**Designation: D5466 – 15**

# Standard Test Method for Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology)[1]

This standard is issued under the fixed designation D5466; 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 standard describes a procedure for sampling and analysis of selected volatile organic compounds (VOCs) in ambient, indoor, and workplace atmospheres. The test method is based on the collection of whole air samples in stainless steel canisters 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 (respectively referred to as pressurized and subatmospheric pressure sampling).[2]

1.2 This test method is applicable to specific VOCs that have been determined to be stable when stored in canisters. Numerous compounds, many of which are chlorinated VOCs, have been successfully tested for storage stability in pressurized canisters (**1-4**).[3] Documentation is also available demonstrating stability of VOCs in subatmospheric pressure canisters. Information on storage stability is available for many polar compounds as well (**5-7**).

1.3 The procedure for collecting the sample involves the use of inlet lines, air filters, flow rate regulators for obtaining time-integrated samples, and in the case of pressurized samples, an air pump. Typical long-term fixed location canister samplers have been designed to automatically start and stop the sample collection process using electronically actuated valves and timers (**8-10**). Temporary or short-term canister samplers may require the user to manually start and stop sample collection. A weatherproof shelter may be required if the sampler is used outdoors. For the purposes of this test method, refer to Practice D1357 for practices and planning ambient sampling events.

1.4 The organic compounds that have been successfully measured at single-digit parts-per-billion by volume (ppbv) levels with this test method are listed in Table 1. The test method is applicable to VOC concentrations ranging from the detection limit to approximately 300 ppbv. Above this concentration, smaller sample aliquots of sample gas may be analyzed or samples can be diluted with dry ultra-high-purity nitrogen or air.

1.5 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.6 *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:*[4]

D1356 Terminology Relating to Sampling and Analysis of Atmospheres

D1357 Practice for Planning the Sampling of the Ambient Atmosphere

E355 Practice for Gas Chromatography Terms and Relationships

2.2 *EPA Documents:*[5]

EPA 600/R-96/010b Compendium of Methods for the Determination to Toxic Organic Compounds in Ambient Air, Method TO-14A

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[1] This test method is under the jurisdiction of ASTM Committee D22 on Air Quality and is the direct responsibility of Subcommittee D22.05 on Indoor Air.

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[2] 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.

[3] The boldface numbers in parentheses refer to the list of references at the end of the standard.

[4] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[5] Produced by United States Environmental Protection Agency (EPA). Available from U.S. Dept. of Commerce, National Technical Information Service, Port Royal Road, Springfield, VA 22161, http://www.cpa.gov/ttn/amtic/airtox.html.

TABLE 1 Typical Volatile Organic Compounds Determined by the Canister Method

| Compound (Synonym) | Formula | Molecular Weight | Boiling Point (°C) | Vaper Pressure kPa at 25°C | Listed in the U.S. EPA TO-14A/TO-15 | CAS Number |
|---|---|---|---|---|---|---|
| Acetylene | | | | | | |
| Propylene | | | | | | |
| Freon 12 (Dichlorodifluoromethane) | $Cl_2CF_2$ | 120.91 | –29.8 | | X/X | |
| Methyl chloride (Chloromethane) | $CH_3Cl$ | 50.49 | –24.2 | | X/X | 74-87-3 |
| Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane) | $ClCF_2CClF_2$ | 170.93 | 4.1 | | X/X | |
| Vinyl chloride (Chloroethylene) | $CH_2=CHCl$ | 62.50 | –13.4 | | X/X | 75-01-4 |
| 1,3-Butadiene | | | | | /X | |
| Methyl bromide (Bromomethane) | $CH_3Br$ | 94.94 | 3.6 | | X/X | 74-83-9 |
| Ethyl chloride (Chloroethane) | $CH_3CH_2Cl$ | 64.52 | 12.3 | | X/X | 75-00-3 |
| Acetonitrile | | | | | /X | |
| Freon 11 (Trichlorofluoromethane) | $CCl_3F$ | 137.38 | 23.7 | | X/X | |
| Acrylonitrile | | | | | | |
| Vinylidene chloride (1,1-Dichloroethene) | $C_2H_2Cl_2$ | 96.95 | 31.7 | | X/X | 75-35-4 |
| Dichloromethane (Methylene chloride) | $CH_2Cl_2$ | 84.94 | 39.8 | | X/X | 75-09-2 |
| Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane) | $CF_2ClCCl_2F$ | 187.38 | 47.7 | | X/X | |
| Trans-1,2-Dichloroethylene | | | | | /X | |
| 1,1-Dichloroethane | $CH_3CHCl_2$ | 98.96 | 57.3 | | X/X | 74-34-3 |
| Methyl *tert*-Butyl Ether | | | | | /X | |
| 2-Butanone Methyl Ethyl Ketone | | | | | /X | |
| Chloroprene | | | | | /X | |
| cis-1,2-Dichloroethylene | $CHCl=CHCl$ | 96.94 | 60.3 | | X/X | |
| Bromochloromethane | | | | | /X | |
| Chloroform (Trichloromethane) | $CHCl_3$ | 119.38 | 61.7 | | X/X | 67-66-3 |
| Ethyl tert-Butyl Ether | | | | | X/X | |
| 1,2-Dichloroethane (Ethylene dichloride) | $ClCH_2CH_2Cl$ | 98.96 | 83.5 | | X/X | 107-06-2 |
| Methyl chloroform (1,1,1,-Trichloroethane) | $CH_3CCl_3$ | 133.41 | 74.1 | | X/X | 71-55-6 |
| Benzene | $C_6H_6$ | 78.12 | 80.1 | | X/X | 71-43-2 |
| Carbon tetrachloride (Tetrachloromethane) | $CCl_4$ | 153.82 | 76.5 | | X/X | 56-23-5 |
| Tert-Amyl Methyl Ether | | | | | /X | |
| 1,2-Dichloropropane (Propylene dichloride) | $CH_3CHClCH_2Cl$ | 112.99 | 96.4 | | X/X | 78-87-5 |
| Ethyl Acrylate | | | | | /X | |
| Trichloroethylene (Trichloroethene) | $ClCH=CCl_2$ | 131.29 | 87 | | X/X | 79-01-6 |
| Methyl Methacrylate | | | | | X/X | |
| cis-1,3-Dichloropropene (cis-1,3-dichloropropylene) | $CH_3CC=CHCl$ | 110.97 | 76 | | X/X | |
| Methyl Methacrylate | | | | | /X | |
| trans-1,3-Dichloropropene (trans-1,3-Dichloropropylene) | $ClCH_2CH=CHCl$ | 110.97 | 112.0 | | X/X | |
| 1,1,2-Trichloroethane (Vinyl trichloride) | $CH_2ClCHCl_2$ | 133.41 | 113.8 | | X/X | 79-00-5 |
| Toluene (Methyl benzene) | $C_6H_5CH_3$ | 92.15 | 110.6 | | X/X | 108-88-3 |
| Dibromochloromethane | | | | | /X | |
| 1,2-Dibromoethane (Ethylene dibromide) | $BrCH_2CH_2Br$ | 187.88 | 131.3 | | X/X | 106-93-4 |
| n-Octane | | | | | X/X | |
| Tetrachloroethylene (Perchloroethylene) | $Cl_2C=CCl_2$ | 165.83 | 121.1 | | X/X | 127-18-4 |
| Chlorobenzene | $C_6H_5Cl$ | 112.56 | 132.0 | | X/X | 108-90-7 |
| Ethylbenzene | $C_6H_5C_2H_5$ | 106.17 | 136.2 | | X/X | 100-41-4 |
| m-Xylene (1,3-Dimethylbenzene) | $1,3\text{-}(CH_3)_2C_6H_4$ | 106.17 | 139.1 | | X/X | |
| p-Xylene (1,4-Dimethylxylene) | $1,4\text{-}(CH_3)_2C_6H_4$ | 106.17 | 138.3 | | X/X | |
| Styrene (Vinyl benzene) | $C_6H_5CH=CH_2$ | 104.16 | 145.2 | | X/X | 100-42-5 |
| 1,1,2,2-Tetrachloroethane | $CHCl_2CHCl_2$ | 167.85 | 146.2 | | X/X | 79-34-5 |
| o-Xylene (1,2-Dimethylbenzene) | $1,2\text{-}(CH_3)_2C_6H_4$ | 106.17 | 144.4 | | X/X | |
| 4-Ethyltoluene | $C_9H_{12}$ | 120.19 | 162 | 3 mm Hg | X | 622–96–8 |
| 1,3,5-Trimethylbenzene (Mesitylene) | $1,3,5\text{-}(CH_3)_3C_6H_6$ | 120.20 | 164.7 | | X/X | 108-67-8 |
| 1,2,4-Trimethylbenzene | $1,2,4\text{-}(CH_3)_3C_6H_6$ | 120.20 | 169.3 | | X/X | 95-63-6 |
| m-Dichlorobenzene (1,3-Dichlorobenzene) | $1,3\text{-}Cl_2C_6H_4$ | 147.01 | 173.0 | | X/X | 541-73-1 |
| Chloromethylbenzene | | | | | /X | |
| Benzyl chloride (α-Chlorotoluene) | $C_6H_5CH_2Cl$ | 126.59 | 179.3 | | X | 100-44-7 |
| o-Dichlorobenzene (1,2-Dichlorobenzene) | $1,2\text{-}Cl_2C_6H_4$ | 147.01 | 180.5 | | X/X | 95-50-1 |
| p-Dichlorobenzene (1,4-Dichlorobenzene) | $1,4\text{-}Cl_2C_6H_4$ | 147.01 | 174.0 | | X/X | 106-46-7 |
| 1,1,2,3,4,4–Hexachloro–1,3-butadiene | $Cl_6C_4$ | 260.76 | 215 | | X | 7-68-3 |
| 1,2,4 - Trichlorbenzene | | | | | /X | |

EPA 625/R-96/010b Compendium of Methods for the Determination to Toxic Organic Compounds in Ambient Air, Second Edition, Compendium Method TO-15

## 3. Terminology

3.1 *Definitions*—For definitions of terms used in this standard, refer to Terminology D1356. 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, n*—*Pg* + *Pa*, where *Pg* = gauge pressure in the canister; (kPa) and *Pa* = barometric pressure.

3.2.2 *absolute pressure, n*—pressure measured with reference to absolute zero pressure (as opposed to atmospheric pressure), expressed as kPa.

3.2.3 *cryogen, n*—a refrigerant used to obtain very low temperatures in the cryogenic trap of the analytical system. Typical cryogens are liquid argon (bp –185.7°C) and liquid nitrogen (bp –195°C).

3.2.4 *dynamic calibration, n*—calibration of an analytical system using calibration gas standards generated by diluting compressed gas standards of known concentration with purified, humidified inert gas. Calibration standards are introduced into the inlet of the sampling or analytical system in the same manner as authentic field samples.

3.2.4.1 *Discussion*—An example is dilution of compressed gas standards into canisters followed by analysis of these canisters.

3.2.5 *gauge pressure, n*—pressure measured above ambient atmospheric pressure (as opposed to absolute pressure). Zero gauge pressure is equal to ambient atmospheric (barometric) pressure.

