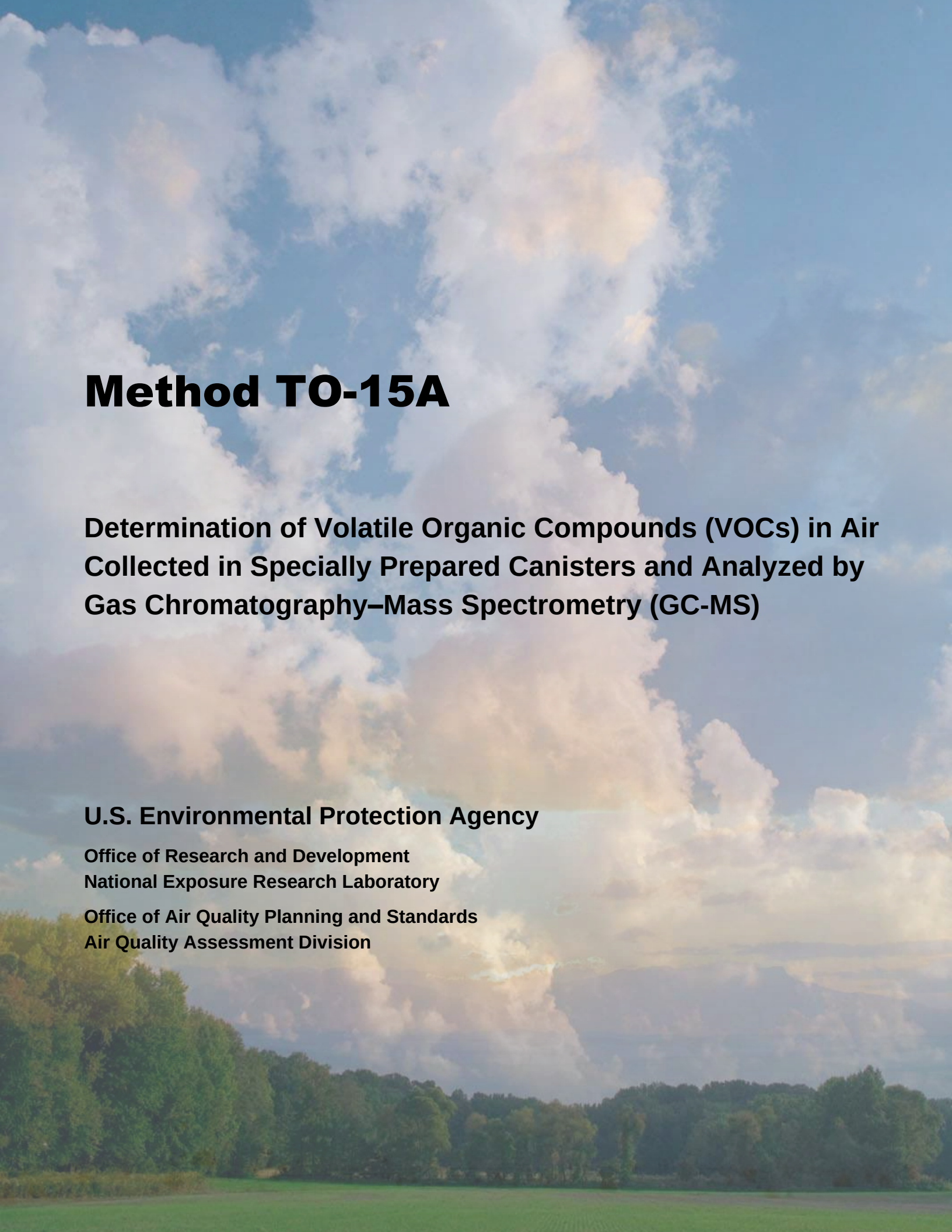

Method TO-15A

Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography–Mass Spectrometry (GC-MS)

U.S. Environmental Protection Agency

Office of Research and Development
National Exposure Research Laboratory

Office of Air Quality Planning and Standards
Air Quality Assessment Division

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This method was initially prepared for publication in the *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air*, Second Edition (EPA/625/R-96/010b), published in 1999. In 2014, U.S. Environmental Protection Agency (EPA) staff from the Office of the Science Advisor (OSA), the Office of Research and Development (ORD), and the Office of Air Quality Planning and Standards (OAQPS) formed a workgroup to focus on method updates. The workgroup members included Lara Phelps, Donald Whitaker, Karen Oliver, David Shelow, and Kevin Cavender. To facilitate the update of the method, the workgroup compiled a list of known needed changes to the method and also requested comments on potential method updates from the air toxics monitoring community to include the best practices and the most up-to-date instruments and procedures. EPA workgroup members considered all the comments that were received and made final decisions on how to incorporate revisions to the method. Battelle prepared an initial draft of the revised method in April 2018 under contract EP-D-13-005, WA No. 5-09. Donald Whitaker, Karen Oliver, and David Shelow prepared the draft final document, which was submitted for peer review in November 2018. Peer-review comments were incorporated by Douglas Turner and Ian MacGregor of Battelle. Donald Whitaker and Karen Oliver reviewed, revised, and prepared the final document.

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Disclaimer

This method has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Acronyms and Abbreviations

BFB	bromofluorobenzene
BP	boiling point
CAS	Chemical Abstracts Service
CB	calibration blank
CCV	continuing calibration verification
CDCF	canister dilution correction factor
COC	chain of custody
DB	dilution blank
EI	electron impact
EPA	U.S. Environmental Protection Agency
FEP	fluorinated ethylene propylene
GC	gas chromatography or gas chromatograph
HAP	hazardous air pollutant
HCF	hydrocarbon-free
HPLC	high-performance liquid chromatography
IB	instrument blank
ICAL	initial calibration
I.D.	inner diameter
ID	identification
IDCF	instrument dilution correction factor
IDL	instrument detection limit
IS	internal standard
MB	method blank
MDL	method detection limit
MFC	mass flow controller
MFCD	mechanical flow controlling device
MFM	mass flow meter
MS	mass spectrometry or mass spectrometer
MW	molecular weight
m/z	mass-to-charge ratio
NATTS	National Air Toxics Trends Stations
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
PAMS	Photochemical Assessment Monitoring Stations
PFA	perfluoroalkoxy
PM	particulate matter
PT	proficiency test
PTFE	polytetrafluoroethylene
QA	quality assurance

QC	quality control
RH	relative humidity
RPD	relative percent difference
RRF	relative response factor
RSD	relative standard deviation
RT	retention time
SIM	selected ion monitoring
SIS	selected ion storage
S:N	signal-to-noise ratio
SOP	standard operating procedure
SSCV	secondary source calibration verification
TO	toxic organic
TOF	time-of-flight
UATMP	Urban Air Toxics Monitoring Program
VOC	volatile organic compound

Units of Measure

*Note: A conversion chart for commonly used vacuums and pressures is included as **Appendix A**.*

amu	atomic mass unit(s)
ata	atmosphere(s) absolute (pressure at sea level, 101.3 kPa or 14.7 psia)
atm	atmosphere(s)
°C	degree(s) Celsius
cc	cubic centimeter(s)
cm	centimeter(s)
eV	electronvolt(s)
g	gram(s)
h	hour(s)
Hz	hertz
in.	inch(es)
in. Hg	inch(es) mercury
K	Kelvin
kPa	kilopascal(s)
L	liter(s)
µL	microliter(s)
µm	micrometer(s)
m	meter(s)
MΩ	megaohm(s)
mbar	millibar(s)
mg	milligram(s)
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mm Hg	millimeter(s) mercury
mol	mole(s)
mTorr	millitorr(s)
ng	nanogram(s)
ppbv	part(s) per billion by volume
ppmv	part(s) per million by volume
pptv	part(s) per trillion by volume
psi	pound(s) per square inch
psia	pound(s) per square inch absolute
psig	pound(s) per square inch gauge
s	second(s)
V	volt(s)

1 Scope

Guidance presented in this 2019 Method TO-15A update of the 1999 Method TO-15 document is intended to provide users with basic canister sampling and analysis information, incorporate current technologies, define performance criteria, and recommend specific procedures associated with collection and analysis of trace levels (approximately 20 to 5,000 parts per trillion by volume [pptv]) of volatile organic compounds (VOCs) in ambient air using specially prepared canisters. However, this method update cannot address all situations analysts might encounter in the present—much less in the future. Therefore, in instances where this guidance is found to be inadequate, development of improved techniques and technologies is encouraged provided that, at a minimum, the performance requirements outlined in this document are met.

This canister air sampling and analysis method provides procedures for measuring a subset of the 97 VOCs included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990 (see **Appendix B** for a list of the 97 compounds). VOCs are defined here as organic compounds with a vapor pressure ≥ 0.1 mm Hg at 25 °C and standard pressure of 760 mm Hg. The subset of toxic organic (TO) VOCs and other environmentally important VOCs that may be measured in ambient air with this method are listed in Table 1-1 in order of highest to lowest vapor pressure. While this list includes compounds usually analyzed in canisters, it does not include many VOCs, notably non-HAP hydrocarbons, such as various ozone precursors including various straight- and branched-chain alkanes, that may be measured with this method. This method's primary application is to measure trace levels of VOCs in ambient air. However, provided the method performance criteria are met, users of TO-15A may, at their discretion, choose to measure other VOCs or implement this method for applications such as vapor intrusion studies, indoor air investigations, and source emissions characterization, among others.

Table 1-1: Volatile Organic Compounds Quantifiable with EPA Method TO-15A

VOC (Alternative Name)[a]	Empirical Formula	CAS[b] Number	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)[c]	Molecular Weight (g/mol)	Typical Ions Monitored
Propene (propylene)	C_3H_6	115-07-1	-48.0	***8686***	42.1	41/39
Dichlorodifluoromethane (Freon 12)	CCl_2F_2	75-71-8	-29.8	4260	120.9	85/87
Chloromethane (methyl chloride)	CH_3Cl	74-87-3	-23.7	3672	50.5	50/52
Chloroethene (vinyl chloride)	C_2H_3Cl	75-01-4	-13.8	2505	62.5	62/64
1,3-Butadiene (butadiene)	C_4H_6	106-99-0	-4.0	1838	54.1	39/54
1,2-Dichlorotetrafluoroethane (Freon 114)	$C_2Cl_2F_4$	76-14-2	4.1	1444	170.9	85/135
Bromomethane (methyl bromide)	CH_3Br	74-83-9	3.5	1420	94.9	94/96
Ethylene oxide	C_2H_4O	75-21-8	10.6	1095	44.1	29/44/15
Chloroethane (ethyl chloride)	C_2H_5Cl	75-00-3	12.5	1000	64.5	64/66
Trichlorofluoromethane (Freon 11)	$CFCl_3$	75-69-4	23.7	690	137.4	101/103
1,1-Dichloroethene (vinylidene chloride)	$C_2H_2Cl_2$	75-35-4	31.7	500	96.9	61/96

VOC (Alternative Name)[a]	Empirical Formula	CAS[b] Number	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)[c]	Molecular Weight (g/mol)	Typical Ions Monitored
Dichloromethane (methylene chloride)	CH_2Cl_2	75-09-2	39.8	350	84.9	49/84
Carbon disulfide (methanedithione)	CS_2	75-15-0	46.0	297	76.1	76/44
1,1,2-Trichlorotrifluoroethane (Freon 113)	$C_2Cl_3F_3$	76-13-1	47.7	285	187.4	101/151
2-Propenal (acrolein)	C_3H_4O	107-02-8	52.3	217	56.1	56/55
2-Methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE)	$C_5H_{12}O$	1634-04-4	55.2	203	88.2	73/41
2-Chloro-1,3-butadiene (chloroprene)	C_4H_5Cl	126-99-8	59.4	188	88.5	88/53
1,1-Dichloroethane (ethylidene chloride)	$C_2H_4Cl_2$	75-34-3	57.4	182	99.0	63/65
cis-1,2-Dichloroethene (*cis*-1,2-dichloroethylene)	$C_2H_2Cl_2$	156-59-2	55.0	180–265	96.9	61/96
trans-1,2-Dichloroethene (*trans*-1,2-dichloroethylene)	$C_2H_2Cl_2$	156-60-5	48.7	180–265	96.9	61/96
2-Propanone (acetone)	C_3H_6O	67-64-1	56.1	180	58.1	43/58
Trichloromethane (chloroform)	$CHCl_3$	67-66-3	61.2	160	119.4	83/85
Tetrahydrofuran (oxolane)	C_4H_8O	109-99-9	66.0	132	72.1	42/41
Hexane	C_6H_{14}	110-54-3	68.7	120	86.2	57/43
Isopropyl ether (diisopropyl ether)	$C_6H_{14}O$	108-20-3	69.0	119	102.2	45/43
1,1,1-Trichloroethane (methyl chloroform)	$C_2H_3Cl_3$	71-55-6	74.0	100	133.4	97/99
2-Ethoxy-2-methylpropane (ethyl *tert*-butyl ether, ETBE)	$C_6H_{14}O$	637-92-3	72.6	96	102.2	59/87
Methanol (methyl alcohol)	CH_4O	67-56-1	64.7	92	32.0	31/29
Carbon tetrachloride (tetrachloromethane)	CCl_4	56-23-5	76.5	91	153.8	117/119
Ethenyl acetate (vinyl acetate)	$C_4H_6O_2$	108-05-4	72.7	83	86.1	43/86
2-Propenenitrile (acrylonitrile)	C_3H_3N	107-13-1	77.3	83	53.1	53/52
2-Butanone (methyl ethyl ketone, MEK)	C_4H_8O	78-93-3	79.6	78	72.1	43/72
Cyclohexane	C_6H_{12}	110-82-7	80.7	78	84.2	56/84
Benzene	C_6H_6	71-43-2	80.1	76	78.1	78/77
Acetonitrile (cyanomethane)	C_2H_3N	75-05-8	81.6	73	41.1	41/40
Ethyl acetate	$C_4H_8O_2$	141-78-6	77.1	73	88.1	43/61
2-Methoxy-2-methylbutane (*tert*-amyl methyl ether)	$C_6H_{14}O$	994-05-8	86.3	68	102.2	73/43
1,2-Dichloroethane (ethylene dichloride)	$C_2H_4Cl_2$	107-06-2	83.5	64	99.0	62/64
1,1,2-Trichloroethene (trichloroethylene)	C_2HCl_3	79-01-6	87.2	58	131.4	130/132
Bromodichloromethane	$CHBrCl_2$	75-27-4	90.0	50	163.8	83/85
Ethanol (ethyl alcohol)	C_2H_6O	64-17-5	78.3	44	46.1	31/45
1,2-Dichloropropane (propylene dichloride)	$C_3H_6Cl_2$	78-87-5	96.0	42	113.0	63/62
Heptane	C_7H_{16}	142-82-5	98.4	35	100.2	43/41
2-Propanol (isopropanol)	C_3H_8O	67-63-0	82.3	33	60.1	45/43
2-Methyl-2-propanol (*tert*-butyl alcohol, TBA)	$C_4H_{10}O$	75-65-0	82.3	31	74.1	59/31
1,4-Dioxane (*p*-dioxane)	$C_4H_8O_2$	123-91-1	101.2	29	88.1	88/58
Methyl methacrylate (methyl 2-methylprop-2-enoate)	$C_5H_8O_2$	80-62-6	100.5	29	100.1	41/69
trans-1,3-Dichloropropene (*trans*-1,3-dichloropropylene)	$C_3H_4Cl_2$	10061-02-6	108.0	28	111.0	75/39
cis-1,3-Dichloropropene (*cis*-1,3-dichloropropylene)	$C_3H_4Cl_2$	10061-01-5	104.3	26	111.0	75/39
Toluene (methylbenzene)	C_7H_8	108-88-3	110.6	21	92.1	91/92
1,1,2-Trichloroethane	$C_2H_3Cl_3$	79-00-5	114.0	19	133.4	97/83

VOC (Alternative Name)[a]	Empirical Formula	CAS[b] Number	Boiling Point (°C)	Vapor Pressure at 20 °C (mm Hg)[c]	Molecular Weight (g/mol)	Typical Ions Monitored
4-Methyl-2-pentanone (methyl isobutyl ketone, MIBK)	$C_6H_{12}O$	108-10-1	116.5	16	100.2	43/58
1,1,1,2-Tetrachloroethane	$C_2H_2Cl_4$	630-20-6	130.5	***14***	167.8	133/131
Tetrachloroethene (perchloroethylene)	C_2Cl_4	127-18-4	121.3	14	165.8	166/164
1,2-Dibromoethane (ethylene dibromide)	$C_2H_4Br_2$	106-93-4	131.0	11	187.9	107/109
Chlorobenzene	C_6H_5Cl	108-90-7	131.6	9	112.6	112/77
m-Xylene (1,3-xylene)	C_8H_{10}	108-38-3	139.1	9	106.2	91/106
p-Xylene (1,4-xylene)	C_8H_{10}	106-42-3	138.3	9	106.2	91/106
Isopropylbenzene (cumene)	C_9H_{12}	98-82-8	152.4	8	120.2	105/120
Ethylbenzene	C_8H_{10}	100-41-4	136.2	7	106.2	91/106
o-Xylene (1,2-xylene)	C_8H_{10}	95-47-6	144.5	7	106.2	91/106
Dibromochloromethane (chlorodibromomethane)	$CHBr_2Cl$	124-48-1	122.0	***6***	208.3	129/127
Styrene (vinylbenzene)	C_8H_8	100-42-5	145.3	5	104.2	104/103
1,1,2,2-Tetrachloroethane (tetrachloroethane)	$C_2H_2Cl_4$	79-34-5	146.0	5	167.9	83/85
Tribromomethane (bromoform)	$CHBr_3$	75-25-2	149.5	5	252.8	173/171
2-Chlorotoluene (1-chloro-2-methylbenzene)	C_7H_7Cl	95-49-8	159.2	3	126.6	91/126
4-Ethyltoluene (1-ethyl-4-methylbenzene)	C_9H_{12}	622-96-8	162.0	***3***[d]	120.2	105/120
n-Propylbenzene	C_9H_{12}	103-65-1	159.2	***3***	120.2	91/120
sec-Butylbenzene (2-phenylbutane)	$C_{10}H_{14}$	135-98-8	173.5	***2***	134.2	105/134
tert-Butylbenzene	$C_{10}H_{14}$	98-06-6	169.1	***2***	134.2	119/91
m-Dichlorobenzene (1,3-dichlorobenzene)	$C_6H_4Cl_2$	541-73-1	173.0	***2***	147.0	146/148
Hexachlorobutadiene (hexachloro-1,3-butadiene)	C_4Cl_6	87-68-3	215.0	2	260.8	225/227
2-Hexanone (methyl butyl ketone, MBK)	$C_6H_{12}O$	591-78-6	127.2	2	100.2	43/58
2-Isopropyltoluene (*o*-cymene)	$C_{10}H_{14}$	527-84-4	178.0	***2***	134.2	119/134
1,2,4-Trimethylbenzene (pseudocumene)	C_9H_{12}	95-63-6	169.0	***2***	120.2	105/120
1,3,5-Trimethylbenzene (mesitylene)	C_9H_{12}	108-67-8	165.0	2	120.2	105/120
n-Butylbenzene	$C_{10}H_{14}$	104-51-8	183.3	***1***	134.2	91/92
Chloromethylbenzene (benzyl chloride)	C_7H_7Cl	100-44-7	179.0	1	126.6	91/92
o-Dichlorobenzene (1,2-dichlorobenzene)	$C_6H_4Cl_2$	95-50-1	180.1	1	147.0	146/148
p-Dichlorobenzene (1,4-dichlorobenzene)	$C_6H_4Cl_2$	106-46-7	174.0	1	147.0	146/148
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	120-82-1	213.0	1	181.4	180/182
Naphthalene (naphthene)	$C_{10}H_8$	91-20-3	218.0	***0.1***	128.2	128/127

[a]Compound information is derived from PubChem (https://pubchem.ncbi.nlm.nih.gov/), an open chemistry database from the National Institutes of Health, U.S. National Library of Medicine, National Center for Biotechnology Information.

[b]Chemical Abstracts Service.

[c]Vapor pressures shown in bold italics are values at 25 °C.

[d]ThermoFisher Scientific, 4-Ethyltoluene Safety Data Sheet, Revised January 26, 2018.

In this method, ambient air samples are collected using specially prepared and precleaned evacuated stainless-steel canisters. VOCs contained in up to 1 L of air are subsequently preconcentrated and injected into a gas chromatograph–mass spectrometer (GC-MS) for separation, identification, and quantitation. The method performance specifications defined in this document have been demonstrated for many of the compounds listed in Table 1-1 at relevant concentrations (pptv and low parts per billion by volume [ppbv]) in ambient air (**Wang and Austin, 2006**; **Ochiai et al., 2002**; **Ochiai et al., 2003**). However, rigorous studies of the temporal stability in and recovery from canisters at pptv concentrations have not been performed for the entire list of compounds. Some of the compounds with higher molecular weight (MW) and lower volatility may behave poorly in the preconcentrator and GC-MS systems. Therefore, users of this method must determine if the method is suitable for a given purpose. To emphasize this point, fitness for purpose is demonstrated by attainment of the method's performance specifications described in this document.

Method performance for a given VOC or suite of VOCs with similar physicochemical properties is driven by several factors, many of which are related to the collection medium. For example, VOC loss and transformation may be caused by adsorption of VOCs to the interior surfaces of the canister, adsorption of VOCs to particulate matter (PM) entrained in the canister, chemical reactions of VOCs within the canister with co-collected reactive species (such as ozone or nitrogen oxides) or other substances in combination with exposed catalytic surfaces within the canister, dissolution of VOCs in water condensed in the canister, and aqueous hydrolysis and biological degradation (**Ochiai et al., 2002**). As a result of loss of certain compounds, reaction byproduct VOCs may form and increase in concentration within the canister.

This method applies under most conditions encountered when sampling ambient air into rigid, opaque containers, typically a specially treated, surface-deactivated stainless-steel canister. Note that glass bottles or similar inert containers may be employed; however, in such cases users may encounter limitations with respect to container pressurization, safety hazards such as increased potential for rupture of the container, and/or an inability to sufficiently decontaminate the container for reuse. While such alternative containers are addressed briefly, this method revision retains the focus on the use of specially prepared and cleaned stainless-steel canisters for collection of whole air samples.

Method performance may be optimized for a specific set of target analytes selected from Table 1-1, and users are encouraged to do so. However, users must consider that optimization, such as selection of preconcentration and GC-MS separation and analysis conditions, may degrade performance for other compounds. For the analysis of alkanes, for example, co-collected moisture likely need not be of primary concern; however, good water management practices are of critical importance for measuring more polar, water-soluble VOCs.

EPA Method TO-15A should be considered for use when a subset of the 97 Title III VOCs constitutes the target list. Applications of this method for the measurement of VOCs in ambient air include assessment of health impacts due to inhalation exposures to HAP source emissions dispersing into downwind areas and long-term monitoring for HAPs at various urban-scale, neighborhood-scale, and regional background, nonsource-impacted sites. These applications form the basis for operation of the U.S. EPA National Air Toxics Trends Stations (NATTS) ambient air monitoring program.

2 Summary of Method

A whole air sample is collected by passing ambient air through a particulate filter into an evacuated, specially prepared stainless-steel canister. Air may be collected as a "grab" sample or as a time-integrated sample, and the final pressures of the collected samples can be subatmospheric, at atmospheric, or pressurized. A grab sample is taken by simply opening the canister valve and allowing the canister to fill quickly (within seconds to minutes) to atmospheric pressure. A time-integrated sample is collected by filling the canister at a constant rate over a known time period (typically over hours or days). Specific information on the air sampling equipment and its cleaning, handling, and preparation are described in **Sections 7** and **10**, respectively.

Subatmospheric sampling employs the canister vacuum to draw the sample into the canister, with the flow regulated by a critical orifice, a mechanical flow controlling device (MFCD), or an electronic mass flow controller (MFC). Note that an adequate pressure differential is necessary with each type of flow controlling device to provide constant flow, and the flow control will fail when the differential falls below the minimum required for that particular device. The final pressure of the canister should be below ambient pressure at the time of sample retrieval.

Pressurized sampling typically employs a commercially available canister sampling unit that uses a pump and a flow regulation system to pressurize the canister. Pressurized sampling requires electrical power to operate the pump system and the MFC that is used to control the flow and pressurize the canister. Users of the method are cautioned that pressurized sampling methods may result in condensed water within the canister, which can have negative effects on the integrity of the VOCs in the sample (**McClenny et al., 1999**).

Whether grab or time-integrated sampling is performed, programmable timers with solenoid valves are commercially available to permit unattended sample collection. For operation when electrical power is not available, battery-powered models are commercially available.

Canister vacuum should be verified prior to sampling, preferably as close to the time of sampling setup as possible and with a high-quality, calibrated vacuum gauge (±0.25% full-scale accuracy). Ideally, sample setup occurs as close to sample collection as possible to ensure the canister remains at vacuum at the commencement of sampling.

Once the air sample is collected, the canister valve is closed, the canister pressure is measured, and the canister is transported to the laboratory for analysis. Upon receipt at the laboratory, the sample collection information is verified, the canister pressure is measured, and the canister is stored at ambient laboratory temperature until analysis. Suitable compound recovery has been demonstrated for many VOCs for storage times of up to 30 days (**Ochiai et al., 2002**; **Ochiai et al., 2003**; **Kelly and Holdren, 1995**). Users are strongly encouraged to demonstrate acceptable performance over storage times applicable to their needs.

For analysis, a known volume of air is directed from the canister into a preconcentrator. The preconcentrator captures VOCs from the sample aliquot and permits most bulk gases (e.g., nitrogen, oxygen, argon, and carbon dioxide) and water vapor to pass through to vent. Following trapping of the VOCs, the preconcentration path should be dry purged with dry carrier gas to further remove water prior to thermally desorbing the VOCs. The VOCs may be trapped further for focusing (to improve

chromatography) or may be introduced to the GC column for separation. Several preconcentrator configurations are described in more detail in Section 14.1.

The analytical strategy for EPA Method TO-15A involves using a high-resolution GC coupled to a low- or high-resolution MS, which may consist of a linear quadrupole, ion trap, or time-of-flight (TOF) system. Target VOCs are identified by a combination of the retention times (RTs) and the associated mass spectra by comparing observed fragmentation patterns to reference spectral patterns and relative ion abundances established during calibration. For any given VOC, the intensity of the observed quantitation ion in the unknown sample is compared with the system response to the same ion for known amounts of the compound. The presence of one or more secondary ions in a known relative abundance to the chosen quantitation ion increases certainty of the identification.

Mass spectrometric detection is considered a more definitive identification technique than nonspecific detectors such as flame ionization detectors, electron capture detectors, photoionization detectors, or a multidetector arrangement of these. The use of both gas chromatographic RTs and the mass fragmentation patterns reduces the likelihood of compound misidentification. If the technique is supported by a comprehensive mass spectral database and a knowledgeable operator, then the correct identification and quantification of VOCs is further enhanced.

3 Significance

EPA Method TO-15A compiles the best practices and lessons learned by users of the method over the past 20 years since Method TO-15 was published in 1999. It also addresses and incorporates improvements in canister, sampling, preconcentration, and analytical instrumentation technology. Many of the method performance specifications, procedures, and best practices described herein were identified through comments submitted by air toxics stakeholders and the community of analysts currently implementing Method TO-15. With the increased availability and improvements in commercially built equipment, most of the diagrams and descriptions of the “home built” systems that were prevalent in the early years of TO-15 have been removed from this method. This revision incorporates advances in measurement technology and the increased availability of commercial instruments and software systems for the various measurements and data-handling needs to perform the method.

This method focuses on the collection and analysis of VOCs in ambient air. The method is written as a performance-based procedure whereby equipment, instruments, operations, best practices, and acceptance and performance criteria are described. Users may modify portions of the method such as using alternative instrumentation or basing their application on a desired suite of target VOCs or concentration ranges for measurement. However, the modified application must meet the quality control (QC) and performance criteria described in Section 18. These criteria have been developed to ensure high-quality data. Laboratories should develop their own standard operating procedure (SOP) documents describing the equipment, desired target VOCs, procedures, and quality assurance (QA) activities specific to that laboratory and instrumentation. Users should describe any modifications or deviations from this guidance within the SOPs.

EPA Method TO-15A is tailored for analysis of the target VOCs listed in Table 1-1 at concentrations present in ambient air, which typically range from approximately 10 to 10,000 pptv (0.010 to 10 ppbv).

Concentrations of certain target VOCs may be present at higher concentrations in ambient air impacted by sources of VOCs such as refineries or chemical production facilities. Some of the compounds that may be measured with this method are present in ambient air at concentrations to which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be greater.

The minimum concentration for which the method is applicable has been reduced from 500 to 20 pptv (0.5 to 0.020 ppbv), and canister cleanliness requirements have been reduced from 200 to 20 pptv (0.2 to 0.020 ppbv). This is in acknowledgment of general reductions to date and expected continued reductions of ambient air concentrations of VOCs in the United States of America as well as improvements in canister technology, canister hygiene practices, and analytical instrument sensitivity. Moisture management and preconcentration techniques are established and robust, and target analyte behavior is better understood. Bench-top MSs have become more sensitive and offer higher resolution than those available when the method was released in 1999.

The target VOCs may also be measured in soil gas during vapor intrusion investigations and in indoor air, both of which are outside the scope of this method. To be suitable for these other purposes, method modifications may be required; such modifications include, but are not limited to, instrument calibration, reduction of the preconcentrated volume, and less aggressive canister cleaning techniques. Furthermore, different method performance specifications may also be applicable to these other uses. For more information on vapor intrusion application, refer to *OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* (**U.S. EPA, 2015**).

4 Applicable Documents

4.1 EPA Documents

- *Quality Assurance Handbook for Air Pollution Measurement Systems*, Volume II, Ambient Air Quality Monitoring Program, U.S. Environmental Protection Agency, EPA-454/B-17-001, January 2017.
- Technical Assistance Document for the National Air Toxics Trends Stations Program, Revision 3, U.S. Environmental Protection Agency, October 2016.
- Clean Air Act Amendments of 1990, U.S. Congress, Washington, D.C., November 1990.

4.2 ASTM Standards

- Method D1356, Standard Terminology Relating to Sampling and Analysis of Atmospheres
- Method E355-96, Standard Practice for Gas Chromatography Terms and Relationships
- Method D5466, Standard Test Method for Determination of Volatile Organic Compounds in Atmospheres (Canister Sampling Methodology)

5 Definitions

Absolute pressure: pressure measured with reference to absolute zero pressure, usually expressed in units of kPa absolute or psia.

Accepted reference value: A value that serves as an agreed-upon reference for comparison and which is derived as follows: (1) a theoretical or established value, based on scientific principles; (2) an assigned or certified value, based on experimental work of some national or international organization; or (3) a consensus or certified value, based on collaborative experimental work under the auspices of a scientific or engineering group (ASTM, 2014).

Audit accuracy: the difference between the concentration measured by the audited laboratory and the theoretical or target value (or other agreed-to reference value, such as the average of all reported results) as determined by the audit authority for an audit sample (typically contained within a canister or high-pressure cylinder), divided by the assigned theoretical or target value and expressed as a percentage.

Collocated precision: precision determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters and collected through two separate sampling inlets (e.g., two MFCDs that are individually attached to two canisters). This determines the precision of the method including the sampling and analysis processes. Collocated precision is determined by calculating the absolute relative percent difference (RPD) for the collocated measurements (the absolute value of the difference between the two collocated sample results divided by their average value and expressed as a percentage).

Cryogen: a refrigerant used to obtain subambient temperatures in the preconcentrator and/or the GC oven. Typical cryogens are liquid nitrogen (boiling point [BP] -195.8 °C), liquid argon (BP -185.7 °C), and liquid carbon dioxide (BP -79.5 °C).

Diluent gas: gas in which target VOCs are mixed, typically consisting of nominally hydrocarbon-free (HCF) synthetic “zero” air or ultrapure nitrogen. Diluent gases should be evaluated to ensure they are fit for use such that various blanks meet method performance specifications of target VOCs < 20 pptv (refer to Section 12.2 and Section 15.3.3).

Duplicate precision: precision determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through the same sampling inlet (e.g., a rack-mounted system that employs one inlet to fill two canisters at the same time). This determines the precision of the method including the sampling and analysis processes. Duplicate precision is determined by calculating the absolute RPD for the duplicate measurements (the absolute value of the difference between the two duplicate sample results divided by their average value and expressed as a percentage).

Dynamic dilution: means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with a diluent gas (such as humidified HCF zero air) in a mixing chamber or manifold so that a flowing stream of calibration mixture is created.

Gauge pressure: pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psig. Gauge pressure is zero-referenced against ambient air pressure; zero is equal to the local atmospheric (barometric) pressure, which is nominally 101.3 kPa absolute or 14.7 psia (standard pressure at sea-level).

Mass spectrometer: instrument that ionizes molecules and atoms (typically into electrically charged fragments), separates these ions according to their mass-to-charge ratio (*m/z* or *m/e*), and responds to the impact of the ions based on their population. MS systems suitable for this method include quadrupole, ion trap, and TOF detectors. Quadrupole and ion trap MS operating modes can be selected to optimize the ion mass collection range:

> **SCAN mode:** mass spectrometric mode of operation in which the quadrupole or ion trap MS is programmed to scan all ions repeatedly over a specified mass range.
>
> **SIM mode:** mass spectrometric mode of operation in which the quadrupole MS is programmed to scan a selected suite of ions repeatedly.
>
> **SIS mode:** mass spectrometric mode of operation in which the ion trap MS is programmed to store a selected suite of ions.

Nominal concentration: a requested, target, or named concentration that approximates the true, reference, or certified concentration. For example, a nominal 200 pptv standard may have an actual certified concentration of 206 pptv.

