



Designation: **D 5466 – 9501**

An American National Standard

## Standard Test Method for Determination of Volatile Organic Chemicals in Atmospheres (Canister Sampling Methodology)<sup>1</sup>

This standard is issued under the fixed designation D 5466; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This test method describes a procedure for sampling and analysis of volatile organic compounds (VOCs) in ambient, indoor, or workplace atmospheres. The test method is based on the collection of air samples in ~~passivated~~ stainless steel canisters. ~~It is with specially treated (passivated) interior surfaces. For sample analysis, a portion of the sample is subsequently removed from the canister and the collected VOCs are selectively concentrated by adsorption or condensation onto a trap, subsequently released by thermal desorption,~~ separated by gas chromatography, and measured by a mass spectrometric detector ~~or other detector(s)~~. This test method describes procedures for sampling into canisters to final pressures both above and below atmospheric pressure

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-22 on Sampling and Analysis of Atmospheres and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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(respectively referred to as pressurized and subatmospheric pressure sampling).<sup>2</sup>

1.2 This test method is applicable to specific VOCs that have been tested and determined to be stable when stored in ~~pressurized and subatmospheric pressure~~ canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters ~~(1, 2)(1-4)~~.<sup>3</sup> **While Although not as extensive, documentation is currently also available demonstrating stability of VOCs in subatmospheric pressure canisters. While initial studies were concentrated on non-polar VOCs, information on storage stability has been extended to many polar compounds as well (5-7).**

1.3 The procedure for collecting the sample involves the use of inlet lines and air filters, flow rate regulators for obtaining time-integrated samples, and in the case of pressurized samples, an air pump. Canister samplers have been designed to automatically start and stop the sample collection process using electronically actuated valves and timers (8-10). A weatherproof shelter is required if the sampler is to be used outside.

1.4 ~~The organic compounds that have been successfully collected in pressurized canisters measured at single-digit parts-per-billion by volume (ppbv) levels with this test method are listed in Table 1. These compounds have been successfully measured at the parts per billion by volume (ppbv) level. This test method is applicable to concentrations of VOC concentrations ranging from the detection limit to 300 ppb by volume. ppbv. Above this concentration, samples require dilution with dry ultra-high-purity nitrogen or air.~~

1.4<sup>5</sup> *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Safety practices should be part of the user's SOP manual.*

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1356 Terminology Relating to Sampling and Analysis of Atmospheres<sup>4</sup>

D 1357 Practice for Planning and Sampling of the Ambient Atmosphere<sup>4</sup>

E 260 Practice for Packed Column Gas Chromatography<sup>5</sup>

E 355 Practice for Gas Chromatography Terms and Relationships<sup>5</sup>

### 2.2 Other Documents:

~~U.S. Environmental Protection Agency Technical Assistance Document for Sampling and Analysis Agency, Compendium of Methods for the Determination to Toxic Organic Compounds in Ambient Air (3)—~~

~~Laboratory and Ambient Air Studies (4-20)— Air, Method TO-14A, EPA 600/R-96/010b <sup>6</sup>~~

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this test method, refer to Terminology D 1356. Other pertinent abbreviations and symbols are defined within this practice at point of use.

### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *absolute canister pressure*— $P_g + P_a$ , where  $P_g$  = gage pressure in the canister. (~~K~~kPa, psi) and  $P_a$  = barometric pressure (see 5.2).

3.2.2 *absolute pressure*—pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), usually expressed as kPa, mm Hg, or psia.

3.2.3 *certification*—the process of demonstrating with humid zero air and humid calibration gases that the sampling systems components and the canister will not change the concentrations of sampled and stored atmospheres.

3.2.4 *cryogen*—a refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. A typical cryogen is liquid argon (bp -185.7°C) or liquid nitrogen (bp -195°C).

3.2.5 *dynamic calibration*—calibration of an analytical system using calibration gas standard concentrations generated by diluting known concentration compressed gas standards with purified, humidified inert gas.

3.2.5.1 *Discussion*—Such standards are in a form identical or very similar to the samples to be analyzed. Calibration standards are introduced into the inlet of the sampling or analytical system in the same manner as authentic field samples.

3.2.6 *gage pressure*—pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gage pressure is equal to ambient atmospheric (barometric) pressure.

3.2.7 *megabore column*—chromatographic column having an internal diameter (I.D.) greater than 0.50 mm.

3.2.7.1 *Discussion*—The Megabore column is a trademark of the J & W Scientific Co. For purposes of this test method, Megabore refers to chromatographic columns with 0.53 mm I.D.

<sup>2</sup> This test method is based on EPA Compendium Method TO-14, "The Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using SUMMA Passivated Canister Sampling and Gas Chromatographic Analysis," May 1988.

<sup>3</sup> The **boldface** numbers in parentheses refer to the list of references at the end of the standard.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>5</sup> *Annual Book of ASTM Standards*, Vol 14.02.

<sup>6</sup> SUMMA<sup>®</sup> process is a registered trademark

<sup>6</sup> Available from the U.S. Dept. of ~~M~~olecetrics Inc., 4000 East 89th St., Cleveland, OH 44105; Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161 or <http://www.cpa.gov/ttn/amtic/airtox.html>.

**TABLE 1 Typical Volatile Organic Compounds Known to Have Been Analyzed by the Canister Method**

Compound (Synonym)	Formula	Molecular Weight	Boiling Point (°C)	Melting Point (°C)	CasAS Number
Freon 12 (Dichlorodifluoromethane)	Cl <sub>2</sub> CF <sub>2</sub>	120.91	-29.8	-158.0	
Methyl chloride (Chloromethane)	CH <sub>3</sub> Cl	50.49	-24.2	-97.1	74-87-3
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	C <sub>2</sub> Cl <sub>2</sub> CF <sub>2</sub>	170.93	4.1	-94.0	
Vinyl chloride (Chloroethylene)	CH <sub>2</sub> =CHCl	62.50	-13.4	-1538.0	75-01-4
Methyl bromide (Bromomethane)	CH <sub>3</sub> Br	94.94	3.6	-93.6	74-83-9
Ethyl chloride (Chloroethane)	CH <sub>3</sub> CH <sub>2</sub> Cl	64.52	12.3	-136.4	75-00-3
Freon 11 (Trichlorofluoromethane)	CCl <sub>3</sub> F	137.38	23.7	-111.0	
Vinylidene chloride (1,1-Dichloroethene)	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	96.95	31.7	-122.5	75-35-4
Dichloromethane (Methylene chloride)	CH <sub>2</sub> Cl <sub>2</sub>	84.94	39.8	-95.1	75-09-2
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	CF <sub>2</sub> ClCCl <sub>2</sub> F	187.38	47.7	-36.4	
1,1-Dichloroethane (Ethylidene chloride)	CH <sub>3</sub> CHCl <sub>2</sub>	-98.96	-57.3	-97.0	74-34-3
1,1-Dichloroethane	CH <sub>3</sub> CHCl <sub>2</sub>	98.96	57.3	-97.0	74-34-3
cis-1,2-Dichloroethylene	CHCl=CHCl	96.94	60.3	-80.5	
Chloroform (Trichloromethane)	CHCl <sub>3</sub>	119.38	61.7	-63.5	67-66-3
1,2-Dichloroethane (Ethylene dichloride)	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	98.96	83.5	-35.3	107-06-2
Methyl chloroform (1,1,1-Trichloroethane)	CH <sub>3</sub> CCl <sub>3</sub>	133.41	74.1	-30.4	71-55-6
Benzene (Cyclohexatriene)	C <sub>6</sub> H <sub>6</sub>	-78.12	-80.4	-5.5	71-43-2
Benzene	C <sub>6</sub> H <sub>6</sub>	78.12	80.1	5.5	71-43-2
Carbon tetrachloride (Tetrachloromethane)	CCl <sub>4</sub>	153.82	76.5	-23.0	56-23-5
1,2-Dichloropropane (Propylene dichloride)	CH <sub>3</sub> CHClCH <sub>2</sub> Cl	112.99	96.4	-100.4	78-87-5
Trichloroethylene (Trichloroethene)	C <sub>2</sub> HCl=CCl <sub>2</sub>	131.29	87	-73.0	79-01-6
cis-1,3-Dichloropropene (cis-1,3-dichloropropylene)	CH <sub>3</sub> CC=CHCl	110.97	76		
trans-1,3-Dichloropropene (trans-1,3-Dichloropropylene)	CH <sub>3</sub> CH=CHCl	110.97	112.0		
trans-1,3-Dichloropropene (trans-1,3-Dichloropropylene)	CH <sub>3</sub> CH=CHCl	110.97	112.0		
1,1,2-Trichloroethane (Vinyl trichloride)	CH <sub>2</sub> ClCHCl <sub>2</sub>	133.41	113.8	-36.5	79-00-5
Toluene (Methyl benzene)	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	92.15	110.6	-95.0	108-88-3
1,2-Dibromoethane (Ethylene dibromide)	BrCH <sub>2</sub> CH <sub>2</sub> Br	187.88	131.3	9.8	106-93-4
Tetrachloroethylene (Perchloroethylene)	C <sub>2</sub> Cl <sub>4</sub>	165.83	121.1	-19.0	127-18-4
Chlorobenzene (Phenyl chloride)	C <sub>6</sub> H <sub>5</sub> Cl	112.56	132.0	-45.6	108-90-7
Chlorobenzene	C <sub>6</sub> H <sub>5</sub> Cl	112.56	132.0	-45.6	108-90-7
Ethylbenzene	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	106.17	136.2	-95.0	100-41-4
m-Xylene (1,3-Dimethylbenzene)	1,3-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	106.17	139.1	-47.9	
p-Xylene (1,4-Dimethylxylene)	1,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	106.17	138.3	13.3	
Styrene (Vinyl benzene)	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	104.16	145.2	-30.6	100-42-5
1,1,2,2-Tetrachloroethane	CHCl <sub>2</sub> CHCl <sub>2</sub>	167.85	146.2	-36.0	79-34-5
o-Xylene (1,2-Dimethylbenzene)	1,2-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	106.17	144.4	-25.2	
1,3,5-Trimethylbenzene (Mesitylene)	1,3,5-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>6</sub>	120.20	164.7	-44.7	108-67-8
1,2,4-Trimethylbenzene (Pseudocumene)	1,2,4-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>6</sub>	120.20	169.3	-43.8	95-63-6
1,2,4-Trimethylbenzene	1,2,4-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>6</sub>	120.20	169.3	-43.8	95-63-6
m-Dichlorobenzene (1,3-Dichlorobenzene)	1,3-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.01	173.0	-24.7	541-73-1
Benzyl chloride (α-Chlorotoluene)	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	126.59	179.3	-39.0	100-44-7
o-Dichlorobenzene (1,2-Dichlorobenzene)	1,2-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.01	180.5	-17.0	95-50-1
p-Dichlorobenzene (1,4-Dichlorobenzene)	1,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	147.01	174.0	53.1	106-46-7
1,2,4-Trichlorobenzene Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)	1,2,4-Cl <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	481.45	213.5	-17.0	420-82-4
1,1,2,3,4,4-Hexachloro-1,3-butadiene	Cl <sub>6</sub> C <sub>4</sub>	260.76	215	-21.0	7-68-3

3.2.8 *MS-SCAN*—the GC is coupled to a Mass Spectrometer (MS) programmed to scan all ions over a preset range repeatedly during the GC run.

3.2.8.1 *Discussion*—As used in the current context, this procedure serves as a qualitative identification and characterization of the sample.

3.2.9 *MS-SIM*—the GC is coupled to a MS programmed to acquire data for only specified ions and to disregard all others. This is performed using selected ion monitoring (SIM) coupled to retention time discriminators. The GC-SIM analysis provides quantitative results for selected constituents of the sample gas as programmed by the user.

3.2.10 *pressurized sampling*—collection of an air sample in a canister with a (final) canister pressure above atmospheric pressure, using a sample pump.

3.2.11 *qualitative accuracy*—the ability of an analytical system to correctly identify compounds.

3.2.12 *quantitative accuracy*—the ability of an analytical system to correctly measure the concentration of an identified compound.

3.2.13 *static calibration*—calibration of an analytical system using standards in a form different than the samples to be analyzed.

3.2.13.1 *Discussion*—An example of a static calibration would be injecting a small volume of a high concentration standard directly onto a GC column, bypassing the sample extraction and preconcentration portion of the analytical system.

3.2.14 *subatmospheric sampling*—collection of an air sample in an evacuated canister to a (final) canister pressure below atmospheric pressure, with or without the assistance of a sampling pump.

3.2.14.1 *Discussion*—The canister is filled as the internal canister pressure increases to ambient or near ambient pressure. An auxiliary vacuum pump may be used as part of the sampling system to flush the inlet tubing prior to or during sample collection.

#### 4. Summary of Test Method

4.1 The method described is taken from published work (1-22) and is the basis of EPA Compendium Method TO-14A. It has been used since the early 1980s in studies to establish long term trends in certain atmospheric gases (11), to determine the prevalence and extent of VOC contributions to ozone production (12), and to assess the toxicity of VOCs in the ambient air (13,14).

4.2 Both subatmospheric pressure and pressurized sampling modes use an evacuated canister. A sampling line less than 2 % of the volume of the canister or a pump-ventilated sample line are used during sample collection. Pressurized sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprising components that regulate the rate and duration of sampling into a precleaned and pre-evacuated **SUMMA<sup>®</sup>** passivated canister.