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

3.2.6.1 *Discussion*—This procedure serves for both qualitative identification and quantitation of VOCs in the sample.

3.2.7 *MS-SIM, n*—the GC is coupled to a MS programmed to acquire data for only specified ions (for example, Table 2) and to disregard all others. This is termed selected ion monitoring (MS-SIM). The MS-SIM analysis provides quantitative results for VOCs that are preselected by the user.

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

3.2.9 *qualitative accuracy, n*—the ability of an analytical system to correctly identify compounds.

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

3.2.11 *static calibration, n*—calibration of an analytical system using standards in a form that is different than the form of the samples to be analyzed.

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

3.2.12 *subatmospheric sampling, n*—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.

3.2.12.1 *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.

3.2.13 *verification, n*—the process of demonstrating with humid zero air and humid calibration gases that the sampling system components and the canister do not contribute positive or negative bias to the analysis results.

## 4. Summary of Test Method

4.1 The method is taken from published work (**1-22**) and is the basis of EPA Compendium Methods TO-14A and TO-15. 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 determine the concentrations of selected VOCs in ambient air (**13**, **14**).

4.2 Both subatmospheric pressure and pressurized sampling modes using a passivated, evacuated canister are described.

4.2.1 Procedures are provided for canister cleaning and performance evaluation.

4.2.2 A sampling line less than 2 % of the volume of the canister, or a pump-ventilated sample line, is used during sample collection. A sample of air is drawn through a sampling train consisting of components that regulate the rate and duration of sampling into a pre-cleaned and pre-evacuated canister.

4.2.3 Pressurized sampling requires an additional pump to provide positive pressure to the canister.

4.3 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.

4.4 Upon receipt at the laboratory, the data on the canister tag are recorded and the canister is attached to a pressure gauge to accurately measure the final canister pressure.

4.5 For analysis, VOCs are concentrated by collection in a trap with or without cryogenic cooling. 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 a flame ionization detector (FID) or an electron capture detector (ECD). Both compound identification and quantitation are performed with this test method. For the purposes of this test method, refer to Practice E355 for terms and practices used in gas chromatography.

4.6 The analytical procedure can be automated (**15-17**) or manual (**18**).

**TABLE 2 Primary and Secondary Ions for Selected VOCs Analyzed by GC-MS**

| Compound[A] | m/z (Primary) | m/z Secondary (amu/% base peak) |
|---|---|---|
| Freon 12 (Dichlorodifluoromethane) | 85 | 87(31) |
| Methyl chloride (Chloromethane) | 50 | 52(34) |
| Freon 114 (1,2-Dichloro-1,1,2,2- tetrafluoroethane) | 85 | 135(56) and 87(33) |
| Vinyl chloride (Chloroethene) | 62 | 27(125) and 64(32) |
| 1,3-Butadiene | 54 | 39(89) |
| Methyl bromide (Bromomethane) | 94 | 96(85) |
| Ethyl chloride (Chloroethane) | 64 | 29(140 and 27(140) |
| Freon 11 (Trichlorofluoromethane) | 101 | 103(67) |
| Acrylonitrile | 53 | 52(85) |
| Vinylidene chloride (1,1-Dichloroethylene) | 61 | 96(55) and 63(31) |
| Dichloromethane (Methylene chloride) | 49 | 84(65) and 86(45) |
| Freon 113 (1,1,2-Trichloro-1,2,2- trifluoroethane) | 151 | 101(140) and 103(90) |
| 1,1-Dichloroethane | 63 | 27(64) and 65(33) |
| Trans-1,2-Dichloroethene | 96 | 61(98) |
| Methyl tert-Butyl Ether | 73 | 57(26) |
| Chloroprene | 53 | 88(63) and 90(21) |
| cis-1,2-Dichloroethene | 61 | 96(60) and 98(44) |
| Chloroform (Trichloromethane) | 83 | 85(65) and 47(35) |
| Ethyl tert-Butyl Ether | 59 | 87(44) and 57(33) |
| 1,2-Dichloroethane (Ethylene dichloride) | 62 | 27(70) and 64(31) |
| Methyl chloroform (1,1,1-Trichloroethane) | 97 | 99(64) and 61(61) |
| Benzene | 78 | 77(25) and 50(35) |
| Carbon tetrachloride (Tetrachloromethane) | 117 | 119(97) |
| Tert-Amyl Methyl Ether | 73 | 87(27) |
| 1,2-Dichloropropane (Propylene dichloride) | 63 | 41(90) and 62(70) |
| Ethyl Acrylate | 55 | 99(8) |
| Bromodichloromethane | 83 | 85(64) and 129(14) |
| Trichloroethylene (Trichloroethene) | 130 | 132(92) and 95(87) |
| Methyl Methacrylate | 41 | 69(26) and 100(8) |
| cis-1,3-Dichloropropene | 75 | 39(70) and 77(30) |
| Methyl Isobutyl Ketone | 75 | 39(70) and 77(30) |
| trans-1,3-Dichloropropene | 75 | 39(70) and 77(30) |
| 1,1,2-Trichloroethane (Vinyl trichloride) | 97 | 83(90) and 61(82) |
| Toluene (Methyl benzene) | 91 | 92(57) |
| Dibromochloromethane | 129 | 127(19) and 131(6) |
| 1,2-Dibromoethane (Ethylene dibromide) | 107 | 109/96 and 27(115) |
| Octane | 43 | 85(51) and 114(4) |
| Tetrachloroethylene (Perchloroethylene) | 166 | 164(74) and 131(60) |
| Chlorobenzene | 112 | 77(62) and 114(32) |
| Ethylbenzene | 91 | 106(28) |
| m,p-Xylene (1,3/1,4-dimethylbenzene) | 91 | 106(40) |
| Bromoform | 173 | 171(51) and 175(49) |
| Styrene (Vinyl benzene) | 104 | 78/60 and 103/49 |
| 1,1,2,2-Tetrachloroethane | 83 | 85(64) |
| o-Xylene (1,2-Dimethylbenzene) | 91 | 106(40) |
| 4-Ethyltoluene | 105 | 120(29) |
| 1,3,5-Trimethylbenzene (Mesitylene) | 105 | 120(42) |
| 1,2,4-Trimethylbenzene | 105 | 120(42) |
| m-Dichlorobenzene (1,3-Dichlorobenzene) | 146 | 148(65) and 111(40) |
| Benzyl chloride (-Chlorotoluene) | 91 | 126(26) |
| p-Dichlorobenzene (1,4-Dichlorobenzene) | 146 | 148(65) and 111(40) |
| o-Dichlorobenzene (1,2-Dichlorobenzene) | 146 | 148(65) and 111(40) |
| 1,2,4-Trichlorobenzene | 180 | 182(98) and 184(30) |
| Hexachlorobutadiene (1,1,2,3,4,4-Hexachloro- 1,3-butadiene) | 225 | 227(66) and 223(60) |

[A] In typical retention time order using a dimethylpolysiloxane-phase column

4.7 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.

4.7.1 *Comparison of GC/MS Technologies:*

4.7.1.1 *GC/MS–SCAN:*

*(1)* Lower sensitivity than GC/MS-SIM,

*(2)* Greater sample volume may be required compared to GC/MS-SIM,

*(3)* Resolution of co-eluting interfering ions is possible,

*(4)* Positive target compound identification,

*(5)* Positive non-target compound identification possible,

*(6)* Quantitative determination of calibrated compounds, and

*(7)* Qualitative and semiquantitative determination of compounds not on calibration list.

4.7.1.2 *GC/MS-SIM:*

*(1)* Can't identify non-target compounds,

*(2)* Less operator interpretation,

*(3)* Higher sensitivity than GC/MS–SCAN,

*(4)* Less sample volume required to obtain same MDLs compared to GC/MS-Scan, and

*(5)* Quantitative determination of calibrated compounds.

4.7.1.3 *GC/TOF MS:*

*(1)* Positive target compound identification,

*(2)* Positive non-target compound identification possible,

*(3)* Resolution of co-eluting interfering ions is possible and superior to GC-MS-Scan,

*(4)* Sensitivity is equal to GC/MS-SIM mode, or better,

*(5)* Less sample volume required to obtain same MDLs compared to GC/MS-Scan,

*(6)* Quantitative determination of calibrated compounds, and

*(7)* Qualitative determination of compounds not contained on calibration list.

4.7.2 The GC/MS–Scan option uses a capillary column GC coupled to a MS operated in a scanning mode which repeatedly acquires a wide mass range of ion data; the acquired mass spectra are supported by spectral library search routines. The GC/TOF MS option uses a capillary column GC coupled to a TOF MS which acquires wide mass range of ion fragment data continuously; the mass spectra are supported by library search routines. These options allow unambiguous compound identification and cover a wide range of compounds as defined by the completeness of the spectral libraries, with GC/TOF MS providing greater sensitivity in most cases. GC/MS-SIM mode is limited to a set of user-selected target compounds; this mode 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. Maximum sensitivity for GC/MS-SIM is achieved when no more than 4 to 5 ions are monitored simultaneously.

## 5. Significance and Use

5.1 VOCs are emitted into ambient, indoor, and workplace air from many different sources. These VOCs are of interest for a variety of reasons including participation in atmospheric chemistry and acute or chronic human health impacts.

5.2 Canisters are particularly well suited for the collection and analysis of very volatile and volatile organic compounds. This test method describes the collection and analysis of whole gas samples and is not subject to high volatility limitations.

5.3 Chemically stable selected VOCs have been 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 through replicate analyses of the same sample by one or several analytical systems, and (*8*) sample collection using a vacuum regulator flow controller if electricity is not available.

5.4 Interior surfaces of the canisters may be treated by any of several proprietary passivation 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 For this standard, VOCs are defined as organic compounds that can be quantitatively recovered from the canisters having a vapor pressure greater than $10^{-2}$ kPa at 25°C and 760 mm Hg.

5.6 Target compound polarity is also a factor in compound recovery. Aliphatic and aromatic hydrocarbons from C1 to C13 have been successfully measured with this standard but are not listed in Table 1 (**21**). Higher polarity target compounds may interact with the canister surface or humidity on the canister surface causing their apparent vapor pressure to decrease. Polar VOCs such as ethers and esters have been successfully measured by this method and are listed in Table 1.

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

## 6. Interferences and Limitations

6.1 Water 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 (for example dehydration traps). The water can restrict and even stop the sample air flow, alter chromatography and GC retention times, remove dissolved polar species and adversely affect the operation of detector systems, especially mass spectrometric systems. In-line permeable membrane dryers have historically been used prior to preconcentration and do not produce artifacts for a number of nonpolar VOCs (**19, 20**). However, in-line permeable dryers may contribute to the loss of polar species as these species may also partition with the water vapor. 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 (**21**).

6.2 For those applications where a membrane dryer is used, interferences can occur in sample analysis if moisture accumulates in the dryer (see 10.1.1.3). This can be avoided by ensuring flow rates of the drying gas are high (for example 5 to 10 times the sample flow rate) and the drying gas has a dew point <–50°C. In extreme circumstances, an automated cleanup procedure that periodically heats the dryer to about 100°C while purging with zero air or an inert gas (such as $N_2$ or He) can help to remove moisture buildup. This procedure does not degrade sample integrity.