Qualitative identification criteria: set of rules or guidelines for establishing the identification or presence of an analyte using a measurement system (U.S. EPA, 2016a).

Quantitative accuracy: the degree of measurement accuracy required to measure the concentration of an identified compound, within a given tolerance of uncertainty, with an analytical system.

Replicate precision: precision determined from repeated analysis of a gas sample from one canister, which may be evaluated by calculating the absolute RPD for pairwise measurements ($N = 2$) or by determining the relative standard deviation (RSD) for replicate measurements where $N \geq 3$. Replicate analyses are used to determine precision of the analysis processes and do not provide information on sampling precision.

Static dilution: means of preparing calibration mixtures in which standard gas(es) and diluent gases are added to a fixed-volume vessel or chamber at a known ratio. Standard and diluent gas amounts may be measured gravimetrically, by volume, and/or by pressure differential from pressurized cylinders or as neat materials and blended with a known amount of diluent gas (such as humidified zero air) in a mixing chamber or manifold.

Target concentration: desired, estimated, or approximate concentration (see “nominal concentration” above).

Theoretical concentration: a reference concentration derived by applying measurements performed with calibrated instruments with known tolerances to a certified reference standard concentration value. Measurements of VOC concentrations are to be determined using a calibration that is developed based on theoretical concentrations.

Time-of-flight mass spectrometry: MS method that determines the ion’s mass-to-charge ratio by measuring the time the ion takes to reach the detector.

Wetted surfaces: surfaces of the flow path, canister, valving, pumps, etc., that contact the gas undergoing collection, mixing, transfer, or analysis.

6 Interferences and Contamination

6.1 Interferences Related to Sample Collection

6.1.1 Leaks in the Sampling Flow Path

Leaks within the sampling flow path will permit air to dilute and likely contaminate field-collected samples. Leaks may also result in unmetered air entering the flow path or canister which may subsequently impact time-integrated sampling. This generally applies to canisters that are placed in an interior location (e.g., sampling shelter) that are drawing outdoor ambient air from a manifold or sampling line.

6.1.2 Contaminants Entering the Flow Path

PM, insect nests, spider webs, and other materials within the sampling flow path may act as sorbents to adsorb VOCs, effectively scrubbing them from the sampled air stream and resulting in a low bias. The VOCs may desorb later from such materials and potentially contaminate subsequent samples. Inlet flow pathways should be inspected for the presence of foreign materials and cleaned regularly. Sintered stainless-steel particulate filters should be installed in the sampling flow path (typically at the canister inlet) to eliminate entrainment of PM into the sampling apparatus. Cleaning of compatible materials is discussed further in **Section 10**.

6.1.3 Contaminants in Co-collected Samples Employing Sorbent Media–Based Methods

Sampling units are commercially available to facilitate simultaneously collecting canister samples and cartridge samples, such as 2,4-dinitrophenylhydrazine-impregnated cartridges for measuring carbonyls. Such instruments may be configured for the two sampling methods to share a common sample introduction manifold. Residual VOCs from the sampling media may be drawn into the sampling manifold during leak checks and/or sampler purges and contaminate the collected canister sample.

6.1.4 Contaminants in the Sampling Apparatus

Sampling unit flow paths should be constructed of inert materials such as borosilicate glass, quartz glass, or chromatographic-grade stainless steel (minimum type 316 or silicon-ceramic coated). Use of Viton, fluorinated ethylene propylene (FEP) and polytetrafluoroethylene (PTFE) Teflon materials should be minimized, and users are cautioned to demonstrate that sampling devices constructed with these materials (such may be employed in seals or gaskets or pump diaphragms) do not unacceptably bias the collected sample as described in **Section 9.5**. Absorption/desorption and permeability issues are associated with Viton and Teflon materials. The user is strongly cautioned against the use of any rubber, plastics, and perfluoroalkoxy (PFA) because of contamination and adsorption issues.

Collection of gas samples containing elevated concentrations of VOCs (relative to typical ambient levels) may result in carryover to subsequent samples, particularly if the sampling apparatus is not purged between samples. Each apparatus should be qualified when initially received and periodically thereafter to demonstrate it is not contributing to measurement bias. Conducting sampling apparatus qualification is discussed further in **Section 9.5**.

6.2 Canister Sampling Media Interferences

Canisters can be the source of interferences resulting from canister manufacturing processes, handling, and/or sampling practices. Such interferences can typically be mitigated by qualifying the canisters when initially purchased and periodically thereafter (as discussed in **Section 9.4**) and by practicing proper canister hygiene as discussed in **Section 10**.

Canister interior surfaces are typically passivated by electropolishing or coating with a silicon-ceramic film. Incomplete surface deactivation treatments, such as those that may occur on canister welds, will result in active sites for adsorption or surfaces that facilitate the decomposition of labile VOCs to form other VOCs within the canister. Other potential sources of active sites include canister valves, valve stems, and ferrules. Damage to the canister interior that exposes untreated surfaces may also result in active sites.

Canisters may show increases of concentrations of oxygenated compounds (e.g., ketones, alcohols, aldehydes) and such has been reported by laboratories. Of particular concern in the canister zero checks is acrolein, which evidence suggests may increase in canisters that are stored for extended periods. The mechanism for this increase in acrolein over time is not completely understood; however, this is widely regarded as problematic in performing ambient concentration analysis.

Introduction of PM into canisters may cause interferences with collected samples. As with PM deposits in the sampling pathway, PM within the canister can behave as a sorbent and adsorb VOCs, making them unavailable in the canister gas phase. Such trapped VOCs can potentially desorb at a later time and result in the inability to achieve canister cleanliness performance specifications and/or contaminate subsequent canister sampling events. Additionally, organic PM can react with co-sampled ozone or other oxidative species to form target VOCs. PM entrained in the canister valve can damage the valve seals, threads, and quick-connect mechanisms designed specifically for ambient air sampling, resulting in leaks. PM can also clog tiny openings in critical or restrictive orifices, which impacts collection flow rates.

Under certain conditions, the composition of an air sample may change upon its introduction into the canister and over time such that the air in the canister no longer represents the ambient air from which it was collected. Such changes may be caused by interactions of the VOCs with the interior canister surface or between chemicals in the air matrix. The activity of the interior canister surface is unique to each canister and is based on several factors, including variability in canister manufacturing defects, differences in canister surface deactivation treatments, the presence of PM in the canister, and artifacts from reactions of VOCs on the canister walls. Notably the presence of co-collected moisture has been found to play a key role in canister performance (**Coutant, 1992**). Under conditions of low humidity, for example, insufficient moisture may be present in the canister to prevent losses of certain VOCs to the interior canister walls, losses that would be less likely and occur to a lesser extent if the relative humidity (RH) of the sample within the canister were higher. However, if the canister is pressurized, condensation of the water present at higher humidities may cause losses of water-soluble compounds.

Condensed water within the canister may result in corrosion of the interior surface of canisters with weak or deficient coatings and may result in the partitioning of hydrophilic polar VOCs to liquid water. Under such circumstances, concentrations of these analytes in the gas phase will be biased low until the condensation is eliminated by reduction of the canister pressure below the vapor saturation pressure of water (**McClenny et al., 1999**). Therefore, pressurized samples should be collected to a pressure approximately 21 kPa above ambient pressure at the sampling location (approximately 3 psi above

ambient pressure at the sampling location) to minimize the likelihood that water will condense within the canister. When this method is used to collect pressurized samples, users should take steps to understand the effect of condensation in the canister on method performance such as VOC recovery (bias), precision, and storage stability over time.

Given that these surface interactions have not been fully characterized on a theoretical basis, an absolute storage stability cannot be assigned to a specific VOC in a specific canister type or specific canister. Rather users of this method must be aware that each canister will have its own specific performance characteristics and be mindful that appropriate cleaning, sampling, and handling procedures are required for attainment of acceptable initial and ongoing method performance. Fortunately, under conditions of normal usage for sampling ambient air, most VOCs covered by this method can be recovered from canisters near their original concentrations after storage times of up to 30 days (**Ochiai et al., 2002**; **Kelly and Holdren, 1995**). Users of this method are encouraged to analyze collected samples as soon as possible after collection to minimize changes that may occur as the canister contents age.

6.3 Analytical Interferences

Interferences in the analytical system can be caused by contamination within the analytical instrument, active sites within the sample introduction or preconcentration flow path, contaminated gases, contaminated water used for humidification, components of the sample matrix such as water or carbon dioxide, or instrument malfunctions:

- Contamination within the analytical system may come from several sources including, but not limited to, offgassing of materials within the sample introduction or preconcentrator flow path, carryover from high-concentration samples or standards, and solvent vapors within the laboratory.
- Active sites within the sample introduction or preconcentration flow path are often caused by use of improper materials or degradation of deactivated surfaces. To minimize the potential for contamination and active sites, analytical system wetted parts should consist of the materials described in **Section 6.1.4**.
- Carrier, diluent, and internal standard (IS) gases may be sources of contaminants. Carrier gases should be dry (dew point < -40 °C) and should be ultrapure (purities > 99.999%). Additional in-line carbon scrubbers and desiccant traps may be necessary to remove residual VOCs and water from the carrier and diluent gases. Impurities in source materials or diluent gases for IS gas mixtures may result in contamination of target VOCs. Qualification of ISs is further discussed in **Section 15.1**.
- Water and the delivery systems used to humidify canisters or diluent gas streams may contaminate the canister contents or humidified gases. Specifications for reagent water are described in **Section 8.7**.
- Moisture in the sample gas may interfere with VOC analysis by GC-MS, whereas a properly configured moisture management system (as discussed in **Section 14.1**) can reduce or eliminate the interference of water. Poor or inconsistent water management during preconcentration can cause peak broadening and RT shifts and result in peak misidentification, particularly for hydrophilic polar compounds. Water management systems

that use semipermeable fluoropolymer membranes are not recommended for use in this method as they remove oxygenated and polar VOCs from the sample matrix and exhibit memory effects for a number of VOCs. VOCs entrained in the fluoropolymer membrane can convert to ketones and alcohols, which are transported across the membrane bidirectionally such that these ketones and alcohols can contaminate the sample stream and VOCs in the sample stream can be adsorbed into the fluoropolymer and removed from the sample stream.

- Carbon dioxide in the collected sample can coelute with more volatile VOCs eluting early in the GC-MS run and interfere with their quantitation.
- Artifacts in chromatograms, such as silanol compounds formed from the breakdown of silicon-ceramic linings of canisters and siloxane compounds from the breakdown of the stationary phase in an analytical column, can interfere with identification and quantitation of less volatile VOCs.

Analysts should be cognizant of compounds that interfere with target analytes when operating in MS modes that do not provide full-scan ion spectra (i.e., selected ion monitoring [SIM] and selected ion storage [SIS]). Such interfering coeluting compounds may share common ions, may have similar mass spectra, and may be difficult or impossible to separate from target VOCs. Examples of such potentially coeluting VOCs that may have identical method-specified quantitation ions include C4 hydrocarbons/1,3-butadiene, propane/propylene, cyclopentane/2,3-dimethylbutane/vinyl acetate, and acetaldehyde/isobutane. When possible, the analyst should add a qualifier ion characteristic to the desired target analyte that is not shared by the interferent. In the case of propane and propylene, however, there is no such ion exclusive to propylene. As propane is ubiquitous in ambient air, propylene concentrations may be overestimated if the two peaks are not sufficiently chromatographically separated. Deconvolution software may assist in distinguishing between minimally resolved peaks; however, users should understand the abilities and limitations of such software, which is generally meant for full-scan spectra. The use of deconvolution software is beyond the scope of this method.

7 Apparatus

7.1 Sample Container

Sample containers should be manufactured expressly for collection and analysis of VOCs in ambient air at trace levels. Before initial use and periodically thereafter, each container and valve combination should be qualified as leak-tight and nonbiasing following the procedure in Section 9.4. This update to TO-15 retains its focus on stainless-steel canisters as the sampling medium of choice, although some information on alternative containers that may meet method performance specifications is also provided.

7.1.1 Stainless-Steel Canisters

Stainless-steel canisters are commercially available with a modest range of options for surface preparation of the canister interior surfaces, valves, and connections. Currently, canister interior surfaces are typically passivated by electropolishing or coating with a silicon-ceramic film. A once common canister surface deactivation process known as SUMMA passivation generated a uniform nickel chromium oxide

surface, which increased the inertness of the canister's inner stainless-steel surface. Note that while a number of laboratories may still own and use SUMMA-passivated canisters, they are not currently being manufactured. In general, canisters with silicon-ceramic passivated interior surfaces have been widely adopted. Silicon-ceramic coatings are applied to the interior canister surface to cover active sites to achieve a passivated surface. While electropolished canisters are commercially available at the time this method was approved, they are not as widely used as silicon-ceramic coated canisters.

Stainless-steel canisters are commercially available in a range of sizes (volumes), shapes (e.g., spherical, oblong, oval), valving configurations, and interior surface treatments. Manufacturers typically state whether the canister is suitable for trace gas analysis. Some manufacturers and vendors of canisters at the time of this document's publication are listed in **Appendix C**. Canisters must withstand numerous cycles of evacuation to high vacuum and pressurization to 377 kPa (40 psig). Canisters may experience pressures higher than 377 kPa (40 psig); however, to meet U.S. Department of Transportation regulations (**49 CFR §173.306 (g)**) for shipment, canister pressures should not exceed 377 kPa (40 psig).

Canister size (volume) should be commensurate with the volume of sample to be removed for each analysis, the number of aliquots to be removed from the canister (such as for replicate analysis), and the pressure range for which the preconcentrator can effectively remove gas from the canister. The most common size employed for ambient canister sampling is 6 L; however, other sizes may be advantageous depending on the intended use. Smaller canisters (e.g., 250 cc) may be less expensive, require less purge gas to clean, and be cleaned and evacuated more quickly than larger canisters. Larger canisters (e.g., 32 L) can hold more sample gas and may be useful for longer-term time-integrated sampling as they permit use of higher flow rates that are easier to properly control. However, larger canisters are more expensive to purchase and ship, they require more time to evacuate and clean, and their size may limit the number of canisters that can be cleaned (some canister cleaners may not accommodate larger canisters at all) and/or connected to an autosampler at one time.

Canisters may be purchased with a variety of valves or combinations of valves for connection to the sampling apparatus and preconcentrator. Valves should be designed specifically for ambient air sampling. They should be of packless design and may be bellows, diaphragm, or quick-connect style. Regardless of the configuration or type, the wetted portions of the valve should, at a minimum, be constructed of chromatographic-grade stainless steel (preferably type 316), and the valve seal surfaces should be metal to metal to minimize absorption and offgassing of VOCs and other potential contaminants. Valve designs should have minimal internal volume and surface area to minimize the risk of contamination. Valves and fittings with complex seals and springs may be difficult to clean if they become contaminated. Several manufacturers also offer new-technology valves designed specifically for canisters that are surface deactivated with silicon-ceramic coatings and minimal wetted surfaces. Amorphous silicon-based coatings are also commercially available that are less susceptible to degradation by acidic sulfur compounds such as hydrogen sulfide and other organo-sulfur compounds. Note that valves with threaded connections will typically be compatible with 1/4-in. compression fittings for connections to sampling and analysis instruments. Quick-connect fittings are usually proprietary and require a compatible fitting for gas-tight connections.

7.1.2 Glass Bottles

Glass bottles or jars are commercially available for collecting gas samples. Glass bottles should be amber to protect the sample from photodegradation and should be purposely constructed and intended for gas sampling. Glass bottles that are not intended for this purpose risk implosion upon evacuation and should

not be pressurized due to the risk of explosion. Valves should comply with those listed above in Section 7.1.1. Users should closely follow manufacturer recommendations to avoid loss of sample or injury due to container breakage. Glass containers must be carefully packaged for shipping to protect from breakage.

7.1.3 Nonrigid Containers

While nonrigid containers such as Tedlar and Mylar (DuPont, Wilmington, DE) or foil bags may be useful for instrument troubleshooting and other sampling and analytical applications, they cannot be used to collect subatmospheric or pressurized samples. Also, these types of containers cannot be cleaned and reused. As such, nonrigid containers are not included in the scope of this method.

7.2 Canister Cleaning System

Canister cleaning systems are commercially available or may be custom built. Commercially available systems are capable of cleaning multiple canisters. Systems should include the following components:

- Manifold constructed of chromatographic-grade stainless-steel tubing and connections for multiple canisters.
- Rough vacuum pump capable of achieving vacuum of approximately 3.4 kPa absolute (1 in. Hg absolute) (note that oil-free pumps are strongly recommended).
- High-vacuum pump (such as a molecular drag pump) to achieve a final canister vacuum of approximately 0.0067 kPa (0.05 mm Hg or 50 mTorr) or less.
- Heating oven or heating jackets to completely contain canister and allow heating of the valve.
- Humidification system such as an impinger humidifier or bubbler.
- Programmable controller that allows selection of temperature and cycle time and automates switching between evacuation and pressurization. Manually operated systems may also be used.
- A pressure release valve to minimize the likelihood of system overpressurization.
- Trap (cryogenic or molecular sieve) to eliminate backstreaming of contaminants into canisters. This is necessary for systems with a vacuum pump that is not oil-free. Note that the use of oil-free vacuum pumps is strongly recommended.
- Chromatographic-grade stainless-steel tubing and connections to minimize dead volume of the system, which reduces pressurization/evacuation time and provides less surface contact area to reduce potential contamination. Note that butyl rubber and PFA should not be used. Viton, Teflon (e.g., PTFE, FEP), or other materials that may adsorb and/or offgas compounds of interest or introduce other potential interferences are not recommended. If needed for connections or seals, use of Viton and Teflon should be minimized.
- Source of clean purge gas such as HCF zero air or ultrapure nitrogen (such as UHP cylinder nitrogen or liquid nitrogen dewar headspace). Additional scrubbing of purge gas is recommended. Charcoal scrubbing and catalytic oxidation of purge gas will ensure trace contaminants are eliminated from the purge gas and avoid introducing contaminants to the canister during pressurization cycles.

7.3 Sampling Apparatus

7.3.1 Grab Sampling

Canister grab sampling is the simplest whole air sample collection technique, and the sample is generally collected over a few seconds or minutes. Grab sampling is useful for scoping (range finding) prior to conducting actual sampling for studies, determining concentrations at a point in time, or complementing measurements made by other instrumentation. Due to the short time interval intended to be represented by the sample, flow control while filling is not required.

Ambient air grab samples are collected by opening the canister valve and allowing the evacuated canister to fill in a matter of seconds to minutes. During grab sampling, the canister is typically allowed to fill to atmospheric pressure or to slightly below atmospheric pressure. Unattended grab sampling may be performed by employing a solenoid valve and timer to begin and end the sampling cycle. Alternatively, the grab sampler may be configured such that sampling is triggered by a signal from another device based on, for example, wind direction from a meteorological station or measured concentrations from a continuous monitor or sensor. If exposure to rain or heavy dew is possible during unattended sampling, an inverted inlet (e.g., cane) should be installed to prevent entry of water droplets into the canister. Regardless of attended or unattended collection, a particulate filter should always be installed on the canister inlet or in the sampling line to eliminate introduction of PM into the canister and valve. If grab sampling is performed through a sampling line, the internal volume of the line should be < ~1% of the canister's collected volume to ensure that the VOCs in the collected sample are representative of those in the ambient air.

7.3.2 Time-Integrated Sampling

Time-integrated sampling generally requires a more developed sampling apparatus than that for grab sampling. To ensure time-integrated samples are representative of the entire time interval of collection, the collection requires controlled, constant flow of ambient air into the evacuated canister. Several vendors offer purpose-built sampling instruments for this application (see **Appendix C**). Ambient air monitoring conducted at fixed sites on a routine schedule, such as for state and national monitoring programs, will typically employ a dedicated rack-mounted or bench-top style sampling unit. These units operate on alternating current power and are installed within a climate-controlled shelter. The sampling unit inlet is then attached to an inlet probe to the ambient atmosphere or to a manifold that is continually flushed with ambient outdoor air. Pressurized or subatmospheric samples may be collected depending on the purpose of the monitor and the requirements of the analytical system. Air samples collected at remote or temporary sites for special studies or investigations may employ stand-alone sampling instruments that operate manually or on battery power and do not require fixed shelters.

All time-integrated sampling apparatus should include the following components:

- A flow controller such as a critical orifice, MFCD, or electronic MFC. The flow control device's operational characteristics should be measured and standardized over the intended pressure range of sample collection. Refer to **Section 9** for information on characterizing and standardizing flow control.
- A wetted flow path consisting of only chromatographic-grade stainless steel (including silicon-ceramic lined steel), borosilicate glass, quartz glass, or Viton (refer to **Section 6.1.4**).
- A stainless-steel particulate filter (2- to 7-µm pore size is recommended).

If unattended sampling is desired, several additional components should be included in the sampling apparatus:

- A clock and timer to control start and stop times.
- An electronic solenoid valve to open and close the flow path to the canister. Solenoid valves should be low-temperature rise coils or latching solenoid valves with Viton seals.
- An elapsed-time indicator.
- A computer and software to operate the system (if required).

To ensure method performance specifications are attained and maintained, sampling units should be checked for cleanliness and bias initially upon receipt before field deployment and periodically thereafter, as described in **Section 9.5**.

The sampling apparatus should be protected from weather conditions that may impact sample collection. Some sampling instruments are designed for installation outdoors and operation in inclement weather; however, many sampling instruments require installation within enclosures that provide shelter from the weather and control of environmental conditions (e.g., controlled temperature and RH). Requirements for installation will be stipulated in the instrument manual.

7.3.2.1 Fixed-Site (Installed) Sampling Systems

Sampling instruments intended for installation inside monitoring shelters are commercially available from several manufacturers (see **Appendix C**) and have been in use for canister sampling at EPA Photochemical Assessment Monitoring Stations (PAMS), NATTS, and Urban Air Toxics Monitoring Program (UATMP) sites for over two decades. For collecting samples to subatmospheric pressure, commercially available systems typically employ an MFC to control sample flow into the canister and include a clock and timer to control start and stop of sampling, an elapsed-time indicator, and a vacuum/pressure gauge or pressure transducer to measure the sample pressure. It is recommended that sampling units incorporate a pump (or other suitable vacuum source) to perform leak checks on the sampling pathway as well as a presampling purge of the sampling inlet. For collecting pressurized samples, sampling units should additionally include a sampling pump that draws ambient air into the sampling unit to pressurize the sample gas upstream of the flow controller. Such systems should be designed with a bypass valve that allows a small percentage of sample flow to be directed to the MFC and canister and the remaining supply of fresh ambient air to exit the system. For pressurized sampling, the sampling pump should be a Viton or PTFE diaphragm type pump or a stainless-steel bellows type pump capable of achieving approximately 3 ata pressure at the outlet (at flow rates through the MFC of ~10 mL/min). The pump must be free of leaks, appropriately clean, and uncontaminated by oils or organic compounds.

Automated samplers are available in various configurations that allow unattended sequential sampling and concurrent collection of other media, such as carbonyl cartridges. The units are often self-contained, rack mounted, and programmed for use by computer interfaces.

7.3.2.2 Portable Sampling Systems

Sampling instruments intended for time-integrated sample collection for short-term studies or investigations should be portable and permit operation manually or on battery power. Manual systems require that the canister valve be physically opened and closed by the operator to start and end sample

collection. Instruments operating on battery power typically consist of a clock/timer, solenoid valve, and a flow-regulating mechanism such as a restrictive or critical orifice. These units are individually programmed to activate the solenoid valves at the designated times to start and end sample collection.

7.3.3 Flow Control

7.3.3.1 Critical Orifices

The most basic of flow control options consists of a critical orifice whereby air flow is controlled based on the pressure differential across a very small orifice. Volumetric flow through the orifice depends on the orifice size, the upstream and downstream pressures, and the temperature. In order for critical orifices to be useful for collection of time-integrated air samples into evacuated canisters, a critical flow through the orifice must be achieved; otherwise, the flow will be continually decreasing as the canister fills.

Critical flow is achieved when the velocity of air through the orifice reaches sonic conditions (velocity of sound in air). For air at 20 °C, critical flow is achieved when the downstream absolute pressure (P2) is 52.8% of the upstream absolute pressure (P1). Expressed as a simple ratio (P2/P1), 0.528 is the pressure ratio necessary for the air flow to reach maximum velocity. As long as the ratio of the canister absolute pressure (downstream) to the ambient absolute pressure (upstream) is ≤ 0.528, the velocity through the orifice will remain constant. Once the absolute pressure ratio increases above 0.528, the flow no longer meets sonic conditions and the air flow to the canister begins to decrease.

For critical orifices installed on evacuated canisters at high vacuum, the critical pressure ratio condition is initially met, and sample flow remains constant until the absolute pressure ratio exceeds 0.528, at which point the critical flow condition fails and the air flow decreases.

Flow must be constant for time-integrated sampling, otherwise the air sample will be biased toward the period of higher flow. Critical orifices permit collection of approximately half the volume of a canister before the critical pressure ratio is exceeded and constant flow is ceased. Therefore, it is not recommended that critical orifices be used for time-integrated sampling when the vacuum of the canister drives the pressure differential (see **Section 9.1** for flow profiles of various types of flow controlling devices, including a critical orifice). In cases where the pressure differential is provided by a pump and the absolute pressure ratio can be maintained below the critical pressure ratio, it may be appropriate to use a critical orifice.

7.3.3.2 Mechanical Flow Controlling Devices

MFCDs designed specifically for use with canisters are available that can maintain constant air flow into an evacuated canister to nearly ambient pressure (17 to 24 kPa below ambient pressure or 5–7 in. Hg vacuum). They are a significant improvement over critical orifices as they are adjustable and extend the range of controlled flow. These devices are effectively used for collecting subatmospheric time-integrated air samples over hours and days, and flow rates are adjustable from < 1 up to several hundred milliliters per minute. MFCDs are designed to maintain a constant pressure drop (and thus a constant flow rate) across a restrictive orifice by allowing a constant leak rate of sample into the canister as the canister vacuum decreases to near ambient pressure. These controllers require no external power to operate as the vacuum of the canister and the resulting pressure differential draws air through the controller into the canister. Battery-powered timers and solenoid valves may be used with these devices to allow remote operation.

MFCDs regulate the air flow with a combination of a restrictive orifice and an adjustable flow mechanism. The flow mechanism consists of a flexible metal diaphragm used in conjunction with an adjustable regulating piston and a precision-bored (typically synthetic sapphire or ruby) flow restrictor. Flow restrictors are available with holes ranging in diameter from 0.0008 to 0.006 in. The flow restrictor determines the approximate flow range, and the piston is adjusted to set the exact flow rate. A diagram of an MFCD is shown in Figure 7-1.

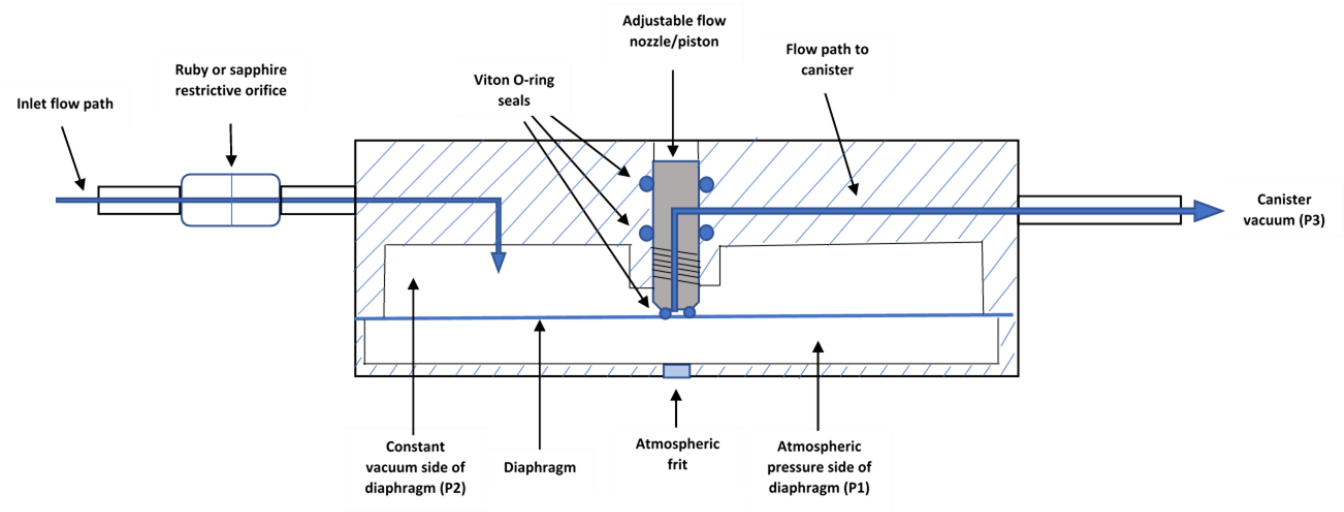

Figure 7-1: Mechanical flow controlling device.

These sampling devices are constructed such that the vacuum of an evacuated canister (P3) draws the air sample in through a stainless-steel particulate filter where it then passes through the restrictive orifice and into the vacuum-regulated chamber (P2). The vacuum in this chamber is balanced by the atmospheric pressure (P1), the vacuum of the canister, and the position of the adjustable piston. The diaphragm is made of thin flexible metal, and one side is open to atmospheric pressure and the other side (sample flow side) is under a slight vacuum as regulated by the piston. The adjustable piston consists of an O-ring that lightly contacts the diaphragm. This piston regulates the vacuum in the chamber, providing the pressure drop that draws the air sample through the restrictor and into the canister. The adjustable piston is moved toward or away from the metal diaphragm by means of screw threads to adjust the vacuum in the chamber. Once set, the pressure drop across the restrictive orifice will be maintained, even with the change in vacuum of the canister, until the vacuum range of the device is exceeded. Figure 7-2 shows the interrelationship of the pressures (P2 and P3) and flow rates of the MFCD/canister system.

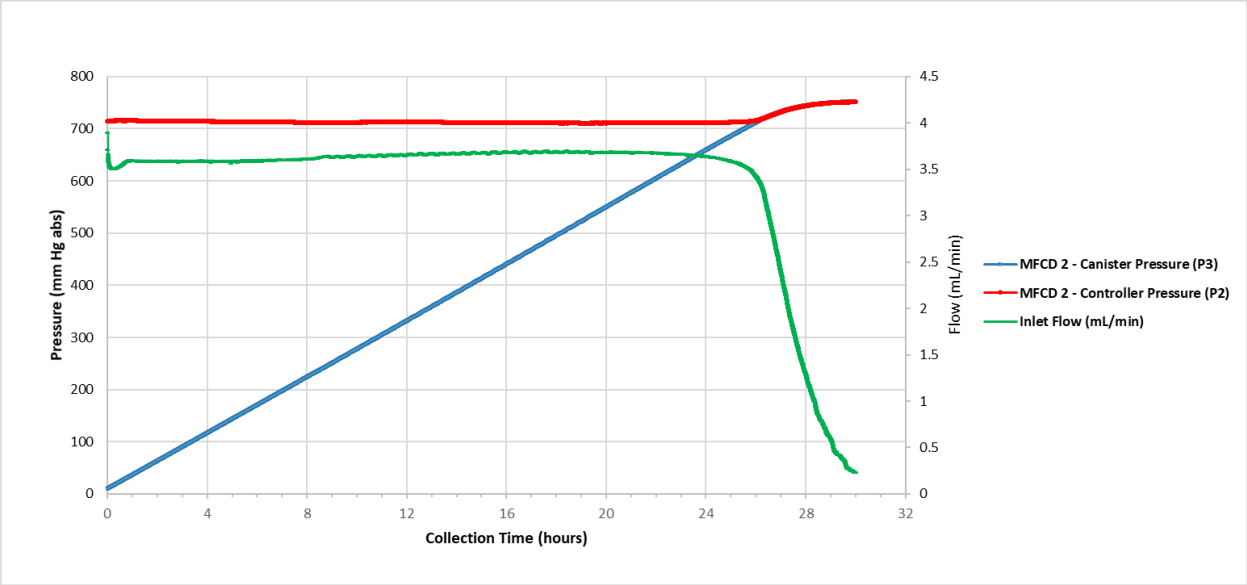

Figure 7-2: MFCD controller chamber pressure, canister pressure, and flow rate during sample collection.

7.3.3.3 Mass Flow Controllers

MFCs regulate flow by sensing the temperature difference across a gas stream and relating this temperature difference to the gas flow according to the density of the gas. MFCs typically perform best when operating at 10% to 90% of the stated flow range. MFCs operate by sensing the change in heat of the metered gas, which is unique to each gas based on the heat capacitance as a function of density, and therefore must be calibrated with the gas for which it will regulate flow. For example, an MFC employed to regulate ambient air flow should not be calibrated with nitrogen as nitrogen is approximately 3% less dense and has a different heat capacitance than air. Such a discrepancy will result in errors in gas flow calibration. MFCs typically require alternating current power, and therefore their use is generally limited to sampling instruments installed for fixed-site or long-term use. MFCs should be able to maintain sample flow to within ±2% of the flow setting over the desired sampling duration. MFC flow characteristics and operation should be precise and predictable such that the selected set point is maintained each time the MFC is employed.