**TABLE 2 Ion/Abundance and Expected Retention Time for Selected VOCs Analyzed by GC-MS-SIM**

Compound	Ion/ Abundance (amu/% base peak)	Expected Retention Time (min)
Freon 12 (Dichlorodifluoromethane)	85/100 87/31	5.01
Methyl chloride (Chloromethane)	50/100 52/34	5.69
Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane)	85/100 135/56 87/33	6.55
Vinyl chloride (Chloroethene)	62/100 27/125 64/32	6.71
Methyl bromide (Bromomethane)	94/100 96/85	7.83
Ethyl chloride (Chloroethane)	64/100 29/140 27/140	8.43
Freon 11 (Trichlorofluoromethane)	101/100 103/67	9.97
Vinylidene chloride (1,1-Dichloroethylene)	61/100 96/55 63/31	10.93
Dichloromethane (Methylene chloride)	49/100 84/65 86/45	11.21
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	151/100 101/140 103/90	11.60
<del>1,1-Dichloroethane (Ethylidene dichloride)</del> <u>1,1-Dichloroethane</u>	<del>63/100</del> <u>63/100</u> 27/64 65/33	<del>12.50</del> <u>12.50</u>
cis-1,2-Dichloroethylene	61/100 96/60 98/44	13.40
Chloroform (Trichloromethane)	83/100 85/65 47/35	13.75
1,2-Dichloroethane (Ethylene dichloride)	62/100 27/70 64/31	14.39
Methyl chloroform (1,1,1-Trichloroethane)	97/100 99/64 61/61	14.62
<del>Benzene (Cyclohexatriene)</del> <u>Benzene</u>	<del>78/100</del> <u>78/100</u> 77/25 50/35	<del>15.04</del> <u>15.04</u>
Carbon tetrachloride (Tetrachloromethane)	117/100 119/97	15.18
1,2-Dichloropropane (Propylene dichloride)	63/100 41/90 62/70	15.83
<del>Trichloroethylene (Trichloroethane)</del> <u>Trichloroethylene (Trichloroethene)</u>	<del>130/100</del> <u>130/100</u> 132/92 95/87	<del>16.10</del> <u>16.10</u>
cis-1,3-Dichloropropene	75/100 39/70 77/30	16.96

**TABLE 2** *Continued*

Compound	Ion/ Abundance (amu/% base peak)	Expected Retention Time (min)
<del>trans-1,3-Dichloropropene (1,3-Dichloro-1-propene)</del>	<del>75/100</del>	<del>17.49</del>
<u>trans-1,3-Dichloropropene</u>	<u>75/100</u>	<u>17.49</u>
	39/70	
	77/30	
1,1,2-Trichloroethane (Vinyl trichloride)	97/100	17.61
	83/90	
	61/82	
Toluene (Methyl benzene)	91/100	17.86
	92/57	
1,2-Dibromoethane (Ethylene dibromide)	107/100	18.48
	109/96	
	27/115	
Tetrachloroethylene (Perchloroethylene)	166/100	19.01
	164/74	
	131/60	
<del>Chlorobenzene (Benzene chloride)</del>	<del>112/100</del>	<del>19.73</del>
<u>Chlorobenzene</u>	<u>112/100</u>	<u>19.73</u>
	77/62	
	114/32	
Ethylbenzene	91/100	20.20
	106/28	
m,p-Xylene (1,3/1,4-dimethylbenzene)	91/100	20.41
	106/40	
Styrene (Vinyl benzene)	104/100	20.81
	78/60	
	103/49	
<del>1,1,2,2-Tetrachloroethane (Tetrachloroethane)</del>	<del>83/100</del>	<del>20.92</del>
<u>1,1,2,2-Tetrachloroethane</u>	<u>83/100</u>	<u>20.92</u>
	85/64	
o-Xylene (1,2-Dimethylbenzene)	91/100	20.92
	106/40	
4-Ethyltoluene	105/100	22.53
	120/29	
1,3,5-Trimethylbenzene (Mesitylene)	105/100	22.65
	120/42	
<del>1,2,4-Trimethylbenzene (Pseudocumene)</del>	<del>105/100</del>	<del>23.18</del>
<u>1,2,4-Trimethylbenzene</u>	<u>105/100</u>	<u>23.18</u>
	120/42	
m-Dichlorobenzene (1,3-Dichlorobenzene)	146/100	23.31
	148/65	
	111/40	
Benzyl chloride ( $\alpha$ -Chlorotoluene)	91/100	23.32
	126/26	
p-Dichlorobenzene (1,4-Dichlorobenzene)	146/100	23.41
	148/65	
	111/40	
o-Dichlorobenzene (1,2-Dichlorobenzene)	146/100	23.88
	148/65	
	111/40	
1,2,4-Trichlorobenzene	180/100	26.71
	182/98	
	184/30	
Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro-1,3-butadiene)	225/100	27.68
	227/66	
	223/60	

4.23 After the air sample is collected, the canister isolation valve is closed, the canister is removed from the sampler, an identification tag is attached to the canister, and the canister is transported to a laboratory for analysis.

4.34 Upon receipt at the laboratory, the data on the canister tag are recorded and the canister is attached to a pressure gage which will allow accurate measurement of the final canister pressure. During analysis, water vapor may be reduced in the gas stream by a Nafion permeable membrane dryer (if applicable), and the VOCs are then concentrated by collection on a sorbent trap or in a cryogenically-cooled trap. ~~The cryogen is then removed and the~~ temperature of the trap is raised, ~~and the~~ VOCs originally collected in the trap are revolatilized, separated on a GC column, and then detected by a mass spectrometer. Compound identification and quantitation are performed with this test method.

#### 4.4 A

4.5 The VOCs are thermally desorbed from the trap into a small volume of carrier gas, separated by gas chromatography, and measured by a mass spectrometric detector or other detector(s) such as the flame ionization detector (FID) or electron capture detector (ECD). The analytical procedure can be automated (15-17) or manual (18). A procedure for measuring total FID response

to a sample without gas chromatographic separation is also documented (19).

4.6 A mass spectrometric detector (MS coupled to a GC) is the principal analytical tool used for qualitative and quantitative analysis because it allows positive compound identification. MS detectors include, but are not limited to, magnetic sector mass analyzers, quadrupole mass filters, combined magnetic sector-electrostatic sector mass analyzers, time-of-flight mass analyzers and ion trap mass spectrometers.

#### 4.46.1 Comparison of GC/MS–Full Scan and GC/MS-SIM:

##### 4.46.1.1 GC/MS–Full Scan:

- (1) Positive nontarget compound identification possible,
- (2) Less sensitivity than GC/MS-SIM,
- (3) Greater sample volume may be required compared to SIM,
- (4) ~~Resolve~~Resolution of co-eluting interfering ions is possible,
- (5) Positive compound identification,
- (6) Quantitative determination of compounds on calibration list, and
- (7) Qualitative and semiquantitative determination of compounds not contained on calibration list.

##### 4.46.1.2 GC/MS-SIM:

- (1) Can't identify non-target compounds,
- (2) Less operator interpretation, and
- (3) Higher sensitivity than GC/MS–full scan.

4.46.2 The GC/MS–full scan option uses a capillary column GC coupled to a MS operated in a scanning mode and supported by spectral library search routines. This option offers the nearest approximation to unambiguous identification and covers a wide range of compounds as defined by the completeness of the spectral library. GC/MS-SIM mode is limited to a set of target compounds which are user defined and is more sensitive than GC/MS-SCAN by virtue of the longer dwell times at the restricted number of m/z values. As the number of ions monitored simultaneously in a GC/MS-SIM analysis increases, the sensitivity of this technique approaches GC/MS-SCAN. The practical limit for GC/MS-SIM is reached at about 4 to 5 ions monitored simultaneously.

## 5. Significance and Use

5.1 VOCs are emitted into the ambient, indoor, and workplace atmosphere from a variety of sources. In addition to the emissions from the use of various products, appliances, and building materials, fugitive or direct emissions from ambient sources such as manufacturing processes further complicate air composition. Many of these VOC compounds are acute or chronic toxins. Therefore, their determination in air is necessary to assess human health impacts.

5.2 The use of canisters is particularly well suited for the collection and analysis of very volatile, stable compounds in atmosphere (for example, vinyl chloride). This test method collects and analyzes whole gas samples and is not subject to high volatility limitations.

5.3 VOCs can be successfully collected in passivated stainless steel canisters. Collection of atmospheric samples in canisters provides for: (1) convenient integration of air samples over a specific time period (for example, 8 to 24 h), (2) remote sampling and central laboratory analysis, (3) ease of storing and shipping samples, (4) unattended sample collection, (5) analysis of samples from multiple sites with one analytical system, (6) dilution or additional sample concentration to keep the sample size introduced into the analytical instrument within the calibration range, (7) collection of sufficient sample volume to allow assessment of measurement precision or analysis, or both, of samples by several analytical systems, and (8) ~~can be performed~~ sample collection in remote access areas using a vacuum regulator flow controller if electricity is not available.

5.4 Interior surfaces of the canisters are treated by ~~the SUMMA® any of several proprietary passivation process,~~ in which a pure chrome-nickel oxide is formed processes including an electropolishing process to remove or cover reactive metal sites on the interior surface of the vessel and a fused silica coating process.

5.5 This test method can be applied to sampling and analysis of compounds that can be quantitatively recovered from the canisters. The typical range of VOC applicable to this test method are ones having saturated vapor pressures at 25°C greater than 15 Pa (10<sup>-1</sup> mm Hg).

5.6 Recovery and stability studies must be conducted on any compound not listed in Table 1 before expanding the use of this test method to additional compounds.

## 6. Interferences and Limitations

6.1 FWater management is a significant analytical problem because VOC preconcentrators typically accumulate water vapor as well as VOCs, especially those preconcentrators that use reduced temperature condensation. The water can restrict and even stop the sample air flow, alter retention times, and affect the operation of detector systems, especially the mass spectrometric systems. In-line permeable membrane dryers are frequently used prior to preconcentration and do not produce artifacts for a number of compounds including those that are on the target list for this method provided certain precautions are observed (20,21). Release of an air sample from a pressurized canister that contains humid air will result in a systematic increase in the humidity of the released sample air as long as condensed water remains on the canister interior (22).

6.2 For those applications where a membrane dryer (for example, Nafion) is used, interferences can occur in sample analysis

if moisture accumulates in the dryer (see 10.1.1.23). An automated cleanup procedure that periodically heats the dryer to about 100°C while purging with zero air eliminates any moisture buildup. This procedure does not degrade sample integrity.

NOTE 1—Removing moisture from samples is not necessary with GC/MS systems that are differentially pumped and which do not employ membrane drying apparatus.

6.23 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (for example, pump and flow controllers) must be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. Instructions for cleaning the canisters and certifying the field sampling system are described in 11.1 and 11.2, respectively. In addition, sufficient system and field blank samples shall be analyzed to detect contamination as soon as it occurs.

6.34 If the GC/MS analytical system employs a Nafion permeable membrane dryer or equivalent to remove water vapor selectively from the sample stream, polar organic compounds will permeate this membrane concurrently with the moisture. Consequently, the analyst must calibrate his or her system with the specific organic constituents under examination. For quantitative analysis of polar compounds analytical systems may not employ Nafion permeable membrane dryers.

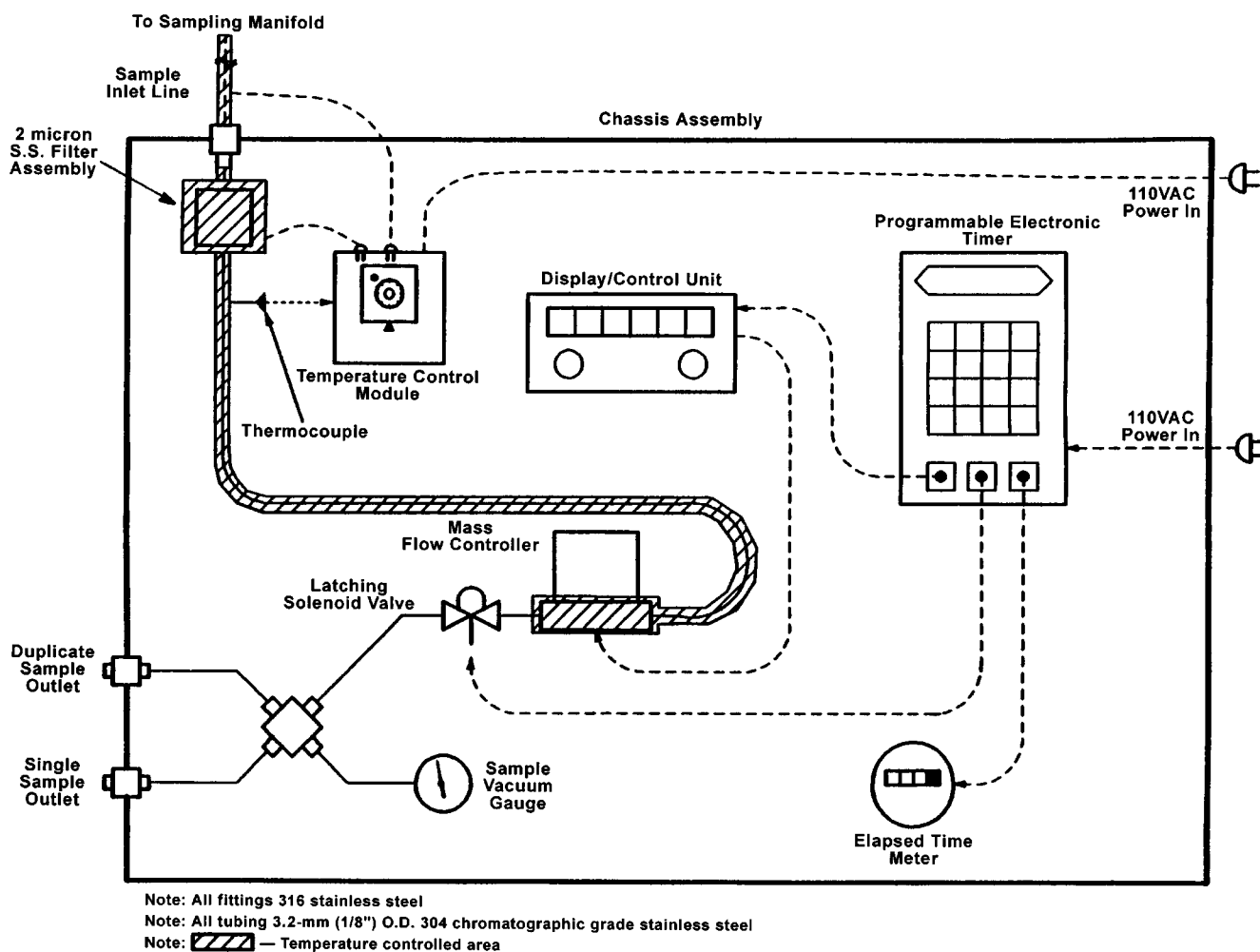


FIG. 1 Sampler Configuration For Subatmospheric Pressure Canister Sampling

## 7. Apparatus

7.1 Stainless steel canisters with interior surfaces passivated by either electropolishing or silica coating, available from various commercial sources.

7.2 Subatmospheric pressure and pressurized canister sampling systems are commercially available and have been certified evaluated for VOC testing in air (28-10). Several configurations of standard hardware can be used successfully as canister sampling units.

