

US EPA ARCHIVE DOCUMENT

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Vapor Intrusion Characterization Work Plan

Chamberlain Manufacturing Corporation

Former Facility at

550 Esther Street

Waterloo Iowa

EPA Docket Nos.

RCRA-07-2010-002

CERCLA-07-2010-0005

May 20, 2010

Revised October 14, 2010

Amended August 1, 2011

Terracon Project No. 07107020

Prepared for:

Chamberlain Manufacturing Corporation

Elmhurst, Illinois

Prepared by:

Terracon Consultants, Inc.

Bettendorf, Iowa

Offices Nationwide
Employee-Owned

Established in 1965
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August 1, 2011

United States Environmental Protection Agency
Region 7
Air, RCRA and Toxics Division
901 North 5th Street
Kansas City, KS 66101

Attention: Mr. Bruce Morrison

Re: Vapor Intrusion Characterization Work Plan
Chamberlain Manufacturing Corporation
Former Facility at 550 Esther Street
Waterloo Iowa
EPA Docket Nos. RCRA-07-2010-002 and CERCLA-07-2010-0005

Dear Mr. Morrison:

Terracon Consultants, Inc. (Terracon) is pleased to submit this revised Vapor Intrusion Characterization Work Plan (VIC Work Plan) for activities in conjunction with the site referenced above. The VIC Work Plan presents a summary of proposed activities related to the installation of sub-slab vapor sampling points and the collection of sub-slab vapor, indoor air, and ambient air samples for chemical analysis.

Should you have any questions or require additional information, please do not hesitate to contact our office.

Sincerely,

Terracon Consultants, Inc.

John F. Brimeyer, PE
Environmental Manager

John B. Sallman, PG
Department Manager

Terracon Consultants, Inc. 870 40th Avenue Bettendorf, Iowa 52722
P [563] 355 0702 F [563] 355 4789 terracon.com

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ACRONYMS & ABBREVIATIONS



CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
City	City of Waterloo
COC	Chain of Custody
EPA	Environmental Protection Agency
Facility	Chamberlain Manufacturing facility
HASP	Health and Safety Plan
NELAC	National Environmental Laboratory Accreditation Conference
PCE	Tetrachloroethene (or Perchloroethene)
PID	Photoionization Detector
ppm	parts per million
QA	Quality Assurance
QAM	Quality Assurance Manual
QAPP	Quality Assurance Project Plan
QC	Quality Control
RCRA	Resource Conservation and Recovery Act
SOP	Standard Operating Procedure
SOW	Statement of Work
TCE	Trichloroethene
TestAmerica	TestAmerica, Inc.
TSOP	Terracon Standard Operating Procedure
UAO	Unilateral Administrative Order
USEPA	United States Environmental Protection Agency
VIC	Vapor Intrusion Characterization
VOC	Volatile Organic Compound



**VAPOR INTRUSION CHARACTERIZATION WORK PLAN
CHAMBERLAIN MANUFACTURING CORPORATION
FORMER FACILITY AT
550 ESTHER STREET
WATERLOO, IOWA**

**Project No. 07107020
May 20, 2010
Revised October 14, 2010
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1.0 INTRODUCTION

Terracon has developed this VIC Work Plan to evaluate the potential existence of a vapor pathway in off-site areas related to shallow groundwater contamination from the former Chamberlain Manufacturing Facility. This VIC Work Plan is submitted in accordance with the requirements of the UAO, Docket Nos. RCRA 07-2010-002 and CERCLA 07-2010-005 dated April 20, 2010 and Task I of the SOW attached to the UAO. Capitalized terms not defined herein have the definitions set for the in the UAO or the SOW.

The VIC Work Plan has been developed in accordance with USEPA guidance including but not limited to:

- CalEPA (California Environmental Protection Agency). 2004. *Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air*. Interim Final. Department of Toxic Substances Control. Sacramento, CA. (Revised February 7, 2005) ("California Guidance")
- ITRC (The Interstate Technology & Regulatory Council). 2007. *Vapor Intrusion Pathway: A Practical Guideline*. Vapor Intrusion Team. Washington, DC. ("ITRC Guidance")
- U.S. EPA. 2002. *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway From Groundwater and Soils (Subsurface Vapor Intrusion Guidance)*. Office of Solid Waste and Emergency Response, Washington, DC.
- U.S. EPA. 2008: *US. EPA's Vapor Intrusion Database: Preliminary Evaluation of Attenuation Factors*. Draft. Office of Solid Waste, Washington, DC.
- U.S. EPA "Development of a Sub-Slab Gas Sampling Protocol to Support Assessment of Vapor Intrusion." (http://www.epa.gov/ahaazvuc/research/waste/research_40.pdf)

1.1 Site Conditions

The Facility is an irregularly shaped parcel containing approximately 22.8 acres and located at 550 Esther Street in Waterloo, Iowa. A Topographic Map is included as Figure 1 in Appendix A. A Site Diagram is included as Figure 2.

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The Facility manufactured metal washer wringers and projectile metal parts from approximately 1919 until 1996 when it was sold to Atlas Warehouse L.C. for use as a storage facility. The Facility was subsequently abandoned and is currently vacant. The City acquired the Facility from Atlas Warehouse L.C in 2005 in an effort to facilitate redevelopment and has demolished a significant portion of the Facility.

The Facility is zoned Heavy Industrial (M-2) by the City. The Facility is adjoined by park land to the north and south, single family residential housing to the west, and Virden Creek followed by a golf course to the east. Virden Creek is within approximately 100 feet of the Facility at its closest point. Gates Park adjoins the Facility to the north across Louise Street, to the east across Virden Creek, and to the south across the railroad tracks. Single family residences are located across East 4th Street to the west of the Facility. Single family residences are also located along the east side of East 4th between Anita and Louise Streets.

1.2 Previous Assessment Activities

Beginning in 2004, the City conducted an environmental assessment of the site using a USEPA Brownfields Grant. Results of assessment activities identified impacts to soil and groundwater at the site including a chlorinated solvent plume that extends to the south and west. Site assessment activities were not completed due to funding restrictions of the Brownfields Grant program.

Subsequently, environmental assessment activities of onsite soil and groundwater conditions and the offsite chlorinated solvent plume were completed by Chamberlain. The lateral extent of the chlorinated solvent plume has been determined to extend south and west from the Facility into an area of residential development. USEPA's preliminary evaluation of the vapor intrusion to indoor air pathway resulting from the groundwater plume identified the potential for vapor intrusion into residential structures.

To further evaluate the vapor intrusion pathway, the USEPA conducted sub-slab vapor sampling of selected residences in November 2008. Due to problems with the sampling and analysis equipment, the sampling activities were repeated in April/May 2009. Sub-slab vapor samples were collected from ten homes located along and near East 4th Street and analyzed for VOCs. In addition, one indoor air sample was collected from one of the ten homes. The results of sampling activities identified PCE and TCE in excess of sub-slab vapor screening levels in seven of the ten residences sampled. The elevated concentrations were generally located within the 2200, 2300, and 2400 block of East 4th Street.

1.3 Project Objectives

The objective of the VIC Work Plan is to develop procedures to define the nature and extent of sub-slab soil gas impact in residential areas adjoining the Facility to the south and west. Results

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of sub-slab vapor sampling will be used to evaluate the need for vapor intrusion interim measures and corrective actions.

2.0 SCOPE OF SERVICES

The VIC Work Plan for the area south and west of the Facility is designed to evaluate the potential vapor intrusion pathway. Activities will include the installation of sub-slab vapor sampling ports and the collection of sub-slab vapor samples. In addition, indoor air samples and corresponding ambient air samples will be collected at representative locations.

2.1 Proposed Study Area

Initially, sub-slab soil gas sampling and analysis will begin with those homes within the limits identified in the SOW, Exhibit 2, included as Figure 3, Appendix A. The area identified includes approximately 72 Residences. A listing of the Residences included in the study area is provided in Appendix B. The ten homes sampled by the IEPA in April/May 2009 are included in the study area and will be offered the opportunity to be resampled for a consistent baseline. If the lateral extent of sub-slab soil gas contamination has not been adequately characterized following completion of sampling in the area set forth in Figure 3, the USEPA will determine which additional adjacent residences, if any, will require vapor intrusion sampling and will notify Chamberlain and Terracon in writing after USEPA's determination is made.

BAM

2.2 Proposed Sampling Activities

2.2.1 Site Access

Prior to site mobilization, the names and addresses for those Residences within the limits identified on Figure 3 will be obtained from a City of Waterloo directory, or similar databases as may be available. Each identified resident will be sent a certified letter explaining the availability of the vapor sampling program, details concerning the procedures to be followed, schedule of proposed activities, and availability of results. A standard Terracon Access Agreement will be included with the letter. The form of the letter is set forth in Appendix C.

Upon approval of the amended VIC Work Plan, Terracon will send another certified letter to those Residences that did not respond to the initial submittal of February 4, 2011 or at which sampling has not been completed to date, except that further offers will not be extended to Residences which have previously denied access. This letter will be substantially in a form approved in advance by EPA.

2.2.2 Sampling Questionnaire

As detailed in the Sections that follow, specific information will be collected in support of the sampling efforts:

- Indoor air surveys documenting the presence/absence and use of household products containing VOCs, including completion of the Occupied Dwelling Questionnaire;
- Ambient outdoor levels of VOCs during sampling;
- Meteorological conditions during sampling; and
- Documentation of physical characteristics of the home being sampled including, but not limited to the type of foundation and its integrity.

2.2.3 Sub-slab Soil Gas, Indoor Air, and Ambient Air Sampling

Each sampling team will arrive at the designated residence at the appointed time. After introductions, one member of the sampling team will complete the Occupied Dwelling Questionnaire attached as Appendix D. The remaining members of the sampling team will proceed with the installation of the sub-slab sampling port.

The sub-slab sampling port will be allowed to cure for at least 48-hours before sampling at the Residence is completed. Indoor air samples and ambient air samples will be collected concurrently at selected Residences.

2.3 Health and Safety

Terracon will prepare a Health and Safety Plan (HASP) for the sampling activities. At this time, we anticipate that all personnel in the work area will require a USEPA Level D work uniform consisting of hard hats, safety glasses, protective gloves, and steel-toed boots.

2.4 Site Access Protocol

Terracon staff will notify the Residences at least 48 hours in advance of the start of assessment activities. City staff will be contacted if issues regarding access to assessment locations are encountered during assessment activities.

3.0 METHODOLOGIES

Project activities will be completed in accordance with the USEPA-approved QAPP, Revision 1 dated August 18, 2006, QAPP Addendum dated August 2, 2010, and relevant TSOPs. The following TSOPs will be used during the assessment.

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Table 3-1 Terracon Standard Operating Procedures

REFERENCE NO.	TITLE OF PROCEDURE
E.10	Project Mobilization
E.20	Standard Safe Operating Procedures for Hazardous Waste Operations
E.30	Chain of Custody Documentation
E.50	Sampling – Environmental Representativeness
E.554	Field Screening – Air / Photoionization Detector
E.2210	General
E.2220	Disposal of Spent Supplies
E.2230	Handling and Storage of Drill Cuttings (Non-Hazardous)
E.2240	Site Security Procedures
E.2405	Cleaning - General
E.2410	Cleaning - Manual Washing

As described in Section 1.5.3 of the QAPP, specific work scopes may require variation of TSOP procedures following relevant state and federal guidance, technical standards, or manufacturer specifications not outlined under a specific TSOP. Accordingly, the following non-TSOPs are incorporated and will be used as a part of the VIC Work Plan.

3.1 Sampling Port Installation

Sub-slab soil gas samples will be collected via a hollow steel sleeve installed through the cement floor slab. The sub-slab inserts will be constructed from a 1-inch outer diameter cylindrical blank that is 4-inches long. The steel blanks are hollowed out to allow for the passage of sub-slab soil gas from beneath the floor slab into sampling apparatus. The top of the sub-slab insert consists of a threaded brass set-screw style cap and rubber O-ring that allows for a flush mounted installation and sealing of insert. Sub-slab inserts also has a one-eighth inch diameter rod welded vertically on their exterior to prevent the insert from spinning loose after the installation process.

Sub-slab inserts will be thoroughly cleaned before installation to remove any residues and contaminants left over from the fabrication processes. The inserts will be installed in holes drilled through the concrete floor slab using a 1¼-inch diameter carbide masonry bit and a rotary hammer drill. The hole will be advanced completely through the concrete floor slab. Silica sand will be used to backfill the hole and obtain the proper level for the insert to be flush mounted. A small piece of wire mesh screen will be placed between the silica sand and insert to prevent silica sand from entering the insert interior. Additional silica sand will be placed around the insert to stabilize the insert in the hole for the remaining installation process. The remaining annular space around the insert will be filled to the concrete surface using neat Portland cement. The Portland cement will be mixed with water until a paste consistency is obtained. The Portland cement will be then placed into a tile grout bag and squeezed into the annular space and finished as a flush mounted unit.

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The sampling port installation will be completed in accordance with the USEPA-approved QAPP Addendum dated August 2, 2010 and consistent with the USEPA document "Assessment of Vapor Intrusion in Homes Near the Raymark Superfund Site Using Basement and Sub-Slab Air Samples" dated March 2006.

3.2 Sub-slab Vapor Sampling

Sub-slab vapor sampling will be conducted in accordance with the ITRC Guidance. The set screw of the flush mounted insert will be removed using an Allen wrench. A threaded nipple with Teflon tubing will be screwed into the flush mounted sub-slab insert. A syringe will be connect to the Teflon tubing and used to purge approximately two volumes of soil gas from the sub-slab soil gas sampling point.

The sample will be collected by attaching the top end of the tubing to a six-liter Summa canister equipped with a 200 cubic centimeter per minute flow control and vacuum gauge with an in-line paper filter/moisture trap. The vacuum in the Summa canister before and after sampling will be recorded on the information form. The valve of the Summa canister will be opened and the sub-slab soil gas allowed to flow into the Summa canister for a period of 30-minutes. The vacuum gauge will be monitored to check progress of the canister filling. The Summa canister valve will be then closed and submitted for laboratory analysis. Sample collection will be completed prior to the full dissipation of vacuum on the summa canisters.

After the soil gas sample has been collected, a photo-ionization detector will be connected to the tubing to measure the organic vapor concentration. A Soil Vapor/Indoor Air Sampling Information Form indicating project information, equipment identifiers, sample location, sample time, etc. will be completed for each soil gas sample. A COC will be also filled out indicating the sample identification, sampling time, equipment identifiers, and soil organic vapor reading. The canisters will then be transported to the laboratory.

Copies of field forms including a Soil Vapor/Indoor Air Sampling Information Form and a standard COC are included as Appendix E.

Sub-slab vapor samples will be collected from each residence that grants access within the limits of the area identified on Figure 3.

3.3 Indoor Air Sampling

Indoor air sampling will be conducted in accordance with the ITRC Guidance. Indoor air samples will be collected using laboratory prepared six-liter Summa canisters and flow controllers. The flow controllers will be pre-set by the laboratory to collect samples over a 24-hour period. Terracon will request that resident occupants close doors and windows and operate the heating, ventilating,

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and air conditioning (HVAC) system for the period beginning 24-hours prior to the start of sample collection to the end of sample collection.

Terracon field personnel will connect the flow controller to the Summa canister by removing the brass cap on the canister and tightening the stainless steel Swagelock fitting on the flow controller to the threads on the canister. This requires the use of a wrench to firmly tighten the fitting. Field personnel will not use Teflon tape, sealant, or over tighten the fitting.

Once a sampling location has been selected, a Terracon air sampling form (project information, equipment identifiers, sample location, and start time) will be filled out and attached to the canister. A Soil Vapor/Indoor Air Sampling Information Form indicating project information, equipment identifiers, sample location, sample time, initial and final vacuum readings, etc. will be completed for each indoor air sample. A COC will be completed indicating the start time for the sample.

To open the canister, the valve will be rotated counter-clockwise at least one full turn or otherwise opened. After the 24-hours have passed, Terracon personnel will return to the Residence, close the valve on the canister and record the time and vacuum remaining in the Summa canister on the Terracon sampling forms and on the COC. The canisters and flow controllers will then be transported to the laboratory.