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

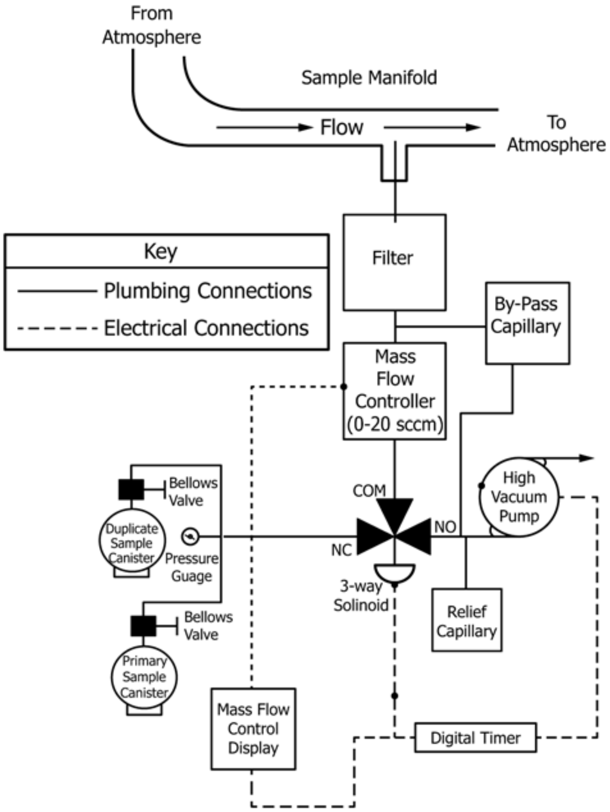


FIG. 1 Example Sampler Configuration for Subatmospheric Pressure Canister Sampling

6.3 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) shall be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples. Instructions for cleaning the canisters and 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.

6.4 If the concentrator-GC/MS analytical system employs a permeable membrane dryer or equivalent to remove water vapor selectively from the sample stream, polar organic compounds will permeate this membrane concurrently with the water. Consequently, the analyst shall calibrate the system with the target VOCs. For quantitative analysis of polar compounds, analytical systems shall not employ permeable membrane dryers.

6.5 The analysis methodology is based upon the identification of a VOC by comparison of its chromatographic retention time and mass spectrum to the retention time and mass spectrum of a pure standard run on the same system using the same analytical conditions. Quantitation is based on pure standard calibrations. Any elements of the air matrix that interfere with the ability to identify the mass spectrum, obtain accurate peak areas, or obtain an accurate retention time of a VOC will affect the performance of the analysis. High concentration interfering compounds generate distorted chromatographic peaks and may affect detector response. Dilution or smaller sample injection size may resolve retention time uncertainty but may adversely affect the method sensitivity. If a co-eluting compound is encountered, the mass spectrum may allow deconvolution of compounds unless the co-eluting compound is an isomer of the compound of interest or the characteristic masses of the interferents and the target compound are the same. Reanalysis of the sample on a different chromatographic column may aid in measurement of target and interfering VOC.

## 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 evaluated for VOC testing in air (**8-10**). Several configurations of standard hardware can be used successfully as canister sampling units.

7.2.1 *Subatmospheric Pressure* (see Fig. 1).

7.2.1.1 *Inlet Line,* stainless steel tubing to connect the sampler to the sample inlet.

7.2.1.2 *Canister,* leak-free stainless steel pressure vessels of desired volume (for example, 6 L), with valve and passivated interior surfaces.

7.2.1.3 *Vacuum/Pressure gauge,* capable of measuring vacuum (–100 to 0 kPa) and pressure (0 to 200 kPa) in the sampling system. Gauges shall be tested clean and leak tight.

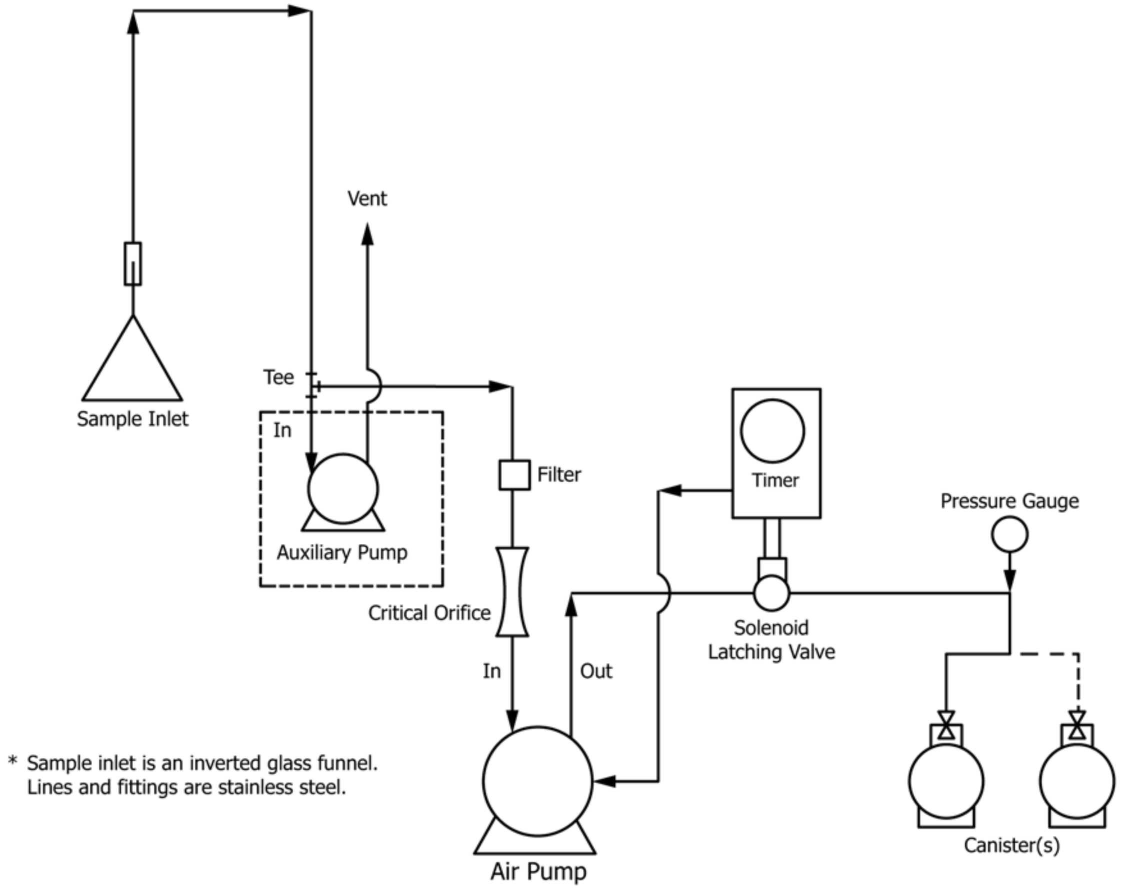


**FIG. 2 Alternative Sampler Configuration for Pressurized Canister Sampling**

7.2.1.4 *Mass Flow Meter and Controller,* capable of maintaining a constant flow rate (±10 %) over a sampling period of up to 24 h and under conditions of changing temperature (20 to 40°C) and humidity.

7.2.1.5 *Filter,* 2-µm sintered stainless-steel in-line filter.

7.2.1.6 *Electronic Timer,* capable of activating a solenoid valve (see 7.2.1.7) to start and stop flow entering a canister, for example, for unattended sample collection.

7.2.1.7 *Solenoid Valve,* electrically operated, latching solenoid valve with fluoroelastomer seat and o-rings, or low temperature solenoid valve with fluoroelastomer seat and o-rings

7.2.1.8 *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.

7.2.1.9 *Heater,* thermostatically controlled to maintain temperature inside insulated sampling enclosure above ambient temperature if needed.

7.2.1.10 *Fan,* for cooling sampling system, if needed.

7.2.1.11 *Thermostat,* automatically regulates fan operation, if needed.

7.2.1.12 *Maximum-Minimum Thermometer,* records highest and lowest temperatures during sampling period.

7.2.1.13 *Shut-Off Valve,* stainless steel—leak free, for vacuum/pressure gauge.

7.2.1.14 *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 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 volume represents less than 5 % of the final sample volume.

7.2.1.15 *Elapsed Time Meter,* capable of measuring the duration of sampling to the nearest second.

7.2.1.16 *Optional Fixed Orifice, Capillary, Adjustable Micrometering Valve, or Vacuum Regulator Manual Flow Controllers,* 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 consume 60 % or less of the total capacity of the canister used for collection. Typically this limits the sample duration to a maximum of 24 h per 6 L canister or 72 h per 15 L canister.

7.2.2 *Pressurized Sampling Apparatus,* see Fig. 2.

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

**TABLE 3 Preconcentration, GC, and MS Operating Condition Guidelines**

| System Component | | | Alternative System Description |
|---|---|---|---|
| Preconcentrator | | Electrically cooled/Non Cryogen systems | Cryogen systems |
| | Focusing trap packing | Multibed trap (for example, porous polymer/ graphitized carbon black/carbon molecular sieve) | |
| | Trap low temperature | –40 to 25°C | –150 to –178°C |
| | Trap high temperature | 280°C | 200°C |
| | Flow path temperature | 160°C | |
| Chromatography Column | | 60-m × 0.32-mm I.D. (1 to 1.8 µm film thickness) cyanopropylphenyl-dimethylpropylsiloxane | 50-m × 0.32-mm I.D. (17 µm film thickness) crosslinked 100 % dimethylpolysiloxane |
| Carrier Gas | | Constant pressure 68.9 kPa | Helium (2.0 cm$^3$/min at 250°C) |
| GC Oven Temperature Program | | | |
| | Initial Column Temperature | 35 to 40°C | –50°C |
| | Initial Hold Time | 5 mins | 2 min |
| | Program | 5 to 8°C/min to 220°C | 8°C/min to 220°C |
| | Final Hold Time | 5 min | 5 min |
| Mass Spectrometer | | | |
| | Mass Range | | |
| | Scan Time | | |
| | EI Condition | 70 eV | |
| | Mass Scan | Follow manufacturer's instruction for selecting | |
| | Detector Mode | mass selective detector (MS) and selected ion | |
| | Scan Time | monitoring (MS-SIM) mode | |
| | EI Condition | Multiple ion detection | |

NOTE 2—Several sampling systems have been developed that result in pressurizing a canister with sample air. The system illustrated in Fig. 2 uses an auxiliary vacuum pump to flush the sample inlet. A non-contaminating air pump pulls air from the inlet tubing, through a critical orifice that regulates the flow into the canister.

7.2.2.2 *Other Supporting Materials,* all other components of the pressurized sampling system are similar to components discussed in 7.2.1.1 – 7.2.1.16.

7.3 *Sample Analysis Equipment:*

7.3.1 *GC/MS-Analytical System (Full Mass Range Data Acquisition and MS-SIM):*

7.3.1.1 The GC/MS-SCAN analytical system shall be capable of acquiring and processing data in the MS–SCAN mode. The GC/MS-SIM analytical system shall be capable of acquiring and processing data in the MS-SIM mode.