7.42.1 Subatmospheric Pressure (see Fig. 1).

7.42.1.1 Inlet Line, Stainless steel tubing to connect the sampler to the sample inlet.

- 7.42.1.2 *Canister*, Leak-free stainless steel pressure vessels of desired volume (for example, 6 L), with valve and passivated interior surfaces.
- 7.42.1.3 *Vacuum/Pressure Gage*, ~~Capable~~ Capable of measuring vacuum (-100 to 0 kPa or 0 to 30 in Hg) and pressure (0 to 200 kPa or 0 to 30 psig) in the sampling system. Gages shall be tested clean and leak tight.
- 7.42.1.4 *Mass Flow Meter and Controller*, ~~Capable~~ Capable of maintaining a constant flow rate ( $\pm 10\%$ ) over a sampling period of up to 24 h and under conditions of changing temperature (20 to 40°C) and humidity.
- 7.42.1.5 *Filter*, 7- $\mu\text{m}$  sintered stainless-steel in-line filter.
- 7.42.1.6 *Electronic Timer*, ~~F~~ Capable of activating a solenoid valve (see 7.2.1.7) to start and stop flow entering a canister, that is, for unattended sample collection.
- 7.42.1.7 *Solenoid Valve*, Electrically operated, bi-stable solenoid valve with fluoroelastomer seat and o-rings, or low temperature solenoid valve.
- 7.42.1.8 *Tubing and Fittings*, Chromatographic grade stainless steel tubing and fittings for interconnections. All such materials in contact with sample, analyte, and support gases prior to analysis shall be chromatographic grade stainless steel.
- 7.42.1.9 *Heater*, ~~t~~ Thermostatically controlled to maintain temperature inside insulated sampler enclosure above ambient temperature if needed.
- 7.42.1.10 *Fan*, For cooling sampling system, if needed.
- 7.42.1.11 *Thermostat*, ~~s~~ Automatically regulates fan operation, if needed.
- 7.42.1.12 *Maximum-Minimum Thermometer*, Records highest and lowest temperatures during sampling period.
- 7.42.1.13 *Shut-Off Valve*—~~Stainless~~, Stainless steel—leak free, for vacuum/pressure gage.
- 7.42.1.14 *Auxiliary Vacuum Pump*—~~(optional)~~, continuously draws air to be sampled 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. 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. Pump is not necessary if the intake manifold represents less than 5 % of the final sample.
- 7.42.1.15 *Elapsed Time Meter*—~~F~~, Capable of measuring the duration of sampling to the nearest second.
- 7.42.1.16 *Optional Fixed Orifice, Capillary, Adjustable Micrometering Valve, or Vacuum Regulator*, May be used in lieu of the electronic flow controller for grab samples or short duration time-integrated samples. Such systems require manual activation and deactivation. In this standard, application of a pumpless simple orifice sampler is appropriate only in situations where samples

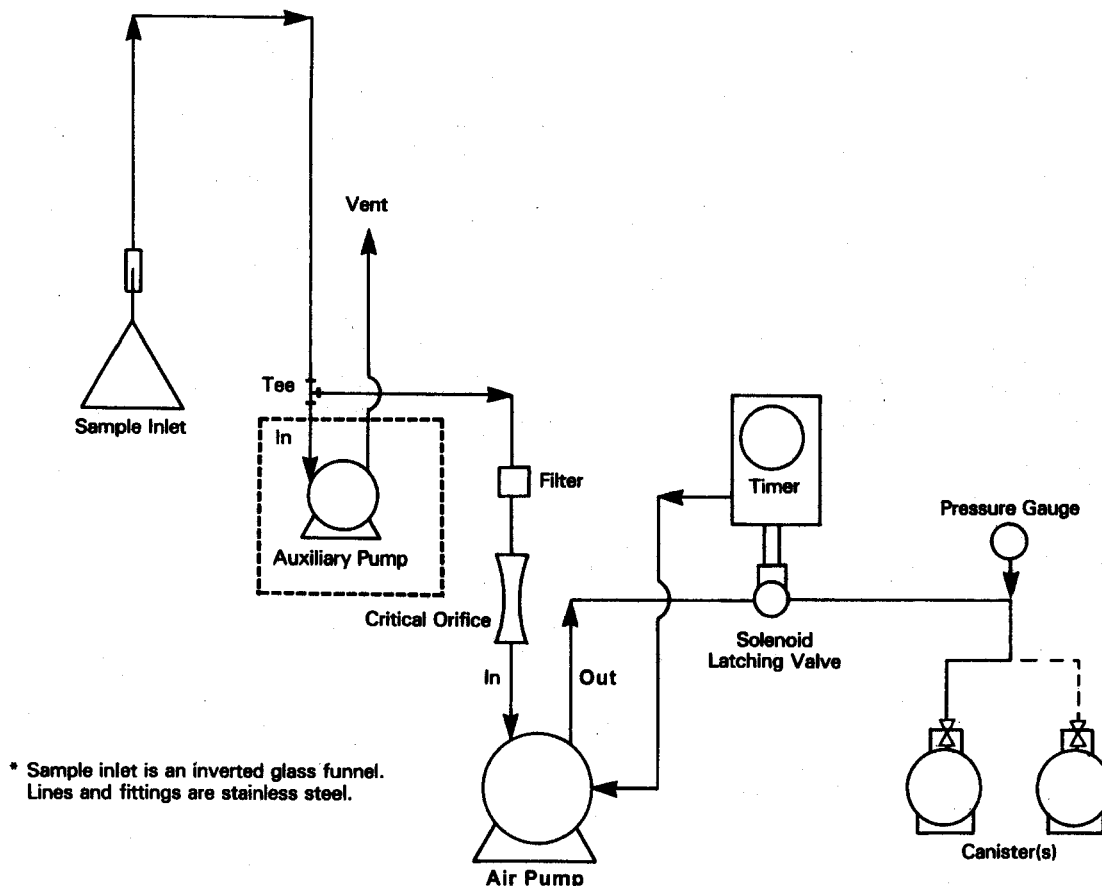


FIG. 2 Alternative Sampler Configuration for Pressurized Canister Sampling



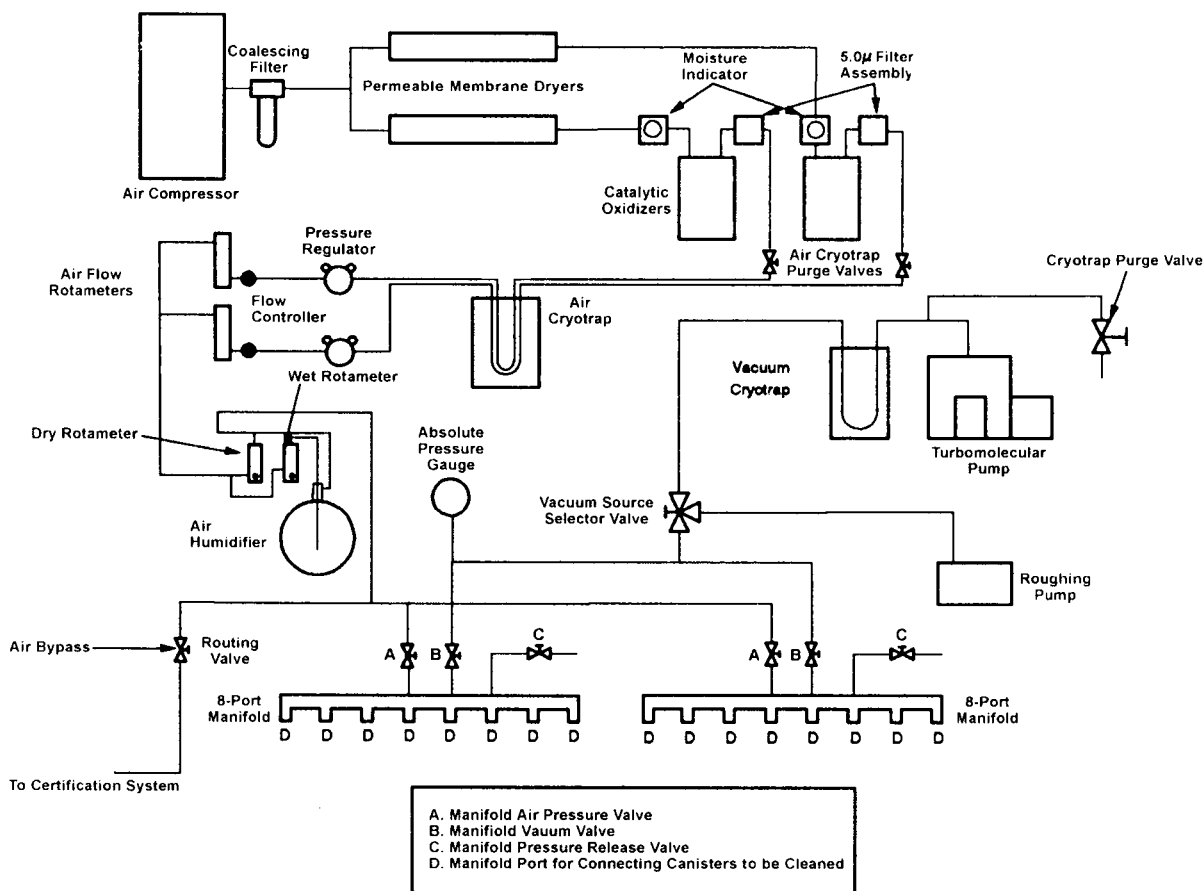


FIG. 3 Canister Cleanup Apparatus

consume 60 % or less of the total capacity of the canister used for collection. Typically this limits the sample duration to a maximum of 8 h per 6 L canister or 20 h per 15 L canister.

7.4.2.2 *Pressurized*— See Fig. 1 and Fig. 2.

7.4.2.2.1 *Sample Pump*, Stainless steel pump head, metal bellows type capable of 200 kPa output pressure. Pump must be free of leaks, clean, and uncontaminated by oil or organic compounds.

NOTE 2—Alternative 2—Several sampling systems have been developed. The Rasmussen sampler (21) is illustrated developed that result in Fig. 2. This flow system uses, in order, pressurizing a pump, a mechanical flow regulator, and a mechanical compensating flow restrictive device. In this configuration the pump is purged canister with a large sample flow, thereby eliminating the need for air. The system illustrated in Fig. 2 uses an auxiliary vacuum pump to flush the sample inlet. The Radian sampler (20) is illustrated in Fig. 3. This system draws a non-contaminating air directly pump pulls air from the inlet tubing, through a mass flow controller critical orifice which regulates the flow, and into an evacuated canister. Interferences using either configuration have been minimal.

7.1.2.2— the canisters.

7.2.2.2 *Other Supporting Materials*— All other components of the pressurized sampling system (Fig. 1, Fig. 2, and Fig. 3) are similar to components discussed in 7.4.2.1.1-7.4.2.1.16.

7.2.3 *Sample Analysis Equipment*:

7.2.3.1 *GC/MS-Analytical System (Full Scan and SIM)*.

7.2.3.1.1 The GC/MS-SCAN analytical system must be capable of acquiring and processing data in the MS-full scan mode. The GC/MS-SIM analytical system must be capable of acquiring and processing data in the MS-SIM mode.

7.2.3.1.2 *Gas Chromatograph*, Capable of sub-ambient temperature programming for the oven, with other standard features such as gas flow regulators, automatic control of valves and integrator, etc. Flame ionization detector optional.

7.2.3.1.3 *Chromatographic Detector*, Mass spectrometric detector equipped with computer and appropriate software. The GC/MS is set in the SCAN mode, where the MS screens the sample for identification and quantitation of VOC species.

7.2.3.1.4 *Cryogenic Trap with Temperature Control Assembly*— Refer to 10.1.1.34 for complete description of trap and temperature control assembly. Traps may be built into the gas chromatograph by the manufacturer or added to existing units.

7.2.3.1.5 *Electronic Mass Flow Controllers (3)*, to maintain constant flow for carrier gas and sample gas and to provide analog output to monitor flow anomalies.

7.2.3.1.6 *Vacuum Pump*, General purpose laboratory pump, capable of evacuating a known volume reservoir (which will be used

for sample transfer) or for drawing the desired sample volume through the cryogenic trap.

**7.23.1.7 Chromatographic Grade Stainless Steel Tubing and Stainless Steel Plumbing Fittings**—<sub>2</sub> Refer to 7.1.2.1.8 for description.

**7.23.1.8 Chromatographic Column** (see Table 3), To provide compound separation such as shown in Table 3—separation.

NOTE 3—Other columns (for example, DB-624) (6 % cyanopropylphenyl/94 % dimethylpolysiloxane) can be used as long as the system meets user needs. The wider M megabore column (that is, 0.53 mm I.D.) is less susceptible to plugging as a result of trapped water, thus eliminating the need for a Nafion permeable membrane dryer in the analytical system. The M megabore column has sample capacity approaching that of a packed column, while retaining much of the peak resolution traits of narrower columns (that is, 0.32 mm I.D.).

**TABLE 3 General GC and MS Operating Conditions**

<i>Chromatography</i>	
—Column	Hewlett-Packard OV-1 crosslinked methyl silicone (50 m by 0.31 mm I.D., 17 µm film thickness), or equivalent
Column	50-m × 0.32-mm I.D. crosslinked 100 % dimethylpolysiloxane (17 µm film thickness)
Carrier Gas	Helium (2.0 cm <sup>3</sup> /min at 250°C)
Injection Volume	Constant (1–3 µL)
Injection Mode	Splitless
<i>Temperature Program</i>	
Initial Column Temperature	–50°C
Initial Hold Time	2 min
Program	8°C/min to 150°C
Final Hold Time	15 min
<i>Mass Spectrometer</i>	
Mass Range	18 to 250 amu
Scan Time	1 s/scan
EI Condition	70 eV
Mass Scan	Follow manufacturer's instruction for selecting mass selective detector (MS) and selected ion monitoring (SIM) mode
Detector Mode	Multiple ion detection
<i>FID System (Optional)</i>	
Hydrogen Flow	30 cm <sup>3</sup> /min
Carrier Flow	30 cm <sup>3</sup> /min
Burner Air	400 cm <sup>3</sup> /min

**7.23.1.9 Stainless Steel Vacuum/Pressure Gage (optional)**,—e Capable of measuring vacuum (–100 to 0 kPa) and pressure (0–200 kPa) in the sampling system. Gages shall be tested clean and leak tight.