One indoor air sample will be collected for every ten sub-slab vapor samples collected from the residences granting access. This is consistent with the guidance listed in the SOW stating that sub-slab soil gas sampling is a preferred approach for evaluating vapor intrusion risks given inherent unreliability of indoor air sampling. See ITRC Guidance (pages 24 to 25). Indoor air sample locations will be randomly selected; except that efforts will be made to uniformly distribute selected locations across the study area.

One indoor air sample will also be collected from each of the seven residences in which the detected concentration of TCE or PCE exceeded the screening level in the April/May 2009 sampling event. These indoor air samples will be in addition to the one sample collected for every 10 homes as noted previously.

3.4 Ambient Air

Ambient (outdoor) air samples will be collected simultaneously with the indoor air samples over a 24-hour period. The sample location will be selected based on a forecast of the prevailing wind direction for the 24-hour sampling period. Since there are no known nearby outdoor sources except for vehicular traffic (no known dry cleaners or other commercial or industrial facilities), one ambient air sample can be representative of ambient air for indoor air samples being collected at the same time (start times within approximately 4 hours of each other) and within two blocks of each other. Ambient air samples will not be collected near buildings or large trees.

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The samples will be collected using individually-certified 6-liter Summa canisters with flow controllers. The inlet to the flow controller will be positioned between 3 and 5 feet above the ground surface.

Up to five ambient air samples will be collected in conjunction with sub-slab vapor and indoor air sampling activities. Ambient air sample locations and sampling schedules will be determined in conjunction scheduling of field activities. To the extent practical, attempts will be made to collect ambient air samples in the general area as indoor air sampling activities.

4.0 LABORATORY ANALYSIS

Sub-slab vapor, indoor air, and ambient air samples will be collected using six-liter Summa canisters. The Summa canisters will be submitted for analysis of PCE, TCE, vinyl chloride, trans-1,2-dichloroethene (trans-DCE), cis-1,2-dichloroethene (cis-DCE), 1,1-dichloroethene, 1,1-dichloroethane, 1,1,1-trichloroethane (TCA), and 1,1,2-trichloroethane, using EPA Method TO-15.

Laboratory procedures will be performed by TestAmerica, Knoxville, Tennessee. TestAmerica is NELAC accredited for the laboratory methods referenced above. The laboratory QAM is on file with the USEPA. A copy of the SOPs for the specified method is included as Appendix F. A copy of the TestAmerica data will be reported in accordance with the QAM and SOP.

5.0 QUALITY ASSURANCE/QUALITY CONTROL

This section sets forth the requirements and provisions for sample quality assurance and quality control in the field and during transport to the laboratory. The transfer of sample custody will be limited between Terracon personnel, laboratory courier and fixed base laboratory personnel. The primary objective of custody requirements for this project is simply to track that samples are handled by authorized personnel and document that handling occurred within the parameters of this Work Plan. In general, the outline for sample handling and custody will be as follows:

- The Terracon project manager will brief sampling personnel on custody procedures.
- Samples will be in the custody of the field team at the site or in secure location until they are transferred to the fixed base laboratory.
- Samples will be removed from the project site on a daily basis and transported to the laboratory.
- The fixed base laboratory will implement tracking and custody documentation
- Post-analysis samples will be disposed of properly.
- COC documentation will be maintained by Terracon after reporting.

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COC protocol will be followed to during all phases of the sample collection, storage, shipment, and analysis procedures. Maintaining the COC in the field will be the responsibility of the Terracon project professional. The Terracon project professional will perform and/or direct the collection, handling, field analysis, and/or shipment of samples collected from the site through the sampling personnel assigned.

Samples collected in the field will be labeled and then stored in secure location from the time of collection through transfer to the fixed base laboratory. Soil gas and air samples will be collected using laboratory prepared Summa canisters or other appropriate vessels. Soil gas and air samples will be kept at ambient temperature.

Table 5-1 Laboratory Sample Requirements.

Analysis and Method	Media	Container	Preservative	Holding Time
VOCs ¹ by EPA Method TO-15	Air	6-Liter Summa Canister Individual Certified	None	14 days ²

¹ - VOCs to include PCE, TCE, vinyl chloride, trans-DCE, cis-DCE, 1,1-dichloroethene, 1,1-dichloroethane, TCA, and 1,1,2-trichloroethane

² - Stability studies indicate TO-15 samples can be held up to 30 days.

A COC record will accompany each set of samples during collection and shipment. Each COC record will be filled out and signed in permanent ink by a Terracon field team member. The COC records will include the following information: project name and number, sample designation, date and time of collection, samplers name, number of sample containers, type of matrix, preservatives, analysis to be performed, signature of laboratory person(s) receiving samples, and inclusive dates / times of possession. Original COC documents placed in laboratory shipping containers will be bagged in Ziplock® plastic bags for protection against moisture and damage. A carbon copy or photocopy will be made of the COC record before sealing and placing it in the shipping container to shipment to the fixed base laboratory.

Various blank, replicate and confirmation samples will be used to monitor the quality assurance and control of the field sampling activities. These samples will be analyzed for VOCs. Table 5-2 lists the type of sample and frequency with which they will be collected.

Table 5-2 Field Quality Control Sample Schedule

QC Sample Type	Media	Analysis	Container	Frequency
Duplicate Samples	Air	VOCs ¹	1-Summa Canister	1 per 20 sub-slab vapor samples 1 per 20 indoor air samples 1 per 20 ambient air samples
Equipment Blank	Air	VOCs ¹	1-Summa Canister	1 per 20 samples collected
Blind Replicate	Air	VOCs ¹	1-Summa Canister	None

¹ - VOCs to include PCE, TCE, vinyl chloride, trans-DCE, cis-DCE, 1,1-dichloroethene, 1,1-dichloroethane, TCA, and 1,1,2-trichloroethane

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Duplicate samples shall be designated using the analytical sample identification followed by “-D”, “-Dup” or other similar common designation. Duplicate sample nomenclature will be clearly identified on analytical data tables as a note.

6.0 DATA VALIDATION AND MANAGEMENT

Data validation activities will focus on verifying the completeness and accuracy of field methods used, sample handling, and fixed base laboratory results. The Terracon Project Manager will be responsible to conduct a full-package review of the field process and data produced for the site and reports from the fixed base laboratory. The TestAmerica QA Officers will conduct validation and reporting consistent with the parameters of the QAM. Data quality QA packages for analytical services will be delivered to the Terracon Project Manager and will be entered into the project record. The Terracon Project Manager is responsible for reviewing and confirming that field and laboratory data meets the data quality objectives for the project.

Field and laboratory data validation procedures will be conducted in accordance with the USEPA-approved QAPP.

7.0 VAPOR INTRUSION CHARACTERIZATION REPORT

In accordance with the schedule in the USEPA-approved VIC Work Plan, Respondent will submit a preliminary VIC Report following completion of the first sampling event and associated confirmatory sampling. The preliminary VIC Report will provide a tabulated summary of sub-slab sampling analytical results, an evaluation of data at locations where confirmatory sub-slab samples are collected, preliminary recommendations for the implementation of interim measures, and a copy of the analytical results.

Following completion of the second sampling event, Respondent will submit a VIC Report which provides the sample locations, sampling information, figures depicting sampling locations, and analysis of data resulting from the characterization of the potential for vapor intrusion. The VIC Report shall define the nature and extent of sub-slab soil vapor contamination greater than the levels set forth in Table 7-1 below and in Table 1A1 of the Statement of Work from the Unilateral Administrative Order for the Chamberlain Manufacturing Site (Docket No. RCRA-07-2010-002 and CERCLA-07-2010-005).

Table 7-1 Interim Measures Screening Levels

Contaminant	Indoor Air Screening Level ($\mu\text{g}/\text{m}^3$) ¹	Sub-Slab Vapor Screening Level ($\mu\text{g}/\text{m}^3$) ²	Analytical Detection Limit ($\mu\text{g}/\text{m}^3$)
Perchloroethene	0.41 c ^{3,5}	4.1	0.540
Trichloroethene	1.2 c	12	0.215

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Contaminant	Indoor Air Screening Level ($\mu\text{g}/\text{m}^3$) ¹	Sub-Slab Vapor Screening Level ($\mu\text{g}/\text{m}^3$) ²	Analytical Detection Limit ($\mu\text{g}/\text{m}^3$)
Vinyl Chloride	0.16 ⁵	1.6	0.204
Trans-1,2-Dichloroethene	63 n ⁴	630	0.317
Cis-1,2-Dichloroethene ⁶	63 n	630	0.317
1,1-Dichloroethene	210 n	2,100	0.317
1,1-Dichloroethane	1.5 c	15	0.324
1,1,1-Trichloroethane	5,200 n	52,000	0.436
1,1,2-Trichloroethane	0.15 c ⁵	1.5	0.360

¹ – Residential Indoor Screening Levels obtained from Regional Screening Table (USEPA 2009).

² – Sub-slab vapor screening level = (Residential Indoor Screening Levels)/ α .

³ – c – based on 10⁻⁶ carcinogenic health effects.

⁴ – n – based on non-carcinogenic health effects.

⁵ – Indoor Air Screening Level is less than Analytical Detection Limit. The USEPA has approved the use of the Analytical Detection Limit as the screening level for this site due to the technical inability to accurately quantify the detection of these compounds at the current USEPA screening level.

⁶ – Trans-1,2-Dichloroethene is used as a surrogate compound for cis-1,2-Dichloroethene.

Residences where sub-slab soil gas sampling results indicate the presence of VOCs at a concentration exceeding USEPA sub-slab screening levels, or where sub-slab soil gas results exceed USEPA indoor air screening levels and a breach¹ in the basement floor to the subsoil is present, shall undergo indoor air sampling (including ambient air sampling) within 30 days of receipt of sub-slab sampling results. Alternatively, an offer to install a vapor intrusion mitigation system may be extended in accordance with the Vapor Intrusion Interim Measures Plan.

7.1 Monthly Reporting

Tabulated summaries of activities completed under this VIC Work Plan will be developed and provided to the USEPA and updated on a monthly basis or such extended period as USEPA may alternatively allow. The tables (in the form of Excel spreadsheets) will include the following:

- Table 1 – Property ID, Property Address, Owner Name, Owner Address, Owner Phone Number, Occupant Name, Occupant Phone Number, and columns to indicate if owner and occupant have approved sampling.
- Table 2 – Property ID, Property Address, Initial Sampling Date, Number and types of samples collected, Follow-up Sampling Dates, Number and types of follow-up samples collected, Date of mitigation offer and Date of Mitigation acceptance.

¹ Breach shall be defined as an unsealed pipe, drain, sump pump pit, or similar floor penetration, a hole, void, or other opening in the concrete floor, or a separated or faulted floor joint or crack of such a nature and extent that it could be reasonably anticipated that sub-slab vapors could be entering a living space.

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- Table 3 - Property ID, Property Address, Date of mitigation system installation, Date of initial indoor air sampling, Dates of system inspections, Dates of annual follow-up monitoring

8.0 POST-SAMPLING ACTIVITIES

8.1 Sample Port Removal

Sub-slab sample ports will be left in place until Terracon is directed by USEPA to remove them; however, collection of additional samples from installed sampling ports is not intended or proposed at this time.

Upon notification by USEPA, Terracon will return to the Residence to remove the sub-slab sampling port. Using hand tools, Terracon will loosen the neat Portland cement placed in the annulus of the hole to allow for removal of the insert. After removal, the hole will be augered out using a 1¼-inch diameter carbide masonry bit and a rotary hammer drill. The hole will be filled to the concrete surface using neat Portland cement and finished flush with the concrete surface.

8.2 Data Transmittal to Residents

Correspondence that provides sampling results to residents and homeowners will only be transmitted by the USEPA, unless prior written approval is provided by the USEPA to Terracon and Chamberlain to perform the transmittal.

Any other written correspondence to residents and owners from Chamberlain and Terracon related to the vapor intrusion sampling and mitigation shall be approved by the USEPA prior to being transmitted. Chamberlain and Terracon will copy the USEPA on any written communications with any residents regarding the property. USEPA will copy Chamberlain and Terracon on any written communications with any residents regarding the property.

9.0 SCHEDULE

Based upon currently available information, the proposed schedule is as follows:

Table 9-1 Schedule

Activity	Days to Complete After USEPA Approval of VIC Work Plan
Submit Letter to Each Residence to be Sampled	30
Deadline for Receipt of Responses from Residents	60

Vapor Intrusion Characterization Work Plan

Former Chamberlain Manufacturing Facility ■ Waterloo, Iowa

May 20, 2010, Revised October 14, 2010, Amended August 1, 2011 ■ Terracon Project No. 07107020



Activity	Days to Complete After USEPA Approval of VIC Work Plan
Schedule Indoor/Sub-slab Air Sampling for Residents who Allow Access and provide notification to USEPA	90
Complete Sub-slab/Indoor Air Sampling Event	120
Receive Analytical Reports	150
Submit Preliminary VIC Report	180
Collect Supplemental Indoor Air Sample ¹	180
Receive USEPA Comments	210
Receive Supplemental Indoor Air Sample Results ¹	210
Submit VIC Report	240 ²

¹ - If sub-slab sample results exceed screening levels and indoor air samples are not collected

² - Assuming USEPA comments are received within 30 days

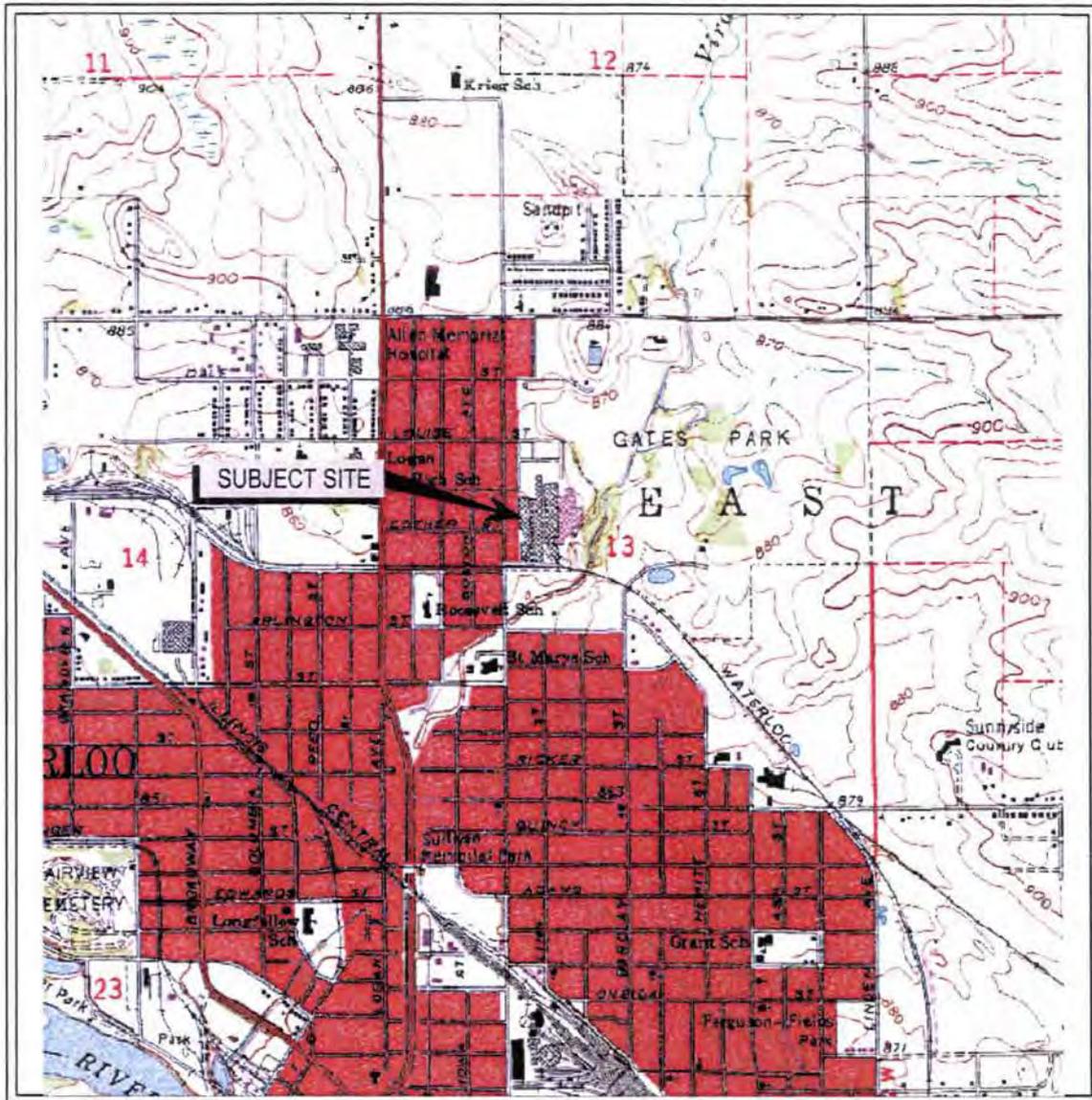
Upon receipt of analytical results, data validation and submittal will be conducted in accordance with Table 9-2. Validated analytical data, including field sampling forms, sample location summary, and a statement that the data has been validated in accordance with the QAPP will be submitted for the USEPA's review and determination of additional activities. If the USEPA determines that additional supplemental sampling is required to further evaluate sampled Residences within the current Study Area or to expand the Study Area, future supplemental sampling will be conducted in accordance with Table 9-2.