7.3.1.2 *Gas Chromatograph,* including standard features such as gas flow regulators, automatic control of valves and oven parameters, etc. Sub ambient temperature programming is optional.

7.3.1.3 *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.

7.3.1.4 *Thermal Desorber/Preconcentrator,* refer to 10.1.1.4 for complete description of the system. Thermal desorbers /preconcentration devices may be added to the GC/MS system or built into the GC by the manufacturer.

7.3.1.5 Complete cryogenic concentrator units are commercially available from several vendors. The characteristics of current concentrators include rapid, "ballistic" heating of the concentrator to release trapped VOC's into a small carrier gas volume. This facilitates the separation of compounds on the gas chromatographic column.

7.3.1.6 *Electronic Mass Flow Controllers,* to maintain constant flow for carrier gas and sample gas and to continuously monitor flow rates.

7.3.1.7 *Vacuum Pump,* general purpose laboratory pump, capable of drawing the desired sample volume through the thermal desorber/preconcentrator.

7.3.1.8 *Chromatographic Grade Stainless Steel Tubing and Stainless Steel Plumbing Fittings,* Refer to 7.2.1.8 for description.

7.3.1.9 *Chromatographic Column* (see Table 3), to provide compound separation.

NOTE 3—Columns other than those in Table 3 (for example, 6 % cyanopropylphenyl/94 % dimethylpolysiloxane) can be used as long as the system meets user needs. Wider megabore columns (that is, greater than 0.530 mm I.D.) are less susceptible to plugging as a result of trapped water, thus potentially eliminating the need for a permeable membrane dryer or other water management procedures in the analytical system. These columns have 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.). Multibed sorbent traps, cold trap dehydration or microscale purge and trap techniques for moisture management in conjunction with 0.32 mm I.D. columns have also been used with no plugging from water.

7.3.1.10 *Stainless Steel Vacuum/Pressure Gauge (optional),* capable of measuring vacuum (–100 to 0 kPa) and pressure (0–200 kPa) in the sampling system. Gauges shall be tested clean and leak tight.

7.3.1.11 *Cylinder Pressure Stainless Steel Regulators,* two-stage cylinder regulators with pressure gauges for helium, zero air, nitrogen, and hydrogen gas cylinders as needed.

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

7.3.1.13 *Low Dead-Volume Tee or Press Fit Splitter (optional),* used to split the exit flow from the GC column.

7.3.1.14 *Dryer (optional),* consisting of permeable membrane tubing coaxially mounted within larger tubing, available commercially. Refer to 10.1.1.3 for description.

7.3.1.15 *Six-Port Gas Chromatographic Valve.*

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

7.4.1 *Vacuum Pump,* capable of evacuating sample canister(s) to an absolute pressure of less than 0.0064 kPa.

7.4.2 *Manifold,* made of stainless steel with connections for simultaneously cleaning several canisters.

7.4.3 *Shut-Off Valve(s),* on-off toggle valves.

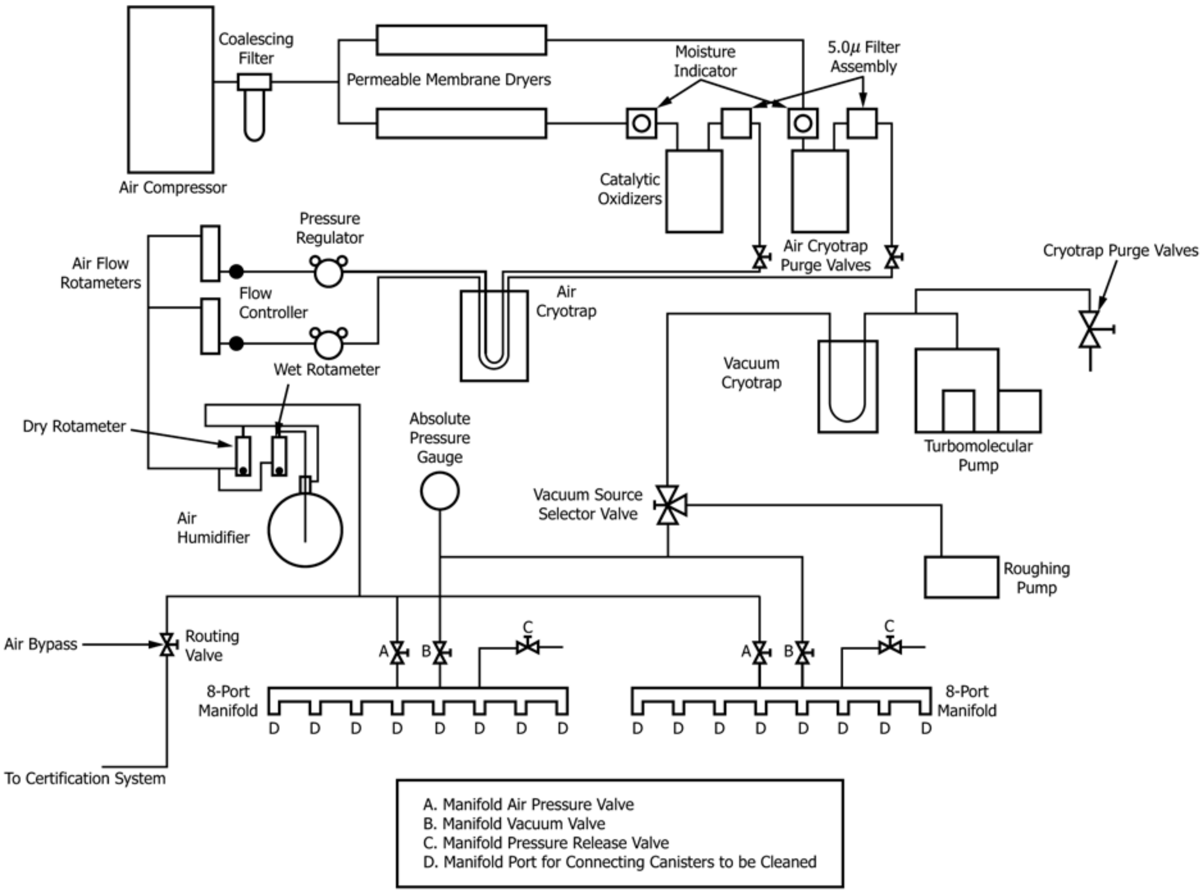


**FIG. 3 Canister Cleanup Apparatus**

7.4.4 *Stainless Steel Vacuum Gauge,* capable of measuring vacuum in the manifold to an absolute pressure of 0.0064 kPa, or less.

7.4.5 *Cryogenic Trap required only for those system using oil-based vacuum pumps or gases that are not sufficient to meet blank criteria),* 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).

7.4.6 *Stainless Steel Pressure Gauges (2),* 0 to 350 kPa to monitor zero air pressure.

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

7.4.8 *Humidifier,* consisting of pressurizable water bubbler, (typically a passivated canister with or without a dip tube and dual valves). Humidifier contains high performance liquid chromatography (HPLC) grade deionized water.

7.4.9 *Isothermal Oven (optional),* for heating canisters.

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

7.5 *Calibration System and Manifold (see Fig. 4):*

7.5.1 *Calibration Manifold,* 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.

7.5.2 *Humidifier,* 500-mL impinger flask containing HPLC grade deionized water or equivalent.

7.5.3 *Electronic Mass Flow Controllers,* to control flow of standard/diluent gas with acceptable flow ranges (for example, one 0 to 5 L/min, one 0 to 50 mL/min).

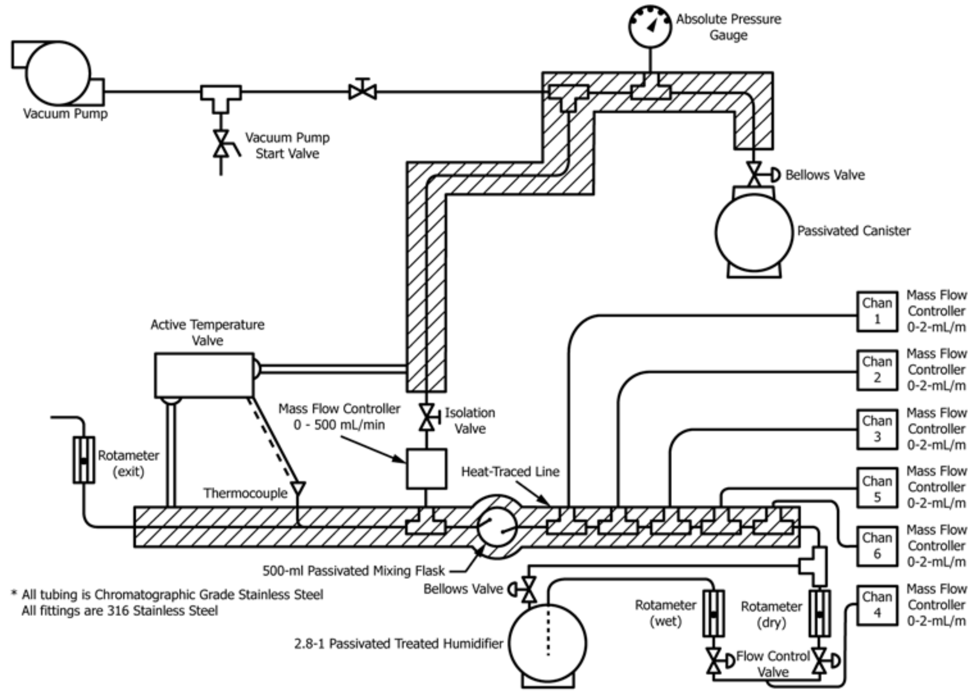
7.5.4 *PTFE–Fluorocarbon Filter(s),* 47-mm TFE–Fluorocarbon filter or sintered stainless steel filter capable of removing particulate matter greater than 2 µm in diameter.

## 8. Reagents and Materials

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

8.2 *Gas Calibration Standards*—cylinder(s) containing approximately 100 ppb to 1.0 ppm of each of the target VOCs. Candidate VOCs are shown in Table 2. Gas calibration standards shall be diluted with sufficient accuracy and precision to meet the performance requirements in this standard at concentrations down to five times the required method detection limit (MDL).

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



* All tubing is Chromatographic Grade Stainless Steel
All fittings are 316 Stainless Steel

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

8.3 *Liquid Nitrogen (bp −195.8°C),* used only for clean air traps and GC oven coolant, and for sample concentration traps requiring active control to maintain –185.7°C.

8.4 *Liquid Argon (bp −185.7°C),* for sample traps that are not actively controlled to –185.7°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 *4-4-Bromofluorobenzene,* used to check GC/MS tuning.

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.

9.1.1.1 In preparation for subatmospheric sample collection in a canister, the canister is evacuated to 0.0064 kPa, or less. When opened to the atmosphere containing the VOCs to be sampled, the differential pressure causes the sample to flow into the canister. Manual initiation and termination of canister sampling can be conducted using a filter, vacuum gauge, and mass flow controller or vacuum regulator connected directly to the canister inlet. The canister valve is manually opened to initiate sampling and closed after the duration is complete and canister is filled to approximately 88.1 kPa. 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.