**7.23.1.10 Cylinder Pressure Stainless Steel Regulators**,—s Standard, two-stage cylinder regulators with pressure gages for helium, zero air, nitrogen, and hydrogen gas cylinders.

**7.23.1.11 Gas Purifiers (4)**, Molecular sieve or carbon used to remove organic impurities and moisture from gas streams.

**7.23.1.12 Low Dead-Volume Tee or Press Fit Splitter (optional)**,—u Used to split the exit flow from the GC column.<sup>7</sup>

**7.2.1.13 Nafion Dryer column.**

**7.3.1.13 Dryer (optional)**,—e Consisting of Nafion permeable membrane tubing coaxially mounted within larger tubing, available commercially. Refer to 10.1.1.23 for description.

**7.23.1.14 Six-Port Gas Chromatographic Valve.**

**7.34 Canister Cleaning System (see Fig. 3):**

**7.34.1 Vacuum Pump**,—e Capable of evacuating sample canister(s) to an absolute pressure of less than 0.0064 kPa (0.05 mm Hg).

**7.34.2 Manifold**,—m Made of stainless steel with connections for simultaneously cleaning several canisters.

**7.34.3 Shut-Off Valve(s)**, On-off toggle valves.

**7.34.4 Stainless Steel Vacuum Gage**,—e Capable of measuring vacuum in the manifold to an absolute pressure of 0.0064 kPa (0.05 mm Hg) or less.

**7.34.5 Cryogenic Trap (2 required)**,—m Made of stainless steel U-shaped open tubular trap cooled with liquid nitrogen, for air purification purposes to prevent contamination from back diffusion of oil from vacuum pump and to provide clean, zero air to sample canister(s).

**7.34.6 Stainless Steel Pressure Gages (2)**, 0 to 350 kPa (0 to 50 psig) to monitor zero air pressure.

**7.34.7 Stainless Steel Flow Control Valve**,—to To regulate flow of zero air into canister(s).

**7.34.8 Humidifier**,<sub>2</sub> Consisting of Pressurizable Water Bubbler, (typically a SUMMA<sup>®</sup> passivated canister equipped with dip tube and dual valves). Humidifier contains high performance liquid chromatography (HPLC) grade deionized water.

**7.34.9 Isothermal Oven (optional)**,—for For heating canisters.

NOTE 4—Oven temperature must not exceed 80°C the manufacturer's recommendation during cleaning to avoid degradation of the passivated canister surface on repeated cleaning.

7.45 Calibration System and Manifold (see Fig. 4):

7.45.1 Calibration Manifold, ~~one~~ Chromatographic grade stainless steel or glass manifold (125 mm I.D. by 660 mm), with sampling ports and internal mixing for flow disturbance to ensure proper mixing.

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

7.45.3 Electronic Mass Flow Controllers, ~~one~~ One 0 to 5 L/min and one 0 to 50 mL/min.

7.45.4 TFE-Fluorocarbon Filter(s), 47-mm TFE-Fluorocarbon filter for particulate control.

## 8. Reagents and Materials

8.1 Gas cylinders of helium, hydrogen, nitrogen, and zero air ultrahigh purity grade.

8.2 Gas calibration standards—cylinder(s) containing approximately 10 ppmv of each of the following compounds of interest:

vinyl chloride	1,2-dibromoethane
vinylidene chloride	tetrachloroethylene
1,1,2-trichloro-1,2,2-trifluoroethane	chlorobenzene
p-dichlorobenzene	benzyl chloride
chloroform	hexachloro-1,3-butadiene
1,2-dichloroethane	methyl chloroform
benzene-carbon	tetrachloride
benzene	carbon tetrachloride
toluene	trichloroethylene
dichlorodifluoromethane	cis-1,3-dichloropropene
methyl chloride	trans-1,3-dichloropropene
ethylbenzene	1,2-dichloro-1,1,2,2-tetrafluoroethane
1,2,4-trichlorobenzene	o-dichlorobenzene
methyl bromide	o-xylene
ethyl chloride	m-xylene
fluorotrichloromethane	p-xylene
dichloromethane	styrene
1,1-dichloroethane	1,1,2,2-tetrachloroethane
cis-1,2-dichloroethylene	1,3,5-trimethylbenzene
1,2-dichloropropane	1,2,4-trimethylbenzene
1,1,2-trichloroethane	m-dichlorobenzene

8.2.1 The cylinder(s) shall be traceable to a National Institute of Standards and Technology (NIST) Standard Reference Material

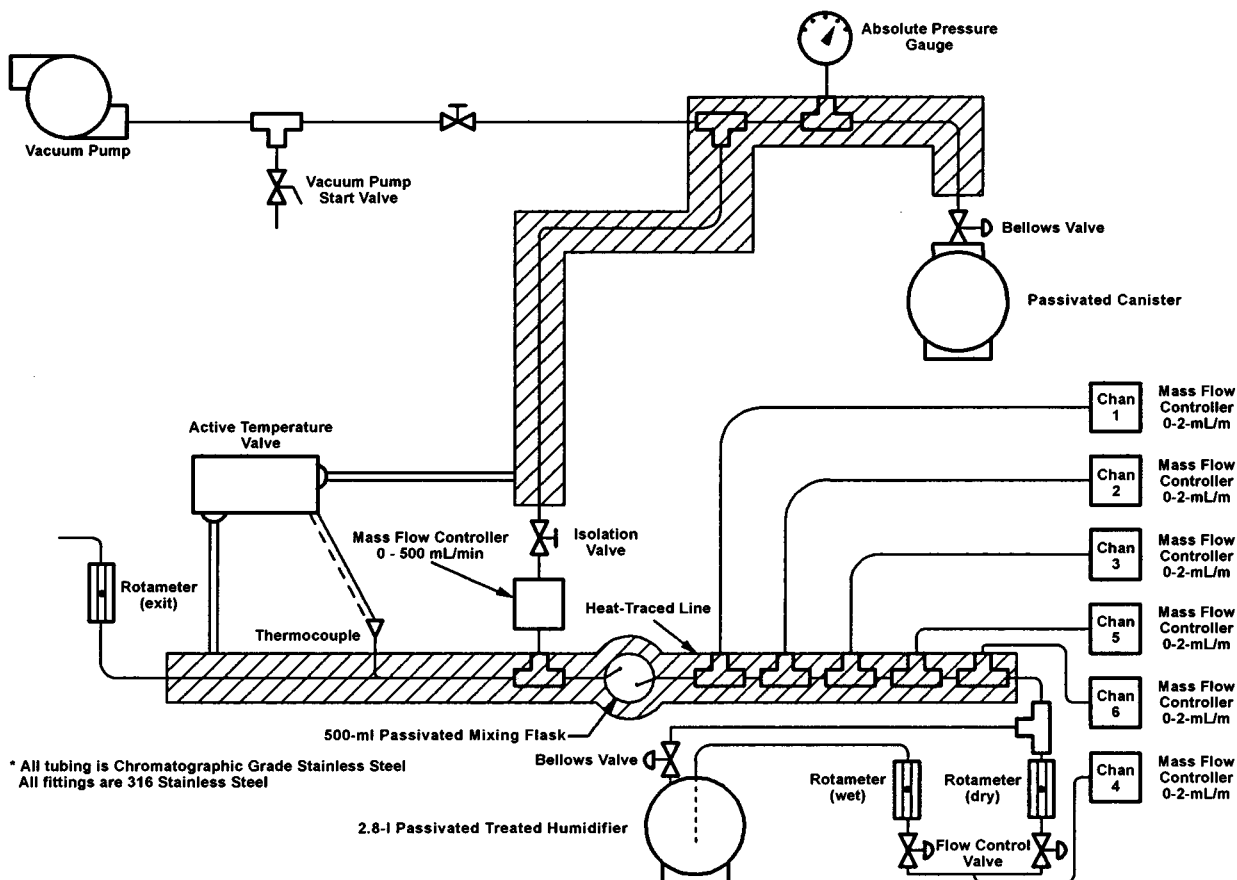


FIG. 4 Schematic of Calibration System and Manifold for (a) Analytical System Calibration, (b) Testing Canister Sampling System and (c) Preparing Canister Transfer Standards

(SRM) or to a NIST/EPA approved Certified Reference Material (CRM). The components may be purchased in one cylinder or may be separated into different cylinders. Refer to manufacturer's specification for guidance on purchasing and mixing VOCs in gas cylinders. Those compounds purchased should match one's own target list.

8.3 *Liquid Nitrogen* (*bp*  $-195.8^{\circ}\text{C}$ ), used only for clean air traps and GC oven coolant, and sample concentration traps requiring active control to maintain  $-185.7^{\circ}\text{C}$ .

8.4 *Liquid Argon* (*bp*  $-185.7^{\circ}\text{C}$ ), for sample traps that are not actively controlled to  $-185.7^{\circ}\text{C}$ .

8.5 *Gas Purifiers*—Molecular sieve or carbon, connected in-line between hydrogen, nitrogen, and zero air gas cylinders and system inlet line, to remove moisture and organic impurities from gas streams.

8.6 *Deionized Water*—High performance liquid chromatography (HPLC) grade, ultrahigh purity (for humidifier).

8.7 *4-Bromofluorobenzene*—Used for tuning GC/MS.

8.8 *Methanol*—For cleaning sampling system components, reagent grade.

## 9. Sampling System

### 9.1 System Description:

#### 9.1.1 Subatmospheric Pressure Sampling—See Fig. 1 or Fig. 2.

9.1.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.0064 kPa (50.05 mm Hg) or less. When 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 s) or time-integrated samples (duration of 12 to 24 h) taken through a flow-restrictive inlet (for example, mass flow controller, vacuum regulator, or critical orifice).

9.1.1.2 With a critical orifice flow restrictor, there will be a decrease in the flow rate if the pressure approaches atmospheric. However, with a mass flow controller the subatmospheric sampling system can be increased since the restrictor size can be adjusted. For example, an electronic flow controller with a flow rate range of 0 to 50 cc/min can maintain a constant (less than 5 % change) flow rate of 5 cc/min from full vacuum to within 7 kPa (1.0 psi) below ambient pressure.

#### 9.1.2 Pressurized Sampling—See Fig. 1.

9.1.2.1 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 100–200 kPa (15–30 psig) final canister pressure. For example, a 6-L evacuated canister can be filled at 7.1 mL/min for 24 h to achieve a final pressure of about 150 67 kPa (10.5 psig).

NOTE 5—Collection of pressurized samples in humid environments may result in condensation of water in sampling canisters. The presence of condensed water may decrease the recovery of polar compounds from the canister and change the retention times of target compounds on the GC column.

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

#### 9.1.3 All Samplers:

9.1.3.1 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:

$$F = (P \times V)/(t \times 60) \quad (1)$$

where:

$F$  = flow rate, mL/min,

$P$  = final canister pressure, atmospheres absolute.  $P$  is approximately equal to [(kPa gage)/100] + 1,

$V$  = volume of the canister, mL, and

$t$  = sample period, h.

9.1.3.2 For example, if a 6-L canister is to be filled to 200 kPa (2 atmospheres) absolute pressure in 24 h, the flow rate can be calculated by:

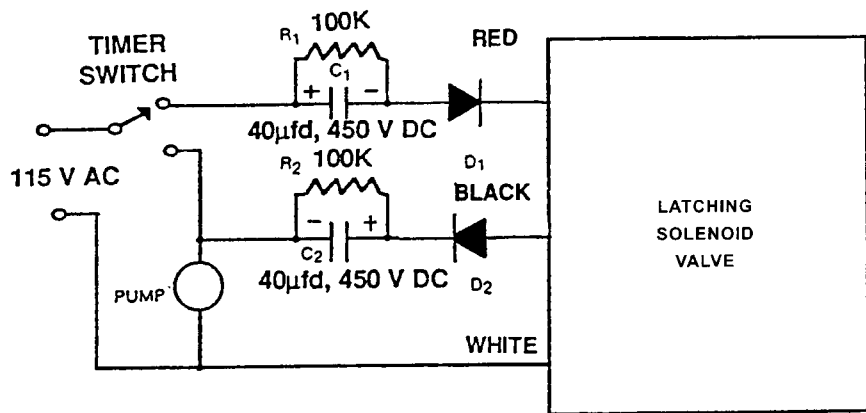
$$F = (2 \times 6000)/(24 \times 60) = 8.3 \text{ mL/min} \quad (2)$$

9.1.3.3 For automatic operation, the timer is wired 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 close the valve when stopping the pump.

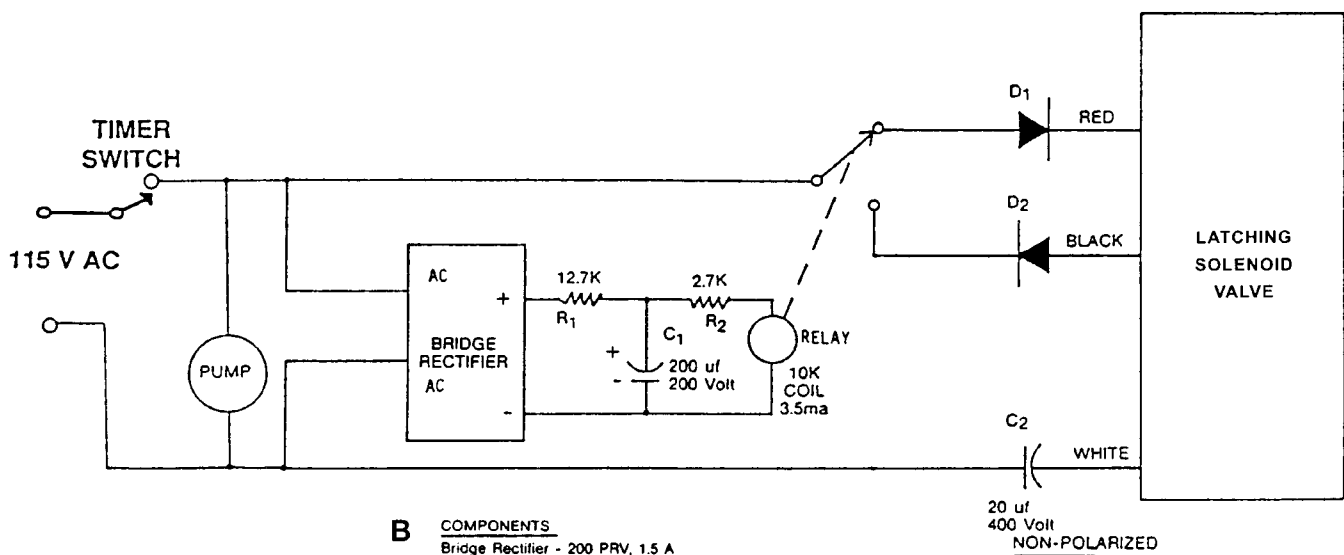
9.1.3.4 The use of a latching solenoid, or low temperature valve, avoids any substantial temperature rise occurring with a conventional, normally energized solenoid during the entire sample period. The temperature rise in the valve could cause outgassing of organic compounds from the ~~Viton~~ valve seat material which must be avoided to reduce background. The ~~Skinner Magnelatch~~ latch solenoid valve requires an electronic timer that can be programmed for short (5 to 60 s) ~~ON~~ "on" periods. ~~A simple~~ Simple electrical pulse circuits for operating the ~~Skinner Magnelatch~~ latching valves with a conventional mechanical timer ~~is~~ are illustrated in Fig. 5.

