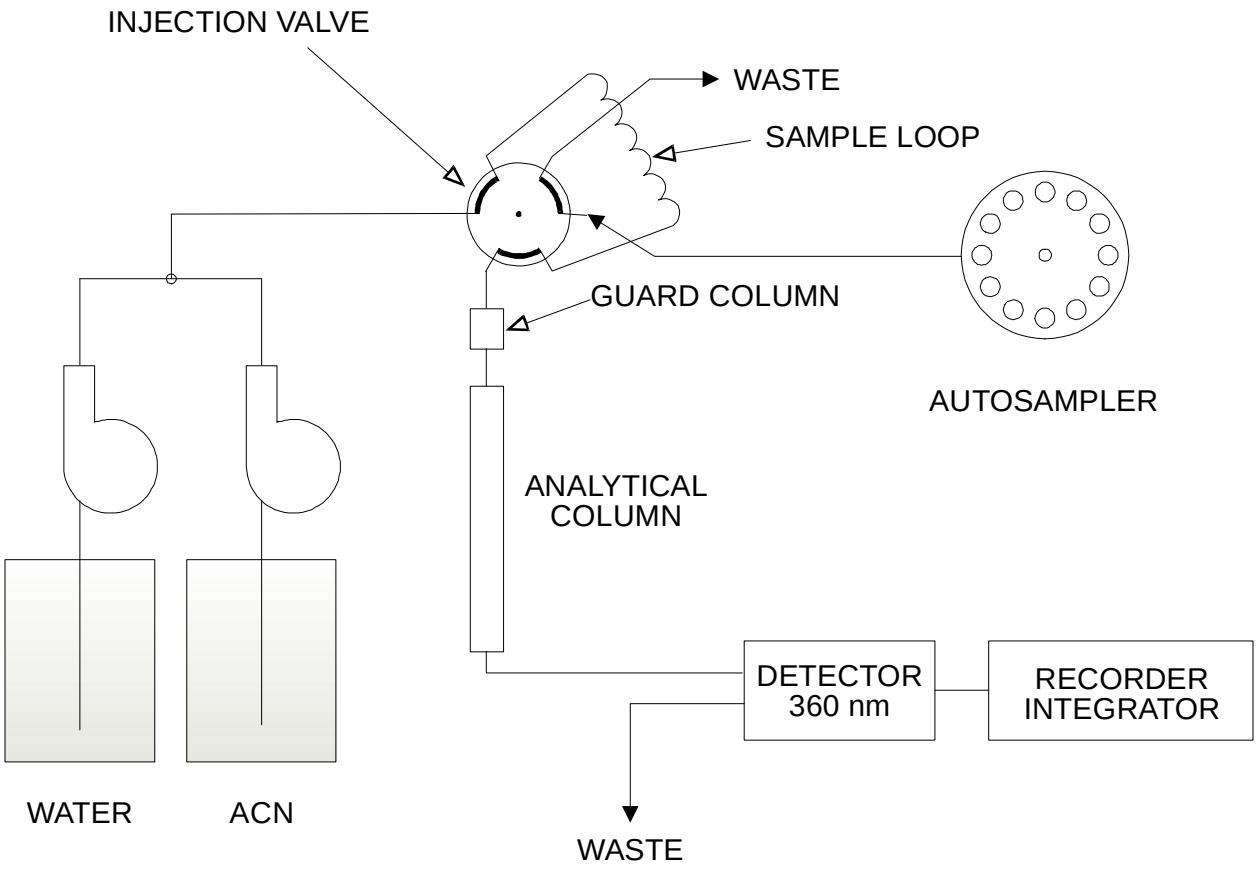


Figure 1. Basic high-performance liquid chromatographic (HPLC) system used for carbonyl analysis.

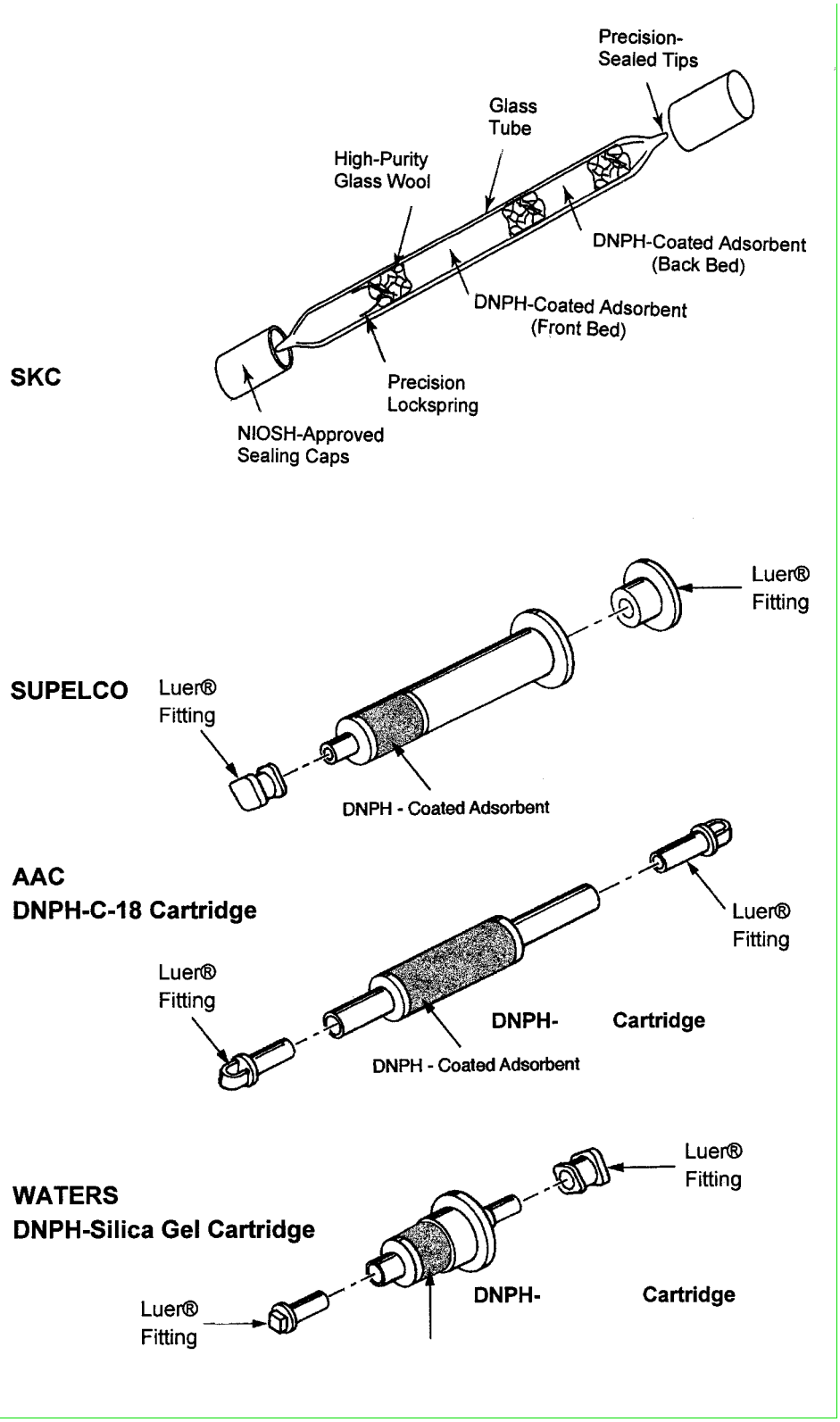


Figure 2. Example of commercially available DNPH-cartridges.

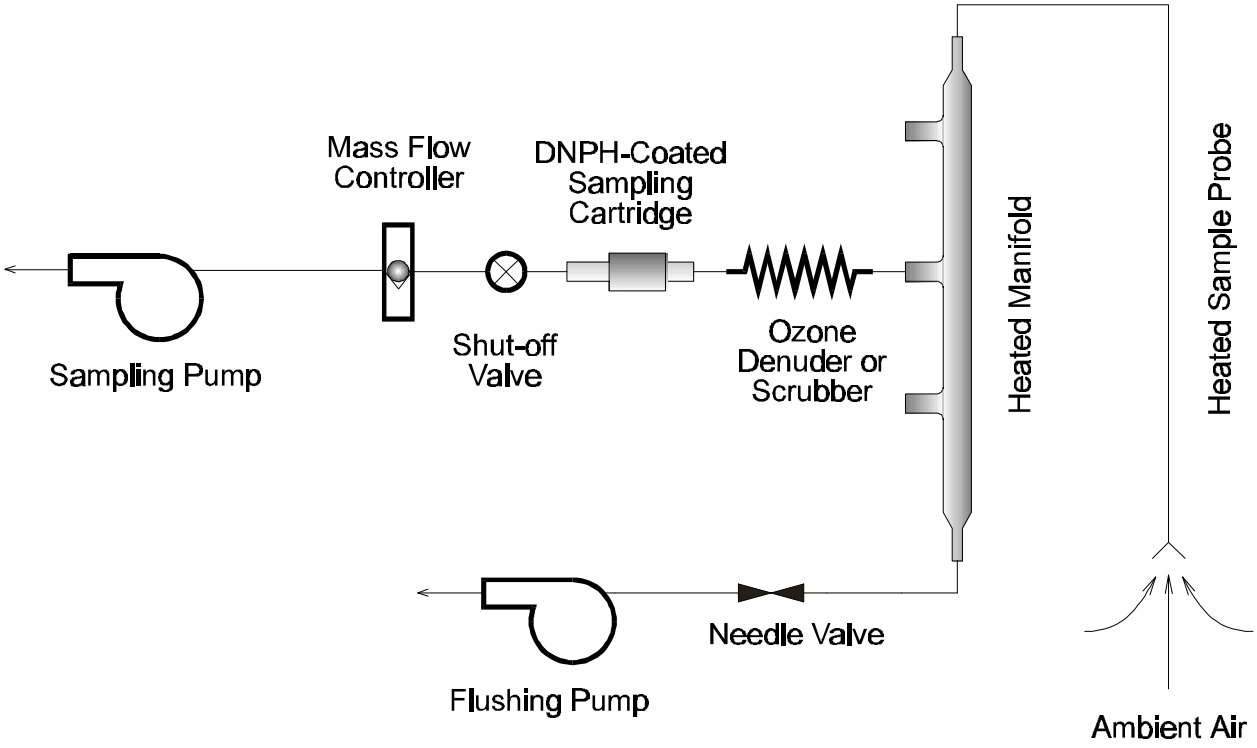


Figure 3. Example of configuration of a single-port carbonyl sampler using DNPH-coated cartridges.

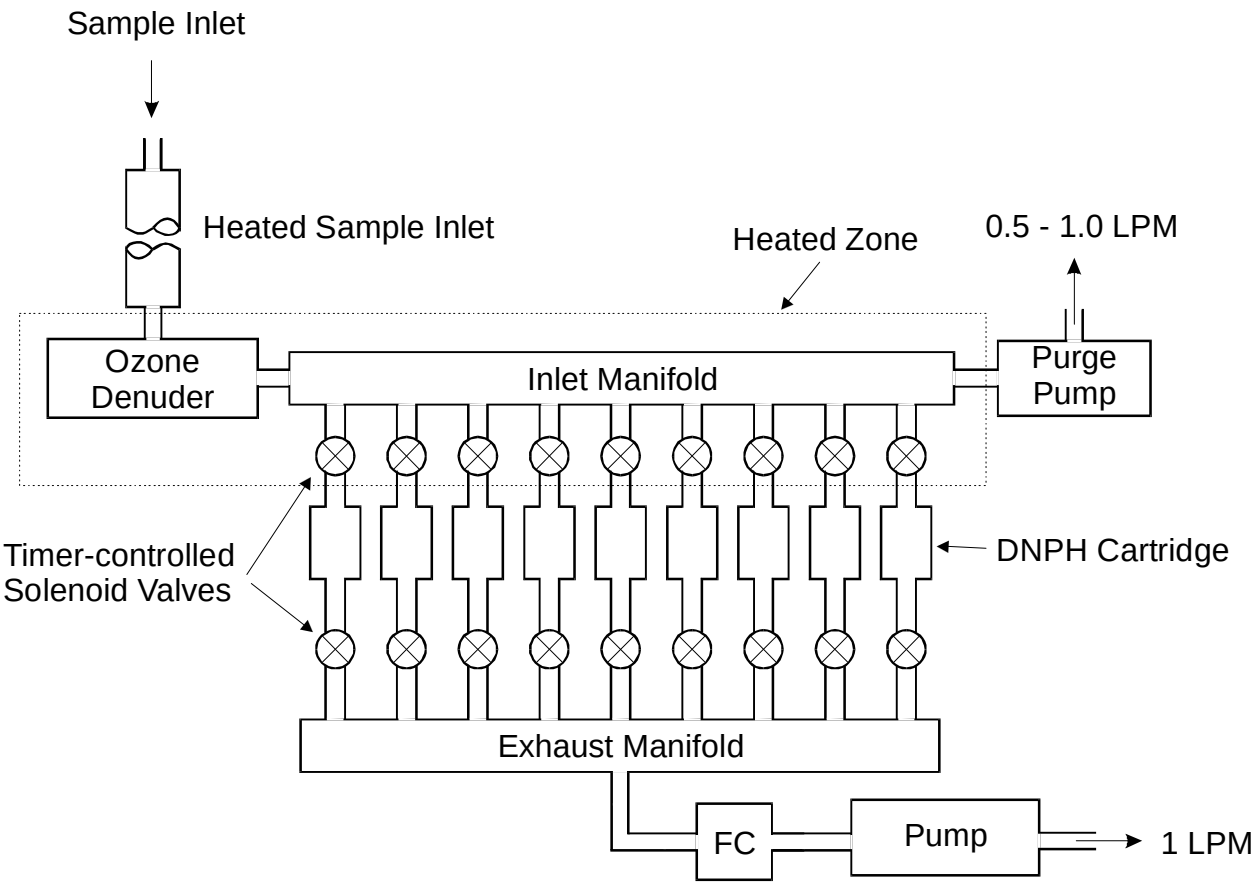


Figure 4. Example of components of an automated multi-port sampler for carbonyls monitoring using DNPH-coated cartridges.

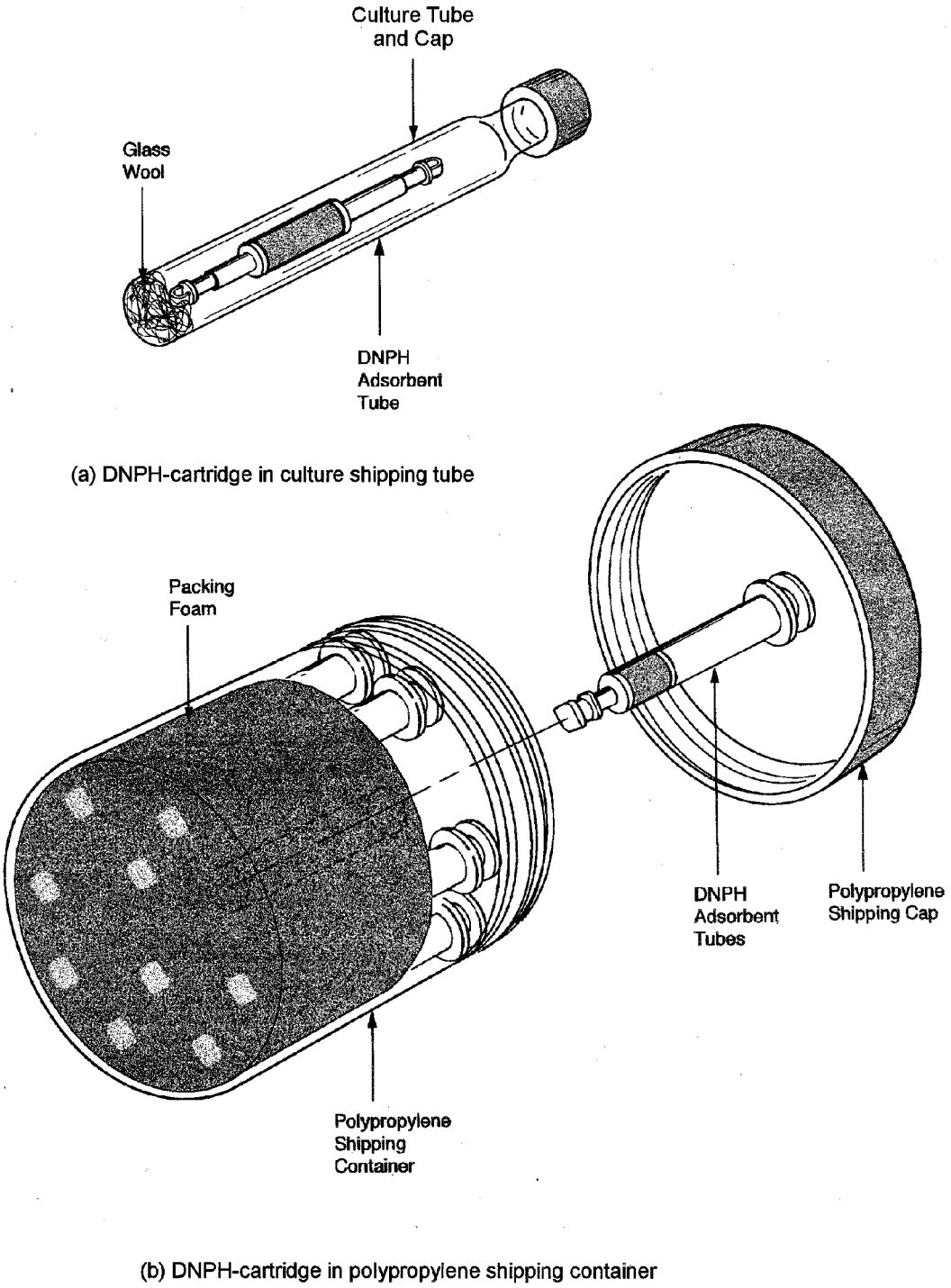
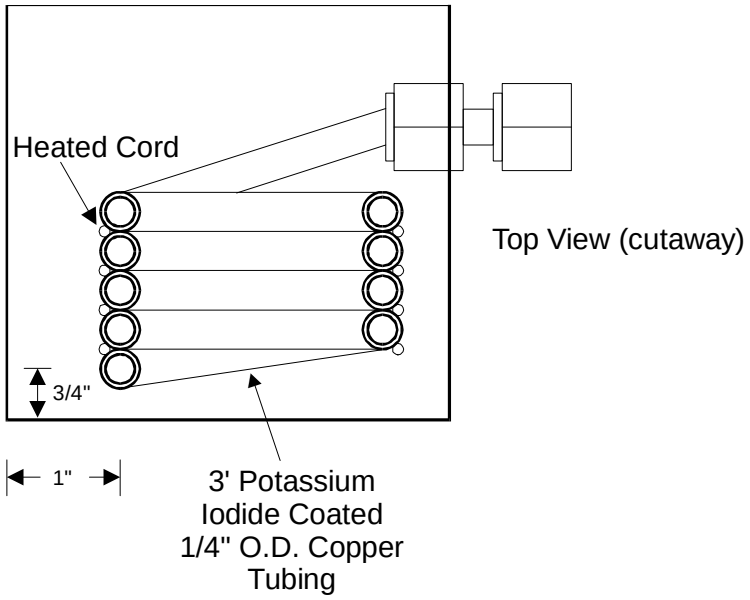
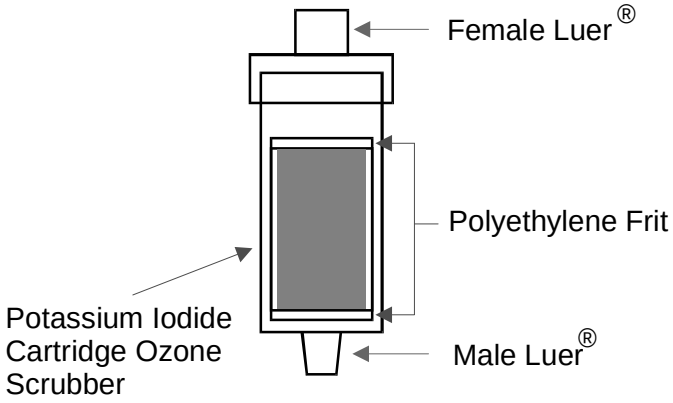


Figure 5. Example of commercially available shipping containers for DNPH cartridges.



(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.

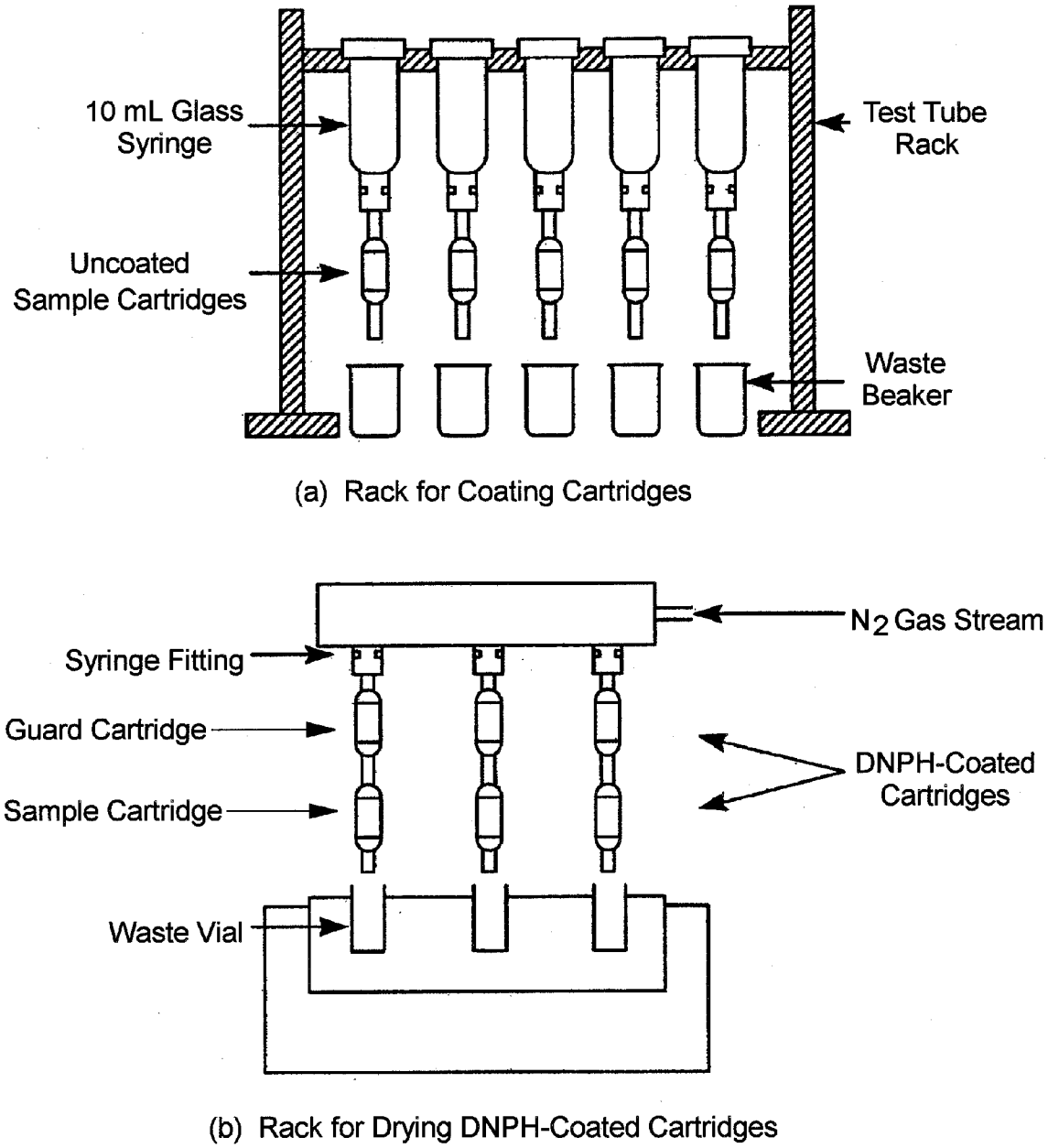


Figure 7. Example of a typical syringe rack for coating (a) and drying (b) sample cartridges.

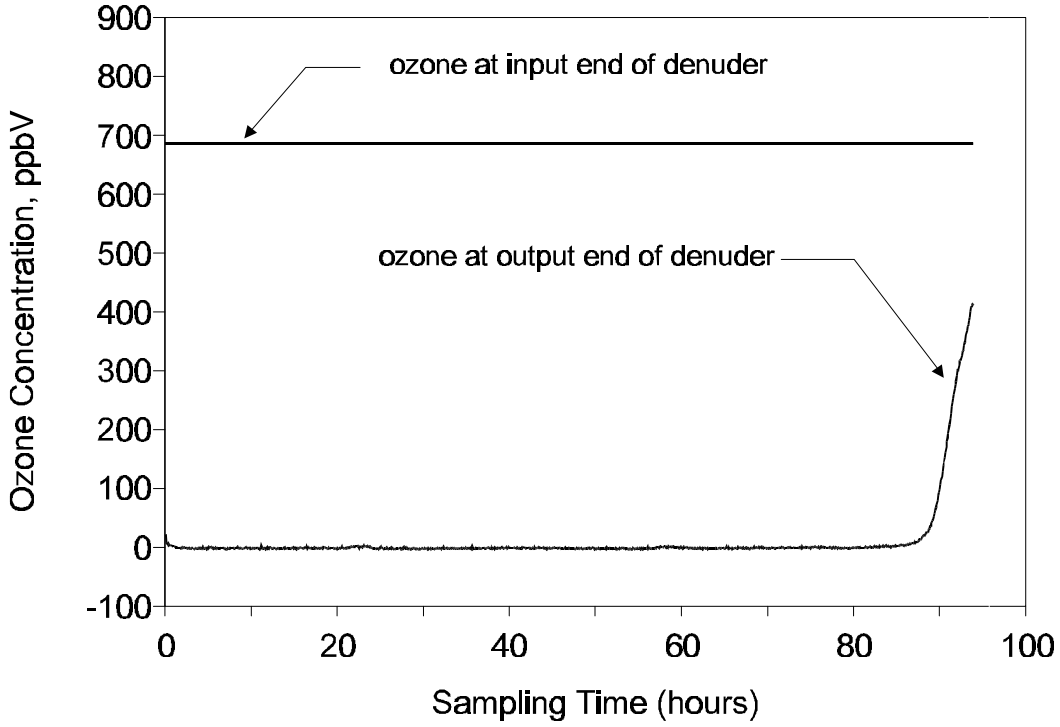


Figure 8. Example of capacity of 3' x 0.25" O.D. x 4.6-mm I.D. copper KI ozone denuder at 2 L/min flow.

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).

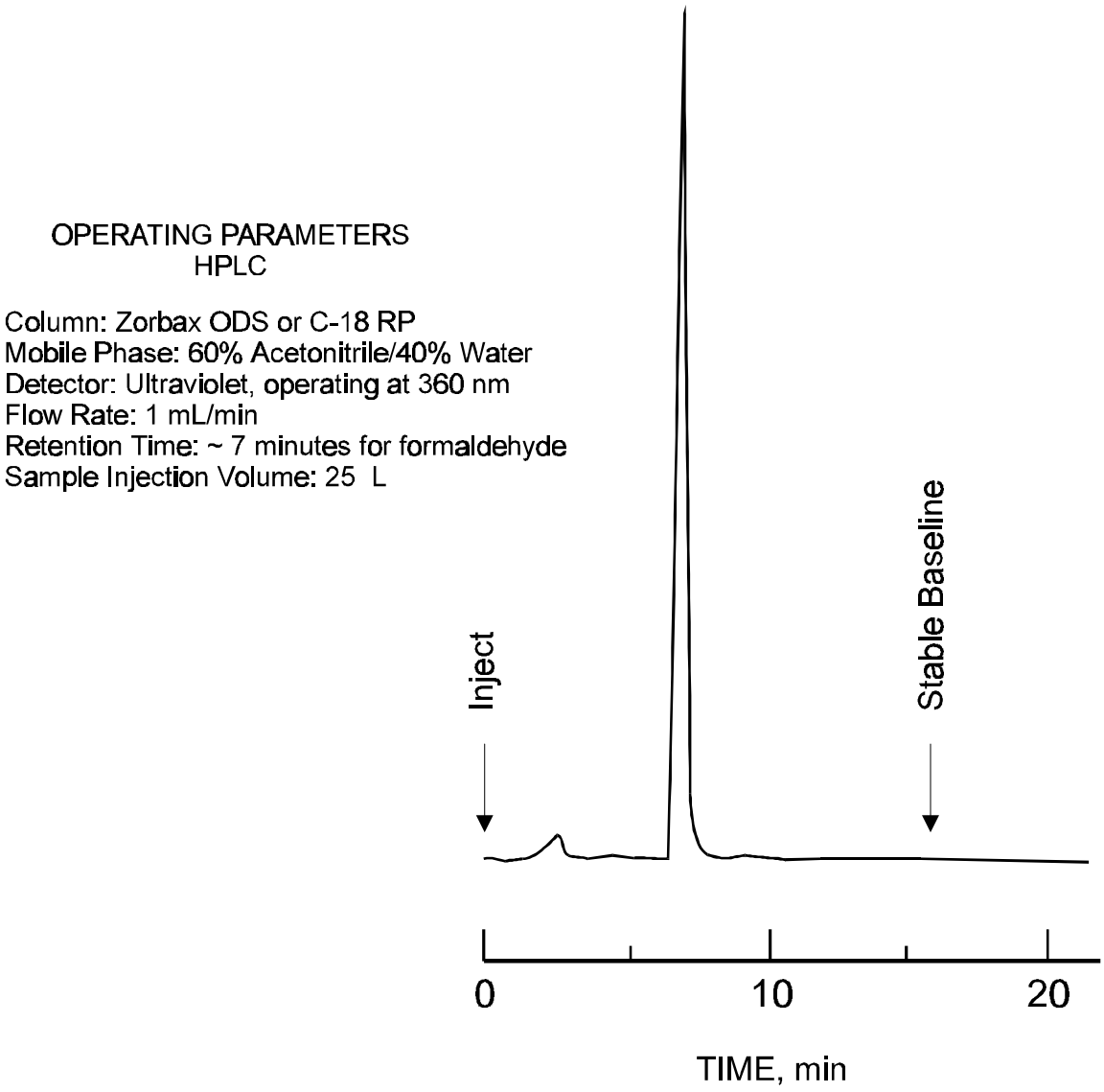


Figure 10. Example of chromatogram of DNPH-formaldehyde derivative.