Table 9-2 Supplemental Sampling Schedule

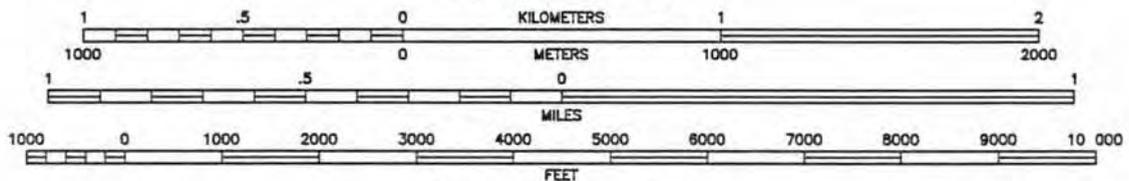
Activity	Days to Complete
Terracon to submit validated data to USEPA	45 days following collection of sample
Terracon to submit access request letter to each residence to be sampled	Within 45 days of notification from USEPA
Schedule sampling with residents who allow access and provide notification to USEPA	Within 60 days of receiving access at each residence
Terracon to perform initial sub-slab/indoor air sampling at each residence	Within 90 days of receiving access at each residence
Terracon to submit validated data to USEPA with completed questionnaires and field sheets	Within 45 days of collecting sample
Schedule follow-up sampling as directed by USEPA and provide notification to USEPA	Within 60 days of notification from USEPA to collect follow-up samples at a particular residence
Terracon to collect follow-up samples at a particular residence	Within 90 days of notification from USEPA to collect follow-up samples at a particular residence

Appendix A

Figures



SCALE 1:24 000



CONTOUR INTERVAL FEET
 NATIONAL GEODETIC VERTICAL DATUM OF 1929
 TOPO LINES REPRESENT 10-FOOT CONTOURS

WATERLOO NORTH QUADRANGLE

7.5 MINUTE SERIES (TOPOGRAPHIC)



Project Mgr:	JFB	Project No.	07107020
Drawn By:	JFB	Scale:	AS SHOWN
Checked By:	JFB	File No.	07107020-T1-FIG1
Approved By:	JFB	Date:	MAY 2010

Terracon
 Consulting Engineers and Scientists

870 40th Avenue Bettendorf, Iowa 52722
 (563) 355-0702 (563) 353-4789

TOPOGRAPHIC VICINITY MAP
 VAPOR INTRUSION CHARACTERIZATION WORK PLAN
 FORMER CHAMBERLAIN MANUFACTURING FACILITY
 550 ESTHER ST.
 WATERLOO, IOWA

FIG. No.
 1



LEGEND

- PROPERTY LINE
- RAILROAD
- ◆ MONITORING WELL
- RES. RESIDENTIAL
- ◆ GEOBROPE SAMPLE LOCATIONS

REV.	DATE	BY	DESCRIPTION

Terracon
Consulting Engineers and Scientists

870 40th Avenue Battendorf, Iowa 52722
(563) 355-0702 (563) 355-4789

SITE DIAGRAM

VAPOR INTRUSION CHARACTERIZATION WORK PLAN
FORMER CHAMBERLAIN MANUFACTURING FACILITY
550 ESTHER STREET

WATERLOO IOWA

FIGURE 2	
PROJECT MGR:	JFB
DRAWN BY:	JFB
APPVD. BY:	JFB
SCALE:	AS SHOWN
DATE:	MAY 2010
PROJECT NO.:	07107020
FILE NAME:	07107020-T1-FIG2
SHEET NO.:	2 OF 3



LEGEND

- PROPERTY LINE
- RAILROAD
- ◆ MONITORING WELL
- RES. RESIDENTIAL
- ◆ FORMER GEOBROPE SAMPLES
- ▨ PROPOSED VAPOR SAMPLING LIMITS

REV.	DATE	BY	DESCRIPTION

Terracon
Consulting Engineers and Scientists

870 40th Avenue Battendorf, Iowa 52722
(563) 355-0702 (563) 355-4789

STUDY AREA LIMITS
VAPOR INTRUSION CHARACTERIZATION WORK PLAN
FORMER CHAMBERLAIN MANUFACTURING FACILITY
550 ESTHER STREET
WATERLOO IOWA

FIGURE 3

PROJECT MGR:	JFB
DRAWN BY:	JFB
APPVD. BY:	JFB
SCALE:	AS SHOWN
DATE:	MAY 2010
PROJECT NO.:	07107020
FILE NAME:	07107020-T1-FIG3
SHEET NO.:	1 OF 3

Appendix B

Listing of Residences in Study Area

Appendix B
Residences in Study Area
Vapor Intrusion Characterization Work Plan
Former Chamberlain Manufacturing Facility

East Arlington Street - Sherman Avenue to East 4th Street	
South Side of Street	North Side of Street
314 East Arlington Street 322 East Arlington Street 400 East Arlington Street	315 East Arlington Street 321 East Arlington Street 401 East Arlington Street 405 East Arlington Street 423 East Arlington Street
Esther Street - Boston Avenue to East 4th Street	
South Side of Street	
410 Esther Street	
Boston Avenue - E. Arlington Street to Hanover Street	
West Side of Street	East Side of Street
211 Boston Avenue 215 Boston Avenue 223 Boston Avenue 227 Boston Avenue 229 Boston Avenue 239 Boston Avenue 245 Boston Avenue 249 Boston Avenue 253 Boston Avenue	212 Boston Avenue 216 Boston Avenue 222 Boston Avenue 226 Boston Avenue 232 Boston Avenue 236 Boston Avenue 240 Boston Avenue 246 Boston Avenue 250 Boston Avenue
Boston Avenue - Hanover Street to Esther Street	
	East Side of Street
	302 Boston Avenue 306 Boston Avenue 312 Boston Avenue 316 Boston Avenue 320 Boston Avenue 326 Boston Avenue
E. 4th Street - E. Arlington Street to Hanover Street	
West Side of Street	
2207 E. 4th Street 2211 E. 4th Street 2215 E. 4th Street 2221 E. 4th Street 2227 E. 4th Street 2233 E. 4th Street 2237 E. 4th Street 2243 E. 4th Street 2247 E. 4th Street 2253 E. 4th Street	

**Appendix B
Residences in Study Area
Vapor Intrusion Characterization Work Plan
Former Chamberlain Manufacturing Facility**

E. 4th Street - Hanover Street to Esther Street	
West Side of Street	
2405 E. 4th Street	
2413 E. 4th Street	
2417 E. 4th Street	
2421 E. 4th Street	
2427 E. 4th Street	
E. 4th Street - Esther Street to Anita Street	
West Side of Street	
2507 E. 4th Street	
2511 E. 4th Street	
2515 E. 4th Street	
2523 E. 4th Street	
2525 E. 4th Street	
2533 E. 4th Street	
2535 E. 4th Street	
E. 4th Street - Anita Street to Louise Street	
West Side of Street	East Side of Street
2601 E. 4th Street	2600 E. 4th Street
2609 E. 4th Street	2610 E. 4th Street
2617 E. 4th Street	2614 E. 4th Street
2621 E. 4th Street	2620 E. 4th Street
2625 E. 4th Street	2626 E. 4th Street
2629 E. 4th Street	2636 E. 4th Street
2635 E. 4th Street	2640 E. 4th Street
2641 E. 4th Street	2646 E. 4th Street
2645 E. 4th Street	

Appendix C

Letter to Residences Regarding Sampling and Access

Terracon

[Date]

Certified Mail/Return Receipt Requested

Certified Mail/Return Receipt Requested

[Owner]
[Address]
[City, State, Zip]

[Current Resident]
[Address]
[City, State, Zip]

Re: Residential Sampling Request

As you may know, the United States Environmental Protection Agency ("EPA") recently asked Chamberlain Manufacturing Corporation to do environmental testing of soil vapors beneath certain homes in your neighborhood near the 550 Esther Street property, once owned and operated by Chamberlain Manufacturing and currently owned by the City of Waterloo. As we understand you are the owner(s) and resident(s) of the residence at [Property Address], we are writing to describe the process and timing for the sampling, should you choose to have us conduct it.

In the next few months, Terracon Consultants, Inc., a licensed and experienced environmental consulting and engineering company, will be in your neighborhood conducting this sampling. The sampling will provide data to help determine if action may be needed. We are requesting your permission to do this sampling in your home.

The sampling, which is completely voluntary, involves two initial visits of about an hour or less each by courteous and experienced professionals who will display proper identification and respect you and your home.

Here's how it works:

Initial Visit: Sampling Port Installation and Questionnaire

On the first visit, we will install a small sample "port" in your home. The port is installed after wet drilling a 1-inch opening in the concrete floor of your basement or the lowest level of your home such as a crawl-space or slab. After installing the port, the voids are then backfilled with sand and concrete, which will set for at least 48 hours. We will clean-up the work area.

We will also ask for your assistance as our field personnel complete a questionnaire about your home. The questionnaire seeks information regarding your home and the presence of chemicals containing volatile organic compounds, such as paints, glues, stored fuels and dry-cleaned clothes. According to EPA, these household products can contribute to indoor air quality problems.

Additional Visit(s): Sample Collection

About two days after the first visit, we will return for about 45 minutes to collect a sample from the port. In some instances, we will also take indoor and outdoor air samples. These indoor and outdoor air samples are collected by small canisters that we would leave at your home for 24-hours and would then return to collect.



Terracon Consultants, Inc. 870 40th Avenue Bettendorf, Iowa 52722
www.terracon.com

Residential Sampling Request

February 4, 2011 ■ Terracon Project No. 07107020

Terracon

Depending on the results of the sampling, one or more additional sampling events may be needed to confirm the results of the previous event. If necessary, we will contact you and make arrangements for any additional sampling events.

Once EPA agrees that sampling in the area is complete, we will remove the sampling port and seal the area where the port was installed, ~~at your request.~~

The results of this sampling will be reviewed by EPA. Following EPA review, a copy of the results will be provided for your records. If the sampling identifies any vapors beneath your home that warrant attention, we will contact you and offer you an EPA-approved system, usually located in your basement, that is designed to reduce any vapors. The system would be installed at no cost to you.

It is important to know that this sampling is a precautionary step. The information we obtain will help us gain a fuller understanding of the conditions in your neighborhood and whether any additional action is needed.

If you would like to have the sampling performed in your home, please complete the enclosed request form and access agreement and mail it to:

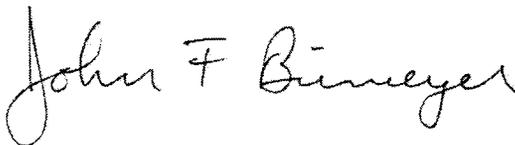
Terracon Consultants, Inc.
870 40th Avenue
Bettendorf, Iowa 52722

We have included separate sampling forms for each party.

In order to facilitate scheduling, we ask that you return the sampling request form no later than [30 days after submittal]. After we receive the form, we will call you to schedule a mutually convenient time for us to meet at your home to begin the sampling process.

We appreciate your cooperation in this process. Please contact John Brimeyer at (563) 355-4852 if you have any questions.

Sincerely,
Terracon Consultants, Inc.



John F. Brimeyer, PE
Environmental Manager

Sampling Request Form for Owner(s)

[Address]

Waterloo, IA 50703

(Please complete and return by [Date])

We hereby provide the City of Waterloo, Chamberlain Manufacturing Corporation, the United States Environmental Protection Agency and their authorized representatives permission to enter the residence listed above at a mutually convenient time for the purpose of collecting samples and completing the questionnaire as outlined in Terracon's letter dated [letter date] and the enclosed access agreement.

Signature of Owner

[Owner]

Telephone:(Day) _____

(Evening) _____

Dated: _____, 2011

Signature of Co-Owner

Print Name (if applicable)

Telephone:(Day) _____

(Evening) _____

Dated: _____, 2011

Sampling Request Form for Resident(s)
[Address]
Waterloo, IA 50703

(Please complete and return by March 11, 2011)

We hereby provide the City of Waterloo, Chamberlain Manufacturing Corporation, the United States Environmental Protection Agency and their authorized representatives permission to enter the residence listed above at a mutually convenient time for the purpose of collecting samples and completing the questionnaire as outlined in Terracon's letter dated [letter date] and the enclosed access agreement.

Signature of Resident

Signature of Co-Resident

Print Name

Print Name (if applicable)

Telephone:(Day) _____

(Evening) _____

Telephone:(Day) _____

(Evening) _____

Dated: _____, 2011

Dated: _____, 2011

ACCESS AGREEMENT

Date: _____

DEFINITIONS

The property to which access is granted is: _____ ("Property").

The Legal Owner(s) of the Property or person/entity with legal authority to grant access to the Property is: _____ ("Grantor").

The services to be conducted on the Property are generally described as follows: Collection of samples as outlined in the _____ letter dated _____. ("Services").

The entity granted access for the purposes of performing the Services is Terracon Consultants, Inc., which shall include its employees, agents, and subcontractors ("Grantee").

AGREEMENTS

By its signature below, Grantor represents it has authority to, and does, grant access to the Property to Grantee for the purpose of performing the Services. Grantor agrees that:

- Grantee may bring sampling equipment on the Property to recover and collect soil, water, and other samples, and perform other actions related to the exploration of surface or subsurface conditions on the Property, as necessary to perform the Services.
- Grantee will make reasonable efforts to restore the property and leave it in a condition suitable for its previous use.
- Grantor will not interfere with any of the activities of Grantee or undertake any actions regarding the use of Property that would endanger the health, safety, or welfare of the Grantee employees, agents, or subcontractors, or damage their equipment, materials, or property.

By its signature below, Grantee agrees:

- That upon completion of Services and activities authorized by this Access Agreement, Grantee will remove all material and equipment utilized by Grantee from the Property, with the exception of ground markers that may be placed on the premises to designate sampling areas,
- Grantee will remove boring spoils that accumulate around the bore holes.
- Grantee will make reasonable efforts to restore the property and leave it in a condition suitable for its previous use.

The Services and field activities authorized under this Access Agreement may begin after signature of Grantor. Access is granted until Services are completed.