9.1.3.5 The connecting lines between the sample inlet and the canister shall be as short as possible to minimize their volume. The flow rate into the canister shall remain relatively constant over the entire sampling period (see 9.1.1.2).

9.1.3.6 As an option, a second electronic timer (see 7.4.2.1.6) may be used to start the auxiliary pump several hours prior to the



- A COMPONENTS**  
 Capacitor C<sub>1</sub> and C<sub>2</sub> - 40 µf, 450 VDC  
 Resistor R<sub>1</sub> and R<sub>2</sub> - 0.5 watt, 5% tolerance  
 Diode D<sub>1</sub> and D<sub>2</sub> - 1000 PRV, 2.5 A



- B COMPONENTS**  
 Bridge Rectifier - 200 PRV, 1.5 A  
 Diode D<sub>1</sub> and D<sub>2</sub> - 1000 PRV, 2.5 A  
 Capacitor C<sub>1</sub> - 200 µf, 250 VDC  
 Capacitor C<sub>2</sub> - 20 µf, 400 VDC Non-Polarized  
 Relay - 10,000 ohm coil, 3.5 ma  
 Resistor R<sub>1</sub> and R<sub>2</sub> - 0.5 watt, 5% tolerance

**FIG. 5 Electrical Pulse Circuits for Driving a Latching Solenoid Valve with a Mechanical Timer**

sampling period to flush and condition the inlet line.

9.1.3.7 Prior to use, each sampling system must pass a humid zero air certification (see 12.2.2, 11.2). All plumbing shall be checked carefully for leaks. The canisters must also pass a humid zero air certification before use (see 12.1.1).

9.2 Sampling Procedure:

9.2.1 The sample canister shall be cleaned and tested according to the procedure in 12.1.1.

9.2.2 A sample collection system is assembled as shown in Fig. 1 (and Fig. 2) and must meet certification requirements as outlined in 11.2.3.

NOTE 6—The sampling system shall be contained in an appropriate enclosure when ambient samples are collected.

9.2.3 Prior to locating the sampling system, the user may want to perform “screening analyses” by taking quick grab samples over a short period of time. The information gathered from the screening samples is used to determine the potential concentration range for analysis and identify potential interferences with the GC/MS analysis. Screening samples should be analyzed using the procedure in this standard. Sampling is performed using a simple sampler described in 7.42.1.16.

9.2.4 Immediately prior to any sample collection record the ambient temperature, humidity, and pressure where the sampler is located.

NOTE 7—The following discussion is related to Fig. 1.

9.2.5 To verify correct sample flow, a “practice” (evacuated) canister is used in the sampling system. Attach a certified mass flow meter to the inlet line of the manifold, just in front of the filter. Open the canister. Start the sampler and compare the reading

of the certified mass flow meter to the sampler mass flow controller. The values shall agree within  $\pm 10\%$ . If not, the sampler mass flow meter shall be recalibrated or the sampler must be repaired if a leak is found in the system.

NOTE 8—For a subatmospheric sampler, the flow meter and practice canister are needed. For the pump-driven system, the practice canister is not needed if the flow can be measured as supplied to the canister.

NOTE 9—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. Adjust the desired canister flow rate to the proper value after a 2 min warm up period, using the sampler flow control unit controller (for example, 3.5 mL/min for 24 h, 7.0 mL/min for 12 h). Measure and record the actual final flow.

9.2.6 Turn the sampler off and reset the elapsed time meter to 000.0.

NOTE 10—Any time the sampler is turned off, wait at least 30 s to turn the sampler back on.

9.2.7 Disconnect the “practice” canister and certified mass flow meter. Attach a clean certified (see 12.1.1) canister to the system.

9.2.8 Open the canister valve and vacuum/pressure gage valve.

9.2.9 Record the pressure/vacuum in the canister as indicated by the sampler vacuum/pressure gage.

9.2.10 Close the vacuum/pressure gage valve and reset the maximum/minimum thermometer to current temperature. Record time of day and elapsed time meter readings.

9.2.11 Set the electronic timer to begin and stop the sampling period at the appropriate times. Sampling commences and stops by the programmed electronic timer.

9.2.12 After the desired sampling period, record the maximum, minimum, current interior temperature and current ambient or indoor temperature. Record the current reading from the flow controller, the ambient or indoor humidity and pressure.

9.2.13 At the end of the sampling period, briefly open and close the vacuum/pressure gage valve on the sampler and record pressure/vacuum in the canister.

NOTE 11—For a subatmospheric sampling system, if the canister is at atmospheric pressure when the final pressure check is performed, the sampling period may be suspect. This information shall be noted on the sampling field data sheet. Time of day and elapsed time meter readings are also recorded.

9.2.14 Close the canister valve. Disconnect the sampling line from the canister and remove the canister from the sampling system. For a subatmospheric system, connect a certified mass flow meter to the inlet manifold in front of the in-line filter and attach a “practice” canister to the valve of the sampling system. Record the final flow rate.

NOTE 12—Attaching a mass flow meter and recording the flow rate is not necessary if the initial and final canister vacuum are recorded.

NOTE 13—For a pressurized system, the final flow may be measured directly before the sampler is turned off.

9.2.15 Attach an identification tag to the canister. Record canister serial number, sample number, location, and date on the tag.

## 10. Analytical System

### 10.1 System Description:

#### 10.1.1 GC/MS System (Full Scan and SIM):

10.1.1.1 The analytical system is comprised of a GC equipped with a mass-spectrometric detector set to operate to detect all mass to charge ratios in the analytical range (full scan mode) or to detect a limited number of ions in each of several segments of any analytical run, referred to as the selected ion monitoring or SIM mode (see Fig. 4). mode. Different types of mass spectrometric systems have different designations for selected ion monitoring. The GC/MS is set up for automatic, repetitive analysis. The GC system is comprised of a GC equipped with ~~an OV-1~~ a crosslinked 100 % dimethylpolysiloxane-phase capillary column (0.32 mm by 50 m), or equivalent. The system also includes a computer and appropriate software for data acquisition, data reduction, and data reporting. In operation, an air sample (usually 250 to 800 mL) is recovered from the canister and routed to the analytical system. The sample air may be passed through a ~~Nafion~~ permeable membrane dryer; however, many polar compounds are not identified using this drying procedure. Sample is routed through a chromatographic valve, then into a cryogenic trap. Concentration of compounds based upon a previously installed calibration table is reported by an automated data reduction program. In full scan mode the GC/MS acquires mass spectral data by continuously scanning a range of masses typically between ~~35~~ 18 and 250 amu. ~~The A~~ A SIM system is programmed to acquire data for only the target compounds and to disregard all others. The sensitivity is typically 1 ppb by volume ppbv or better for a 500 mL air sample.

10.1.1.2 SIM analysis is based on a combination of retention times and relative abundances of selected ions (see Table 2). These qualifiers are stored on the hard disk of the GC/MS computer and are compared to sample data for identification of each chromatographic peak. The retention time qualifier is determined to be, for example  $\pm 0.10$  min of the library retention time of the compound. The acceptance level for relative abundance is determined to be, for example  $\pm 15\%$  of the expected abundance, except for vinyl chloride and methylene chloride, which is determined to be, for example  $\pm 25\%$ . Three ions are measured for most of the forty compounds. When compound identification is made by the computer, any peak that fails any of the qualifying tests is flagged (for example, with an asterisk). All the data shall be manually examined by the analyst to determine the reason for the flag and whether the compound can be reported as found. While this adds some subjective judgment to the analysis, computer-generated identification problems must be clarified by an experienced operator. Manual inspection of the quantitative results must also be performed to verify concentrations outside the expected range. To realize the maximum sensitivity of SIM, retention time windows shall be chosen for each compound or group of compounds so that the number of ions monitored during a scan is kept to three or four.

10.1.1.3 A ~~Nafion~~ permeable membrane dryer may be used to remove water vapor selectively from the sample stream. The permeable membrane consists of ~~Nafion~~ tubing ~~(a made of a copolymer of tetrafluoroethylene and fluorosulfonyl monomer)~~ that is coaxially mounted within larger tubing. The sample stream is passed through the interior of the ~~Nafion~~ permeable membrane tubing, allowing water (and other light, polar compounds) to permeate through the walls into a dry air purge stream flowing through the annular space between the ~~Nafion~~ semipermeable membrane and outer tubing. To prevent excessive moisture build-up and any memory effects in the dryer, a cleanup procedure involving periodic heating of the dryer (100°C for 20 min) while purging with dry zero air (500 mL/min) shall be implemented as part of the user's standard operating procedure (SOP) manual. The clean-up procedure is repeated during each analysis ~~(see Section 14, Ref analysis. However, care must be taken when heating the dryer (7)-(21). Another method for drying the air sample involves freezeout of water in a pre-trap followed by raising the temperature and purging target compounds that move into the gas phase to a downstream trap while leaving most of the water behind. Removal of water with a Nafion-type permeable membrane-type dryer shall not be performed for compounds other than those on the list in Table 1 unless recovery studies are performed to validate analysis of these compounds. Polar compounds are particularly susceptible to loss through the Nafion permeable membrane interface.~~

NOTE 14—Recent studies have indicated no substantial loss of targeted VOCs utilizing the above water clean-up procedure (7). This 14—A cleanup procedure is particularly useful when employing cryogenic preconcentration of VOCs with subsequent GC analysis because excess accumulated water can cause trap and column blockage and also adversely affect detector precision. This is a particular problem using GC/MSD systems. In addition, the improvement in water removal from the sampling stream will allow analyses of much larger volumes of sample air in the event that greater system sensitivity is required for targeted compounds.

NOTE 15—While a differentially pumped GC/MS analytical system does not need a ~~Nafion~~ permeable membrane dryer for drying the sample gas stream, such a dryer may be used with GC/Mass Selective Detector (GC/MSD) type GC/MS systems because GC/MSD units are far more sensitive to excessive moisture than the GC/MS analytical systems. Moisture can adversely affect detector precision.

10.1.1.4 The cryogenic sample trap is heated to at least 120°C and no more than 200°C in approximately 60 s and the analyte is injected onto the ~~DB-5~~ capillary column ~~(0.53 mm by 60 m); column.~~ Rapid heating of the trap provides efficient transfer of the sample components onto the gas chromatographic column. Upon sample injection onto the column, the MS computer is signaled by the GC computer to begin detection of compounds which elute from the column. The gas stream from the GC is scanned within a preselected range of atomic mass units (amu). For detection of compounds in Table 1, the range shall be 18 to 250 amu, resulting in a 1.5 Hz repetition rate. Six scans per eluting chromatographic peak are provided at this rate. Automated computer peak selection, or manual selection of each target compound is performed according to the instrument manufacturer's specifications. A library search is then performed and up to ten of the best matches for each peak are listed. A qualitative characterization of the sample is provided by this procedure.

10.1.1.5 Packed metal tubing is used for reduced temperature trapping of VOCs. The cooling unit is comprised of a 32 mm outside diameter (O.D.) nickel tubing loop packed with 60–80 mesh borosilicate glass beads.

NOTE 16—The nickel tubing loop can be placed in an aluminum or brass block containing a tube heater (500 to 1000 watt) or wound onto a cylindrically formed tube heater (250 watt). A cartridge heater (25 watt) is required for the cylindrically wound trap. This low watt heater is sandwiched between pieces of metal plate at the trap inlet and outlet to provide additional heat to eliminate cold spots in the transfer tubing. Rapid heating (–178 to +120°C in 55 s) is accomplished by direct thermal contact between the heater and the trap tubing. Cooling of aluminum or brass mounted traps is achieved by immersion in liquid cryogen. Cooling of cylindrically wound traps is achieved by vaporization around or submersion of the trap in the cryogen. In the shell, efficient cooling (+120 to –178°C in 225 s) is facilitated by confining the vaporized cryogen to the small open volume surrounding the trap assembly. The trap assembly and chromatographic valve are mounted on a baseplate fitted into the injection and auxiliary zones of the GC on an insulated pad directly above the column oven when used with the Hewlett-Packard 5880 GC.

10.1.1.6 As an option, the analyst may wish to split the gas stream exiting the column with a low dead-volume tee, passing one-third of the sample gas (1.0 mL/min) to the mass selective detector and the remaining two-thirds (2.0 mL/min) through a flame ionization detector, ~~as illustrated as an option in Fig. 4; detector.~~ The use of the specific detector (MS-SCAN) coupled with the nonspecific detector (FID) enables enhancement of data acquired from a single analysis. In particular, the FID provides the user with the following:

- (1) Semi-real time picture of the progress of the analytical scheme,
- (2) Confirmation by the concurrent MS analysis of other labs that can provide only FID results, and
- (3) Ability to compare GC-FID with other analytical laboratories with only GC-FID capability.

## 10.2 GC/MS-SCAN-SIM System Performance Criteria:

### 10.2.1 GC/MS System Operation:

10.2.1.1 Prior to analysis, assemble and check the GC/MS system according to manufacturer's instructions.

10.2.1.2 Table 3 outlines general operating conditions for the GC/MS-SCAN-SIM system with optional FID.

10.2.1.3 Challenge the GC/MS system with humid zero air (see 11.2.2). ~~The humid zero air challenged Results of this challenge must contain indicate less than 0.2 ppb by volume ppbv of targeted VOCs prior to sample analysis.~~

### 10.2.2 Daily GC/MS Tuning:

10.2.2.1 At the beginning of each day or prior to a calibration, tune the GC/MS system to verify that acceptable performance criteria are achieved.