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

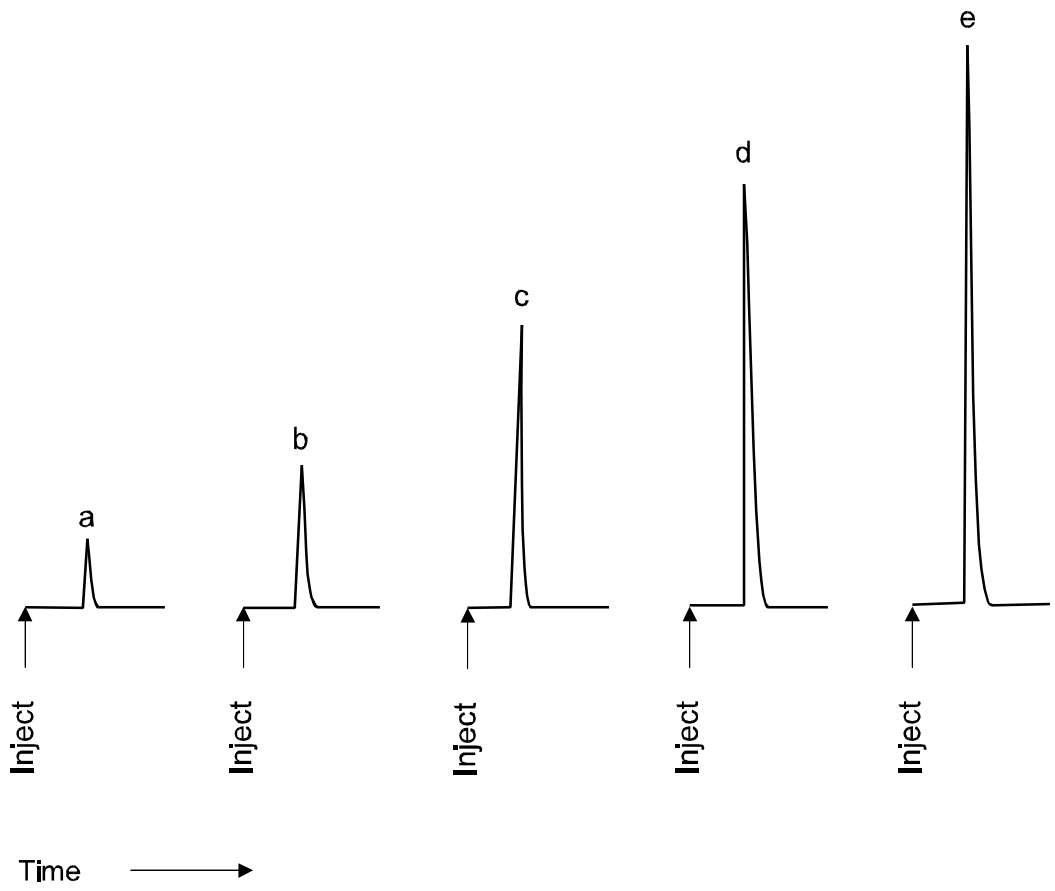


Figure 11. Example of HPLC chromatogram of varying concentration of DNPH-formaldehyde derivative.

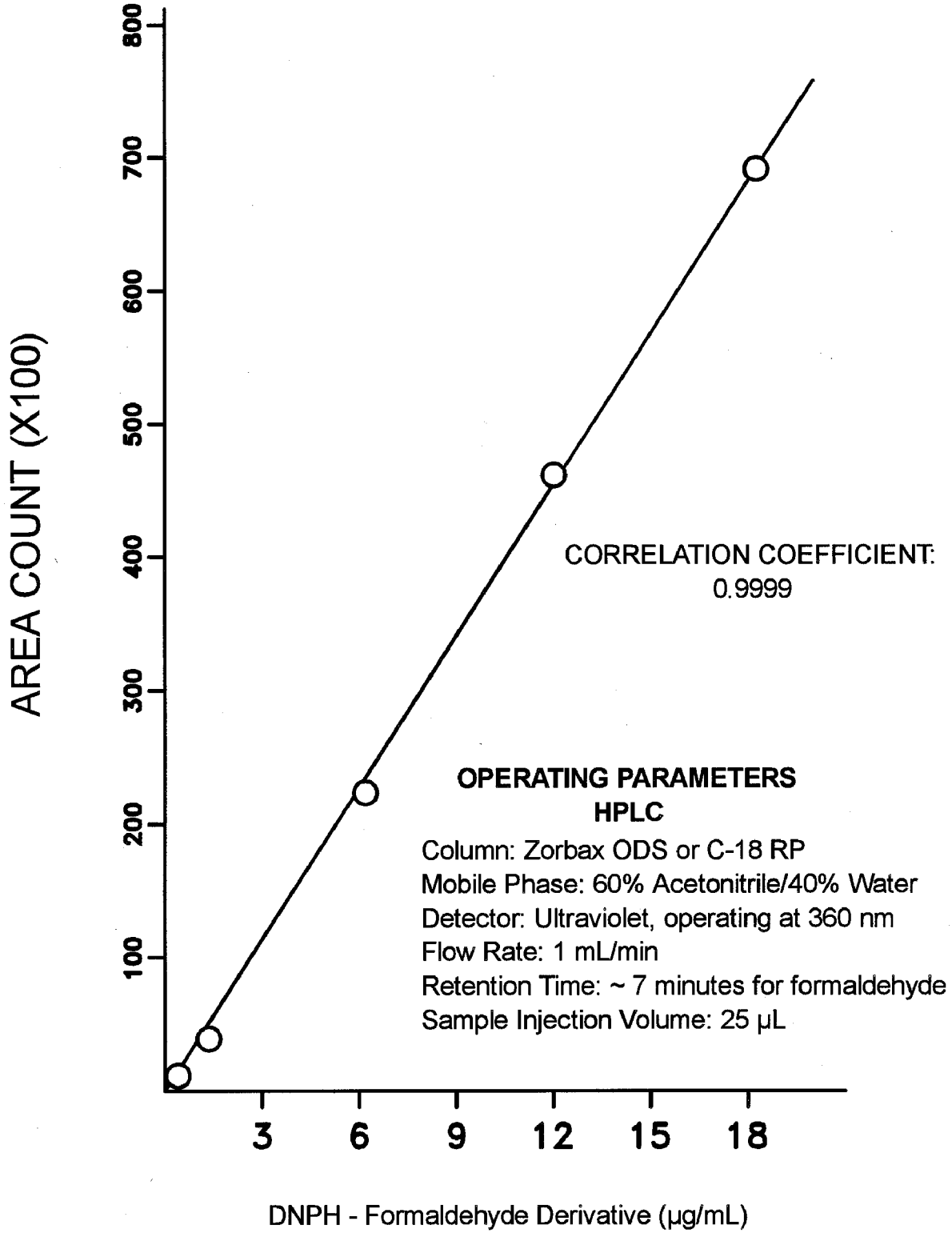


Figure 12. Example of calibration curve for formaldehyde.

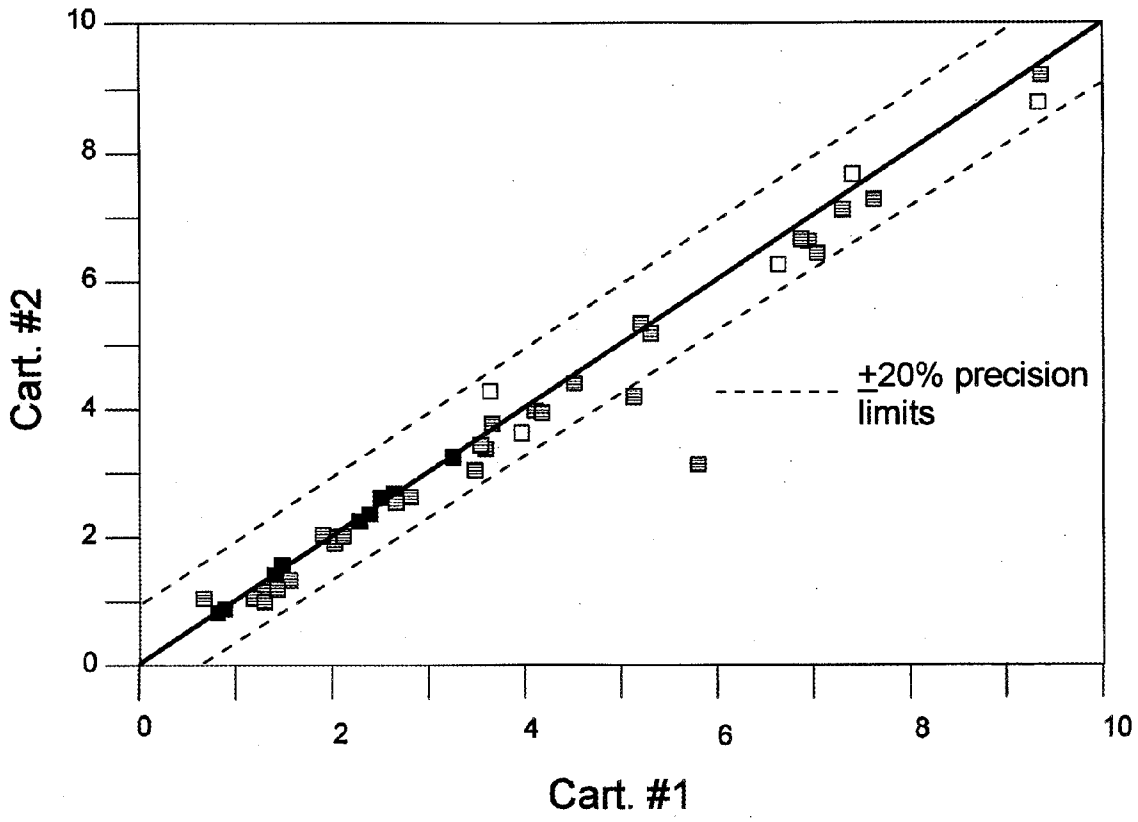


Figure 13. Historical data associated with collocated samples for formaldehyde (ppbv) in establishing 20% precision.

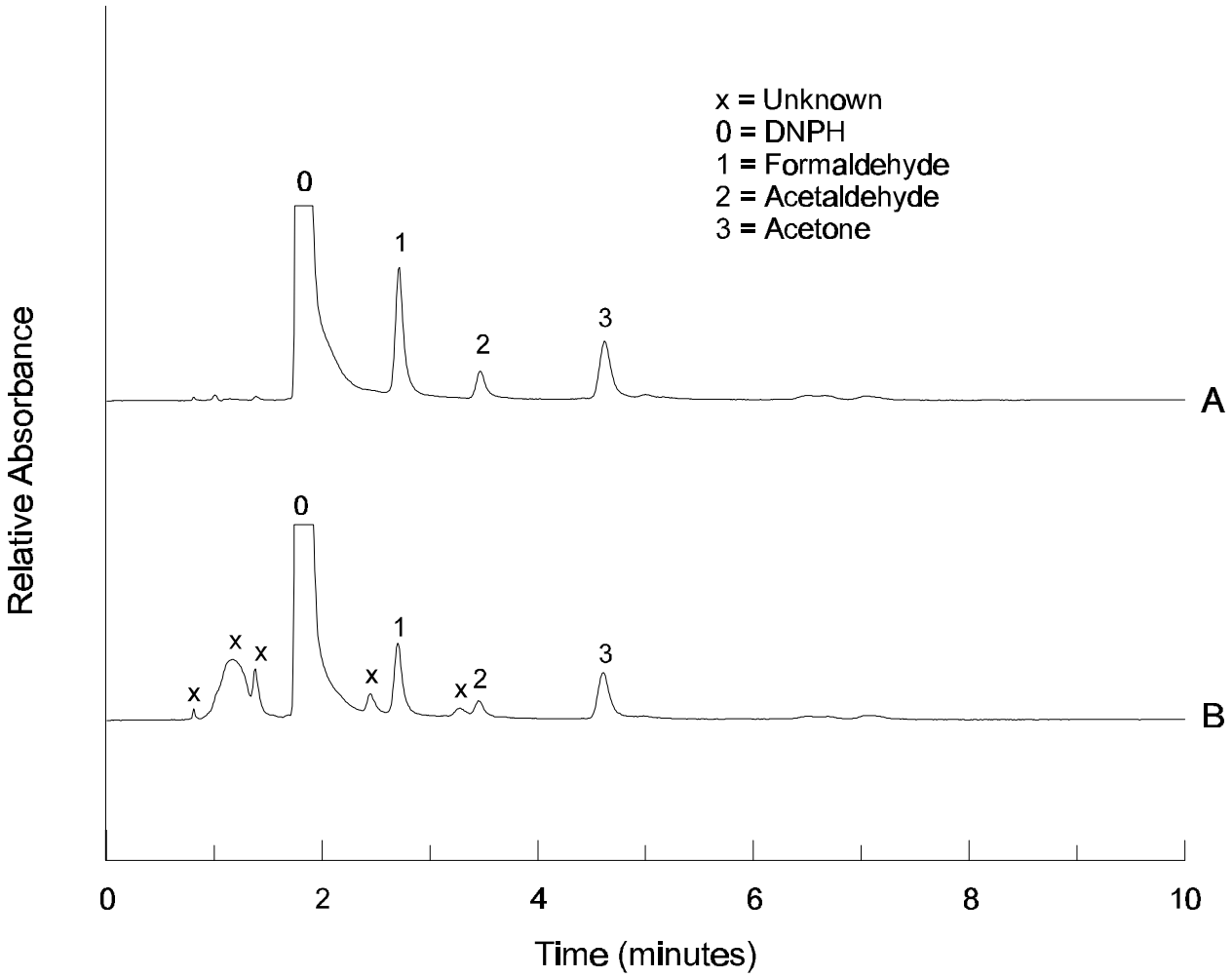


Figure 14. Example of analysis demonstrating DNPH-coated cartridges sampling air with (A) and without (B) ozone denuders, in the determination of formaldehyde.

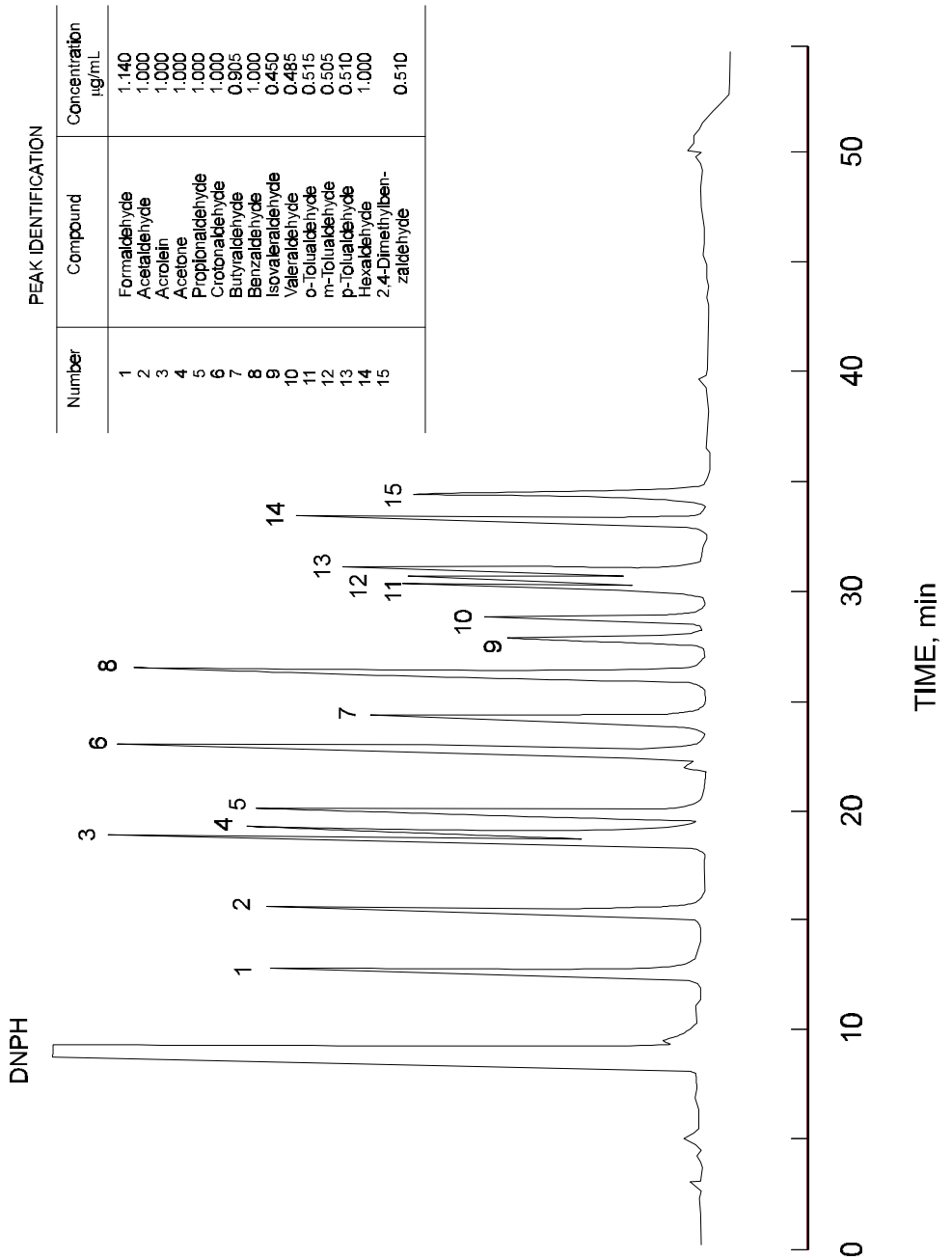


Figure 15. Typical chromatogram of a linear gradient program for analyzing other aldehydes/ketones from a DNPH-coated cartridge.

Sampling Guide – EPA Compendium Method TO-11A

Summary: Formaldehyde and other carbonyl compounds (aldehydes and ketones) in air are collected by drawing sample through a DNPH-coated silica gel cartridge using a sampling pump.

Application: TO-11A can be applied to indoor air, ambient air, and source-impacted sites. Longer collection times up to 24 hours are used for low ppbv environments, and short-term sampling (5 to 60 minutes) can be used for higher concentration sites.

Interferences: Atmospheric ozone can result in a loss of formaldehyde and other carbonyl derivatives. An ozone scrubber is recommended to minimize interference. Particulate-laden atmospheres (>50 ug/m3) may result in flow drops during sampling. Additionally, acrolein and crotonaldehyde may partially degrade using DNPH-coated silica gel cartridges.

Special Considerations: Compound breakthrough can occur if too much volume is collected and the sorbent becomes overloaded. If breakthrough is a concern, cartridges may be sampled as a train. The two cartridges are analyzed separately by the laboratory to monitor breakthrough.

Media	Sep-Pak cartridges (DNPH-coated silica gel) with optional ozone scrubber
Sampling Rate	Range: 0.1 to 2 L/min Typical rate for ambient/indoor air <1 L/min when using a personal sampling pump due to possible flow drops at higher rates.
Cartridge capacity	S10 Supelco = Approximately 75 ug total carbonyls Cartridges with higher capacity are available. If breakthrough is a concern, use a back-up tube.
Sample Handling	Cap ends, place in foil-lined envelope included in shipment. Label envelope with sample information. Keep chilled at ~ 4ºC and keep out of sunlight.
Media Hold Time	Manufacturer's expiration date listed on cartridge
Sample Hold Time	14 days
Field QC Samples	Field Blank – Treat in the same manner as samples, but do not draw air through cartridge. Field Duplicate – Collect a collocated sample using a second sampling port attached to the sample pump. Back-up tube – If breakthrough is a concern, a back-up tube can be connected to the sample tube.
Sampling QC	Measure and record the flow rate before and after sample collection. Flow rates should not vary more than 10% over the sampling duration.

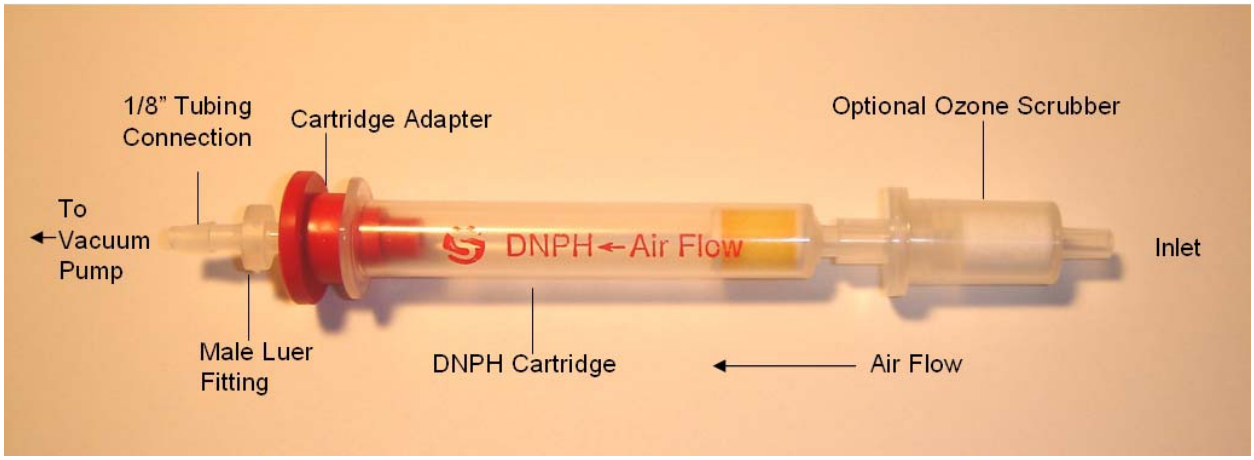


Figure 1. TO-11A sampling equipment set-up

Worksheet to calculate sampling parameters

1) Calculate Minimum Sample Volume

$$\text{Minimum Volume (L)} = \frac{\text{Reporting Limit}^a\ (\text{ug})}{\text{Action Level (ug/m}^3)} * \frac{1000\ \text{L}}{\text{m}^3}$$

Example: Screening Level = 0.08 ug/m^3

$$\text{Minimum Volume (L)} = \frac{0.05\ \text{ug}}{0.08\ \text{ug/m}^3} * \frac{1000\ \text{L}}{\text{m}^3} = 625\ \text{Liters}$$

2) Calculate Minimum Flow Rate if time duration is set.

$$\text{Minimum Flow Rate (L/min)} = \frac{\text{Minimum Volume (L)}}{\text{Duration (min)}}$$

Example: TWA of 24 hours

$$\text{Minimum Flow Rate (L/min)} = \frac{625\ \text{L}}{24\ \text{hour}} * \frac{\text{hour}}{60\ \text{min}} = 0.44\ \text{L/min}$$

Suggest sampling at a flow rate of 0.5 to 0.8 L/min for 24 hours to meet a screening level of 0.08 ug/m^3.

3) For a source-impacted environment, calculate if overloading of tube is possible. Estimate concentration of total aldehydes to estimate maximum volume. A safe sampling volume is considered to be 75% or less of the cartridge capacity. The standard TO-11A cartridge supplied by Air Toxics has a capacity of approximately 75 ug total carbonyls.

$$\text{Estimated maximum volume (L)} = \frac{(0.75 * 75\ \text{ug})}{\text{Est. Form. Conc (ug/m}^3)} * \frac{1000\ \text{L}}{\text{m}^3}$$

Example: Source-impacted site 3 ppmv (3700 ug/m^3) Formaldehyde

$$\text{Estimated maximum volume (L)} = \frac{0.75 * 75\ \text{ug}}{3700\ \text{ug/m}^3} * \frac{1000\ \text{L}}{\text{m}^3} = 15\ \text{L}$$

[a]Reporting Limits for TO-11A
Formaldehyde = 0.05 ug
Acetaldehyde = 0.10 ug
Other Carbonyls = 0.25 ug

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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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.

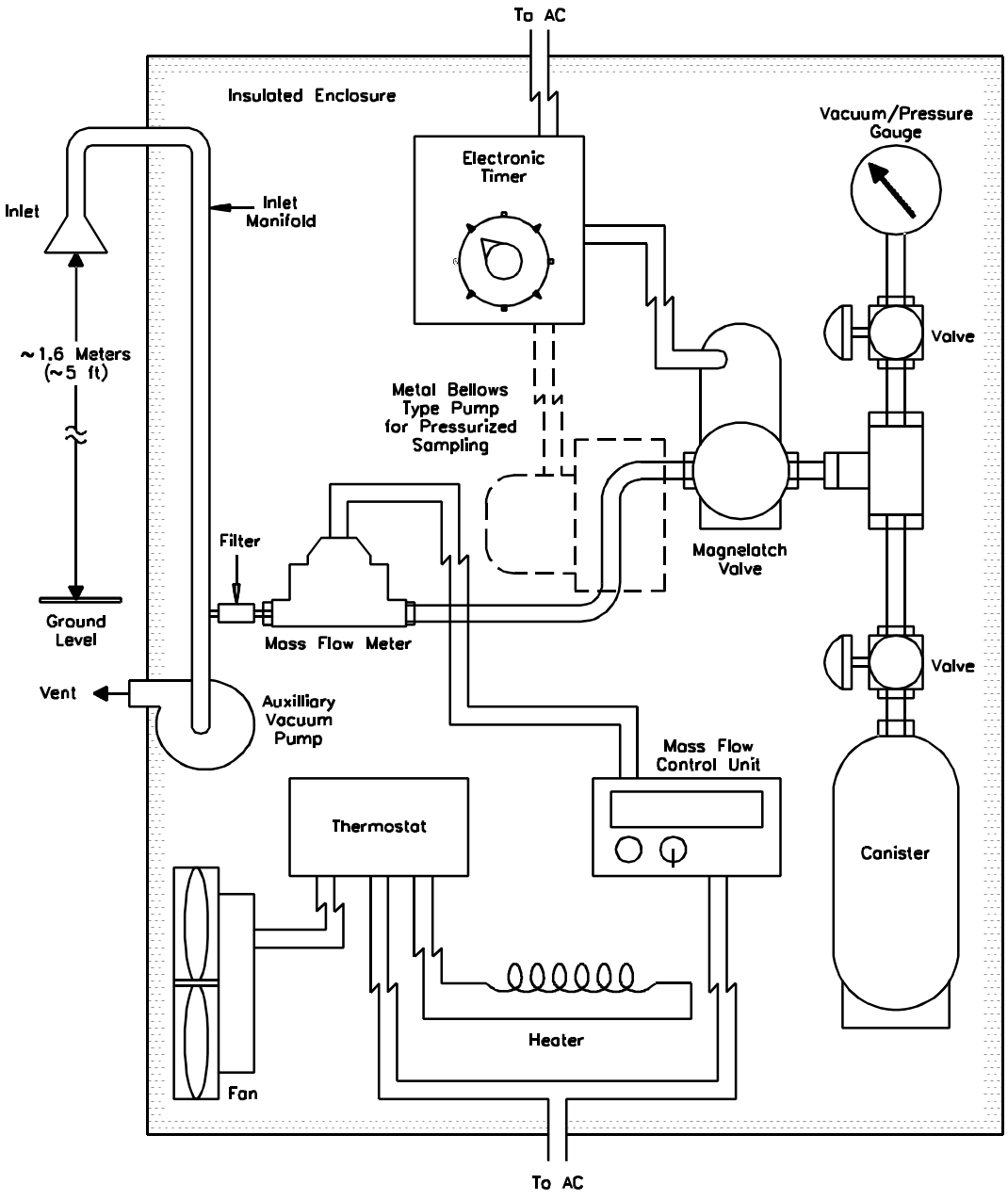
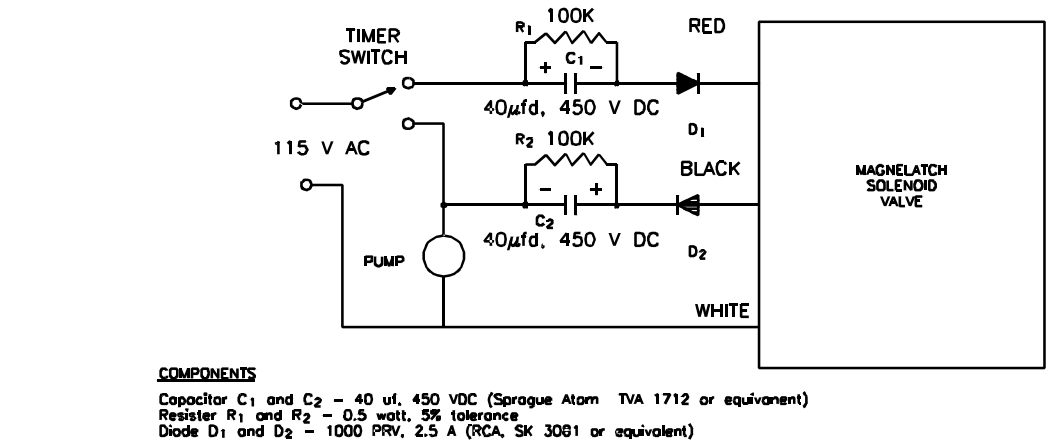
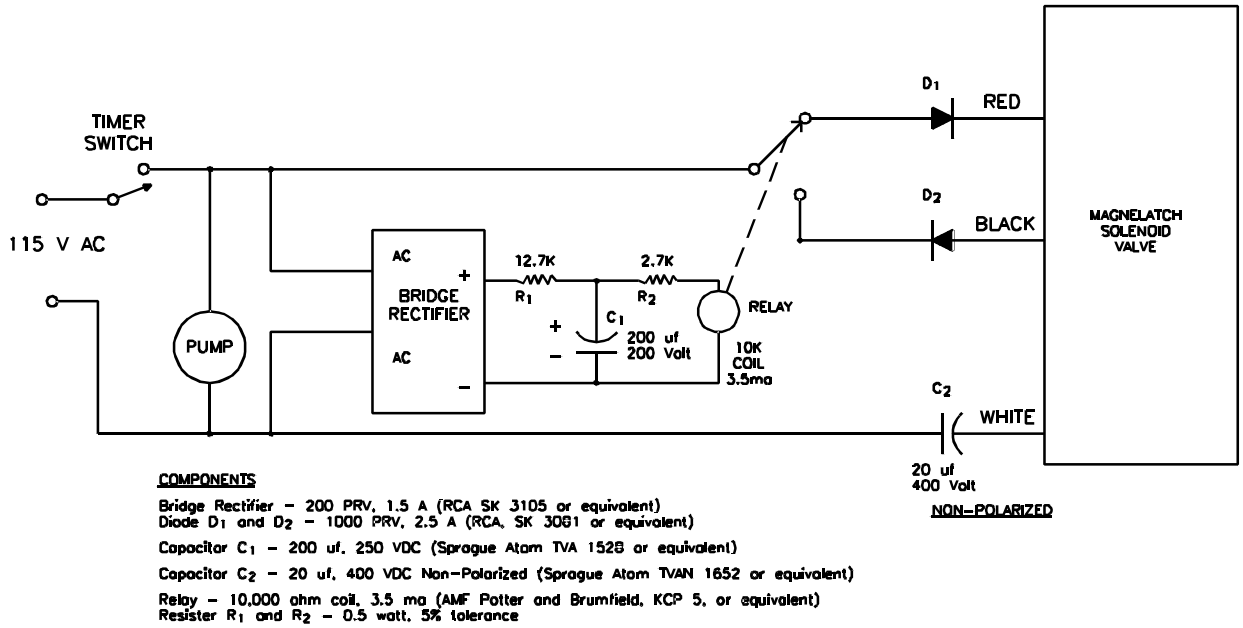


Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.