9.1.1.2 With a critical orifice flow restrictor, the flow rate decreases as the canister pressure approaches atmospheric pressure. With a mass flow controller, the flow rate varies to compensate for reduced canister vacuum. 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 below ambient pressure.

9.1.2 *Pressurized Sampling*—See Fig. 2.

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 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 67 kPa.

NOTE 5—Collection of pressurized samples in humid environments may result in condensation of water in canisters. The presence of condensed water may decrease the recovery of polar compounds from the canister and adversely impact chromatography.

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 canister.

9.1.3 *All Samplers:*

9.1.3.1 A flow control device is used to maintain a relatively constant flow into the canister over the desired sample period. This flow rate is determined so the canister is filled (to about 88.1 kPa for subatmospheric pressure sampling or to about one atmosphere above ambient pressure for pressurized sampling) over the desired sample period. The flow rate can be calculated by:

$$F = \frac{(P \times V)}{(t \times 60)} \tag{1}$$

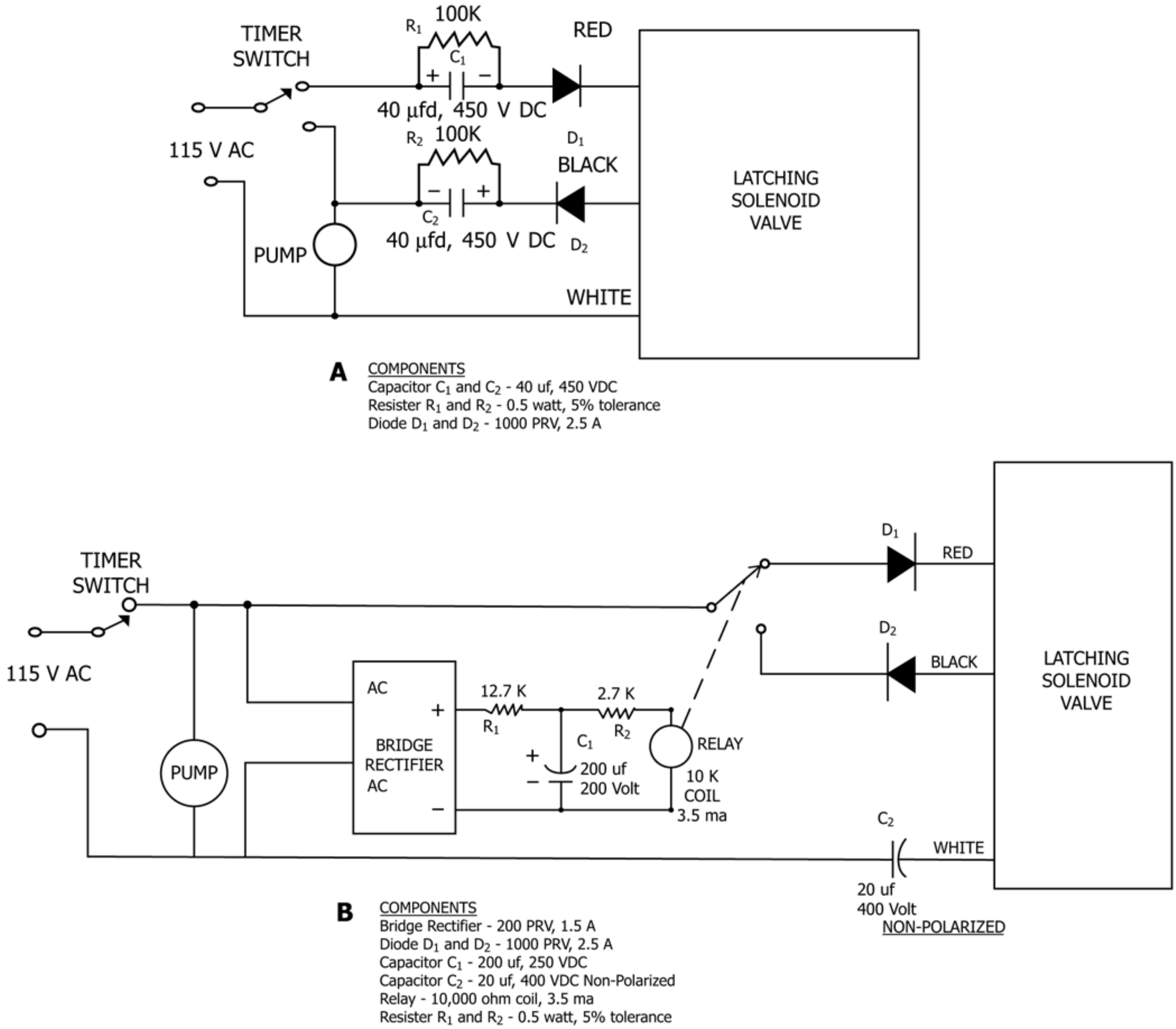


**FIG. 5 Electrical Pulse Circuits for Driving a Latching Solenoid Valve with a Mechanical Timer**

where:

$F$ = flow rate, mL/min,

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

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

$t$ = sample period, h (×60 min/h).

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

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

9.1.3.3 For automatic operation, the timer is programmed to start and stop the pump at appropriate times for the desired sample period. The timer shall also control the solenoid valve, to open the valve when starting the pump and to close the valve when stopping the pump.

9.1.3.4 The use of a latching solenoid valve, or low temperature valve, avoids a substantial temperature rise as will occur with a conventional solenoid that is energized throughout the entire sample period. The temperature rise in the valve can cause outgassing of organic compounds from the valve seat material and shall be avoided. The latching solenoid valve requires an electronic timer that can be programmed for short (5 to 60 s) "on" periods. Simple electrical pulse circuits for operating latching valves with a conventional mechanical timer 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 7.2.1.6) may be used to start the auxiliary pump prior to sampling and operate it for a sufficient period to flush and condition the inlet line.

9.1.3.7 Prior to use, each sampling system shall pass a humid zero air verification procedure (see 11.2). All plumbing shall be checked for leaks. The canisters shall meet verification requirements as outlined in 11.1 before use.

9.2 *Sampling Procedure:*

9.2.1 The sample canister shall be cleaned and tested according to the procedure in 11.1.

9.2.1.1 Immediately prior to sample collection, the canister pressure shall be checked for leaks. If leak tight, the pressure shall not vary more than ±13.8 kPa. Canisters failing this field leak check shall not be used for sample collection.

9.2.2 A sample collection system is assembled as shown in Fig. 1 (and Fig. 2) and shall meet verification requirements as outlined in 11.2.

NOTE 6—Sampling system shall be contained in an appropriate enclosure for ambient air sampling.

9.2.3 Prior to initiating a sampling program, samples collected over a short period of time can be used as "screening samples." The information gathered from the screening samples is used to determine the potential concentration range for analysis and to identify potential interferents with the GC/MS analysis. Sampling is performed using a simple sampler described in 7.2.1.16.

9.2.4 Immediately prior to any sample collection record the ambient temperature, humidity, and atmospheric 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. This function may be performed by the laboratory during equipment preparation prior to sending the equipment to the field. 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 ±10 %. If not, the sampler mass flow meter shall be recalibrated or the sampler shall 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 to the canister can be measured.

NOTE 9—Mass flow meter zero set points may drift. Check the zero reading and add or subtract the zero reading when reading or adjusting the sampling flow rate, to compensate for drift. Adjust the canister flow rate to the desired 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 rate.

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

NOTE 10—Any time the sampling system is turned off, wait at least 30 s before turning on the system.

9.2.7 Disconnect the "practice" canister and the certified mass flow meter. Attach a clean canister (see 11.1) to the system.

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

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

9.2.10 Close the vacuum/pressure gauge valve and reset the maximum/minimum thermometer to the 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, and current temperature of the sampler housing, if any, and the current ambient or indoor temperature. Record the current reading from the flow controller and the ambient or indoor humidity and pressure.

9.2.13 At the end of the sampling period, briefly open and close the vacuum/pressure gauge 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 sample may be suspect. This information shall be noted on the sampling 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—The procedure in 9.2.14 is not necessary if the initial and final canister vacuum pressures 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 (MS-SCAN and MS-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 or MS-SCAN mode) or to detect a limited number of ions in each of several segments of the analytical run, referred to as the selected ion monitoring or MS-SIM mode. Different types of mass spectrometric systems have different designations for selected ion monitoring. In full scan mode, the GC/MS acquires mass spectral data by continuously scanning a range of masses typically between 35 and 300 amu. A MS-SIM system is programmed to acquire data for only the target compounds and to disregard all others. The sensitivity of a MS-SIM system is typically 1 ppbv or better for a 500 mL air sample. The GC system is comprised of a GC equipped with a suitable column, (for example, as described in Table 3, 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 100 to 1000 mL) is recovered from the canister and routed to the analytical system. The sample air may be passed through a permeable membrane dryer; however, many polar compounds cannot be quantitated using this drying procedure. The sample is routed through a chromatographic valve, and the VOCs are concentrated on an electrically cooled (Peltier) or cryogenic trap. The trap is then heated rapidly to release the VOCS and backflushed to inject the VOCs onto the GC column. Concentrations of compounds based upon a previously installed calibration table is reported by an automated data reduction program.

10.1.1.2 MS-SIM analysis is based on a combination of chromatographic retention times and the relative abundances of selected primary and secondary ions (see Table 2) for the target VOCs. A minimum of one primary and one secondary ion are monitored for each target compound. The response parameters for each VOC peak are recorded and are compared to data obtained for the standard compound analyzed on the same system with the same GC and MS operating conditions. The acceptance level for retention time is determined to be, for example, ±0.10 min of the expected retention time of the compound. The acceptance level for relative abundance of a qualifier ions to the primary ion is determined to be, for example, ±20 % of the expected abundance. Any peak that fails any of the qualifying tests is flagged. All the data shall be manually examined by an experienced operator to determine the reason for the flag and whether the compound can be reported as found. Manual inspection of the quantitative results shall also be performed to verify concentrations outside the expected range. To realize the maximum sensitivity of MS-SIM, a retention time windows shall be selected for each compound or group of compounds so that a maximum of four ions are monitored during a scan.

10.1.1.3 An optional permeable membrane dryer may be used to remove water vapor selectively from the air sample stream. The permeable membrane consists of tubing 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 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 semipermeable membrane and outer tubing. To prevent excessive moisture build-up and any memory effects in the dryer, the drying gas flow rate is set at 5 to 10 times the sample gas flow rate. In extreme circumstances, a cleanup procedure involving periodic heating of the dryer (100°C for 20 min) while purging with dry zero air (500 mL/min) may be required. However, care must be taken when heating the dryer (**21**). Another method for drying the air sampling stream involves freezeout of water in a pre-trap followed by raising the temperature of the pre-trap and purging VOCs that move into the gas phase to a downstream trap while leaving most of the water behind. Removal of water with a permeable membrane-type dryer shall not be performed for compounds other than those listed in Table 1 unless recovery studies are performed to validate analysis of these compounds. Polar compounds are particularly susceptible to losses through the permeable membrane interface and by using freeze out techniques.