SIGNATURES

Grantor:

By: _____ Date: _____

Name/Title: _____

Address: _____

Phone: _____ Fax: _____

Terracon Consultants, Inc. :

By: _____ Date: _____

Name/Title: _____

Address: **870 40th Avenue**

Bettendorf, Iowa 52722

Phone: **563.355.0702** Fax: **563.355.4789**

Terracon

Appendix D
Occupied Dwelling Questionnaire

OCCUPIED DWELLING QUESTIONNAIRE

Indoor Air Assessment Survey

Date: _____

1. Name: _____

Address: _____

Home Phone: _____ Work Phone: _____

2. What is the best time to call to speak with you? _____ At: Work or Home ?

3. Are you the Owner , Renter , Other (please specify) _____
of this Home/Structure?

4. Total number of occupants/persons at this location? _____
Number of children? _____ Ages? _____

5. How long have you lived at this location? _____

General Home Description

6. Type of Home/Structure (check only one): Single Family Home , Duplex ,
Condominium , Townhouse , Other _____

7. Home/Structure Description: number of floors _____

Basement? Yes No

Crawl Space? Yes No

If Yes, under how much of the house's area? ____%

8. Age of Home/Structure: _____ years, Not sure/Unknown

9. General Above-Ground Home/Structure construction (check all that apply):
Wood , Brick , Concrete , Cement block , Other _____

10. Foundation Construction (check all that apply):

Concrete slab

Fieldstone

Concrete block

- Elevated above ground/grade
- Other _____
11. What is the source of your drinking water (check all that apply)?
 Public water supply
 Private well
 Bottled water
 Other, please specify _____
12. Do you have a private well for purposes other than drinking?
 Yes No
 If yes, please describe what you use the well
 for: _____

13. Do you have a septic system? Yes No Not used Unknown
14. Do you have standing water outside your home (pond, ditch, swale)? Yes No

Basement Description, please check appropriate boxes.
If you do not have a basement go to question 23.

15. Is the basement finished or unfinished ?
16. If finished, how many rooms are in the basement? _____
 How many are used for more than 2 hours/day? _____
17. Is the basement floor (check all that apply) concrete , tile , carpeted , dirt ,
 other (describe) _____?
18. Are the basement walls poured concrete , cement block , stone , wood , brick ,
 other _____?
19. Does the basement have a moisture problem (check one only)?
 Yes, frequently (3 or more times/yr)
 Yes, occasionally (1-2 times/yr)
 Yes, rarely (less than 1 time/yr)
 No
20. Does the basement ever flood (check one only)?
 Yes, frequently (3 or more times/yr)
 Yes, occasionally (1-2 times/yr)
 Yes, rarely (less than 1 time/yr)
 No
21. Does the basement have any of the following? (check all that apply) Floor cracks ,
 Wall cracks , Sump , Floor drain , Other hole/opening in floor
 (describe) _____

22. Are any of the following used or stored in the basement (check all that apply)
 Paint Paint stripper/remover Paint thinner
 Metal degreaser/cleaner Gasoline Diesel fuel Solvents Glue
 Laundry spot removers Drain cleaners Pesticides
23. Have you recently (within the last six months) done any painting or remodeling in your home? Yes No
 If yes, please specify what was done, where in the home, and what month:

24. Have you installed new carpeting in your home within the last year? Yes No
 If yes, when and where? _____
25. Do you regularly use or work in a dry cleaning service (check only one box)?
 Yes, use dry-cleaning regularly (at least weekly)
 Yes, use dry-cleaning infrequently (monthly or less)
 Yes, work at a dry cleaning service
 No
26. Does anyone in your home use solvents at work?
 Yes If yes, how many persons _____
 No If no, go to question 28
27. If yes for question 26 above, are the work clothes washed at home? Yes No
28. Where is the washer/dryer located?
 Basement
 Upstairs utility room
 Kitchen
 Garage
 Use a Laundromat
 Other, please specify _____
29. If you have a dryer, is it vented to the outdoors? Yes No
30. What type(s) of home heating do you have (check all that apply)
 Fuel type: Gas , Oil , Electric , Wood , Coal , Other _____
 Heat conveyance system: Forced hot air
 Forced hot water
 Steam
 Radiant floor heat
 Wood stove
 Coal furnace
 Fireplace
 Other _____

31. Do you have air conditioning? Yes No . If yes, please check the appropriate type(s)
 Central air conditioning
 Window air conditioning unit(s)
 Other , please specify _____
32. Do you use any of the following? Room fans , Ceiling fans , Attic fan
 Do you ventilate using the fan-only mode of your central air conditioning or forced air heating system? Yes No
33. Has your home had termite or other pesticide treatment: Yes No Unknown
 If yes, please specify type of pest controlled, _____
 and approximate date of service _____
34. Water Heater Type: Gas , Electric , By furnace , Other

 Water heater location: Basement , Upstairs utility room , Garage , Other (please describe) _____
35. What type of cooking appliance do you have? Electric , Gas , Other

36. Is there a stove exhaust hood present? Yes No
 Does it vent to the outdoors? Yes No
37. Smoking in Home:
 None , Rare (only guests) , Moderate (residents light smokers) ,
 Heavy (at least one heavy smoker in household)
38. If yes to above, what do they smoke?
 Cigarettes Cigars
 Pipe Other
39. Do you regularly use air fresheners? Yes No
40. Does anyone in the home have indoor home hobbies of crafts involving: None
 Heating , soldering , welding , model glues , paint , spray paint,
 wood finishing , Other Please specify what type of hobby: _____

41. General family/home use of consumer products (please circle appropriate): Assume that
Never = never used, **Hardly ever** = less than once/month, **Occasionally** = about
 once/month, **Regularly** = about once/week, and **Often** = more than once/week.

Product _____ Frequency of Use

Spray-on deodorant Never Hardly ever Occasionally Regularly Often

Aerosol deodorizers	Never	Hardly ever	Occasionally	Regularly	Often
Insecticides	Never	Hardly ever	Occasionally	Regularly	Often
Disinfectants	Never	Hardly ever	Occasionally	Regularly	Often

(Question 41, continued)

<u>Product</u>	<u>Frequency of Use</u>				
Window cleaners	Never	Hardly ever	Occasionally	Regularly	Often
Spray-on oven cleaners	Never	Hardly ever	Occasionally	Regularly	Often
Nail polish remover	Never	Hardly ever	Occasionally	Regularly	Often
Hair sprays	Never	Hardly ever	Occasionally	Regularly	Often

42. Please check weekly household cleaning practices:

- Dusting
- Dry sweeping
- Vacuuming
- Polishing (furniture, etc)
- Washing/waxing floors
- Other _____

43. Other comments: _____

Appendix E
Typical Field Forms

**VAPOR INTRUSION CHARACTERIZATION WORK PLAN
 CHAMBERLAIN MANUFACTURING CORPORATION
 FORMER FACILITY AT
 550 ESTHER STREET
 WATERLOO, IOWA**

Soil Vapor/Indoor Air Sampling Information Form

Residence ID:		Address:	
Sample ID:		Location:	
Date:		Time:	
Sampler(s):		Summa Canister ID:	
Flow Controller ID:		Flow Controller Rate Setting (cc/min):	
Start Time:		Finish Time:	
Pre-Sampling Vacuum (in Hg):		Post-Sampling Vacuum (in Hg):	
Organic Vapor Reading (ppm):		PID used:	
Summa Canister went to Ambient?	Yes / No	Method:	Grab
Comments:			
Sketch:			

DO NOT TOUCH

SAMPLE IN PROGRESS

TERRACON PROJECT NUMBER: _____

PROJECT LOCATION: _____

DATE INSTALLED: _____

TIME INSTALLED: _____

ADDRESS INSTALLED: _____

SAMPLE ID: _____

SAMPLE LOCATION: _____

DEVICE #: _____ CONTROLLER#: _____

LAB ID #: _____

RETRIEVAL DATE: _____

PLANNED RETRIEVAL TIME: _____

ACTUAL RETRIEVAL TIME: _____

TERRACON REPRESENTATIVE: _____

COMMENTS:

Terracon
Consulting Engineers & Scientists

FOR INFORMATION CALL 651-770-1500

3535 Hoffman Rd E
White Bear Lake, MN 55110

Appendix F

Laboratory Standard Operating Procedures

**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

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Author(s)

- William A. McClenny, U.S. EPA, NERL, RTP, NC
- Michael W. Holdren, Battelle, Columbus, OH

Peer Reviewers

- Karen Oliver, ManTech, RTP, NC
- Jim Cheney, Corps of Engineers, Omaha, NB
- Elizabeth Almasi, Varian Chromatography Systems, Walnut Creek, CA
- Norm Kirshen, Varian Chromatography Systems, Walnut Creek, CA
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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-15

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

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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 cryogenes 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 ($\pm 10\%$) 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- μ m 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.

7.2.1.7.1 A 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/Amborsorb 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.

7.2.2.3.1 Linear 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.

7.2.2.3.2 Ion 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 $\pm 10\%$. 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 refocused on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocused 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-d₅, 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, $\text{mg}/\mu\text{L}$.

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:

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

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

Desorb Temperature	120°C
Desorb Flow Rate	~ 3 mL/min He
Desorb Time	<60 sec

Adsorbent Trap

Desorb Temperature	Variable
Desorb Flow Rate	~ 3 mL/min He
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

Initial bakeout	120°C (24 hrs)
Variable (24 hrs)	
After each run	120°C (5 min)

Adsorbent Trap

Initial bakeout	
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.

<u>Item</u>	<u>Condition</u>
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:

<u>Item</u>	<u>Condition</u>
-------------	------------------

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:

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

where: $\overline{\text{RRT}}$ = 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 ($\overline{\text{RT}}$). Calculate the mean of the retention times ($\overline{\text{RT}}$) for each internal standard over the initial calibration range using the following equation:

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

where: $\overline{\text{RT}}$ = 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 within 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 valve 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 μ L) 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 <0.05 mm 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 <0.2 mm 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 0.05 mm 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 <10 ppbC. 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); CH ₃ Cl	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); C ₂ H ₃ Cl	75-01-4	-14.0	3.2 x 10	62.5	X	X
Diazomethane; CH ₂ N ₂	334-88-3	-23.0	2.8 x 10	42.1		
Formaldehyde; CH ₂ O	50-00-0	-19.5	2.7 x 10	30		
1,3-Butadiene; C ₄ H ₆	106-99-0	-4.5	2.0 x 10	54		X
Methyl bromide (bromomethane); CH ₃ Br	74-83-9	3.6	1.8 x 10	94.9	X	X
Phosgene; CCl ₂ O	75-44-5	8.2	1.2 x 10	99		
Vinyl bromide (bromoethene); C ₂ H ₃ Br	593-60-2	15.8	1.1 x 10	107		
Ethylene oxide; C ₂ H ₄ O	75-21-8	10.7	1.1 x 10	44		
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	75-00-3	12.5	1.0 x 10	64.5	X	X
Acetaldehyde (ethanal); C ₂ H ₄ O	75-07-0	21.0	952	44		
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	75-35-4	31.7	500	97	X	X
Propylene oxide; C ₃ H ₆ O	75-56-9	34.2	445	58		
Methyl iodide (iodomethane); CH ₃ I	74-88-4	42.4	400	141.9		
Methylene chloride; CH ₂ Cl ₂	75-09-2	40.0	349	84.9	X	X
Methyl isocyanate; C ₂ H ₃ NO	624-83-9	59.6	348	57.1		
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	107-05-1	44.5	340	76.5	X	X
Carbon disulfide; CS ₂	75-15-0	46.5	260	76		
Methyl tert-butyl ether; C ₅ H ₁₂ O	1634-04-4	55.2	249	86		
Propionaldehyde; C ₂ H ₅ CHO	123-38-6	49.0	235	58.1		
Ethylidene dichloride (1,1-dichloroethane); C ₂ H ₄ Cl ₂	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); C ₄ H ₅ Cl	126-99-8	59.4	226	88.5		
Chloromethyl methyl ether; C ₂ H ₅ ClO	107-30-2	59.0	224	80.5		
Acrolein (2-propenal); C ₃ H ₄ O	107-02-8	52.5	220	56		X
1,2-Epoxybutane (1,2-butylene oxide); C ₄ H ₈ O	106-88-7	63.0	163	72		
Chloroform; CHCl ₃	67-66-3	61.2	160	119	X	X
Ethyleneimine (aziridine); C ₂ H ₅ N	151-56-4	56	160.0	43		
1,1-Dimethylhydrazine; C ₂ H ₈ N ₂	57-14-7	63	157.0	60.0		
Hexane; C ₆ H ₁₄	110-54-3	69.0	120	86.2	X	
1,2-Propyleneimine (2-methylaziridine); C ₃ H ₇ N	75-55-8	66.0	112	57.1		
Acrylonitrile (2-propenenitrile); C ₃ H ₃ N	107-13-1	77.3	100	53	X	
Methyl chloroform (1,1,1-trichloroethane); C ₂ H ₃ Cl ₃	71-55-6	74.1	100	133.4	X	X
Methanol; CH ₄ O	67-56-1	65.0	92.0	32		X
Carbon tetrachloride; CCl ₄	56-23-5	76.7	90.0	153.8	X	X
Vinyl acetate; C ₄ H ₆ O ₂	108-05-4	72.2	83.0	86		X
Methyl ethyl ketone (2-butanone); C ₄ H ₈ O	78-93-3	79.6	77.5	72		X
Benzene; C ₆ H ₆	71-43-2	80.1	76.0	78	X	X
Acetonitrile (cyanomethane); C ₂ H ₃ N	75-05-8	82	74.0	41.0		X
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	107-06-2	83.5	61.5	99	X	X
Triethylamine; C ₆ H ₁₅ N	121-44-8	89.5	54.0	101.2		
Methylhydrazine; CH ₆ N ₂	60-34-4	87.8	49.6	46.1		
Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂	78-87-5	97.0	42.0	113	X	X
2,2,4-Trimethyl pentane C ₈ H ₁₈	540-84-1	99.2	40.6	114		
1,4-Dioxane (1,4-Diethylene oxide); C ₄ H ₈ O ₂	123-91-1	101	37.0	88		
Bis(chloromethyl) ether; C ₂ H ₄ Cl ₂ O	542-88-1	104	30.0	115		
Ethyl acrylate; C ₅ H ₈ O ₂	140-88-5	100	29.3	100		
Methyl methacrylate; C ₅ H ₈ O ₂	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; C ₅ H ₈ O ₂	80-62-101	101	28.0	100.1		
1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (cis)	542-75-6	112	27.8	111	X	X
Toluene; C ₇ H ₈	108-88-3	111	22.0	92	X	X
Trichloroethylene; C ₂ HCl ₃	79-01-6	87.0	20.0	131.4	X	X
1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃	79-00-5	114	19.0	133.4	X	X
Tetrachloroethylene; C ₂ Cl ₄	127-18-4	121	14.0	165.8	X	X
Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO	106-89-8	117	12.0	92.5		
Ethylene dibromide (1,2-dibromoethane); C ₂ H ₄ Br ₂	106-93-4	132	11.0	187.9	X	X
N-Nitroso-N-methylurea; C ₂ H ₅ N ₃ O ₂	684-93-5	124	10.0	103		
2-Nitropropane; C ₃ H ₇ NO ₂	79-46-9	120	10.0	89		
Chlorobenzene; C ₆ H ₅ Cl	108-90-7	132	8.8	112.6	X	X
Ethylbenzene; C ₈ H ₁₀	100-41-4	136	7.0	106	X	X
Xylenes (isomer & mixtures); C ₈ H ₁₀	1330-20-7	142	6.7	106.2	X	X
Styrene; C ₈ H ₈	100-42-5	145	6.6	104	X	X
p-Xylene; C ₈ H ₁₀	106-42-3	138	6.5	106.2	X	X
m-Xylene; C ₈ H ₁₀	108-38-3	139	6.0	106.2	X	X
Methyl isobutyl ketone (hexone); C ₆ H ₁₂ O	108-10-1	117	6.0	100.2		
Bromoform (tribromomethane); CHBr ₃	75-25-2	149	5.6	252.8		
1,1,2,2-Tetrachloroethane; C ₂ H ₂ Cl ₄	79-34-5	146	5.0	167.9	X	X
o-Xylene; C ₈ H ₁₀	95-47-6	144	5.0	106.2	X	X
Dimethylcarbonyl chloride; C ₃ H ₆ Cl ₂ O	79-44-7	166	4.9	107.6		
N-Nitrosodimethylamine; C ₂ H ₆ N ₂ O	62-75-9	152	3.7	74		
Beta-Propiolactone; C ₃ H ₄ O ₂	57-57-8	Decomposes at 162	3.4	72		
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	153	3.2	120		

TABLE 1. (continued)