10.2.2.2 For tuning the GC/MS, introduce gas from a cylinder containing 4-bromofluorobenzene by way of a sample loop valve injection system. Obtain a background corrected mass spectrum of 4-bromofluorobenzene and check that all key ion abundance

criteria are met. BFB calibration requirements are listed in Table 4. If the criteria are not achieved, the analyst shall retune the mass spectrometer and repeat the test until all criteria are achieved:

~~NOTE 17—Some achieved. Some systems allow are configured for auto-tuning to facilitate this process. The key ions and ion abundance criteria that must be met are illustrated in Table 5. Analysis shall not begin until all those criteria are met.~~

10.2.2.3 The performance criteria shall be achieved before any samples, blanks or standards are analyzed. If process.

10.2.2.3 If any key ion abundance observed for the daily 4-bromofluorobenzene mass tuning check differs by more than 10 % absolute abundance from that observed during the previous daily tuning, retune the instrument or reanalyze the sample or calibration gases, or both, until the above condition is met.

10.2.2.4 The GC/MS tuning standard may also be used to assess GC column performance (chromatographic check) and as an internal standard.

10.2.3 GC/MS Calibration:

10.2.3.1 Initial Calibration—Initially, a multipoint dynamic calibration (three to five levels plus humid zero air) is performed

**TABLE 4 Resp4-Bronse Factmofluors (ppobv/area count) azend  
Expect Ked Retenti Ion Time for GC-MS-Ss and lMon  
Abundalytincale Configuraiteriona**

CompoundMass	Response Factor (pp Abv/area count)	Expected Retention Time (m Crinutes)ria
Freon 12- 50	0.67055-01 15 to 40 % of mass 95	
Methyl chloride- 75	4.0 93 30 to 60 % of mass 93	5.64 5
Freon 114- 95	0.4928 Base Peak, 10.4928	6.55 6.550 %RelativeAbundance
Vinyl chloride- 96	2.343 2.343	6.71 6.715 to 9 % ofmass95
Methyl bromide 173	2.64 77.83 <2 % of mass 174	
Ethyl chloride 174	2. 954 >50 % of mass 954	8.43 8.43
Freon14 175	0.5145 5145	9.8 7 to 9 % ofmass 174
Vinylidene chloride 176	1.037 >95 % but <1037	10.93 1 % of mass 174
Dichloromethane 177	2.255 55	11.21 11.21
Trichloro trifluoroethane	-0. 9031	11.50
Trichloro toroethane	-0. 9031	11.50
1,1-Dichl oroethane	-1.273	12.50
1,1-Dichl % oroethane	-1.273	12.50
cis-1,2-Dichloroethylene	-1.363	13.40
Chlorofor m0.7911	13.75	
Chlorof m0.7911	13.75	
1,2-Dichloroethane	-1.017	14.39
Methyl chloroform	-0.7078	14.62
Benzene	-1.236	15.04
Carbon tetrachloride	-0.5880	15.18
1,2-Dichloropropane	-2.400	15.83
Trichloroethylene	-1.383	16.10
cis-1,3-Dichloropropene	-1.877	16.96
trans- 1,3-Dichloropropene	-1.338	17.49
trans 1,3-Dichloropropene	-1.338	17.49
1,1,2-Trichloroethane	-1.891	17.61
Toluene	-0.9406	17.86
1,2-Dibromoethane (EDB)	-0.8662	18.48
Tetrachloroethylene	-0.7357	19.01
Chlorobenzene	-0.8558	19.73
Ethylbenzene	-0.6243	20.20
m,p-Xylene	-0.7367	20.41
Styrene	-1.888	20.80
1,1,2,2-Tetrachloroethane	-1.035	20.92
o-Xylene	-0.7498	20.92
4-Ethyltoluene	-0.6181	22.53
1,3,5-Trimethylbenzene	-0.7088	22.65
1,2,4-Trimethylbenzene	-0.7536	23.18
m-Dichlorobenzene	-0.9643	23.31
Benzyl chloride	-1.420	23.32
p-Dichlorobenzene	-0.8912	23.41
o-Dichlorobenzene	-1.004	23.88
1,2,4-Trichlorobenzene	-2.150	26.71
Hexachlorobutadiene	-0.4117	27.68



on the GC/MS system, before sample analysis, with the assistance of a calibration system (see Fig. 4). The calibration system uses National Institute of Standards and Technology (NIST) traceable standards or NIST/EPA CRMs in pressurized cylinders [containing a mixture of the targeted VOCs at nominal concentrations of 10 ppm by volume in nitrogen (8.2)] as working standards to be diluted with humid zero air. The contents of the working standard cylinder(s) are metered (2 mL/min) into the heated mixing chamber where they are mixed with a 2 L/min humidified zero air gas stream to achieve a nominal 10 ~~ppb by volume per compound~~ ppbv per compound calibration mixture (see Fig. 4). This nominal 10 ~~ppb by volume~~ ppbv standard mixture is allowed to flow and equilibrate for a minimum of 24 h. After the equilibration period, the gas standard mixture is sampled and analyzed by the real-time GC/MS system (see Fig. 4(a) and 7.2.1). (7.3.1). The results of the analyses are averaged, flow audits are performed on the mass flow meters and the calculated concentration compared to generated values. After the GC/MS is calibrated at three to five concentration levels, a second humid zero air sample is passed through the system and analyzed. The second humid zero air test is used to verify that the GC/MS system is certified clean (less than 0.2 ~~ppb by volume~~ ppbv of target compounds).

NOTE 187—Alternative approaches for generation of calibration standards are acceptable as long as the calibration range (0–100 ~~ppb by volume~~ ppbv) and humidity are accurately maintained.

10.2.3.2 As an alternative, a multipoint humid static calibration (three to five levels plus zero humid air) can be performed on the GC/MS system. During the humid static calibration analyses, three (3) SUMMA<sup>®</sup> passivated canisters are filled each at a different concentration between 1 to 20 ~~ppb by volume~~ ppbv from the calibration manifold using a pump and mass flow control arrangement [see Fig. 4(c)]. The canisters are then delivered to the GC/MS to serve as calibration standards. The canisters are analyzed by the MS in the SIM mode, each analyzed twice. The expected retention time and ion abundance (see Table 2.4 and Table 5) are used to verify proper operation of the GC/MS system. A calibration response factor is determined for each analyte, as illustrated in Table 5.

10.2.3.3 *Routine Calibration*—The GC/MS system is calibrated daily (and before sample analysis) with a one point calibration. The GC/MS system is calibrated either with the dynamic calibration procedure [see Fig. 4(a)] 4] or with a 6 L-SUMMA<sup>®</sup> passivated canister filled with humid calibration standards from the calibration manifold (see 10.2.3.2). After the single point calibration, the GC/MS analytical system is challenged with a humidified zero gas stream to ensure the analytical system returns to specification (less than 0.2 ~~ppb by volume~~ ppbv of selective organics).

### 10.3 Analytical Procedures:

#### 10.3.1 Canister Receipt:

10.3.1.1 The overall condition of each sample canister is observed. Each canister must be received with an attached sample identification tag.

10.3.1.2 Each canister is recorded in the dedicated laboratory logbook. Also noted on the identification tag are date received and initials of recipient.

NOTE 198—A log containing the usage and history of each canister shall be kept. This historical record will assist in ensuring that canisters used for source sampling are not mixed with canisters used for indoor or ambient air. Samples used for high level standards or to acquire high level VOC samples should be flagged to receive individual blanking quality control checks after sample analysis.

10.3.1.3 The pressure of the canister is checked by attaching a pressure gage to the canister inlet. The canister valve is opened briefly and the pressure (kPa, psig) is recorded.

NOTE 20—If 19—If pressure is <83 kPa (<12 psig), the user may wish to pressurize the canisters, as an option, with zero grade nitrogen up to 137 kPa (20 psig) to ensure that enough sample is available for analysis. However, pressurizing the canister can introduce additional error, increase the minimum detection limit (MDL), and is time consuming. The user must consider these limitations as part of his program objectives before pressurizing. Final cylinder pressure is recorded.

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

$$DF = Y_d/X_a \quad (3)$$

where:

$X_a$  = canister pressure absolute before dilution, kPa, psia and

$Y_a$  = canister pressure absolute after dilution, kPa, psia.

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

#### 10.3.2 GC/MS-SCAN and SIM Analysis:

10.3.2.1 When the MS is placed in the full scan mode (SCAN) all ions are scanned between the preset windows for monitoring. The characteristic mass spectrum of any compound or group of compounds reaching the MS detector are recorded and can be interpreted for both qualitative identification and quantitative determination. In the SIM mode of operation, the MS monitors only preselected ions, rather than scanning all masses continuously between two mass limits. As a result, increased sensitivity and improved quantitative analysis can be achieved at the expense of identifying and quantifying unknown compounds.

10.3.2.2 The analytical system shall be properly assembled, humid zero air certified (see 4.2.3; 11.2), operated (see Table 3), and calibrated for accurate VOC determination.

10.3.2.3 The mass flow controllers are checked and adjusted to provide correct flow rates for the system.

10.3.2.4 The sample canister is connected to the inlet of the GC/MS-SCAN or GC/MS-SIM analytical system. For pressurized

**TABLE 5 4-BrResponse Factor fluoros (ppbv/arenzene Key la  
count) and Expected Retention Time for GC-MS-SIM  
Abundantly Confitegration**

Mass Compounds	Response Factor (ppbv/area count)	Expected Retention Time (minutes)
Freon 12	0.6705	5.01
Methyl chloride	4.093	5.64
Freon 114	0.4928	6.55
Vinyl chloride	2.343	6.71
Methyl bromide	2.647	7.83
Ethyl chloride	2.954	8.43
Freon 11	0.5145	9.87
Vinylidene chloride	0.037	10.93
Dichloromethane	2.255	11.21
Trichloroethane	0.9034	11.50
Trichlorotrifluoroethane	0.081	11.50
1,1-Dichloroethane	0.273	12.50
cis-1,2-Dichloroethylene	0.666	13.40
Chloroform	0.7911	13.75
1,2-Dichloroethane	0.017	14.39
Methyl chloroform	0.7078	14.62
Benzene	1.236	15.04
Carbon tetrachloride	0.5880	15.18
1,2-Dichloropropane	0.400	15.83
Trichloroethylene	1.383	16.10
cis-1,3-Dichloropropane	0.076	16.96
trans-1,3-Dichloropropane	0.086	17.49
trans-1,3-Dichlorobutene	0.086	17.49
1,1,2-Trichloroethane	0.091	17.61
Toluene	0.9406	17.86
1,2-Dibromoethane	0.8662	18.48
Tetrachloroethylene	0.7357	19.01
Chlorobenzene	0.8558	19.73
Ethylbenzene	0.6243	20.20
m,p-Xylene	0.7367	20.41
Styrene	1.888	20.80
1,1,2,2-Tetrachloroethane	0.076	20.92
o-Xylene	0.7498	20.92
4-Ethyltoluene	0.6181	22.53
1,3,5-Trimethylbenzene	0.208	22.65
1,2,4-Trimethylbenzene	0.256	23.18
m-Dichlorobenzene	0.9643	23.31
Benzyl chloride	1.420	23.32
p-Dichlorobenzene	0.8912	23.41
o-Dichlorobenzene	0.004	23.88
1,2,4-Trichlorobenzene	0.216	26.71
Hexachlorobutadiene	0.4117	27.68

samples, a mass flow controller is placed on the canister, the canister valve is opened and the canister flow is vented past a tee inlet to the analytical system at a flow of 75 mL/min so that the inlet system up to the six-port sample injection valve is flushed with sample gas (typically 40 mL). The cryogenic trap is connected and verified to be operating properly while cooled with cryogen through the system.

NOTE 2—Flow rate is not as important as acquiring sufficient sample volume.

10.3.2.5 Sub-ambient pressure samples are connected directly to the inlet. The sample system Sample flow from the canister is controlled to allow sample air to pass through the concentration loop to an evacuated (lower pressure) reservoir downstream of the loop. A pressure increase in the downstream reservoir is often used to collect or monitor the sample on volume that is pulled through the concentration loop.

10.3.2.6 The GC oven and cryogenic trap (inject position) are cooled to their set points of  $-50^{\circ}\text{C}$  and  $-178^{\circ}\text{C}$ , respectively.

10.3.2.7 As soon as the cryogenic trap reaches its lower set point of  $-178^{\circ}\text{C}$ , the six-port chromatographic valve is turned to its fill position to initiate sample collection.

10.3.2.8 A ten-minute collection period of canister sample is utilized.

NOTE 221—More or less canister sample is used for analysis depending on the sensitivity of the mass detection unit and the concentration of the target analytes in the sample.

10.3.2.9 After the sample is preconcentrated in the cryogenic trap, the GC sampling valve is cycled to the inject position and the cryogenic trap is heated. The trapped analytes are thermally desorbed onto the head of the ~~OV-1 or equivalent~~ capillary column (~~0.31 mm I.D. by 50 m length~~) column. The GC oven is programmed to start at  $-50^{\circ}\text{C}$  and after 2 min to heat to  $150^{\circ}\text{C}$  at a rate of  $8^{\circ}\text{C}$  per minute.

10.3.2.10 Upon sample injection onto the column, the MS is signaled by the computer to start data acquisition. In the SCAN mode, the eluting carrier gas passing through the mass spectrometer source is scanned from ~~35~~ 38 to 250 amu, resulting in a 1.5 Hz repetition rate. This corresponds to about 6 scans per eluting chromatographic peak.

10.3.2.11 The individual analyses are handled in three phases: data acquisition, data reduction, and data reporting.

10.3.2.12 Primary identification is based upon retention time and relative abundance of eluting ions as compared to the spectral library stored on the hard disk of the GC/MS data computer. In the SIM, the data acquisition software is set to monitor specific compound fragments at specific times in the analytical run. Data reduction is coordinated by the postprocessing program that is automatically accessed after data acquisition is completed at the end of the GC run. Resulting ion profiles are extracted, peaks are identified and integrated, and an integration report is generated by the computer software. A reconstructed ion chromatogram for hard copy reference is prepared by the program and various parameters of interest such as time, date, and integration constants are printed. At the completion of the program, the data reporting software is accessed. The appropriate calibration table is retrieved by the data reporting program from the computer's hard disk storage and the proper retention time and response factor parameters are applied to the macro program's integration file. With reference to certain pre-set acceptance criteria, peaks are automatically identified and quantified and a final summary report is prepared.