NOTE 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 response. 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.

10.1.1.4 Concentration of VOCs is typically performed using a sorbent trap that can be cooled using various techniques (Peltier or cryogen). Some systems allow concentration of target VOCs at ambient temperature using multiple sorbents in a trap and back flushing the VOCs with heating into the GC. The sorbent trap is constructed of an inert material, such as quartz, and is designed to facilitate high linear velocity through the trap during thermal desorption. The trap is heated rapidly at rates approaching 60°C/s using resistive heaters to ensure rapid release and transfer of VOCs. Other concentration devices may employ a nickel loop packed with a suitable sorbent.

10.1.1.5 Upon sample injection onto the column and any selected delay time, the MS computer is signaled by the GC computer to begin detection of compounds that 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 35 amu to a minimum of 300 amu and a minimum of 1.5 Hz repetition rate. Approximately, six full mass range data acquisitions 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 can be performed and a list the best matches for each peak can be generated.

10.1.1.6 As an option, the gas stream exiting the column may be split with a low dead-volume tee, passing a fraction of the sample gas stream to the mass selective detector and the remainder to FID. The use of the specific detector (MS-SCAN) coupled with the nonspecific detector FID provides additional data:

*(1)* Semi-real time picture of the progress of the analysis,

*(2)* FID has broader dynamic range than MS,

*(3)* Response may be more stable over time when using external standard calibration, and

*(4)* Simultaneous determination of hydrocarbons by FID for comparison to results obtained by other laboratories using only GC-FID.

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.

10.2.1.3 Challenge the GC/MS system with humid zero air (see 11.2.1). Results of this challenge shall indicate less than 5 times the MDL or less than 50 % of the project specific

**TABLE 4 4-Bromofluorobenzene Key Ions and Ion Abundance Criteria[A]**

| Target Mass | Rel. To Mass | Lower Limit % | Upper Limit % |
|---|---|---|---|
| 50 | 95 | 8 | 40 |
| 75 | 95 | 30 | 66 |
| 95 | 95 | 100 | 100 |
| 96 | 95 | 5 | 9 |
| 173 | 174 | 0 | 2 |
| 174 | 95 | 45 | 120 |
| 175 | 174 | 4 | 9 |
| 176 | 174 | 93 | 101 |
| 177 | 176 | 5 | 9 |

[A] All ion abundances shall be normalized to m/z 95,the nominal base peak, even though the ion abundance of m/z 174 may be up to 120 % that of m/z 95.

reporting limit requirement for each target compound or less than 50 % of the project specific data quality requirement for target compound quantitation.

10.2.2 *Daily GC/MS Tune Check:*

10.2.2.1 Prior to a calibration, tune the GC/MS system according to manufacturer's specifications if required. Verify the MS instrument performance by analyzing a 50 µg injection of 4-bromofluorobenzene (BFB) and comparing the response to the criteria in Table 4. This mass is recommended but may be altered based on the capabilities or requirements of the specific instrument. Also, prior to the beginning of each analytical sequence and every 24 hours during continuous GC/MS operation, demonstrate that the instrument meets the criteria in Table 4.

10.2.2.2 BFB 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 before sample analysis, a multipoint dynamic calibration (five concentrations) is performed. A calibration system is shown in Fig. 4. The calibration system uses NIST traceable standards or NIST/EPA CRMs in pressurized cylinders containing a mixture of the target VOCs in nitrogen (8.2) as working standards to be diluted with humid zero air. One approach to prepare calibration standards is to meter the working standard cylinder(s) into the heated mixing chamber where it is mixed with humidified zero air gas stream to achieve a compound calibration mixture (see Fig. 4). This nominal standard mixture is allowed to flow and equilibrate for a minimum of 2 h. After the equilibration period, the gas standard mixture is sampled with a canister and analyzed. Calibration ranges shall span the measured sample concentrations. An example calibration range is approximately 0.25, 0.5, 1, 2.5, 5, and 10 ppbv for each compound. Flow audits are performed on the calibration system mass flow meters, and the calculated concentrations are compared to the generated values. After the GC/MS is calibrated at five concentration levels, a humid zero air sample is passed through the system, sampled and analyzed. The humid zero air sample is used to verify that the GC/MS system is clean, that is, there is less than 5 times the MDL or less than 50 % of the project required reporting limit for each target compound or less than 50 % of the project specific data quality requirement for target compound quantitation.

NOTE 15—Alternative approaches for generation of calibration standards are acceptable as long as the calibration range spans the sample concentrations of interest and humidity is accurately maintained.

10.2.3.2 For both dynamic and static calibrations, the calculations are performed in the data system. Relative response factors are typically used assuming linear calibration responses. Response factors can be manually calculated to check automated calculations using Eq 3:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s} \tag{3}$$

where:

$A_s$ = peak area for the characteristic ion of the analyte,
$A_{is}$ = peak area for the characteristic ion of the internal standard,
$C_s$ = concentration of the analyte (ppbv), and
$C_{is}$ = concentration of the internal standard (ppbv).

10.2.3.3 *Relative Response Factor or Linear Calibration Fit*—The acceptance criteria (% RSD) for the relative response factor for each compound is 30 % or less with an exception of no more than 5 % of the total number of calibrated compounds above a limit of 40 %. The acceptance criteria using a linear model is a correlation coefficient, $r^2 \geq 0.995$.

10.2.3.4 *Non-Linear Calibration Fit Using an Internal Standard Approach*—Some VOCs will not be able to meet the performance requirements for a consistent average relative response factor or linear calibration. These VOCs may require the use of a quadratic calibration model. The user shall ensure that the use of the quadratic model is not the result of poor instrument performance but rather due to the characteristics of a specific compound or set of compounds.

10.2.3.5 *Routine Calibration Verification*—The GC/MS system calibration is verified daily prior to the beginning of sample analysis and every 24 hours thereafter during continuous GC/MS operation with a one-point second source calibration standard whose concentration is no more than 50 % of the initial highest calibration standard. Calibration verification analysis results shall agree within ±30 % of the known standard concentration with no more than two exceptions deviating by no more than ±40 %. Some compounds analyzed by this procedure may not meet the performance requirements. The use of statistically derived control limits that meet project quality requirements are an acceptable performance based alternative for routine calibration verification. After the single point calibration verification analysis, the GC/MS analytical system is challenged with a humidified zero gas stream to ensure the analytical system is clean, that is, less than 5 times the MDL or less than 50 % of the project required reporting limit for each target compound or less than 50 % of the project specific data quality requirement for target compound quantitation.

10.3 *Analytical Procedures:*

10.3.1 *Method Detection Limit (MDL):*

10.3.1.1 The MDL for this standard is the minimum concentration necessary to confirm the presence of a target compound with 99 % confidence. MDLs typically fall in the range of 0.01 to 0.1 ppbv.

10.3.1.2 Determine the MDL following the general approach described in 40 CFR Part 136 Appendix B, the Code of Federal Regulations.

10.3.1.3 Determine the MDL by analyzing a minimum of seven replicate canisters prepared with target concentrations as standards within a factor of five times the estimated MDL.

10.3.1.4 Calculate the MDL by multiplying the standard deviation of the replicate canister measurements by the appropriate student's t value for 99 % one-sided confidence interval for the degrees of freedom of the MDL study.

10.3.1.5 If the MDL calculated by this procedure is less than five times the lowest concentration standard used for the study, repeat the MDL study with a lower concentration standard.

10.3.1.6 MDLs include the uncertainty in a laboratory's ability to prepare replicate low level standards.

10.3.1.7 MDLs calculated as described assume that blank target concentrations are below the MDL. If a measurable blank concentration is consistently present in clean canisters, the effective detection limit is the sum of the average blank concentration and the calculated MDL.

10.3.2 *Canister Receipt:*

10.3.2.1 The overall condition of each received sample canister is observed. Each canister shall have an attached sample identification tag.

10.3.2.2 Each canister is recorded in a dedicated laboratory logbook or electronic information management system. The record shall indicate the date received and the individual who received the sample.

NOTE 16—A log containing the usage and history of each canister shall be kept. This historical record assists in ensuring that canisters used for source sampling or other high concentration VOC sampling are not mixed with canisters used for indoor or ambient air sampling. Canisters used for high level standards or to acquire high level VOC samples shall be flagged to receive individual blanking quality control checks after analysis or segregated for restricted use.

10.3.2.3 The pressure of the canister is checked by attaching a pressure gauge to the canister inlet. The canister valve is opened briefly and the pressure (kPa) is recorded.

NOTE 17—If pressure is <83 kPa, the canister may be pressurized, as an option, with zero grade nitrogen up to atmospheric pressure to ensure that enough sample is available for analysis. However, pressurizing the canister may introduce additional error and increase the MDL. Record final canister pressure.

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

$$DF = Y_a / X_a \tag{4}$$

where:

$X_a$ = canister pressure absolute before dilution, kPa, and
$Y_a$ = canister pressure absolute after dilution, kPa.

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

10.3.3 *GC/MS-SCAN and MS-SIM Analysis:*

10.3.3.1 When the MS is operated in the full scan mode all ions within a preset window are scanned. The characteristic mass spectra of compounds or group of compounds 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.

10.3.3.2 The analytical system shall be properly assembled. The instrument performance check standard, the daily calibration standard, and the humid air zero standard shall all meet their acceptance criteria before sample analysis may begin.

10.3.3.3 Check and adjust the mass flow controllers to provide correct flow rates for the system.

10.3.3.4 Connect the sample canister to the autosampler device attached to the GC/MS analytical system. Purge the sample lines with the sample to ensure that only the sample is collected and to remove any carrier gas from the prior leak test/post sampling line purge. Pressurized samples can also use a pump but it is not always necessary, for example, when sampling using a gas sample loop.

10.3.3.5 Several types of sample introduction are available: Loop, Mass Flow Controller (MFC) or Fixed Volume Reservoir.

*(1)* Loop sample introduction can be used with pressurized samples. A mass flow controller or other flow controlling device is placed on the canister, the canister valve is opened and the canister flow is vented through a bypass before the inlet to the analytical system. For example, use a flow of 75 mL/min so that the inlet system up to the loop sample injection valve is flushed with sample gas equal to seven (7) or more times the dead volume of the loop and connecting tubing (typically 40 mL).

*(2)* Mass Flow Controller introduction can be used with samples at or below atmospheric pressure. Purge canister samples using a pump and MFC positioned after the VOC focusing trap to control the flow. Sample flow from the canister is controlled to allow sample air to pass through the VOC concentration trap.

*(3)* Fixed Volume Reservoir introduction can be used with samples above, at or below atmospheric pressure. Sample flow from the canister is controlled to allow the sample to pass through the VOC concentration trap to an evacuated vessel. A pressure increase in the downstream reservoir is used to monitor and determine the sample volume pulled through the trap.

10.3.3.6 Set the GC oven and focusing trap to their initial method conditions (example shown in Table 3).

10.3.3.7 Sampling of VOCs from the canister begins when the focusing trap reaches its initial temperature set point.

10.3.3.8 The sample collection time depends upon the desired volume and the flow rate (if applicable); typically it requires ten minutes to collect a 500 mL sample.