(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.

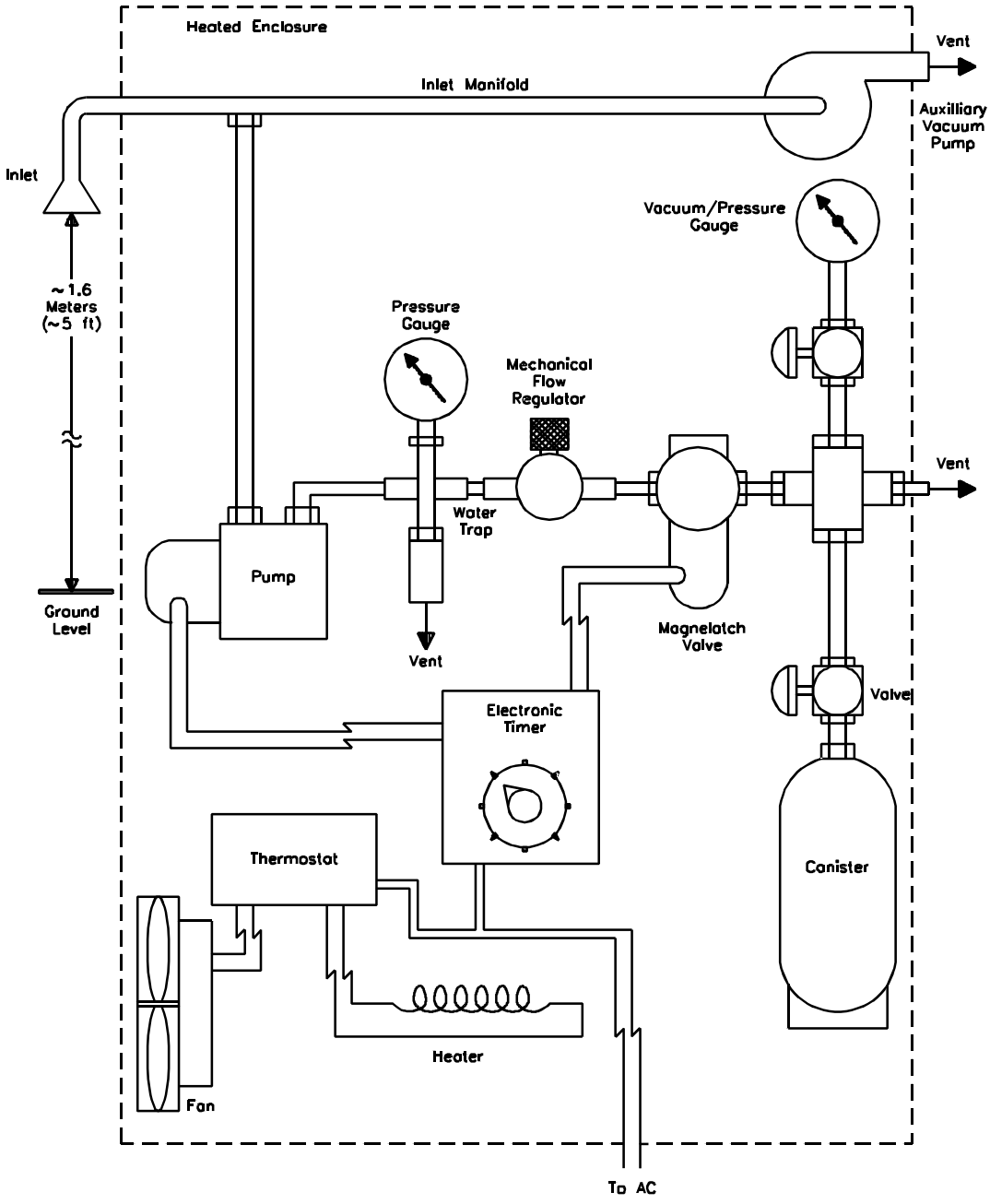


Figure 3. Alternative sampler configuration for pressurized canister sampling.

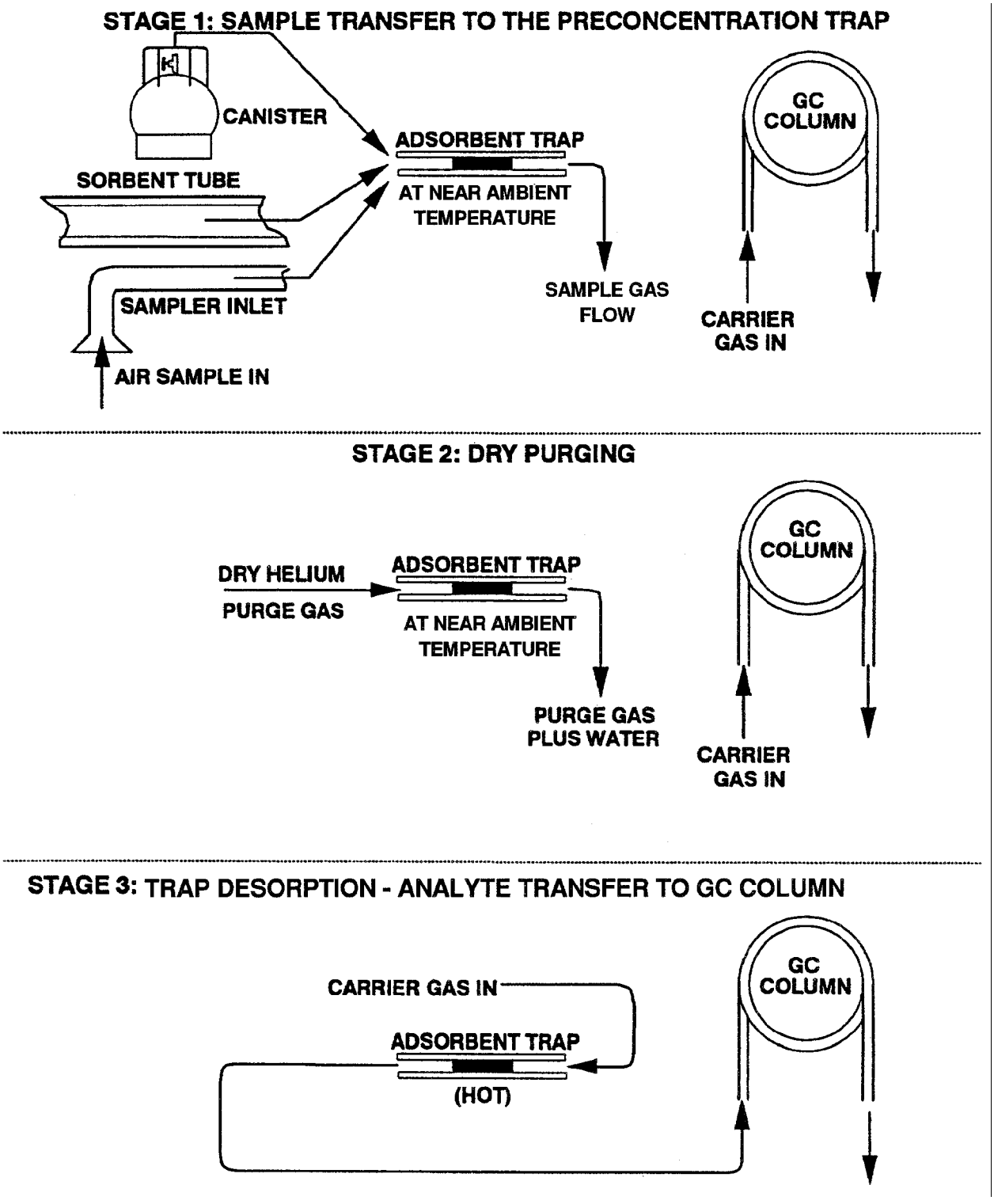


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

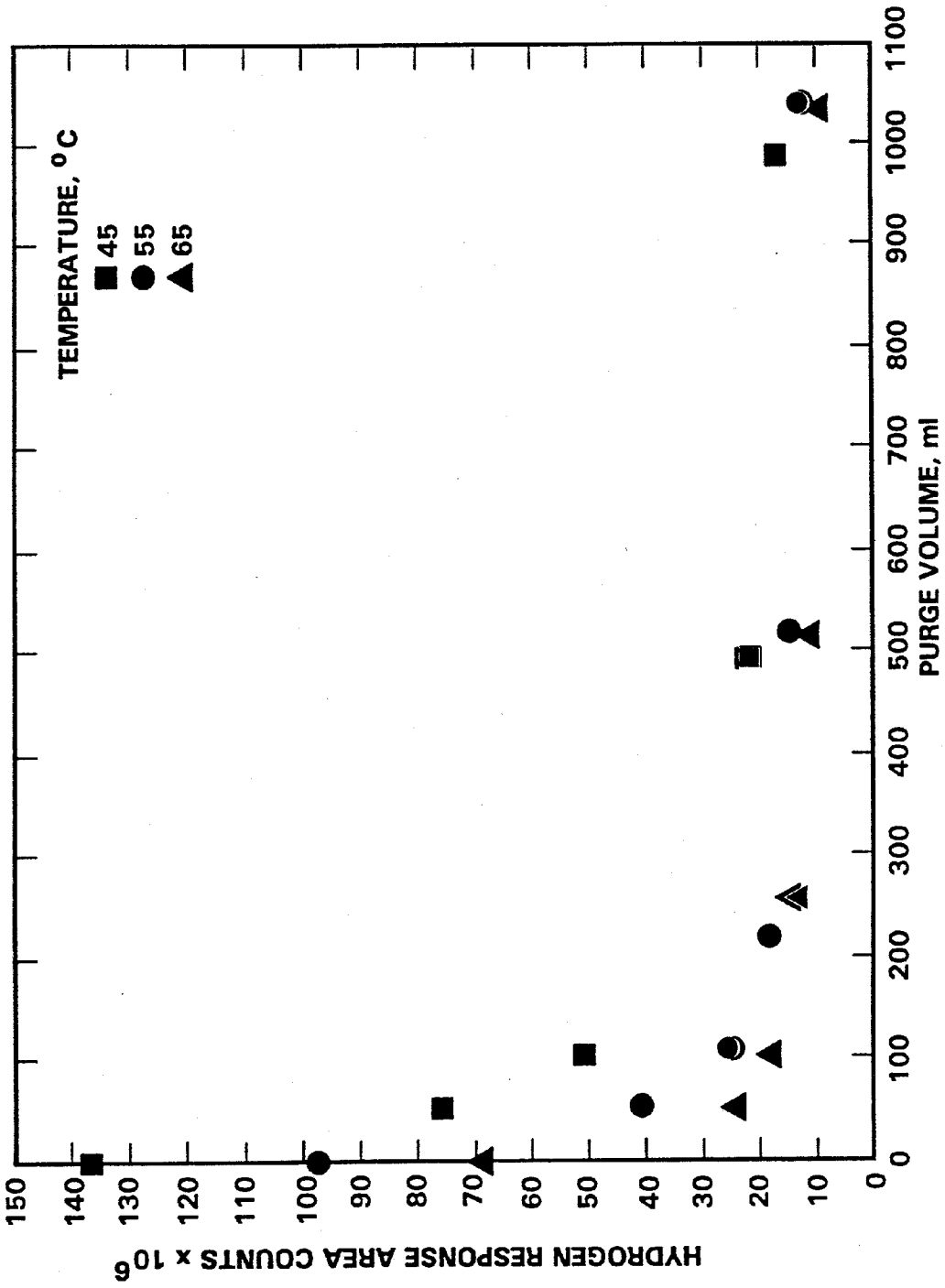


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

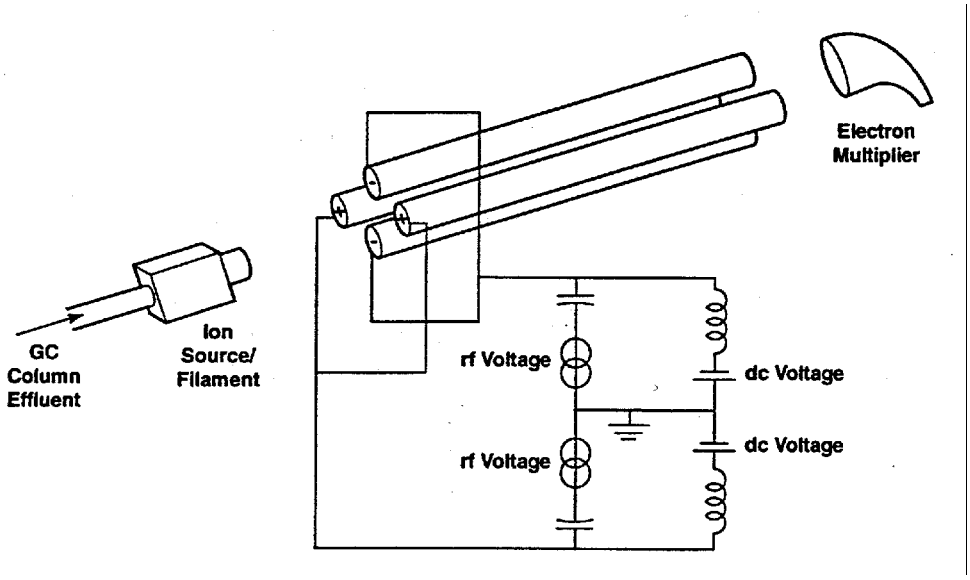


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

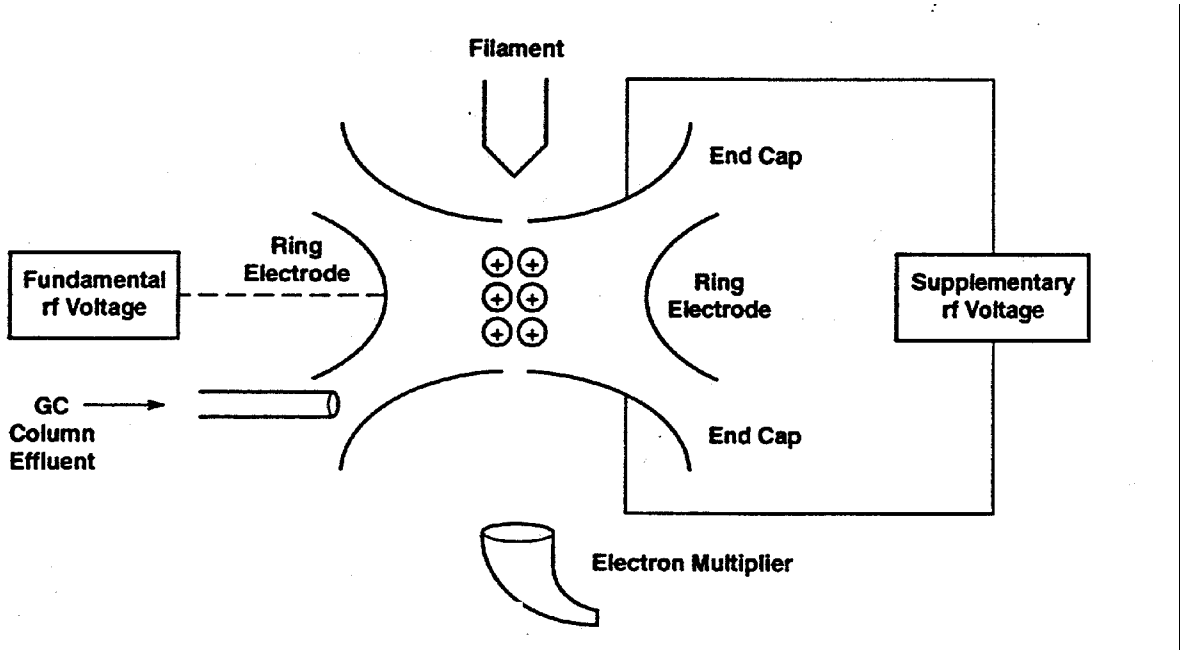


Figure 7. Simplified diagram of an ion trap mass spectrometer.

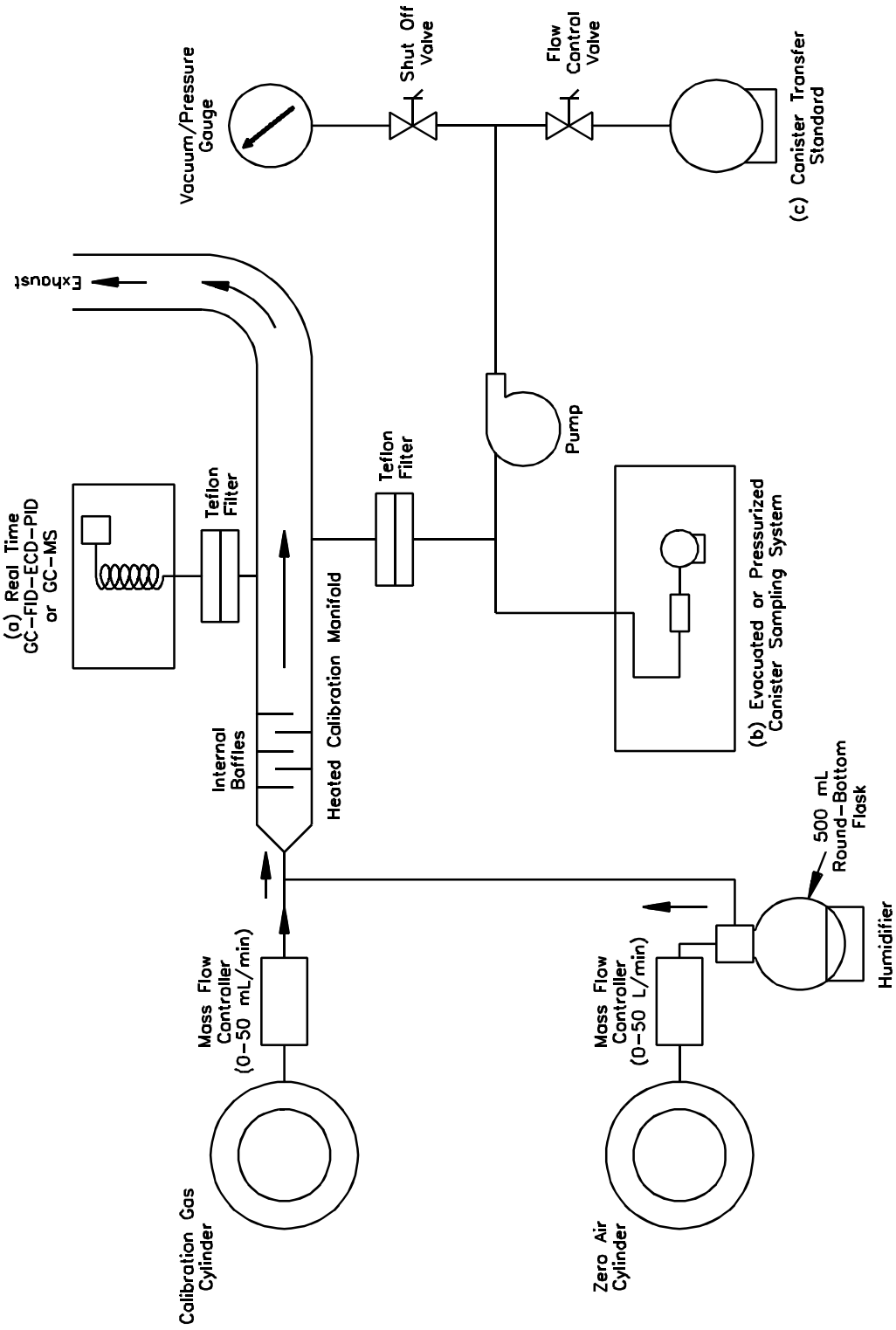


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

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).

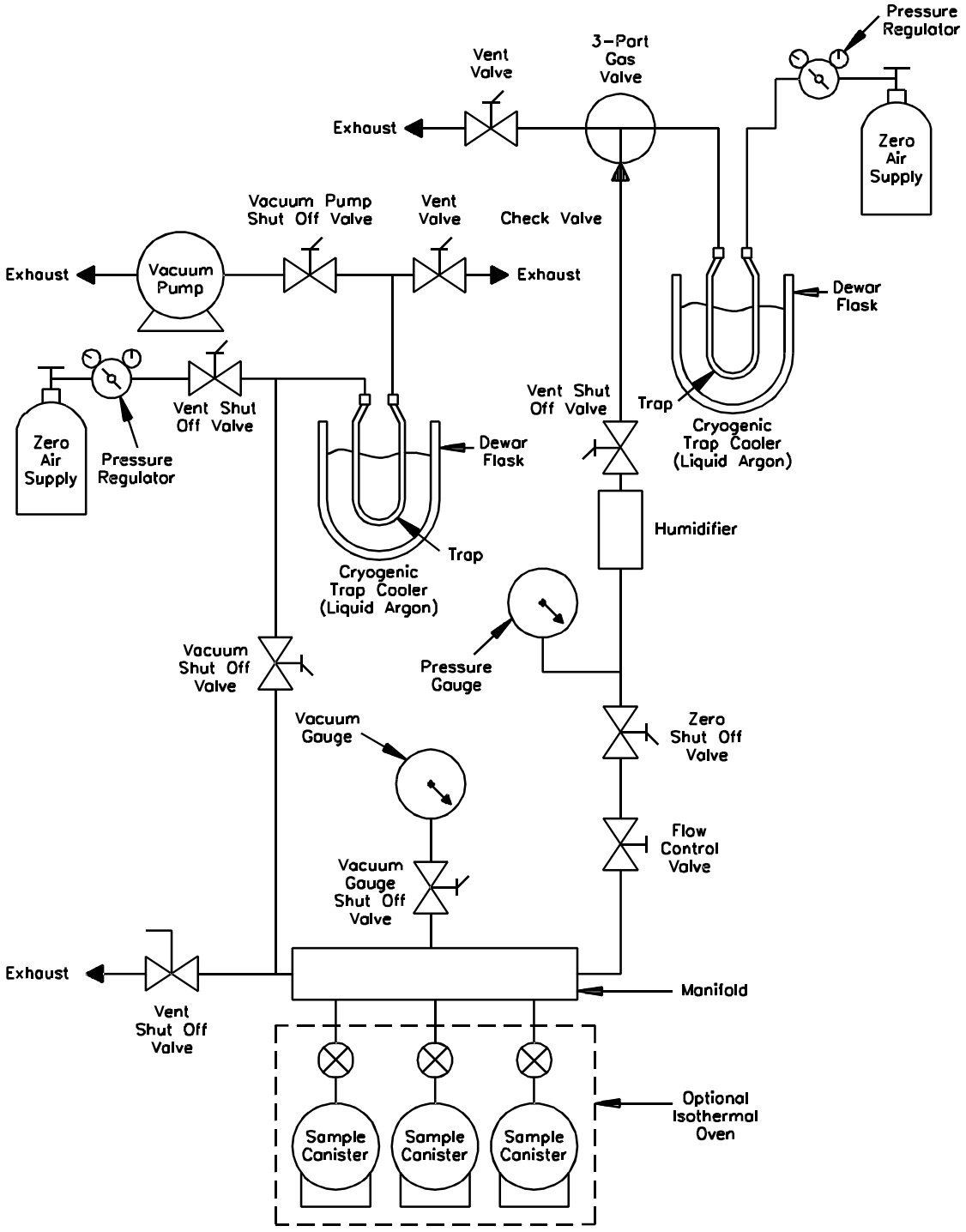


Figure 10. Canister cleaning system.

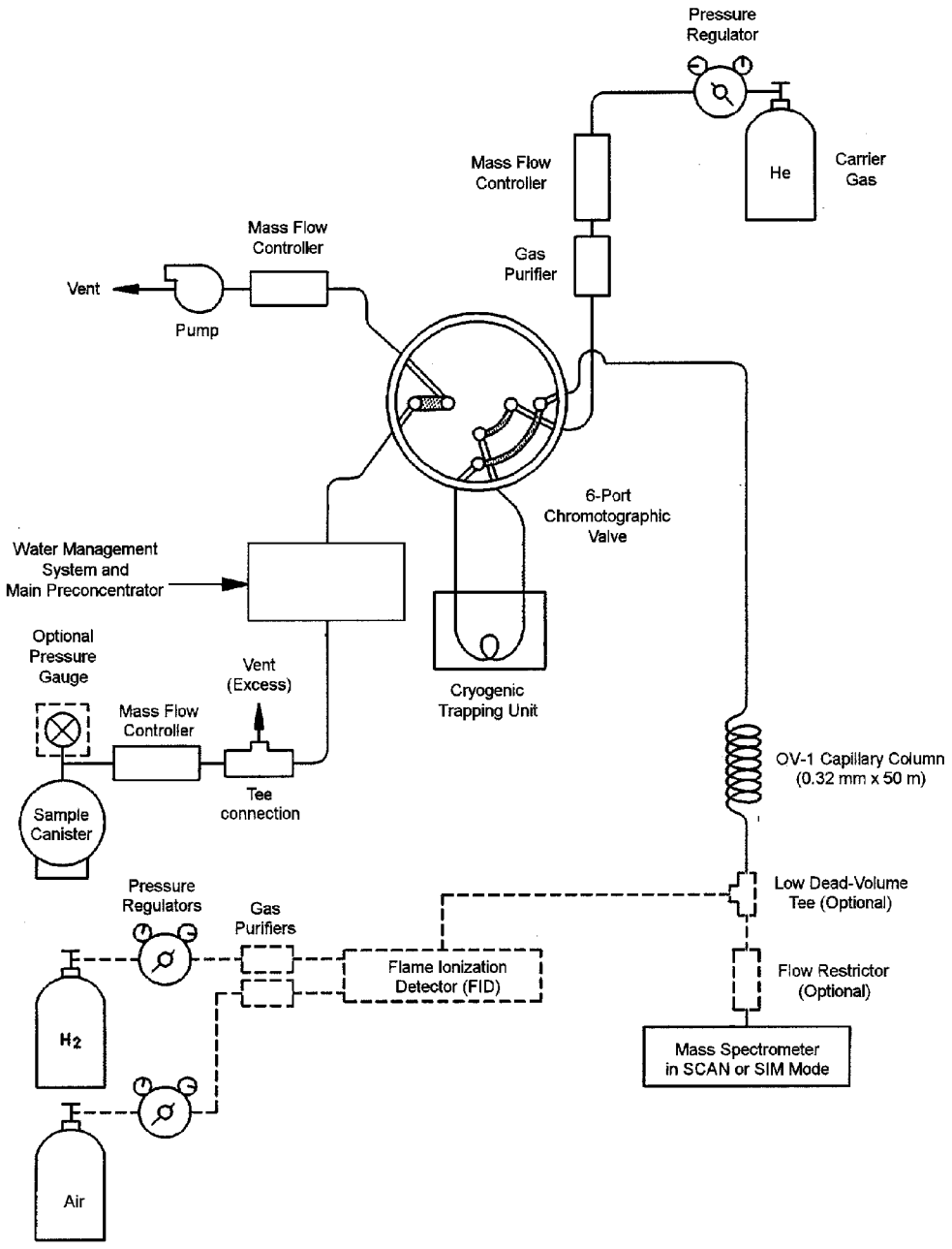
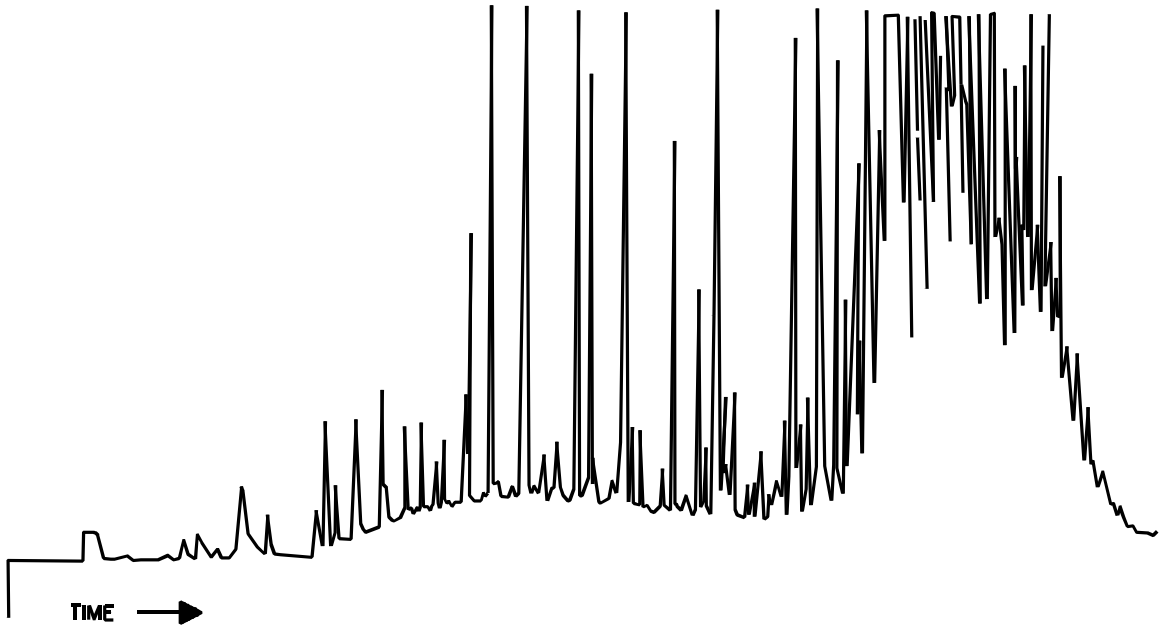


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
[Alternative analytical system illustrated in Figure 16.]