10.3.2.13 ~~Approximately 64 min are required for each sample analysis, 15 min for system initialization, 14 min for sample collection, 30 min for analysis, and 5 min for post run equilibration, during which a report is printed.~~

10.3.2.14 ~~The helium and sample mass flow controllers are checked and adjusted to provide correct flow rates for the system. Helium is used to purge residual air from the trap at the end of the sampling phase and to carry the revolatilized VOCs from the trap onto the GC column.~~

10.3.2.15 ~~The~~

10.3.2.13 ~~The concentration (ppb by volume) (ppbv) is calculated using the previously established response factors (see 10.2.3.2), as illustrated in Table 5.~~

NOTE 232—If the canister is diluted before analysis, an appropriate multiplier is applied to correct for the volume dilution of the canister (10.3.1.4).

10.3.2.14 ~~In a typical analysis, approximately 64 min are required for each sample analysis, 15 min for system initialization, 14 min for sample collection, 30 min for analysis, and 5 min for post run equilibration, during which a report is printed.~~

## 11. Cleaning and Certification Program

### 11.1 Canister Cleaning and Certification:

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

11.1.2 All canisters are leak tested by pressurizing them to approximately 200 kPa (30 psig) with zero air.

NOTE 243—The canister cleaning system in Fig. 3 can be used for this task. The initial pressure is measured, the canister valve is closed, and the final pressure is checked after 24 h. If leak tight, the pressure shall not vary more than  $\pm 13.8$  kPa ( $\pm 2$  psig) over the 24-h period.

11.1.3 A canister cleaning system may be assembled as illustrated in Fig. 3. 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 less than 0.0064 kPa (~~50.05~~ mm Hg) for at least one hour.

NOTE 254—On a daily basis, or more often if necessary, the cryogenic traps shall be purged with zero air to remove any trapped water from previous canister cleaning cycles.

11.1.4 The vacuum and vacuum/pressure gage 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 200 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.

11.1.5 The zero 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. Steps 11.1.3-11.1.5 are repeated two additional times for a total of three evacuation/pressurization cycles for each set of canisters.

11.1.6 At the end of the evacuation/pressurization cycle, the canister is pressurized to 200 kPa (30 psig) with humid zero air. Analyze the canister with the GC/MS or GC-FID-ECD analytical system. Any canister that has not tested clean (compared to direct

analysis of humidified zero air of less than ~~0.2 ppb by volume~~ ppbv of targeted VOCs) shall not be used. As a “blank” check of the canister(s) and cleanup procedure, analyze the final humid zero air fill of 100 % of the canisters until the cleanup system and canisters are proven reliable (less than ~~0.2 ppb by volume~~ ppbv of target VOCs). This blank check may be reduced to one canister per batch after the blank criterion has been met on one entire batch.

11.1.7 Reattach the canister to the manifold and reevacuate to less than 0.0064 kPa (50.05 mm Hg). The canister valve is closed. Remove the canister from the cleaning system and cap the canister connection with a stainless steel fitting. The canister is now ready for collection of an air sample. Attach an identification tag to the neck of each canister for field notes and chain-of-custody purposes. Retain the canister in this condition until used.

11.1.8 As an option to the humid zero air cleaning procedures, heat the canisters in an isothermal oven to no greater than 100°C using the apparatus described in 11.1.3.

NOTE 265—For sampling heavier, more complex VOC mixtures, the canisters shall be heated to 250°C during 11.1.3-11.1.7. Canister valves shall not be heated during this cleaning process. Once heated, the canisters are evacuated to 0.0064 kPa (50.05 mm Hg). At the end of the heated/evacuated cycle, pressurize the canisters with humid zero air and analyze by the blanking procedures in this standard. Any canister that has not tested clean (less than ~~0.2 ppb by volume~~ ppbv of targeted compounds) shall not be used. Once tested clean, reevacuate the canisters to 0.0064 kPa (0.05 mm Hg) or less and retain in the evacuated state until used. Repeated heating of canisters may degrade the ~~SUMMA®~~ treated surface of the canister and premature degradation of samples may ensue. Periodic (yearly) check of calibration standard stability shall be performed in canisters that are repeatedly heat treated.

## 11.2 Sampling System Cleaning and Certification:

### 11.2.1 Cleaning Sampling System Components:

11.2.1.1 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 hexane in an ultrasonic bath for 15 min. This procedure is repeated with methanol as the solvent.

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

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

### 11.2.2 Humid Zero Air Certification:

11.2.2.1 The system is “certified” if ~~no significant additions or deletions (less less than 0.2 ppb by volume ppbv of targeted compounds) have occurred~~ compounds is measured for each compound when the system is challenged with the ultra high purity humidified air test stream. The cleanliness of the sampling system is determined by testing the sampler with humid zero air with an evacuated canister, as follows.

11.2.2.2 The calibration system and manifold are assembled as illustrated in Fig. 4. The sampler (with an evacuated sampling canister) is connected to the manifold and the zero air cylinder activated to generate a humid gas stream (2 L/min) to the calibration manifold [see Fig. 4(b)] ~~manifold.~~

11.2.2.3 The humid zero gas stream passes through the calibration manifold, through the sampling system and is collected in a clean evacuated sampling canister (see 10.2.2.1). ~~After the sample (a minimum of 250 mL) is preconcentrated on the trap, the trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. Since the column is at -50°C, the VOCs are cryofocussed on the column. Then, the oven temperature (programmed) increases and the VOCs begin to elute and are detected by a GC/MS (see 10.2). The analytical system must not detect greater than 0.2 ppb by volume of targeted VOCs in order for the sampling system to pass the humid zero air certification test.~~ canister. 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 (for example, 5.0 to 20 ~~ppb by volume~~ ppbv) as outlined in 11.2.3.

NOTE 276—As an alternative to save the use of GC/MS time, a GC-FID-ECD may be used for canister analysis of certification standards. Such a system must include a sample concentration interface identical to the one used for GC/MS analysis (10.3). It must also be calibrated with standards prepared in the same way as those used for GC/MS analysis. Retention time is verified with known standard ~~compounds and used to identify certification standards or analyzed zero test samples.~~ compounds.

### 11.2.3 Sampler System Certification with Humid Calibration Gas Standards:

11.2.3.1 Assemble the dynamic calibration system and manifold as illustrated in Fig. 4.

NOTE 287—The certification manifold will often become contaminated with certification compounds in the process of certifying samplers. Separate manifolds shall be used for zero certification and humid calibration gas challenge to avoid erroneous results caused by carryover of compounds in the test manifold. Alternatively, one manifold may be used; however, the manifold must be certified as clean prior to the start of a zero certification test.

NOTE 298—Manifold components and flow regulators must be heated during humid calibration gas standards certification to ensure complete vaporization of challenge gas components.

11.2.3.2 Verify that the calibration system is clean (less than ~~0.2 ppb by volume ppbv~~ of targeted compounds) by sampling a humidified gas stream, without gas calibration standards, with a previously certified clean canister (see 12.1.1).

11.2.3.3 The assembled dynamic calibration system is certified clean if less than ~~0.2 ppb by volume ppbv~~ of targeted compounds are found.

11.2.3.4 For generating the humidified calibration standards, the calibration gas cylinder(s) (see 8.2) containing nominal concentrations of 10 ppm by volume in nitrogen of selected VOCs are attached to the calibration ~~system, as outlined in 10.2.3.1.~~ system. The gas cylinders are opened and the gas mixtures are passed through 0 to 50 mL/min certified mass flow controllers to generate ppbv levels of calibration standards.

11.2.3.5 After the appropriate equilibration period, attach the sampling system (containing a certified evacuated canister) to the manifold, as illustrated in Fig. 4(a)-4.

11.2.3.6 Sample the dynamic calibration gas stream with the sampling system according to 9.2.1.

~~Note 30—To conserve generated calibration gas, bypass the canister sampling system manifold and attach the sampling system to the calibration gas stream at the inlet of the in-line filter of the sampling system so the flow will be less than 500 mL/min. 9.2.~~

11.2.3.7 Concurrent with the sampling system operation, real time monitoring of the calibration gas stream is accomplished by collection of a canister sample connected directly to a mass flow controller and the certification test gas feed line. Analysis of this check sample must be performed to confirm the concentration of standard gas delivered to the samplers being certified.

11.2.3.8 At the end of the sampling period (normally same time period used for anticipated sampling), the sampling system canister is analyzed and compared to the reference canister results to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system.

11.2.3.9 A recovery of between 85 % and 115 % is expected for the average of all targeted VOCs. Individual compounds must fall within the range of 80 % and 120 % for acceptable certification.

## 12. Performance Criteria and Quality Assurance

### 12.1 Standard Operating Procedures (SOPs):

12.1.1 SOPs must be generated in each laboratory describing and documenting the following activities: (1) assembly, calibration, leak check, and operation of specific sampling systems and equipment used, (2) preparation, storage, shipment, and handling of samples, (3) assembly, leak-check, calibration, and operation of the analytical system, addressing the specific equipment used, (4) canister storage and cleaning, and (5) all aspects of data recording and processing, including lists of computer hardware and software used.

12.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the laboratory personnel conducting the work.

### 12.2 Method Relative Accuracy and Linearity:

12.2.1 Accuracy can be determined by injecting VOC standards (see 8.2) from an audit cylinder into a sampler. The contents are then analyzed for the components contained in the audit canister. Percent relative accuracy is calculated:

$$\% \text{ Relative Accuracy} = (X - Y)/X \times 100 \quad (4)$$

where:

$Y$  = concentration of the targeted compound recovered from sampler, and

$X$  = concentration of VOC-targeted compound in the NIST-SRM or EPA-CRM audit cylinders.

12.2.2 If the relative accuracy does not fall between 80 and 120 %, the sampler should be removed from use, cleaned, and recertified according to initial certification procedures outlined in 11.2.2 and 11.2.3.

### 12.3 Method Modification:

#### 12.3.1 Sampling:

12.3.1.1 *Urban Air Toxics Sampler*—The sampling system described in this test method (Fig. 1) may be modified like the sampler in EPA’s FY-90 Urban Air Toxics Pollutant Program (see Fig. 6).

#### 12.3.1.2 Analysis:

(1) Heat inlet tubing from the calibration manifold to 50°C (same temperature as the calibration manifold) to prevent condensation on the internal walls of the system.

(2) The analytical strategy for this test method involves positive identification and quantitation by GC/MS-SCAN or -SIM mode. This is a highly specific and sensitive detection technique. Because a specific detector system (GC/MS-SCAN or -SIM) is more complicated and expensive than the use of non-specific detectors (GC-FID-ECD-PID), the analyst may perform a screening analysis and preliminary quantitation of VOC species in the sample, including any polar compounds, by utilizing the GC-multidetector (GC-FID-ECD-PID) analytical system prior to GC/MS analysis. This multidetector system can be used for approximate quantitation. The GC-FID-ECD-PID provides a “snapshot” of the constituents in the sample, allowing the analyst to determine:

(a) (a) Whether the constituents are within the calibration range of the anticipated GC/MS-SCAN-SIM analysis or does the sample require further dilution, and

(b) (b) Are there unexpected peaks which need further identification through GC/MS-SCAN or will GC/MS-SIM be adequate.

### 12.4 Quality Assurance (See Fig. 7):

#### 12.4.1 Sampling System:

12.4.1.1 Paragraph 9.2 requires pre- and post-sampling measurements with a certified mass flow controller for flow verification of sampling system.

12.4.1.2 Paragraph 11.1 requires all canisters to be pressure tested to 200 kPa ± 14 kPa (30 psig ± 2 psig) over a period of 24 h.

12.4.1.3 Paragraph 11.1 requires that all canisters be certified clean (containing less than 0.2 ~~ppb by volume~~ ppbv of targeted VOCs) through a humid zero air certification program.

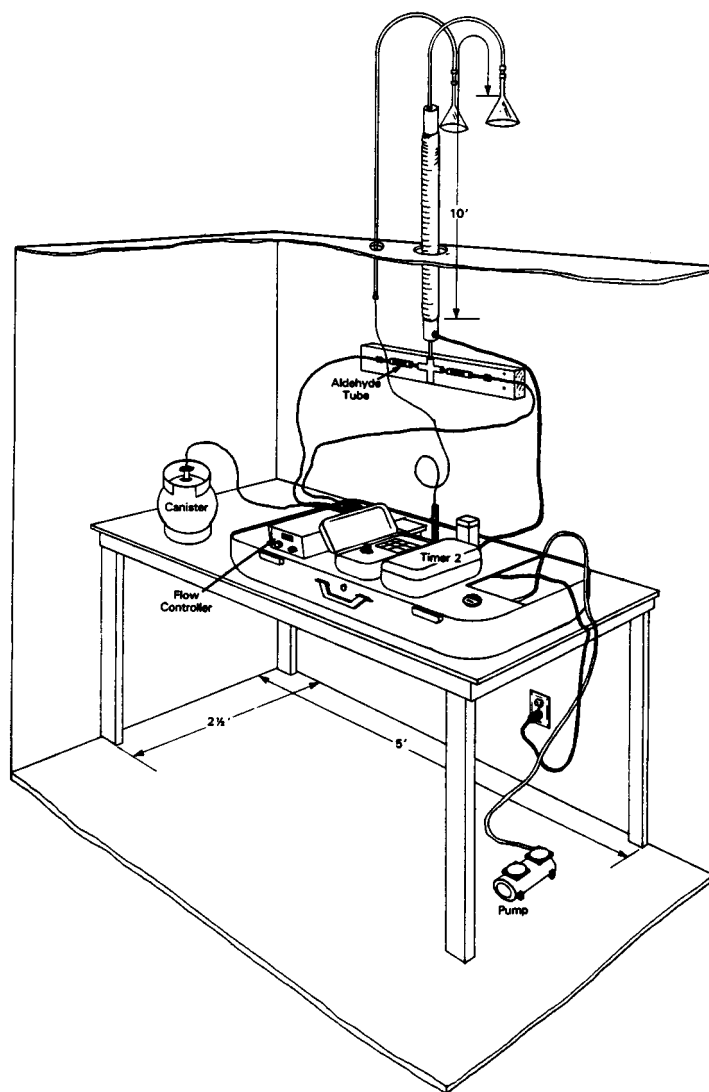


FIG. 6 Perspective View of UATMP Sampler

12.4.1.4 Paragraph 11.2.2 requires all sampling systems to be certified initially clean (containing less than 0.2 ~~ppb by volume~~ ppbv of targeted VOCs) through a humid zero air certification program.