Compound	CAS No.	BP (°C)	v.p. (mmHg)	MW ¹	TO-14A	CLP-SOW
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	153	3.2	120		
Acrylic acid; C ₃ H ₄ O ₂	79-10-7	141	3.2	72		
N,N-Dimethylformamide; C ₃ H ₇ NO	68-12-2	153	2.7	73		
1,3-Propane sultone; C ₃ H ₆ O ₃ S	1120-71-4	180/30mm	2.0	122.1		
Acetophenone; C ₈ H ₈ O	98-86-2	202	1.0	120		
Dimethyl sulfate; C ₂ H ₆ O ₄ S	77-78-1	188	1.0	126.1		
Benzyl chloride (a-chlorotoluene); C ₇ H ₇ Cl	100-44-7	179	1.0	126.6	X	X
1,2-Dibromo-3-chloropropane; C ₃ H ₅ Br ₂ Cl	96-12-8	196	0.80	236.4		
Bis(2-Chloroethyl)ether; C ₄ H ₈ Cl ₂ O	111-44-4	178	0.71	143		
Chloroacetic acid; C ₂ H ₃ ClO ₂	79-11-8	189	0.69	94.5		
Aniline (aminobenzene); C ₆ H ₇ N	62-53-3	184	0.67	93		
1,4-Dichlorobenzene (p-); C ₆ H ₄ Cl ₂	106-46-7	173	0.60	147	X	X
Ethyl carbamate (urethane); C ₃ H ₇ NO ₂	51-79-6	183	0.54	89		
Acrylamide; C ₃ H ₅ NO	79-06-1	125/25 mm	0.53	71		
N,N-Dimethylaniline; C ₈ H ₁₁ N	121-69-7	192	0.50	121		
Hexachloroethane; C ₂ Cl ₆	67-72-1	Sublimes at 186	0.40	236.7		
Hexachlorobutadiene; C ₄ Cl ₆	87-68-3	215	0.40	260.8	X	X
Isophorone; C ₉ H ₁₄ O	78-59-1	215	0.38	138.2		
N-Nitrosomorpholine; C ₄ H ₈ N ₂ O ₂	59-89-2	225	0.32	116.1		
Styrene oxide; C ₈ H ₈ O	96-09-3	194	0.30	120.2		
Diethyl sulfate; C ₄ H ₁₀ O ₄ S	64-67-5	208	0.29	154		
Cresylic acid (cresol isomer mixture); C ₇ H ₈ O	1319-77-3	202	0.26	108		
o-Cresol; C ₇ H ₈ O	95-48-7	191	0.24	108		
Catechol (o-hydroxyphenol); C ₆ H ₆ O ₂	120-80-9	240	0.22	110		
Phenol; C ₆ H ₆ O	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); C ₆ H ₆ O ₂	120-80-9	240	0.22	110		
Phenol; C ₆ H ₆ O	108-95-2	182	0.20	94		
1,2,4-Trichlorobenzene; C ₆ H ₃ Cl ₃	120-82-1	213	0.18	181.5	X	X
nitrobenzene C ₆ H ₅ NO ₂	98-95-3	211	0.15	123		

¹Vapor 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); CH ₃ Cl	74-87-3	50	52
Carbonyl sulfide; COS	463-88-1	60	62
Vinyl chloride (chloroethene); C ₂ H ₃ Cl	75-01-4	62	64
Diazomethane; CH ₂ N ₂	334-88-3	42	41
Formaldehyde; CH ₂ O	50-00-0	29	30
1,3-Butadiene; C ₄ H ₆	106-99-0	39	54
Methyl bromide (bromomethane); CH ₃ Br	74-83-9	94	96
Phosgene; CCl ₂ O	75-44-5	63	65
Vinyl bromide (bromoethene); C ₂ H ₃ Br	593-60-2	106	108
Ethylene oxide; C ₂ H ₄ O	75-21-8	29	44
Ethyl chloride (chloroethane); C ₂ H ₅ Cl	75-00-3	64	66
Acetaldehyde (ethanal); C ₂ H ₄ O	75-07-0	44	29, 43
Vinylidene chloride (1,1-dichloroethylene); C ₂ H ₂ Cl ₂	75-35-4	61	96
Propylene oxide; C ₃ H ₆ O	75-56-9	58	57
Methyl iodide (iodomethane); CH ₃ I	74-88-4	142	127
Methylene chloride; CH ₂ Cl ₂	75-09-2	49	84, 86
Methyl isocyanate; C ₂ H ₃ NO	624-83-9	57	56
Allyl chloride (3-chloropropene); C ₃ H ₅ Cl	107-05-1	76	41, 78
Carbon disulfide; CS ₂	75-15-0	76	44, 78
Methyl tert-butyl ether; C ₅ H ₁₂ O	1634-04-4	73	41, 53
Propionaldehyde; C ₂ H ₅ CHO	123-38-6	58	29, 57
Ethylidene dichloride (1,1-dichloroethane); C ₂ H ₄ Cl ₂	75-34-3	63	65, 27
Chloroprene (2-chloro-1,3-butadiene); C ₄ H ₅ Cl	126-99-8	88	53, 90
Chloromethyl methyl ether; C ₂ H ₅ ClO	107-30-2	45	29, 49
Acrolein (2-propenal); C ₃ H ₄ O	107-02-8	56	55
1,2-Epoxybutane (1,2-butylene oxide); C ₄ H ₈ O	106-88-7	42	41, 72
Chloroform; CHCl ₃	67-66-3	83	85, 47
Ethyleneimine (aziridine); C ₂ H ₅ N	151-56-4	42	43
1,1-Dimethylhydrazine; C ₂ H ₈ N ₂	57-14-7	60	45, 59
Hexane; C ₆ H ₁₄	110-54-3	57	41, 43
1,2-Propyleneimine (2-methylaziridine); C ₃ H ₇ N	75-55-8	56	57, 42
Acrylonitrile (2-propenenitrile); C ₃ H ₃ N	107-13-1	53	52
Methyl chloroform (1,1,1 trichloroethane); C ₂ H ₃ Cl ₃	71-55-6	97	99, 61
Methanol; CH ₄ O	67-56-1	31	29
Carbon tetrachloride; CCl ₄	56-23-5	117	119
Vinyl acetate; C ₄ H ₆ O ₂	108-05-4	43	86
Methyl ethyl ketone (2-butanone); C ₄ H ₈ O	78-93-3	43	72

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Benzene; C ₆ H ₆	71-43-2	78	77, 50
Acetonitrile (cyanomethane); C ₂ H ₃ N	75-05-8	41	40
Ethylene dichloride (1,2-dichloroethane); C ₂ H ₄ Cl ₂	107-06-2	62	64, 27
Triethylamine; C ₆ H ₁₅ N	121-44-8	86	58, 101
Methylhydrazine; CH ₆ N ₂	60-34-4	46	31, 45
Propylene dichloride (1,2-dichloropropane); C ₃ H ₆ Cl ₂	78-87-5	63	41, 62
2,2,4-Trimethyl pentane; C ₈ H ₁₈	540-84-1	57	41, 56
1,4-Dioxane (1,4 Diethylene oxide); C ₄ H ₈ O ₂	123-91-1	88	58
Bis(chloromethyl) ether; C ₂ H ₄ Cl ₂ O	542-88-1	79	49, 81
Ethyl acrylate; C ₅ H ₈ O ₂	140-88-5	55	73
Methyl methacrylate; C ₅ H ₈ O ₂	80-62-6	41	69, 100
1,3-Dichloropropene; C ₃ H ₄ Cl ₂ (cis)	542-75-6	75	39, 77
Toluene; C ₇ H ₈	108-88-3	91	92
Trichloroethylene; C ₂ HCl ₃	79-01-6	130	132, 95
1,1,2-Trichloroethane; C ₂ H ₃ Cl ₃	79-00-5	97	83, 61
Tetrachloroethylene; C ₂ Cl ₄	127-18-4	166	164, 131
Epichlorohydrin (1-chloro-2,3-epoxy propane); C ₃ H ₅ ClO	106-89-8	57	49, 62
Ethylene dibromide (1,2-dibromoethane); C ₂ H ₄ Br ₂	106-93-4	107	109
N-Nitroso-N-methylurea; C ₂ H ₅ N ₃ O ₂	684-93-5	60	44, 103
2-Nitropropane; C ₃ H ₇ NO ₂	79-46-9	43	41
Chlorobenzene; C ₆ H ₅ Cl	108-90-7	112	77, 114
Ethylbenzene; C ₈ H ₁₀	100-41-4	91	106
Xylenes (isomer & mixtures); C ₈ H ₁₀	1330-20-7	91	106
Styrene; C ₈ H ₈	100-42-5	104	78, 103
p-Xylene; C ₈ H ₁₀	106-42-3	91	106
m-Xylene; C ₈ H ₁₀	108-38-3	91	106
Methyl isobutyl ketone (hexone); C ₆ H ₁₂ O	108-10-1	43	58, 100
Bromoform (tribromomethane); CHBr ₃	75-25-2	173	171, 175
1,1,2,2-Tetrachloroethane; C ₂ H ₂ Cl ₄	79-34-5	83	85
o-Xylene; C ₈ H ₁₀	95-47-6	91	106
Dimethylcarbonyl chloride; C ₃ H ₆ ClNO	79-44-7	72	107
N-Nitrosodimethylamine; C ₂ H ₆ N ₂ O	62-75-9	74	42
Beta-Propiolactone; C ₃ H ₄ O ₂	57-57-8	42	43
Cumene (isopropylbenzene); C ₉ H ₁₂	98-82-8	105	120
Acrylic acid; C ₃ H ₄ O ₂	79-10-7	72	45, 55
N,N-Dimethylformamide; C ₃ H ₇ NO	68-12-2	73	42, 44
1,3-Propane sultone; C ₃ H ₆ O ₃ S	1120-71-4	58	65, 122

TABLE 2. (continued)

Compound	CAS No.	Primary Ion	Secondary Ion
Acetophenone; C ₈ H ₈ O	98-86-2	105	77,120
Dimethyl sulfate; C ₂ H ₆ O ₄ S	77-78-1	95	66,96
Benzyl chloride (a-chlorotoluene); C ₇ H ₇ Cl	100-44-7	91	126
1,2-Dibromo-3-chloropropane; C ₃ H ₅ Br ₂ Cl	96-12-8	57	155, 157
Bis(2-Chloroethyl)ether; C ₄ H ₈ Cl ₂ O	111-44-4	93	63, 95
Chloroacetic acid; C ₂ H ₃ ClO ₂	79-11-8	50	45, 60
Aniline (aminobenzene); C ₆ H ₇ N	62-53-3	93	66
1,4-Dichlorobenzene (p-); C ₆ H ₄ Cl ₂	106-46-7	146	148, 111
Ethyl carbamate (urethane); C ₃ H ₇ NO ₂	51-79-6	31	44, 62
Acrylamide; C ₃ H ₅ NO	79-06-1	44	55, 71
N,N-Dimethylaniline; C ₈ H ₁₁ N	121-69-7	120	77, 121
Hexachloroethane; C ₂ Cl ₆	67-72-1	201	199, 203
Hexachlorobutadiene; C ₄ Cl ₆	87-68-3	225	227, 223
Isophorone; C ₉ H ₁₄ O	78-59-1	82	138
N-Nitrosomorpholine; C ₄ H ₈ N ₂ O ₂	59-89-2	56	86, 116
Styrene oxide; C ₈ H ₈ O	96-09-3	91	120
Diethyl sulfate; C ₄ H ₁₀ O ₄ S	64-67-5	45	59, 139
Cresylic acid (cresol isomer mixture); C ₇ H ₈ O	1319-77-3		
o-Cresol; C ₇ H ₈ O	95-48-7	108	107
Catechol (o-hydroxyphenol); C ₆ H ₆ O ₂	120-80-9	110	64
Phenol; C ₆ H ₆ O	108-95-2	94	66
1,2,4-Trichlorobenzene; C ₆ H ₃ Cl ₃	120-82-1	180	182, 184
Nitrobenzene; C ₆ H ₅ NO ₂	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

¹All 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

¹Method 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 OPERATIONS¹**

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	--	--	--

¹Denotes 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.

²Styrene 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) VALUES¹ 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

¹Audit 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.

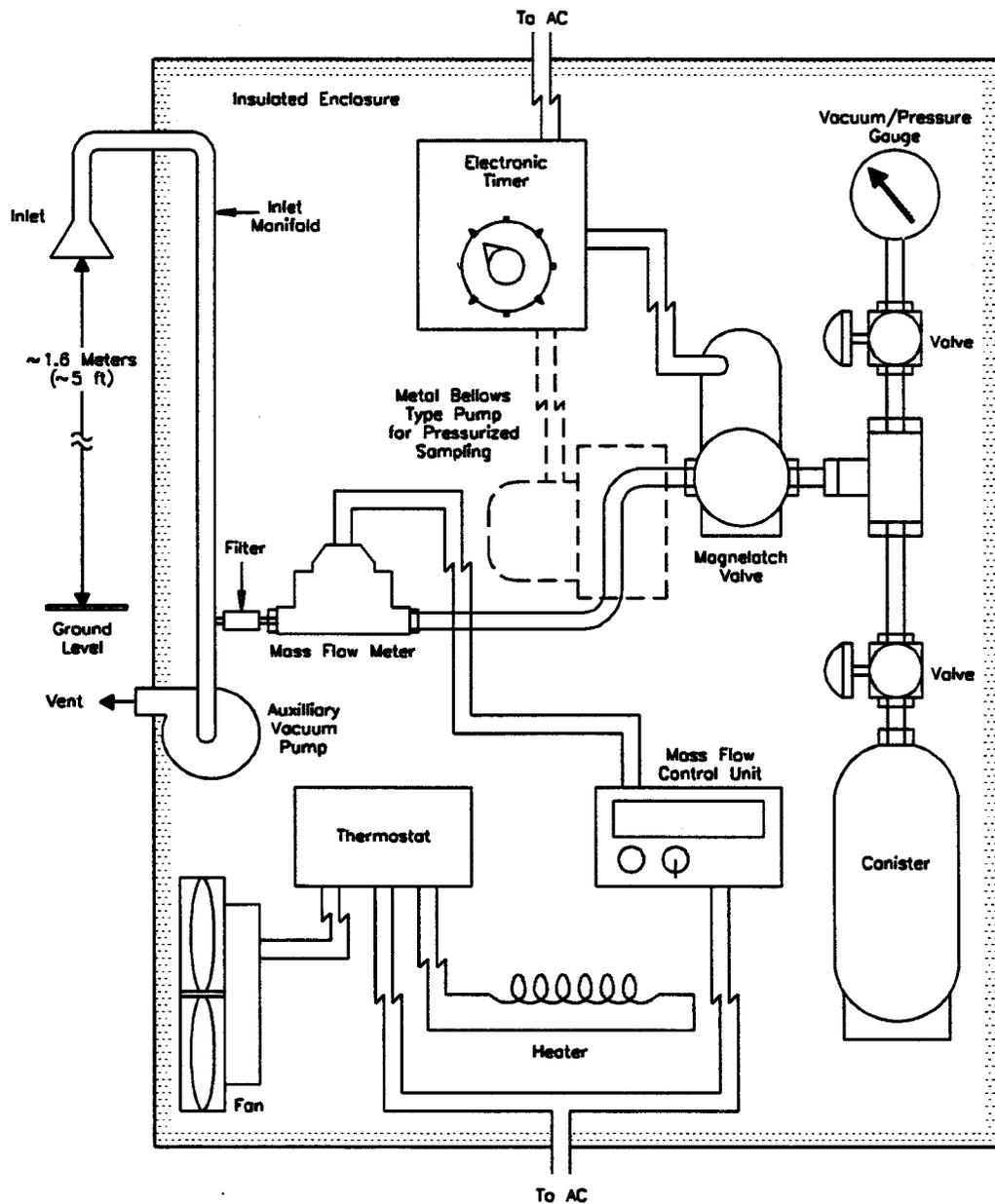
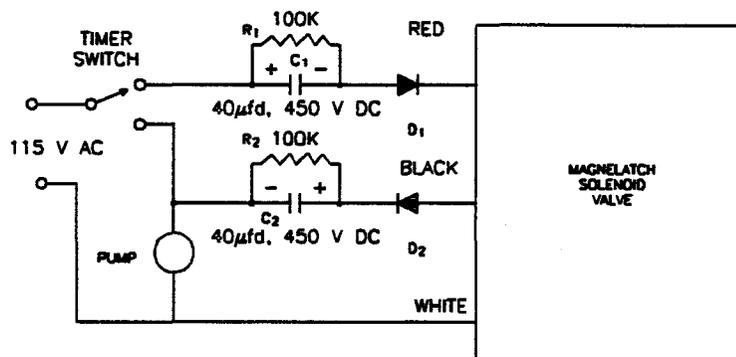