7.4 Vacuum/Pressure Gauges

To verify canister pressure or vacuum, high-quality (accuracy of ±0.25% full scale), calibrated vacuum/pressure gauges or pressure transducers are needed. Gauges may be digital or analog. Commercially available digital gauges that allow programming/selection of units are very useful. Such a gauge or combination of gauges is needed to measure the key pressures, as described in Section 11.3. Gauges for accomplishing these measurements may be incorporated into sampling units, installed on canisters, connected to cleaning manifolds, or be stand-alone and attached at the time of use. For critical processes such as the preparation of standards, the dilution of samples, the determination of acceptable leak rates, and the assessment of minimum canister pressures for analysis, the gauge or combination of gauges should be calibrated over the range of use for the application and have sufficient resolution to

permit the user to measure pressure differentials precisely. To verify the accuracy of the laboratory's commonly used gauges, it is recommended that users of the method maintain a National Institute of Standards and Technology (NIST)–certified precision test gauge with accuracy of ±0.1% full scale or better and a range of at least 0 to 207 kPa absolute (0 to 30 psia) or an equivalent electronic digital pressure transducer.

7.5 Gas Regulators, Tubing, and Fittings

Regulators for high-pressure cylinders of dilution gas, stock standard gases, and IS gases should be high-purity stainless steel and may be silicon-ceramic lined (which may be required when analyzing sulfonated VOCs). Regulators should be dedicated to a specific task and labeled for use. For example, a regulator used on a high-concentration stock VOC standard cylinder should not be used on a low-concentration stock VOC cylinder. Teflon products such as PTFE and FEP seals and diaphragms should be avoided where possible to minimize memory effects; PFA should not be used. Regulators for connections to high-pressure cylinders for carrier and make-up gases should be brass or stainless steel and be rated for the pressure and flow used.

Connecting tubing and fittings for dilution gas and standard gases should be of chromatographic-grade stainless steel (preferably 316 type), which includes silicon-ceramic–treated stainless steel. Note that the lining of silicon-ceramic–treated stainless steel tubing can be damaged by bending the tubing too tightly. Follow the manufacturer's recommendations for working with silicon-ceramic–treated tubing. Connections should be metal to metal; PTFE thread sealants and Buna-N rubber components should be avoided.

7.6 Analytical Instrumentation

Analysis by this method may be accomplished with any combination of preconcentrator, GC, and MS provided the performance specifications of the method are met.

7.6.1 Sample Introduction

Commercially available preconcentrator units typically include several ports for the connection of standards, blanks, samples, and ISs. Some users may find the number of ports to be limiting, particularly laboratories with high sample throughput. The connection capacity may be increased by the addition of one or more commercially available multiposition autosamplers.

7.6.2 Sample Preconcentrator

To measure the target VOCs collected within the canister, an aliquot of air is removed and passed through a trap or series of traps where the VOCs are retained (concentrated) while the bulk gases and water are effectively removed. The VOCs are then desorbed from the trap(s) and injected into a GC-MS system.

Several preconcentrator units for this purpose are commercially available. Preconcentrator traps consist of quartz or stainless-steel tubing that may be empty or filled with sorbent material (or combinations of sorbents), such as glass beads, styrene-divinyl copolymers, and graphitized carbon. The traps may also be coated capillary tubing. Parts or all of these traps may be selectively cooled to increase retention of VOCs. Cooling may be accomplished thermoelectrically (for example, with the Peltier effect) or with cryogens such as liquid nitrogen, liquid argon, or liquid carbon dioxide.

Preconcentrators require a vacuum source and a source of clean, dry carrier gas. Vacuum is typically provided by an oil-free pump that meets the manufacturer's specifications for flow and achievable vacuum. Carrier gases may be supplied in high-pressure cylinders or by gas generation systems. Preconcentrators are typically computer controlled to facilitate creating and executing analysis sequences of standards, field-collected canisters, and laboratory QC samples.

7.6.3 Gas Chromatographic–Mass Spectrometric System

7.6.3.1 Gas Chromatograph

The GC must allow temperature programming with quick and accurate temperature ramping. If needed for separation of very light VOCs (such as ethane), the GC should be capable of subambient cooling (e.g., -50 °C). The GC will typically be a stand-alone instrument that is connected to the preconcentrator by a heated chromatographic-grade stainless-steel transfer line or equivalent, such as a length of unlined capillary column, as specified by the preconcentrator or GC manufacturer. Carrier gas connections should be of stainless-steel or copper tubing.

7.6.3.2 Chromatographic Column

A range of suitable capillary chromatographic columns is commercially available for separation of the target analytes. Typical columns are 100% methylpolysiloxane or 5% diphenyl and 95% dimethylpolysiloxane, and the column should have an inner diameter (I.D.) of 0.18 to 0.32 mm for separation of nonpolar compounds. If separation of polar VOCs is desired, the operator may select other stationary phases, as appropriate, such as 6% cyanopropylphenyl–94% dimethylpolysiloxane. The recommended column length is 60 m, but appropriate separation may be achieved by shorter columns (e.g., 30 m), which have the advantage of a shorter GC analysis time. Longer columns (e.g., 100 m) may be employed for better separations, albeit at the cost of longer GC analysis times. However, considering the diversity of the desired target analyte list, the operator should choose a column that is suitable for separating the compounds of interest to meet the performance standards given in **Section 18**.

7.6.3.3 Mass Spectrometer

The MS may consist of a linear quadrupole, ion trap, or TOF unit. The chosen detector should cover the mass range required to evaluate the characteristic ions for each desired target VOC and should have minimum resolution of 1 amu or less. The typical mass range used for monitoring the VOCs in Table 1-1 is 35 to 270 amu; however, depending on the desired suite of target analytes, the range may require adjustment to include lower masses (e.g., down to approximately 20 amu) or higher masses (e.g., up to approximately 300 amu) when characterizing high-MW nontarget VOCs. The upper limit of the range may be preferentially limited to 200 amu, which will increase dwell time and MS sensitivity for quadrupole and ion trap MSs. The MS must be capable of analyzing the desired mass range every 1 s or less and ideally would operate with an acquisition rate such that at least 10 (**Boyd et al., 2008**), and preferably 12 or more, measurements are performed over a typical 6-s-wide (full width at half maximum) chromatographic peak. Quadrupole and ion trap systems employing electron impact (EI) ionization mode should provide 70 V (nominal) electron energy in EI mode to produce a mass spectrum that meets all the instrument performance acceptance criteria as specified by the manufacturer.

Quadrupole MS units may be operated in full-scan (SCAN) mode, which monitors for all ions in the chosen scan range, or SIM mode, which permits the operator to define the ions to be monitored at various time points in the chromatogram. With SIM, the dwell times are increased when compared to SCAN, which consequently increases signal strength of the desired ions and decreases the background

noise, leading to lower detection capabilities. SIM historically has had the advantage of providing additional sensitivity for the selected ions; however, it does not provide information on ions that were not purposely selected for monitoring. More sophisticated quadrupole systems are available that allow operation in SCAN and SIM modes simultaneously, which provides the full ion profiles of SCAN and the sensitivity benefits of SIM. If qualitative identification of nontarget VOCs is desired, the MS instrument should be capable of full-scan mode and producing library-searchable mass spectra, which are typically based on a quadrupole MS operated with EI at 70 eV. Note that some instrument systems may also permit the use of "soft" ionization techniques with EI of < 70 eV; however, users of the method should note that ion spectra libraries typically contain spectra generated with EI at 70 eV.

Ion trap MS units similarly may operate in full-scan or SIS mode. As with the quadrupole MS in SIM, SIS provides greater sensitivity than full-scan mode by eliminating unselected ions from the detector and thereby increasing the signal-to-noise ratio (S:N) of the desired ions.

TOF instruments operate on a different measurement principle than the quadrupole and ion trap MS units. TOF instrument operation does not involve filtering the ion fragments as is done with quadrupole and ion trap MSs. All ion fragments impact the detector, and thus TOFs are more sensitive than the quadrupole and ion trap counterparts. The instrument measures the duration from when the ions are electrically pulsed into the analyzer until impact at the detector and correlates the time of impact with the ion *m/z*, providing ion measurement ranges from single-digit *m/z* to approximately 1000 *m/z*, at a resolution that varies according to *m/z* and the analyzer design. The ionization and detection cycles can occur thousands of times per second, resulting in thousands of spectra per analyte peak, which may be co-added to report the spectra at more modest acquisition rates.

7.6.4 Calibration Gas Standard Preparation Equipment

The GC-MS may be calibrated by several conventions, all of which involve varying a known mass of target VOCs introduced to the instrument for analysis. This section discusses the methods of preparing working-level standards for calibrating the GC-MS by dilution of a higher concentration stock standard gas. This dilution can be performed dynamically or statically using commercially available dilution instruments or a custom-built unit constructed of individual components. Refer to **Section 13** for calculations for preparing dilutions.

7.6.4.1 Dynamic Dilution Instrumentation

Dynamic dilution preparation methods involve mixing a known standard gas stream or streams with a diluent gas at known flow rates to effectively dilute the standard gas to the desired concentration. The combined gas streams are typically routed through a chamber or area of the flow path with baffles or other turbulence-inducing features to encourage thorough mixing of the resulting gas stream. The diluted gas mixture can be plumbed directly to the preconcentrator inlet or captured in an evacuated canister for later introduction to the preconcentrator. The diluent gas should be humidified to approximately 40% to 50% RH to ensure proper quantitative transfer of target VOCs through the dilution system. The humidity aids in transfer of VOCs with higher BPs from the mixing area to the canister or directly to the preconcentrator. Refer to **Section 8.7** for humidification of diluent gases. Deionized water can be added to the canister to adjust the humidity level as needed, as described in **Section 13.1**.

For dynamic dilution, the system requires, at a minimum, a flow control device for the diluent gas flow and each standard gas to be diluted and a mixing area such as a manifold where the gases and diluent can be sufficiently mixed before introduction to the preconcentrator or canister. Connection tubing should be

of chromatographic-grade or silicon-ceramic–coated stainless steel. Mixing chambers or manifolds should be of chromatographic-grade or silicon-ceramic–coated stainless steel, borosilicate, or quartz glass.

Dynamic dilution gas flows are typically controlled by calibrated electronic MFCs with flow ranges appropriate to achieve the desired dilution factor(s). Purpose-built dynamic dilution systems are commercially available with MFCs to meter standard and diluent gases into an included mixing chamber. Such systems should be chosen to provide the desired dilution factor ranges. For example, if a 25 pptv (0.025 ppbv) standard concentration is desired and the stock gas concentration is 100,000 pptv (100 ppbv), the dilution system will need to provide a 1:4000 dilution. Periodic recertification of MFCs is required unless flows are verified with a flow calibration device each time gas standards are prepared.

Alternatively, mechanical flow devices such as needle valves may be used. If these devices are used, flows must be manually adjusted and verified. Use of MFCs is generally preferable as flows are automatically adjusted to maintain a specified rate, whereas mechanical flow devices require an initial manual adjustment and are assumed to maintain the set flow.

7.6.4.2 Static Dilution Instrumentation

Static dilution preparation methods involve the delivery of precise volumes of gas or liquid standards and diluent gas into a container of constant volume. Static dilution of standards is performed in a fixed-volume vessel such as a canister or through a manifold where known amounts of certified standards are transferred. The known amounts may be measured based on partial pressure measurements, volumetric transfers, and/or mass difference. Precise and sensitive pressure transducers or pressure gauges are used to measure the partial pressures of added standard and dilution gases. Volumetrically certified gas-tight syringes may be employed when transferring known volumes of liquids or small gas volumes into vessels for dilution. Sensitive high-capacity analytical balances may be employed to measure masses of added neat materials and diluent gases.

At least four types of static dilution approaches can be used for preparation of standard gas dilutions:

- **Static dilution performed directly into canisters based on partial pressures.** Gas volumes are measured using pressure transducers or pressure gauges to determine the gas volumes added. A pressure transducer or gauge is connected to an evacuated canister, and the canister pressure is monitored and recorded before and after each standard and diluent gas is added. These pressures are input into the calculation of the dilution factor and final concentrations.
- **Static dilution through a manifold based on partial pressures.** A pressure transducer or combination of pressure transducers is employed to monitor the pressures of added standard and diluent gases plumbed through valves into a manifold constructed of chromatographic-grade or silicon-ceramic–coated stainless steel. A canister is attached to the manifold to receive the diluted standard gas. Commercially available static diluters designed for the preparation of calibration gas standards operate on this principle and meter gas standards and dilution gases into canisters based on precise measurements of pressures with pressure transducers.
- **Static dilution into canisters based on known standard volumes.** A known volume of standard gas is added to an evacuated canister with a gas-tight syringe, and the diluent gas is added to a known final pressure. The final pressure of the diluted canister is used to calculate a final volume of the mixture, assuming the volume of the canister is known. Users

are cautioned that this method of dilution preparation is difficult to perform reproducibly and requires practice and excellent technique to perform accurately and consistently. Additionally, due to deviation from the indicated volume of the canister (e.g., 6 L), this method may be subject to errors in the final theoretical concentration as the canister is not volumetrically certified. This is not the preferred method for standards preparation, and it is highly recommended that standards prepared in this manner be verified against standards prepared in a robust manner.

- **Static dilution into canisters based on gravimetric methods.** Gravimetric dilution of standards requires access to a high-sensitivity, high-capacity analytical balance that can resolve and register the addition of small amounts of gas or neat material to a fixed-volume vessel such as a canister or cylinder. Known masses of standard gases or neat materials are added to the vessel. The vessel's mass is measured before and after addition of each material and the added mass is calculated by difference. The vessel mass is then measured prior to and following the addition of diluent gas to determine the final concentration(s). This convention, especially when using neat source material, requires excellent technique and hygiene to prepare an accurate and contaminant-free standard. In general, preparation of standards should be performed by diluting gaseous standards unless exploratory or experimental work is to be conducted for which gaseous standards are not commercially available.

8 Standards, Materials, and Reagents

Standards and reagents should be used within their expiration period. Working-level standards prepared in canisters should be evaluated within 30 days of preparation.

8.1 VOC Standard Stock Gas Mixtures

Standard gaseous mixtures with certified concentrations of desired target VOCs can be sourced from reputable gas vendors (see **Appendix C**). The concentrations of the VOCs in the mixture should be commensurate with the anticipated dilution factor achievable by the laboratory needed to dilute the mixture to the desired working range. Typical concentrations of the stock standard gas mixtures range from approximately 100 ppbv to 1 ppmv, and analytical accuracy is typically cited to be within ±10% tolerance. Note that gas vendors may cite wider allowable deviations for certain labile analytes. When available, standard mixtures of target VOCs in high-pressure cylinders should be traceably certified to a NIST Standard Reference Material or to a NIST/EPA-approved Certified Reference Material. Gas standard certificates of analysis should be retained.

Several gas vendors maintain a readily available stock calibration gas mixture with a predetermined suite of approximately 65 VOCs. The balance of these gas mixtures is ultrapure nitrogen, and the gas mixtures are typically given an expiration of 1 year from certification or production. Note that certain labile analytes may be given shorter or no expiration periods. Gas vendors or third-party certification laboratories may offer recertification services of the target compound concentrations and extend the expiration of the cylinder contents. Recertification is particularly useful and typically costs less than sourcing a new

standard if large cylinders of standard gas are purchased. Gas standards that are in use must not have exceeded their current expiration period.

8.2 Neat Materials

Neat VOCs can be procured from reputable chemical providers as gases or neat liquids. The purity for the neat materials should be ≥ 98% and be evidenced by a certificate of analysis or purity. These neat materials are diluted to desired concentrations in evacuated fixed-volume vessels. Masses of these neat materials are added to the canister or cylinder with calibrated glass gas-tight syringes, by pressure differential, or gravimetrically as described in **Section 13.3**. The expiration of a prepared gas mixture is the earliest expiration date of the parent materials.

8.3 Internal Standards

Standard gaseous mixtures with certified concentrations of IS compounds in ultrapure nitrogen are available from reputable gas vendors. IS gases should be sufficiently free of target VOCs. IS compounds chosen should represent the MW range of the desired target VOC suite and may be deuterated isotopes of target analytes or VOCs that are not expected to be found in unknown samples.

8.4 Secondary Source Gas Standard

A secondary source calibration verification (SSCV) is used as a QC measure to verify the accuracy of the primary VOC standard used for quantitation. A best practice is to procure the certified secondary source stock calibration standard from a different supplier than that of the primary calibration standard. A less desirable option is to obtain a second certified standard from the same supplier but from a different lot. The standard must meet the criteria listed in **Section 8.1**. The SSCV should contain all compounds in the calibration mix. As with the calibration stock gases, at time of use the secondary source stock must be within the expiration period of the most recent certification or recertification.

8.5 Gases

Carrier gas: Helium is used as a carrier gas in the GC. Ultrapure (99.999% pure or better) helium is available in high-pressure cylinders. Hydrogen and nitrogen may also be used as carrier gases if all performance criteria are met.

Air: HCF zero air may be purchased in high-pressure cylinders from reputable gas vendors or may be prepared by passing ambient air through molecular sieves, catalytic oxidizers, and subsequent charcoal filters or similar substrate to effectively remove impurities to a concentration of < 20 pptv per compound of interest.

Nitrogen: Ultrapure (99.999% pure or better) nitrogen may be sourced from cylinders procured from commercial gas vendors or from the headspace gas from a liquid nitrogen dewar. (*Note: Dewar headspace is theoretically VOC-free as VOCs in the source nitrogen gas should stay frozen in the liquid phase of the dewar contents. Users are encouraged to analyze headspace gas from each dewar or dewar refill prior to use to ensure the gas is fit for use in this method.*)

8.6 Cryogens

Cryogens such as liquid nitrogen, liquid argon, and liquid carbon dioxide will be specified by the instrument manufacturer, if needed.

8.7 Water for Humidification

Water used to humidify canister contents and diluent gases or to clean canisters should be high-performance liquid chromatography (HPLC) grade or ASTM Type I (resistivity ≥ 18 MΩ·cm), ultrapure, or equivalent. Water should be evaluated for potential VOC contamination by analyzing humidified zero air samples. If VOC contamination is found, removal may be attempted by boiling for approximately 10 min to degas or by sparging for approximately 10 min (or until the VOC background is reduced) with ultrapure helium or nitrogen.

9 Physical and Chemical Characterization and Qualification of Field and Analytical Instruments and Canisters

Prior to field deployment, sampling apparatus flow profiles should be characterized, instrumentation flow rates set or calibrated, and the instrumentation qualified to be nonbiasing. Similarly, analytical instrumentation and canisters should be qualified as nonbiasing prior to use.

9.1 Characterization of Sampling Devices and Systems

The goal for time-integrated sampling is to achieve a constant flow rate during the desired sampling time period. For subatmospheric sampling, when the evacuated canister provides the differential pressure to draw air into the canister, a constant flow rate should be maintained until at least 75% of the canister volume is collected, which is equivalent to approximately 28 kPa (4 psi or 7 in. Hg) below atmospheric pressure. Manufacturers typically provide instructions regarding recommended fill times and flow rates based on designated restrictors and canister sizes. This is addressed in greater detail in Section 11.1.2.

To verify that the flow controlling device is operating properly, the sampling device may be characterized by assembling an evacuated canister, a calibrated vacuum/pressure gauge, the flow controlling device to be tested, a particulate filter, and a certified flow meter, as shown in Figure 9-1. The canister pressure downstream of the flow controlling device and the flow upstream of the flow controlling device are monitored and manually or electronically logged over the desired sample collection period. To verify flow control systems intended for very low flows, such as those required for a two-week sampling period, the flow verification may be performed on an accelerated schedule by employing a smaller-volume canister. The differential pressure is the critical variable for determining flow rate, so a smaller canister will enable the user to verify flow control across the desired pressure differential (vacuum) range in a shorter period due to the more rapid filling of smaller-volume canisters when compared to larger-volume canisters (e.g., 0.4 L vs 6 L).

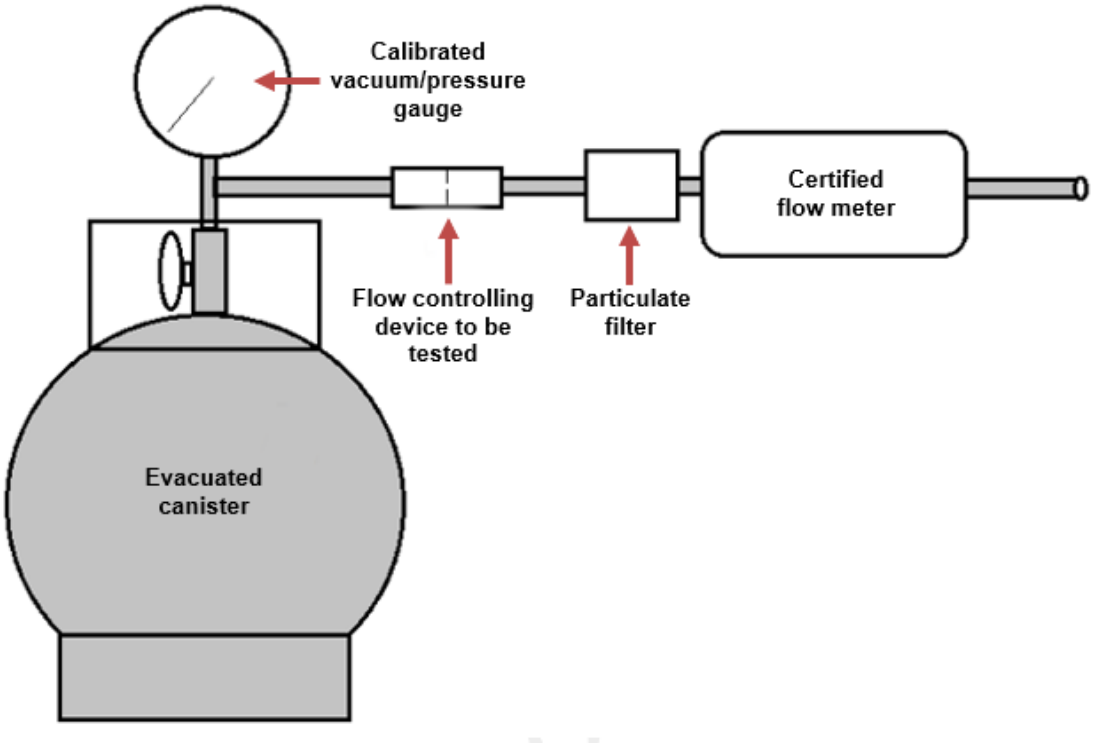

Figure 9-1: Flow controlling device characterization apparatus.

A certified flow meter should be employed, which may consist of a calibrated mass flow meter (MFM), a dry piston meter, or other similar measurement device with the calibrated measurement range appropriate to measure the flow (typically in low single-digit milliliters per minute). For low flow rates (single-digit), the flow measurement device itself must not interfere with the flow measurement—that is, the pressure drop across the measuring device should not be such that it impacts the flow being measured.

An example of a simple test system for characterizing sampling devices can be constructed that continuously logs the output signals from an electronic vacuum/pressure gauge and calibrated MFM using a datalogger to record the pressure (vacuum) of the canister, the flow passing through the controlling device, and the time. Pressure and flow measurement data collection should be of sufficient frequency (e.g., readings every hour or more frequently) to ensure adequate time resolution for determining the critical pressure differential—the pressure ratio above which flow rate is no longer constant. Example plots of flow vs. pressure for various types of flow controlling devices experimentally determined using this test system are shown in Figure 9-2.

Characterization of the flow/pressure profiles for pump-driven canister sampling systems is not necessary as these systems generally maintain a constant flow across the desired flow range. Commercially available rack-mounted canister sampling systems should have been tested and characterized by the manufacturer.

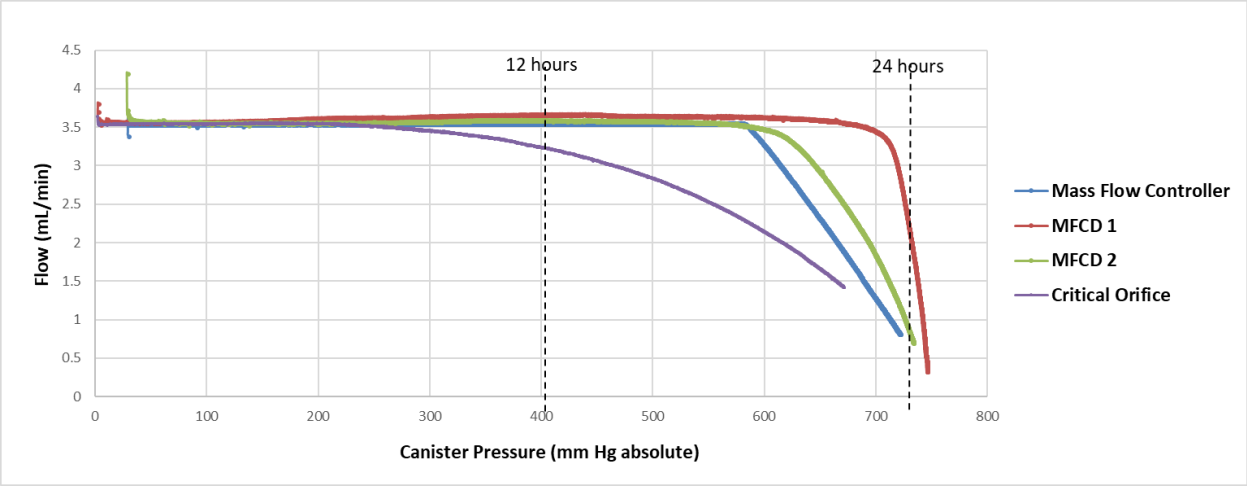

Figure 9-2: Examples of flow vs. pressure plots for various flow controllers.

9.2 Calibration of Flow Controlling Devices and Systems

9.2.1 Calibration and Verification of Mass Flow Controllers

If calibration of an MFC is required, the unit should be sent to the manufacturer or a third-party metrology laboratory. The chosen metrology laboratory should be accredited and have the capability to adjust or repair the MFC in the event it is found to be out of tolerance.

To establish or verify calibration of an MFC, the user should supply air pressure or vacuum to the MFC in the appropriate operating range as stated by the manufacturer and that approximates the pressure during routine use. If the MFC is an integral part of a sampling system, flow verifications should be conducted while it is installed in the system. If the MFC is used as a stand-alone controller attached to an individual canister, it should be verified using the power source and readout that will be used during sampling. The direction of flow indicated on the MFC must be observed and will depend on whether the source of air is pushed or pulled through it. If pressure is applied, the output flow downstream of the MFC is measured with a calibrated flow measurement device. If vacuum is applied, the inlet flow upstream of the MFC is measured with a calibrated flow measurement device.

Preferred flow measurement devices are graphite piston flow calibrators (positive displacement technology such as DryCal technology [Mesa Labs, Butler, NJ]) and calibrated MFMs capable of accurately measuring flow rates under both vacuum and pressure conditions. In either case, a calibrator or MFM of the appropriate calibration range must be used. For very low air flow rates (10 mL/min and below), the pressure drop across the measuring device must be considered as the measurement device may change the performance of the flow control device undergoing verification such that the performance is not representative of the performance under conditions of use.

If verification of flow measurement demonstrates that the MFC readout display is accurate, flows may be set directly using the MFC digital display. However, if the MFC-displayed readings are outside the flow tolerance specified in Section 7.3.3.3 or the manufacturer-defined tolerance from the measured flow, the unit should be returned to the manufacturer or metrology laboratory for recalibration or it may be necessary to measure the flow during each use.

If the MFC-displayed readings are outside of the acceptable tolerance, flows can be measured and set at each use by adjusting the flows according to calibration device measurements. Alternatively, calibration verification can be accomplished by measurement at a minimum of three different flow rates: two flows bracketing the intended flow and one at the intended flow. The MFC display reading is then plotted against the actual measured flow, and the points are modeled by linear regression. The linear regression is then used to provide the corresponding readout display setting for the desired flow rate.

9.2.2 Adjustment and Verification of Mechanical Flow Controlling Devices

Flow rates for MFCDs must be set and/or verified prior to each use. The adjustment process requires that the MFCD be attached to an evacuated canister (or other vacuum source) and a calibration device of the appropriate flow range be attached to the inlet of the MFCD. The canister valve is opened, and as the air is drawn through the flow calibration device, the flow adjustment piston of the MFCD is carefully adjusted until the desired flow is attained. Initial flow adjustment for MFCDs is typically performed prior to sample deployment with the sampling unit attached to an evacuated test canister. This allows adjustments to be made without impacting sample collection. If flows are initially set at an off-site location prior to deployment, it is strongly recommended that flow rates be verified at the sampling location at the time of deployment. If the flow rate has changed and is outside the desired range, the controller will need to be adjusted.

Typical flow measurement devices that meet the necessary criteria for setting and verifying MFCD flow rates are graphite piston flow calibrators (positive displacement technology such as DryCal Technology [Mesa Labs, Butler, NJ]) and calibrated MFMs. Suitable devices for flow measurement must be noncontaminating; therefore, bubble flow devices should not be used. They must also operate based on vacuum and have a sufficiently low pressure drop so as not to impact the flow being measured. Flow measurement devices must be in the appropriate operating range for the target flow range, typically 0–10 mL/min or 0–100 mL/min, depending on the canister volume and sampling duration. Adjustment of MFCDs to flows below 1 mL/min is challenging and requires special measurement devices. MFMs are commercially available that are capable of measuring flows below 1 mL/min.

A simple technique can be used to verify that the MFCD is properly set at time of deployment. This technique requires an evacuated canister, the MFCD with vacuum/pressure gauge, and a timing device. The MFCD is installed on the evacuated canister, and the canister valve is momentarily opened, allowing a vacuum to be established in the controller. The canister valve is then closed, and the time required for the vacuum reading to rise 34 kPa (10 in. Hg) is measured. The time is then referenced to a chart developed by the user specifically for the controller design that relates the leak rate to the flow rate. For this technique to work, the internal volume of the system between the canister valve and the restrictor must always be the same.

9.3 Qualification of Analytical Instrumentation

9.3.1 Zero-Air Challenge of Analytical Instrumentation

To fundamentally demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not a source of contamination (positive bias), humidified (40% to 50% RH) HCF zero air from a known clean source (e.g., certified clean canister, clean cylinder gas, zero-air generator) is analyzed to confirm the cleanliness of the system. This procedure should be conducted at installation prior to initial use of the instrument. This basic evaluation does not require establishing calibration or determining quantitative

results to assess potential positive bias. This check should be performed by connection of the clean humidified gas sample to the preconcentrator to verify that the analytical instrument and all connections are sufficiently clean. The volume of air analyzed should be consistent with the laboratory's typical canister sample injection volume. Compounds that appear in this zero-air challenge sample indicate contamination attributable to the analytical instrumentation.

Analysis must show that any detected target compounds in the zero-air challenge sample are at response levels that are expected to be < 20 pptv or preferably not detected. Users should examine chromatograms for interferences and other chromatographic artifacts such as nontarget peak responses, large peaks or rises in the chromatogram due to undifferentiated compounds, and baseline anomalies. Where exceedances are noted in the zero-air challenge sample for target compounds, steps should be taken to remove the contamination attributable to the analytical instrumentation by following the manufacturer's instructions. Such steps may include analyzing replicates of humidified clean gas until the contamination is eliminated, which is indicated by measuring decreasing concentrations in subsequent analyses of the target VOCs until a stable concentration (preferably not detected) is reached. The analytical system zero-air challenge is then repeated to ensure that any problems have been mitigated before the analytical instrumentation is suitable for use.

Once the analytical system has been demonstrated to have minimal to no positive bias for target VOCs, the system should be tested with a known standard of target compounds to check for any negative bias.

9.3.2 Known-Standard Challenge of Analytical Instrumentation

To fundamentally demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not causing loss of compounds (negative bias), a humidified (40% to 50% RH) reference standard of known integrity containing all target compounds is analyzed to verify that all target compounds are detected by the system, that they respond consistently upon repeated injection, and that they exhibit sufficient response to be quantifiable at low concentrations. This procedure should be conducted at installation prior to initial use of the instrument. This basic evaluation does not require establishing calibration or determining quantitative results to assess potential negative bias. It is recommended that the challenge gas contain all target VOCs at approximately 100 to 500 pptv each, chosen in consideration of the expected concentration in ambient air. The volume of air analyzed should be consistent with the laboratory's typical canister sample injection volume. Compounds demonstrating poor response as indicated by peak absence or minimal peak area may be a result of active sites in the analytical system, cold spots in transfer lines, gas impurities, improper choice of preconcentrator sorbent traps or GC columns, system leaks, and/or poor moisture management. If problems are noted, the instrument manufacturer should be consulted on the necessary steps to eliminate the bias.

9.3.3 Qualification of Autosamplers Associated with Analytical Instrumentation

Once the system has been shown to be fundamentally nonbiasing (positive or negative), the system should be calibrated and evaluated as described in Sections 13 through 16 in order to conduct the canister and sampling device and system qualifications. If an autosampler is used to facilitate analysis of multiple canisters, all ports of the autosampler should be tested once the analytical system has been calibrated and prior to conducting the canister and sampling device and system qualifications.

After establishing the initial calibration (ICAL), each port of the autosampler should be tested to demonstrate cleanliness (positive bias) by analyzing humidified zero air. This is performed by connecting the clean humidified gas sample to the port to verify that transfer lines and all connections are sufficiently

clean. Each target VOC's concentration should be < 20 pptv or preferably not detected. This check is performed prior to initial use, upon replacement of transfer lines, or after analysis of potentially contaminating samples.

Next, each port of the autosampler is challenged with a reference standard (approximately 100 to 500 pptv) to demonstrate that the autosampler is not causing bias (typically loss of compounds, or negative bias). Each target VOC's concentration should be within ±15% of theoretical concentration. This is performed prior to initial use and upon replacement of transfer lines.

9.4 Qualification of Canisters

To establish an inventory of canisters suitable for use under Method TO-15A, each canister should be qualified to ensure sample validity. Since canisters may develop problems with use, it is strongly recommended that they be qualified frequently. Canisters that are qualified have been demonstrated to be acceptably leak-tight and nonbiasing. All canisters in use should be qualified at least every 3 years. New canisters should be qualified before initial use and every 3 years thereafter. All canisters in the inventory need not be qualified at the same time but rather a subset of the canister inventory can be qualified on a rolling basis such that all canisters are qualified within a 3-year period. Canisters in an existing inventory that have not been qualified in the past 3 years should be qualified as soon as possible.