(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).

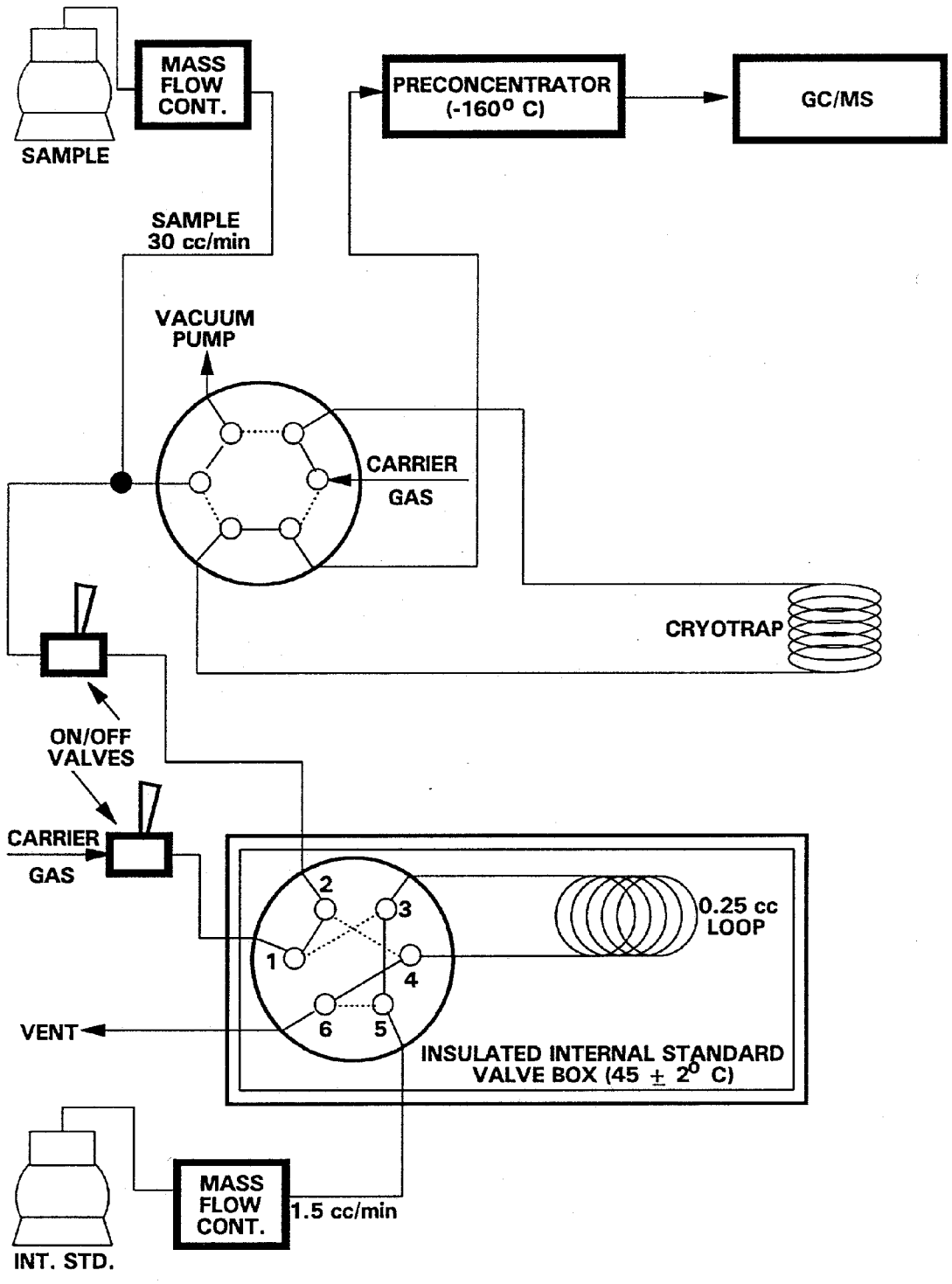


Figure 13. Diagram of design for internal standard addition.

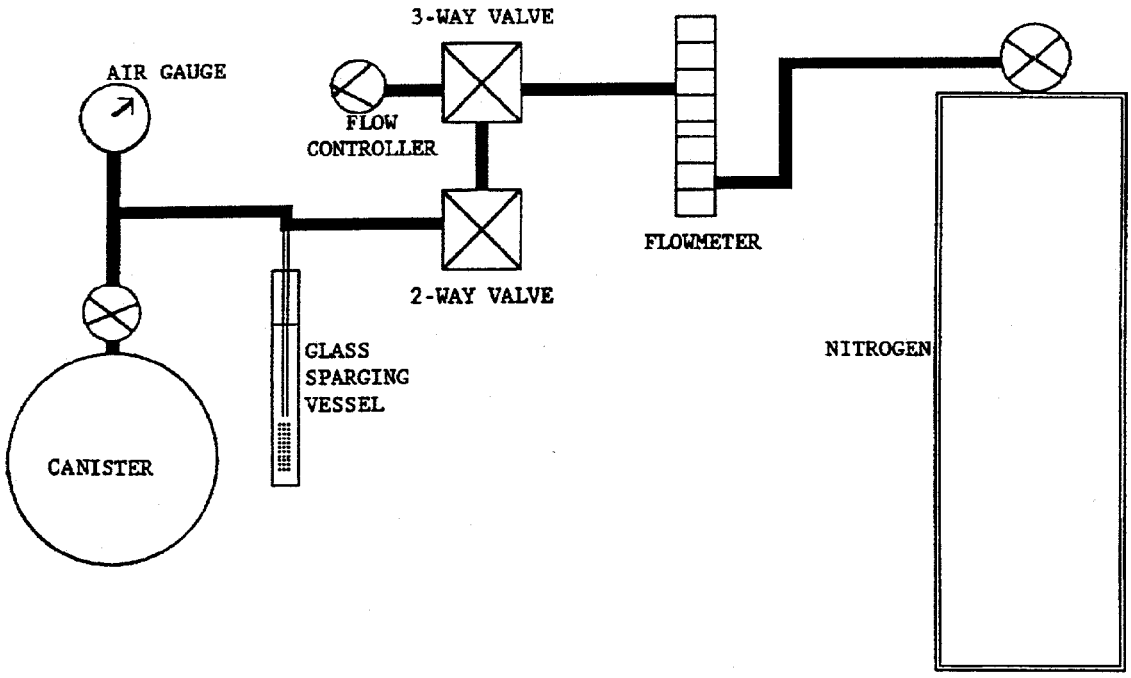


Figure 14. Water method of standard preparation in canisters.

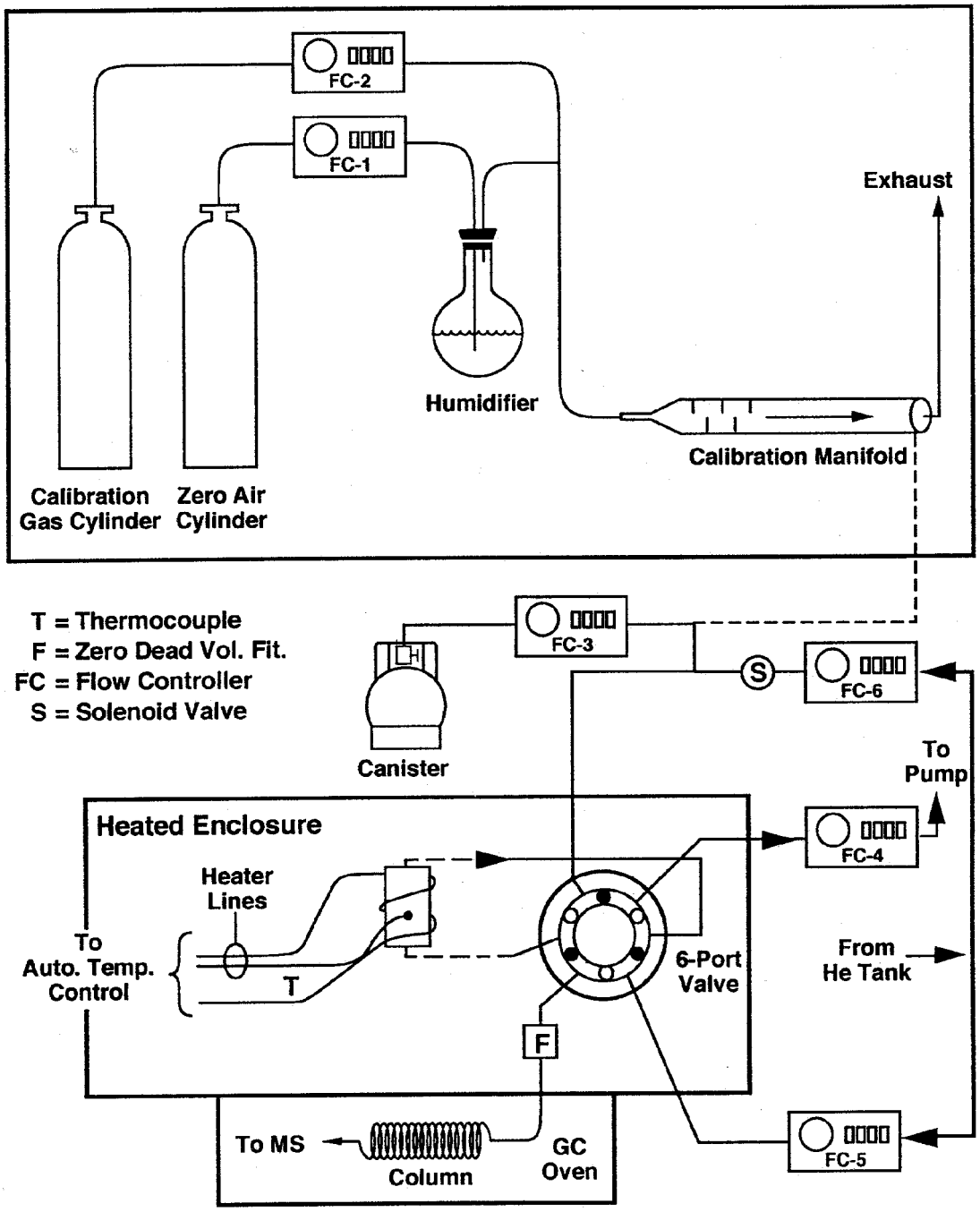


Figure 15. Diagram of the GC/MS analytical system.

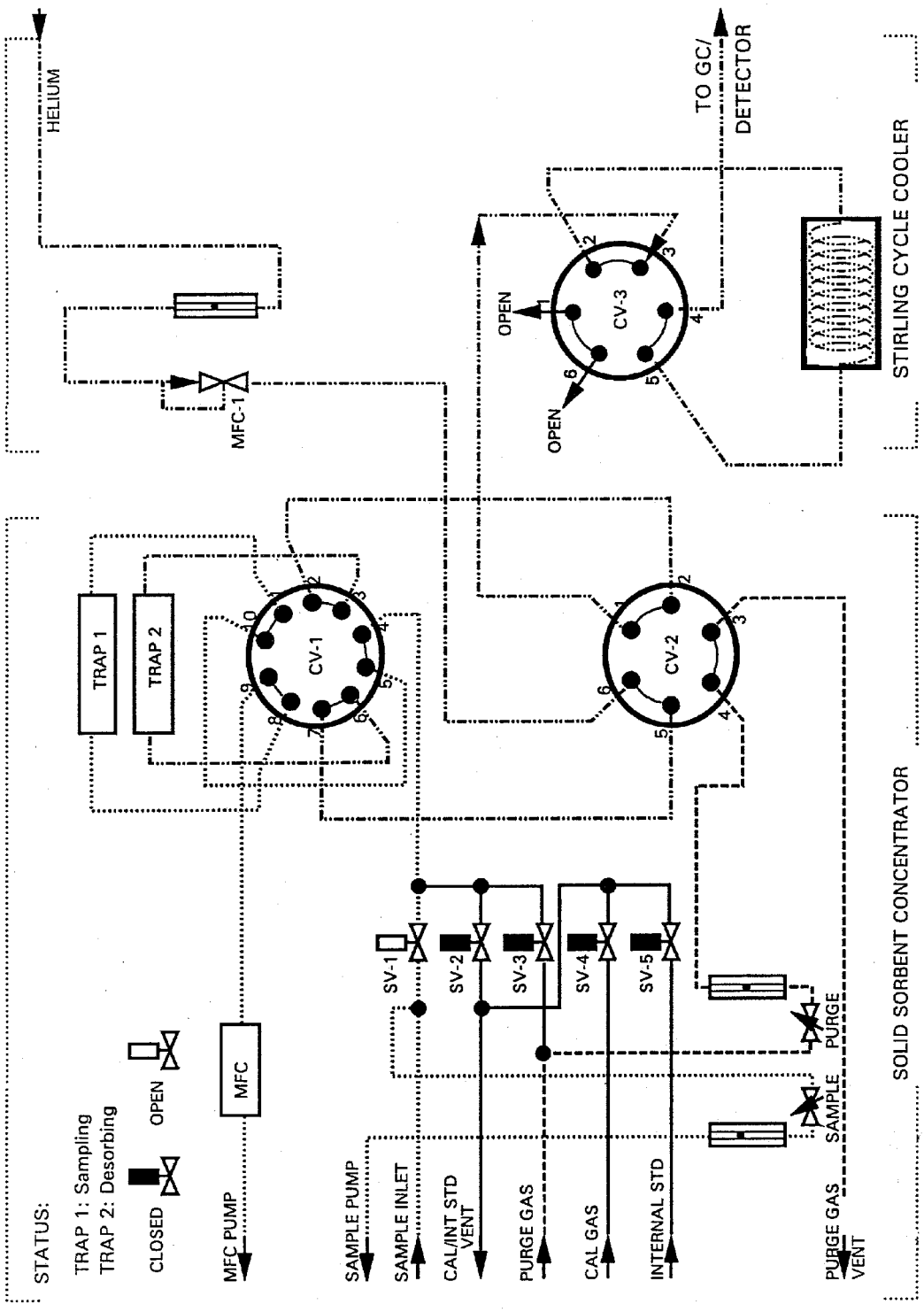


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).

EPA/625/R-96/010a

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

Compendium Method IO-3.3

DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

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

June 1999

Method IO-3.3

Acknowledgments

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

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

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Method IO-3.3
Determination of Metals in Ambient Particulate Matter Using
X-Ray Fluorescence (XRF) Spectroscopy

TABLE OF CONTENTS

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Chapter IO-3
CHEMICAL SPECIES ANALYSIS OF FILTER-COLLECTED SPM

Method IO-3.3
DETERMINATION OF METALS IN AMBIENT PARTICULATE MATTER USING X-RAY FLUORESCENCE (XRF) SPECTROSCOPY

1. Scope

1.1 During a span of more than two decades, the U. S. Environmental Protection Agency (EPA) has developed and applied x-ray fluorescence (XRF) to the analysis of ambient and source aerosols using both energy and wavelength dispersive spectrometers. Inorganic Compendium Method IO-3.3 briefly describes the agency's experience with XRF and informs the reader of its capability in elemental aerosol analysis and attempts to give a brief account of what is involved in its application. The procedures described have been in a continual state of evolution beginning with those in use on a special purpose spectrometer designed by Lawrence Berkeley Laboratory (LBL) and eventually applied to a commercially available instrument manufactured by Kevex. It is for the Kevex spectrometer to which this method applies.

1.2 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.

1.3 Suspended particulate matter (SPM) in air generally is considered to consist of 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 microns to 100 (0.01 Fm to 100 Fm) microns and larger. Historically, measurement of SPM has concentrated on total suspended particulates (TSP) with no preference to size selection.

1.4 The most commonly used device for sampling TSP in ambient air 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-hour sample. The sample is weighed to determine concentration of TSP and is usually analyzed chemically to determine concentration of various inorganic compounds. When EPA first regulated TSP, the National Ambient Air Quality Standard (NAAQS) was stated in terms of SPM with aerodynamic particle size of < 100 Fm captured on a filter as defined by the high-volume TSP sampler. Therefore, the high-volume TSP sampler was the reference method. The method is codified in 40CFR50, Appendix B.

1.5 More recently, 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 of < 10 Fm. These particles are referred to as PM_{10}. It is now generally recognized that, except for toxic materials, it is this PM_{10} fraction of the total particulate loading that is of major significance in health effects. The reference method for PM_{10} is codified in 40CFR50, Appendix J and specifies a measurement principle based on extracting an ambient air sample with a powered sampler that incorporates inertial separation of PM_{10} size range particles and collection of these particles on a filter for a 24-hour period. Again, the sample is weighed to determine concentration of PM_{10} and is usually analyzed chemically to determine concentration of various inorganic compounds.

1.6 Further research now strongly suggests that atmospheric particles commonly occur in two distinct modes, the fine (< 2.5 µm) mode and the coarse (2.5 to 10.0 Fm) mode. The fine or accumulation mode (also termed the respirable particles) is attributed to growth of particles from the gas phase and subsequent agglomerization, whereas the coarse mode is made up of mechanically abraded or ground particles. Because of their initially gaseous origin, the fine range of particle sizes includes inorganic ions such as sulfate, nitrate, and ammonium as well as combustion-form carbon, organic aerosols, metals, and other combustion products. Coarse particles, on the other hand, normally consist of finely divided minerals such as oxides of aluminum, silicon, iron, calcium, and potassium. Samplers which separate SPM into two size fractions of 0-2.5 µm and 2.5-10 µm are called dichotomous samplers. In 1997, the EPA promulgated a new standard with fine particles. The new $PM_{2.5}$ standard replaced the previously NAAQS for PM_{10}.

1.7 Airborne particulate materials retained on a sampling filter, whether TSP, PM_{10}, $PM_{2.5}$, or dichotomous size fractions, may be examined by a variety of analytical methods. This method describes the procedures for XRF analysis as the analytical technique. The XRF method provides analytical procedures for determining concentration in ng/m^3 for 44 elements that might be captured on typical filter materials used in fine particle or dichotomous sampling devices. With the sample as a thin layer of particles matrix effects substantially disappear so the method is applicable to elemental analysis of a broad range of particulate material. The method applies to energy dispersive XRF analysis of ambient aerosols sampled with fine particle (< 2.5 µm) samplers, dichotomous and VAPS (versatile air pollution sampler) samplers with a 10 µm upper cut point and PM_{10} samples.

1.8 The analysis of ambient aerosol samples captured on filterable material should be performed by a scientist that has been trained in energy dispersive x-ray fluorescence spectroscopy and its associated data processing system. The training should be performed by a scientist with an advance degree in the physical sciences with a minimum of 5 years experience in x-ray spectroscopy.

2. Applicable Documents

2.1 ASTM Documents

- D4096 Application of 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.

2.2 U.S. Government 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 B.
- "Reference Method for the Determination of Particulate Matter in the Atmosphere (PM_{10} Method)," *Code of Federal Regulations*, 40 *CFR* 50, Appendix J.
- "1978 Reference Method for the Determination of Lead in Suspended Particulate Matter Collected From Ambient Air." *Federal Register* 43 (194):46262-3.
- *Test Methods for Evaluating Solid Waste, Method 9022*, EPA Laboratory Manual, Vol. 1-A, SW-846.

2.3 Other Documents

- Kevex XRF TOOLBOX II Reference Manual
- Kevex 771-EDX Spectrometer User's Guide and Tutorial

3. Summary of Method

[Note: This method was developed using the Kevex spectrometer. EPA has experience in the use of the Kevex spectrometer associated with various field monitoring programs involving analysis of filterable particulate matter for metals over the last two decades. The use of other manufacturers of x-ray spectrometers should work as well as long as the quality assurance and quality control specifications identified in Sections 12 through 14 of Method 10-3.3 are met. However, modifications to Compendium Method IO-3.3 procedures may be necessary if another commercial x-ray spectrometer is used.]

The method described is x-ray fluorescence applied to PM_{10}, fine (< 2.5 µm) and coarse (2.5-10 µm) aerosols particles captured on membrane filters for research purposes in source apportionment. The samplers which collect these particles are designed to separate particles on their inertial flow characteristics producing size ranges which simplify x-ray analysis. The instrument is a commercially available Kevex EDX-771 energy dispersive x-ray spectrometer which utilizes secondary excitation from selectable targets or fluorescers and is calibrated with thin metal foils and salts for 44 chemical elements. Spectra are acquired by menu-driven procedures and stored for off-line processing. Spectral deconvolution is accomplished by a least squares algorithm which fits stored pure element library spectra and background to the sample spectrum under analysis. X-ray attenuation corrections are tailored to the fine particle layer and the discrete coarse particle fraction. Spectral interferences are corrected by a subtractive coefficient determined during calibration. The detection limits are determined by propagation of errors in which the magnitude of error from all measured quantities is calculated or estimated as appropriate. Data are reported in ng/m^3 for all samples. Comprehensive quality control measures are taken to provide data on a broad range of parameters, excitation conditions and elements.

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 are based on these data.

4.2 Inhalable ambient air particulate matter (< 10 µm) can be collected on Teflon® filters by sampling with a dichotomous sampler and analyzed for specific metals by X-ray fluorescence. The dichotomous sampler collects particles in two size ranges - fine (< 2.5 µm) and coarse (2.5-10 µm). The trace element concentrations of each fraction are determined using the nondestructive energy dispersive X-ray fluorescence spectrometer.

4.3 The detectability and sensitivity of specific elements may vary from instrument to instrument depending upon X-ray generator frequency, multichannel analyzer sensitivity, sample interferences, etc.

5. Definitions

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

5.1 Accuracy. The agreement between an experimentally determined value and the accepted reference value.

5.2 Attenuation. Reduction of amplitude or change in wave form due to energy dissipation or distance with time.

5.3 Calibration. The process of comparing a standard or instrument with one of greater accuracy (smaller uncertainty) for the purpose of obtaining 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.

5.4 10 µm Dichotomous Sampler. An inertial sizing device that collects suspended inhalable particles (< 10 µm) and separates them into coarse (2.5-10 µm) and fine (< 2.5 µm) particle-size fractions.

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

5.6 Filter. A porous medium for collecting particulate matter.

5.7 Fluorescent X-Rays (Fluorescent Analysis). Characteristic X-rays excited by radiation of wavelength shorter than the corresponding absorption edge.

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

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

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

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

5.12 Traceability to NIST. A documented procedure by which a standard is related to a more reliable standard verified by the National Institute of Standards and Technology (NIST).

5.13 Uncertainty. An allowance assigned to a measured value to take into account two major components of error: (1) the systematic error, and (2) the random error attributed to the imprecision of the measurement process.

5.14 Chi-square. A statistic which is a function of the sum of squares of the differences of the fitted and measured spectrum.

5.15 Fluorescer. A secondary target excited by the x-ray source and in turn excites the sample.

5.16 FWHM. Full width at half maximum, a measure of spectral resolution.

5.17 NIST. National Institute of Standards and Technology.

5.18 Shape. The actual shape of a background corrected pulse height spectrum for an element.

5.19 SRMs. Standard reference materials.

5.20 Teflo®. Trade name of a Teflon filter.

5.21 Unknown. A sample submitted for analysis whose elemental concentration is not known.

5.22 XRF. X-ray fluorescence.

6. Description of Spectrometer

The x-ray analyzer is a Kevex EDX-771 energy dispersive spectrometer with a 200 watt rhodium target tube as an excitation source. The machine has multiple modes of excitation including direct, filtered direct, and secondary which utilizes up to 7 targets or fluorescers. To minimize radiation damage to delicate aerosol samples only the secondary mode is used. Table 1 provides a listing of the fluorescers and the elements which they excite associated with energy dispersive spectrometers. Analysis atmospheres are selectable with choices of helium, vacuum or air; helium is used for all targets except Gd where air is employed because it gives a lower background. The detector is cryogenically cooled lithium-drifted silicon with a 5 μm Be window and a resolution of 158 eV at Fe K_{α} and comes with two manually changeable collimators. A 16 position rotating wheel accommodates the samples and provides sample changing.

The machine is operated by procedure files (or programs) written in Kevex's proprietary Job Control Language (JCL) which runs in a Windows 3.1 environment and provides setting of the analytical conditions and data acquisition. Using the JCL language, procedures have been written in-house to perform all the

functions necessary to acquire spectra and to assign to them file names in a structured manner to facilitate future spectral processing. These procedures are invoked in menu form.

7. Caveats

7.1 The type of samplers mentioned in Section 1.7 must be operated in accordance with Inorganic Compendium Method IO-2.2 Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler, or severe errors in x-ray analysis may occur. For example, errors in flow rate will not only give erroneous volumes but will cause a more serious condition of altering the cut points upon which the coarse particle x-ray attenuations are based. If samples are intended for x-ray analysis then the sampling protocol must conform to the constraints inherent within this method. Furthermore, the type of filter on which the sample is collected is very important. In general, thin membrane filters (Teflo® and Nuclepore®) are required so that the background is low and penetration of particles into the matrix of the filter is small. Thick depth filters such as quartz or glass fiber not only have high background but also allow particles to penetrate into the matrix of the filter - a condition which the spectral processing program cannot accommodate.

7.2 Some internal contaminations consisting of Sn, Ni, Cu and Fe are present which sometimes appear in blanks. Routine analysis of blanks with samples will give the magnitude of the correction necessary to compensate for this.

7.3 In general the elements analyzed by the Gd fluorescer have higher detection limits than the other fluorescers (see Table 2). The reason for this is due to limitations in the upper voltage limit of the x-ray tube power supply and the use of rhodium instead of a heavier element such as tungsten as a target material for the x-ray tube. As a secondary consequence of this, there are also higher detection limits for many of the elements below chromium because they overlap the elements analyzed by Gd.

7.4 An inherent problem with a helium atmosphere is the diffusion of He through the detector window causing detector degradation and necessitating replacement. A lifetime of 3 to 4 years is expected.

7.5 Due to an x-ray leak around the anode area of the x-ray tube the head must be shielded with additional lead cladding to prevent unwanted excitation of internal parts. This leak posed no threat to personnel but caused high background when operating at the maximum voltage. The additional shielding proved very effective at improving detection limits.

7.6 Experience with wavelength dispersive spectrometers (WDXRF) has shown good agreement with energy dispersive instruments (EDXRF) over a broad range of elements. In spite of this agreement and the simpler spectral processing requirements of wavelength machines the preference remains with energy dispersive equipment for a variety of reasons. The very low power tubes in EDXRF machines leaves the sample intact and unaffected whereas in WDXRF the high power excitation embrittles the filter itself after 15 - 30 min exposure raising the possibility of altering particle morphology. This is a concern if electron microscopy is considered. Also, the vacuum environment, necessary for WDXRF, causes loss of some volatile materials.

8. Sample Preparation

8.1 Sample preparation begins with the correct operation of the samplers employed. Inorganic Compendium Method IO-2.2, Sampling for Suspended Particulate Matter in Ambient Air Using a Dichotomous Sampler, covering the option of the samplers in the field and subsequent collection of ambient air particles on 37-mm Teflon® filter for XRF analysis. One of the greatest advantages of analyzing aerosols by XRF is that the sample can, in theory, be collected in a manner most advantageous to XRF by sampling for a duration that produces an ideal mass loading on the filter. An approximate maximum target mass is about 100 $\mu g/cm^2$ although much less is often collected in many environments.

8.2 The types of filters used for aerosol sampling are 37-mm or 47-mm Teflo® with a pore size of 2 microns and, if electron microscopy is planned for the coarse fraction, then a 0.6 micron pore size Nuclepore® filter is used. The sample should be collected on the side of the Teflo® filter with the supporting ring to maintain the proper distance between the sample and detector during analysis. A properly collected sample will be a uniform deposit over the entire collection area of at least 25-mm in diameter. Samples which are not uniformly deposited over the whole collection area are not quantitatively analyzable.

8.3 All filter samples received for analysis are removed with tweezers from their container and are checked for any invalidating conditions such as holes, tears, or a non-uniform deposit which would prevent quantitative analysis. If such a condition is found the sample is noted as invalid on the XRF data entry form; data from such samples are not reported. Teflo® filters are easily handled because of the supporting ring, however, Nuclepore® filters must have a supporting ring applied to them (after gravimetric assay) to help maintain their flatness and to securely hold them in the frame. The sample is then placed in a custom-designed commercially available two-part sample frame which snaps together holding the filter securely in place.