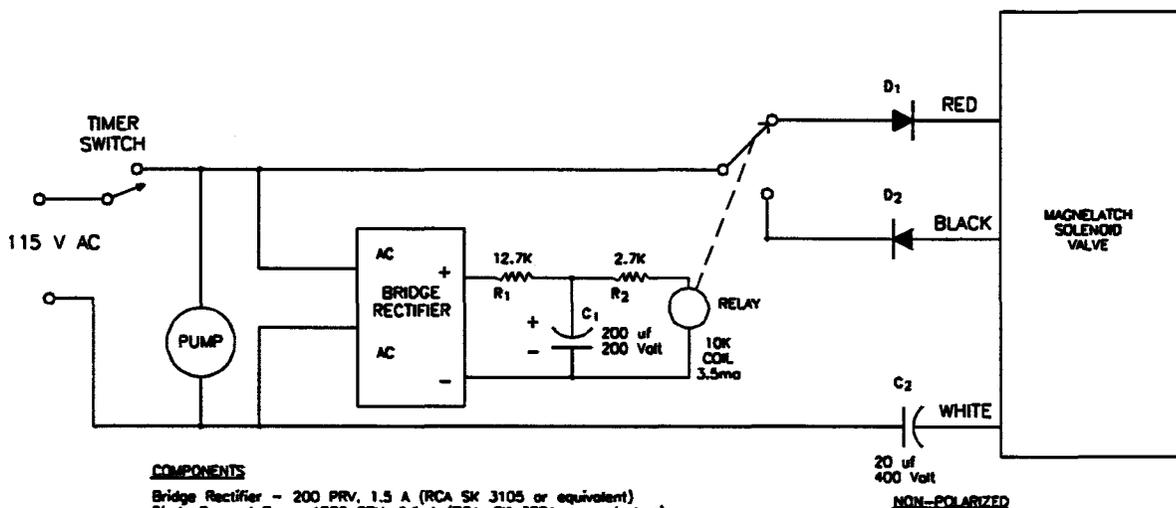
Figure 1. Sampler configuration for subatmospheric pressure or pressurized canister sampling.



COMPONENTS

Capacitor C₁ and C₂ - 40 uf, 450 VDC (Sprague Atom TVA 1712 or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)

(a). Simple Circuit for Operating Magnelatch Valve



COMPONENTS

Bridge Rectifier - 200 PRV, 1.5 A (RCA SK 3105 or equivalent)
 Diode D₁ and D₂ - 1000 PRV, 2.5 A (RCA, SK 3081 or equivalent)
 Capacitor C₁ - 200 uf, 250 VDC (Sprague Atom TVA 1528 or equivalent)
 Capacitor C₂ - 20 uf, 400 VDC Non-Polarized (Sprague Atom TVAN 1652 or equivalent)
 Relay - 10,000 ohm coil, 3.5 ma (AMF Potter and Brumfield, KCP 5, or equivalent)
 Resistor R₁ and R₂ - 0.5 watt, 5% tolerance

(b). Improved Circuit Designed to Handle Power Interruptions

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

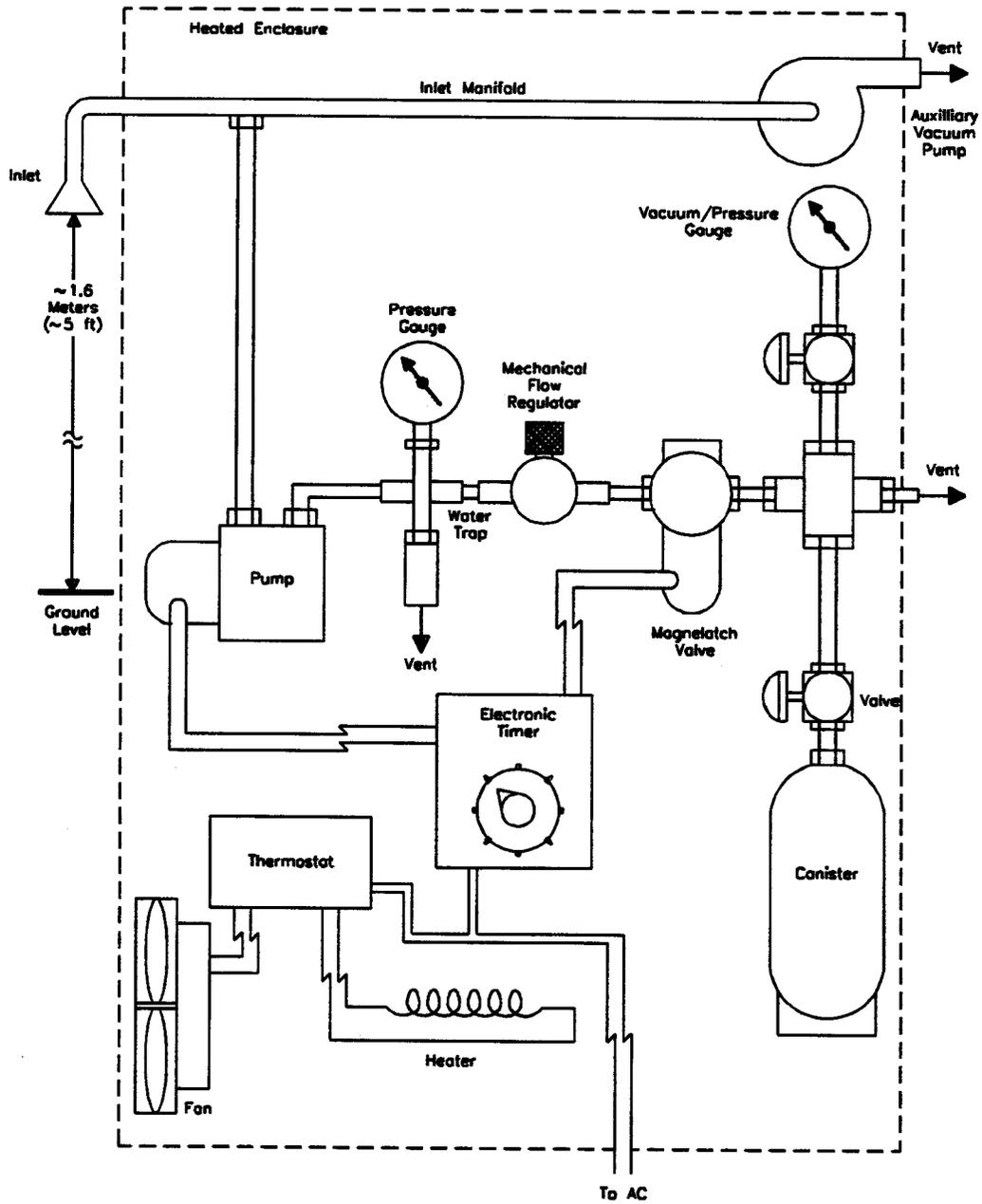


Figure 3. Alternative sampler configuration for pressurized canister sampling.

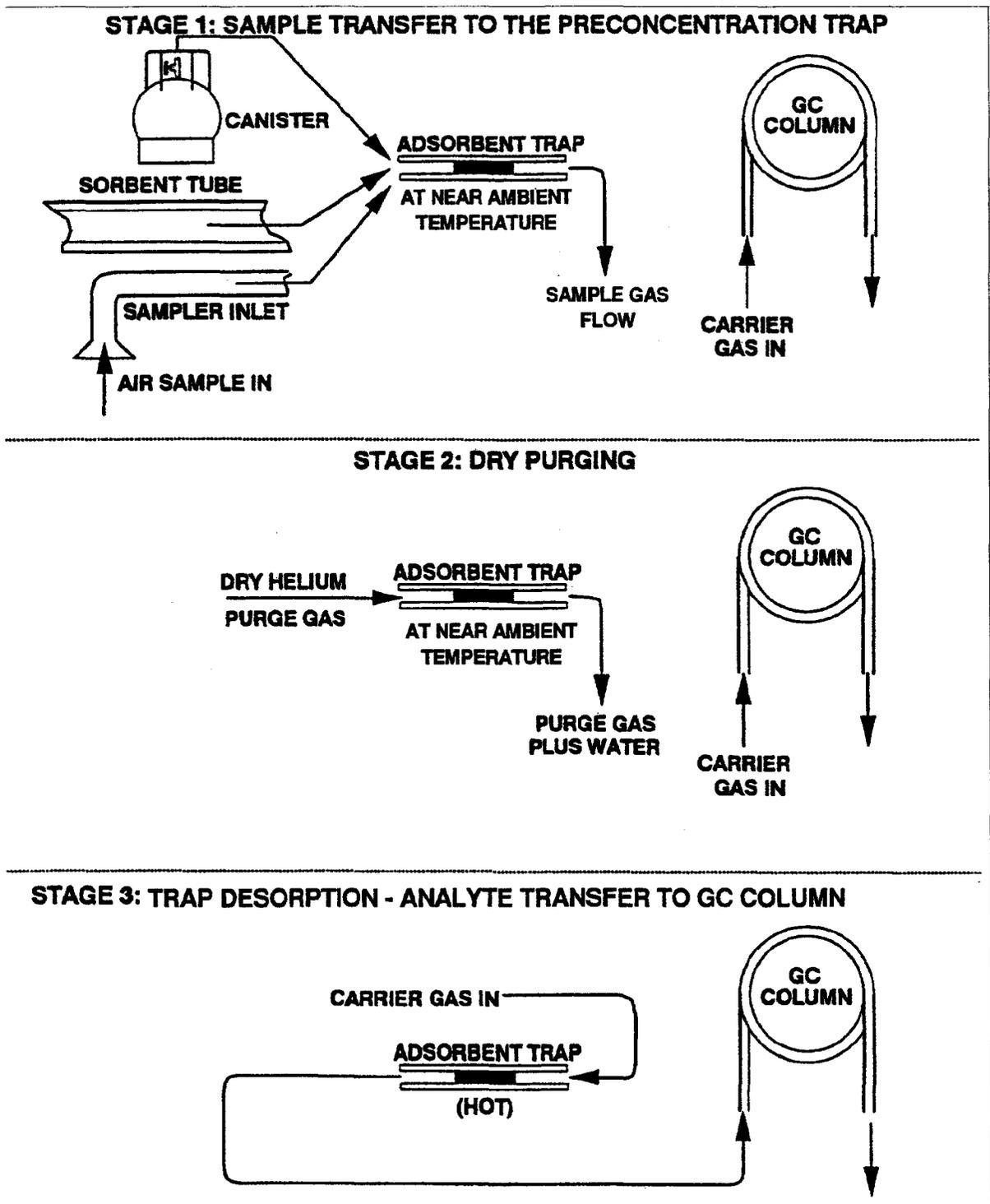


Figure 4. Illustration of three stages of dry purging of adsorbent trap.

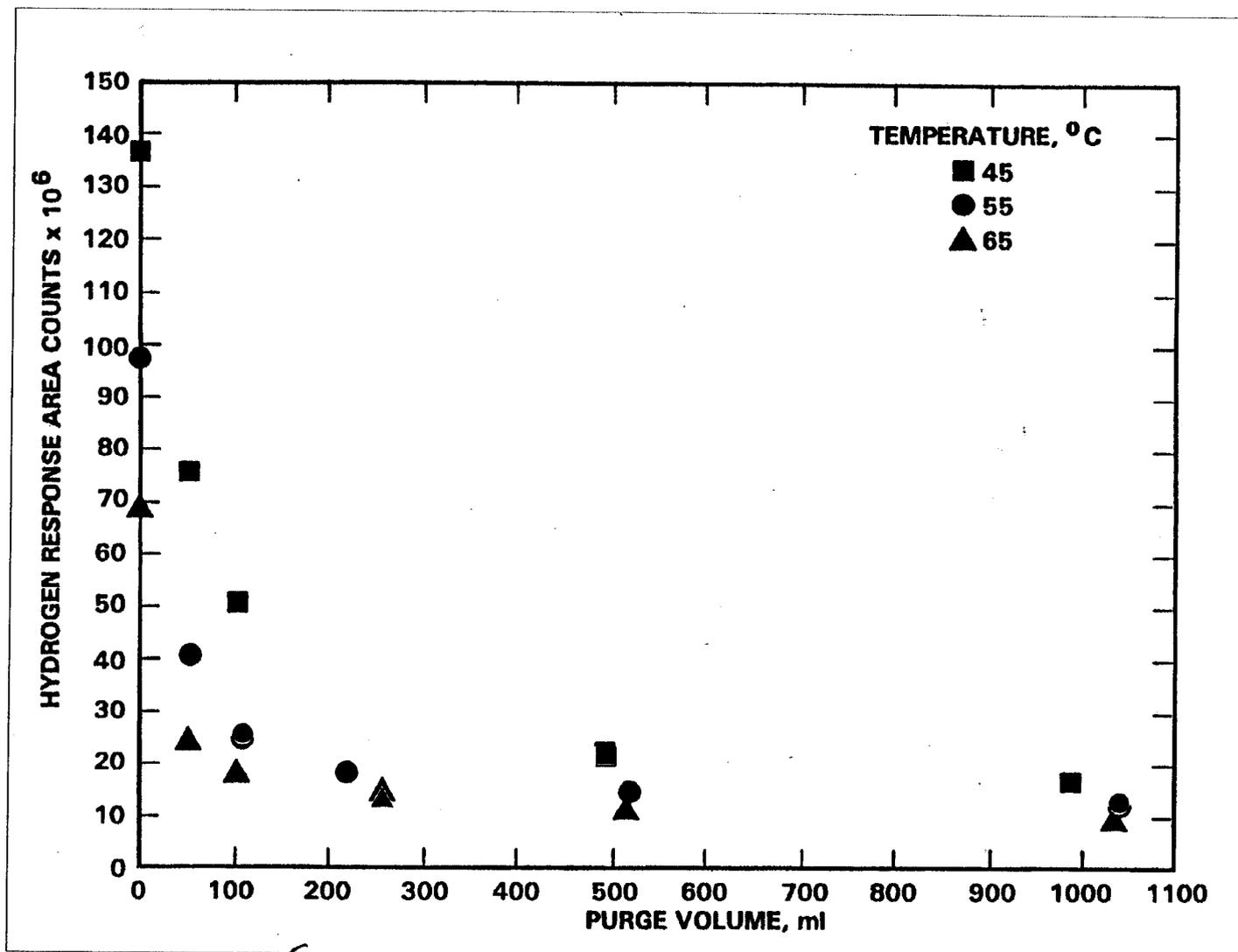


Figure 5. Residual water vapor on VOC concentrator vs. dry He purge volume.

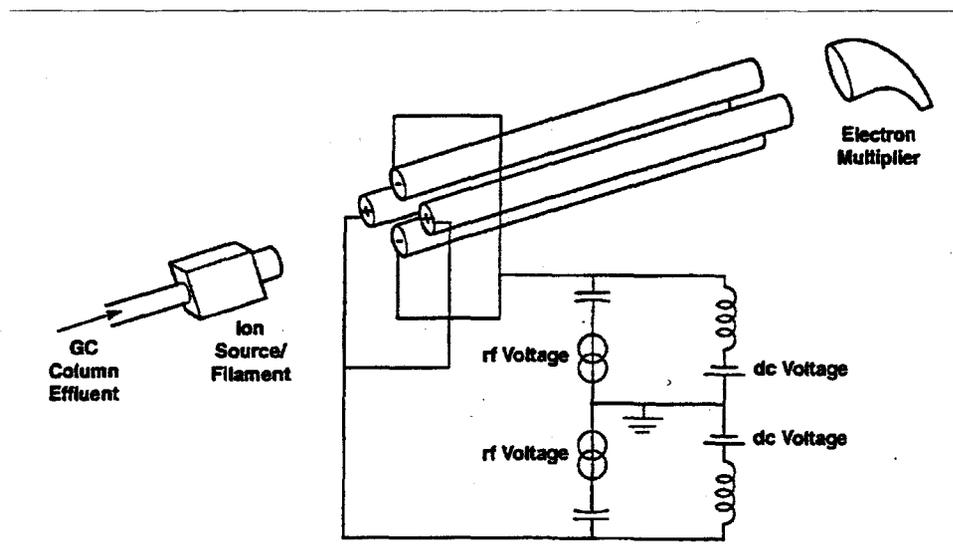


Figure 6. Simplified diagram of a quadrupole mass spectrometer.