9.4.1 Canister Leak Check

Prior to initial use, new canisters should be verified to be leak-free by performing a pressure decay test. This is accomplished by either evacuating or pressurizing the canister. If the evacuation method is used, the canister is evacuated, preferably to high vacuum ≤ 0.0067 kPa absolute (0.05 mm Hg or 50 mTorr), the valve is closed, the vacuum/pressure gauge is attached, the valve is opened, and the initial vacuum is measured and recorded. The valve is then closed, the vacuum/pressure gauge is removed, and the canister valve is left loosely capped until the next pressure reading several days later. In the pressurization method, the procedure is identical except that instead of evacuated, the canister is pressurized to approximately 203 kPa absolute (29.4 psia) with clean fill gas. It is critical that canister valves are loosely capped (brass cap) to ensure that leakage through the valve is accurately assessed while avoiding potential entry of debris into the valve. Vacuum/pressure should be measured with a high-quality, calibrated vacuum/pressure gauge or transducer. Vacuum/pressure should not change by more than 0.69 kPa/day (0.1 psi/day), otherwise the canister leak rate is excessive, and the canister should be removed from service and repaired. As an aid in identifying the location of leaks for possible repair, the canister can be pressurized with helium, which permits quick pinpointing of any leaks with a helium leak detector.

9.4.2 Zero-Air Challenge of Canisters

Canister zero-air challenges are performed by pressurizing clean evacuated canisters with humidified (40% to 50% RH) HCF zero air. Note that performing this qualification with ultrapure nitrogen does not adequately test the canister as the inert nitrogen atmosphere does not permit reactions within the canister that may occur when ambient air is sampled. Each canister should be allowed to equilibrate for a minimum of 24 h prior to an initial analysis. This initial analysis should demonstrate that the target VOCs meet the cleanliness criteria specified in **Section 10.2**. After the initial analysis, it is recommended that one subsequent analysis be performed for each canister following a holding period equal to or exceeding the typical laboratory holding time, nominally 30 days from the canister fill date. Laboratories may tailor

the time of the subsequent analysis to be representative of the maximum holding time experienced by the laboratory (e.g., 21 days if all samples are analyzed within this time frame from sample collection). For this second analysis, the results should continue to meet the cleanliness criteria specified in Section 10.2. Canisters that fail the zero-air challenge should be recleaned and retested. If necessary, more aggressive cleaning techniques such as water rinses or other rinses as specified by manufacturers may be tried. If a canister continues to fail the zero-air challenges for Method TO-15A, it may need to be removed from service or repurposed for other applications. It is recommended that all canisters in the active inventory be retested in this manner at least every 3 years. This can be accomplished by testing a subset of canisters on a periodic basis. This may be coordinated with the cleanliness verification checks that are routinely performed as described in Section 10.2.

9.4.3 Known-Standard Challenge of Canisters

Following the canister zero-air challenge described in Section 9.4.2, it is strongly recommended that canister bias be assessed by filling a clean evacuated canister with a humidified (40% to 50% RH) standard gas in HCF zero air with each target VOC at approximately 100 to 500 pptv. The selected challenge concentration should be chosen to consider the expected measured concentration in ambient air. The canister is filled with the challenge standard and analyzed at least 24 h after preparation. This initial analysis should show that the measured concentrations of the target analytes are within ±30% of the theoretical spiked concentration. After the initial analysis, it is recommended that one subsequent analysis be performed for each canister following a holding period equal to or exceeding the typical laboratory holding time, nominally 30 days from the canister fill date. Laboratories may tailor the time of the subsequent analysis to be representative of the maximum holding time experienced by the laboratory (e.g., 21 days if all samples are analyzed within this time frame from sample collection). For this second analysis, the results should remain within ±30% of the original theoretical value for each target compound. It is recommended that all canisters in the active inventory be retested in this manner at least every 3 years. This can be accomplished by testing a subset of canisters on a periodic basis. Note that the criterion of ±30% is chosen based on the continuing calibration verification (CCV) criterion for acceptable variability in instrument response; however, analysts may choose to set a more stringent criterion for the initial analysis based on the stability of their instrument.

9.5 Qualification of Sampling Devices and Sampling Systems

Prior to use, sampling devices and sampling systems should be determined to be leak-free and nonbiasing. Leak checks should be performed prior to each use. Bias checks should be performed prior to first use and periodically thereafter. Sampling systems that are operated routinely year-round should undergo these checks annually, typically to be conducted after annual calibration and maintenance. Any canisters used during this process should be canisters that have been qualified as described in Section 9.4. Bias checks should be conducted by challenging the systems with humidified zero air and known standards. Ideally the units should not contaminate or adsorb target compounds during sampling.

9.5.1 Leak Checks for Sampling Devices and Sampling Systems

Performance of leak checks on sampling devices and systems during qualification permits users to repair sampling equipment prior to field deployment. Leak checks should also be performed at the time of sample collection, as discussed in Section 11.

A simple technique for leak testing MFCDs with vacuum/pressure gauges is to place the MFCD on an evacuated canister, cap the inlet to the MFCD, open and close the canister valve, and observe the vacuum/pressure gauge for a minimum of 2 min. Ideally there should be no perceivable pressure increase. If a pressure increase is observed, then the device does not qualify, and attempts may be made to determine and eliminate the source of the leak prior to retesting the device.

For qualification of automated rack-mount or bench-top systems, follow the manufacturer's instructions to conduct a leak check to ensure the internal flow path is acceptably leak-free. Ideally, there should be no perceivable leak; however, any leak that is detected should not contribute more than 5% of the total volume collected in the canister. Since manufacturers' leak rates are expressed in psi/min, the user may need to contact the manufacturer to determine the leak rate (psi/min) criteria required to meet the 5% benchmark for a chosen canister volume. Manufacturers' instructions should be followed to correct leaks in the system.

9.5.2 Zero-Air Challenge of Sampling Devices and Sampling Systems

To ensure the sampling device or system is not a source of contamination (positive bias), humidified (40% to 50% RH) HCF zero air collected through the sampling device is analyzed and compared with a reference humidified air sample from the same source. The volume of air analyzed should be consistent with the laboratory's typical canister sample injection volume. Compounds that show increased concentrations in the challenge sample compared to the reference sample indicate contamination attributable to the sampling unit. This challenge should be conducted prior to initial use and on an annual basis thereafter, as well as after cleaning, replacement of components, and collection of potentially contaminating samples.

One technique is to provide humidified zero air flow to a challenge manifold constructed of chromatographic-grade stainless steel or borosilicate or quartz glass. The manifold should include, at a minimum, two ports to be used for connections to the sampling device or system and to a reference canister or analytical system, and a vent to ensure that the manifold remains at ambient pressure. Zero air is to be supplied such that there is excess flow to the manifold at all times as indicated by visible means such as a rotameter, MFM, or piece of tubing inserted in a flask filled with water (bubbling to indicate flow) on the vent. If using a reference canister, its flow should be controlled to approximately the same flow rate as the sampling unit with an MFC or other flow controller. At a minimum, the reference canister should collect a grab sample of the humidified zero-air challenge gas from the manifold. An alternative to using a reference canister is to collect the humidified air directly from the manifold into the VOC preconcentration/analytical system.

Analysis by GC-MS for target compounds must show that the target compounds in the zero-air challenge sample collected through the sampling unit are not > 20 pptv higher than the concentration in the reference sample. Where exceedances are noted in the zero-air challenge sample for target compounds, steps should be taken to remove the contamination attributable to the sampling unit. The sampling unit zero-air challenge is then repeated to ensure the criterion is met before the sampling unit is deployed for sampling. Initial steps to clean the system would involve purging overnight or for longer durations with humidified HCF zero air. If extended purging durations are not adequate to eliminate contaminants, then disassembling and cleaning according to **Section 10.6** is recommended. If the unit cannot be cleaned to meet the specifications, then it should be retired from use or repurposed for source sampling.

9.5.3 Known-Standard Challenge of Sampling Devices and Sampling Systems

To ensure the sampling device or system is not causing loss, degradation, or enhancement of compounds, a humidified (40% to 50% RH) standard gas collected through the sampling device is analyzed and compared with a reference sample from the same source. Compounds that show decreased concentrations in the challenge sample as compared to the reference sample indicate that active sites or absorbing materials are present. Increased concentrations as compared to the reference sample indicate contamination or offgassing of target VOCs. This challenge should be conducted prior to initial use, after cleaning or significant maintenance, and after collection of damaging sample matrices that may impact the activity of the flow path surfaces.

The manifold system similar to that described in Section 9.5.2 may be used to accomplish the challenge of the sampling device or system. It is recommended that the challenge gas contain all target VOCs at 100 to 500 pptv each and that the selected challenge concentration be chosen to consider the expected measured concentration in ambient air.

Analysis by GC-MS for target compounds should demonstrate that each VOC in the challenge sample collected through the sampling device or system is within ±15% of the concentration in the reference sample. For compounds exceeding this criterion, steps should be taken to eliminate the bias. This may include cleaning as recommended in Section 10.6 or replacement of compromised parts. Note that this criterion is intentionally tighter than the CCV criterion of ±30%, which characterizes the acceptable drift in instrument calibration response. The reference and challenge canisters are typically analyzed in the same analysis sequence, and therefore calibration drift is expected to not exceed the CCV criterion.

Following completion of the known-standard challenge, the sampling device or system should be flushed with humidified (40% to 50% RH) HCF zero air or ultrapure nitrogen for a minimum of 24 h before field deployment.

10 Cleaning, Handling, and Maintenance of Canisters and Sampling Components

10.1 Canister Cleaning

Canister cleanliness is a critical aspect of Method TO-15A as it directly impacts the quality of VOC measurements. Important cleaning parameters that must be considered are pressure, temperature, humidity, and the number of cleaning cycles. The number of cleaning cycles in particular greatly impacts the final cleanliness of the canisters. Definitive studies have not been published to date recommending specific superior canister cleaning procedures. The canister cleaning recommendations in this section were assembled based on the experience of analysts and procedures generally accepted to be effective. Use of the following procedures should provide canisters of sufficient cleanliness to meet the criteria specified in Section 18. Canister cleaning procedures are discussed below and summarized in Table 10-1.

10.1.1 Gas Source for Canister Cleaning, Pressurization, and Flushing

The purge gas for canister cleaning should be high-purity HCF zero air or nitrogen. Ultrapure nitrogen may be sourced from cylinders, nitrogen generators, or the headspace gas from a liquid nitrogen dewar. Air is generally sourced from cylinders or air generators. Scrubbing of purge gas with additional hydrocarbon traps, moisture traps, and/or catalytic oxidation may be necessary to obtain sufficiently clean purge gas, which should be < 20 pptv for each target analyte. Purge gas cleanliness should be verified upon initial setup by direct analysis if possible or indirectly by filling and analyzing a known clean canister. After initial demonstration of purge gas cleanliness, acceptable canister batch blanks (individual target VOCs ≤ 20 pptv at 101.3 kPa absolute) provide continuing indirect confirmation that the purge gas is suitably clean.

If used, gas scrubbers should be replaced on a regular maintenance schedule. In the event of changes in gas sourcing or after the replacement of scrubbers such as hydrocarbon traps and moisture traps, additional cleanliness verifications may be necessary.

The purge gas should be humidified to approximately 30% to 70% RH; higher humidity levels within this range generally are considered more effective for cleaning canisters. The water assists in removal of polar and high-BP VOCs that may otherwise remain in the canister. Commercial canister cleaning systems usually incorporate a humidifier; however, the supplied humidity may vary considerably based on the type of humidifier that is used. There are generally two types of humidification processes: (1) bubbler humidification systems that incorporate an impinger submerged in water that humidifies by bubbling the purge gas through the water and (2) headspace humidification systems whereby air is simply blown over the surface of the water. Bubbler systems generate higher humidities than headspace systems.

Water for the humidification device should be deionized, distilled, or HPLC grade as specified by the cleaning system manufacturer. If a bubbler-type humidifier is employed, care should be taken to ensure the downstream pressure is lower than the humidifier upstream pressure to avoid backflow of the water. It is recommended that the humidity of the purge gas be measured with a calibrated hygrometer to ensure the desired humidity is attained. Such a measurement can be made by placing a hygrometer probe in the humidified gas stream.

10.1.2 Pre-evacuation of Canisters

Canisters should be pre-evacuated prior to connection to the canister cleaning system to reduce the potential for contamination of the system. Pre-evacuation should be performed on all canisters regardless of whether the contents are ambient air, standards, or samples of high concentrations. Canisters are pre-evacuated by attaching them to an oil-free roughing pump and evacuating to approximately 7 kPa absolute (28 in. Hg vacuum) with the exhaust of the pump directed to a fume hood or passed through a charcoal trap. Canisters are then refilled to ambient pressure with HCF zero air or nitrogen. The pre-evacuation process may need to be repeated for canisters that contain VOCs at higher concentrations. Once the canisters have been pre-evacuated and filled, they are attached to the cleaning system.

10.1.3 Heated Canister Cleaning

Canisters should be heated during cleaning as the heat facilitates removal of compounds. Heating is generally achieved by placing canisters in enclosed ovens. Heating to 80 °C is generally sufficient for cleaning canisters used for ambient air sample collection. Higher temperatures may be used; however, interactions within the canister and the humidified purge gas at temperatures of ≥ 100 °C are not well understood and do not appear to increase cleaning effectiveness. The temperature to which the canister

may be subjected during cleaning depends on whether the canister is silicon-ceramic lined, SUMMA, or electropolished; the temperature rating of the valve and vacuum/pressure gauge (if so equipped); and the heating method employed. If using humidified HCF zero air during canister cleaning (specifically in the canister pressurization steps), silicon-ceramic–lined canisters should not be heated above 80 °C as damage to the surface coating due to oxidation may occur, leading to active sites within the canister (**Restek, 2010**).

Canisters used for collection of source-level samples (ppmv concentrations of VOCs) or samples with matrices that include high-MW compounds with high BPs (such as semivolatile organic compounds) may require heating to higher temperatures (100 °C or higher, if permitted by the canister and valve) or specialized cleaning processes. Such canisters typically cannot be sufficiently cleaned with the pressurization and evacuation procedures described in the following sections and should not be used for collecting ambient samples. A best practice is to segregate canister inventories such that canisters used for collection of source-level samples are not used for collection of ambient air samples.

Users are cautioned regarding the following types of heating methods. Heat bands may cause hot spots on the canister where the band contacts the canister, do not evenly heat canister surfaces farther from the bands, and may not adequately heat the valve. Heating jackets and ovens heat the canister evenly but may not be able to isolate the valve from the heat source, which may cause damage to the valve if cleaning is performed at excessive temperatures (> 80 ºC). Some heating jackets or ovens allow the valve to protrude from the heated space and the valve to be exposed only to radiant heat. This may result in cold spots where higher-BP VOCs can accumulate.

10.1.4 Cycles of Evacuation and Pressurization

In general, the greater the number of evacuation and pressurization cycles, the more effective the cleaning. Canisters should be evacuated to minimally 7 kPa absolute (28 in. Hg vacuum) during each evacuation cycle, and higher vacuum is recommended. This vacuum should be maintained for a minimum of 1 min before the pressurization step. Canisters should be pressurized to ≤ 30 psig with humidified purge gas for each pressurization cycle. This pressure should be maintained for a minimum of 1 min before the next evacuation step. At least five cycles of evacuation and pressurization are recommended and 10 or more have been shown to be effective in removing stubborn oxygenated compounds such as ketones, alcohols, and aldehydes (**U.S. EPA, 2016b**). Following the principle of extraction efficiency, in which each cycle recovers a specific percentage of each compound (e.g., 85%), additional evacuation and pressurization cycles (up to 20) may be performed to achieve sufficiently clean canisters. Canisters should undergo final evacuation to ≤ 0.0067 kPa (≤ 50 mTorr). Canisters may be held at this high vacuum for a short period prior to closing the canister valves; however, extended periods (> approximately 5 min) at high vacuum with open connection to the cleaning manifold may result in diffusion of contaminants into the canisters from elsewhere in the manifold. Canisters maintained on the cleaning system at high vacuum for extended periods should be subjected to a subsequent cycle of pressurization prior to final evacuation and closing canister valves. Automated canister cleaning systems are advantageous as they can be programmed to include additional cycles or customize vacuum hold times and thresholds.

For canisters that will be stored for use at a later time, an alternative to storing the canisters under high vacuum is to pressurize the canisters with clean humidified HCF zero air or ultrapure nitrogen purge gas. The stored pressurized canisters are then evacuated to ≤ 0.0067 kPa (≤ 50 mTorr), as stated above, just prior to field deployment.

Table 10-1: Recommended Canister Cleaning Parameters

Canister Type	Pre-evacuate Canister	Temperature[a]		Humidity	Minimum Number of Pressure/Evacuation Cycles	Cycle Time
		Air Purge Gas	Nitrogen Purge Gas			
Silicon-ceramic coated	Yes	≤ 80 °C	≤ 100 °C	50%	5	Varies by system
SUMMA	Yes	≤ 100 °C	≤ 100 °C	50%	5	Varies by system
Electropolished	Yes	≤ 100 °C	≤ 100 °C	50%	5	Varies by system

[a]Do not exceed the manufacturer's recommended maximum temperatures for component parts such as valves and gauges.

10.2 Verification of Canister Cleanliness Prior to Sample Collection

Upon cleaning a batch of canisters, one or more canisters are selected to be pressurized with humidified HCF zero air or nitrogen and analyzed after a minimum of 24 h to verify acceptability of the batch for use. A batch is defined as a set of canisters connected to the same manifold and vacuum source and cleaned simultaneously. At least one canister per batch of up to eight canisters is selected for verification. For batches of 9 to16 canisters, two canisters are selected for verification; for batches of 17 to 24 canisters, three canisters are selected; and so on. This is summarized in Table 10-2.

Table 10-2: Recommended Number of Canisters Verified per Cleaning Batch

Number of Canisters in Batch	Minimum Number Selected for Cleanliness Verification
1 to 8	1
9 to 16	2
17 to 24	3
25 to 36	4

Analysis of more than one canister from each batch is highly recommended. Selection of batch blank canisters for analysis may be random or targeted. Targeted canisters should be those that previously contained high-concentration samples or high-BP VOCs. Targeted canisters may also be those that are to be requalified on a rotating basis as described in Section 9.4. Verification of every canister is a best practice and may be necessary for certain studies, depending on the QA requirements.

The canister cleaning criterion is ≤ 20 pptv (0.02 ppbv) per target VOC when a canister is filled to standard ambient pressure (101.3 kPa absolute or 14.7 psia). The criterion is set to meet the challenges of accurately characterizing the ever-lower concentrations of VOCs in ambient air, since the VOC background in canisters should be insignificant in comparison to expected ambient concentrations. Every effort should be made to meet the cleanliness criterion for all compounds of interest. If not achievable, the data must be flagged for those compounds not meeting the criterion.

To maintain more uniform cleaning acceptance criteria across the range of pressures that laboratories may ultimately choose to use for sample collection, the acceptance criterion will vary depending on the final pressure chosen for verifying the canister cleaning batch blanks. This criterion is based on demonstrating that the amount of any given target VOC in a canister is sufficiently low when normalized to the canister volume at ambient pressure at sea level. Filling of canisters to pressures higher than this will dilute the contaminants in the canister, so the acceptance criterion concentration will need to be proportionally reduced. These values (in pptv) are shown in Table 10-3. Canister volumes are included in

the table to illustrate the approximate volume of gas in common canister sizes at various absolute pressures.

The acceptable concentration values are based on the fact that increased pressures in a canister correlate with increased volumes of gas that dilute the background contamination. All concentrations stated at the pressures listed in Table 10-3 represent a uniform concentration that is equivalent to 20 pptv at 101.3 kPa absolute (14.7 psia). For example, if a fill pressure of 207 kPa absolute (30 psia) is used for verification of canister cleanliness, then the laboratory would need to meet the cleanliness criterion of ≤ 9.8 pptv for each target compound of interest.

Table 10-3: Canister Blank Acceptance Criteria

Canister Pressure (kPa absolute)	Canister Pressure (psia)	Canister Gauge Pressure (psig)[a]	Final Air/Nitrogen Volume (approx.)				Acceptable Concentration (pptv)
			1-L Canister	2.7-L Canister	6-L Canister	15-L Canister	
310	45.0	30.3	3.1	8.3	18.4	45.9	≤ 6.5
276	40.0	25.3	2.7	7.3	16.3	40.8	≤ 7.4
241	35.0	20.3	2.4	6.4	14.3	35.7	≤ 8.4
207	30.0	15.3	2.0	5.5	12.2	30.6	≤ 9.8
172	25.0	10.3	1.7	4.6	10.2	25.5	≤ 11.8
138	20.0	5.3	1.4	3.7	8.2	20.4	≤ 14.7
101.3	**14.7**	**0**	**1.0**	**2.7**	**6.0**	**15.0**	**≤ 20.0**
89.7	13.0	-1.7	0.9	2.4	5.2	13.3	≤ 23.0

[a]Gauge pressures shown represent those expected at sea level for barometric pressure at standard pressure, 101.3 kPa absolute. Gauge pressure readings under barometric pressure conditions other than sea level will need to be adjusted based on the ambient barometric pressure at a specific location.

The equation used for calculating the canister final air/nitrogen volume (V_{calc}) is given below. It may be used to calculate approximate volumes in the canisters at a given pressure and the acceptance concentration criteria for pressures not shown in Table 10-3:

$$V_{calc} = \left(\left((P_{clean} - P_{std})/P_{std}\right) * V_{can}\right) + V_{can}$$

where:

V_{calc} = approximate calculated volume of gas contained in the canister (L)

P_{clean} = absolute pressure of canister cleaning batch blank, kPa absolute

P_{std} = 101.3 kPa absolute, standard atmospheric pressure

V_{can} = nominal canister volume (L)

The equation used for calculating the acceptable concentration criterion (C_{acc}) is given below. It may be used to calculate acceptance concentration values for pressures not shown in Table 10-3. Calculations are based on the pressure change and specified target concentration of 20 pptv relative to 101.3 kPa absolute (14.7 psia):

$$C_{acc} = C_{atm} * (P_{std}/P_{clean})$$

where:

C_{acc} = acceptance limit concentration at measured canister pressure (pptv)

C_{atm} = 20 pptv, acceptance limit concentration at standard atmospheric pressure

P_{std} = 101.3 kPa absolute, standard atmospheric pressure

P_{clean} = absolute pressure of canister cleaning batch blank, kPa absolute

For example, a laboratory pressurizes cleaned canisters to 178 kPa absolute for batch cleaning analysis. The acceptance criterion for each target VOC is ≤ 11.4 pptv (20 pptv · 101.3 kPa/178 kPa).

The canister cleanliness criterion should be commensurate with the intended measurements to be characterized. Air samples with generally higher concentrations may not require such rigorous canister cleaning. In this case, the laboratory should ensure that canister background levels are kept to ≤ 5% of the concentration measured in the sample.

Canisters that meet the batch blank criterion are ready to be evacuated for use. If one canister representing the batch fails, either the entire batch can be recleaned (recommended) or two additional canisters from the batch can be selected and analyzed to determine whether the batch meets the criterion. If both canisters meet the cleanliness criterion, only the failing canister should be recleaned. If either canister fails, however, the entire batch should be recleaned. If each cleaned canister from the batch is tested, only those canisters that fail the criterion should be subjected to further cleaning. Actions should be taken to investigate an ongoing failure of batch blanks to meet the cleanliness criterion. In a system where batch blanks normally meet the cleanliness verification criterion, continued failure of batch blanks may indicate that the purge gas, cleaning manifold, or other system components have become contaminated. If it is determined that failures are related to specific canisters, more aggressive cleaning techniques such as water rinses or other rinses as specified by manufacturers may be tried.

10.3 Cleaning of Glass Bottles

Prior to cleaning glass bottles, vacuum or pressurization must be released and the vessel must be at atmospheric pressure. Bottles containing standards or unknown contents exceeding ambient pressure should be vented into a fume hood or other exhaust outlet. Once at atmospheric pressure, the cap and valving hardware are removed from the bottle. Bottles are then placed into a heated oven at approximately 75 °C and flushed with humidified purge gas for approximately 12 h. Valving hardware should be connected to a source of humidified purge gas and flushed for several hours. Following cleaning, the bottle and valving should be reassembled, the bottle evacuated to ≤ 0.0067 kPa absolute (≤ 50 mTorr), the bottle filled with a clean diluent gas to the pressure of ambient field samples, and the contents analyzed to ensure all target VOCs are ≤ 20 pptv at standard ambient pressure (101.3 kPa absolute), as discussed in **Section 10.2**. Once demonstrated to be clean, the bottle assembly is ready for evacuation and field deployment.

10.4 Canister Preventive Maintenance and Best Practices

Maintenance of canisters involves a combination of preventive and routine actions and best practices. The following subsections detail activities and best practices related to canister qualification, sample collection, cleaning, and general handling.

10.4.1 Particulate Filters

Whole air sampling into canisters should be performed using a particulate filter, as discussed in Section 7.3, because particulates are difficult to remove with typical evacuation and pressurization cleaning techniques once they have been drawn into a canister. With use, particulate filters will trap airborne particles and become partially clogged, potentially impacting the concentrations of compounds being drawn into the canister. Particulate filters should be cleaned or replaced frequently to reduce the likelihood of negative impacts on the air sample being collected. Replacement of the filter element is preferred due to the ease of replacement and associated difficulty with cleaning and decontaminating the filter element. If cleaned, sintered metal filters should be removed from the sampling inlet and sonicated in water and/or methanol for 15 min, after which they should be rinsed with fresh methanol, dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 h, and flushed for several hours with humidified HCF zero air or nitrogen.

Particulate residue inside a canister creates active sites that may have a detrimental effect on target VOC recovery. Particulates may deposit into canister valves, potentially damaging threads and seals, which results in leaks. Furthermore, typical cleaning techniques that employ evacuation and pressurization of canisters do little to remove particulate residue interferences, which may result in canister compound behavior indistinguishable from that caused by degradation of the interior surfaces of the canister. Canisters that cannot be remediated successfully may need to be retired. Alternatively, canister manufacturers offer canister reconditioning and valve replacement parts or services that can restore canisters to new condition.

10.4.2 Canister Valves

Valves currently supplied with new canisters have been specifically designed for canister use to address common issues with early valves that were adapted from other technologies. Early valves were typically of a stainless-steel bellows design, and overtightening the valve damaged valve seats, which caused leaks. Older SUMMA canisters still in service may have valves of the original bellows design, so care must be taken not to overtighten them. Newer valves are generally of a stainless-steel diaphragm design that are often silicon-ceramic coated and have minimal wetted surface area. These valves are less prone to damage from improper tightening; however, the proper torque required to close the valve depends on the specific valve design, and the manufacturer's recommendation should be followed. Valves should only be hand tightened to close—never tightened with tools (e.g., adjustable or locking pliers).

Faulty or leaking valves generally fall into two categories: (1) those with damaged internal valve seat components or (2) those with damaged external threads. Valves with damaged valve seat components should either be replaced entirely or rebuilt using kits available from the manufacturer. Valves with damaged external threads due to careless handling or deformation from overtightening of sampling inlets require replacement of the entire valve. Using a thread chaser to restore damaged threads is rarely effective in reversing the thread damage and is not recommended.

When not connected for cleaning, sample collection, or analysis, the canister valve opening should always be capped with a brass plug to protect the exposed threads and to ensure particulates do not deposit into the valve opening. Care must be used to properly tighten the brass plugs and to attach the canister to sampling devices and cleaning ovens to minimize chances of distortion of the threads. To avoid galling or cross-threading the threads of the valve connection, caps, plugs, or nuts should be finger tightened and then snugged slightly with a wrench.

10.5 General Canister Handling

Canisters should be handled with care to ensure that the interior canister surface is not compromised, the valve-to-canister connection remains intact, and weld integrity is maintained. Excessive torque on unbraced canister valve stems when making connections to the canister may cause damage and potentially leaks in the valve stem weld or at the ferrule sealing the canister valve and canister stem. Shocks resulting in dents to the surface of the canister may damage welds or create small cracks in the interior canister surface that may expose active sites.

Shipment of canisters in protective hard-shell boxes and/or sturdy cardboard boxes is required to ensure canister longevity. Boxes that have lost integrity or rigidity should be replaced.

10.6 Cleaning of Sampling Components

The manufacturer's instructions should be followed for cleaning components such as flow controllers and sampling unit parts. Note that disassembly of such instruments may void warranties or calibrations.

Metallic and glass components of sampling units, canister cleaning apparatuses, and wetted pathways such as stainless-steel tubing, sintered particulate filters, critical orifices, and connecting components should be flushed with humidified HCF zero air or ultrapure nitrogen to remove contamination. They may be further cleaned by disassembling and sonicating in water and/or methanol for 15 min, after which they should be rinsed with fresh methanol and dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 h. Ovens may be set to higher temperatures if the components can withstand the temperatures. To avoid damage to deactivated stainless-steel components due to oxidation in the presence of oxygen-containing atmospheres (e.g., HCF zero air), components treated with silicon-ceramic coatings should not be heated above 80 °C unless evacuated or under an inert atmosphere (e.g., nitrogen).

Nonmetallic components such as Viton seals and O-rings should be disassembled and inspected for cracks, abrasions, and residue (such as from PM) and sonicated in ASTM Type I water for 15 min. After sonication, components should be rinsed with fresh ASTM Type I water and dried in an oven (preferably a vacuum oven) set to approximately 50 °C for a minimum of 12 h.

Following drying, components should be inspected (e.g., to be sure critical orifices are not cracked or compromised), reassembled, and flushed with humidified HCF air or ultrapure nitrogen for at least 12 h.

11 Sample Collection

Before any sample collection is undertaken, decisions need to be made and activities performed to ensure success. Planning and attention to details are important for the generation of high-quality and trusted data. This section addresses the application of the many components and operations previously discussed in **Sections 7**, **9**, and **10**. In addition to the actual collection of samples, the associated presampling and postsampling activities are described.

11.1 Presampling Activities

11.1.1 Preparing SOPs and Quality Assurance Project Plan

Prior to collection of samples, SOPs should be prepared for each process (e.g., canister cleaning, standards preparation, operation of canister air sampling device) specific to the project or program. Additionally, a quality assurance project plan should be prepared that establishes the overall project details and the QA and QC aspects of the process.

11.1.2 Determining Sample Collection Specifics

- Determine the type of sampling to be conducted (subatmospheric, grab, or pressurized).
- Determine the type of sample collection apparatus to be used (MFCD, MFC, commercially available rack-mount or bench-top sampling system). Refer to Section 7.3 for discussion.
- Determine the number of canisters and sampling apparatus required.
- Determine the required sampling time and flow rates needed. *Note: Flow controllers should be calibrated against a reference flow standard prior to field deployment. If the flow controllers are calibrated and shipped to a sampling location, flows must be verified at local conditions and adjusted as necessary prior to deployment.*
  - For subatmospheric sampling, refer to Table 11-1 for typical sampling flow rates for commercially available MFCDs and common canister sizes and sampling times.

Table 11-1: Typical Sampling Flow Rates (mL/min) for Subatmospheric Sampling Using Common MFCDs

Canister Size (L)	Sampling Time					
	1 h	8 h	12 h	24 h	1 week	2 weeks
1	13.2 to 14.9	1.6 to 1.9	1.1 to 1.2	0.56 to 0.62	—	—
2.7	35.5 to 40.2	4.4 to 5.0	3.0 to 3.4	1.5 to 1.7	0.21 to 0.24	—
3	39.5 to 44.7	4.9 to 5.6	3.3 to 3.7	1.6 to 1.9	0.23 to 0.27	—
3.2	42.1 to 47.2	5.3 to 6.0	3.5 to 4.0	1.8 to 2.0	0.25 to 0.28	—
6	78.9 to 89.5	9.9 to 11.2	6.6 to 7.5	3.3 to 3.7	0.47 to 0.53	0.23 to 0.27
15	197.4 to 223.7	24.7 to 28.0	16.4 to 18.6	8.2 to 9.3	1.8 to 1.3	0.59 to 0.67

Note: Values populating Table 11-1 are calculated based on the actual flow vs. pressure plots of MFCDs 1 and 2 shown in Figure 9-2. Flow adjustments may need to be made for sampling at higher elevations or at low temperatures. These flows should result in time-integrated canister samples at a slight vacuum (10 to 20 kPa below ambient or 3 to 6 in. Hg vacuum). For the MFCDs, the pressure at which the flow controller ceases to maintain constant flow is used as the final canister pressure. It is recommended that laboratories determine the flow vs. pressure characteristics for MFCDs in their inventories and apply the results as appropriate to establish the sampling flow rates for desired sampling volumes and times.

- For samples collected at high elevations, the flow rates may need to be adjusted to account for changes in ambient pressures due to elevation. As a general rule, approximately a 0.2 L decrease in potential collection volume occurs for each 305-m (1000-ft) rise in elevation. For example, at 1524 m (5000 ft), a maximum of approximately 5 L of gas at standard conditions can be collected in a 6-L canister due to the lower

ambient pressure and the differential required to drive MFCDs. Larger volumes can be collected if pumps are used.