9. Spectral Acquisition and Processing

9.1 Spectra are acquired in sets of 15 samples each. Up to 7 spectra are acquired for each sample depending on how many secondary excitation targets are selected. Utilizing all seven fluorescers requires approximately 4 hours machine time for 44 elements analyzed plus atmospheric argon.

9.2 Elemental intensities are determined by spectral deconvolution with a least squares algorithm which utilizes experimentally determined elemental shape functions instead of the mathematical Gaussian function. This approach has been successfully implemented for many years on an earlier machine and is described in Section 15, Citation 10. Since the spectral shape is not a pure Gaussian the experimental shapes are a more realistic representation of a spectrum. In addition to this library of elemental shape spectra there is also a background shape spectrum for each of the types of filters. It is assumed that the background on an unknown sample is due to the filter and not to the sample. (This is one of the reasons for avoiding heavily loaded filters.) The least squares algorithm synthesizes the spectrum of the sample under analysis by taking a linear combination of all the elemental shapes spectra and the background shape spectrum. The coefficients on the linear combination of elemental shapes and background spectra are scaling factors determined by minimizing chi-square thus producing the best fit possible by least square minimization. Values of the chi-square statistic are calculated for each sample and fluorescer to give an indication of the quality of the fit.

9.3 X-ray attenuation corrections are performed as described in Section 15, Citation 10 and are briefly described here. The mass absorption coefficients for the layer of fine particles is based on a typical composition of ambient aerosol particles so the actual x-ray attenuations on a given sample are simply a function of the mass loading. Coarse particle attenuations are more complex in that they are based on x-ray

attenuation by spherical particles with compositions of common crustal minerals with various size distributions. An average attenuation and uncertainty for each coarse particle element is based on this broad range of crustal minerals and is therefore a one-time calculation giving an attenuation factor useable for all subsequent coarse (2.5-10 µm) particle analyses. This treatment assumes low coarse particle loading so that the particles do not shadow one another - yet another reason for assuring that the sample mass loading is not too high. Attenuation corrections on PM_{10} particles are deduced from elemental concentration data from samples taken with collocated PM_{10} and dichotomous samplers.

9.4 The need for interference corrections arises from overlaps that are not deconvoluted by the least squares algorithm. This can best be illustrated by an example: Barium and titanium are analyzed by the gadolinium and iron fluorescers, respectively. The barium L x-rays overlap with the K x-rays of titanium and require an interference correction because the elements analyzed by gadolinium do not include titanium. The interference correction technique is described by Gilfrich in Section 15, Citation 29. The interference coefficient, determined during calibration, represents the fraction of the concentration of an affecting element (barium in the present example) which must be subtracted from the concentration of the affected element concentration (titanium) to compensate for the interference.

9.5 When samples are collected by the dichotomous or other samplers using virtual impaction, an additional correction must be employed because these type of samplers do not perfectly separate the fine and coarse particles. Due to virtual impaction requirements, about 10% of the fine particle mass is deposited on the coarse filter. Therefore, the attenuation corrections used for the particles on the coarse filter "over-correct" the attenuation because of these residual fines on the coarse filter. These effects are compensated for by the flow fraction correction.

10. Data Reporting

[Note: In other Inorganic Compendium methods, the authors have provided detailed examples of calculations involving final metal concentration (in terms of µg/m^3) from filterable materials. However, due to the nature of overlapping spectra which is characteristic of energy dispersive spectormeters, calculations are required to be performed by computer due to the complexity of the deconvolution of the recorded spectra which uses least square algorithm involving experimentally determined elemental shape functions instead of the mathematical Gaussian function. To perform by hand would require second order calculus and considerable time and manpower. Thus, the application of a computer is mandatory to determine elemental intensities and the elemental concentrations by a polynomial fit using a model based on the fundamentals of x-ray physics process (see Section 11 for further explanation).]

The two most important data output files are an ASCII file which contains a recapitulation of the field data and the final sample concentrations in ng/m^3 and a Lotus file with only the sample data. An example printout of a fine/coarse sample pair is shown in Table 3.

The uncertainty reported with each concentration is a 1F (68% confidence level) uncertainty and is determined by propagating the errors given in Section 12. Elements with concentrations below 3 times the uncertainty are flagged with an asterisk (*) on the printed record. If the true elemental concentration is zero then the fitting procedure implies that negative and positive results are equally probable. Therefore, negative numbers may be reported.

11. Calibration

11.1 Calibration is performed only when a change in fluorescers or x-ray tubes or detector is made or a serious malfunction occurs requiring significant repairs. Calibration establishes the elemental sensitivity factors and the magnitude of the interference or overlap coefficients. It takes approximately 2 weeks to complete a calibration.

11.2 Thin film standards are used for calibration because they most closely resemble the layer of particles on a filter. There are two types of calibration standards in use. One type consists of thin films deposited on Nuclepore substrates (Micromatter Co., Eastsound, WA). These standards are available for almost all the elements analyzed ranging in atomic number from 11 (Na) to 82 (Pb) with deposit masses gravimetrically determined to ± 5%. Another type consists of polymer films that contain known amounts of two elements in the form of organo-metallic compounds dissolved in a polymer and are not commercially available but their preparation is described in Section 15, Citation 9. These standards have been prepared for elements with atomic numbers above 21 (titanium and heavier). The same set of standards is used every time the spectrometer is calibrated. The standards are sufficiently durable to last many years, however occasionally one must be replaced due to accidents in handling. Approximately 200 calibration standards for 44 elements are in use (see Table 4.) and the acquisition of their spectra requires several days.

11.3 The background files which are used for background fitting are created at calibration time. Thirty clean Teflo® and Nuclepore® blanks are kept sealed in a plastic bag and are used exclusively for background measurement. After acquiring spectra for all 7 fluorescers the spectra are added together to produce a single spectrum for each fluorescer. Options are available to omit a spectrum from the sum if one shows a contamination. It is these summed spectra that are fitted to the background during spectral processing.

11.4 The shapes standards are thin film standards consisting of ultra pure elemental materials for the purpose of determining the physical shape of the pulse height spectrum. For this purpose it is not necessary for the concentration of the standard to be known - only that it be pure. A slight contaminant in the region of interest in a shape standard can have serious effect on the ability of the least squares fitting algorithm to fit the shapes to the unknown. For this reason the Se and elemental As standards, whose compounds are volatile, are kept in separate plastic bags in a freezer to prevent contamination of other standards; the Au standard, which will slowly amalgamate with atmospheric Hg, is kept in a desiccator. The shape standards are acquired for sufficiently long times to provide a large number of counts in the peaks of interest. It is these elemental shapes spectra that are fitted to the peaks in an unknown sample during spectral processing.

11.5 The spectra from the calibration standards are deconvoluted to get elemental intensities as described in Section 9.2. Using these intensities and the elemental concentration in the standards the sensitivities are determined by a polynomial fit using a model based on the fundamentals of the x-ray physics process as well as measurements on the calibration standards. This approach allows the calculation of sensitivities for elements for which there are poor or no standards such as volatile ones like Se and elemental As well as improving on elements with good standards.

11.6 The overlap coefficients are determined during calibration and represent the extent of interference that exists between overlapping spectral peaks. During calibration an affecting element (barium, to continue with the example of Section 9.4) is measured both at the analyte line peak for barium and at the titanium peak. The coefficient is expressed as the ratio of the concentration of the affected element (titanium) to the

concentration of the affecting element (barium). All elements requiring overlap coefficient determination are calculated in this manner.

12. Detection Limits

The detection limits are determined by propagation of errors. The sources of random error which are considered are: calibration uncertainty (± 5%); long term system stability (± 5%); peak and background counting statistics; uncertainty in attenuation corrections; uncertainty in overlap corrections; uncertainty in flow rate; and uncertainty in coarse fraction due to flow fraction correction (paired samples only). Table 2 outlines typical 1F (68% confidence level) detection limits on a Teflo® blank for fine particles and a Nuclepore® blank for coarse (2.5 µm-10 µm) particles. These detection limits are defined in terms of the uncertainty in the blank. This ignores the effect of other elements which generally is small except for the light elements (potassium and lower) where overlapping spectral lines will increase the detection limit.

[Note: The difference in the detection limits between the two filters in Table 2 is due more to the difference in sensitivity to fine and coarse particles and less to the difference in filter material.]

Higher confidence levels may be chosen for the detection limits by multiplying the 1F limits by 2 for a 2F (or 95% level) or by 3 for 3F (or 99.7% level). To convert the detection limits to more useful units one can use the typical deposit areas for 37-mm and 47-mm diameter filters of 6.5 cm^2 and 12.0 cm^2 respectively.

13. Quality Control

13.1 A comprehensive quality control program is in effect consisting of many measured parameters covering all measurement conditions and automatically produces control charts for all such measurements. All plotted data are normalized to the mean to give a rapid assessment of relative change.

13.2 Run-time quality control gives an indication of instrument performance at the time of data acquisition by measurements on stable qualitative standards. The parameters which are measured and their significance are: peak areas (monitors change in sensitivity), background areas (monitors contamination or background changes), centroid (monitors gain and zero adjustment to insure that spectra are assigned the correct channel), and FWHM, (monitors degradation of the detector resolution). These four parameters are measured for elements ranging from sodium to lead and include atmospheric argon. An example of plots of run-time QC data are illustrated in Figures 1 through 4 and Table 5, for the target and tolerance values for the parameters measured.

13.3 In addition to the run-time quality control procedure the analysis results of Standard Reference Materials SRM1833 and SRM1832 are included in the data reports. These results provide an overall check of the spectral processing program for the elements which are certified in the standards. The sole purpose of the SRMs is to provide a quality control measure; the standards are not used for calibration. Typical results of these SRMs are documented in Tables 6 and 7, and plotted in Figure 5.

13.4 The run-time quality control procedures serve as an indicator of possible emerging problems by flagging deviations greater than 3 tolerance units as defined for each element in Table 5. Persistently increasing trends are investigated to determine their cause(s) before they impact the results of SRM analyses.

13.5 The acceptance criteria of results for the elements certified in the SRMs is that the uncertainty intervals for the analytical results and those of the certified values should overlap each other. If any element fails this then the run of unknowns is repeated. Repeated failures indicate the need for recalibration.

13.6 A value for chi-square is calculated and reported with the data to indicate the quality of the fit. Chi-square values that are much larger than 1.0 indicate a problem in the fitting procedure. Changes in detector resolution or gain in the amplifier produce large values for chi-square; however such changes would be detected by the run-time quality control procedure. Also, large chi-square values can accompany results for heavily loaded filters even though the relative errors are typical. In addition, elements analyzed by the titanium and the iron fluorescers may experience large chi-square values due to interferences from overlapping elements. Chi-square is a more useful measure of goodness-of-fit for the other fluorescers for this reason.

13.7 To acquire more information about fitting problems the fitted spectra can be viewed on the screen or a hard copy printed. Such plots can be compared to the unknown spectra, background spectra, or to the library shape standards to help elucidate the suspected problem. Various statistics such as the correlation coefficient can be calculated on the fitted and measured spectra as a additional measure of the goodness-of-fit. Fitted spectrum superposed on its measured spectrum along with the associated statistics is illustrated in Figure 6.

14. Precision and Accuracy

Precision varies with the element and concentration. At high concentrations (greater than 1 $\mu g/cm^2$) a precision of 7.1% can be expected for elements analyzed by one fluorescer and 5.0% can be expected for those analyzed by two. Refer to Table 1 for a listing of the elements and the fluorescers which analyze them. Based upon the analysis of NIST SRMs the accuracy is ± 10%.

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TABLE 1. EXAMPLE OF FLUORESCER USAGE

Element	Fluorescer Al	Ti	Fe	Ge	Ag	Zr	Gd
Na	x						
Mg	x						
Al	x						
Si	x						
P	x	x					
S	x	x					
Cl	x	x					
Ar	x	x					
K	x	x					
Ca	x	x					
Sc	x	x					
Ti			x	x			
V			x	x			
Cr			x	x			
Mn				x		x	
Fe				x		x	
Co				x		x	
Ni				x		x	
Cu				x		x	
Zn						x	
Ga						x	
Ge						x	
As						x	
Se						x	
Br						x	
Rb					x	x	
Sr					x		x
Y					x		
Zr					x		x
Mo					x		x
Rh							x
Pd							x
Ag							x
Cd							x
Sn							x
Sb							x
Te							x
I							x
Cs							x
Ba							x
La							x
W					x	x	
Au					x	x	
Hg					x	x	
Pb					x	x	

[Note: The 'x' marks the fluorescers that analyze each element.]

TABLE 2. METHOD DETECTION LIMITS (MDL) FOR TEFLO® AND NUCLEPORE® BLANK FILTERS (1F)

Teflo® - fine element Method Detection Limits (MDL)			Nuclepore® - coarse element Method Detection Limits (MDL)		
	ng/cm^2	ng/m^3[1]		ng/cm^2	ng/m^3[2]
Na	5.3	1.59	Na	17.4	47.12
Mg	3.2	0.96	Mg	7.9	21.34
Al	17.6	5.29	Al	46.7	126.48
Si	8.0	2.41	Si	21.2	50.40
P	2.6	0.78	P	4.1	11.10
S	2.6	0.78	S	6.9	16.56
Cl	4.8	1.44	Cl	5.6	13.44
K	6.3	1.89	K	5.6	15.17
Ca	9.0	2.71	Ca	8.7	23.56
Sc	1.5	0.45	Sc	1.3	3.52
Ti	16.9	5.08	Ti	18.7	42.52
V	5.3	1.59	V	5.5	14.89
Cr	3.0	0.90	Cr	3.0	8.12
Mn	.8	0.24	Mn	.8	2.17
Fe	.7	0.21	Fe	1.0	2.71
Co	.4	0.12	Co	.4	1.08
Ni	.6	0.18	Ni	.7	1.89
Cu	.7	0.21	Cu	.8	2.17
Zn	1.0	0.30	Zn	1.1	2.98
Ga	1.6	0.48	Ga	1.5	4.06
Ge	1.1	0.33	Ge	1.0	2.71
As	.8	0.24	As	.9	2.44
Se	.7	0.21	Se	.6	1.62
Br	.6	0.18	Br	.7	1.89
Rb	.7	0.21	Rb	.7	1.89
Sr	1.1	0.33	Sr	.9	2.44
Y	1.2	0.36	Y	1.1	2.98
Zr	1.2	0.36	Zr	1.1	2.98
Mo	1.6	0.48	Mo	1.5	4.06
Rh	25.9	7.79	Rh	26.5	71.70
Pd	22.9	6.89	Pd	18.7	50.65
Ag	20.2	6.02	Ag	20.3	54.98
Cd	22.0	6.62	Cd	19.2	52.00
Sn	30.5	9.18	Sn	31.5	85.31
Sb	31.4	9.45	Sb	26.7	72.31
Te	26.3	7.91	Te	27.6	66.62
I	35.5	10.68	I	34.4	93.17
Cs	48.9	14.62	Cs	50.9	137.85
Ba	51.8	15.59	Ba	58.3	157.89
La	70.6	2.12	La	68.9	186.60
W	3.4	10.23	W	3.3	8.93
Au	1.7	0.51	Au	1.5	4.06
Hg	1.5	0.45	Hg	1.4	3.79
Pb	1.5	0.45	Pb	1.5	4.06

[1]Based upon dichotomous sampling for 24-hrs. using a 37-mm Teflo® filter at a sampling rate of 0.9 m^3/hr.
[2]Based upon dichotomous sampling for 24-hrs using a 37-mm Nuclepore® filter at a sampling rate of 0.1 m^3/hr.

TABLE 3. DATA REPORT FORMAT FOR A FINE/COARSE PAIRED SAMPLE

KEVEX SUMMARY: ADOBE FLATS URBAN PARTICULATE STUDY

SITE = ADB
DURATION (MIN) = 714.0 SAMPLE DATE = 3/20/92 AND 1900 HOURS
FLOW FRAC = .0869 FLOW (L/MIN) = 37.105 +- .500
XRF ID = 999906 XRF ID = 999956
SAMPLE ID = T0033 SAMPLE ID = NU0033

FINE, NG/M³				COARSE, NG/M³			
MASS	77912.	+-	1962.	MASS	11347.	+-	812.
*NA	211.9	+-	71.4	*NA	53.3	+-	27.1
MG	564.6	+-	89.4	MG	443.9	+-	40.8
*AL	162.2	+-	74.1	AL	539.9	+-	173.8
SI	213.4	+-	40.4	SI	909.5	+-	232.7
* P	12.1	+-	18.5	* P	-5.5	+-	11.3
S	2653.4	+-	183.7	S	285.7	+-	84.9
CL	1164.4	+-	79.3	*CL	34.8	+-	24.6
K	193.6	+-	13.8	K	63.5	+-	8.9
CA	43.4	+-	5.6	CA	181.7	+-	13.9
*SC	3.6	+-	4.1	*SC	-1.3	+-	2.2
*TI	17.6	+-	6.6	TI	54.7	+-	9.6
* V	4.6	+-	2.3	* V	3.2	+-	1.7
*CR	2.0	+-	1.0	CR	9.8	+-	1.6
MN	10.0	+-	1.4	MN	10.1	+-	1.3
FE	243.7	+-	21.9	FE	783.5	+-	78.2
*CO	2.8	+-	1.8	*CO	4.8	+-	1.7
NI	3.8	+-	1.2	*NI	.3	+-	.6
CU	14.3	+-	1.9	CU	8.8	+-	1.3
ZN	167.5	+-	14.9	ZN	27.6	+-	4.9
*GA	2.4	+-	1.0	*GA	-.0	+-	.4
*GE	3.3	+-	1.3	*GE	.0	+-	.6
AS	24.7	+-	3.6	*AS	1.8	+-	1.2
SE	4.7	+-	.8	*SE	.7	+-	.4
BR	29.0	+-	2.8	BR	7.9	+-	1.1
*RB	1.7	+-	.8	*RB	1.0	+-	.4
SR	2.9	+-	.9	SR	2.2	+-	.5
* Y	12.4	+-	6.1	* Y	3.9	+-	2.9
*ZR	2.9	+-	4.8	*ZR	4.3	+-	2.6
*MO	7.3	+-	4.8	*MO	-3.2	+-	2.2
*RH	.0	+-	3.2	*RH	-1.2	+-	1.6
*PD	-3.6	+-	3.1	*PD	-1.0	+-	1.7
*AG	-6.4	+-	3.4	*AG	1.2	+-	1.9
*CD	8.5	+-	4.5	*CD	-.7	+-	2.2
SN	54.3	+-	9.4	*SN	2.3	+-	3.9
*SB	-1.6	+-	6.4	*SB	-.6	+-	3.3
*TE	2.5	+-	7.5	*TE	-7.2	+-	3.8
* I	25.0	+-	9.6	* I	2.4	+-	4.7
*CS	-4.0	+-	11.2	*CS	12.4	+-	5.9
*BA	-7.7	+-	13.7	BA	25.1	+-	7.4
*LA	-4.8	+-	34.5	*LA	22.6	+-	17.9
* W	-1.1	+-	2.6	* W	1.5	+-	1.3

```
        *AU       -.9 +-     1.8       *AU        .2 +-      .9
        *HG       -.4 +-     1.9       *HG       1.5 +-     1.0
         PB     221.6 +-    19.7        PB      46.0 +-     6.2
* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
  XRF DATE= 04/29/1992  16:35 RBK   (F):  04/29/1992  20:35 RBK   (C)
  SPECTRAL ANALYSIS DATE=  5/20/1992
```

TABLE 4. CALIBRATION STANDARDS AND CONCENTRATIONS

Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²
CaF237	F	18.00	CuS1124	S	31.90	Cr 85	Cr	85.00	RbNO311	Rb	69.00
CaF2 29	F	14.10	CuS58.6	S	16.50	Cr 84	Cr	84.00	RbNO322	Rb	12.90
CaF2 90	F	43.80	CuS57.6	S	13.90	Cr 75	Cr	75.00	RbNO3 a	Rb	24.90
CaF2 91	F	44.30	CuS58.2	S	14.00	Cr 74	Cr	74.00	RbNO3 b	Rb	24.90
CaF2102	F	49.60	NaCl 57	Cl	34.60	Cr 122	Cr	122.00	RbNO3 c	Rb	24.90
CaF2 66	F	32.10	NaCl 87	Cl	52.80	CrCu32a	Cr	9.19	SrF2 57	Sr	39.80
CaF2 28	F	13.60	NaCl446	Cl	27.10	CrCu26g	Cr	8.14	SbSr29z	Sr	4.97
CaF2 33	F	16.10	NaCl715	Cl	43.40	MnZn24b	Mn	8.57	SrF2 50	Sr	34.90
CaF2 39	F	19.00	NaCl497	Cl	30.20	Mn 57	Mn	57.00	SbSr31y	Sr	5.14
CaF2 54	F	26.30	NaCl501	Cl	30.40	Mn 183	Mn	183.00	SrF2137	Sr	95.60
CaF2291	F	14.10	NaCl 51	Cl	31.00	MnZn27x	Mn	9.10	SrF2184	Sr	12.80
CaF2 30	F	14.60	NaCl512	Cl	31.10	Mn 43	Mn	43.00	SrF2 92	Sr	64.20
CaF2 52	F	25.30	NaCl519	Cl	31.50	Mn 46.9	Mn	46.90	SrF2103	Sr	71.80
CaF2 48	F	23.40	KCl 45	Cl	21.40	Mn 44.5	Mn	44.50	YF3 46	Y	28.00
CaF2 45	F	21.90	KCl53.3	Cl	25.40	Mn 46.6	Mn	46.60	ZrCd24c	Zr	9.85
CaF2 36	F	17.50	KCl 70	Cl	33.30	Mn 43.7	Mn	43.70	ZrCd20w	Zr	10.77
CaF2134	F	65.20	KCl 49	Cl	23.30	Mn 69	Mn	69.00	MoO3145	Mo	96.70
CaF2110	F	53.50	KCl48.7	Cl	23.20	FePb37y	Fe	7.72	MoO3106	Mo	70.70
NaCl 57	Na	22.40	KCl47.9	Cl	22.80	Fe 107	Fe	107.00	MoO3110	Mo	73.30
NaCl 87	Na	34.20	KCl 48	Cl	22.80	Fe 127	Fe	127.00	MoO3 59	Mo	39.30
NaCl446	Na	17.60	KCl47.6	Cl	22.60	Fe 46	Fe	46.00	MoO3 54	Mo	36.00
NaCl715	Na	28.10	KCl 45	K	23.60	Fe 88	Fe	88.00	Rh 16	Rh	16.00
NaCl497	Na	19.60	KCl53.3	K	28.00	FePb38y	Fe	7.71	Pd 33	Pd	33.00
NaCl501	Na	19.70	KCl 70	K	36.70	Co 45a	Co	45.00	Pd 198	Pd	198.00
NaCl 51	Na	20.10	KCl 49	K	25.70	Co 45b	Co	45.00	Ag 35	Ag	35.00
NaCl512	Na	20.10	KCl48.7	K	25.50	RbCo29c	Co	7.43	Ag 132	Ag	132.00
NaCl519	Na	20.40	KCl47.9	K	25.10	RbCo25b	Co	7.65	Cd 83	Cd	83.00
Mg 81	Mg	81.00	KCl 48	K	25.20	Ni 54	Ni	54.00	ZrCd20w	Cd	9.15
Mg 41	Mg	41.00	KCl47.6	K	25.00	Ni 88	Ni	88.00	ZrCd24c	Cd	8.38
Mg 41.3	Mg	41.30	CaF2 37	Ca	19.00	NiV 21c	Ni	5.77	Cd 77	Cd	77.00
Mg 43	Mg	43.00	CaF2 29	Ca	14.90	Ni 101	Ni	101.00	Sn 40	Sn	40.00
Mg 43.8	Mg	43.80	CaF2 90	Ca	46.20	Cu 96	Cu	96.00	Sn 185	Sn	185.00
Mg 60.2	Mg	60.20	CaF2 91	Ca	46.70	Cu 104	Cu	104.00	Sn 97a	Sn	97.00
Al 57	Al	57.00	CaF2102	Ca	52.40	Cu 128	Cu	128.00	Sn 97b	Sn	97.00
Al 37.9	Al	37.90	CaF2 66	Ca	33.90	CrCu26g	Cu	7.65	Sn 79	Sn	79.00
Al 37.4	Al	37.40	CaF2 28	Ca	14.40	CrCu32a	Cu	8.63	Sb 194	Sb	194.00
Al 29	Al	29.00	CaF2 33	Ca	16.90	Cu 38	Cu	38.00	Sb 47	Sb	47.00
Al 43.2	Al	43.20	CaF2 39	Ca	20.00	Zn 51	Zn	51.00	Sb 147	Sb	147.00
Al 62	Al	62.00	CaF2 54	Ca	27.20	Zn 125	Zn	125.00	Sb 42	Sb	42.00
Al 75	Al	75.00	CaF2291	Ca	14.90	MnZn27x	Zn	8.46	SbSr29z	Sb	5.01
SiO 46	Si	29.30	CaF2 30	Ca	15.40	MnZn24b	Zn	7.97	SbSr31y	Sb	5.18
SiO 47	Si	29.90	CaF2 52	Ca	26.70	GaP 34	Ga	23.50	Te 53	Te	53.00
SiO 51a	Si	32.50	CaF2 48	Ca	24.60	GaP 40	Ga	27.70	KI 46	I	35.20
SiO 51b	Si	32.50	CaF2 45	Ca	23.10	GaP 70	Ga	48.50	CsBr 53	Cs	33.10
SiO 56	Si	35.70	CaF2 36	Ca	18.50	GaP 105	Ga	72.70	CsBr 54	Cs	33.70
SiO 80	Si	51.00	CaF2134	Ca	68.60	Ge 37	Ge	37.00	CsBr 51	Cs	31.90
SiO27.6	Si	17.60	CaF2110	Ca	56.50	TiGe33d	Ge	6.22	BaF2108	Ba	84.60
SiO46.1	Si	29.40	ScF3 57	Sc	25.10	TiGe29x	Ge	5.94	BaF2 48	Ba	37.60
SiO72.2	Si	46.00	Ti 39	Ti	39.00	Ge 140	Ge	140.00	BaF2 60	Ba	47.00
GaP 34	P	10.50	Ti 95	Ti	95.00	BaAs23y	As	5.60	BaF2 57	Ba	44.70
GaP 40	P	12.30	TiGe33d	Ti	2.46	BaAs36w	As	5.52	BaF2143	Ba	112.00
GaP 70	P	21.50	TiGe29x	Ti	2.36	CsBr 53	Br	19.90	BaF2114	Ba	89.40
GaP 105	P	32.30	V 45	V	45.00	CsBr 54	Br	20.30	BaAs23y	Ba	4.98

TABLE 4. (continued)

Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²	Standard ID	Element	µg/cm²
CuS1052	S	30.80	V 53	V	53.00	CsBr 51	Br	19.10	BaAs36w	Ba	4.91
CuS 48	S	13.00	NiV 21c	V	6.64	RbNO346	Rb	26.60	LaF3157	La	111.30
CuS 136	S	33.00	Cr 30	Cr	30.00	RbCo25b	Rb	7.88	LaF3 62	La	44.00
CuS39.6	S	10.20	Cr 53	Cr	53.00	RbCo29c	Rb	7.65			

TABLE 5. TARGET AND TOLERANCE VALUES FOR QC RESULTS

(TARGET VALUES)

FILE: 0:QCBEGTGT					FILE: 0:QCENDTGT				
STDEL ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)	STD ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)
1833	Pb	31112.12	10.5449	207.4653	1832	Cu	17548.85	8.0411	174.1389
1833	Zn	31772.52	8.6306	179.6835	1832		5303.84	6.9247	167.1478
1833	Fe	313475.41	6.3935	159.4537	1832	Mn	86202.33	5.8891	154.6347
1833	Ti	216978.09	4.5037	142.4946	1832	Ca	217562.00	3.6847	135.3520
1833	Si	69021.60	1.7322	121.7406	1832	V	99761.96	4.9443	146.1904
1833	K	220344.80	3.3069	132.4137	1832	Al	16562.45	1.4779	119.5793
BLKt	Sn	111.52	0.0000	0.0000	1832	Si	67688.42	1.7319	118.4960
BLKt	Pb	85.82	0.0000	0.0000	1832	Na	10332.21	1.0256	114.4485
BLKt	Cu	497.06	0.0000	0.0000	BLKn	Ba	183.14	0.0000	0.0000
BLKt	Sr	72.92	0.0000	0.0000	BLKn	W	241.42	0.0000	0.0000
BLKt	Ni	648.99	0.0000	0.0000	BLKn	Zn	148.48	0.0000	0.0000
BLKt	Fe	459.10	0.0000	0.0000	BLKn	Sr	83.00	0.0000	0.0000
BLKt	S	266.76	0.0000	0.0000	BLKn	Ni	654.44	0.0000	0.0000
BLKt	Al	396.30	0.0000	0.0000	BLKn	Fe	603.55	0.0000	0.0000
BLKt	Ar	747.74	0.0000	0.0000	BLKn	S	3047.53	0.0000	0.0000
BLKt	Na	120.85	0.0000	0.0000	BLKn	Si	936.48	0.0000	0.0000
BaNa	Na	27711.44	1.0278	107.2698	BLKn	Ar	751.18	0.0000	0.0000
BaNa	Ba	7369.12	32.0701	670.6336	BLKn	Mg	3622.12	0.0000	0.0000
					BaSr	Sr	210871.20	14.1410	227.8625
					BaSr	Ba	7464.85	32.0692	671.0372

(TOLERANCE UNITS in %)