12.4.1.5 Paragraph 11.2.3 requires all sampling systems to pass an initial humidified calibration gas certification [at VOC concentration levels expected in the field (for example, 0.5 to 20 ~~ppb by volume~~) ppbv] with a percent recovery of greater than 90.

12.4.2 *GC/MS-SCAN-SIM System Performance Criteria:*

12.4.2.1 Paragraph 10.2.1 requires the GC/MS analytical system to be certified clean (less than 0.2 ~~ppb by volume~~ ppbv of targeted VOCs) prior to sample analysis, through a humid zero air certification.

12.4.2.2 Paragraph 10.2.2 requires the tuning of the GC/MS with 4-bromofluorobenzene (4-BFB) and that it meets the key ions and ion abundance criteria (10%) outlined in Table 5-4.

12.4.2.3 Paragraph 10.2.3 requires both an initial multipoint humid static calibration (three levels plus humid zero air) and a daily calibration (one point) of the GC/MS analytical system.

12.4.2.4 Paragraph 10.2.3.3 requires that a calibration check sample in the mid range of the calibration curve is analyzed once each day or once every eight samples to ensure the calibration of the GC/MS is still valid and under control.

### 13. Precision and Bias

13.1 The precision of replicate gas sample analysis will vary depending on the volatile organic compound being determined. Typical precision reported as %CV should be  $\pm 30\%$ , for determinations made on the same sample over an 8-h period. If the GC/MS analysis does not meet or exceed these criteria, the instrument should be retuned and recalibrated. Precision measured for seven replicate analyses analyzed over a 10-h period are reported in Table 6.

13.2 Tests performed to measure the bias of this procedure have been conducted with a performance audit sample prepared by

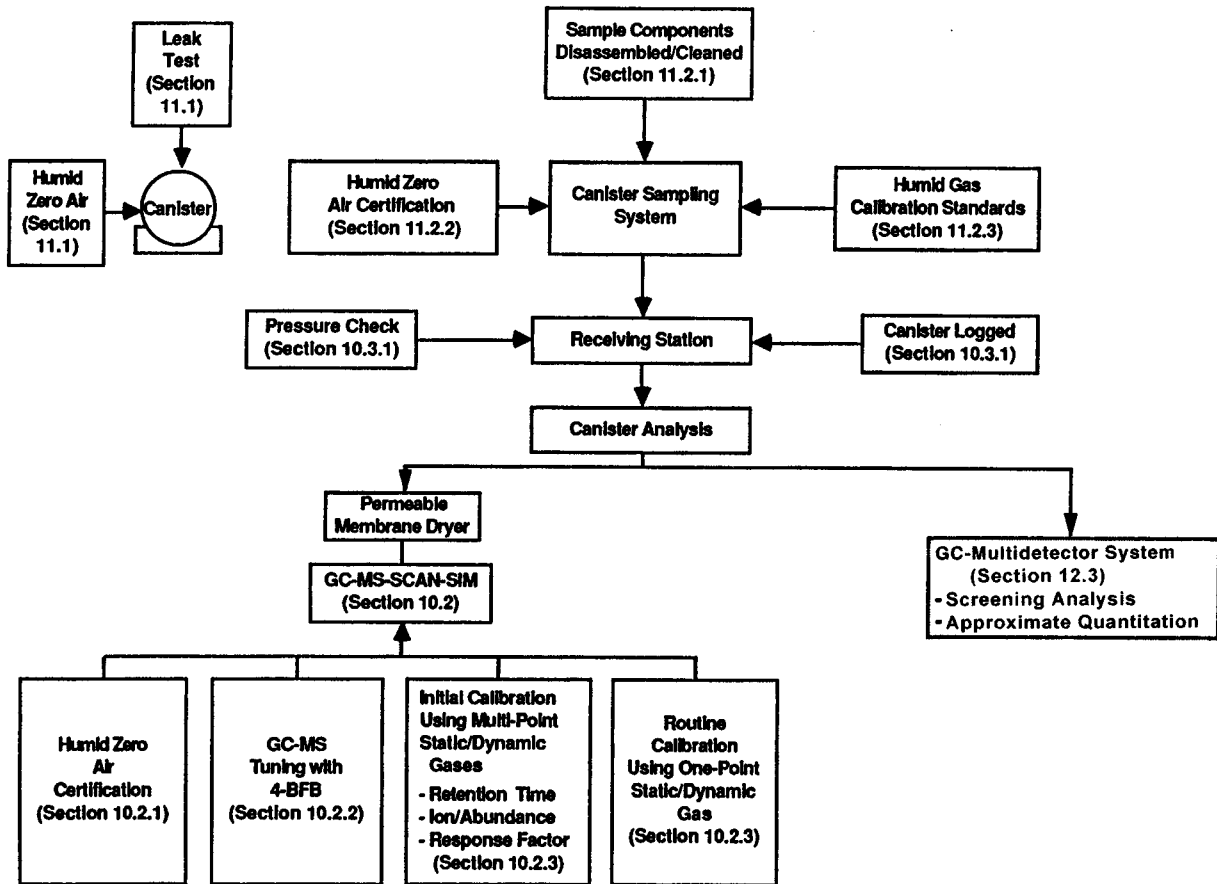


FIG. 7 System Quality Assurance/Quality Control (QA/QC) Activities Associated with Various Analytical Systems

U.S. EPA and referenced to a primary standard gas mixture prepared by NIST. Humidified gas performance standards were analyzed in a GC/MS system configured in accordance with this standard, following the procedure without the use of a Nafion permeable membrane dryer. Four performance samples ranging in concentration from 2 to 10 ppb by volume ppbv were analyzed one sample every other month over a period of 10 months. The test results shown in Tables 7 and Table 88 were obtained using this system.

**TABLE 6 Precision Results for Canister VOC Method (Example)**

Compound	Standard Deviation	% CV	Instrument Detection Limit
1,3-butadiene	0.15	12.5	0.20
1,3-Butadiene	0.15	12.5	0.20
vinyl chloride	0.11	12.3	0.38
Vinyl chloride	0.11	12.3	0.38
propylene	0.18	16.8	0.95
Propylene	0.18	16.8	0.95
chloromethane	0.13	12.4	0.48
Chloromethane	0.13	12.4	0.48
chloroethane	0.12	7.8	0.56
Chloroethane	0.12	7.8	0.56
bromomethane	0.07	18.5	0.22
Bromomethane	0.07	18.5	0.22
methylene chloride	0.44	49.7	0.23
Methylene chloride	0.44	49.7	0.23
trans-1,2-dichloroethane	0.22	16.4	0.66
trans-1,2-Dichloroethane	0.22	16.4	0.66
1,1-dichloroethane	0.08	6.3	0.26
1,1-Dichloroethane	0.08	6.3	0.26
chloroprene	0.08	8.2	0.26
Chloroprene	0.08	8.2	0.26
bromochloromethane	0.06	4.3	0.23
Bromochloromethane	0.06	4.3	0.23
chloroform	0.26	6.1	0.81
Chloroform	0.26	6.1	0.81
1,1,1-trichloroethane	0.20	15.9	0.72
1,1,1-Trichloroethane	0.20	15.9	0.72
carbon tetrachloride	0.03	9.2	0.09
Carbon tetrachloride	0.03	9.2	0.09
benzene	0.04	9.0	0.12
Benzene	0.04	9.0	0.12
1,2-dichloroethane	0.08	5.2	0.21
1,2-Dichloroethane	0.08	5.2	0.21
trichloroethene	0.04	14.0	0.15
Trichloroethene	0.04	14.0	0.15
1,2-dichloropropane	0.07	6.1	0.16
1,2-Dichloropropane	0.07	6.1	0.16
bromodichloromethane	0.14	9.7	0.46
Bromodichloromethane	0.14	9.7	0.46
trans-1,3-dichloropropene	0.07	5.7	0.23
trans-1,3-Dichloropropene	0.07	5.7	0.23
toluene	0.17	24.5	0.52
Toluene	0.17	24.5	0.52
n-octane	0.32	22.7	1.01
n-Octane	0.32	22.7	1.01
cis-1,3-dichloropropene	0.05	8.4	0.14
cis-1,3-Dichloropropene	0.05	8.4	0.14
1,1,2-trichloroethane	0.31	12.0	0.96
1,1,2-Trichloroethane	0.31	12.0	0.96
tetrachloroethene	0.08	19.0	0.27
Tetrachloroethene	0.08	19.0	0.27
dibromochloromethane	0.04	26.3	0.11
Dibromochloromethane	0.04	26.3	0.11
chlorobenzene	0.07	7.5	0.22
Chlorobenzene	0.07	7.5	0.22
ethylbenzene	0.23	7.9	0.73
Ethylbenzene	0.23	7.9	0.73
m-p-xylene	0.41	11.1	1.03
m-p-Xylene	0.41	11.1	1.03
styrene	0.15	37.9	0.46
Styrene	0.15	37.9	0.46
o-xylene	0.23	16.2	0.71
o-Xylene	0.23	16.2	0.71
bromoform	0.03	6.5	0.10
Bromoform	0.03	6.5	0.10
1,1,2,2-tetrachloroethane	0.09	6.7	0.22
1,1,2,2-Tetrachloroethane	0.09	6.7	0.22
m-dichlorobenzene	0.09	8.7	0.27
m-Dichlorobenzene	0.09	8.7	0.27
p-dichlorobenzene	0.04	12.9	0.11
p-Dichlorobenzene	0.04	12.9	0.11
o-dichlorobenzene	0.14	8.9	0.38
o-Dichlorobenzene	0.14	8.9	0.38
1,1-dichloroethene	0.05	4.2	0.17
1,1-Dichloroethene	0.05	4.2	0.17
1,2-dichloroethane	0.08	6.7	0.24
1,2-Dichloroethane	0.08	6.7	0.24
cis-1,2-dichloroethene	0.06	5.0	0.19
cis-1,2-Dichloroethene	0.06	5.0	0.19
Halocarbon 11 (trichlorofluoromethane)	0.06	4.8	0.18
Freon 11 (Trichlorofluoromethane)	0.06	4.8	0.18





TABLE 7 NIST Traceable GC/MS Audit Results

Compound	Audit #1164			Audit #1252			Audit #1366			Audit #1496		
	Ref. (ppb-by volume)	Rep. (ppb-by volume)	% Bias	Ref. (ppb-by volume)	Rep. (ppb-by volume)	% Bias	Ref. (ppb-by volume)	Rep. (ppb-by volume)	% Bias	Ref. (ppb-by volume)	Rep. (ppb-by volume)	% Bias
Vinyl chloride	3.6	2.8	-22.0	4.9	4.5	-8.16	3.6	3.2	-11.11	2.4	2.1	-12.20
Bromomethane	3.6	3.5	-2.8	4.8	4.2	-12.50	3.5	3.1	-11.43	2.4	1.1	-54.17 <sup>A</sup>
Methylene chloride	7.2	7.9	4.2	9.8	9.1	-7.14	7.2	6.7	-6.94	4.9	5.6	14.29
trans-1,2-Dichloroethylene	6.9	7.0	1.4	9.3	7.6	-18.28	7.6	5.4	-20.59	4.9	5.1	8.51
1,1-Dichloroethane	3.8	3.3	-13.0	5.1	3.9	-23.53	3.9	2.9	-27.03	2.6	2.6	0.00
Chloroform	3.5	3.8	8.6	4.8	5.4	12.50	3.5	4.3	22.86	2.4	2.9	20.83
1,1,1-Trichloroethane	3.6	4.1	14.0	4.8	4.9	2.08	3.6	4.0	11.11	2.4	2.7	12.50
Carbon tetrachloride	3.3	3.4	3.0	4.5	3.6	-20.00	3.3	3.7	12.12	2.3	2.6	13.04
Benzene	7.3	7.0	-4.1	9.9	10.5	6.06	7.3	8.2	12.33	4.9	4.5	-8.16
Trichloroethylene	3.6	3.6	0.0	10.0	10.1	1.00	3.6	6.0	66.67	2.4	2.1	-12.50
1,2-Dichloropropane	7.4	7.2	-2.7	4.9	5.9	20.41	7.3	8.8	20.55	5.0	4.1	-18.00
Toluene	3.8	4.1	7.9	5.1	4.6	-9.80	3.8	3.6	-5.26	2.6	2.5	-3.85
Tetrachloroethylene	3.8	5.3	39.0 <sup>A</sup>	5.2	5.6	7.69	3.8	4.6	21.05	2.6	2.8	7.69
Chlorobenzene	7.6	9.5	25.0	10.3	6.6	-35.92 <sup>A</sup>	7.5	5.5	-26.67	5.1	4.4	-13.72
Styrene	3.7	2.0	-46.0 <sup>A</sup>	5.0	4.6	-8.00	3.7	0.5	-86.49	2.5	2.4	-4.00
o-Xylene	8.8	8.0	-9.1	12.0	8.9	-25.83	8.8	6.9	-21.59	6.0	6.1	1.67
Ethylbenzene	7.8	6.8	-13.0	10.5	7.2	-31.43	7.7	5.7	-25.97	5.3	5.1	-3.77

<sup>A</sup> Greater than the  $\pm 30\%$  data quality objectives.

TABLE 8 Average Performance on Audits

	Average Deviation	Standard	n
Vinyl chloride	-3.9	14.4	8
Bromomethane	5.5	19.7	8
Methylene chloride	5.9	9.9	8
trans-1,2-Dichloroethylene	-4.2	10.9	8
1,1-Dichloroethane	-7.9	12.5	8
Chloroform	15.9	5.3	5
1,1,1-Trichloroethane	8.9	5.6	8
Carbon tetrachloride	6.0	12.6	8
Benzene	5.6	12.5	8
Trichloroethylene	9.1	24.2	8
1,2-Dichloropropane	7.0	15.0	8
Toluene	1.6	12.3	8
Tetrachloroethylene	18.3	15.1	7
Chlorobenzene	4.2	22.4	6
Styrene	25.7	30.9	7
o-Xylene	-13.7	10.8	4
Ethylbenzene	-13.7	9.7	8

## 14. Keywords

14.1 ambient atmospheres; analysis; atmospheres; canister sampling; gas chromatography–mass spectrometry;

indoor atmospheres; sampling; volatile organic compounds; workplace atmospheres



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