NOTE 18—The gas volume used for analysis depends upon the sensitivity of the mass detection unit and the concentration of the target analytes in the sample.

10.3.3.9 After the sample is preconcentrated in the focusing trap, the valve moves to the inject position and the focusing trap is heated rapidly to desorb the VOCs onto the head of the capillary column. The GC oven program is started (see Table 3 for typical oven conditions).

10.3.3.10 Upon sample injection onto the column and including any delay time, MS data acquisition is initiated.

10.3.3.11 The VOC analyses are handled in three phases: data acquisition, data processing, and data reporting.

*(1)* In the MS-SCAN mode, the instrument acquires data from 35 amu to a minimum of 300 amu at a minimum 1.5 Hz scan rate. This rate corresponds to about 6 scans per eluting chromatographic peak. Primary VOC identifications are based upon retention times and relative abundances of eluting ions compared to data in a user-generated electronic library that is constructed by analysis of standards using the same operating conditions. Commercial mass spectral libraries can be used to tentatively identify unknown peaks.

*(2)* In the MS-SIM, the data acquisition software is set to monitor specific compound fragments at specific times in the analytical run.

10.3.3.12 The acquired data are automatically processed after data acquisition is completed at the end of the GC run. Resulting ion profiles are extracted, ion peaks are identified and integrated, and an integration report is internally generated. Other parameters such as time, date, and integration constants are included. A reconstructed total-ion-current chromatogram is generated for MS-SCAN analysis. The data reporting software may be automatically accessed at this time. The appropriate calibration table is retrieved and the processed retention times and response factors are applied to the macro program's integration file. With reference to pre-set acceptance criteria, peaks are automatically identified and quantified and a final summary report is prepared.

10.3.3.13 VOC concentrations (ppbv) are calculated using the previously established response factors (see 10.2.3.2).

NOTE 19—If the canister was diluted before analysis, the appropriate dilution factor is applied (10.3.2.4).

10.3.3.14 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 generated. Preconcentration systems may allow overlap of runs, for example, after a run has started, the preconcentration device can be preparing the next sample for collection. Once collected, the sample is ready for injection when the GC returns to run start conditions. Sequencing sample concentration in this manner can reduce the run-to-run time to less than 40 min.

## 11. Cleaning and Verification Procedures

11.1 *Canister Cleaning and Verification:*

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

11.1.2 All canisters shall be leak tested by pressurizing them to approximately 200 kPa with zero air.

NOTE 20—The canister cleaning system in Fig. 3 can be used for leak testing. 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 ±13.8 kPa over the 24-h period. Alternatively a vacuum leak check can be performed with an acceptance criterion of less than 0.7 kPa vacuum loss.

11.1.3 A canister cleaning system may be assembled as illustrated in Fig. 3. Cryogen is added to both the vacuum pump and the zero air supply traps. The canister(s) is 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. The vent shut-off valve is then closed and the vacuum shut-off valve is opened. The canister(s) is evacuated to less than 0.0064 kPa for at least one hour. Alternatively commercially available cleaning systems may be used; some do not require cryogen.

NOTE 21—On a daily basis, or more often as required, cryogenic traps shall be purged with zero air to remove trapped water from previous canister cleaning cycles.

11.1.4 The vacuum and vacuum/pressure gauge shut-off valves are closed and the zero air shut-off valve is opened to pressurize the canister(s) with humid zero air to approximately 200 kPa. If a zero gas generator system is used, the flow rate may need to be regulated 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 a minimum of two additional times for a total of at least three evacuation/pressurization cycles for each canister(s).

11.1.6 At the end of the evacuation/pressurization cycle, the canister(s) is pressurized to 200 kPa with humid zero air. Analyze each canister with the GC/MS or GC-FID-ECD analytical system. The results are compared to the direct analysis of humidified zero air, which has the requirement of less than 3 times the MDL or less than 50 % of the project required reporting limit for each target compound or less than 50 % of the project specific data quality requirement for target compound quantitation. A canister that does not meet the same requirement shall not be used. As a "blank" check of the canister(s) and the cleanup procedure, analyze the final humid zero air fill of 100 % of the canisters until the cleanup system and canisters are proven reliable (that is, less than 3 times the MDL for each target compound). This blank check may be reduced to one canister per batch of cleaned canisters after the blank criterion has been met on one entire batch.

11.1.7 Reattach the canister to the manifold and re-evacuate to less than 0.0064 kPa. Close the canister valve. Remove the canister from the cleaning system and cap the canister connection with a metal 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. Maintain 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 22—For sampling less volatile, 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. At the end of the heating/evacuation cycle, pressurize the canisters with humid zero air and analyze by the blank procedures in 11.1.6. Do not use any canister that is not clean based on the requirement of less than 5 times the MDL or less than 50 % of the project required reporting limit for each target compound or less than 50 % of the project specific data quality requirement for target compound quantitation. Once tested clean, re-evacuate the canisters to 0.0064 kPa, or less, and maintain them in the evacuated state until used. Repeated heating of canisters may degrade the treated interior surface and degradation of samples may ensue. Canisters that are repeatedly heat treated shall be periodically (yearly) checked to measure calibration standard stability

11.1.9 *Canister Verification:*

11.1.9.1 Before the first use and once every two years (24 months), evaluate canister performance by cleaning according to 11.1.3 – 11.1.8 and adding the lowest calibration standard gas or a calibration gas at 10 times the MDL for each target compound to the canister. Store the spiked canister for 14 days followed by analysis. Canister results greater than ±30 % of the spiked concentration fail the verification and require canister maintenance followed by retesting or canister retirement.

11.1.9.2 Perform a canister zero challenge test by retaining the canister prepared in 11.1.6, storing the canister for 14 days and reanalyzing the canister. Canister results greater than 120 % of the initial zero gas analysis fail the verification and require canister maintenance followed by retesting or canister retirement.

11.2 *Sampling System Verification:*

11.2.1 *Humid Zero Air Verification:*

11.2.1.1 The sampling system is "verified" to be clean if less than 5 times the MDL for each target compound or less than 10 % of the project specific data quality requirement for target compound quantitation is measured when the system is challenged with the humid zero air stream. The cleanliness of the sampling system is determined as follows:

11.2.1.2 The dynamic calibration system and manifold are assembled as illustrated in Fig. 4. The sampling system (with a clean, evacuated canister) is connected to the manifold and the zero air cylinder is activated to deliver a humid gas stream (2 L/min) to the manifold.

11.2.1.3 The humid zero gas stream passes through the manifold, through the sampling system and is collected in the canister. The canister is analyzed. If the analysis shows the sampling system passes the humid zero air test, the system is tested with humid calibration gas standards containing selected VOCs as outlined in 11.2.2.

11.2.2 *Humid Calibration Gas Standard Verification:*

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

NOTE 23—The calibration system manifold may become contaminated with verification compounds in the process of verifying the sampling system. Separate manifolds shall be used for zero air verification and humid calibration gas verification to avoid erroneous results caused by carryover. Alternatively, one manifold may be used provided that the manifold is demonstrated to be clean prior to the start of a verification test.

NOTE 24—Calibration system manifold components and flow regulators shall be heated during humid calibration gas standard verification to ensure complete vaporization of challenge gas components.

11.2.2.2 Demonstrate that the calibration system itself is clean (that is, less than 3 times the MDL of each target compound or less than 10% of the project specific data quality requirement for target compound detection) prior to starting the procedure.

11.2.2.3 For generating the humidified calibration standards, the calibration gas cylinder(s) (see 8.2) is attached to the calibration system. The gas cylinder is opened and the gas mixture is passed through 0 to 50 mL/min certified mass flow controllers to generate ppbv levels of calibration standards that are two to five times the reporting limit of each compound.

11.2.2.4 After an appropriate equilibration period, attach the sampling system (containing a verified evacuated canister) to the manifold, as illustrated in Fig. 4.

11.2.2.5 Sample the dynamic calibration gas stream with the sampling system according to 9.2.

11.2.2.6 Concurrent with the sampling system operation, a reference air sample is collected in a verified evacuated canister that is connected directly to a mass flow controller and the calibration gas feed line.

11.2.2.7 At the end of the sampling period (typically same time period as used for sampling), the sampling system canister is removed and analyzed. The results are compared to the results for the reference canister to determine if the concentration of the targeted VOCs were increased or decreased by the sampling system.

11.2.2.8 A recovery of between 85 % and 115 % is expected for the average of all targeted VOCs. Individual compounds shall fall within the range of 70 % and 130 % for acceptable verification.

11.2.3 Humid Zero Air Verification and Humid Calibration Gas Standard Verification shall be performed upon receipt or replacement of any major component of the sampling system and biannually thereafter for each sampling system.

## 12. Documentation, Proficiency Testing and Quality Assurance

12.1 *Standard Operating Procedures (SOPs):*

12.1.1 Each laboratory shall generate SOPs documenting the details of their systems and procedures that are not fully described in applicable standards. SOPS shall cover activities including: (*1*) assembly, calibration, leak checking, and operation of specific sampling systems including system descriptions, (*2*) cleaning, preparation, storage, shipment, and handling of canisters and air samples, (*3*) assembly, leak-checking, calibration, and operation of the analytical system, including descriptions of specific equipment, and (*4*) all aspects of data recording and processing, including lists of computer hardware and software.

12.1.2 SOPs shall document all modifications to equipment and procedures described in this and other applicable standards.

12.1.3 SOPs shall provide specific stepwise instructions. Laboratory personnel conducting the work shall be trained to the SOPs and shall have ready access these documents.