FILE: 0:QCBEGTOL					FILE: 0:QCENDTOL				
STDEL ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)	STD ID	EL	AREA (cts)	CENTROID (keV)	FWHM (ev)
1833	Pb	1.66	0.0313	0.9901	1832	Cu	1.66	0.0104	1.9331
1833	Zn	1.66	0.0131	1.7328	1832	Co	1.70	0.0308	2.4345
1833	Fe	1.66	0.0224	0.9361	1832	Mn	1.66	0.0198	1.3536
1833	Ti	1.66	0.0259	0.9768	1832	Ca	1.66	0.0253	1.1311
1833	Si	1.66	0.0616	1.4120	1832	V	1.66	0.0243	1.1031
1833	K	1.66	0.0323	0.9235	1832	Al	2.02	0.1173	3.3722
BLKt	Sn	12.98	0.0000	0.0000	1832	Si	1.66	0.0481	0.8888
BLKt	Pb	8.93	0.0000	0.0000	1832	Na	1.78	0.1560	1.5333
BLKt	Cu	4.95	0.0000	0.0000	BLKn	Ba	9.92	0.0000	0.0000
BLKt	Sr	17.61	0.0000	0.0000	BLKn	W	8.20	0.0000	0.0000
BLKt	Ni	3.81	0.0000	0.0000	BLKn	Zn	11.45	0.0000	0.0000
BLKt	Fe	7.57	0.0000	0.0000	BLKn	Sr	10.88	0.0000	0.0000
BLKt	S	8.71	0.0000	0.0000	BLKn	Ni	6.55	0.0000	0.0000
BLKt	Al	7.23	0.0000	0.0000	BLKn	Fe	5.63	0.0000	0.0000
BLKt	Ar	17.39	0.0000	0.0000	BLKn	S	2.88	0.0000	0.0000
BLKt	Na	16.00	0.0000	0.0000	BLKn	Si	6.75	0.0000	0.0000
BaNa	N	1.66	0.1103	1.2599	BLKn	Ar	22.14	0.0000	0.0000
BaNa	Ba	2.53	0.0979	3.9782	BLKn	Mg	5.64	0.0000	0.0000
					BaSr	Sr	1.66	0.0073	0.4538
					BaSr	Ba	1.86	0.0279	2.8094

TABLE 6. EXAMPLE PRINTOUT OF SRM 1833

KEVEX SUMMARY: TEFLO® BLANKS LOT #457803 (NEW TUBE)

SITE =
DURATION (MIN) = .0 SAMPLE DATE = 99/99/99 AND 9999 HOURS
FLOW FRAC = .0000 FLOW (L/MIN) = .000 +- .200
XRF ID = 112141
SAMPLE ID = SRM1833

	FINE, NG/CM^2			NIST CERTIFIED VALUES			
MASS	0.	+-	398.	MASS	15447		
*NA	-801.2	+-	326.4	NA	.0	+-	.0
MG	161.3	+-	18.2	MG	.0	+-	.0
AL	1027.5	+-	102.2	AL	.0	+-	.0
SI	34806.8	+-	3023.4	SI	33366.0	+-	2163.0
P	79.8	+-	19.9	P	.0	+-	.0
*S	-28.2	+-	782.8	S	.0	+-	.0
*CL	-68.6	+-	113.8	CL	.0	+-	.0
K	16734.7	+-	1018.7	K	17147.0	+-	1699.0
*CA	-3.9	+-	61.4	CA	.0	+-	.0
*SC	-17.1	+-	5.4	SC	.0	+-	.0
TI	12852.9	+-	822.1	TI	12821.0	+-	1854.0
*V	46.0	+-	52.2	V	.0	+-	.0
CR	108.2	+-	12.7	CR	.0	+-	.0
MN	13.8	+-	2.9	MN	.0	+-	.0
FE	14332.4	+-	872.4	FE	14212.0	+-	463.0
*CO	-2.6	+-	2.9	CO	.0	+-	.0
NI	62.5	+-	4.6	NI	.0	+-	.0
*CU	3.8	+-	1.5	CU	.0	+-	.0
ZN	3800.9	+-	327.7	ZN	3862.0	+-	309.0
*GA	-30.9	+-	7.7	GA	.0	+-	.0
*GE	5.9	+-	3.6	GE	.0	+-	.0
*AS	5.7	+-	14.6	AS	.0	+-	.0
*SE	-2.0	+-	2.6	SE	.0	+-	.0
*BR	-2.3	+-	2.5	BR	.0	+-	.0
*RB	.5	+-	1.4	RB	.0	+-	.0
*SR	-5.0	+-	2.9	SR	.0	+-	.0
* Y	-2.6	+-	7.5	Y	.0	+-	.0
*ZR	-7.6	+-	3.5	ZR	.0	+-	.0
MO	45.4	+-	5.6	MO	.0	+-	.0
*RH	156.7	+-	69.5	RH	.0	+-	.0
*PD	79.2	+-	67.1	PD	.0	+-	.0
*AG	114.0	+-	69.7	AG	.0	+-	.0

TABLE 6. (continued)

	FINE, NG/CM^2				NIST CERTIFIED VALUES		
*CD	24.7	+-	66.3	CD	.0	+-	.0
*SN	-1496.1	+-	188.1	SN	.0	+-	.0
*SB	88.2	+-	96.2	SB	.0	+-	.0
*TE	240.8	+-	93.8	TE	.0	+-	.0
* I	134.8	+-	107.5	I	.0	+-	.0
*CS	-209.3	+-	106.6	CS	.0	+-	.0
*BA	-5098.1	+-	517.8	BA	.0	+-	.0
*LA	-1416.4	+-	202.2	LA	.0	+-	.0
W	59.9	+-	17.6	W	.0	+-	.0
*AU	8.7	+-	6.8	AU	.0	+-	.0
*HG	-30.6	+-	5.9	HG	.0	+-	.0
PB	16886.2	+-	1028.1	PB	16374.0	+-	772.0

* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
XRF DATE = 28-SEP-93 10:58:37 RBK
SPECTRAL ANALYSIS DATE = 12/14/1993

TABLE 7. EXAMPLE PRINTOUT OF SRM 1832

KEVEX SUMMARY: TEFLO® BLANKS LOT #457803 (NEW TUBE)

SITE	=		
DURATION (MIN)	= .0	SAMPLE DATE	= 99/99/99 AND 9999 HOURS
FLOW FRAC	= .0000	FLOW (L/MIN)	= .000 +- .200
XRF ID	= 112191		
SAMPLE ID	= SRM1832		

	FINE, NG/CM^2				NIST CERTIFIED VALUES		
MASS	0.	+-	398.	MASS	16431		
NA	11891.5	+-	1035.0	NA	11173.0	+-	.0
MG	92.2	+-	13.0	MG	.0	+-	.0
AL	15856.5	+-	1373.2	AL	14953.0	+-	986.0
SI	34398.8	+-	2964.2	SI	35491.0	+-	1150.0
P	492.0	+-	32.1	P	.0	+-	.0
S	402.1	+-	27.3	S	.0	+-	.0
CL	156.8	+-	15.9	CL	.0	+-	.0
* K	18.5	+-	18.0	K	.0	+-	.0
CA	20011.7	+-	1218.2	CA	19225.0	+-	1315.0
*SC	-21.8	+-	5.6	SC	.0	+-	.0
*TI	-4.7	+-	130.6	TI	.0	+-	.0
V	4593.6	+-	281.1	V	4272.0	+-	493.0
*CR	7.4	+-	7.3	CR	.0	+-	.0
MN	4959.3	+-	302.4	MN	4437.0	+-	493.0
FE	30.5	+-	3.9	FE	.0	+-	.0
CO	1055.1	+-	64.7	CO	970.0	+-	66.0
*NI	-6.8	+-	1.8	NI	.0	+-	.0
CU	2400.1	+-	146.3	CU	2300.0	+-	164.0
ZN	9.3	+-	2.7	ZN	.0	+-	.0
*GA	2.1	+-	2.1	GA	.0	+-	.0
*GE	.3	+-	2.4	GE	.0	+-	.0
*AS	-3.7	+-	2.2	AS	.0	+-	.0
*SE	1.0	+-	1.2	SE	.0	+-	.0
BR	10.7	+-	1.8	BR	.0	+-	.0
*RB	-.2	+-	.9	RB	.0	+-	.0
*SR	2.8	+-	2.3	SR	.0	+-	.0
* Y	-5.0	+-	1.6	Y	.0	+-	.0
*ZR	-6.5	+-	1.8	ZR	.0	+-	.0
MO	26.8	+-	4.2	MO	.0	+-	.0
*RH	25.2	+-	58.2	RH	.0	+-	.0

TABLE 7. (continued)

	FINE, NG/CM^2			NIST CERTIFIED VALUES			
*PD	-69.0	+-	54.7	PD	.0	+-	.0
*AG	151.2	+-	63.4	AG	.0	+-	.0
*CD	24.2	+-	58.2	CD	.0	+-	.0
*SN	-640.8	+-	138.6	SN	.0	+-	.0
*SB	-73.5	+-	81.3	SB	.0	+-	.0
*TE	-9.3	+-	73.9	TE	.0	+-	.0
* I	-46.6	+-	91.6	I	.0	+-	.0
*CS	3.6	+-	96.7	CS	.0	+-	.0
*BA	-2352.9	+-	328.6	BA	.0	+-	.0
*LA	-509.9	+-	156.5	LA	.0	+-	.0
W	40.0	+-	12.9	W	.0	+-	.0
*AU	-5.6	+-	2.5	AU	.0	+-	.0
*HG	-5.4	+-	3.0	HG	.0	+-	.0
*PB	-10.4	+-	4.2	PB	.0	+-	.0

* INDICATES THAT THE CONCENTRATION IS BELOW 3 TIMES THE UNCERTAINTY.
XRF DATE = 29-SEP-93 13:27:55 RBK
SPECTRAL ANALYSIS DATE = 12/14/1993

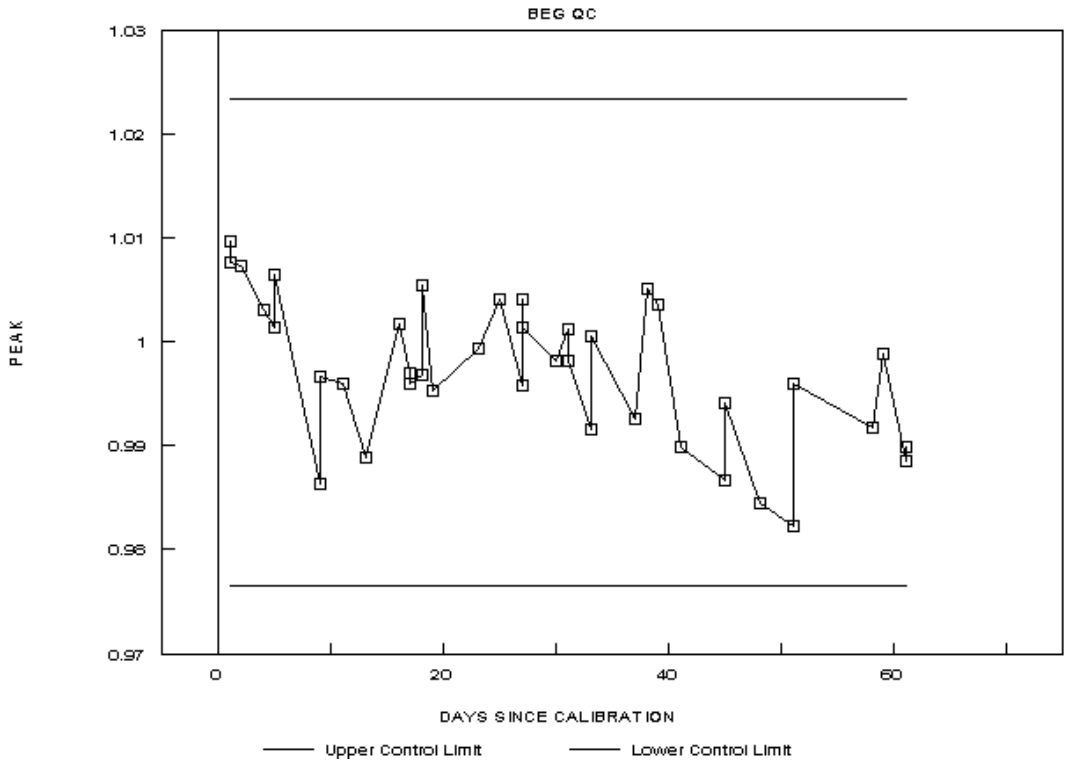


Figure 1. Quality control indicator associated with Fe peak area.

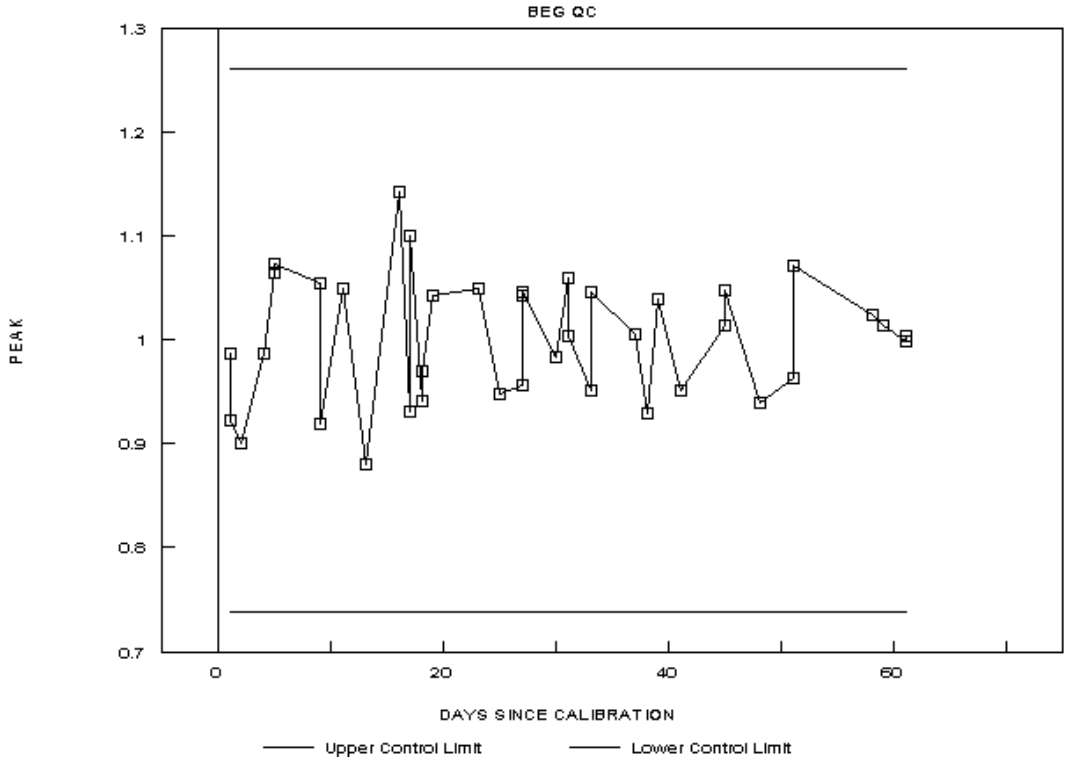


Figure 2. Quality control indicator associated with S background area.

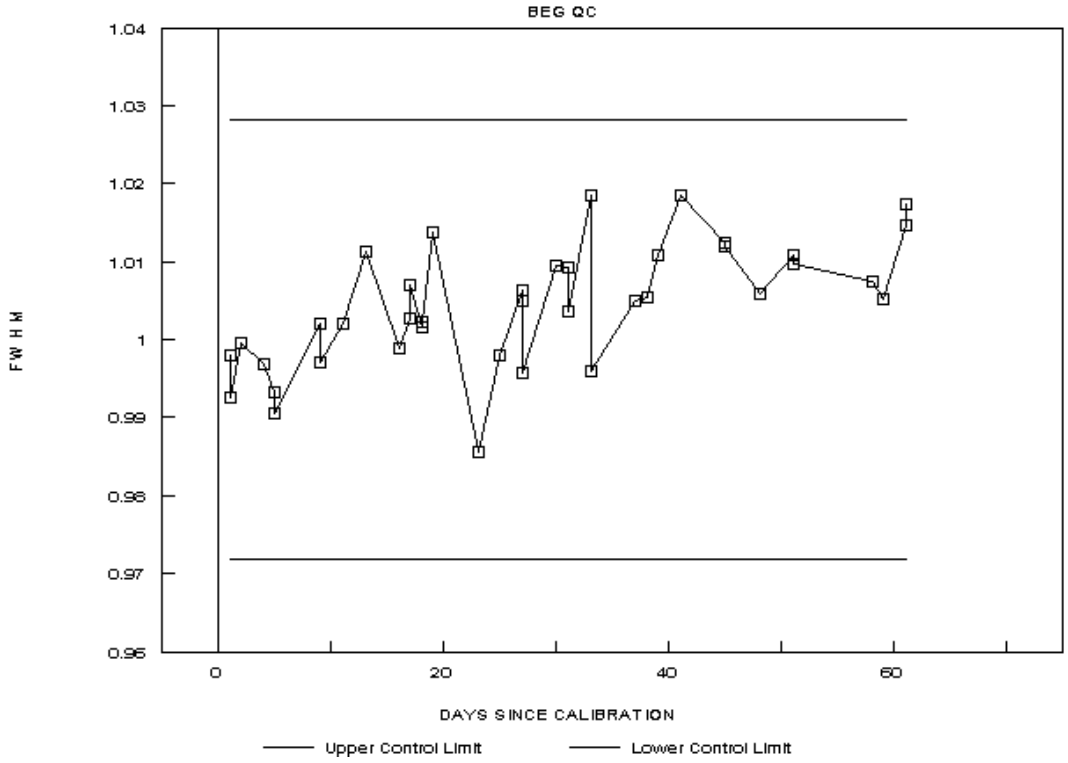


Figure 3. Quality control indicator associated with Fe FWHM.

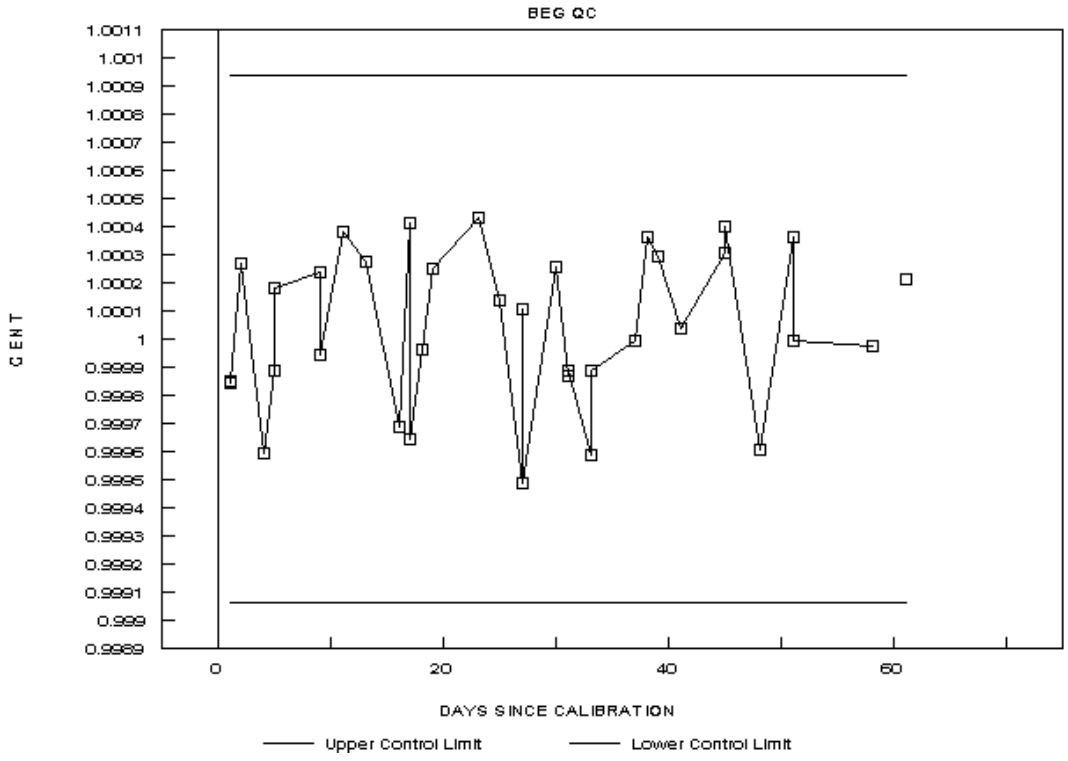


Figure 4. Quality control indicator associated with Pb centroid.

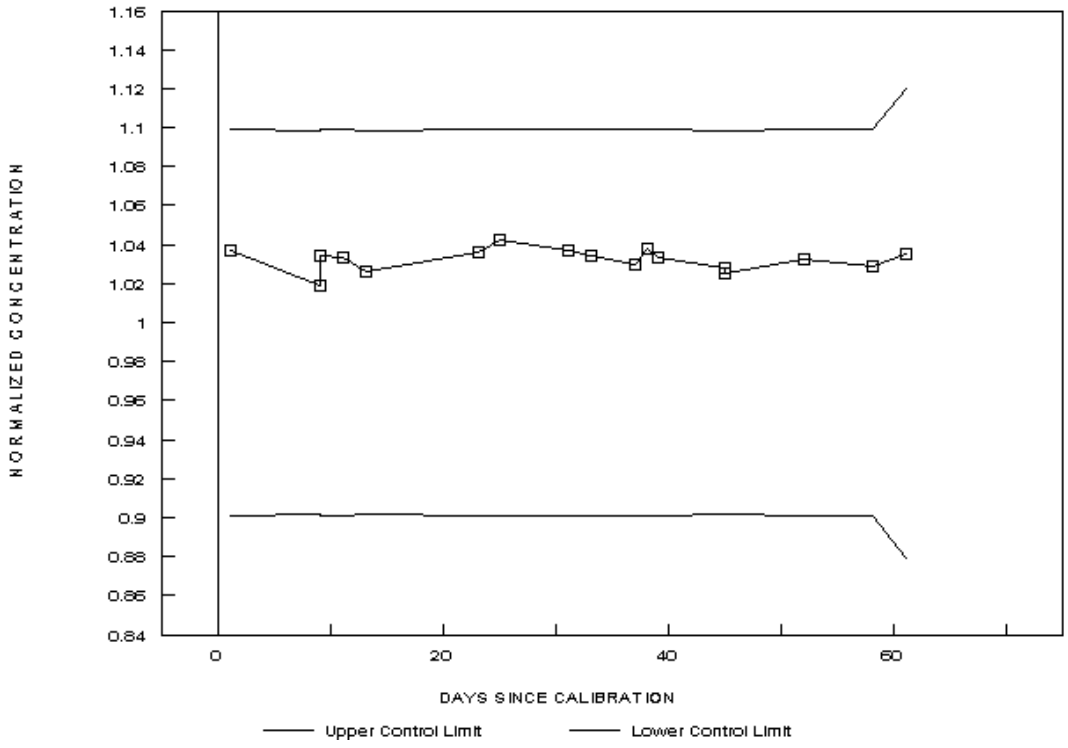


Figure 5. Quality control indicator associated with Pb in SRMs.

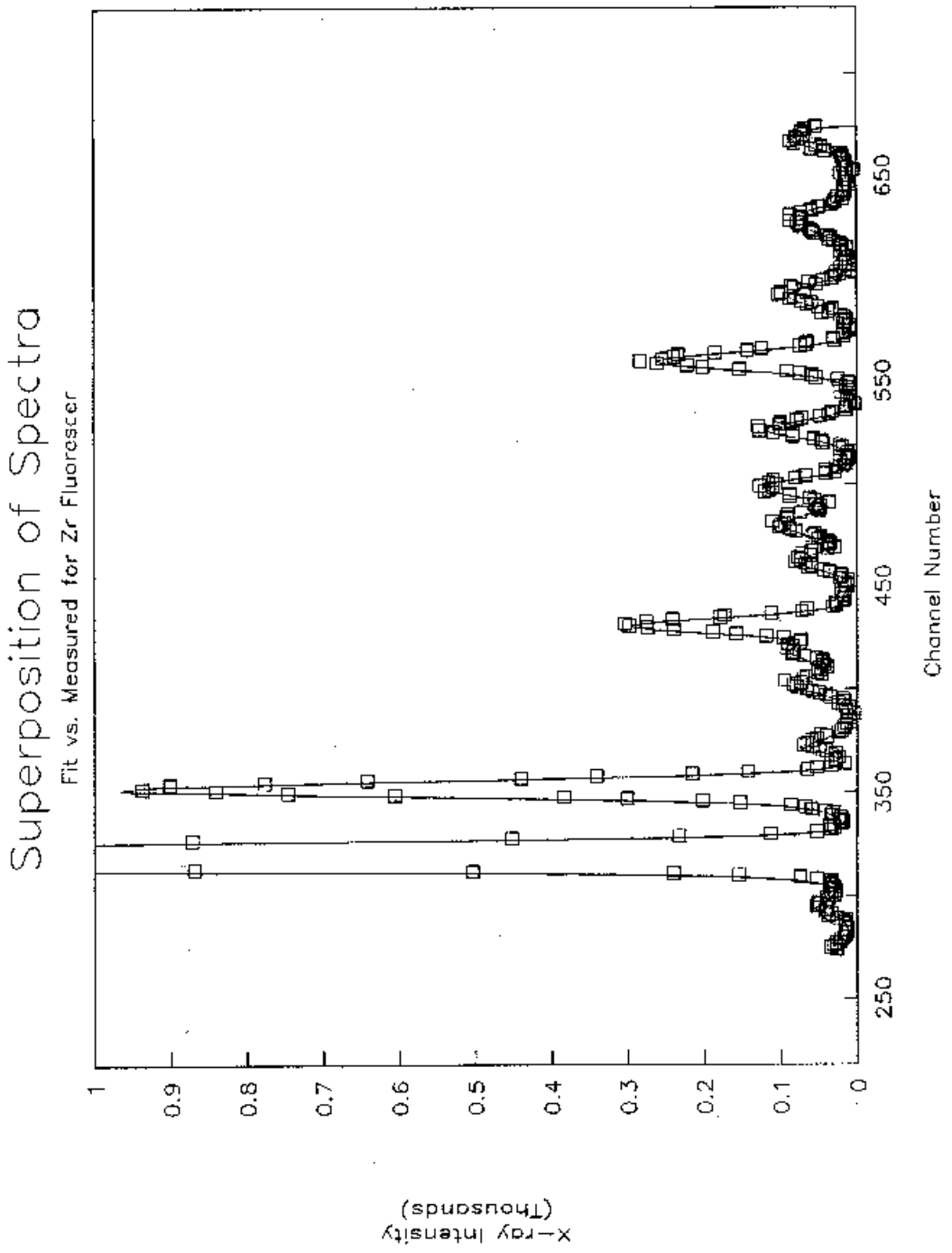


Figure 6. Quality control indicator associated with superposition of fitted and measured spectrum.

APPENDIX B

STANDARD OPERATING PROCEDURES AND INSTRUCTION MANUALS FOR AIRMETRICS SAMPLERS, SKC SAMPLE PUMPS, AND SUMMA CANISTERS

TETRA TECH EM INC.

STANDARD OPERATING PROCEDURES
AIRMETRICS MINI-VOL PARTICULATE SAMPLER

Objectives:

1. Terminal Learning Objective. Demonstrate awareness of the methods to sample ambient air with the Airmetrics Mini-Vol Particulate Sampling Unit IAW manufacturer's operating instructions

2. Enabling Learning Objectives.

   a. Given a Mini-Vol particulate sampling device, demonstrate the proper techniques for operating and maintaining the equipment IAW manufacturer's operating instructions.

   b. Given a list, select the correct pre-sampling site procedures for the Mini-Vol particulate sampling device IAW manufacturer's operating instructions.

   c. Given a list, select the correct sampling site procedures for the Mini-Vol particulate sampling device IAW manufacturer's operating instructions.

   d. Given a list, select the correct post-sampling site procedures for the Mini-Vol particulate sampling device IAW manufacturer's operating instructions.

   e. Given a list, select the correct filter installation procedures for the Mini-Vol particulate sampling device IAW manufacturer's operating instructions.

   f. Given a list, select the correct filter recovery procedures for the Mini-Vol particulate sampling device IAW manufacturer's operating instructions.

   g. Given a list, select the correct quality control/quality assurance procedures for the Mini-Vol particulate sampling device IAW manufacturer's operating instructions.

NOTES

A. Airmetrics Mini-Vol Particulate Sampler Characteristics

1. Samples air at 5 liters per minute
2. Samples for particulate matter (TSP, PM10, PM 2.5)
3. Portable and battery operated
4. Not EPA approved, but ...