- For pressurized sampling and for canister sizes or times not listed in Table 11-1, the following equation can be used to calculate the required flow rate at local conditions for sample collection. The flow rate is determined so the canister is filled to the desired final pressure over the specified sampling period. Note that this formula does not correct for differences in temperature:

$$F = \frac{P_c \cdot V}{P_a \cdot D}$$

where:

F = flow rate (mL/min) at local conditions

P_c = final absolute canister pressure (kPa absolute)

V = volume of the canister (mL) at standard conditions (101.3 kPa absolute and 25 °C)

P_a = atmospheric pressure (kPa absolute) at time of sampling

D = sampling duration (min)

For example, if a 6-L canister is to be filled to 21 kPa (3 psi) above ambient (122 kPa [17.7 psia] for ambient pressure of 101.3 kPa [14.7 psia]) in 24 h, the flow rate can be calculated as follows:

$$F = \frac{122\ \text{kPa} \cdot 6000\ \text{mL}}{101.3\ \text{kPa} \cdot 1440\ \text{min}} = 5.0\ \text{mL/min}$$

Note: Users are strongly encouraged to limit final pressures of pressurized samples to ≤ 21 kPa above ambient pressure (3 psig) to minimize the likelihood of condensation within the canister as discussed in Section 6.2.

11.1.3 Preparing Field Materials and Supplies for Use

- Clean canisters and verify that cleanliness and vacuum criteria are met (refer to Section 10.2 and Table 10-3).
- If canisters were previously cleaned and stored pressurized while awaiting use, evacuate prior to field deployment. If canisters were stored at vacuum, verify that they still meet vacuum threshold requirements.

Note: It is recommended that at the time of canister cleaning and preparation, an identification (ID) tag such as a 2 3/8-in. x 4 3/4-in. manila or plastic shipping tag with wire (or similar tag) be attached to each canister to provide a convenient place to record the cleaning date, canister pressure, and other information associated with each canister. This also provides a suitable location to attach sample labels without defacing the canister.

- Establish sample codes (unique identifiers) and develop chain of custody (COC)/sample collection data form(s) (hardcopy and/or electronic).
- *(Optional)* Prepare field QC samples (canister field blanks and field spikes) by filling canisters with clean air or standards as described in Section 15.3.5.

- Clean and verify the cleanliness of sample collection devices (MFCD, rack-mount or bench-top system, etc.) that will be used. Ensure a clean particulate filter is in place.
- Preset flow rates and test the operation of sample collection devices.
- If timers and solenoid valves are used, test their operation. Ensure batteries have adequate voltage to operate the timer and solenoid for the duration of sample collection or replace as necessary. Preprogram time/day and sampling times if practical.
- Prepare at least one backup timer and sample collection device for use in the event that problems arise during deployment (e.g., failed solenoid valve) and replacement is required.
- Assemble wrenches and other needed tools, flow calibration devices, and spare components such as batteries, fittings, etc., to accommodate moderate field repairs in the event of problems during deployment.

11.2 Sample Setup Activities

11.2.1 Extra Samples

It may be desirable to collect a few extra samples at the beginning of a study or when sampling in a new area to provide additional analyses that address analytical method development such as unexpected target compounds, tweaks to analysis volumes, or fine-tuning of GC programs for compound separations. Collection of extra samples depends on the specific project and may not be necessary as generally multiple analyses can be made from a single canister, and one of the initial collected canisters may suffice for this purpose.

11.2.2 Sampling Site Requirements

Specific site requirements generally depend on the project goals; regardless of the goals, it is important that sampler placement provides samples that are representative of the air being monitored. Refer to **Section 7.3.2** for a general description of time-integrated sampling apparatus and general sampling considerations.

11.2.2.1 Existing Air Monitoring Shelters

Many sites where canister samples are collected are associated with existing air monitoring shelters that have been established using EPA guidelines as outlined in the *Code of Federal Regulations,* Network Design Criteria for Ambient Air Quality Monitoring (**40 CFR Part 58 Appendices D and E**), and Sections 6 and 7 of *EPA's Quality Assurance Handbook for Air Pollution Measurement Systems* (**U.S. EPA, 2017**). The requirements for these sites have generally already been determined, and the primary VOC canister sampling decisions deal with whether the air samples are drawn from a multiuse manifold or a dedicated collection line. The canisters are typically placed inside a climate-controlled shelter. For established shelters, the manifold/collection line intake should be positioned so that it is not impacted by local sources such as roadways; parking lots (vehicle exhaust); shelter roofing materials; heating, ventilation, and air conditioning units/building exhausts; outdoor fuel storage areas; and outdoor smoking areas, to name a few. Also, there should be no nearby obstructions such as buildings or vegetation that block air flow. Manifold or dedicated sampling line intakes must be located to avoid bias to the sample. Intakes must extend beyond building overhangs.

11.2.2.2 Special Studies or Investigations

For air samples collected for special studies or investigations using temporary sampling sites, the following criteria should be considered:

- The canister should be placed in a secure location that protects the canister and sampling inlet from unwanted tampering, damage, or theft.
- Canister and sampling inlets are typically designed to withstand outdoor elements (rain, snow, sun exposure) but should be further protected from the elements by being placed under shelter if possible. Air flow around inlets should not be restricted, and inlets should not be located under building overhangs. The level of protection required will depend on the type of sampling devices used.
- Canister MFCD inlets and manifold intakes should be protected to prevent rain from being drawn directly into the MFCD or manifold. Commercial units are typically designed to address this.
- Consider the use of sturdy speaker tripod stands or metal sign posts modified with hook bolts to hang the canisters. Be aware that any posts that are driven into the ground must be in an area known to be free of underground wiring and/or plumbing.
- There should be no biasing sources in the immediate vicinity, such as outdoor smoking areas; vehicle exhaust; heating, ventilation, and air conditioning units/building exhaust; outdoor fuel storage areas; shelter roofing materials; or exhaust from other sample collection devices. In general, horizontal distances should be > 10 m from biasing sources.
- Placement near vegetation or structures that block or significantly restrict air flow should be avoided.
- Inlet height placement is generally project specific. At temporary locations such as residential indoor or outdoor monitoring sites, inlet heights should be in the breathing zone, approximately 1 to 2 m above ground level. For special studies conducted at established monitoring shelters, inlet heights generally should be between 2 and 6 m. For collection of collocated samples, inlets should be placed as close together as possible, generally within 12 in. (both vertically and horizontally).
- Length and diameter of any tubing used to connect to manifolds or penetrate through shelters should be minimized to maximize linear velocity, thus minimizing residence time of the sampled air in the sampling line. Use inert silicon-ceramic–coated tubing (preferred) or high-grade stainless steel for this purpose. Do not use PTFE, PFA, FEP, or polyethylene tubing. Use of tubing with 1/16- or 1/8-in. outer diameter is recommended.

11.2.3 Sample Setup and Deployment

Whether using manual or automated techniques to collect canister air samples, certain prescribed steps should be followed to ensure successful deployment and sample collection. Deployment of canisters with insufficient starting vacuums, use of improperly functioning sampling apparatus, or improperly labeled samples may result in invalid samples.

Canisters scheduled for deployment can be tracked from cleaning to the point of deployment using the manufacturer-assigned serial number found on each canister, an identifier created by the laboratory's

information management system, or some other convention. Regardless of the identifier used, it must be unique. As noted in Section 11.1.3 an ID tag such as a 2 3/8-in. x 4 3/4-in. manila or plastic shipping tag with wire (or similar tag) provides a convenient place to record the canister identifier, cleaning date, canister pressure, and other information associated with each canister until the time of deployment.

At the time of successful deployment, the canister must be assigned a unique sample code that either includes information or links to information providing when and where the sample was collected. This code should also link the sample with any other pertinent collection information and should be affixed to the canister or canister tag as a label that is water resistant or waterproof. A COC form (see Figure 11-1 for an example) should accompany the canisters during shipment and collection to document sample handling and transport. COC forms may be electronic or hard copy.

Canister vacuum should be verified prior to deployment and must be measured at the time of setup to minimize contamination, bias, and/or incomplete sample volumes due to leakage and inadequate starting vacuum. If using a sampling apparatus with an incorporated calibrated vacuum/pressure gauge, the canister vacuum should be read and recorded at the time the canister is connected to the sampling apparatus. Automated computerized sampling units may include routines to facilitate measuring and verifying canister vacuum upon sample setup. If the sampling apparatus does not have an incorporated gauge or if the gauge is not calibrated or functioning properly, the vacuum should be measured and recorded using an auxiliary calibrated digital or analog gauge just prior to connecting the canister to the sampling apparatus. Automated rack-mount and bench-top canister samplers may be programmed to automatically test and record vacuum prior to sample collection.

Starting canister pressure should ideally be high vacuum (≤ 0.0067 kPa absolute or ≤ 50 mTorr) and should not permit more than an overall 5% dilution of the sample collected into the canister. Such a dilution is equivalent to a starting canister pressure of approximately 4 kPa absolute (0.6 psia) for samples collected to a subatmospheric pressure of 81 kPa absolute (11.7 psia) or approximately 7 kPa absolute (1 psia) for samples collected to 122 kPa absolute (17.7 psia). Starting canister pressure should not exceed 7 kPa absolute, which is equivalent to 28 in. Hg vacuum at standard barometric pressure.

The sampling apparatus should be tested for proper connection to the canister and the connection verified to be leak free. If battery-powered timers and solenoids are used, verify that sufficient battery charge is available and that programmed times are correct.

Perform the following steps at the time of sample setup and deployment:

1. Ensure each canister is labeled with unique canister and sample ID codes.
2. Measure and record the canister vacuum to verify that the canister has not leaked and has sufficient vacuum to collect the sample (refer to Table 11-2). Replace the canister if the initial vacuum criterion is not met.
3. Connect the canister to the sampling apparatus (if not already performed as part of the measurement of the canister vacuum).
4. Conduct a leak check.
    - For MFCDs:
        - Tightly cap the inlet.
        - If the gauge is upstream of the solenoid, manually activate the solenoid (if so equipped).
        - Open and close the canister valve to generate a vacuum at the gauge.

- Observe the gauge to assess the leak rate. There should be no perceivable pressure increase.
- If there is a leak, gently snug the fittings and retest. If the leak persists, replace the sampling apparatus and/or canister and test.
- Following a successful leak check, remove the inlet cap.

- For rack-mount or bench-top sampling instruments:
  - Follow the manufacturer's instructions for performing onboard automated leak check routines, if so equipped.
  - Open and close the canister valve, or, if so equipped, activate the vacuum pump to generate a vacuum in the system.
  - Observe the gauge to assess the leak rate.

5. Open the canister valve.
6. Record the time that the valve is opened as the start time if the sampling apparatus is manually operated. If the sampling apparatus is controlled by a timer, record the time that the timer is scheduled to turn on as the start time.
7. If the sampling apparatus uses a timer to activate the solenoid, verify the timer program and flow rate (if possible). (Refer to **Section 9.2.2** for a discussion on flow measurements.)
8. Document pertinent information (listed below) on the COC/sample collection data form(s) and canister tag.

Sampling details should be documented on the COC/sample collection data form(s) (refer to the example form shown in Figure 11-1). The following are typical parameters that should be recorded along with the operator's initials and date recorded:

- Unique sample ID
- Unique canister ID
- Date canister cleaned
- Unique sampling unit ID (MFCD, orifice, rack-mount or bench-top unit, and channel)
- Initial canister vacuum measured at time of sample setup
- Gauge/transducer ID used for initial canister vacuum measurement
- Acceptable canister vacuum threshold met/not met (optional)
- Date/time canister was installed on sampling unit
- Performance of a leak check and pass/fail status
- Confirmation of opening canister valve (as applicable)
- Sample collection start time and date
- Sample collection end time and date
- Sample retrieval time and date (may be the same or different from collection end time)
- Canister vacuum/pressure upon retrieval
- Acceptable final canister pressure threshold met/not met *(optional)*
- Sampling flags or error messages provided by the sampling unit
- Comments such as unusual events or conditions that may impact sample results

Sample collection details, or a portion of them, may also be recorded on the tag attached to the canister (see Section 11.1.3). It is recommended that the following information, at a minimum, be recorded on the canister tag: unique sample ID; canister ID; date, time, and vacuum at time of deployment; and date, time and vacuum/pressure at time of retrieval.

EXAMPLE TO-15A SAMPLE COLLECTION FORM

		Initials/Date
Sample ID		
Canister ID		
Date Canister Cleaned		

Sample Set Up Details				
Sampling Unit ID				
Sampling Location				
Initial Canister Pressure (kPa absolute)		Does this pressure meet the criterion (≤ 7 kPa absolute)? [Y/N]		
Pressure Gauge or Transducer ID		Pressure Gauge or Transducer Calibration Date:		
Time/Date Canister Installed on Sampling Unit				
Leak Check Performed [Y/N]				
Leak Check Starting Pressure (kPa absolute)		Leak Check Ending Pressure (kPa absolute)		
Leak Check Duration		Does this leak rate meet the criterion (≤ 0.69 kPa/minute)? [Y/N]		
Canister Valve Opened? [Y/N]				

Sample Collection Details		
Sample Start Time/Date		
Sample End Time/Date		

Sample Retrieval Details				
Canister Pressure Upon Retrieval (psia)		Does this pressure meet the criterion (≥ 69 and ≤ 83 kPa absolute)? [Y/N]		
Sampling Unit Flags or Errors				
Comments:				

Figure 11-1: Example TO-15A COC/sample collection data form.

11.3 Sample Retrieval

If canister air samples are collected using a manually operated sampling apparatus, meaning that a valve (e.g., the canister valve) must be manually opened and closed to collect the sample, it is important that the operator be present at the designated time to close the canister valve. If the samples are collected using a flow control device attached to a programmed solenoid valve timer, the solenoid valve will close at the programmed time and the operator does not need to be present at the designated stop time to close the canister valve. However, the operator should return within a reasonable amount of time (within 1 to 2 days) to close the canister valve. Operators should ensure that the solenoid is not programmed to open again prior to retrieval.

If using a manually operated sampling apparatus with a calibrated vacuum/pressure gauge attached, the vacuum/pressure reading should be recorded before closing the canister valve. For sampling apparatus with a programmed solenoid timer, if the gauge is on the upstream side of the solenoid and the solenoid is closed, a temporary override (or manual activation) will be necessary to open the solenoid to measure the vacuum/pressure. For automated sampling devices with vacuum/pressure gauges downstream of the solenoid, the vacuum/pressure can be read directly. For sampling systems without gauges or with improperly functioning gauges, or as an alternative to using an incorporated gauge, the canister vacuum/pressure can be measured using an auxiliary calibrated digital or analog vacuum/pressure gauge.

The following steps should be performed at the time of retrieval for sampling apparatus with properly functioning calibrated incorporated vacuum/pressure gauges:

1. Read and record the final canister vacuum/pressure measurement.
2. Close the canister valve (and record the time if closing the valve concludes the sampling period).
3. Disconnect the sampling apparatus from the canister.
4. Cap the canister valve inlet with a brass plug cap.

The following steps are performed at the time of retrieval when an auxiliary digital or analog vacuum/pressure gauge is used for vacuum/pressure measurements:

1. Close the canister valve.
2. Record the sampling end time (if closing the canister valve stops the sample collection).
3. Disconnect the sampling apparatus from the canister.
4. Attach the calibrated vacuum/pressure gauge.
5. Momentarily open the canister valve.
6. Allow the vacuum/pressure reading to stabilize and record the final measurement.
7. Close the canister valve and remove the gauge.
8. Cap the canister valve inlet with a brass plug cap.

The following steps are performed at the time of retrieval when an automated rack-mount or bench-top system is used for sample collection:

1. Close the canister valve(s).
2. Disconnect the canister(s) from the sampling apparatus.
3. Cap the canister valve inlet with a brass plug cap.

4. Retrieve and record pertinent sampling information stored by the system on the COC/sample collection data form(s).
5. Transfer electronic data collection files from the sampler system to a backup device.

The ending vacuum/pressure reading is compared to the expected ending reading to evaluate whether the sample was collected appropriately. Refer to Table 11-2 for typical pressure ranges for collected samples. An additional conversion chart is provided in **Appendix A**. Sampling units that log the sampling flow rate and canister pressure should be checked for error messages or alarms (flags) that may be generated due to sampling errors. As a final step, the canister air samples should be prepared and secured for the transport method of choice.

Table 11-2: Key Pressure Measurements and Gauge Ranges Expressed in Commonly Used Units (approximate conversions)

Measurement	Typical Pressure Use Ranges							
	kPa		psi		in. Hg		mm Hg (Torr)	
	Absolute	Gauge[a]	Absolute	Gauge[a]	Absolute	Gauge[a]	Absolute	Gauge[a]
Cleaning – final evacuation	≤ 0.0067	~ –101	≤ 0.001	~ –14.7	≤ 0.02	~ –29.9	≤ 0.05 (≤ 50 mTorr)	~ –760
Canister vacuum prior to sample collection	≤ 7	≤ ~ –94.1	≤ 1	≤ ~ –13.7	≤ 2	≤ ~ –28	≤ 52	≤ ~ –708
Subatmospheric sampling pressure range at completion	64 to 88	–37 to –13	9 to 13	–5 to –2	19 to 26	–11 to –4	484 to 662	–276 to –98
Pressurized sampling pressure range at completion[b]	110 to 122	9 to 21	16 to 18	1 to 3	32 to 36	2 to 6	827 to 915	67 to 155

[a]Gauge reading = (absolute pressure) – (atmospheric pressure at sea level); conversions obtained from the ENDMEMO website, http://www.endmemo.com/.

[b]Users of the method are cautioned that pressurized sampling methods may result in condensed water within the canister, which may have negative effects on the integrity of the VOCs in the sample.

12 Canister Receipt and Preparation for Analysis

12.1 Measurement of Canister Receipt Pressure

Upon receipt at the laboratory, the sample custodian should review the sample collection information documented on the COC/sample collection data form(s) for completeness and accuracy. The sample custodian should also compare the canister label with the sample collection data sheet and verify that the canister and sample IDs are correct, that the sample collection start and stop times are reasonable, and that the starting and ending sample pressures are as expected.

The canister pressure is then measured with a calibrated vacuum/pressure gauge or transducer and recorded. For samples collected to subatmospheric pressure, the measured canister absolute pressure must be within ±3.5 kPa (0.5 psi) of that measured upon retrieval. This criterion permits a change of pressure (and therefore volume change, or potential dilution) equivalent to approximately 5% of the total

pressure of a sample collected to 90 kPa absolute. Pressure differences exceeding this criterion indicate the canister has leaked, permitting contamination of the collected sample. Results from subatmospheric pressure samples exhibiting leaks should be flagged as invalid unless the pressure difference can be confidently attributed to a temperature difference from sample collection to measurement in the laboratory. Note that for samples collected in a temperature-controlled monitoring shelter, a temperature difference is not expected to contribute to a discernible pressure change.

For canisters collected to pressures above atmospheric pressure, the absolute pressure measured upon receipt should ideally also be within ±3.5 kPa (0.5 psi) of that measured at sample retrieval but should minimally exceed ambient pressure at the laboratory. Results from positive pressure samples that have leaked to atmospheric pressure may be suspect and should, at a minimum, be flagged as an “estimated” value for conditional use unless the pressure difference can be confidently attributed to a temperature difference from collection location to laboratory pressure measurement as noted above for subatmospheric pressure sampling.

12.2 Dilution of Canister Samples

Canister samples collected at subatmospheric pressures may require pressurization with HCF zero air or ultrapure nitrogen to provide sufficient pressure for analysis. Minimum sample pressures will depend on the size of the canister and the capability of the preconcentrator to remove the desired aliquot of the sample and will be indicated by the instrument manufacturer. Canisters with target VOC concentrations exceeding the calibration curve range may also require dilution.

When such dilution is performed, the source of diluent gas must be demonstrated to be free of contaminants to ensure that the dilution process does not contaminate the collected samples. This may be done by collecting diluent gas in a separate certified clean canister as a dilution blank (DB) and analyzing. The DB should not be prepared through a dilution system used for preparing standards. The concentrations of the target VOCs in the DB must be < 20 pptv. Ideally a DB is prepared and analyzed with each set of samples that are diluted and at a minimum is prepared and analyzed when the source gas and/or filters are changed.

The canister pressure must be measured with a calibrated vacuum/pressure gauge or pressure transducer just prior to dilution and immediately following dilution. A canister dilution correction factor (CDCF) is calculated from the two absolute pressure readings as follows:

$$\mathrm{CDCF} = \frac{P_d}{P_i}$$

where:

P_d = pressure of the canister following dilution (kPa)

P_i = pressure of the canister immediately preceding dilution (kPa)

Diluted canisters should be equilibrated minimally overnight and preferably 24 h before analysis.

13 Preparation of Calibration Standards

Calibration standards will typically be prepared from stock standard gases by dilution using humidified HCF zero air or ultrapure nitrogen. Standards may be prepared by dynamic or static dilution methods employing the equipment described in Section 7.6.4. Dynamic dilution techniques involve blending the standard gas mixture with the diluent gas in a manifold prior to transfer to the canister. Static dilution techniques involve dilution of the standard gas mixture with the diluent gas directly in the canister. Standards should be humidified to approximately 40% to 50% RH. Following preparation, it is recommended that each canister be allowed to equilibrate for a minimum of 24 h prior to an initial analysis.

13.1 Humidification of Canisters

The humidity of the gas within a canister is important in the preparation of calibration standards and impacts analysis in several ways. First, water vapor within a canister displaces gases from the interior surfaces of the canister, retaining them in the gas phase. This is especially important for VOCs with higher BPs and for electropolished canisters (Ochiai et al., 2002). Insufficient humidification of calibration standards may result in incomplete quantitative transfer of VOCs from the calibration manifold and/or canister(s) containing the calibration mixture to the preconcentrator. Insufficient humidification may also impact transfer to or from subsequent canisters when canister gas standards serve as intermediates for preparing lower level standards. Second, depending on the meteorological conditions at the time of collection, ambient air samples will include some humidity, typically above 10% RH and may be saturated to 100% RH. Since matrix matching between collected samples and the associated standards and blanks is desirable, standard and blank canisters should be humidified to approximately 40% to 50% RH at ambient laboratory temperature. The range of 40% to 50% RH represents a practical compromise to ensure sufficient humidification given the impracticality of matching humidity for the variety of humidity levels possible in collected samples. This helps ensure that hydrophilic and high-BP VOCs meet relevant method performance specifications.

Humidification can be accomplished in several ways: employing a bubbler or impinger within the dilution gas stream, addition of deionized water to the canister, or a combination of these two methods. Adding water to canisters with a syringe via rubber septum is not recommended as the syringe needle can core the septum and result in deposits of rubber into the canister and valve. This may lead to potentially irreproducible and biased VOC recoveries from the canister. For direct injection of water into a canister with a syringe, a high-pressure PTFE-sealed septum (such as a Merlin Microseal [Merlin Instrument Company, Newark, DE]) should be installed on the canister. For canisters to be connected to a gas source for pressurization via a dynamic or static dilution system, the water can be added to the valve opening of the evacuated canister prior to connecting to the dilution system. Once connected, the valve is opened, and the water is pulled into the canister along with the diluted standard gas.

The following formula is used to determine the volume of water to add to a canister to achieve the desired % RH (Herrington, 2013):

$$V_w = D_{sat} \cdot RH_d \cdot V_c \cdot \frac{P_c}{P_s} \cdot \frac{1}{D_w}$$

where:

V_w = water volume to add to canister (µL)

D_{sat} = saturation vapor density of water (mg/µL) at ambient laboratory temperature (refer to Table 13-1)

RH_d = desired RH level expressed as a decimal

V_c = nominal internal volume of canister (L)

P_c = final pressure of canister (kPa absolute)

P_s = standard ambient pressure (101.3 kPa absolute)

D_w = density of water (1 mg/µL)

*Notes: The formula above does not correct the density of water for the ambient temperature and assumes the density of water to be 1 g/mL. It also assumes that 100% of the added water is in the gas phase. Water may condense inside the canister if the temperature is reduced to the point at which the amount of water in the canister exceeds the saturation density. For more information regarding canister humidity, refer to "Variation of the Relative Humidity of Air Released from Canisters after Ambient Sampling" (**McClenny et al., 1999**).*

Table 13-1: Water Saturation Vapor Density at Various Temperatures

Temperature (°C)	Water Saturation Vapor Density (mg/L)[a]
15	12.8
16	13.6
17	14.4
18	15.3
19	16.3
20	17.3
21	18.3
22	19.4
23	20.6
24	21.8
25	23.1
26	24.4
27	25.9
28	27.3
29	28.9
30	30.5
31	32.2
32	34.0
33	35.8

[a]Values are generated according to the following formula (Nave, 2017):

$$vapor\ density\ (mg/L) = 5.018 + 0.32321 \cdot T + 8.1847 \times 10^{-3} T^2 + 3.1243 \times 10^{-4} T^3$$

where: T = temperature in °C

Example:

An analyst prepares a VOC standard in a 6-L canister, diluting to a final pressure of 202.6 kPa (2 ata) with dry HCF zero air. The laboratory temperature is 25 °C and the analyst wants the standard to be 50% RH. The volume of water needed is calculated as follows:

$$V_W = 23.1\ \text{mg/L} \cdot 0.50 \cdot 6\ \text{L} \cdot 1\ \mu\text{L/mg} = 139\ \mu\text{L}$$

13.2 Dynamic Dilution

13.2.1 Calibration of Dynamic Dilution Systems

For dynamic dilution, the system requires a separate flow control device for the diluent gas and each gas standard to be diluted as well as a mixing area such as a manifold where the gases can be sufficiently mixed before introduction to the preconcentrator or canister. Dynamic dilution gas flows are typically controlled by employing calibrated electronic MFCs with flow ranges appropriate to achieve the desired dilution factor(s).

MFCs in dynamic dilution systems should be calibrated, with the calibration verified at least annually by comparison to a certified or primary reference flow standard. MFCs that fail a calibration check criterion of ±2% should be recalibrated. For commercially available dilution instruments, the manufacturer's instructions should be followed for recalibration. For laboratory-built systems that employ MFCs, the controllers may either be removed and shipped to a manufacturer or third party for recertification. Alternatively, a regression calibration curve can be generated by challenging the MFC with the appropriate gas, recording the MFC setting, and measuring the flow with a flow calibrator for a minimum of five points covering the 10% to 100% portion of the flow range of the MFC. The resulting regression slope and intercept is then used to provide the MFC setting for a given desired flow. As a best practice, flows should be measured at each use with a primary reference flow standard if possible, depending on the system configuration and accessibility to the MFCs.

13.2.2 Standards Preparation by Dynamic Dilution

Dynamic dilution systems should be powered on and the diluent and stock gases allowed to flow through the respective MFCs for a minimum of 1 h prior to use. A best practice is to experimentally determine the actual equilibration times necessary for each concentration level and document this in the SOP as appropriate. This equilibration period allows passivation and equilibration of the system to ensure the concentrations of the VOCs in the blended gas are stable prior to transferring to the canister (or directly to the preconcentrator).

Before proceeding with the preparation of canister standards by dynamic dilution, determine the method of humidification to be used as discussed in **Section 13.1**. Standards should be prepared from low concentration to high concentration. When changing stock gas flow rate(s) to prepare a different concentration, calibration gas should flow through the system for a minimum of 30 min prior to preparation of the working calibration canister (or delivering the working standard directly to the preconcentrator). These equilibration times are particularly important for laboratories analyzing compounds with higher BPs such as hexachlorobutadiene and 1,2,4-trichlorobenzene. Extended equilibration times may be necessary to fully passivate the flow path and mixing chamber of the dynamic dilution system when higher BP compounds are included in the standard.

Note: Final pressures of calibration standard canisters must not exceed the maximum pressure permitted by the preconcentrator unit. Closely matching the pressure of the calibration standard canisters to the expected pressure of the collected field samples is recommended when analysis is performed with preconcentrators that measure volumes with MFCs. Consult the preconcentrator instrument manual for further guidance on matching canister pressures.

The final concentration of the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot F_s}{F_s + F_d}$$

where:

C_f = final diluted standard concentration (pptv)

C_s = certified concentration of stock standard (pptv)

F_s = flow of stock standard (mL/min)

F_d = flow of diluent gas (mL/min)

Note: If multiple gas standards are combined for dilution, the denominator is the sum of all gas flows combined for preparing the dilution.

13.3 Static Dilution

Static dilution methods involve the precise measurement of the pressure changes in, or delivery of known volumes of gas into, a container of known constant volume. Static dilution is performed into a fixed-volume vessel such as a canister or into a manifold where the known volumes or partial pressures of each gas are measured. Before proceeding with the preparation of canister standards by static dilution, determine the method of humidification to be used as discussed in Section 13.1.

13.3.1 Static Dilution by Addition of Partial Pressures into Canisters

Starting with an evacuated canister, a pressure transducer or gauge is connected to the canister to monitor the canister pressure as gases are added. Stock and diluent gases are added separately by direct connection of the gas to the canister. The canister pressure is measured before and after standard and diluent gases are bled into the canister, and these pressures are input into the calculation of the dilution factor and final concentrations.

The final concentration of each VOC in the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot (P_{sa} - P_{sb})}{P_f}$$

where:

C_f = final diluted standard concentration (pptv)

C_s = certified concentration of stock standard (pptv)

P_{sa} = absolute pressure of canister after adding standard gas (kPa)

P_{sb} = absolute pressure of canister before adding standard gas (kPa)

P_f = final absolute pressure of canister after adding standard and diluent gases (kPa)

13.3.2 Static Dilution by Addition of Partial Pressures into Manifolds

Diluent gas and standard gas(es) are introduced stepwise into a manifold constructed of chromatographic-grade stainless steel or silicon-ceramic–coated stainless steel to which a canister is connected. The pressure of the manifold and canister is measured with a pressure transducer or combination of pressure transducers prior to and after the addition of each gas to the manifold.

The final concentration of the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot (P_{sa} - P_{sb})}{(P_{sa} - P_{sb}) + (P_{da} - P_{db})}$$

where:

C_f = final diluted standard concentration (pptv)

C_s = certified concentration of stock standard (pptv)

P_{sa} = absolute pressure of manifold and canister after adding standard gas (kPa)

P_{sb} = absolute pressure of manifold and canister before adding standard gas (kPa)

P_{da} = final absolute pressure of manifold and canister after adding diluent (kPa)

P_{db} = absolute pressure of manifold and canister before adding diluent (kPa)

13.3.3 Static Dilution by Addition of Known Volumes into Canisters

Note: This method of dilution preparation is difficult to perform reproducibly and requires practice and excellent technique to perform consistently. Additionally, due to deviation from the vendor-stated volume of the canister (e.g., 6 L), this method may be subject to errors in the final theoretical concentration as the canister is not volumetrically certified.

A known volume of standard gas is added to an evacuated canister with a gas-tight syringe through a septum, and the diluent gas is added to a known final pressure. The canister contents should be humidified as described in Section 13.1. The final concentration of the diluted standard is calculated as follows:

$$C_f = \frac{C_s \cdot V_s}{V_c(\frac{P_f}{P_a})}$$

where:

C_f = final diluted standard concentration (pptv)

C_s = certified concentration of stock standard (pptv)

V_s = volume of stock standard added to canister (mL)

V_c = nominal volume of canister (mL)

P_f = absolute pressure of final dilution (kPa)

P_a = ambient absolute pressure (kPa)

13.3.4 Static Dilution into Canisters by Gravimetric Methods

Gravimetric dilution of standards requires access to a high-sensitivity, high-capacity analytical balance that can resolve and register the addition of small amounts of gas or neat material to a fixed-volume vessel such as a canister or cylinder. Known masses of standard gases or neat materials are added to

the canister. The canister mass is measured before and after addition of each material, and the added mass is calculated by difference. The canister mass or pressure is measured before and after the addition of diluent gas to determine the final concentration in the canister. This convention, especially when using neat source material, requires excellent technique and hygiene to prepare an accurate and contaminant-free standard. In general, this technique is employed for experimental or exploratory work for which diluted standard gases are not available from commercial sources.

The masses of the added standard and diluent materials are measured directly with the analytical balance, if all materials are gases. Liquid standard material masses may be measured directly with the analytical balance when added to the canister or may be measured volumetrically and the mass determined according to the density of the liquid material at the temperature when weighed according to the following equation:

$$m_{std} = V_{ls} \cdot d_{ls}$$

where:

m_{std} = mass of standard material (g)
V_{ls} = liquid volume of neat standard material at temperature of preparation (mL)
d_{ls} = density of the neat standard (g/mL) at temperature of preparation

For example, 0.0100 mL of 1,2,4-trichlorobenzene at 25 °C (density of 1.46 g/mL at 25 °C) is added to a canister.

0.00100 mL · 1.46 g/mL = 0.0146 g 1,2,4-trichlorobenzene

The gaseous volumes of the standards and diluent are determined from the mass of each gas added to the fixed-volume vessel according to the following equation. Gaseous volumes of standards are corrected according to their purity listed on the certificate of analysis. Diluent gases are assumed to have 100% purity:

$$V = \frac{m \cdot R \cdot T \cdot p}{MW \cdot P_s}$$

where:

V = gaseous volume of added gas at 25 °C and 101.3 kPa absolute (L)
m = mass of the gas added (g)
R = gas constant, 8.314 L-kPa/mol·K
T = standard temperature, 298 K
P_s = standard pressure, 101.3 kPa absolute (1 atm)
MW = molecular weight of the gas (g/mol)
p = purity of neat material as listed on the certificate of analysis (as a decimal)

For example, 0.0114 grams of 99.2% pure benzene (MW 78.11 g/mol), 0.0146 grams of 99.7% pure 1,2,4-trichlorobenzene (MW 181.45 g/mol), and 4585.12 grams of high-purity nitrogen (MW 28.013 g/mol) are added to a cylinder:

(0.0146 g · 8.314 L-kPa/mol·K ·298 K · 0.997)/(181.45 g/mol · 101.3 kPa) = 0.00196 L 1,2,4-trichlorobenzene

(0.0114 g · 8.314 L-kPa/mol·K ·298 K · 0.992)/(78.11 g/mol · 101.3 kPa) = 0.00354 L benzene

(4585.12 g · 8.314 L-kPa/mol·K ·298 K · 1.00)/(28.013 g/mol · 101.3 kPa) = 3999.25 L nitrogen

The final concentration (in pptv) is then calculated using the following equation:

$$C_f = \frac{V_s}{V_t} \cdot 10^{12}$$

where:

C_f = final diluted standard concentration (pptv)

V_s = volume of stock standard gas added to vessel at 25 °C and 101.3 kPa absolute (L)

V_t = total volume of standard and diluent gases at 25 °C and 101.3 kPa absolute (L)

For the example above, the concentrations of 1,2,4-trichlorobenzene and benzene are 490,000 pptv (0.00196 L/3999.26 L · 10^{12}) and 885,000 pptv (0.00354 L/3999.26 L · 10^{12}), respectively.