12.2 *Proficiency Testing:*

12.2.1 Bias for a laboratory's analysis of canister samples shall be determined by the analysis of audit canisters prepared by a third party, preferably an accredited standards provider, or by the analysis of canisters used to sample the gas from a NIST traceable audit cylinder (see 8.2). Dry gas audit samples shall be humidified before analysis. Percent relative bias is calculated as:

$$\%\ Relative\ Bias = \frac{(X - Y)}{X} \times 100 \tag{5}$$

where:

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

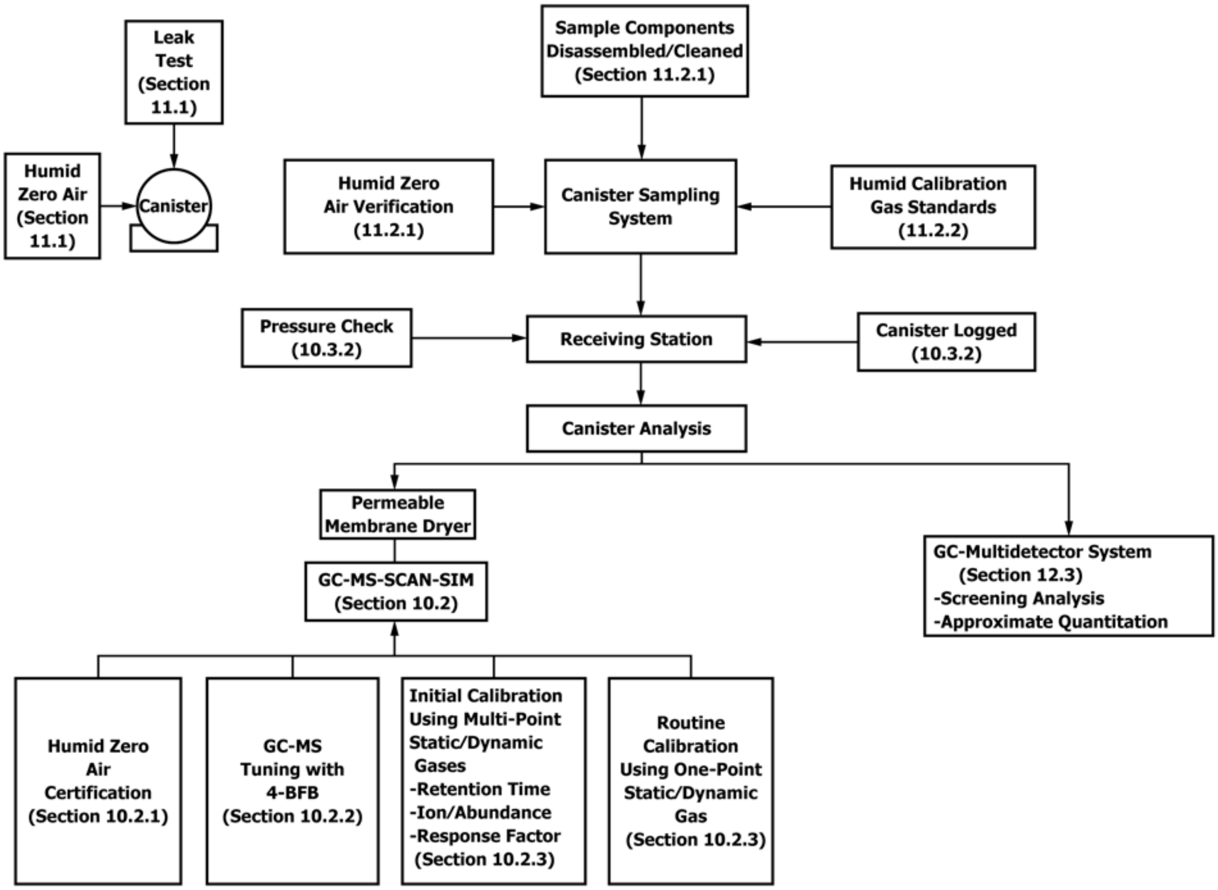


**FIG. 6 System Quality Assurance/Quality Control (QA/QC) Critical Components and Activities**

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

12.2.2 The canisters used for the determination of bias shall be analyzed in replicate (three or more analyses) to document analytical precision. Additionally, precision for the analysis of replicate samples drawn from a single canister sample of atmospheric air and for the analysis of replicate canister samples of atmospheric air shall be routinely determined and documented by the laboratory.

12.3 *Quality Assurance/Quality Control (See Flow Chart in Fig. 6):*

12.3.1 *Sampling System:*

12.3.1.1 Section 9.2 requires pre- and post-sampling measurements with a certified mass flow controller for flow verification of the sampling system. For subambient pressure samples, attaching a mass flow meter and recording the flow rate is not necessary if the initial and final canister vacuum are recorded.

12.3.1.2 Section 11.1 requires all canisters to be pressure tested to 200 kPa ± 14 kPa over a period of 24 h. Alternately, a vacuum leak check can be performed with an acceptance criterion of less than 0.7 kPa vacuum loss.

12.3.1.3 Section 11.1 requires that all canisters be verified to be clean (that is, less than 3 times the MDL or less than 50 % of the project required reporting limit for each target compound or less than 50 % of the project specific quality requirement for target compound quantitation).

12.3.1.4 Section 11.1.9 requires that all canisters initially and biannually be verified to be inert (that is, recover 70 % to 130 % of targeted VOCs spiked at the lowest calibration standard or 10 times the MDL) using a humid calibration gas standard.

12.3.1.5 Section 11.2.2 requires all sampling systems be verified to be initially clean (that is, contain less than 3 times the MDL or less than 50 % of the project required reporting limit for each target compound or less than 50 % of the project specific data quality requirement for target compound detection) through a humid zero air verification program.

12.3.1.6 Section 11.2.3 requires all sampling systems to pass an initial and biannual humidified calibration gas verification with a percent recovery of 70 % to 130 %.

12.3.2 *GC/MS-SCAN and GC/MS-SIM System:*

12.3.2.1 Section 10.2.1 requires the GC/MS analytical system be verified to be clean (that is, less than 3 times the MDL or 50 % of the project required reporting limit for each target compound or less than 50 % of the project specific data quality requirement for target compound quantitation) through a humid zero air verification.

**TABLE 5 Precision Results for Canister VOC Method (Example)**

| Compound | Standard Deviation | % CV | Instrument Detection Limit (ppbv) |
|---|---|---|---|
| 1,3-Butadiene | 0.15 | 12.5 | 0.20 |
| Vinyl chloride | 0.11 | 12.3 | 0.38 |
| Propylene | 0.18 | 16.8 | 0.95 |
| Chloromethane | 0.13 | 12.4 | 0.48 |
| Chloroethane | 0.12 | 7.8 | 0.56 |
| Bromomethane | 0.07 | 18.5 | 0.22 |
| Methylene chloride | 0.44 | 49.7 | 0.23 |
| trans-1,2-Dichloroethane | 0.22 | 16.4 | 0.66 |
| 1,1-Dichloroethane | 0.08 | 6.3 | 0.26 |
| Chloroprene | 0.08 | 8.2 | 0.26 |
| Bromochloromethane | 0.06 | 4.3 | 0.23 |
| Chloroform | 0.26 | 6.1 | 0.81 |
| 1,1,1-Trichloroethane | 0.20 | 15.9 | 0.72 |
| Carbon tetrachloride | 0.03 | 9.2 | 0.09 |
| Benzene | 0.04 | 9.0 | 0.12 |
| 1,2-Dichloroethane | 0.08 | 5.2 | 0.21 |
| Trichloroethene | 0.04 | 14.0 | 0.15 |
| 1,2-Dichloropropane | 0.07 | 6.1 | 0.16 |
| Bromodichloromethane | 0.14 | 9.7 | 0.46 |
| trans-1,3-Dichloropropene | 0.07 | 5.7 | 0.23 |
| Toluene | 0.17 | 24.5 | 0.52 |
| *n*-Octane | 0.32 | 22.7 | 1.01 |
| cis-1,3-Dichloropropene | 0.05 | 8.4 | 0.14 |
| 1,1,2-Trichloroethane | 0.31 | 12.0 | 0.96 |
| Tetrachloroethene | 0.08 | 19.0 | 0.27 |
| Dibromochloromethane | 0.04 | 26.3 | 0.11 |
| Chlorobenzene | 0.07 | 7.5 | 0.22 |
| Ethylbenzene | 0.23 | 7.9 | 0.73 |
| *m*-/ *p*-Xylene | 0.41 | 11.1 | 1.03 |
| Styrene | 0.15 | 37.9 | 0.46 |
| *o*-Xylene | 0.23 | 16.2 | 0.71 |
| Bromoform | 0.03 | 6.5 | 0.10 |
| 1,1,2,2-Tetrachloroethane | 0.09 | 6.7 | 0.22 |
| *m*-Dichlorobenzene | 0.09 | 8.7 | 0.27 |
| *p*-Dichlorobenzene | 0.04 | 12.9 | 0.11 |
| *o*-Dichlorobenzene | 0.14 | 8.9 | 0.38 |
| 1,1-Dichloroethene | 0.05 | 4.2 | 0.17 |
| 1,2-Dichloroethane | 0.08 | 6.7 | 0.24 |
| cis-1,2-Dichloroethene | 0.06 | 5.0 | 0.19 |
| Freon 11 (Trichlorofluoromethane) | 0.06 | 4.8 | 0.18 |
| Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane) | 0.06 | 5.3 | 0.20 |
| Freon 114 (1,2-Dichloro-1,1,2,2-tetrafluoroethane) | 0.09 | 7.5 | 0.27 |
| Freon 12 (Dichlorodifluoromethane) | 0.08 | 6.9 | 0.26 |
| Acetonitrile | 0.20 | 16.7 | 0.63 |
| Acrylonitrile | 0.09 | 7.2 | 0.27 |
| Benzyl chloride | 0.06 | 4.8 | 0.18 |
| 4-Ethyltoluene | 0.13 | 10.9 | 0.41 |
| 1,2,4-Trichlorobenzene | 0.32 | 26.8 | 1.01 |
| 1,2,4–Trimethylbenzene | 0.17 | 13.8 | 0.52 |
| 1,3,5–Trimethylbenzene | 0.13 | 10.6 | 0.40 |
| Hexachloro-1,3-butadiene | 0.32 | 16.8 | 1.01 |

12.3.2.2 Section 10.2.2 requires the GC/MS tune to be verified with BFB and for the BFB response to meet the key ion and ion abundance criteria given in Table 4.

12.3.2.3 Section 10.2.3 requires both an initial multipoint humid static calibration (five levels plus humid zero air) and a daily calibration verification (one point) of the GC/MS analytical system. The percent deviation for the actual concentration of each compound compared to the calibration curve calculated concentration shall be less than or equal to ±30 %. Calibration verification analysis results shall agree within ±30 % of the known standard concentration with no more than two exceptions deviating more than ±40 %. A daily second source verification standard shall be performed. The acceptance criterion for the verification analysis is ±30 % when compared to the actual standard concentration.

## 13. Precision and Bias

13.1 The precision of replicate gas sample analysis varies depending upon the VOCs being determined. Often, the analysis of more polar compounds is less precise. Precision data obtained by the U.S. EPA for 51 VOCs using this method are shown in Table 5 as an example.

13.2 The bias of this test method was demonstrated with performance audit samples prepared by the U.S. EPA and referenced to a primary standard gas mixture prepared by

TABLE 6 NIST Traceable GC/MS Audit Results

| Compound | Audit #1164 | | | Audit #1252 | | | Audit #1366 | | | Audit #1496 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ref. (ppbv) | Rep. (ppbv) | % Bias | Ref. (ppbv) | Rep. (ppbv) | % Bias | Ref. (ppbv) | Rep. (ppbv) | % Bias | Ref. (ppbv) | Rep. (ppbv) | % 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[A] |
| 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[A] | 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[A] | 7.5 | 5.5 | –26.67 | 5.1 | 4.4 | –13.72 |
| Styrene | 3.7 | 2.0 | –46.0[A] | 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 |

[A] Greater than the ±30 % data quality objectives.

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 permeable membrane dryer. Four performance samples ranging in concentration from 2 to 10 ppbv were analyzed over a period of 10 months. The performance results shown in Tables 6 and 7 were obtained using this system.

## 14. Keywords

14.1 ambient atmospheres; air analysis; canister analysis; canister sampling; gas chromatography–mass spectrometry; indoor atmospheres; volatile organic compounds; workplace atmospheres

TABLE 7 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 |

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