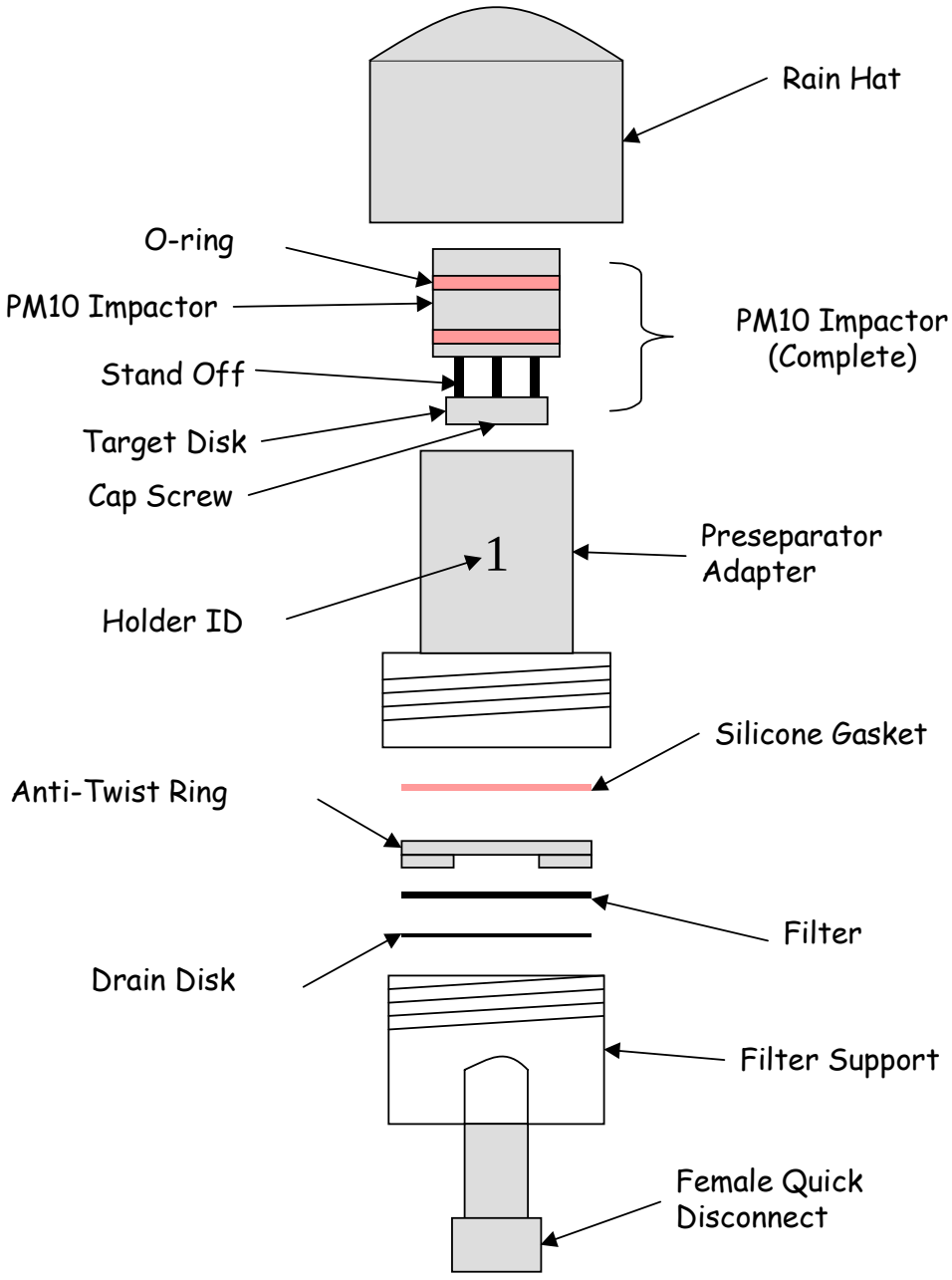
B. Pre-Sampling Site Procedures

1. TSP Sampling
2. PM_{10} Sampling
3. $PM_{2.5}$ Sampling
4. Installing 47-mm filters into Filter Assembly

C. Required Equipment

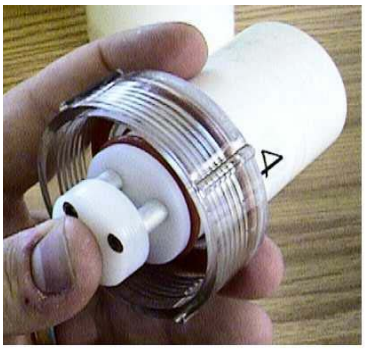
ITEM DESCRIPTION	QUANTITY
MiniVol Sampler unit	2
MiniVol Batteries	2
Preseperator/filter assemblies with rain hats (PM10, PM2.5, or TSP)	2
47-mm quartz filters pre-weighed on a 0.01 ug balance	2
Miniflow Calibration kit or dry calibrator or Gilibrator	1
Tripods or Y-shaped mounting brackets	2
Spare parts kit	1
Operating manual	1
Sampling Instructions	1
Field data sheets	2
Thermometer/Barometer	1
Mini-Screwdriver	1
Utility Wipes	2
Plastic Bags (4″ x 4″)	2
Plastic Bags (4″ x 9″)	4
Permanent Marker	1

D. Pre-Separator/Filter Holder Assembly



G. Assembling Pre-separator for TSP Sampling - The assembly should not have any impactors if TSP sampling is to be performed.

H. Assembling Pre-separator for PM 10 Sampling - Place the PM 10 impactor in the pre-separator/filter holder assembly prior to sampling.



I. Assembling Pre-separator for PM 2.5 Sampling - The assembly for the PM 2.5 sampling uses both the PM 10 and PM 2.5 impactors in sequence.

J. Preparation

1. Perform work in a vehicle or indoor work area

   a. reduces contamination

   b. simplifies assembly

The “Pre-separator/Filter Holder Assembly should be dismantled and the impactor cleaned and greased at regular intervals (*i.e.*, at minimum after every seventh sampling episode, but if heavy particulate loadings are observed on the target disk, as often as appropriate).

2. Unscrew the “Pre-separator Adapter” section from the “Filter Support” assembly and remove the “Rain Hat”.

3. Pushing with your thumb from the bottom, remove the “Impactor” through the top of the housing into the palm of your free hand.

4. Rinse the impactor from top to bottom with a solvent (hexane, white gas, lantern gas) using a squeeze bottle, paying particular attention to the impactor’s target disk.

5. Let the impactor air-dry.

6. Prepare a mixture of solvent and impactor grease (Apiezon®M, Glisseal®Ht) in a dropper bottle until thoroughly mixed and of a fluid consistency. Use a 1-inch length of grease to 100 ml of solvent. Vigorously shake the mixture until an opaque, uniform suspension, free from grease globs, is obtained. Other low-vapor pressure greases, such as silicone, are acceptable. However, removing the dirty grease from the impactor parts may be more difficult.

7. Put two or three drops of the cloudy solution on the impactor’s target disk. The drops should saturate the disk, flowing freely to the edge.

8. Let the target disk "dry" by allowing the solvent to volatilize, leaving a thin film of grease on the target disk.

9. Re-insert “Impactor” into the “Pre-separator Adapter”

K. Installing 47-mm filters into Filter Assembly

1. Select a filter/petri slide and remove cover from petri slide.

2. Remove the “Anti-Twist Ring” from the “Filter Support Assembly”.

3. Using forceps, install the new filter onto the "Drain Disk" which rests on the filter support grid, taking care not to shred or damage the edges of the filter.

4. Replace the "Anti-Twist Ring" by lining up the notches on the ring with the holder so that the ring does not move. Improper alignment could cause filters to tear.

5. Replace "Pre-separator Adapter" ensuring the "Silicone Gasket" is properly secured and aligned at the base of the "Pre-separator Adapter" and screw down hand-tight. Reattach the "Rain Hat"

6. If a unique ID does not already exist on the "Pre-separator Adapter", assign and place a unique identifying number on the filter holder. This establishes a relationship between the filter number and the "Pre-separator Adapter".

7. Record the following information on the field data sheet:

– *Sample ID* - Sample ID number XXX_YYYY_DDDD_ZZ

Where:

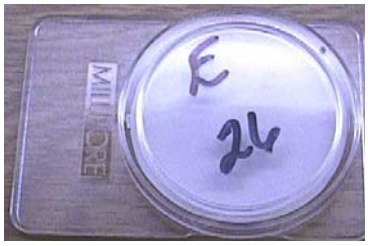
XXX - Camp abbreviation (i.e. first three letters of camp name)
YYYY - Method type (e.g. PM10, PM25, TSP)
DDDD - jday code, first digit is the last number of the year and remaining three digits are the jday of the year (e.g. 1-Jan-1999 = jday 9001).

ZZ – Sample type:
P – Primary sample, if collocated
C – Collocated sample, if collocated
FB – Field Blank
TB – Trip Blank

– *Location* - Camp or location sampled (not required)
– *Country* – Country of camp or location sample (not required)
– *Operation* – Name of operation, if applicable (not required)
– *Collected By* – Unit collecting the sample (e.g. TAML, 71st MEDDET, etc).
– *Unit Spec ID* – Unit specific ID associated with the sample if any (not required).
– *Mission ID* – Unit mission ID associated with the sample if any (not required).
– *Sample Notes* – Any notes or comments associated with the sample (e.g. short holding time, unusual circumstances, etc).
– *Filter Number* – The filter ID # obtained from the filter cassette (e.g. QM-01)
– *Filter Type* – Type of filter, one of the following types (not required)
  © TF- Teflon
  © QM – Quartz
  © GF – Glass Fiber
  © CE – Cellulose Ester
– *Holder ID* – The ID associated with the filter holder assembly
– *Sample Type* – Type of particulate sampler (not required)
  © PM10 – Particulate matter less than 10 microns (DEFAULT)
  © TSP – Total Suspended Particulate
  © PM2.5 – Particulate matter less than 2.5 microns

1. Place the entire assembly into a plastic bag

2. Keep assembly in a vertical position during transport



K. Sampling Site Procedures

1. Carefully transport the following equipment to the sampling site:

   a. Sampling unit

   b. Pre-separator/Filter Holder Assembly

   c. Battery

   d. Flow meter (e.g. Gilibrator)

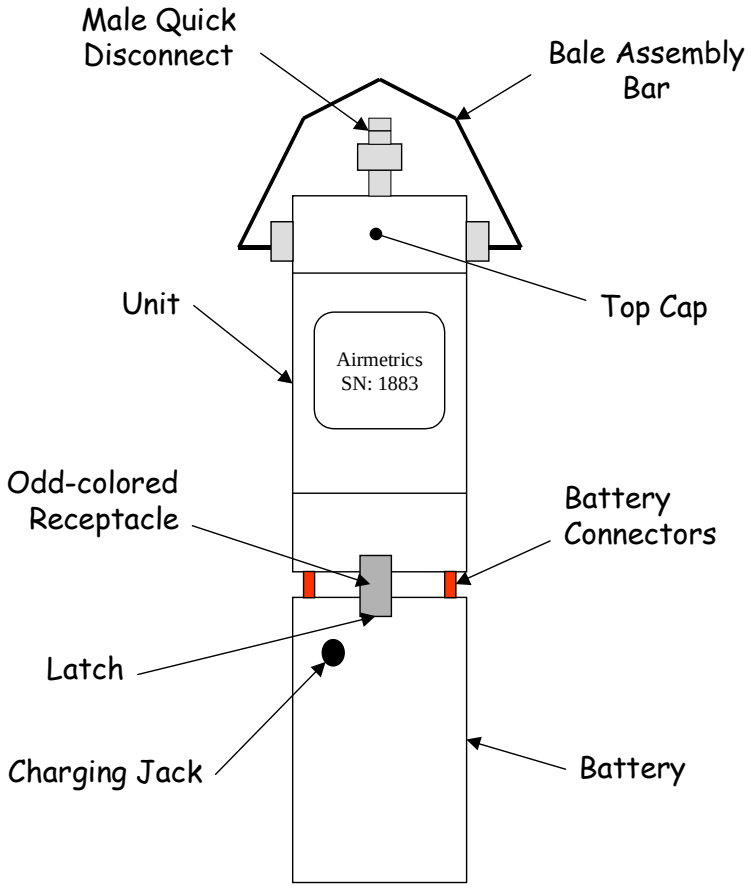
   e. Flow meter adapter

   f. Sampler mounting cradle and associated support equipment

   g. Thermometer/barometer

2. Establish a location for the sampler using the mounting cradle. Verify that the sampler when finally installed in the mounting cradle will be positioned at least 5 feet off the ground with the intake upward in an unobstructed area at least 30 cm from any obstacle to air flow.

3. Place the battery on a firm level surface and secure the sampling pump to the battery using the two latches at the base of the sampler. Ensure that the pin behind the front latch is inserted into the “Odd-colored Receptacle” on the battery pack.

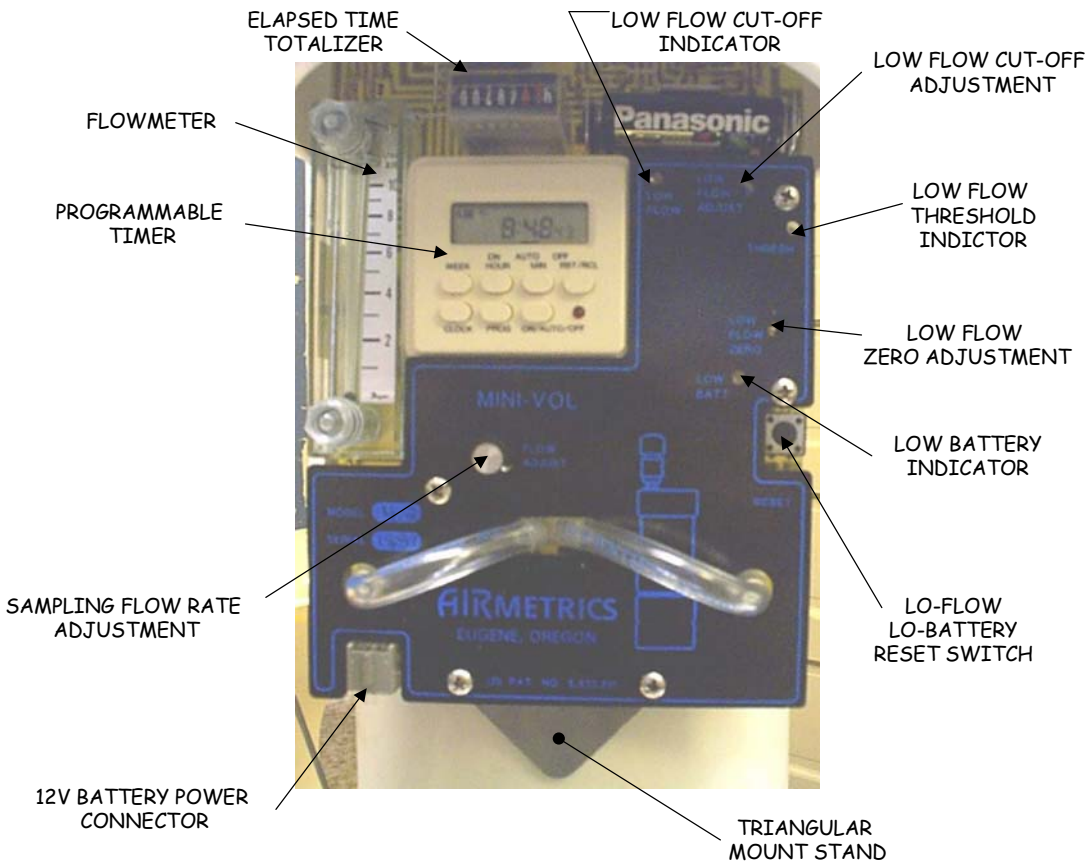


4. Unscrew either cap of the “Bale Assembly Bar” and remove the assembly.

5. Lift the pump and timer assembly out by the 6" diameter “Top Cap” and rest it on the edge of the sampler casing, using the triangular mount stand. Take care not to pull the connecting wire loose or jar the pump hose fittings. Hold the “Top Cap” and do NOT grasp the center of the circuit board.

6. Check the sampler faceplate for any error conditions. If an error condition exists, refer to the "Error Conditions" section of the operating manual.

7. Turn the sampler on by pressing the “ On/Auto/Off” button [Figure 4]. Verify the sampler flow rate is approximately 5.0 liters per minutes (lpm) ±5% by reading the “Flowmeter” to the nearest tenth at center of ball. If flow is outside the flow range use the “Flow Rate Adjustment” control to set the flowmeter flow within required flow range (5.0 lpm ±5%)



8. Turn off the pump by pressing the " On/Auto/Off" button.

9. Remove the clean "Pre-separator/Filter Holder Assembly" from the plastic transport bag or case. Attach the assembly to the "Male Quick Disconnect" orifice on the top of the sampler.

10. Record the following on the field data sheet:

- *Operator* - Name of person operating the equipment.
- *Unit Type* - Type of sampling unit ("Airmetrics")
- *Unit ID* – The serial number off the sampler (e.g. 1884) or leave blank if the sample is a field blank
- *Battery ID* – The battery number (BATT#) off the top of the battery used (e.g. 97-421)

Note: specific location can be entered in Latitude/Longitude or MGRS. LATITUDE/LONGITUDE IN DEGREES AND MINUTES IS PREFERRED.

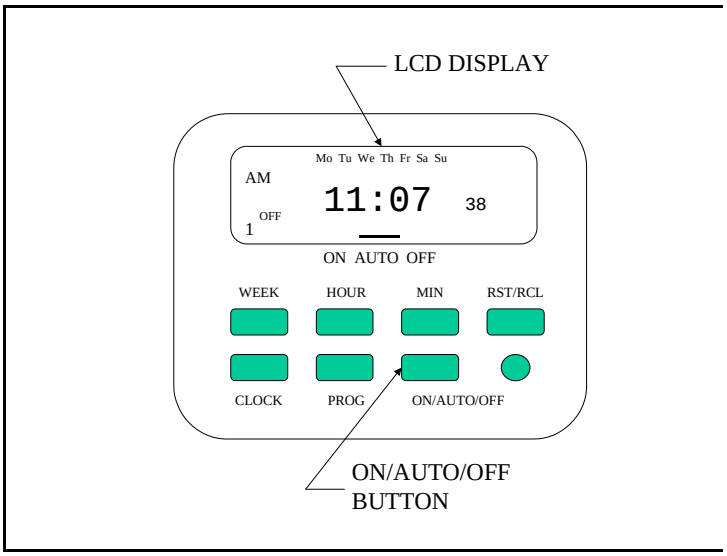
- *Latitude (degrees)* – Sample latitude location in degrees (from GPS).
- *Latitude (minutes)* - Sample latitude location in minutes (from GPS).

- *Longitude (degrees)* - Sample longitude location in degrees (from GPS).
- *Longitude (minutes)* - Sample longitude location in minutes (from GPS).

---OR---

- *MGRS* – Location in Military Grid Reference System (MGRS) from GPS, eight to ten digit grid with grid square identifier (e.g. BQ1234567890)

11. Verify correct time and day of week on time LCD.



12. Program the “Programmable Timer” if applicable or press the “ On/Auto/Off” button to start the pump and initiate the sampling period. If the pump is started manually skip the programming section and record the necessary information on the field data sheet. If the timer is programmed press the “ON/AUTO/OFF” button to set the timer to "Auto" mode, it is very important to place the sampler in “Auto” mode if it is programmed.

Note: It is recommended that the sampler be operated using the “Programmable Timer” this allows documentation of the sampling time if an error occurs and the sampler shuts down.

13. To program the sampler, using the “Programmable Timer”.

- Set the sample start time.

  © Press the “PROG” button, 1^{on} will appear on the bottom-left corner of the LCD display
  © Using the “WEEK” button select the sample start day.
  © Using the “HOUR” button select the hour the sample will start. Pay particular attention that the correct time of day (i.e. AM or PM) is selected.
  © Using the “MIN” button select the minute the sample will start.

- Set the sample end time.
  - © Press the "PROG" button, 1^{off} will appear on the bottom-left corner of the LCD display
  - © Using the "WEEK" button select the sample end day, this should be the day after the start day.
  - © Using the "HOUR" button select the hour the sample will start, this should be 24-hours after the start hour. Pay particular attention that the correct time of day (i.e. AM or PM) is selected.
  - © Using the "MIN" button select the minute the sample will start, this should be same minute as the start time.
- Verify other Programs are "OFF"
- Press the "CLOCK" button to return to clock display on the LCD.
- Press the "PROG" button to toggle through the sample start and end times to verify they were entered correctly.
- Press the "CLOCK" button to return to clock display on the LCD.
- Press the "ON/AUTO/OFF" button to put the sampler in "AUTO" mode.

14. Record the following on the field data sheet:

- *Start Date* – The day the sample was started, same as the "Sampling Date"
- *Start Time* - Time of day sample was started in 24-hour time (e.g. 0800), same as "Sampling Time"
- *Pre Ambient Temperature (^{o}C)* - Ambient Temp in degrees C from thermometer at the start of the sampling episode
- *Pre Ambient Pressure (inches Hg)* - Ambient Pressure in inches Hg from barometer at the start of the sampling episode
- *Pre Elapsed Time Reading (hours)* - Pre-sampling Elapsed Time Reading in hours from sampler's "Elapsed Time Totalizer" at the start of the sampling episode
- *Field Notes* - Notes relating to sampling episode (e.g. unusual circumstance, weather, potential pollution sources, etc), if applicable.

15. If the sampler was not programmed, start the sampler and place it vertically, read the "Flowmeter" (to the nearest tenth at center of ball). If a Gilibrator is available use it and the adapter to acquire the flow rate. Record the flow rate in "*Pre Flow Meter Reading (lpm)*" field on the field data sheet. Record in Pre Time Totalizer readout on Field Data Sheet.

16. If the sampler was programmed, wait for the sampler to start and read the "Flowmeter" (to the nearest tenth at center of ball). If a Gilibrator is available use it and the adapter to acquire the flow rate. Record the flow rate in "*Pre Flow Meter Reading (lpm)*" field on the field data sheet.

Errors: If the "Flowmeter", which should be in the vertical position, indicates zero or a very low reading, check for restrictions in the tubing, or improperly seated screw fittings between the pump and the "Flowmeter". If a RED LIGHT is lit (either low flow or low battery), press the Reset button to start pump.

17. Place the pump and timer assembly back into the sampler body and replace the "Bale Assembly Bar".

18. Using the hoisting pole, hook the "Bale Assembly Bar" and raise the sampler, as vertically as possible, to the mounting cradle. This position not only more easily accommodates the sampler's weight, but also prevents the hook from hitting and possibly dislodging or breaking the "Pre-separator/Filter Holder Assembly".

Note: The sampler should run for 24-hours and events noted.

L. Post Sampling Site Procedures

1. SAMPLE RETRIEVAL

   a. Arrive at the sampling location approximately 5-10 minutes before the sampling episode is scheduled to end.

   b. Remove the sampler from the mounting cradle using the hoisting pole. Position yourself directly under the sampler, hook the "Bale Assembly Bar", and lower the sampler as vertically as possible. This vertical take-away not only accommodates the sampler's weight, but also prevents the hook from dislodging the "Rain Hat" or damaging the "Pre-separator/Filter Holder Assembly".

2. Place the sampler on a firm level surface.

3. If the sampler is still running use a Gilibrator and adapter to acquire the flow rate. Record the flow rate in "*Post Flow Meter Reading (lpm)*" field on the field data sheet. If the sampler is not running go to the next step.

4. Unscrew either cap of the bale assembly bar and remove the bar.

5. Lift the pump and timer assembly out by the "Top Cap" and rest it on the edge of sampler body using the triangular mount stand. Take care not to pull the connecting wires loose and hold the "Top Cap".

6. Check the sampler faceplate for any error conditions. If an error condition exists, refer to the "Error Conditions" section in the operating manual and record the error in the "*Invalid Sample*" field on the field data sheet.

7. Verify the correct time and day of week on the LCD.

8. Record the following on the field data sheet:

- *End Date* - The day the sample was ended
- *End Time* - Time of day sample was ended in 24-hour time (e.g. 0800)
- *Post Ambient Temperature (^{o}C)* - Ambient Temp in degrees C from thermometer at the end of the sampling episode
- *Post Ambient Pressure (inches Hg)* - Ambient Pressure in inches Hg from barometer at the end of the sampling episode
- *Post Elapsed Time Reading (hours)* - Pre-sampling Elapsed Time Reading in hours from sampler's "Elapsed Time Totalizer" at the end of the sampling episode
- *Field Notes* - Notes relating to sampling episode (e.g. unusual circumstance, weather, potential pollution sources, etc), if applicable.

9. If a Gilibrator was not available to obtain the "Post-Flow Rate", place the sampler vertically and press the ON/AUTO/OFF button twice to start the pump. Read the "Flowmeter" (to the nearest tenth at center of ball). Record the flow rate in "*Post Flow Meter Reading (lpm)*" field on the field data sheet. Press the ON/AUTO/OFF button twice to stop the pump.

10. Place the pump and timer assembly into the sampler body and reassemble the "Bale Assembly Bar". Record the Time Totalizer readout on the Field Data Sheet.

11. Remove the clean "Pre-separator/Filter Holder Assembly" from the sampling unit and place in the original plastic transport bag or other case. Keep the assembly upright at all times during transport.

12. Transport the following back to the work area.
    a. Sampling unit (not required if sampler is placed in a secure area)
    b. Pre-separator/Filter Holder Assembly
    c. Battery
    d. Flow meter (e.g. Gilibrator)
    e. Flow meter adapter
    f. Sampler mounting cradle and associated support equipment (not required unless additional samples are not to be collected).
    g. Thermometer/barometer
13. Sampling episode is complete, re-apply directions to next sampling episode.

DO NOT store the battery while attached to the sampler, as this will cause irreparable damage to the battery. The indicator lights that remain on when the battery is connected to the sampler will discharge the batter past its 10.3-volt safety cut-off point

M. Filter Recovery Procedure – In the lab.

1. In the laboratory, unscrew the "Pre-separator Adapter" from the "Filter Support" assembly.

2. Locate the appropriate numbered petri slide associated with the sample filter. Use the relation between the filter number and the "Holder ID" to verify the appropriate filter is place in the proper petri slide.

3. Lift off the "Anti-twist Ring" from the base.

4. Using tweezers, carefully remove the exposed filter from the "Drain Disk" and place it into its original petri slide, replacing the petri slide lid when finished. (Be sure to replace the "Drain Disk" back on the filter support grid in the "Filter Support" assembly if it came off when the filter was removed). Scrape any pieces off of "Support Assembly" and "Anti-Twist Ring" and place in the petri dish.

5. Replace the "Anti-twist Ring" and screw the "Pre-separator Adapter" onto the "Filter Support" assembly.

N. Battery Maintenance

1. After each sampling episode, the used battery pack should be charged for a minimum of 18 hours or overnight.

2. A single AA battery on the circuit board operates the "Programmable Timer". The lifetime for this battery is approximately six months when it is left in place on the circuit board.

3. Battery light blinks or goes out when charging is complete.

O. Quality Assurance/ Quality Control Procedures

1. Note in the *"Invalid Sample"* field the appropriate code of sampler malfunction or filter damage.

2. Ensure all required fields on the "Air – Particulate Sampling (Low Volume) Field Data Sheet" are complete and legible.

3. Enter field data sheet information into "Deployment Environmental Surveillance

Database" if applicable.

4. Complete datasheets as required for field blanks, and indicate the type of blank in the "*Blank*" field on the field data sheet.

P. Error Conditions

1. Should the "Low Battery Indicator" be ON at the end of a sampling period, check the "Elapsed Time Totalizer" to determine the length of time the sampler ran before shutting off. If the time is short (*e.g.*, only 12 hours out of a programmed 24 hours), perhaps the battery was not completely charged or is failing to hold a charge. Note the battery number and, after recharging in the lab, observe performance in the next sampling period. If the battery fails again, it is most likely defective and should be replaced.

2. If a different battery performs in the same manner after shown to be fully charged, the pump motor is perhaps drawing more current than it should. If possible, install a pump from another sampler. If this solves the problem, the previous pump motor is likely defective and should be replaced. If the problem continues, a more serious fault is occurring which should be referred to the manufacturer or CHPPM.

3. Low Flow Indicator ON - Should the "Low Flow Indicator" be found ON at the end of sampling period, first check the "Elapsed Time Totalizer" to determine the length of time the sampler ran before shutting off. Check the operating manual for a more detailed explanation of Low Flow errors.

Q. Packing Samples for Shipment

1. Filters should be replaced in their respective petri dishes and sealed.

2. Include datasheets with respective filters in packing box.

3. Include enough packing material in shipping box to ensure that filters do not move in shipping container.

R. Air related Web sites

1. CHPPM-Air Programs Web Page http://chppm-www.apgea.army.mil/air/ap_home.htm

2. EPA Technology Transfer Network http://chppm-www.apgea.army.mil/air/ap_home.htm

3. EPA Office of Air and Radiation http://chppm-www.apgea.army.mil/air/ap_home.htm

S. Field Data Sheet

Air - Particulate Sampling (Low Volume)

Administrative Data

Sample ID:		Collected By:		Lab ID:	
Location:		Unit Spec ID:		Job No:	
Country:		Mission ID:		Project No:	
Operation:		Shipping ID:		Europe ID:	
Sampling Date:		Sample Notes:			
Sampling Time:					

Latitude: Longitude:

Field Data

Filter No:		Sample Type:		Unit ID:	
Filter Type:		Operator:		Battery ID:	
Holder ID:		Unit Type:		Blank?:	
				Invalid Sample?:	

	Start/Pre	End/Post	Average
Date:			
Time:			
Ambient Temperature (oC):			
Ambient Pressure (inHg):			
Flow Meter Reading (lpm):			
Elapsed Time Reading (hrs):			
Field Notes:			

	Degrees	Minutes
Latitude:		
Longitude:		

-or-

MGRS:

Filter Weighting

Tare Weight:		ug
Gross Weight:		ug
Net Weight:		ug

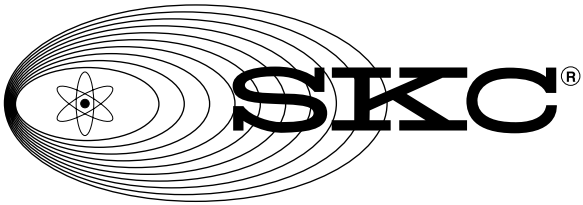
Concentration Calculation

Q(standard):		lpm	K(ambient):	
V(standard):		m3	V(ambient):	
Conc(standard):		ug/m3	Conc(ambient):	

Notes: Grey areas are calculated fields or obtained from calibration data

Bold boxes are required entries.