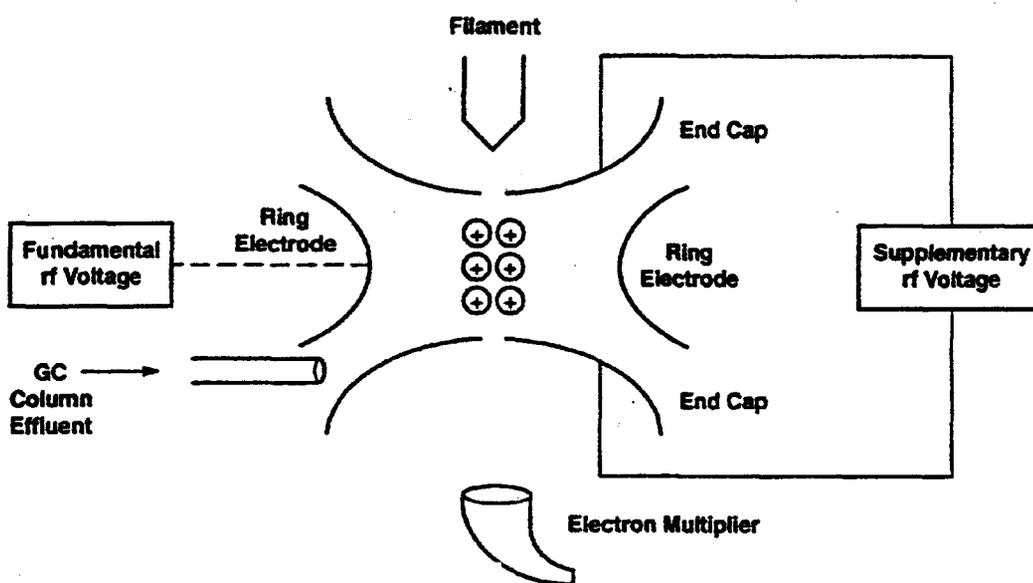


Figure 7. Simplified diagram of an ion trap mass spectrometer.

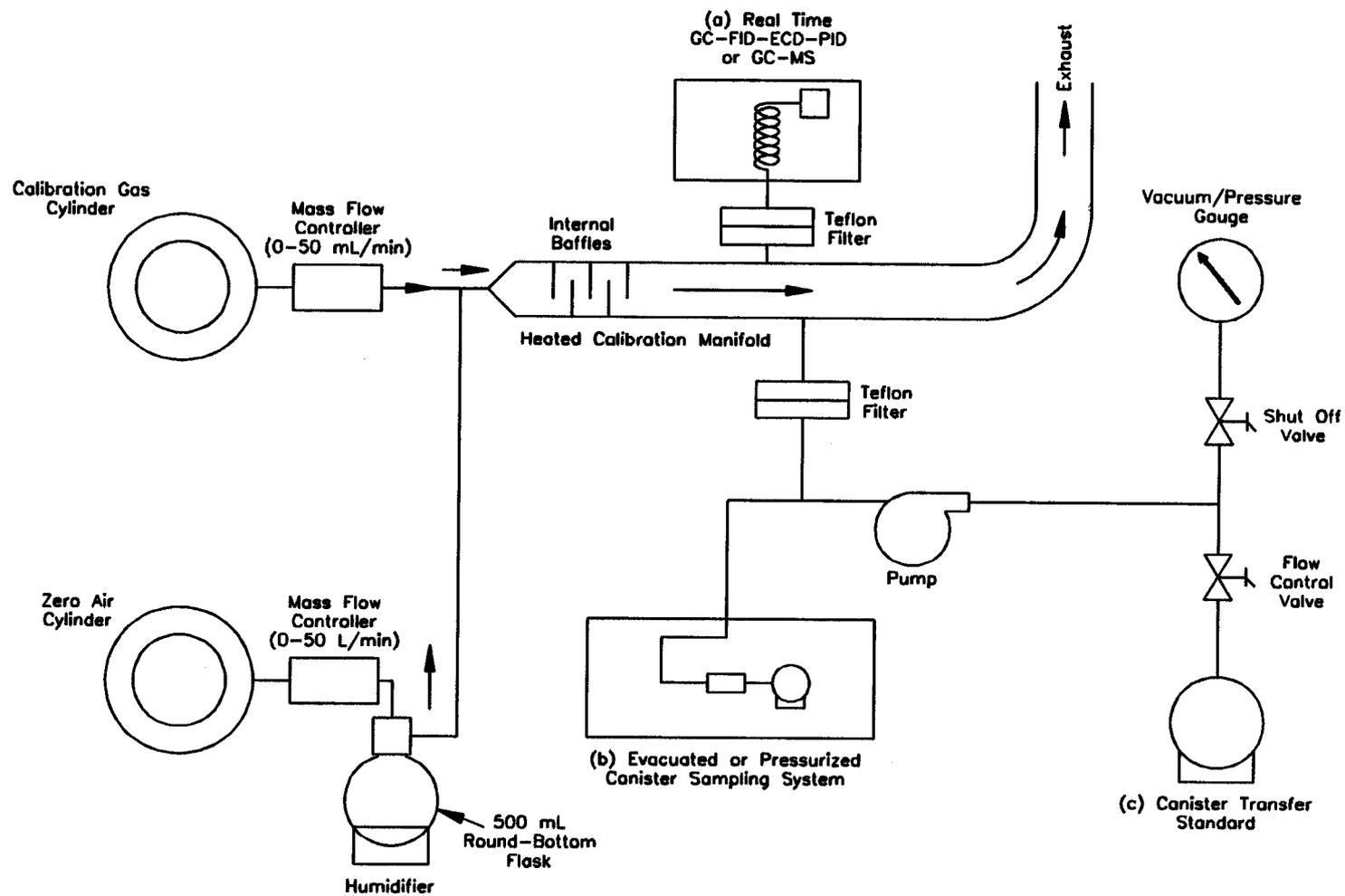


Figure 8. Schematic diagram of calibration system and manifold for (a) analytical system calibration, (b) testing canister sampling system and (c) preparing canister transfer standards.

**COMPENDIUM METHOD TO-15
CANISTER SAMPLING FIELD TEST DATA SHEET**

A. GENERAL INFORMATION

SITE LOCATION: _____ SHIPPING DATE: _____
 SITE ADDRESS: _____ CANISTER SERIAL NO.: _____
 _____ SAMPLER ID: _____
 SAMPLING DATE: _____ 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).

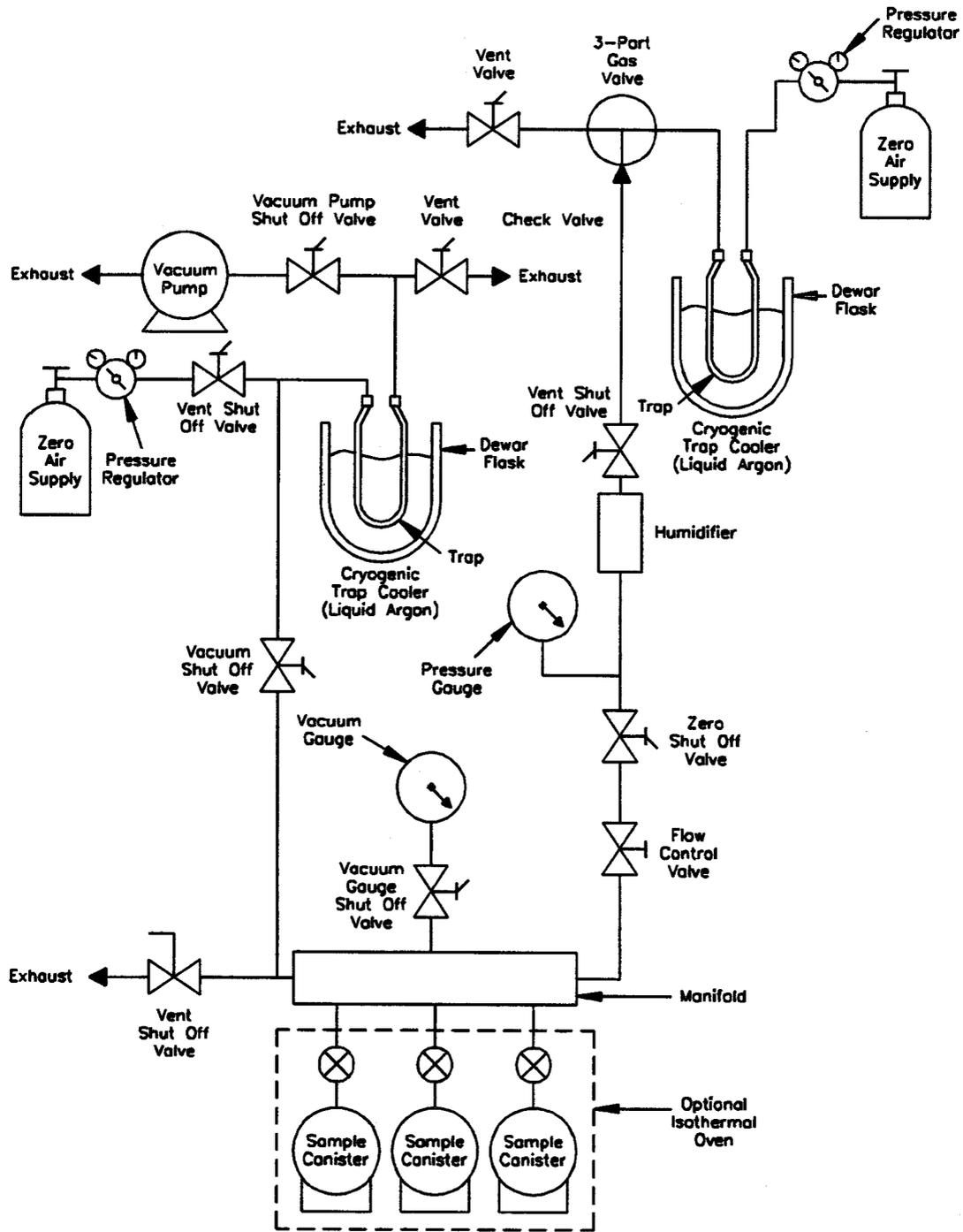


Figure 10. Canister cleaning system.

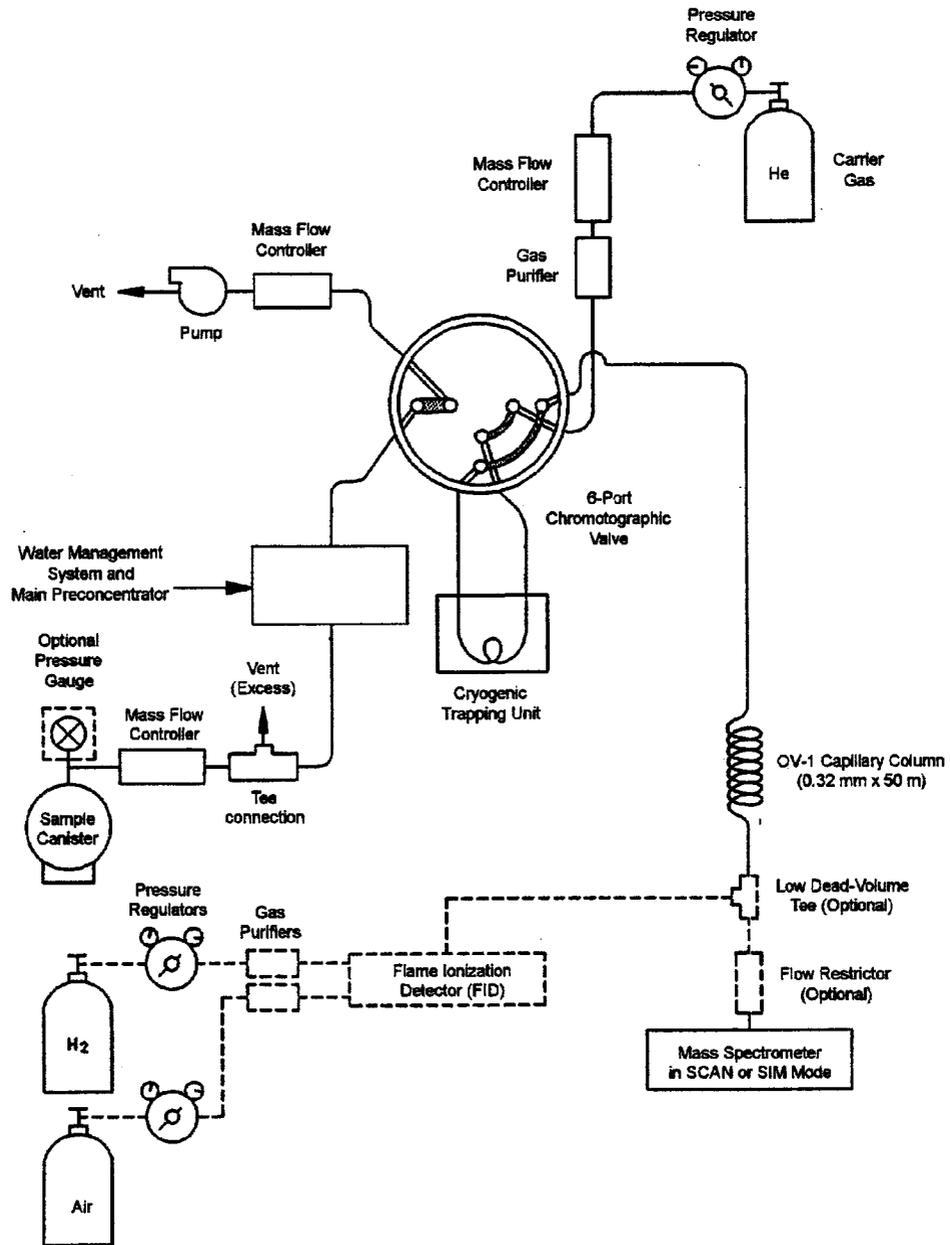
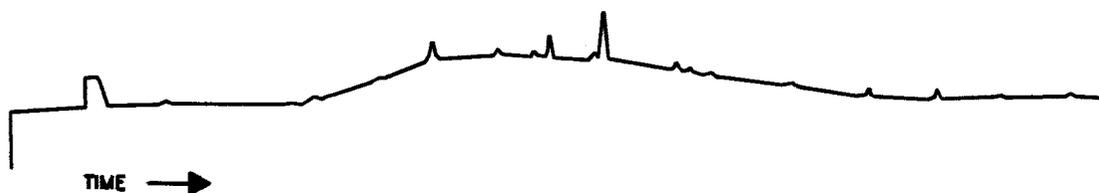
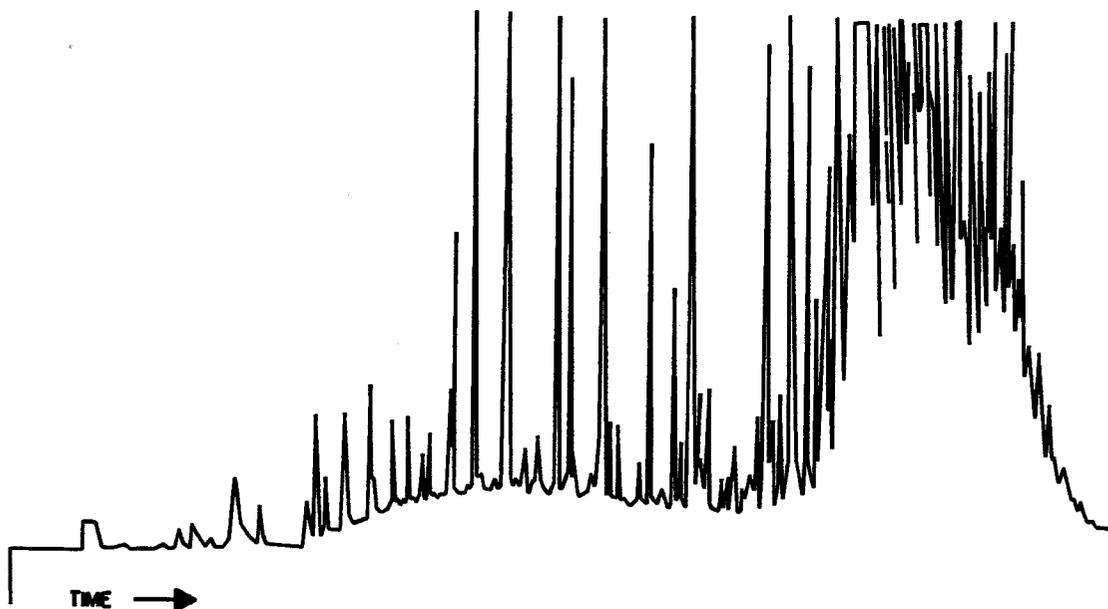


Figure 11. Canister analysis utilizing GC/MS/SCAN/SIM analytical system with optional flame ionization detector with 6-port chromatographic valve in the sample desorption mode.
 [Alternative analytical system illustrated in Figure 16.]



(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).

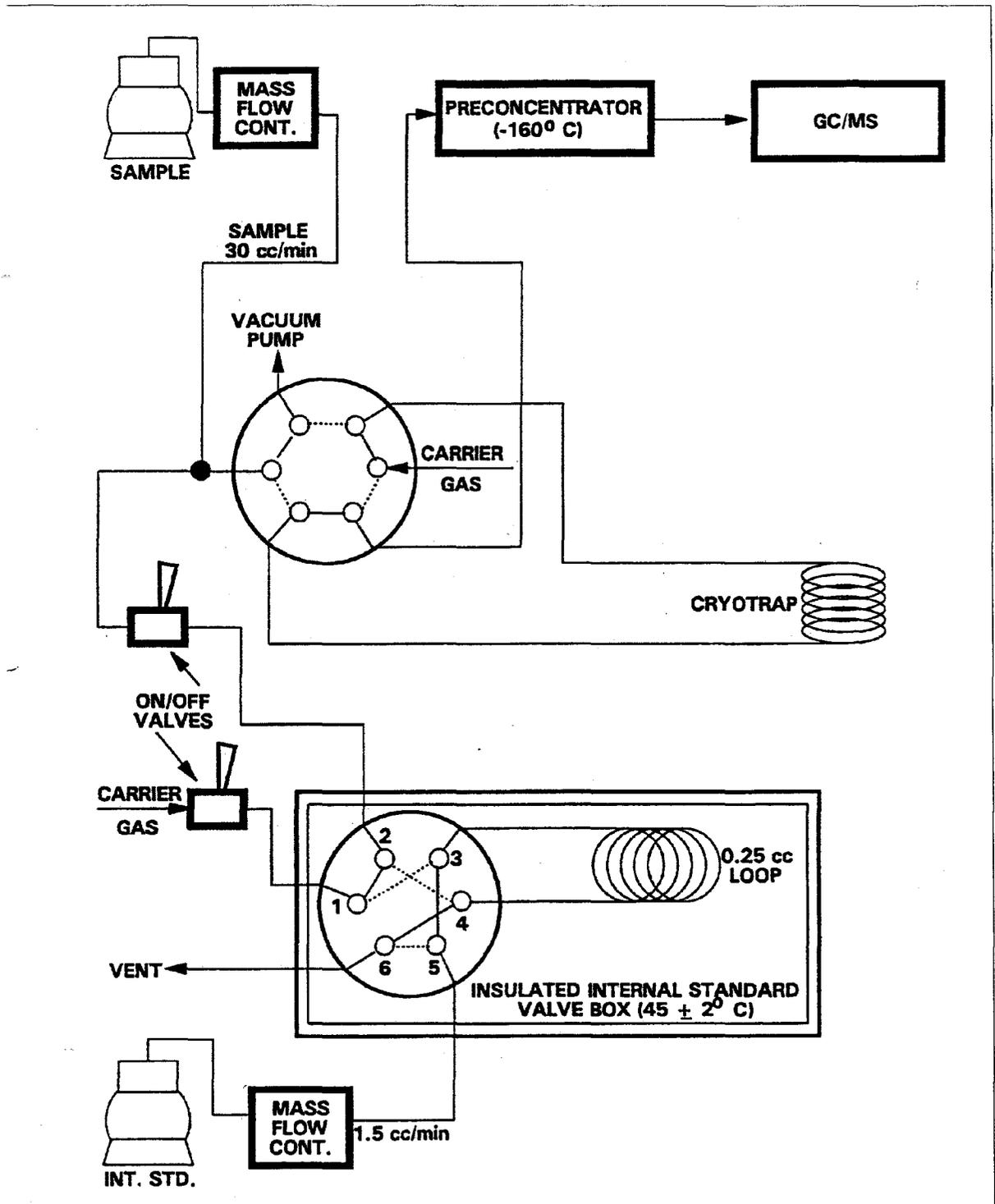


Figure 13. Diagram of design for internal standard addition.

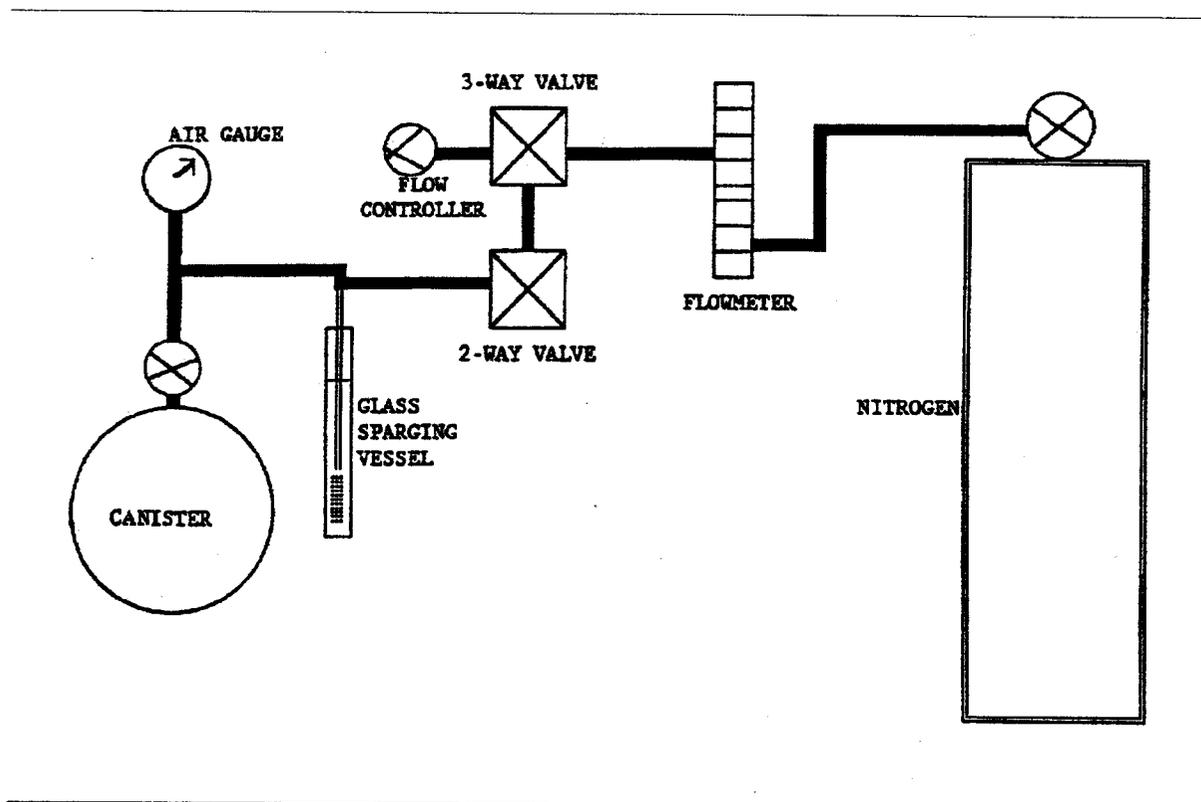


Figure 14. Water method of standard preparation in canisters.

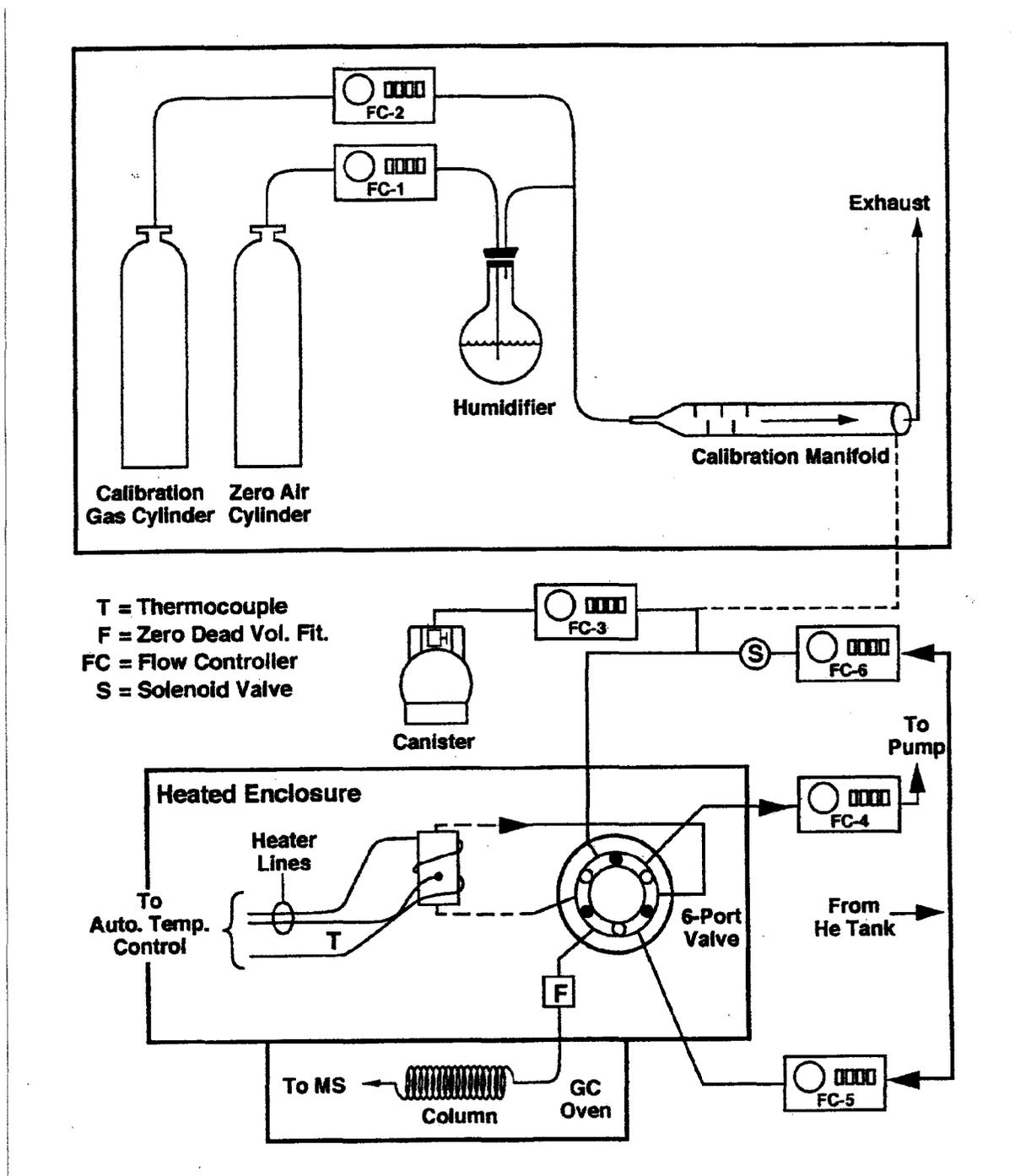


Figure 15. Diagram of the GC/MS analytical system.

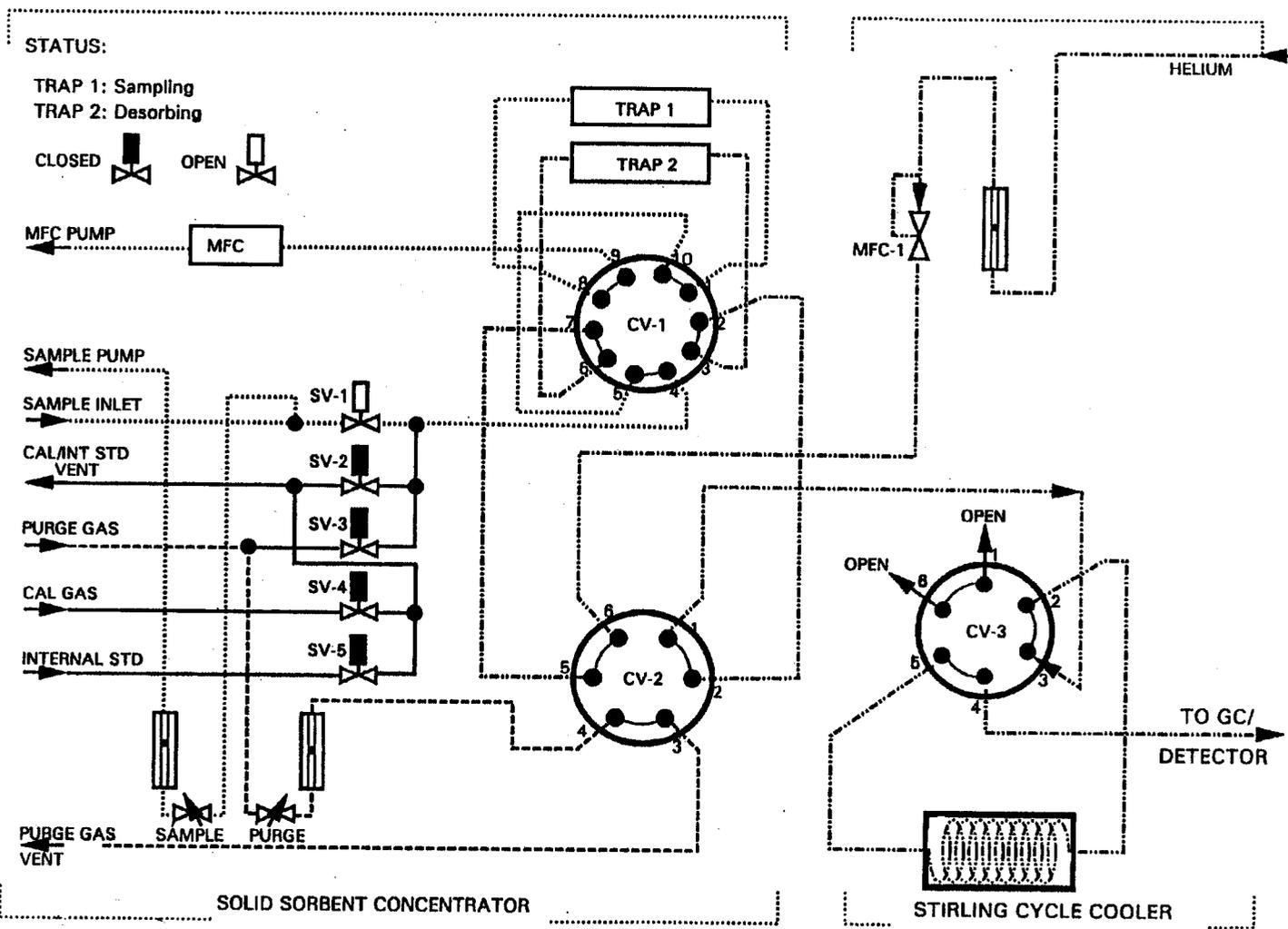


Figure 16. Sample flow diagram of a commercially available concentrator showing the combination of multisorbent tube and cooler (Trap 1 sampling; Trap 2 desorbing).