13.4 Storage of Standards

Standards prepared in canisters should be stored at ambient laboratory conditions for up to 30 days. Users should note that many target VOCs may not be stable over this time frame, so it is strongly recommended that users demonstrate storage stability in the canisters to be employed by following the canister bias checks described in Section 9.4. Storage locations should be free of potential contaminants.

14 Sample Preconcentration and Analytical System Operation

The introduction of standards and samples to the analytical system is handled by a preconcentrator unit configured as a multitrap system whose function is to quantitatively trap the target VOCs while allowing bulk gases and water to pass through the system. Elimination of bulk gases and water improves the GC separation of the target VOCs. Target VOCs with high temporal resolution are separated with fused-silica capillary columns and detected by a linear quadrupole, ion trap, or TOF MS.

14.1 Sample Preconcentration

A measured aliquot of the whole air sample (typically 100 to 1000 mL) is drawn from the sample canister by vacuum through a preconcentrator. Moisture and bulk atmospheric gases such as oxygen, nitrogen, argon, and carbon dioxide must be largely removed from the sample aliquot prior to introduction of the target VOCs to the GC. Instrument manufacturers have developed different methods for removal of moisture and bulk gases, most of which typically involve freezing water from the sample aliquot by cryogenic or electronic cooling.

One general convention passes the sample aliquot through an empty metal or quartz trap cooled to approximately -30 to -50 °C to freeze the water but permit the target VOCs and bulk gases to pass through to a sorbent bed trap. The empty trap containing the ice is then isolated from the sorbent bed

trap, warmed to melt the ice, swept with a dry purge gas to vent, and readied for the next sample (**Entech Instruments, 2015**).

In another convention, the sample aliquot is routed through an empty trap or a trap packed with glass beads that is cooled to approximately -110 to -160 °C to retain all of the target VOCs and water while permitting the bulk gases to pass through. The trap is then warmed slightly above the freezing point of water and flushed with dry carrier gas to sweep the target VOCs onto a subsequent sorbent bed trap and retain most of the water on the first trap (**Agilent Technologies, 2017**).

In either convention described above, the second trap may contain sorbent beds with one or more sorbents arranged to selectively trap the target VOCs and permit water and the bulk gases to pass through. Following trapping of the target VOCs on this second trap, it is isolated, heated quickly to desorb the target VOCs, and backflushed to the GC column or to a subsequent focusing trap (typically a cooled empty trap). The focusing step delivers the VOCs to the GC column in a small volume of carrier gas, which facilitates sharp chromatographic peaks and improved baseline separation of peaks. If multiple sorbents are employed in the trap, the sorbents are arranged such that the sample aliquot first enters the weakest sorbent and then successively stronger sorbents. This configuration permits trapping of the higher-BP VOCs in the weaker sorbent. Lower-BP VOCs are not retained as completely on the weaker sorbents and partially pass through to the stronger sorbents where they are retained. Once trapping is complete, the trap may be purged with dry carrier gas to remove excess moisture, or the preconcentration may progress directly to heated desorption. During heated desorption, the trap is rapidly heated and backflushed to release the target VOCs from the sorbents. Such multisorbent bed arrangements allow efficient trapping and desorption of target VOCs. Sorbent configurations, trap cooling temperatures, flush volumes, and desorption temperatures are recommended by the preconcentrator instrument manufacturers and are tailored to the suite of target VOCs desired for quantification.

A third type of preconcentration uses a series of capillary columns to trap and maintain target VOCs while allowing water and bulk gases to pass through. Upon backflushing, the target VOCs are trapped onto a second series of capillary columns for focusing and then backflushed for injection onto the GC column.

Preconcentrator instrument manufacturers will typically indicate the optimum factory default settings for the sample aliquot volume, trapping time, trapping temperature, gas flows, and additional preconcentration parameters. Each of these variables may be adjusted based on the needs of the individual user and the suite of desired VOCs for measurement.

14.2 Preconcentration System Operation

Preconcentrator traps should be conditioned when first installed to eliminate contaminants that act as interferences or chromatographic artifacts. Conditioning may be performed with prolonged baking of the trap at an elevated temperature (e.g., 200 to 300 °C) while flowing dry, inert carrier gas (hydrogen or helium as recommended by the manufacturer) through the trap. The conditioning temperature depends on the sorbents in the trap and is typically recommended by the sorbent or trap manufacturer. Note that preconcentrator traps with multiple sorbent beds should be conditioned at the lowest temperature of the sorbents contained in the trap (**Brown, 2013**). For example, if a sorbent trap contains both Tenax-TA (MilliporeSigma, St. Louis, MO, recommended conditioning temperature 320 °C) and Carbopack (available from MilliporeSigma, St. Louis, MO, recommended conditioning temperature 350 °C), the trap conditioning temperature should not exceed 320 °C. The temperature during conditioning should be

raised slowly in a stepwise manner (e.g., 20 °C/h) until the conditioning temperature is achieved. Bakeout periods of approximately 48 h at the conditioning temperature have shown to be effective; however, manufacturer recommendations should be followed. After this 48-h period, most of the trap contamination will have been removed. Lower concentration (sub-ppbv) levels of target compounds may still evolve from the trap for an extended period following conditioning. Analysis of instrument blanks (IBs) and method blanks (MBs) will demonstrate sufficient trap conditioning when criteria in Table 18-1 are met.

Differing configurations of preconcentrator systems and the associated sorbent traps and conventions for moisture management require the operating conditions and settings of the preconcentrator to be optimized based on the desired suite of target VOCs. The manufacturer's guidelines should be used as a starting point.

14.3 GC-MS System

The instrument operator should optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methylpolysiloxane stationary phase is an indication of acceptable chromatographic performance. GC carrier gas flows, oven temperature program, and instrument run time should be based on the manufacturer's recommendations and customized for separating the list of desired target VOCs. In general, heated transfer lines from the preconcentrator to the GC should be set to manufacturer recommendations, typically approximately 80 to 100 °C.

14.3.1 Example GC Conditions

Example GC analytical conditions are given in Table 14-1 for carrier gas, carrier gas flow rate, and oven program. These conditions assume the use of a 60-m length fused-silica column with an I.D. of 0.25 or 0.32 mm and a polydimethylsiloxane film thickness of 1 µm.

Table 14-1: Example GC Analytical Conditions

Parameter	Specification	
Carrier gas:	Helium	
Carrier gas flow rate:	1–3 mL/min as recommended by manufacturer	
Oven temperature program:	Initial temperature[a]:	35 °C
	Initial hold time:	2 min
	Ramp rate:	8 °C/min
	Final temperature:	220 °C
	Final hold time:	Until all target compounds elute

[a]This is a default initial temperature, and users may need to employ a subambient initial oven temperature to effectively separate VOCs and interferences eluting in the early portion of the chromatogram.

14.3.2 Example MS Conditions

The MS instrument manufacturer's recommendations should be followed for detection of the desired suite of target VOCs. The following are examples of MS settings for linear quadrupole, ion trap, and TOF MS detectors:

- Linear quadrupole MS instruments should be operated in EI mode at nominal ionization energy of 70 eV. The scan range should be commensurate with the target analytes; the recommended range is 35 to 270 amu unless the desired target VOCs require a different scan range. Scan ranges that include *m/z* 28 and 32 may experience interference problems with nitrogen and oxygen, respectively. Creation of custom scan ranges that are tailored to specific analyte RTs may be appropriate and may avoid these interferences when an expanded scan range is needed. The MS should be configured to perform at least one scan per second. Ideally, the scan rate should be fast enough that at least 10 (**Boyd et al., 2008**), and preferably 12 or more, scans are available for each peak.
- Ion trap MS instruments should be operated in EI mode at nominal ionization energy of 70 eV. As with linear quadrupole instruments, the scan range should cover the desired target VOC suite, and the recommended range is 35 to 270 amu unless an expanded range is needed. The same interferences with nitrogen and oxygen apply when including lower masses in the scan range. The scan time should be set to approximately 0.4 to 1 s/scan; faster scan rates will provide improved resolution. Axial modulation, manifold temperature, and emission current should be adjusted to the manufacturer's recommendations.
- TOF MS instruments should be configured to the manufacturer's recommendations. The following are typical settings: EI setting of 70 eV, ion source temperature of 260 °C, and transfer line temperature of 260 °C. Spectral acquisition rates of approximately 2 to 4 Hz (2 to 4 scansets/s) or higher will provide appropriate resolution for eluting peaks.

14.3.3 Data Acquisition Method

Based on the type of MS that is in use, the analyst must decide on a specific data acquisition method (SIM, full scan, SIM/SCAN, SIS) as discussed in **Section 7.6.3.3**. The data acquisition parameters are set up based on the manufacturer's specific software package. Typically monitored ions are listed in **Table 1-1**.

14.4 Tuning/Optimizing the Mass Spectrometer and Verifying the Tune

14.4.1 General Mass Spectrometer Tuning/Optimizing Considerations

The MS (quadrupole, ion trap, or TOF MS) is tuned/optimized according to the manufacturer's specifications upon initial installation of the instrument and following significant preventive maintenance or repair activities that impact the performance of the GC-MS system. This includes, but is not limited to, cleaning the ion source or analyzer, trimming or replacing the capillary column, and adjusting MS tune or optimization parameters. Once optimized, the MS tune should be verified according to the manufacturer's specifications each day of use. The purpose of MS tuning is to demonstrate acceptable performance across the selected ion mass range, where acceptable performance demonstrates sufficient responses of desired masses, correct mass ratios, and adequately low vacuum leak rates.

Note: The analytical instrument (quadrupole, ion trap, or TOF MS) should be tuned/optimized according to the manufacturer's specifications. Method TO-15 previously required a bromofluorobenzene (BFB) tune verification. This BFB tune verification is no longer required in Method TO-15A, although analysts may choose to continue using this protocol as outlined below.

14.4.2 Optional Tune Verification Using BFB

To confirm that the MS meets tuning and standard mass spectral abundance criteria prior to initiating data collection, the GC-MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the system are then verified by analysis of the tuning check compound, BFB. Most modern MS systems include an automatic tuning optimization routine that is operated through the instrument software. The use of BFB as the tuning compound is specific to ensure acceptable MS response ratios up to approximately 200 amu.

14.4.2.1 Introducing the BFB

If the BFB is included in the IS stock gas mixture, it is introduced to the preconcentrator with the IS mixture through the dedicated port. If not a component of the IS mixture, BFB can be purchased as a stand-alone compound in a high-pressure cylinder and introduced to the preconcentrator through a step-down regulator or diluted appropriately into a canister. The tuning check is performed by introducing 1 to 2 ng into the preconcentrator and analyzing the standard using the preconcentrator, GC, and MS parameters established and used for the analysis of calibration standards, QC samples, and field samples. The method integration and analysis parameters employed should also be those for routine analysis of standards, QC samples, and field samples.

14.4.2.2 BFB Tuning Verification Frequency

Before analyzing samples, blanks, or calibration standards on each day of analysis, the analyst should confirm that the GC-MS system meets the mass spectral ion abundance criteria, as listed in Table 14-2, for the BFB tuning check for linear quadrupole or ion trap MS instruments. The tuning check should be analyzed and pass criteria before the ICAL and every 24 h of analysis thereafter. The 24-h time period for the tuning check begins at the injection (acquisition time) of the BFB.

Table 14-2: BFB Tuning Check Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria[a]
50	8.0% to 40.0% of *m/z* 95
75	30.0% to 66.0% of *m/z* 95
95	Base peak, 100% relative abundance
96	5.0% to 9.0% percent of *m/z* 95
173	< 2.0% of *m/z* 174
174	50.0% to 120.0% of *m/z* 95
175	4.0% to 9.0% of *m/z* 174
176	93.0% to 101.0% of *m/z* 174
177	5.0% to 9.0% of *m/z* 176
[a]All ion abundances must be normalized to *m/z* 95, the nominal base peak, even though the ion abundance of *m/z* 174 may be up to 120% that of *m/z* 95.	

14.4.2.3 BFB Tuning Corrective Action

If the BFB tuning criteria in Table 14-2 are not met, the analyst should adjust the tune of the MS, which may require adjusting the ion focus or lens settings, for example. Repeated failure to meet tuning abundance acceptance criteria requires corrective action, which may include cleaning the ion source, checking for leaks, and/or servicing the MS vacuum pump. If the analyst cannot attain an acceptable MS tune after performing instrument maintenance, a service technician visit may be required. The

manufacturer's manual should be consulted for assistance with instrument troubleshooting. Automated tuning routines may be helpful in adjusting MS tuning parameters to achieve an acceptable tune.

15 Internal Standards, Calibration, and Quality Control

Method users should strive to meet acceptance criteria for the calibration and QC listed in the following section for the suite of target VOCs; however, method users may identify target VOCs of importance that they require to meet calibration and QC criteria to continue analysis and may identify other target VOCs that are still of interest but need not meet the most stringent calibration and QC criteria to continue analysis. In all cases, sample measurements for target VOCs associated with nonconformance of calibration and/or QC criteria should be flagged to indicate the criteria failure(s).

15.1 Selection and Use of Internal Standards

ISs are added to the air matrix during preconcentration to permit tracking of and correction for variability in instrument performance and detector response over time. IS compounds should be selected to include a minimum of three VOCs covering the approximate early, middle, and late elution range of the target VOC elution order. At a minimum, a single IS compound should be used. ISs should be VOCs that are not expected to be present in collected field samples and should either be deuterated VOCs or VOCs that are chromatographically similar to, but are not, target VOCs. Three typical VOC ISs are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d_5. Other suitable IS compounds include 1,2-dichloroethane-d_4, hexane-d_{14}, toluene-d_8, and 1,2-dichlorobenzene-d_4.

IS stock gases are commercially available at 100 ppbv in ultrapure nitrogen or can be purchased with a custom suite of compounds at desired concentrations from reputable gas providers. IS stock gases should be evaluated upon receipt for the presence of contaminants that may interfere with the quantitation of target VOCs. This evaluation can be performed by analyzing increasing volumes of the IS (e.g., 25, 50, 100, 250 mL) and examining the results for VOC contaminants whose responses increase proportionally with the increasing volume of IS analyzed. IS gas standards that contribute unacceptable levels of target VOCs, such that, for instance, MBs fail acceptance criteria, should not be employed for analysis and should be replaced. Typical contaminants in IS mixtures include methylene chloride and carbon disulfide.

The IS is added at the same concentration to each injection (standard, sample, blank, etc.) to monitor instrument sensitivity and assess potential matrix effects. Significant changes in the IS RT and response may be warning signs of chromatographic issues such as leaks, column degradation, or insufficient water management techniques. ISs are not added directly to the sample canister but instead are introduced through a different dedicated nonsample port in the preconcentrator and trapped along with the sample aliquot on the trapping module in the preconcentrator. The concentration of IS added to each injection should be chosen such that the IS compound peak area response approximates target compound area responses in the lower half of the calibration curve range, but that minimally provides a peak that is on scale and does not exceed the area response of the highest calibration standard.

15.1.1 Internal Standard Retention Time

Each IS compound in each injection should be within ±2 seconds of the average RT for each IS compound in the ICAL. An occasional outlier may not be problematic but may indicate a poor injection, in which case the analysis should be repeated. If RTs are consistently outside of this window of the average RT, then the operator should further investigate possible reasons for the shift.

The average RT for each IS in the ICAL is calculated using the following equation:

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

where:

$\overline{RT}$ = average RT for the IS compound (min)

RT_i = RT for the IS compound for each calibration level (min)

n = number of concentration values used to generate the calibration (minimum of 5)

15.1.2 Internal Standard Response

The area response for each IS compound in each injection (calibration standard, field sample, blank, CCV, etc.) must be within ±40% of the mean area response of the IS compound determined from the ICAL per the following equation:

$$\overline{Y} = \sum_{i=1}^{n} \frac{Y_i}{n}$$

where:

$\overline{Y}$ = average area response for the given IS compound

Y_i = area response for the IS for each calibration level

n = number of concentration values used to generate the calibration (minimum of 5)

The quantitation ion for each IS compound is chosen as the most abundant ion (base peak) unless there is a spectral interference from a coeluting or nearby compound or interference that impacts the quantitation of the base peak. In such cases, another abundant ion that is distinguishable from the other compounds may be selected for quantitation.

Changes in the IS response may be due to leaks in the system, issues associated with the IS delivery, matrix effects, or a decline in detector sensitivity. It is advised that a control chart of all IS area responses (temporal plot of IS response vs. chronological sample analyses), such as that shown in Figure 15-1, be maintained and monitored on a daily basis to aid in the detection and diagnosis of problems. Erratic increases and decreases of approximately 15% in IS response can indicate system leaks, issues with delivery of the IS, and/or other problems with the analytical system. A trending decline of IS responses typically indicates a decline in detector sensitivity. If there is a trending decline, sequences involving multiple samples should not be started if there is a likelihood that the IS responses (based on the indicated trend) will fall outside the ±40% range. Otherwise samples falling outside this range will need to be reanalyzed once the instrument sensitivity is restored. In any event, IS responses should be evaluated and appropriate action taken to resolve issues before analysis is resumed. Any samples for which the IS area response differs by more than 40% from the mean IS area response as determined from the ICAL should be reanalyzed or flagged.

Note that while changes in the instrument sensitivity are quantitatively adjusted using the IS response through the use of relative response factors (RRFs) (see Section 15.2.3), loss of sensitivity due to detector issues can cause some low-concentration compounds to produce reduced signals that fall below detection levels. Maintaining a tight IS response range minimizes the impact of this effect and improves the comparability of data. In light of this, laboratories may choose to implement a ±30% acceptance criterion for IS response tracking.

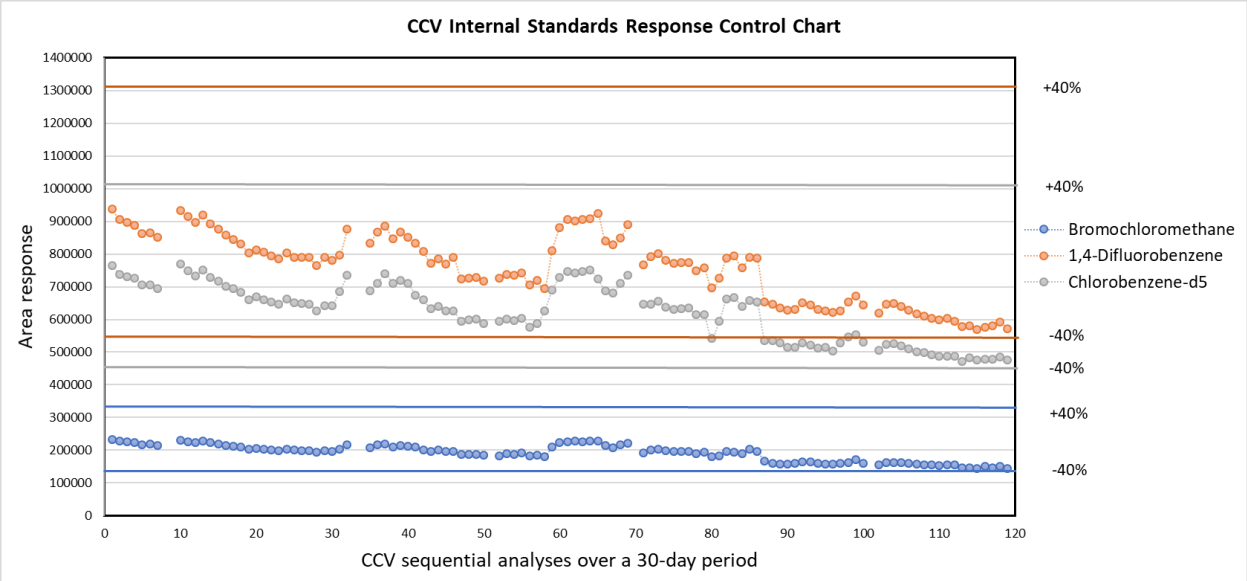

Figure 15-1: Example control chart for internal standards response.

15.2 Establishing Calibration

The GC-MS is calibrated initially and when the system is out of control as indicated by IS responses or CCV standards failing acceptance criteria. Once the decision has been made to calibrate or after the instrument has been tuned/optimized, it is recommended that a sufficient number of humidified HCF zero air blanks or humidified check standards be analyzed to verify that instrument sensitivity is stable, as indicated by IS response. This will minimize potential instrument drift during the ICAL. When this has been completed, the ICAL can proceed as discussed below.

15.2.1 Preparation for Calibration

The calibration curve is prepared by analysis of different concentration levels covering the concentration range desired by the laboratory as determined by the expected concentration of the samples, the sensitivity of the instrumentation, and the mass of analytes delivered to the column. A typical calibration range for ambient air analysis is approximately 20 to not more than 5000 pptv (ranging from tens of picograms to tens of nanograms on column). A best practice is to include a calibration point to approximate concentrations of target VOCs typically measured in ambient air, approximately 20 pptv. Five levels must be included in the ICAL at a minimum, and more levels are recommended, especially at the lower end of the calibration curve if the lowest standard concentration is in the tens of pptv. If a quadratic

regression is used to model the curve, a minimum of eight levels is recommended. While not required, analysis of up to three replicates at each calibration level should be considered to verify injection precision and provide a more robust calibration curve.

The inclusion of a true zero calibration point (a calibration blank [CB], which is a humidified matrix blank with no standards added, as discussed in **Section 15.3.3.3**) should be considered for calibration models that permit inclusion of a zero concentration point (note that calibrations employing the average RRF cannot accommodate a zero concentration point). However, even if the calibration model does not allow a zero point to be used as a data point, a zero point may still be analyzed and used for assessment purposes since the zero-concentration point should ideally demonstrate no target VOC detections.

Calibration curves may be established on the instrument by two conventions:

- **Individual standards method.** Prepare a separate canister for each level of the calibration curve and analyze the same volume from each canister. This method is straightforward. For example, to establish an eight-level calibration curve, the analyst prepares canisters at concentrations of 20, 50, 100, 250, 1000, 2000, and 5000 pptv and analyzes the same volume (e.g., 250 mL) of each standard as is performed for field samples.
- **Effective dilution method.** Prepare canisters at different concentrations from which proportional volumes are analyzed to establish the calibration curve. For example, the analyst prepares two standard canisters: 250 and 5000 pptv. The typical injection volume for samples is 250 mL; therefore, to establish a calibration curve of 20, 50, 100, 250, 1000, 2000, and 5000 pptv, the analyst injects 20, 50, 100, and 250 mL from the 250 pptv canister and 50, 100, and 250 mL from the 5000 pptv canister. Users should employ a minimum of two different canisters for generating calibration curves. When using a single canister for introducing standards, an error in preparation of the canister will not be apparent as the calibration will meet the technical linearity and accuracy criteria. When employing a single standard canister to generate the calibration curve, it is necessary to verify the calibration with a canister prepared independently from the primary calibration canister. The SSCV described in **Section 15.3.1** can serve this purpose.

Note that when the individual standards method is employed to establish calibration, the same gas volume from each canister is delivered to the preconcentrator resulting in the same amount of moisture and the same degree of penetration of compounds onto the preconcentrator sorbent trap. When the effective dilution standards method is employed to establish calibration, various gas volumes are delivered to the preconcentrator resulting in differing amounts of moisture and degrees of penetration of the compounds on the preconcentrator sorbent trap. As a result, it is important to demonstrate that the sample introduction volume measurements are reproducible, linear, and proportional and that the moisture and penetration do not impact the analysis. To accomplish this, analysts should follow any manufacturer procedures for demonstrating linear and proportional volume metering of gases for preconcentration. Acceptance should also be demonstrated by establishing a calibration based on the individual standards method followed by establishing a second calibration based on the effective dilution method by injecting various volumes of the individual standard method's high calibration standard. A comparison of the two calibration curves should demonstrate linearity of compounds covering the volatility range of the target analyte suite. This demonstration then validates the effective dilution is appropriate.

For measuring low (tens of pptv) levels of VOCs as is needed for ambient air analysis, it is important to properly characterize instrument response at these lower concentrations by including a greater number of

calibration points toward the bottom of the calibration curve (as shown in the examples above). Including more lower concentration points better defines the calibration curve at the low end and minimizes calibration bias due to the influence of the higher concentration standards.

Note: To establish the calibration curve, the theoretical concentrations of the working calibration standards should be calculated using the certified concentration from the gas vendor or neat standard provider. Certificates of analysis for stock standard gas mixtures typically include both a nominal (or "requested") concentration (e.g., 100 ppbv) for each analyte and a certified concentration (e.g., 108 ppbv), which should be within a specified tolerance (e.g., ±10%). These tolerances may permit the certified concentration to differ from the nominal concentration by 10% to 20%, resulting in final theoretical concentration errors for the working-level standards when the nominal concentration is input into standard concentration calculations instead of the certified concentration. Calibration standards prepared with neat materials must account for the standard purity when calculating the working standard concentrations.

15.2.2 Analysis of Calibration Standards

Once the calibration convention has been decided and standards have been prepared, the calibration standards are analyzed to establish the ICAL.

An air/water check of the MS also should be performed prior to any analyses to ensure that the system is leak-free. Prior to starting the ICAL analytical sequence, the operator should conduct a thorough system bakeout per the manufacturer's instructions for the preconcentrator and also ramp the GC column temperature. This readies the system by effectively removing any accumulated impurities in the analytical system. Analysis of an IB (**Section 15.3.3.1**) or performing a BFB tune check (**Section 14.4.2**) accomplishes this as well. An MB (**Section 15.3.3.2**) should be analyzed before beginning the analysis of the calibration standards. Analysis of the MB should demonstrate that the system is acceptably clean and meets the canister blank acceptance criteria in **Table 10-3** (i.e., ≤ 20 pptv at 101.3 kPa absolute). Once the criteria have been met, analysis of the calibration standards from lowest to highest concentration can be performed. It is recommended that an additional MB be analyzed following the highest calibration standard in preparation for analysis of the SSCV, as discussed in **Section 15.3.1** (strongly recommended after ICAL). If calibration standards and samples are to be analyzed sequentially, analyze field samples and additional CCV standards and MBs to complete the sequence, ending with a CCV, as discussed in **Section 15.3.2**.

The recommended steps for readying the system and performing the GC-MS analytical sequence are as follows:

1. Perform an air/water check.
2. Bake out the system.
3. Analyze a preliminary IB or perform the BFB instrument tuning check.
4. Analyze a laboratory MB.
5. Analyze the calibration standards to establish the ICAL (includes CB).
6. Analyze a laboratory MB.
7. Analyze a SSCV.
8. Analyze field samples, CCV standards (every 10 samples), and MBs, ending with a CCV. (*Note: This step is applicable for laboratories that run samples immediately following an ICAL.*)

15.2.3 Calibration Curve Models

Following analysis of all calibration standards, a calibration curve is prepared for each target analyte by determining the RRF of each concentration level. Following data acquisition for the calibration standards, the RRF of each target compound in each calibration level is determined as follows:

$$\mathrm{RRF} = \frac{\mathrm{A_s} \cdot \mathrm{C_{IS}}}{\mathrm{A_{IS}} \cdot \mathrm{C_s}}$$

where:

A_s = peak area for quantitation ion of the target compound

C_{IS} = concentration of the assigned IS compound (pptv)

A_{IS} = peak area for quantitation ion of the assigned IS compound

C_s = concentration of the target compound (pptv)

The quantitation ion for each target VOC is chosen as the most abundant ion (base peak) unless there is a spectral interference from a coeluting or nearby compound or interference that impacts the quantitation of the base peak. In such cases, another abundant ion that is distinguishable from the other compounds may be selected for quantitation.

Method TO-15 previously required the use of an average RRF calibration model. This calibration model is no longer required in Method TO-15A. Analysts should use their professional judgment to select an appropriate calibration model, which may include using average RRFs or linear or quadratic regressions.

If using an average RRF calibration model, the RSD of the RRF for each target VOC should be ≤ 30%. Chromatographic software programs typically include these calculations and can be configured to generate the RRF at each level, the average RRF for all calibration standards, and the RSD of the RRF for each target compound and to flag calibrations that exceed the RSD criterion.

Note that the calibration model using average RRF assumes the curve intercept goes through the origin. For analytes with calibration behavior known to demonstrate background or other behavior where the curve is not expected to pass through the origin, the analyst should carefully consider an alternative calibration model. For example, a calibration curve may be prepared by linear or quadratic regression of the ratios A_S/A_{IS} as the dependent variables and the ratios C_S/C_{IS} as the independent variables. The user should be aware that use of quadratic regression may mask nonlinear behavior that is due to errors in standards preparation or introduction and is not a function of the compound behavior or instrument limitations. The coefficient of determination (R^2) for linear or quadratic curves should be ≥ 0.995 for each target VOC. Such linear or quadratic curves may be weighted (e.g., 1/concentration or 1/concentration^2) to provide better representation at the low end of the curve. However, better representation at the low end of the curve may be achieved without employing weighted regression models by including more calibration levels at the low end, as described in **Section 15.2.1**, where half the calibration levels are less than or equal to 100 pptv.

Linear or quadratic curves should pass through the origin unless the system exhibits consistent elevated background levels of target VOCs. Consistent low-concentration background levels in the calibration may be introduced from contamination in canisters, diluent gas, humidification processes, or the analytical system. Presence of background may be confirmed by analysis of a CB (see **Section 15.3.3.3**) canister prepared identically to calibration standards without introduction of standard gas (i.e., only containing standard diluent gas), which is the zero-calibration point (see **Section 15.2.1**) when employed in the

calibration curve. In such cases, the calibration behavior may be better characterized with a calibration regression curve fit using a calculated y-intercept, which will typically be positive in magnitude. However, analysts should use caution when employing calculated intercepts and calibration models including a zero point, especially in situations where the compound background is an artifact of the calibration process (such as in dilution gases, canisters selected for preparing calibration standards, or the gas dilution system) and not a consistent behavior of the measurement system that affects all measurements (such as low-level contamination in the preconcentrator, ISs, or transfer line). In instances where the positive calibration y-intercept is due to the calibration process (including any contribution from a zero-calibration point), negative concentration measurements may result when measuring individual samples that do not exhibit the same level of background contamination.

Irrespective of the curve-fit method selected, the calculated concentration for each VOC at each calibration level should be within ±30% of the theoretical concentration when quantitated against the resulting calibration curve. Exclusion of calibration standard levels is not permitted unless justifiable (for example, a known error in standard preparation or a known poor injection of the standard). This evaluation of each concentration level is important to properly demonstrate calibration curve accuracy across the chosen concentration levels as both the coefficient of determination and RSD assessment of linear regression are poor overall estimation of the goodness of fit of the curve. Corrective action should be taken for target compounds that fail this criterion.

Note: Since this method may be employed to analyze numerous target VOCs with a wide range of chemical properties (volatility, polarity, etc.), some target VOCs may not meet the calibration criteria. Target VOCs of high importance to the laboratory should meet the calibration criteria; however, compounds of lesser importance may fail the criteria. In such instances of failed calibration criteria, the concentrations measured in samples should be labeled (flagged) accordingly based on the laboratory policy.

15.3 Quality Control

15.3.1 Second Source Calibration Verification Standard

Following each successful calibration, it is strongly recommended that an SSCV standard be analyzed to verify the ICAL for each target VOC. The SSCV standard should be prepared independently from the calibration standards using a certified secondary source calibration standard. A humidified SSCV standard is prepared in a canister at a concentration in the lower third of the calibration curve. The SSCV standard should contain all compounds in the calibration mixture. Each target VOC in the SSCV standard should be recovered within ±30% of the theoretical concentration.

15.3.2 Continuing Calibration Verification Standard

On a daily basis, the operator should verify that the system continues to meet sensitivity and quantitation criteria for each target VOC prior to analyzing samples. This is accomplished through analysis of a CCV standard. Sensitivity is based on monitoring the IS responses, and quantitation is based on comparing the measured amount of target compounds to the theoretical amount. A humidified CCV standard is prepared as a dilution of a certified standard in a canister at a concentration in the lower third of the calibration curve. This certified standard is preferably the cylinder that was used for the ICAL standards but may be another certified cylinder standard containing the target VOCs.

At a minimum, a CCV standard is analyzed at the beginning and end of the analytical sequence unless the sequence begins with an ICAL. Additionally, and as a best practice, it is recommended that a CCV standard be analyzed after every 10 sample injections. The IS area responses for each CCV standard should meet the criteria outlined in **Section 15.1.2**, and the quantitated concentrations of the target compounds for each CCV standard should be within ±30% of the theoretical concentrations. CCV failures indicate a drift in calibration response or degradation of the gas within the CCV standard canister. Therefore, corrective action should be taken to investigate and address CCV failures, including, for example, reanalyzing the CCV, preparing and analyzing a new CCV or standard canister, and preparing a new ICAL. Additional steps may require system maintenance including, for example, trimming or replacing the column, cleaning MS components followed by retuning the MS, or replacing preconcentrator traps, all of which require establishing a new ICAL.

The following equation is used to calculate the percent difference of the measured concentration of each target VOC in the CCV standard ($\%D_{CCV}$) from the theoretical concentration:

$$\%D_{CCV} = \frac{C_{CCV} - C_{theoretical}}{C_{theoretical}} \times 100$$

where:

C_{CCV} = measured concentration of the CCV for each target VOC (pptv)

$C_{theoretical}$ = theoretical concentration of the CCV for each target VOC (pptv)

Alternatively, percent recoveries may be calculated as follows and should fall between 70% and 130%:

$$\%Recovery_{CCV} = \frac{C_{CCV}}{C_{theoretical}} \times 100$$

where:

C_{CCV} = measured concentration of the CCV for each target VOC (pptv)

$C_{theoretical}$ = theoretical concentration of the CCV for each target VOC (pptv)

15.3.3 Blank Analyses

Blank analyses confirm for the analyst that the analytical system and reagent gases are suitably clean and free of interferences. Analysis of all blanks should demonstrate each target compound is < 20 pptv.

15.3.3.1 Instrument Blank

An IB should be analyzed at the beginning of the sequence and prior to analysis of the ICAL and daily CCV standard as a preliminary demonstration that the carrier gas and analytical system show acceptably low levels of target VOCs and potential interferences. The IB is a preconcentration analysis cycle performed where all preconcentration steps are taken without introduction of diluent (e.g., HCF zero air or ultrapure nitrogen) or sample gas into the preconcentrator. Preconcentration traps are desorbed and swept with carrier gas to the GC to evaluate contaminants within the preconcentrator sample introduction and concentration pathways. ISs should be included in this injection to ensure proper quantitation of contaminants and to aid in conditioning the IS lines and loop.

15.3.3.2 Method Blank

A laboratory MB is analyzed at least once in each analytical sequence. The MB not only indicates possible laboratory contamination but also fully verifies that target VOCs and potential interferences are

acceptably low in the system as a whole. The MB consists of a canister filled with humidified (40% to 50% RH) clean diluent gas and is analyzed via the same instrument method as the standards and field samples in the analytical sequence (i.e., if 250 mL of field sample are typically analyzed, the MB analysis volume will also be 250 mL). The humidified air of the MB more fully characterizes and purges the system of contaminants than analysis of the dry carrier gas in the IB.

The MB is analyzed prior to and following the ICAL in an ICAL sequence or prior to the initial daily CCV standard. This should demonstrate acceptably low carryover in the analytical system prior to analysis of samples (ICAL standards, CCVs/SSCVs, and field samples). Samples with expected high concentrations of target VOCs may be followed by one or more MB injections to flush the analytical system. In such instances where a blank is used to clean the instrument, additional MB aliquots should be run until the instrument is demonstrated to be acceptably clean. This will ensure the analyst's confidence in the subsequent data.

15.3.3.3 Calibration Blank

A CB is prepared with each set of standard canisters to be used for an ICAL. The CB used for this purpose is a canister filled with the humidified (40% to 50% RH) clean diluent gas sourced through the dilution system employed to prepare standards. For laboratories that do not employ a dynamic or automated static dilution system, the CB consists of a humidified canister of the gas used to dilute the calibration standard. The purpose of the CB is to demonstrate that the diluent gas and dilution apparatus (if employed) is sufficiently clean such that little or no positive bias is imparted to the calibration. The CB is analyzed via the same instrument method as standards and field samples when the ICAL is established and may be included in the calibration curve as a zero-concentration level (this is optional). The typical analysis volume is to be analyzed (i.e., if 250 mL of field sample are typically analyzed, the CB analysis volume will also be 250 mL).

15.3.4 Precision Measurements

Precision of the method may be assessed by analysis of collocated or duplicate samples as well as replicate sample analyses, as defined in **Section 5**. Precision is evaluated by calculating the absolute RPD of the measurement pair using the following formula:

$$\text{RPD} = \left| \frac{X_1 - X_2}{\left(\frac{X_1 + X_2}{2}\right)} \right| \times 100$$

where:

X_1 = target VOC concentration measured in first measurement of the precision pair (pptv)

X_2 = target VOC concentration measured in second measurement of the precision pair (pptv)

Acceptable precision analyses will demonstrate RPD ≤ 25% for each target analyte when both measurements are ≥ fivefold the method detection limit (MDL). Failure to meet this criterion should prompt the analyst to investigate the reason for the discrepancy. Associated results should be flagged to indicate poor precision was observed.

15.3.4.1 Field Sample Precision

Precision of the method inclusive of the field collection activities is evaluated through measurements of collocated or duplicate samples. When collecting samples for a study, a number of samples equal to

approximately 5% of the total samples (at minimum three) are collected as duplicate or collocated samples.

15.3.4.2 Laboratory Analysis Precision

Replicate analyses are used to demonstrate precision of the instrumental analysis and do not provide information on field-sampling precision. Each analysis sequence should include a replicate analysis of a field-collected sample. Each analytical sequence should include analysis of either one replicate or replicates of 5% of the field samples, whichever is greater.

15.3.5 Field Quality Control Samples

Note: Field QC samples are optional but may be required by QA/QC staff for particular projects or as outlined in a quality assurance project plan.

Field QC samples provide additional verification that the data which are being collected are reliable. The canister valve is not opened in the field; therefore, field QC samples should not become contaminated or otherwise compromised. Field QC samples that do not meet acceptance criteria should prompt users to examine the preparation and sample handling procedures and to qualify the concentration data reported for associated field collected samples (those samples accompanying the field QC samples through handling and transport).

- **Canister field blank.** Blank field QC sample prepared by filling a canister with humidified clean diluent gas (prepared in the same manner as an MB as described in Section 15.3.3.2). The canister is transported to the field site(s) to accompany field-collected canisters and treated identically to field-collected samples in the field and laboratory. The field blank canister valve is not opened in the field (users may remove and reinstall the brass plug, if so equipped). The field blanks are analyzed by interspersing them among the field samples. Field blank acceptance criteria should be approximately 20 pptv or less.
- **Field spike.** Positive field QC sample prepared by filling a canister with humidified standard gas at a concentration in the lower third of the calibration curve. The field spike canister is transported to the field site(s) to accompany field-collected canisters and treated identically to field-collected samples in the field and laboratory. The field spike canister is not opened in the field (users may remove and reinstall the brass plug, if so equipped). The field spikes are analyzed by interspersing them among the field samples. Field spike acceptance criteria should be within ±30% of the theoretical spiked concentrations.

15.3.6 Audit Accuracy

A measure of analytical accuracy is the degree of agreement with an independently prepared audit standard. An audit standard is prepared by an individual or entity other than the analyst, and the concentrations can be known or blind to the analyst. These samples are also known as performance evaluation or proficiency test (PT) samples. The results measured by the analyst are compared to an accepted reference value to evaluate the analytical method bias, which is defined as the difference between the target compound's accepted reference value and the measured value divided by the accepted reference value and expressed as a percentage as follows:

$$\text{Audit Accuracy (\%)} = \frac{\text{Measured Value} - \text{Accepted Reference Value}}{\text{Accepted Reference Value}} \text{ x } 100$$

The recommended audit accuracy criterion for this method is that the analyzed result be within ±30% of the accepted reference value, which is in agreement with the bias specification for the calibration standard levels, SSCV, and CCV.

Aggregated audit accuracy data from the NATTS PT Program from 2016 and 2017 are shown in Table 15-1. The NATTS PT Program requires the measurement of 15 target VOCs and requires that measurements provided by participating laboratories be within ±25% of the accepted reference value for an acceptable evaluation. *N* is the is the number of participating laboratories measuring and reporting a concentration value for the analyte.

Table 15-1: Example Proficiency Test/Audit Accuracy Results for Trace-Level VOC Analysis

National Air Toxics Trends Stations (NATTS) Proficiency Test (PT) Mean Percent Difference of Participating Laboratories' Reported Values from Accepted Reference Values Calendar Year (CY) 2016 and 2017, Calendar Quarters (QTR) 1 and 3												
Target VOC	**CY2016 QTR1**			**CY2016 QTR3**			**CY2017 QTR1**			**CY2017 QTR3**		
	RV[a] (pptv)	**Bias %**	***N***	**RV[a] (pptv)**	**Bias %**	***N***	**RV[a] (pptv)**	**Bias %**	***N***	**RV[a] (pptv)**	**Bias %**	***N***
2-Propenal	261	44.4	20	313	16.1	18	NS[b]	N/A	N/A	NS[b]	N/A	N/A
Benzene	228	–1.6	26	507	0.4	22	256	–7.4	21	438	0.4	22
1,3-Butadiene	366	3.1	25	572	–5.5	21	460	–12.3	21	539	–8.9	22
Carbon tetrachloride	NS[b]	N/A	N/A	86	32.2	22	59.7	16.5	21	219	7.0	23
Trichloromethane	667	–1.9	26	409	0.1	23	192	2.4	22	590	2.8	23
1,2-Dibromoethane	906	–0.8	25	344	–3.1	22	345	–6.1	21	567	–5.2	22
1,2-Dichloroethane	524	–3.8	25	351	1.7	22	286	–3.7	22	346	0.3	23
Dichloromethane	363	–5.2	25	117	13.9	21	186	67.4	22	NS[b]	N/A	N/A
1,2-Dichloropropane	421	2.2	22	434	1.2	21	547	–10.4	20	473	–0.3	20
***cis*-1,3-Dichloropropene**	735	–12.4	25	541	–12.7	21	430	–17.2	20	380	–1.9	20
***trans*-1,3-Dichloropropene**	426	–4.2	25	399	–8.2	21	243	–5.6	19	597	–12.5	20
1,1,2,2-Tetrachloroethane	291	–1.0	24	124	14.0	21	37.2	43.4	16	89.3	–4.8	20
Tetrachloroethene	211	0.3	26	460	–1.8	22	268	–7.6	21	379	1.3	22
1,1,2-Trichloroethene	264	–6.2	26	442	–8.5	23	246	–8.2	22	447	–7.3	23
Chloroethene	366	1.6	26	344	2.5	22	425	–6.0	21	270	–3.9	22

[a]RV = reference value.

[b]NS = not spiked. VOC not included in PT to evaluate laboratories incorrectly reporting false-positive detections.

15.3.7 Ambient Air Check

Several of the chlorofluorocarbon VOCs are ubiquitous in ambient air due to their long half-life in the atmosphere. These compounds include trichlorofluoromethane (Freon 11), dichlorodifluoromethane (Freon 12), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon 113), carbon tetrachloride, and 1,2-dichloro-1,1,2,2-tetrafluoroethane (Freon 114). The National Oceanic and Atmospheric Administration (NOAA) periodically updates the global background concentrations of these compounds, which can be queried at the NOAA halocarbon website, **https://www.esrl.noaa.gov/gmd/hats/**. Analysts can compare their measured concentrations of these analytes to the values reported by NOAA to increase confidence in the representativeness of the field-collected sample and in the precision, accuracy, and sensitivity of the

collection and analysis methods. However, this comparison should not serve as the basis for invalidation of sample data.

16 Sample Analysis and Compound Identification and Quantitation

16.1 Sample Analysis

This section addresses the analysis of samples after an ICAL has been established. See Section 15.2.2 for discussion of sample analysis when an ICAL is performed at the beginning of each sequence.

Samples are analyzed using the same acquisition methods as were used for establishing calibration. This includes the preconcentrator operation parameters, GC oven program, MS parameters, and integration methods. Field-collected samples and QC samples should be at ambient laboratory temperature for analysis. A typical sample aliquot volume is used for all samples. Adjustment of this sample aliquot volume requires adjustment of a dilution factor to account for the difference in relative analyzed volume, as discussed in Section 16.1.4.

16.1.1 Sample Introduction

Sample canisters are connected to the preconcentration unit through a port. Instrument manufacturers offer configurations that consist of a single port or a series of ports on a manifold, with each port connected through a rotary valve, solenoid valve, or other means that permits connection of sample canisters. Regardless of the sample introduction configuration, each canister should be isolated and verified to have a leak-free connection prior to beginning the analysis sequence.

The sample aliquot volume should be accurately measured for analysis. This can be accomplished by metering the sample with an MFC or with the combination of a fixed-volume vessel and a pressure transducer. Sample introduction volume measurements must be reproducible to ensure that analyzed volumes of samples and standards are consistent. It is critical that the metering system operates reproducibly, linearly, and proportionally. This is particularly important if the effective dilution method is employed for samples that fall outside the calibration range.

16.1.2 Leak Check of Preconcentrator Connections

Prior to beginning an analytical sequence, including an ICAL sequence, each canister connection must be verified as leak-free through the preconcentrator. Manufacturers generally incorporate a leak test routine in their software. During the leak check, canisters are connected to the autosampler or sample introduction lines and the canister valves are kept closed. Each port of the autosampler or sample introduction line is evacuated, and the pressure is monitored over 30 s to 1 min for a change in pressure. Pressure changes of < 3.4 kPa/min (0.5 psi/min) are generally acceptable although no change in pressure is preferable. Should a canister fail the leak check, a typical corrective action includes rechecking the tightness of all fittings and then retesting. If leaks persist, then other troubleshooting measures should be undertaken as per the manufacturer's recommendations. Analysis must not be performed using any canister connection that does not pass the leak check. Canisters that do not pass the leak check may leak to atmospheric pressure, allowing laboratory air into the analyzed sample

stream. Many preconcentration control software systems include a leak check function that provides standard QC reports. Following the leak check, all autosampler ports or sample introduction lines are evacuated and the canister valves are opened. Leak check results should be documented in the analysis records.

16.1.3 Analysis of Field Samples

An air/water check of the MS should be performed prior to any analyses to ensure that the system is acceptably leak-free. Prior to starting an analytical sequence, the operator should conduct a thorough system bakeout per the manufacturer's instructions for the preconcentrator and also ramp the GC column temperature. This readies the system by effectively removing any accumulated impurities in the analytical system. Analysis of an IB (Section 15.3.3.1) or performing a BFB tune check (Section 14.4.2) accomplishes this as well. An MB (Section 15.3.3.2) should be analyzed before beginning the analysis of the samples. Analysis of the MB should demonstrate that the system is acceptably clean and that each target compound is < 20 pptv. Once these checks meet criteria (summarized in Table 18-1), the instrument calibration is verified by analysis of a CCV and sample analysis can begin.

The recommended steps for readying the system and performing the GC-MS analytical sequence are as follows:

1. Perform an air/water check.
2. Bake out the system.
3. Analyze a preliminary IB or perform the BFB instrument tuning check.
4. Analyze a laboratory MB.
5. Analyze a CCV to verify the calibration.
6. Analyze field samples and additional CCV standards (every 10 samples) and MBs to complete the sequence, ending with a CCV, as discussed in Section 15.3.2.

16.1.4 Sample Dilution

If the on-column concentration of any compound in any sample exceeds the calibration range, the sample should be diluted for reanalysis. A dilution can be performed either by reducing the sample aliquot volume for an effective dilution or adding diluent gas to the sample canister to physically dilute the sample. To select an appropriate dilution factor, the analyst should estimate the concentration of the sample requiring dilution and aim to have diluted concentrations fall into the upper third of the calibration range (e.g., 3500 pptv for a calibration with a 5000 pptv high standard). The dilution factor is then equal to the estimated concentration divided by this desired diluted concentration.

It is recommended that an effective dilution be used first, if an appropriate dilution factor can be achieved. This eliminates the need to add diluent gas to the canister. Note that this dilution method is limited by the ability of the preconcentrator to accurately extract smaller volumes from the canister. For some preconcentrators this lower limit is approximately 20 mL. For example, if an analyst needs to perform a 10-fold dilution on a sample and the typical injection volume is 250 mL, the analyst would inject 25 mL. If a larger dilution is necessary, physical dilution of the canister sample with diluent gas may be necessary in combination with effective dilution, as described in Section 12.2. If a 30-fold dilution is needed, for example, a twofold physical dilution (doubling the sample pressure) is suggested, followed by a 15-fold effective dilution. These dilution factors are multiplied to calculate the total dilution factor. Refer to Section 16.3 for resulting sample concentration calculations.

16.2 Compound Identification

Once data acquisition is complete, each chromatogram should be examined. Chromatographic peaks should be appropriately resolved, and integration should not include peak shoulders or inflections indicative of a coelution. Subject to the judgment of an experienced operator, any peaks that have not been integrated properly may need to be manually integrated. Deconvolution techniques may be available to the operator to help resolve compound coelutions, depending on the particular instrument and chromatography software package that is in use.

Target VOCs are identified based on their RT and the relative abundance of their characteristic ions from the MS. Four criteria must be met to positively identify a target compound qualitatively:

1. The RT of the compound must be within the RT window of ±2 s as determined from the ICAL average.
2. The relative abundance ratio of qualifier ion response to target ion response for at least one qualifier ion must be within ±30% of the average relative abundance ratio from the ICAL.
3. The S:N of the target and qualifier ions must be > 3:1, preferably > 5:1.
4. The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other) (**Axys Analytical Services, 1992**).

Figure 16-1 shows an example of the qualitative identification criteria listed above. The RT is within the RT window defined by the method (red box A), and the relative abundance ratios of the qualifier ions are within ±30% of the ICAL average relative abundance ratio (red box B). The S:N of the peak is shown to be > 5:1 (red oval C), and the target and qualifier ion peaks are co-maximized (dotted purple line D). Note that it is critical that ion abundance ratios are relative to the average relative abundances established with the ICAL. Incorrectly assigning abundance ratios as absolute abundance percentages will lead to improperly wide or narrow acceptance ranges. Improperly wide acceptance ranges may include an abundance ratio of 0%, which the chromatography data systems/software may show as an acceptable identification even though the qualifier ion may not in fact be present. For the example in Figure 16-1, the average relative abundance of *m/z* 49 and 86 are 141.1% and 64.1%, respectively. Calculating lower and upper relative abundance ranges based on these averages results in acceptance ranges of 97.9% to 181.7% and 45.1% to 83.7%, respectively.

Refer to Figure 16-2 for the following example for determining the S:N. To determine the S:N, the characteristic height of the noise of the baseline (A) just before the peak and the height of the analyte peak (B) are measured. The ratio of the analyte peak height (B) is divided by the noise height (A) to calculate the S:N. In the example, the peak at 17 min is discernible from the noise but is not well resolved and is very close to an S:N of 3. In the example, the peak heights of the noise and the analyte peaks (at approximately 17 min) are approximately 700 units and 1700 units, respectively, for an S:N of 2.4. Analysts may choose instead to determine the S:N by determining the average area of a selected portion of the chromatogram characteristic of the noise (e.g., 0.2 minutes before the target peak) and the area of the target peak.

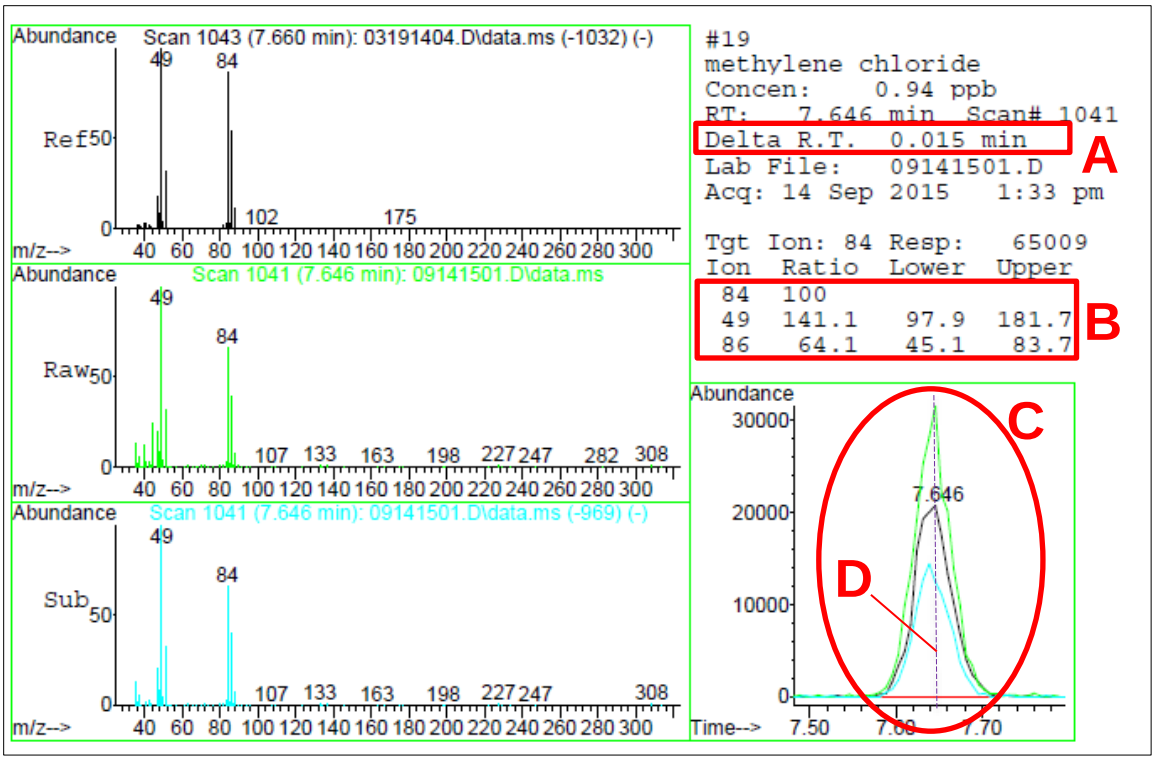

Figure 16-1: Qualitative identification of GC-MS target analytes.

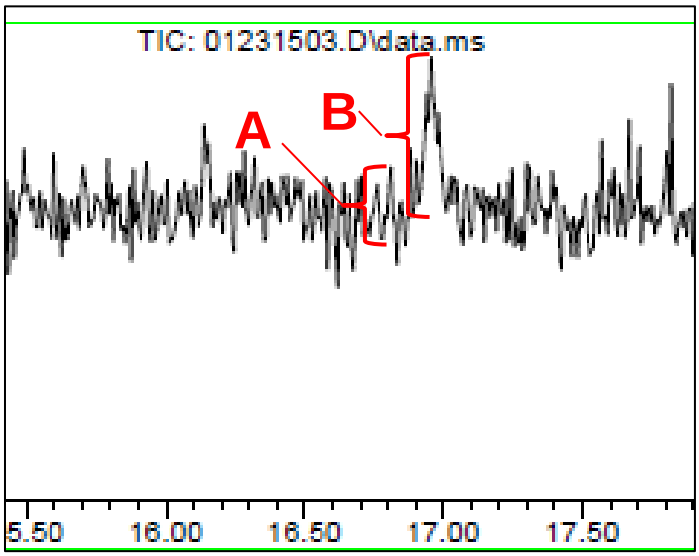

Figure 16-2: Determination of chromatographic peak signal-to-noise ratio.

Determining the S:N is somewhat subjective based on an individual analyst's characterization of the noise and analyte peak. Some chromatography data systems/software programs include S:N functions that require the analyst to assign the noise range in the chromatogram and target peak. For well-resolved peaks, the S:N will greatly exceed 5:1 and does not need to be measured. For peaks with low S:N that are questionable as to whether they meet criterion 3 above, the 3:1 S:N is only a guideline; it is unnecessary to measure each peak, and the experienced analyst's opinion should weigh heavily on whether the peak meets the S:N criterion.

As with the S:N determination, evaluation of whether target and qualifier ion peaks are co-maximized does not need to be rigorously evaluated with each peak. Rather interpretation by an experienced analyst is sufficient for deciding whether the qualifier ion peaks are co-maximized with the target ion.

Evaluation of criteria 1 (RT) and 2 (relative ion abundances) may be automated by the analytical data system such that they are automatically flagged when exceeded. Such automation reduces the time required for analyst data review; however, it is important that the RT windows and ion abundances be updated with each new ICAL.

If any of the four criteria are not met, the compound cannot be positively identified. The only exception to this is when the compound is positively identified in the opinion of an experienced analyst. The rationale for such an exception should be documented and the associated reported data flagged to indicate that identification criteria were not met. Note that in some instances of large peaks where the detector response is saturated or close to saturation, the relative ion abundances may not fall within the ±30% range. Such peaks typically require dilution of the sample and reanalysis. If the abundance criterion is not met and the sample cannot be reanalyzed, the experienced analyst's opinion should be considered for compound identification.

16.3 Compound Quantitation

16.3.1 Quantitation Using Relative Response Factors

Once the peak areas are determined, the quantitation process is initiated using the software package of choice to provide quantitative results based on the selected calibration model (see **Section 15.2.3**). Quantitation of the target VOC concentration is performed by relating the area response ratio of each target ion (typically the base peak, or most abundant, ion) and assigned IS in the unknown sample to the RRF of the ICAL curve as follows:

$$C_D = \frac{A_t \cdot C_{IS}}{A_{IS} \cdot RRF}$$

where:

C_D = instrument-detected analyte concentration (pptv)

A_t = area response of target compound quantitation ion

C_{IS} = concentration of assigned IS (pptv)

A_{IS} = area response of assigned IS quantitation ion

RRF = RRF from the ICAL curve

16.3.2 Dilution Correction Factors

If an aliquot is analyzed from the sample canister that is different from the typical analysis volume (as described in Section 16.1.4 for performing effective dilution), an instrument dilution correction factor (IDCF) is calculated:

$$\mathrm{IDCF} = \frac{\mathrm{V_{nom}}}{\mathrm{V_{inj}}}$$

where:

V_{nom} = nominal volume of sample injected (typical volume analyzed)

V_{inj} = volume of sample injected

The final concentration of each target compound in air is determined by multiplying the instrument-detected concentration by the CDCF (see Section 12.2) and the IDCF:

$$\mathrm{C_F} = \mathrm{C_D} \cdot \mathrm{CDCF} \cdot \mathrm{IDCF}$$

where:

C_F = concentration of the target compound in air (pptv)

C_D = concentration measured at the instrument (pptv)

CDCF = canister dilution correction factor

IDCF = instrument dilution correction factor

Note: The MDL reported with the final concentration data will be corrected by multiplying the MDL by the CDCF and IDCF applied to the sample concentrations. For example, if the benzene MDL is 9.1 pptv for an undiluted sample and the sample was diluted by 2.5, the MDL becomes 23 pptv.

17 Method Detection Limits

17.1 Overview

MDLs for VOCs are determined as part of the initial validation of the method and annually thereafter by following the guidance from EPA's Office of Water listed in the *Code of Federal Regulations* (U.S. EPA, 2016a; 40 CFR Part 136 Appendix B). The MDL procedure described was updated in August 2017 to address shortcomings of the original MDL process first promulgated in 1984. The purpose of the MDL is to capture the routine variability in the method and is defined as the minimum measured amount of a target analyte that is distinguishable above background (MB) levels with 99% confidence. The MDL process involves estimating the MDL concentration, preparing and analyzing a series of blanks and known-standard "spike" samples prepared in matrix (e.g., humidified HCF zero air), calculating the MDL for each target VOC, and confirming the representativeness of the MDL.

The MDL process is designed to account for background contaminants present in the canisters themselves as well as the contaminants that may be introduced during canister handling, preparation, and analysis. Statistical confidence is estimated from the observed method variability across instruments, operators, and time and requires that canisters be selected randomly from among a laboratory's inventory of canisters in routine use. Separate spiked canisters and MBs must be prepared using the same

procedures as those with which field-collected canisters are prepared and analyzed. It is not acceptable to analyze replicate samples from a single canister, to intentionally choose the best-performing canisters, or to select only a specific vendor's canisters for determining MDLs.

To initially determine the MDL, laboratories must prepare a minimum of seven MB canisters and seven spiked canisters in at least three batches on three separate calendar dates. These canisters are analyzed on at least three separate calendar dates. Separate MDLs are calculated for each target VOC based on the results from the spiked canisters and the MBs (MDL_{sp} [Section 17.6] and MDL_b [Section 17.7], respectively), and the higher of the two concentrations is chosen as the laboratory MDL.

All steps performed in the preparation and analysis of field sample canisters (such as dilution) must be included in the MDL procedure. Canisters are prepared at the selected spiking concentration with humidified (40% to 50% RH) HCF zero air. While the MDL capabilities of each laboratory may vary due to a number of factors (canister hygiene, condition of equipment, cleanliness of diluent gases, etc.), spiking concentrations for VOC MDLs of approximately 10 to 100 pptv are typical to achieve realistic MDLs. It is not appropriate to prepare a higher concentration spike and analyze a smaller aliquot than analyzed for field-collected samples (e.g., perform an effective dilution). For example, laboratories that analyze 250 mL of field-collected sample should choose a spike concentration of 60 pptv. The spiked canisters should be prepared at 60 pptv with humidified HCF zero air, and 250 mL should be analyzed. It would not be acceptable for the laboratory to prepare spikes at 300 pptv and analyze only 50 mL of the sample as this would not be representative of the procedure for field-collected samples. This would underrepresent any potential contamination that may remain in the canisters from inadequate canister cleaning. Moreover, potentially anomalous canister behavior will be more evident at lower concentrations, thereby better representing the expected behavior of VOCs in ambient air at concentrations near MDLs.

17.2 Frequency of Method Detection Limit Determination

MDLs are determined initially and, at a minimum, annually thereafter or when changes to the instrument or preparation procedure result in significant changes to the sensitivity of the instrument and/or procedure. Situations that require redetermination of the MDL include, but are not limited to, the following:

- Detector replacement or major preventive maintenance activities
- Replacement of the entire analytical instrument
- Replacement of a large (e.g., > 50%) portion of a laboratory's canister inventory
- A change to the cleaning procedure for sample collection media or labware that results in a marked reduction in contamination levels

After the initial MDL determination, laboratories may choose to perform and update MDLs on an ongoing basis. This may be beneficial for laboratories that run samples routinely. In this scenario MDL spiked canister samples are prepared and analyzed along with scheduled MBs that are interspersed with samples. The MDL samples are analyzed over the course of days or weeks. After a minimum of seven data points have been collected for the MDL spikes and for seven associated MBs, the MDLs for each can be calculated. This eliminates the need to dedicate a significant continuous block of time to preparing and analyzing MDL samples and MBs. All criteria outlined in Section 17.1 must be met.

For laboratories that do not run samples continuously but rather are more research focused, determining MDLs for each new calibration or project may be more appropriate. In this situation, the laboratory should repeat the process for determining the initial MDL.

17.3 Selecting a Spiking Level

An estimated spiking level for the replicate canister samples must be determined before preparing the spiked MDL canisters for analysis. If the analyst chooses a spiking level that is too low, the analyte may not be reliably detected. If a spiking level is chosen that is too high, the variability of the method near the actual limits of detection may not be properly characterized. An appropriate spiking level may be selected by considering the following (in order of importance):

1. Concentration at which the instrument S:N is threefold to fivefold for the analyte.
2. Concentration at which qualitative identification criteria for the analyte are lost. (Note that this will be approximately the concentration determined from the MDL process absent of blank contamination.)
3. The concentration estimated as the equivalent of three times the standard deviation of the area response from the analysis of at least three MBs.
4. Concentrations from previously acceptable MDL studies and related experience.

Note that the MDL spiking level should not be within the calibration curve; rather the MDL spiking level should be less than the lowest calibration standard (excluding a potential zero calibration point) to best approximate the MDL. Concentrations within the calibration curve will meet precision and bias acceptance criteria and are of a high enough concentration that qualitative identification is certain. Note that it is expected and acceptable that the relative abundance and S:N for qualifier ions may not meet the identification criteria listed in **Section 16.2**; however, the RT and qualifier ion (when of sufficient S:N) must be met.

At least once per year the spiking level should be reevaluated by analyzing samples at the MDL spike level. If more than 5% of the spiked samples do not provide positive numerical results that meet all the method qualification criteria (see **Section 16.2**), then the spiking level must be increased and the initial MDL redetermined.

17.4 Preparing the Spiked and Method Blank Samples

A minimum of seven separate spiked samples (at the level determined in **Section 17.3**) and a minimum of seven separate MB samples are prepared for analysis to determine the MDL. To best mimic field-collected samples, each spiked and blank sample must include, to the extent feasible, all portions of the sample matrix and be subjected to the same procedures performed to process field samples in preparation for analysis. MBs and spiked samples should be prepared over the course of three different preparation batches, preferably on nonconsecutive days.

The following should be considered when preparing MDL samples:

- Spiked samples must be prepared in matrix (humidified HCF zero air in a canister). Following preparation, it is recommended that each canister be allowed to equilibrate for a minimum of 24 h prior to initial analysis.

- Selection of canisters should include as much variety as possible (e.g., different canister manufacturers or types of canisters such as electropolished and silicon-ceramic lined) to best characterize the variability of the method attributable to the use of field-collection sample media.
- MBs that do not meet cleanliness criteria for a given target VOC should trigger root-cause analysis to determine the source of the contamination and should not be used to determine the MB portion of the MDL.

17.5 Analyzing MDL Samples

The MDL samples (blanks and spikes) are analyzed against a valid calibration curve on three separate calendar dates. QC criteria for the analytical sequences should be met. All MDL calculations should be performed in the final units (e.g., pptv).

*Note: The MDL Method Update (**U.S. EPA, 2016a**; **40 CFR Part 136 Appendix B**) allows multiple instruments in the same laboratory to be assigned the same MDL values if the results of the required seven MDL spike and seven MB analyses are distributed across the instruments (minimum two spikes and two blanks per instrument) and the resulting standard deviation from the combined instrument data is used to calculate the MDLs. This is not a recommended practice for Method TO-15A.*

17.6 Calculating MDLs from Spiked Samples (MDL_{sp})

After acquisition of the concentration data for each of the seven or more spiked canisters, the standard deviation of the concentrations for the spiked samples (S_{sp}) is calculated. All replicates are included unless a technically justified reason can be cited (faulty injection, unacceptably low IS response, etc.) or if a result can be statistically excluded as an outlier.

The MDL for the spiked samples (MDL_{sp}) is calculated by multiplying S_{sp} by the Student's *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n - 1$ degrees of freedom corresponding to the number of spiked samples analyzed according to Table 17-1. Other values of *t* for additional samples ($n > 13$) may be found in standard statistical tables.

$$MDL_{sp} = t_{(n-1,1-\alpha=0.99)} S_{sp}$$

where:

$t_{(n-1,1-\alpha=0.99)}$ = the Student's' *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n - 1$ degrees of freedom

S_{sp} = sample standard deviation of the replicate spiked sample measured concentrations

The analyst compares the resulting calculated MDL_{sp} value to the theoretical spiked amount. The theoretical spiked level must be greater than MDL_{sp} and less than 10-fold MDL_{sp}, otherwise the determination of MDL_{sp} must be repeated with an adjusted spiking concentration. For MDL_{sp} values greater than the theoretical spike level, the MDL spiking level should be adjusted higher by approximately twofold or threefold. For theoretical spike levels that are greater than 10-fold the MDL_{sp}, the MDL spiking level should be adjusted lower by approximately twofold or threefold. The goal is to spike at a

concentration within approximately three times the MDL_{sp} to best estimate the method variability at concentrations near the MDL.

Table 17-1: Single-Tailed 99th Percentile Student's *t*-Statistics

Number of MDL Samples (*n*)	Degrees of Freedom (*n* – 1)	$t_{(n-1,1-\alpha=0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
12	11	2.718
13	12	2.681

17.7 Calculating MDLs from Method Blanks (MDL_b)

There are three scenarios for determining MDL values for the MBs: (1) if none of the MBs provides numerical results, (2) if some (but not all) of the MBs provide numerical results, and (3) if all the MBs provide numerical results.

Non-numerical values such as "ND" (not detected) are reported when the analyte is not positively identified and only those target VOCs having peaks in the MB that meet the specified qualitative criteria for identification listed in Section 16.2 are given a numerical result. A numerical result includes both positive and negative values for analytes that are positively identified.

The procedure to calculate MDL_b for each of the three scenarios is as follows:

1. If none of the MBs provides a numerical result for the individual analyte, the MDL_b does not apply.
2. If some, but not all, of the MBs provide numerical results for an individual analyte, the MDL_b is set to the highest of the MB concentration results. If 100 or more MB results are available for the analyte, the MDL_b is set to the level that is no less than the 99th percentile concentration of the MBs. In other words, for *n* MBs where $n \geq 100$, the concentrations should be rank ordered with all non-numerical and zero results placed before the lowest numerical result. The value of the 99th percentile concentration ($n \cdot 0.99$) is the MDL_b. For example, to determine MDL_b from a set of 129 MBs where the highest ranked MB concentrations are … 1.10, 1.15, 1.62, 1.63, and 2.16, the 99th percentile concentration is the 128th value ($129 \cdot 0.99 = 127.7$, which rounds to 128), or 1.63. Alternatively, spreadsheet programs may be employed to interpolate the MDL_b more precisely.
3. If all concentration values for the MBs are numeric values, the MDL_b is calculated as follows:
   - Calculate the average concentration of the MBs ($\bar{x}_b$). If $\bar{x}_b < 0$, let $\bar{x}_b = 0$.
   - Calculate the standard deviation of the MB concentrations, S_b.
   - Multiply S_b by the Student's *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n - 1$ degrees of freedom corresponding to the

number of blanks analyzed according to Table 17-1. Other values of *t* for additional samples ($n > 13$) may be found in standard statistical tables.

- Calculate MDL_b as follows:

  $$MDL_b = \bar{x}_b + t_{(n-1,1-\alpha=0.99)} S_b$$

  where:

  $\bar{x}_b$ = average concentration of the MBs

  $t_{(n-1,1-\alpha=0.99)}$ = the Student's *t*-value appropriate for the single-tailed 99th percentile *t*-statistic and a standard deviation estimate with $n - 1$ degrees of freedom

  S_b = sample standard deviation of the replicate MB concentrations

- As an option, if $n \geq 100$, MDL_b may be determined as in procedure 2 above.

17.8 Selecting and Confirming the MDL

MDL_{sp} and MDL_b are compared and the higher of the two values is selected as the MDL for a given analyte. If MDL_{sp} is determined to be the MDL, laboratories may choose to perform a confirmation of the determined MDL as follows:

1. Prepare one or more spiked samples at onefold to fivefold the determined MDL and analyze the sample per the method to ensure the determined MDL is reasonable. At the MDL_{sp} concentration, there is a 50% chance that the analyte will not be detected (i.e., meet the qualitative identification criteria listed in Section 16.2) (Keith, 1991); however, the analyte should be reliably detected at twofold to fivefold the determined MDL_{sp}.
2. Develop a reasonable acceptance criterion for the measured concentrations in the MDL_{sp} verification. An appropriate starting point for acceptance limits is to double or triple the acceptance window prescribed by the method for the given analyte. For example, 40% to 160% recovery doubles the method bias criteria of ±30% (see Section 15.3.6).
3. Examine the MDL_{sp} procedure for reasonableness if the verification sample is outside the laboratory-defined acceptance criteria. Such an examination might include investigating the S:N of the analyte response in the spiked samples, comparing the MDL_{sp} to the existing instrument detection limit (IDL) (if known, as discussed in #4 below), and relying on the analyst's experience and expertise to evaluate the MDL_{sp} procedure and select a different spiking level. The MDL_{sp} portion of the study should then be repeated with a different spiking level. A very low S:N for the spiked samples may indicate the MDL_{sp} is not representative of the estimated MDL and that the chosen spiking concentration was too low and should be increased several-fold. If the MDL_{sp} is several-fold higher than the IDL, canister hygiene or the standards preparation process should be investigated. If the canister and standards preparation issues cannot be resolved, the spiking concentration may need to be increased several-fold.
4. Troubleshooting may include determination of the IDL to evaluate whether the poor or elevated recovery is due to the instrument. The IDL is determined by analyzing seven or more aliquots of a standard from the same canister, calculating the standard deviation of the measurements, and multiplying the standard deviation by the appropriate Student's *t*-value. The IDL is an estimate of the concentration that can be detected above instrument background and is typically much lower than the MDL_{sp} since it does not involve the variability of multiple canisters and preparation steps.

The MDL_{sp} should not theoretically be less than the IDL, and if such is the case, it indicates the MDL_{sp} measurements are overly precise and the spiking level should be decreased several-fold.

MDLs determined by a NATTS laboratory employing a quadrupole MS in SIM mode are shown in Table 17-2. Analytes were spiked in seven separate canisters at a target concentration of 10 pptv except *m,p*-xylenes, which were spiked at 20 pptv.

Table 17-2: Example MDLs for EPA Method TO-15A

Compound	MDL (pptv)
Dichlorodifluoromethane	2
Chloromethane	4
1,2-Dichlorotetrafluoroethane	2
Chloroethene	3
1,3-Butadiene	7
Bromomethane	2
Chloroethane	1
2-Propenal	7
Trichlorofluoromethane	2
2-Propenenitrile	2
1,1-Dichloroethene	1
Dichloromethane	3
1,1,2-Trichlorotrifluoroethane	2
1,1-Dichloroethane	2
cis-1,2-Dichloroethene	1
Trichloromethane	2
1,2-Dichloroethane	2
1,1,1-Trichloroethane	1
Benzene	2
Carbon tetrachloride	1
1,2-Dichloropropane	1
1,1,2-Trichloroethene	2
cis-1,3-Dichloropropene	2
trans-1,3-Dichloropropene	2
1,1,2-Trichloroethane	2
Toluene	3
1,2-Dibromoethane	2
Tetrachloroethene	2
Chlorobenzene	2
Ethyl benzene	1
m,p-Xylenes	4
Styrene	2
o-Xylene	2
1,1,2,2-Tetrachloroethane	2
1,3,5-Trimethylbenzene	2
1,2,4-Trimethylbenzene	6
m-Dichlorobenzene	2
p-Dichlorobenzene	2
o-Dichlorobenzene	2
1,2,4-Trichlorobenzene	4
Hexachlorobutadiene	2

17.9 Reporting Concentrations Outside the Calibration Range

Measured concentrations between the determined MDL and the lowest calibration standard and measurements exceeding the calibration range are not expected to meet method specifications for bias and precision. Depending on the reporting requirements, laboratories may opt to report a non-numeric value for concentrations below the lowest calibration standard, also referred to as the lower limit of quantitation. Laboratories reporting concentrations measured below the lowest calibration level should identify such measurements and should also identify reported concentrations measured below the MDL. Additionally, concentrations exceeding the calibration range that were not diluted into the calibration range for measurement should be identified when reported.

18 Method Quality Control Parameters and Performance Specifications

Method QC parameters and performance specifications for TO-15A are listed in Table 18-1.

Table 18-1: Quality Control Parameters and Performance Specifications for EPA Method TO-15A

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Zero-air challenge of analytical instrument systems	Test of instrumentation to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the preconcentrator to verify that the analytical instrument and all connections are sufficiently clean	At installation prior to initial use of the instrument	Analysis must show that any detected target compounds in the zero-air challenge sample are at response levels that are expected to be < 20 pptv or preferably not detected (see Section 9.3.1)
Known-standard challenge of analytical instrument systems	Test to demonstrate that the analytical instrumentation (preconcentrator and GC-MS system) is not causing loss of compounds (negative bias)	At installation prior to initial use of the instrument	Verifies that all target compounds are detected by the system, that they respond consistently upon repeated injection, and that they exhibit sufficient response to be quantifiable at low concentrations (see Section 9.3.2)
Zero-air challenge of autosamplers associated with analytical instrument systems	After establishing the ICAL, each port of the autosampler is tested to demonstrate cleanliness (positive bias) by analyzing humidified zero air; performed by connecting the clean humidified gas sample to the port to verify that transfer lines and all connections are sufficiently clean	Prior to initial use, upon replacement of transfer lines, or after analysis of potentially contaminating samples	Each target VOC's concentration should be < 20 pptv or preferably not detected (see Section 9.3.3)
Known-standard challenge of autosamplers associated with analytical instrument systems	After establishing the ICAL, each port of the autosampler is tested with a reference standard (approximately 100 to 500 pptv) to demonstrate that the autosampler is not causing bias (typically loss of compounds or negative bias)	Prior to initial use and upon replacement of transfer lines	Each target VOC's concentration within ±15% of theoretical concentration (see Section 9.3.3)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Canister leak check	Verification that canisters are leak-free by performing a pressure decay test of a canister pressurized to approximately 203 kPa absolute (29.4 psia) over the course of several days	Prior to initial use and recommended periodically thereafter (e.g., every 3 years)	Remove from service and repair any canister that exhibits a pressure change ≥ 0.69 kPa/day (see Section 9.4.1)
Zero-air challenge of canisters for qualification	Test of canisters to determine that they remain acceptably clean (show acceptably low positive bias) over the course of a known time period, typically 30 days or the laboratory holding time, by filling with humidified zero air (not nitrogen)	Initially upon receipt in the laboratory and every 3 years thereafter	Upon initial analysis after a minimum of 24 h and a subsequent time period (e.g., 30 days), each target VOC's concentration ≤ 20 pptv at 101.3 kPa absolute (14.7 psia) (refer to Table 10-3 and Section 9.4.2)
Known-standard challenge of canisters for qualification	Test of canisters to determine bias by filling with a known reference standard (approximately 100 to 500 pptv) prepared in humidified zero air (not nitrogen) and analyzing	Initially upon receipt in the laboratory and every 3 years thereafter	Upon initial analysis after a minimum of 24 h and subsequent analysis at 30 days or typical laboratory holding time, each target VOC's concentration must remain within ±30% of theoretical concentration (see Section 9.4.3)
Zero-air challenge of sampling devices/systems	Assessment of positive bias of sampling system by collecting humidified zero air through the sampling device/system and comparing it to the reference sample collected upstream of the sampling device/system	Prior to initial field deployment and periodically thereafter (e.g., annually), following maintenance (component replacement), or after collection of potentially contaminating samples	Analysis must show that the target compounds in the zero-air challenge sample collected through the sampling unit are not > 20 pptv higher than the concentration in the reference sample (see Section 9.5.2)
Known-standard challenge of sampling devices/systems	Assessment of bias of sampling system by collecting a known reference standard (approximately 100 to 500 pptv) through the sampling device/system and comparing it to the reference standard collected upstream of the sampling device/system	Prior to initial field deployment and periodically thereafter (e.g., annually), following maintenance (component replacement), or after collection of potentially contaminating samples or damaging sample matrices that may impact the activity of the flow path surfaces	Each target VOC's concentration within ±15% of concentrations in the reference sample (see Section 9.5.3)
Purge gas check	Analysis of canister cleaning purge gas to ensure contaminants are acceptably low	Verified upon initial setup and in the event of changes in gas sourcing or after the replacement of scrubbers such as hydrocarbon traps and moisture traps, or following maintenance of zero-air generator	Each target VOC's concentration < 20 pptv (see Section 10.1.1)
Canister cleaning batch blank	Analysis of a sample of humidified diluent gas in a canister from a given batch of clean canisters to ensure acceptably low levels of VOCs in the batch of cleaned canisters	One or more canisters from each batch of cleaned canisters (chosen canister should represent no more than eight total canisters) Alternatively, each canister checked for cleanliness	Upon analysis 24 h after filling, each target VOC's concentration should meet the canister blank acceptance criterion in Table 10-3 (i.e., ≤ 20 pptv at 101.3 kPa absolute, 14.7 psia) (see Section 10.2)
Dilution blank (DB)	Canister filled with clean, humidified diluent gas that is used to dilute samples; indicates that diluent gas and dilution apparatus do not contribute target VOCs to the samples; the DB should not be prepared through a dilution system used for preparing standards	Ideally one DB is prepared and analyzed with each set of samples that are diluted, and at minimum one DB is prepared and analyzed when source and/or filters are changed	DB should be sufficiently clean such that no positive bias is imparted to the samples; each target VOC's concentration should be < 20 pptv (see Section 12.2).

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Holding time	Duration from end of sample collection or canister preparation to analysis	Each field-collected or laboratory QC (standard or blank) canister	≤ 30 days unless longer stability can be demonstrated (see Section 13.4)
MS tune check, as applicable	May be accomplished by injection of 1 to 2 ng BFB for tune verification of quadrupole or ion trap MS detector	Prior to ICAL and prior to each day's analysis	Abundance criteria for BFB listed in Table 14-2 (see Section 14.4.2)
Retention time (RT)	RT of each IS and target compound	All qualitatively identified compounds and internal standards	IS compounds within ±2 s of their mean ICAL RTs (see Section 15.1.1) Target VOCs within ±2 s of their mean ICAL RTs (see Section 16.2)
Internal standards (IS)	Deuterated or other compounds not typically found in ambient air co-analyzed with samples to monitor instrument response and assess matrix effects	Co-analyzed along with all calibration standards, laboratory QC samples, and field-collected samples	Area response for each IS compound preferably within ±30% of the average response as determined from the ICAL and may not exceed ±40% (see Section 15.1.2)
Initial calibration (ICAL)	Analysis of a minimum of five calibration levels (minimum eight levels if using quadratic regression) covering approximately 20 to 5000 pptv	Before sample analysis; following failed BFB tune check (as applicable), failed IS criteria, or failed CCV criteria; or when changes/maintenance to the instrument affect calibration response	Average RRF ≤ 30% RSD and each calibration level within ±30% of theoretical concentration; for quadratic or linear curves, coefficient of determination ≥ 0.995, and each calibration level within ±30% of theoretical concentration (see Section 15.2.3)
Second source calibration verification (SSCV)	Analysis of a secondary source standard in the lower third of the calibration curve to verify ICAL accuracy for each target analyte	Immediately after each ICAL	Measured concentrations of VOCs should be within ±30% of theoretical concentration (see Section 15.3.1)
Continuing calibration verification (CCV)	Analysis of a known standard in the lower third of the calibration curve to verify ongoing instrument calibration for each target analyte	Prior to analyzing samples in an analytical sequence and at the end of a sequence; recommended after every 10 sample injections	Measured concentrations of VOCs within ±30% of theoretical concentration (see Section 15.3.2)
Instrument blank (IB)	Analysis of an injection where no sample or standard is introduced to the preconcentrator to preliminarily demonstrate the carrier gas and instrument are sufficiently clean to begin analysis	Prior to ICAL and at the beginning of an analytical sequence	Each target VOC's concentration should be < 20 pptv (see Section 15.3.3.1)
Method blank (MB)	Canister filled with clean, humidified gas; indicates that target VOCs and potential interferences are at acceptably low levels in the system as a whole; the MB is to help assess overall quality of the data	Prior to and following the ICAL and prior to the initial daily CCV/SSCV	This should demonstrate acceptably low carryover in the analytical system prior to analysis of samples; each target VOC's concentration should generally be < 20 pptv (see Section 15.3.3.2)
Calibration blank (CB)	Canister filled with clean, humidified diluent gas; indicates that diluent gas and dilution apparatus do not contribute target VOCs, imparting a positive bias to the ICAL; may also serve as zero point in the ICAL	Prepare one CB with each set of calibration standard canisters and analyze with each ICAL	CB should be sufficiently clean such that little or no positive bias is imparted to the calibration (see Section 15.3.3.3)

Parameter	Description and Details	Required Frequency	Acceptance Criteria
Method precision	Duplicate samples: precision is determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through the same sampling inlet (e.g., a rack-mounted system that employs one inlet to fill two canisters at the same time; this determines the precision of the sampling and analysis processes OR Collocated samples: precision is determined from the analyzed concentrations of samples collected simultaneously from the same air mass using two discrete canisters collected through two separate sampling inlets (e.g., two MFCDs that are individually attached to two canisters); this determines the precision of the sampling and analysis processes	Applicable to the collection of samples: collect approximately 5% of total samples or minimum of three samples	Precision ≤ 25% RPD of target VOCs in the compared samples when both measurements are ≥ fivefold MDL (see Section 15.3.4)
Instrument precision	Precision is determined from repeated analyses of a gas sample from one canister; replicate analyses are used to determine precision of the analysis processes and do not provide information on sampling precision	One replicate analysis with each analytical sequence or 5% of field samples in each analytical sequence, whichever is greater	Precision ≤ 25% RPD for target VOCs when both measurements are ≥ fivefold MDL (see Section 15.3.4)
Field blank	Canister filled with clean, humidified diluent gas transported to the field site(s) with field collected samples; indicates that sample handling practices do not contaminate samples	*Optional:* prepared for transport with field-collected samples; frequency determined by method user	Each target VOC's concentration should be approximately 20 pptv or less (see Section 15.3.5)
Field spike	Canister filled with humidified standard gas at a concentration in the lower third of the calibration curve and transported to the field site(s) with field collected samples; indicates that sample handling practices do not deteriorate sample integrity	*Optional:* prepared for transport with field-collected samples; frequency determined by method user	Measured concentrations of VOCs within ±30% of theoretical spiked concentrations (see Section 15.3.5)
Audit accuracy	Analysis of an independently prepared audit standard to determine analytical accuracy	Annually at a minimum	Within ±30% of accepted reference value (see Section 15.3.6)
Preconcentrator leak check	Pressurize or evacuate the canister connection to verify as leak-free	Each canister connected to the instrument prior to analysis	< 3.4 kPa (0.5 psi) change per minute or as recommended by the manufacturer (see Section 16.1.2)
Method detection limit (MDL)	Establishes the minimum amount of a target analyte distinguishable above background with 99% confidence; determined from spiked canisters and MB canisters	Annually at a minimum	MDLs are recommended to be < 20 pptv or should meet program goals (see Table 17-2 for example MDLs)
MDL confirmation sample	Known standard prepared at approximately onefold to fivefold the determined MDL_{sp} to confirm the determined MDL is reasonable	*Not required* but recommended for MDLs determined as the MDL_{sp} (and not for those determined as the MDL_b)	Recommended recovery within 40% to 160% or other in-house defined limits (see Section 17.8)

19 References and Supporting Documentation

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Appendix A: Vacuum and Pressure Units Conversion Chart

% Vacuum[a]	in. Hg Vacuum[a]	in. Hg (absolute)	mm Hg and Torr (absolute)	mbar (absolute)	psia (absolute)	kPa (absolute)
0%	0	29.92	760	1013.3	14.7	101.325
10%	2.99	26.93	684	912.2	13.23	91.217
20%	5.98	23.94	608	810.8	11.76	81.082
30%	8.98	20.94	532	709.5	10.29	70.947
40%	11.97	17.95	456	608.1	8.82	60.812
50%	14.96	14.96	380	506.8	7.35	50.676
60%	17.95	11.97	304	405.4	5.88	40.541
70%	20.94	8.98	228	304.1	4.41	30.406
80%	23.94	5.98	152	202.7	2.94	20.271
90%	26.93	2.99	76.0	101.4	1.47	10.135
91%	27.23	2.69	68.4	91.0	1.32	9.101
92%	27.53	2.39	60.8	81.4	1.18	8.136
93%	27.83	2.09	53.2	71.0	1.03	7.102
94%	28.13	1.79	45.6	60.7	0.88	6.067
95%	28.42	1.50	38.0	50.3	0.73	5.033
96%	28.72	1.20	30.4	40.7	0.59	4.068
97%	29.02	0.90	22.8	30.3	0.44	3.034
98%	29.32	0.60	15.2	20.0	0.29	1.999
99%	29.62	0.30	7.6	10.3	0.15	1.034
99.10%	29.65	0.27	6.8	8.96	0.13	0.896
99.20%	29.68	0.24	6.1	8.27	0.12	0.827
99.30%	29.71	0.21	5.3	6.89	0.10	0.689
99.40%	29.74	0.18	4.6	6.21	0.09	0.621
99.50%	29.77	0.15	3.8	4.83	0.07	0.483
99.60%	29.80	0.12	3.0	4.14	0.06	0.414
99.70%	29.83	0.09	2.3	2.76	0.04	0.276
99.80%	29.86	0.06	1.5	2.07	0.03	0.207
99.90%	29.89	0.03	0.8	0.69	0.01	0.069
100%	29.92	0	0	0	0	0

[a]The % vacuum and in. Hg vacuum assume that the reference barometric pressure is at standard conditions of 101.325 kPa.

Appendix B: The 97 VOCs Included in the 189 Hazardous Air Pollutants Listed in the Clean Air Act Amendments

Compound (Alternative Name)[a]	Empirical Formula	CAS Number
Chloromethane (methyl chloride)	CH_3Cl	74-87-3
Carbonyl sulfide	COS	463-58-1
Chloroethene (vinyl chloride)	C_2H_3Cl	75-01-4
Diazomethane	CH_2N_2	334-88-3
Formaldehyde	CH_2O	50-00-0
1,3-Butadiene (butadiene)	C_4H_6	106-99-0
Bromomethane (methyl bromide)	CH_3Br	74-83-9
Phosgene (carbonyl dichloride)	CCl_2O	75-44-5
Vinyl bromide (bromoethene)	C_2H_3Br	593-60-2
Ethylene oxide	C_2H_4O	75-21-8
Chloroethane (ethyl chloride)	C_2H_5Cl	75-00-3
Acetaldehyde (ethanal)	C_2H_4O	75-07-0
1,1-Dichloroethene (vinylidene chloride)	$C_2H_2Cl_2$	75-35-4
Propylene oxide	C_3H_6O	75-56-9
Methyl iodide (iodomethane)	CH_3I	74-88-4
Dichloromethane (methylene chloride)	CH_2Cl_2	75-09-2
Methyl isocyanate	C_2H_3NO	624-83-9
Allyl chloride (3-chloropropene)	C_3H_5Cl	107-05-1
Carbon disulfide (methanedithione)	CS_2	75-15-0
2-Methoxy-2-methylpropane (methyl *tert*-butyl ether, MTBE)	$C_5H_{12}O$	1634-04-4
Propionaldehyde (propanal)	C_3H_6O	123-38-6
1,1-Dichloroethane (ethylidene chloride)	$C_2H_4Cl_2$	75-34-3
2-Chloro-1,3-butadiene (chloroprene)	C_4H_5Cl	126-99-8
Chloromethyl methyl ether (chloro(methoxy)methane)	C_2H_5ClO	107-30-2
2-Propenal (acrolein)	C_3H_4O	107-02-8
1,2-Epoxybutane (1,2-butylene oxide)	C_4H_8O	106-88-7
Trichloromethane (chloroform)	$CHCl_3$	67-66-3
Ethyleneimine (aziridine)	C_2H_5N	151-56-4
1,1-Dimethylhydrazine	$C_2H_8N_2$	57-14-7
Hexane	C_6H_{14}	110-54-3
Propyleneimine (2-methylaziridine)	C_3H_7N	75-55-8
2-Propenenitrile (acrylonitrile)	C_3H_3N	107-13-1
1,1,1-Trichloroethane (methyl chloroform)	$C_2H_3Cl_3$	71-55-6
Methanol (methyl alcohol)	CH_4O	67-56-1
Carbon tetrachloride (tetrachloromethane)	CCl_4	56-23-5
Ethenyl acetate (vinyl acetate)	$C_4H_6O_2$	108-05-4
2-Butanone (methyl ethyl ketone, MEK)	C_4H_8O	78-93-3

Compound (Alternative Name)[a]	Empirical Formula	CAS Number
Benzene	C_6H_6	71-43-2
Acetonitrile (cyanomethane)	C_2H_3N	75-05-8
1,2-Dichloroethane (ethylene dichloride)	$C_2H_4Cl_2$	107-06-2
Triethylamine (N,N-diethylethanamine)	$C_6H_{15}N$	121-44-8
Methylhydrazine	CH_6N_2	60-34-4
1,2-Dichloropropane (propylene dichloride)	$C_3H_6Cl_2$	78-87-5
2,2,4-Trimethylpentane (isooctane)	C_8H_{18}	540-84-1
1,4-Dioxane (*p*-dioxane)	$C_4H_8O_2$	123-91-1
bis(Chloromethyl) ether (chloro(chloromethoxy)methane)	$C_2H_4Cl_2O$	542-88-1
Ethyl acrylate (ethyl prop-2-enoate)	$C_5H_8O_2$	140-88-5
Methyl methacrylate (methyl 2-methylprop-2-enoate)	$C_5H_8O_2$	80-62-6
cis-1,3-Dichloropropene (*cis*-1,3-dichloropropylene)	$C_3H_4Cl_2$	10061-01-5
Toluene (methylbenzene)	C_7H_8	108-88-3
1,1,2-Trichloroethene (trichloroethene)	C_2HCl_3	79-01-6
1,1,2-Trichloroethane	$C_2H_3Cl_3$	79-00-5
Tetrachloroethene (perchloroethylene)	C_2Cl_4	127-18-4
Epichlorohydrin (2-(chloromethyl)oxirane)	C_3H_5ClO	106-89-8
1,2-Dibromoethane (ethylene dibromide)	$C_2H_4Br_2$	106-93-4
N-Nitroso-N-methylurea (1-methyl-1-nitrosourea)	$C_2H_5N_3O_2$	684-93-5
2-Nitropropane	$C_3H_7NO_2$	79-46-9
Chlorobenzene	C_6H_5Cl	108-90-7
Ethylbenzene	C_8H_{10}	100-41-4
Xylenes (isomer and mixtures)	C_8H_{10}	1330-20-7
Styrene (vinylbenzene)	C_8H_8	100-42-5
p-Xylene (1,4-xylene)	C_8H_{10}	106-42-3
m-Xylene (1,3-xylene)	C_8H_{10}	108-38-3
4-Methyl-2-pentanone (methyl isobutyl ketone, MBK)	$C_6H_{12}O$	108-10-1
Tribromomethane (bromoform)	$CHBr_3$	75-25-2
1,1,2,2-Tetrachloroethane (tetrachloroethane)	$C_2H_2Cl_4$	79-34-5
o-Xylene (1,2-xylene)	C_8H_{10}	95-47-6
Dimethylcarbamoyl chloride (dimethylcarbamyl chloride)	C_3H_6ClNO	79-44-7
N-Nitrosodimethylamine (N,N-dimethylnitrous amide)	$C_2H_6N_2O$	62-75-9
beta-Propiolactone	$C_3H_4O_2$	57-57-8
Isopropylbenzene (cumene)	C_9H_{12}	98-82-8
Acrylic acid (2-propenoic acid)	$C_3H_4O_2$	79-10-7
N,N-Dimethylformamide	C_3H_7NO	68-12-2
1,3-Propane sultone	$C_3H_6O_3S$	1120-71-4
Acetophenone	C_8H_8O	98-86-2
Dimethyl sulfate	$C_2H_6O_4S$	77-78-1
Chloromethylbenzene (benzyl chloride)	C_7H_7Cl	100-44-7
1,2-Dibromo-3-chloropropane	$C_3H_5Br_2Cl$	96-12-8
bis(2-Chloroethyl)ether	$C_4H_8Cl_2O$	111-44-4

Compound (Alternative Name)[a]	Empirical Formula	CAS Number
2-Chloroacetic acid	$C_2H_3ClO_2$	79-11-8
Aniline (aminobenzene)	C_6H_7N	62-53-3
p-Dichlorobenzene (1,4-dichlorobenzene)	$C_6H_4Cl_2$	106-46-7
Ethyl carbamate (urethane)	$C_3H_7NO_2$	51-79-6
Acrylamide (2-propenamide)	C_3H_5NO	79-06-1
N,N-Dimethylaniline	$C_8H_{11}N$	121-69-7
Hexachloroethane (1,1,1,2,2,2-hexachloroethane)	C_2Cl_6	67-72-1
Hexachlorobutadiene (hexachloro-1,3-butadiene)	C_4Cl_6	87-68-3
Isophorone	$C_9H_{14}O$	78-59-1
N-Nitrosomorpholine (4-nitrosomorpholine)	$C_4H_8N_2O_2$	59-89-2
Styrene oxide (2-phenyloxirane)	C_8H_8O	96-09-3
Diethyl sulfate	$C_4H_{10}O_4S$	64-67-5
Cresylic acid (cresol isomer mixture)	C_7H_8O	1319-77-3
o-Cresol (2-methylphenol)	C_7H_8O	95-48-7
Catechol (1,2-dihydroxybenzene)	$C_6H_6O_2$	120-80-9
Phenol	C_6H_6O	108-95-2
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	120-82-1
Nitrobenzene	$C_6H_5NO_2$	98-95-3

[a]Compound information is derived from PubChem (https://pubchem.ncbi.nlm.nih.gov/), an open chemistry database from the National Institutes of Health, U.S. National Library of Medicine, National Center for Biotechnology Information.

Appendix C: Some Commercial Vendors of Analytical and Sample Collection Instruments and Supplies

Agilent
5301 Stevens Creek Blvd
Santa Clara, CA 95051
(877) 424-4536
www.agilent.com
[GC, MS]

Airgas USA, LLC
(formerly Air Liquide America, LLC)
259 N. Radnor-Chester Road, Suite 100
Radnor, PA 19087
800 255-2165
www.airgas.com
[Scott calibration standards]

Apel Riemer Environmental, Inc.
1295 NW 163rd Street
Miami, FL 33169
(786) 925-6201
Email: riemer@apelriemerenvironmental.com
[VOC standards]

ATEC
9727 Cotharin Road
Malibu, CA 90265
(310) 457-2671
www.atec-online.com
[sampling instruments]

Bruker BioSpin Corporation
15 Fortune Drive
Billerica, MA 01821
(978) 667-9580
www.bruker.com
[preconcentration, GC, MS]

Entech Instruments, Inc
2207 Agate Court
Simi Valley, CA 93065
(805) 527-5939
www.entechinst.com
[sampling hardware, preconcentration, canister cleaner]

Essex Industries
7700 Gravois Road
St. Louis, MO 63123
(314) 832-4500
www.essexindustries.com
[sampling media]

Lab Commerce, Inc.
681 E. Brokaw Road
San Jose, CA 95112
(408) 265-6482
www.labcommerce.com
[sampling media, sampling instruments]

LECO Corporation
3000 Lakeview Avenue
Saint Joseph, MI 49085
(269) 985-5496
www.leco.com
[MS]

Markes International, Inc.
2355 Gold Meadow Way
Gold River, Sacramento, CA 95670
(866) 483-5684
www.markes.com
[preconcentration, GC, MS]

Messer North America, Inc.
(formerly Linde North America, Inc.)
200 Somerset Boulevard, Suite 7000
Bridgewater, NJ 08807
(800) 755-9277
www.messer-us.com
[environmental/VOC standards]

NuTech
651 N. Plano Road #429
Richardson, TX 75081
(972) 480-8908
http://www.nutechins.com
[sampling instruments, preconcentration]

PerkinElmer
710 Bridgeport Avenue
Shelton, CT 06484-4794
(203) 925-4600
www.perkinelmer.com
[GC, MS]

Restek Corporation
110 Benner Circle
Bellefonte, PA 16823
(800) 356-1688
www.restek.com
[sampling hardware, GC, canister cleaner]

Shimadzu Scientific Instruments, Inc.
7102 Riverwood Drive
Columbia, MD 21046
(800) 477-1227
www.ssi.shimadzu.com
[GC, MS]

ThermoFisher Scientific
(formerly Finnigan/ThermoQuest)
168 Third Avenue
Waltham, MA 02451
https://www.thermofisher.com
(800) 678-5599
[GC, MS]

Tisch Environmental
145 South Miami Avenue
Cleves, OH 45002
(877) 263-7610
tisch-env.com
[sampling instruments]

Wasson-ECE Instrumentation
101 Rome Court
Fort Collins, CO 80524
(970) 221-9179
wasson-ece.com
[canister cleaner]

Xonteck, Inc.
4009 Clipper Court
Fremont, CA 94538
(805) 547-2022
www.xonteck.com
[sampling instruments, canister cleaner]