16-Jun-99



Operating Instructions
Universal Sample Pump
Catalog No. 224-PCXR8

SKC Inc.
863 Valley View Road
Eighty Four, PA 15330 USA

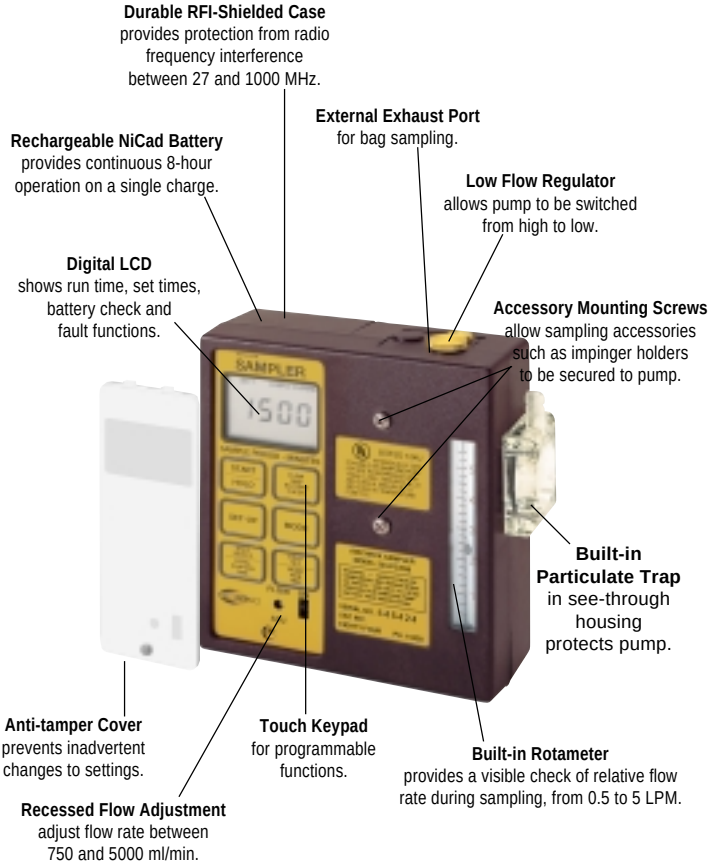
Form #37713 Rev 0008

Table of Contents

Description

The result of extensive research and development, the PCXR8 is a constant flow air sampler suited for a broad range of applications. It is ideal for industrial hygiene studies as well as environmental testing.

Specifically designed for "on worker" and "fenceline" applications, the PCXR8 is typically used with collecting devices such as filters, impingers, sorbent sample tubes and sample bags.



Specifications

Operating Range:	5-5000 ml/min (5-500 ml/min requires adjustable low flow holder)
Weight:	34 oz (964 gm)
Dimensions:	1.9 x 4.7 x 5.1 inches; 46.5 cubic inches (4.9 x 11.9 x 13 cm, 758 cubic cm)
Compensation Range:	750 to 2500 ml/min—to 40 inches water back pressure 2500 to 4000 ml/min—to 20 in water back pressure
Flow Control:	±5% set point constant flow
Run Time:	8 hrs min at 4000 ml/min & 20 in water back pressure
Flow Indicator:	Built-in flow indicator with 250 ml division; scale marked at 1, 2, 3, 4, and 5 LPM
Battery Assembly:	Plug in battery pack, rechargeable NiCad 2.0 Ah, 6.0 V UL Listed.
Intrinsically Safe:	UL Listed for: Class I, Groups A, B, C, D; Class II, Groups E, F, G; and Class III. Temp Code T3C.
Operating Temp:	-20 C to 45 C (-4 F to 113 F)
Storage Temp:	-40 C to 45 C (-40 F to 113 F)
Charging Temp:	5 C to 45 C (41 F to 113 F)
Operating Humidity:	0 to 95% Relative
Multiple Sampling:	Built-in constant pressure regulator allows user to take up to four simultaneous samples at different flow rates up to 500 ml/min (maximum total combined flow 1350 ml/min) using optional low flow control.
RFI-Shielding Performance:	Complies with requirements of EN 55022, FCC Part 15 Class B, EN 50082-1, Frequency range of the radiated susceptibility test was 27 MHz to 1000 MHz. CE approved.

Specifications (cont)

Flow Fault: Fault shutdown with LCD indicator and time display retention if flow is restricted.

Battery Test: LCD shows battery condition prior to sampling.

Time Display: LCD shows sampler run time in minutes for sampler period elapsed time, pump run-time or total elapsed time including delayed start time.

Timing Accuracy: ±0.05% (±45 seconds/day)

Sampling Pause: Allows user to temporarily halt sampling without loss of timing data. Restart does not require resetting time.

Timed Shutdown: Allows user to select minutes of operation before automatic shutdown.

Delay on: Allows user to select minutes to delay of test up to 9999 minutes (7 days).

Intermittent Sampling: Programmable to allow user to extend short term samples over an extended period of time to meet time weighted average (TWA) requirements with a reduced number of samples. Elapsed time maximum is 9999 minutes (7 days).

Operation

High Flow Applications (750-5000 ml/min)

Setup

Fully charge the battery by connecting the charger plug to the sampler charging jack (Figure 1, #22). Use only an SKC charger designated for this model. **CAUTION: DO NOT CHARGE IN A HAZARDOUS ENVIRONMENT.** Using flexible tubing, connect the sampling media to the pump intake (Figure 1, #13). Make sure the pump is set for high flow. (See "Return to High Flow" p. 7).

Setting the Flow Rate

Test the battery pack by turning the sampler on using the ON/OFF switch (Figure 1, #8). Press the START/HOLD key (Figure 1, #3) then the FLOW AND BATTERY CHECK key (Figure 1, #2). Adjust the flow to 2 L/min using the FLOW ADJUST SCREW (Figure 1, #11). The LCD should indicate "BATT OK" in the upper left corner, if not, recharge the battery. Press the FLOW AND BATTERY CHECK key to place the pump in "HOLD" mode.

Connect a flowmeter to the intake of the sampling media using flexible tubing. [For pressure applications, insert the exhaust port fitting into the exhaust port (Figure 1, #19) and connect the sample bag to this fitting.] Press the FLOW AND BATTERY CHECK key to start the pump and set the flow rate using the FLOW ADJUST SCREW. When the flow rate is set, press the FLOW AND BATTERY CHECK key to place the pump in "HOLD".

Caution: When using impingers, place an in-line trap between the pump and the impinger to protect the sampler from liquid or vapors. **FAILURE TO USE THE IMPINGER TRAP VOIDS THE WARRANTY.** The impinger and trap may be mounted to the sampler using the accessory mounting screws (Figure 1, #12).

Programming the PCXR8

From HOLD, press the SET-UP key (Figure 1, #5) to enter the "Delayed Start" mode. Enter the number of minutes delay before the sampling period begins by pressing the DIGIT SELECT (Figure1, #7) and DIGIT SET (Figure 1, #6) keys. The DIGIT SELECT key advances the flashing digit and the DIGIT SET key increases the value of the flashing digit. Press the MODE (Figure 1, #4) key to enter the "Sample Period" mode. Press the DIGIT SELECT and DIGIT SET keys to enter the sampling time period in minutes. **Note:** The sample period is the total period in which sampling is performed and not the pump run time. Press the MODE key to enter the "Pump Period" mode. This is the actual running time of the pump. Use the DIGIT SELECT and DIGIT SET keys to enter the pump run time in minutes. If intermittent sampling is not desired, set the sampling period to equal the pump period. If the pump running time is less than the sampling period, the computer will automatically calculate and control the

on/off cycling to complete the pump run time during the sampling period. Pressing the MODE key will scroll through the program sequence.

Sampling

For personal sampling, clip the sample collection media to the worker in the breathing zone. While the LCD shows "HOLD," start the test cycle by pressing the START/HOLD key. If a time delay has been programmed, the "DELAYED START" indicator will flash and the LCD displays the amount of time remaining until the sampling period starts. "SAMPLE RUNNING" will display when the delay sequence has ended. The time display will automatically track the sampling period time elapsed.

User options during sampling:
Pause - pause (shutdown) by pressing the START/HOLD key. All timing data will freeze. To resume sampling press the START/HOLD key, timing data will resume.

Fault shutdown - during restricted flow or low battery conditions the sampler will shut down. "HOLD" will display on the LCD and timing functions will pause. "LO BATT" or "FLOW FAULT" will display on the LCD depending on the cause of the shutdown. To restart a pump in "FLOW FAULT," correct the flow blockage and press the START/HOLD key. A pump displaying "LO BATT" must be recharged before sampling.

Display times - The LCD continuously shows the elapsed sampling period. Press and hold the PUMP RUN TIME (Figure 1, #6) key to display the pump run time. Press and hold the TOTAL ELAPSED TIME (Figure 1, #7) key to display the total elapsed time, including the delayed start time.

Low Flow Applications (5-500 ml/min)

Setup

Low Flow applications (only) require an adjustable low flow holder (Fig. 2). Fully charge the battery by connecting the charger plug to the sampler charging jack (Figure 1, #22). Use only an SKC charger designated for this model. **CAUTION: DO NOT CHARGE IN A HAZARDOUS ENVIRONMENT.**

Test the battery pack by turning the sampler on using the ON/OFF switch (Figure 1, #8). Press the START/HOLD key (Figure 1, #3) then the FLOW AND BATTERY CHECK key (Figure 1, #2) and adjust the flow to 1.5 L/min using the FLOW ADJUST SCREW (Figure 1, #11). If performing multiple sampling using an adjustable flow tube holder (dual, tri, or quad), the flow rate of the pump must be greater than the sum of the flow rates through the tubes; the flow rate through any one tube cannot exceed 500 ml/min. The LCD should indicate "BATT OK" in the upper left corner. If not, recharge the battery. Press the FLOW AND BATTERY CHECK key to place the pump in "HOLD" mode.

Remove the screw cap (Figure 1, # 18) covering the regulator isolation valve. Turn the exposed screw 4-5 turns counterclockwise. Replace the screw cap. The pump is now set for low flow. Connect an adjustable low flow holder (Figure 2) to the pump intake (Figure 1, #13) using flexible tubing. Insert an opened sorbent tube into the rubber sleeve (Figure 2, #3) of the low flow holder so the arrow on the tube points toward the holder.

Caution! Long duration color detector tubes require a special tube cover which accommodates an in-line trap tube. The trap tube protects the pump from caustic fumes which are often released from detector tubes. **FAILURE TO USE THE TRAP TUBE VOIDS THE WARRANTY.**

Setting the Flow Rate

Connect a flowmeter to the exposed end of the sorbent tube. Loosen the screw on the low flow holder, for Tri and Quad models first rotate the anti-tamper cover (Figure 2, #1) to expose the brass screw(s) (Figure 2, #2). Activate the pump by pressing the FLOW AND BATTERY CHECK key and adjust the flow rate by turning the brass screw until the flowmeter indicates the desired flow. Do not adjust the flow on the pump. Adjust the flow only by using the brass screw (Figure 2, #2) on the low flow holder.

When the flow rate is set, place the pump in "HOLD" by pressing the FLOW AND BATTERY CHECK key and disconnect the flowmeter. Replace the sorbent tube used for setting the flow with a new sorbent tube for sample collection. Place the appropriate size tube cover (Figure 2, #5) over the tube, and screw it in place on the low flow holder.

Programming the PCXR8

From HOLD, press the SET-UP key (Figure 1, #5) to enter the "Delayed Start" mode. Enter the number of minutes delay before the sampling period begins by pressing the

DIGIT SELECT (Figure1, #7) and DIGIT SET (Figure 1, #6) keys. The DIGIT SELECT key advances the flashing digit and the DIGIT SET key increases the value of the flashing digit. Press the MODE (Figure 1, #4) key to enter the "Sample Period" mode. Press the DIGIT SELECT and DIGIT SET keys to enter the sampling time period in minutes. **Note:** The sample period is the total period in which sampling is performed and not the pump run time. Press the MODE key to enter the "Pump Period" mode. This is the actual running time of the pump. Use the DIGIT SELECT and DIGIT SET keys to enter the pump run time in minutes. If intermittent sampling is not desired, set the sampling period to equal the pump period. If the pump running time is less than the sampling period, the computer will automatically calculate and control the on/off cycling to complete the pump run time during the sampling period. Pressing the MODE key will scroll through the program sequence.

Sampling

For personal sampling, clip the sample collection media to the worker in the breathing zone. While the LCD shows "HOLD," start the test cycle by pressing the START/HOLD key. If a time delay has been programmed, the "DELAYED START" indicator will flash and the LCD displays the amount of time remaining until the sampling period starts. "SAMPLE RUNNING" will display when the delay sequence has ended. The time display will automatically track the sampling period time elapsed.

User options during sampling:
Pause - pause (shutdown) by pressing the START/HOLD key. All timing data will freeze. To resume sampling press the START/HOLD key, timing data will resume.

Fault shutdown - during restricted flow or low battery conditions the sampler will shut down. "HOLD" will display on the LCD and timing functions will pause. "LO BATT" or "FLOW FAULT" will display on the LCD depending on the cause of the shutdown. To restart a pump in "FLOW FAULT," correct the flow blockage and press the START/HOLD key. A pump displaying "LO BATT" must be recharged before sampling.

Display times - The LCD continuously shows the elapsed sampling period. Press PUMP RUN TIME (Figure 1, #6) key to display the pump run time. Press the TOTAL ELAPSED TIME (Figure 1, #7) key to display the total elapsed time, including the delayed start time.

Return to High Flow

Remove the low flow holder. To return to High Flow, remove the screw cap (Figure 1, # 18) covering the regulator isolation valve. Turn the exposed screw clockwise until it stops. (Do not over-tighten.) Replace the screw cap. The pump is now set for high flow.

Bag Sampling by Positive Pressure

Using flexible tubing, connect the sampling media to the pump intake (Figure 1,#13). [For sample bags using positive pressure filling, insert the exhaust fitting into the exhaust port (Figure 1, #19). After setting the flow rate, you will connect the sample bag to this fitting instead.]

Preventive Maintenance

Battery Pack Maintenance

Removal—Remove the two screws (Figure 1, #20) which secure the battery pack (Figure 1, #21) and loosen the four case screws above and below the belt clip (Figure 1, #23). Carefully slide the battery pack out from under the belt clip being careful to keep it straight.

Replacement—Slip the front edge of the battery pack under the belt clip and rotate the battery pack so the rails engage the slots on the case front. Push the battery pack until it is properly located. Reinstall battery screws (Figure 1, #20) and tighten the case screws.

Charge Maintenance

For proper maintenance of battery packs, SKC produces an optional cycling charger (Catalog No. 223-426) which discharges and recharges the battery automatically to protect against memory effects.

Rotate the use of any spare pack to avoid idle periods in excess of one month. Fully charge packs before or after use or storage.

SKC UL listed battery packs (SKC Catalog No. P21661) contain a fuse which blows to prevent fires resulting from a short-circuit while the pump is in use. If the indicator light on the charger will not light while charging, either the battery pack, charger, or wall outlet is inoperative. If you are unable to determine which is inoperative, please contact SKC Technical Support at 724-941-9701 or e-mail skctech@skcinc.com.

Caution: Do not charge in a hazardous environment.

Warning: Using a non-approved charger voids the SKC warranty.

Warning: Tampering with the battery pack voids the SKC warranty and the UL Intrinsic Safety listing.

Pump Inlet Filter

The SKC sampler is fitted with a filter/trap inside the clear plastic intake port housing. This prevents particulates from being drawn into the pump mechanism. Occasionally, the filter should be visually checked to assure that it does not become clogged. If maintenance is necessary:

1. Clean all dust and debris from around the filter housing.
2. Remove the four screws (Figure 1, #14) and the front filter housing.
3. Remove and discard the filter membrane (Figure 1, #16) and O-ring (Figure 1, #15).
4. Clean the filter housing.
5. Insert a new filter membrane and o-ring.
   (Filter Replacement Kit, SKC Catalog No. P22409)
6. Reattach the front filter housing and cross-tighten the four screws.

Pump Service

Pumps under warranty should be sent to SKC Inc. for servicing (see Service p. 4). For further information on pump maintenance, testing and replacing pump components, and troubleshooting, request the Universal Pump Service Manual (SKC Publication No. 1377).

Diagrams/Part Description for Figure 1
Model 224-PCXR8

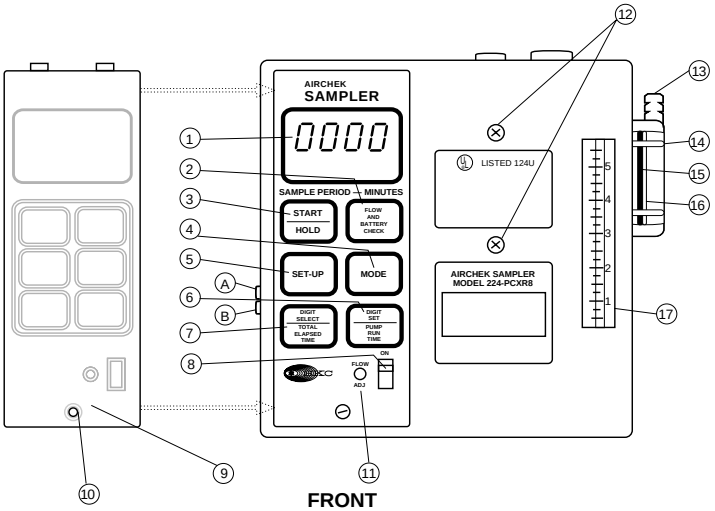
No. Description

1. **LCD**: Indicators for all sampler functions.
2. **FLOW AND BATTERY CHECK Key:** Allows setting flow rate and testing battery condition.
3. **START/HOLD Key:** Used when ready to begin the sampling cycle, pause the sampling cycle and restart the cycle after pause.
4. **Mode Key.** During set-up allows changing between delayed start, pump run time and total elapsed time.
5. **Set-up Key.** Allows setting the delayed start, pump run time and total elapsed time desired.
6. **Digit Set/Pump Run Time Key.** Allows setting the flashing digit to the desired value or viewing the actual pump run time during the actual sampling cycle.
7. **Digit Select/Total Elapsed Time Key.** Allows selecting which time digit is being set when in set-up mode or viewing total elapsed time during the actual sampling cycle.
8. **ON/OFF Switch:** Allows the pump to be shut down completely, clears time display.
9. **Anti-tamper Cover:** Protects controls from incidental contact or tampering.
10. **Cover Screw:** Fastens anti-tamper cover.
11. **Flow Adjustment Control:** Adjusts flow from 750-5000 ml/min.
12. **Accessory Mounting Screws (2):** Secure accessories such as impinger and trap holders.
13. **Filter Housing (intake):** Air intake port and trap.
14. **Filter Housing Screws (4):** Secure filter housing.
15. **Filter O-ring:** Leak seal for filter in housing.
16. **Filter (10 micron nylon):** Filters particulates before entering pump.
17. **Built-in Flowmeter:** Monitors flow changes.
18. **Regulator Isolation Cap:** Accesses regulator isolation valve.
19. **Exhaust Port Cap:** Accesses exhaust port.
20. **Battery Pack Screws (2):** Secures pack to pump.
21. **Battery Pack Assembly:** Provides power to pump.
22. **Charging Jack:** Connector for battery charger.
23. **Belt Clip:** Secures pump to worker.

A **Compensation Pot A:** Adjusts pump compensation which is factory set. Access screw guards against accidental contact or tampering.

B **Compensation Pot B:** Adjusts pump compensation which is factory set. Access screw guards against accidental contact or tampering.

Figure 1


AIRCHEK
SAMPLER
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SAMPLE PERIOD — MINUTES
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HOLD
FLOW AND BATTERY CHECK
SET-UP
MODE
DIGIT SELECT TOTAL ELAPSED TIME
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AIRCHEK SAMPLER
MODEL 224-PCXR8
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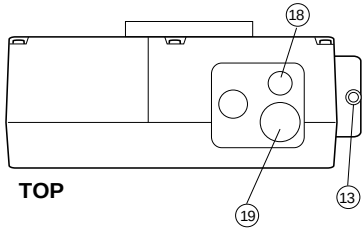
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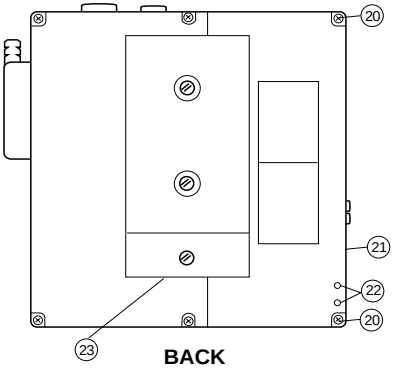
TOP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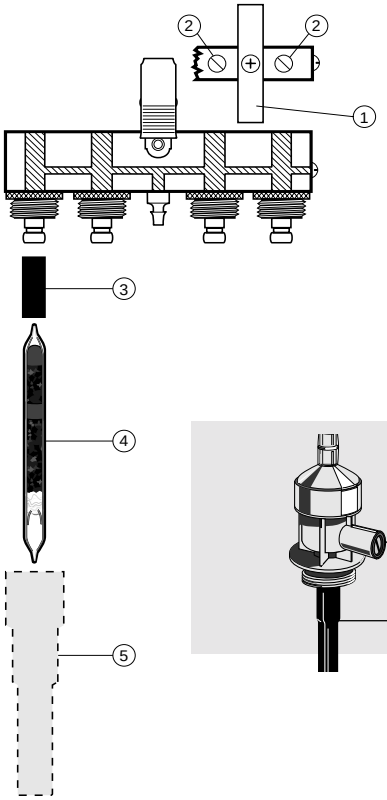
BACK

Figure 2



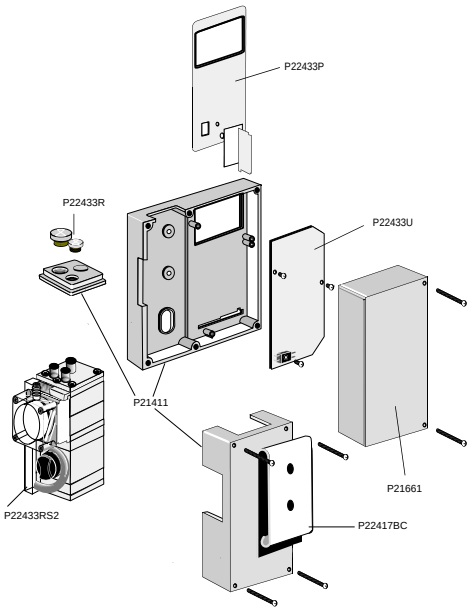
Quad Adjustable Low Flow Holder

Single Adjustable Low Flow Holder

Figure 2 - Adjustable Low Flow Holder

1. Anti-tamper Cover (tri and quad only)
2. Manifold Flow Adjustment
3. Rubber Sleeve
4. Sorbent Sample Tube
5. Protective Cover (not included)

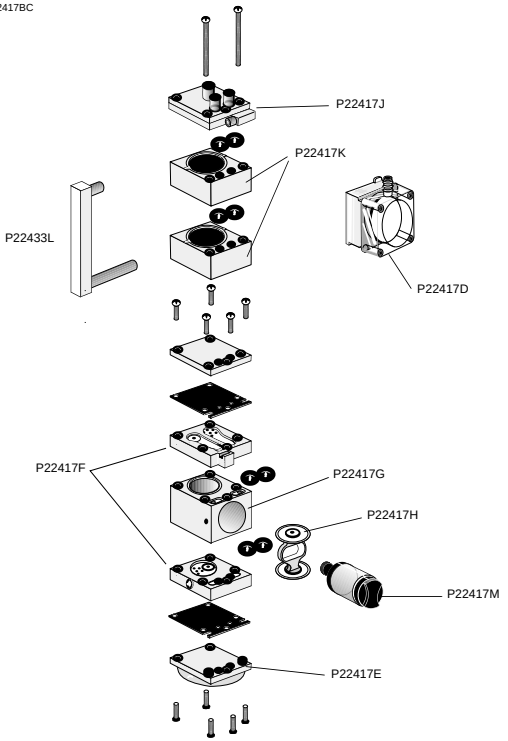
Figure 3 — Replacement Parts for 224-PCXR8



Part Description for Figure 3

Replacement Parts

P2240901*	Replacement FIlters (pk/10)
P2240902	Replacement Filter Kit (with O-rings)
P22433R	Cap Screws (set of 2)
P22417C*	Exhaust Port Fitting
P22417D	Filter Housing Assembly
P22417E	Pressure Switch Assembly
P22417F	Valve Plate Assembly
P22417G	Pump Body
P22417H	Diaphragm/Yoke Assembly
P22417J	Regulator Assembly
P22417K	Pulsation Dampener Assembly (2)
P22417M	Motor/Eccentric Assembly
P21661	Battery Pack Assembly
P21411	Case Parts (excluding Battery Case)
P22417L	Flowmeter Assembly



Exploded view of stack # P22433RS2

For further information on testing and replacing pump components, request the Universal Pump Service Manual (SKC Publication No. 1377).

Optional Accessories

Adjustable Flow Holders:
224-26-01 Single Holder
224-26-02 Dual Holder
224-26-03 Tri Holder
224-26-04 Quad Holder

Protective Covers:
224-29A 70 mm long
224-29B 110 mm long
224-29C 150 mm long
224-29D 220 mm long
224-29T 115 mm with tandem trap tube cover

Battery Chargers:
223-226 Single Battery Charger 115 V
223-227 Single Battery Charger 230 V
223-426 Deluxe 5 Station Battery Charger, Switchable for 115 or 230 V operation

Miscellaneous:
224-11 Sampler Tool Kit
224-95 Protective Nylon Pouch with belt and shoulder strap, brown
224-95A Protective Nylon Pouch-red

Service

Product to be serviced should be sent, freight prepaid, to:

SKC Inc.
National Service Center
863 Valley View Road
Eighty Four, PA 15330

Care should be taken in packaging to prevent damage in transit. Please include a contact name and phone number, shipping address, and a brief description of the problem. For nonwarranty repairs, a purchase order number and billing address is also required. The Service Center will contact nonwarranty customers with an estimate before proceeding with repairs.

SKC QualityCare
QualityCare is a cost-effective preventive maintenance program that assures that pumps are tested, repaired, and calibrated on an annual basis. Participants will receive certificates of compliance for each pump, each year, to demonstrate adherence to Occupational Health and Safety Management Systems or company quality programs.

For more information on QualityCare call our SKC Customer Service Team at 724-941-9701.

Note: *SKC Inc. will accept for repair any SKC product which is not contaminated with hazardous materials. Products determined to be contaminated will be returned unserviced.*

Universal Pump Service Manual
Customers who wish to self-service their out-of-warranty pumps should request the Universal Pump Service Manual (SKC Publication No. 1377).

SKC INC. LIMITED ONE YEAR WARRANTY

1. SKC warrants that its instruments provided for industrial hygiene, air pollution, gas analysis, and safety and health applications are free from defects in workmanship and materials under normal and proper use in accordance with operating instructions provided with said instruments. The term of this warranty begins on the date the instrument is delivered to the buyer and continues for a period of one (1) year.

This warranty does not cover claims due to abuse, misuse, neglect, alteration, accident, or use in application for which the instrument was neither designed nor approved by SKC Inc. This warranty does not cover the buyer's failure to provide for normal maintenance, or improper selection or misapplication. This warranty shall further be void if changes or adjustments to the instrument are made by other than an employee of the seller, or if the operating instructions furnished at the time of installation are not complied with.

2. SKC Inc. hereby disclaims all warranties either expressed or implied, including any implied warranties of merchantability or fitness for a particular purpose, and neither assumes nor authorizes any other person to assume for it any liability in connection with the sale of these instruments. No description of the goods being sold has been made a part of the basis of the bargain or has created or amounted to an express warranty that the goods will conform to any such description. Buyer shall not be entitled to recover from SKC Inc. any consequential damages, damages to property, damages for loss of use, loss of time, loss of profits, loss of income, or other incidental damages. Nor shall buyer be entitled to recover from SKC Inc. any consequential damages resulting from defect of the instrument including, but not limited to, any recovery under section 402A of the Restatement, Second of Torts.

3. This warranty extends only to the original purchaser of the warranted instrument during the term of the warranty. The buyer may be required to present proof of purchase in the form of a paid receipt for the instrument.

4. This warranty covers the instrument purchased and each of its component parts.

5. In the event of a defect, malfunction, or other failure of the instrument not caused by any misuse or damage to the instrument while in possession of the buyer, SKC Inc. will remedy the failure or defect without charge to the buyer. The remedy will consist of service or replacement of the instrument. SKC Inc. may elect refund of the purchase price if unable to provide replacement and repair is not commercially practicable.

6. (a) To obtain performance of any obligation under this warranty, the buyer shall return the instrument, freight prepaid, to SKC Inc., at the following address:

SKC Inc., National Service Center
863 Valley View Road
Eighty Four, PA 15330 USA

(b) To obtain further information on the warranty performance you may telephone 412- 941-9701 at the address above.

7. This warranty shall be construed under the laws of the Commonwealth of Pennsylvania which shall be deemed to be the situs of the contract for purchase of SKC Inc. instruments.

8. No other warranty is given by SKC Inc. in conjunction with this sale.

Form #3755 Rev 9612

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.

APPENDIX C

AIR SAMPLING FIELD DATA LOG SHEETS

TETRA TECH EM INC.
AIR QUALITY SAMPLE DOCUMENTATION SHEET
RICHMOND FIELD STATION

SITE INFORMATION

Sample Location:	
Sample Start Date/Time:	Sample Stop Date/Time:
Sample ID # (all media):	Field Technician:
Average Daily Temp. (deg C):	Ambient Baro. Press. (in. Hg):

Air Metric PM_{10} Sampler

PM_{10} Filter ID #:	Beginning Flow Rate (LPM):
Timer Beginning Time:	Ending Flow Rate (LPM):
Timer Ending Time:	Sampler Serial #:

Summa Canister (VOC) Sampler

Canister ID #:	Beginning Canister Pressure(in. Hg):
Flow Meter ID #:	Ending Canister Pressure(in. Hg):

Formaldehyde/SKC Sampler

Formaldehyde Lot ID #:	Beginning Timer Reading:
Beginning Flow Rate (LPM):	Ending Timer Reading:
Ending Flow Rate (LPM):	SKC Pump Serial #:

FIELD NOTES:

SIGNATURE: