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"When Quality Counts"

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McCampbell Analytical Inc.

Volatile Organic Compounds in Air
TO 15

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VOCs in Air by GC/MS (TO-15)

1. Scope and Application:

1.1. This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to 1 L of a sample volume. The VOC concentration range for ambient air includes the concentration at which continuous exposure over a lifetime is estimated to constitute a 10^{-6} or higher lifetime risk of developing cancer in humans. Under circumstances in which many hazardous VOCs are present at 10^{-6} risk concentrations, the total risk may be significantly greater.

1.2. Solid adsorbents can be used in lieu of canisters for sample of VOCs, provided that the solid adsorbent packings, usually multisorbent packings in metal or glass tubes, can meet the performance criteria specified in Compendium Method TO-17.

2. Cleaning and Certification Program:

2.1.1. Canister Cleaning and Certification:

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

2.1.1.2. Leak test the canisters by pressurizing them to ~206 kPa (30 psig) with zero air. Measure the initial pressure, close the canister valve, and check the final pressure after 24 hours. If acceptable, the pressure should not vary more than ± 13.8 kPa (± 2 psig) over the 24 hour period (we don't check the canisters over 24hr period)

2.1.1.3. Add cryogen to both the vacuum pump and zero air supply traps. Connect the canister(s) to the manifold. Start the vent shut-off and then close the vent shut-off valve and open vacuum shut-off valve. Evacuate the canister(s) to < 0.05 mmHg for at least 1 hour.

2.1.1.4. Close the vacuum and vacuum/pressure gauge shut-off valves and open the zero air shut-off valve to pressurize the canister(s) with humid zero air to ~206 kPa (30 psig). If a zero gas generator system is used, the flow rate may need to be limited to maintain the zero air quality.

2.1.1.5. Close the zero air shut-off valve and allow the canister (s) to vent down to atmospheric pressure through the vent shut-off valve. Close the vent shut-off valve. Repeat 2.3.1.3 to 2.3.1.5 two more times.

2.1.1.6. At the end of the evacuation/pressurization cycle, pressurize the canister to 206 kPa (30 psig) with humid zero air. Analyze the canister by GC/MS. Any canister that has not tested clean (compared to direct analysis of humidified zero air of < 0.2 ppbv of targeted VOCs) should not be used. As a blank check of the canister(s) and cleanup procedure, analyze the final humid zero air fill of 100% of the canisters until the cleanup system

and canisters are proven reliable (< 0.2 ppbv of any target VOC). The check can then be performed for every batch of 10 canisters.

2.1.1.7. Reattach the canister to the cleaning manifold and then re-evacuate to < 0.05 mmHg and let remain in this condition until use. Close the canister valve. Remove the canister from the cleaning system and cap the canister connection with a stainless steel fitting. The canister is now ready for air sample collection. Attach an identification tag. Alternatively, store the canisters and re-evacuate them just prior to next use.

2.1.1.8. As an option to the humid zero air cleaning procedures, heat the canisters with a heating band up while they are being evacuated to ensure that high molecular weight compounds are not retained on the canister walls. Once heated, evacuate the canisters to < 0.05 mmHg and maintain there for 1 hour. At the end of the heated/evacuated cycle, pressurize the canisters with humid zero air and analyze by GC/MS. Any canister that has not tested clean should not be used. Once tested clean, re-evacuate canisters to < 0.05 mmHg and keep evacuated until use.

2.1.2. Cleaning Sampling System Components:

2.1.2.1. Sample components are disassembled and cleaned before the sampler is assembled. Rinse nonmetallic parts with HPLC grade DI water and dry in a vacuum oven at 50ºC. Typically, stainless steel parts and fittings are cleaned by placing them in a beaker of methanol in an ultrasonic bath for 15 minutes. This procedure is repeated with hexane as the solvent.

2.1.2.2. Rinse the parts with HPLC grade DI water and dry in a vacuum oven at 100ºC for 12-24 hours.

2.1.2.3. Once the sampler is assembled, purge the entire system with humid zero air for 24 hours.

2.1.3. Zero Air Certification:

2.1.3.1. The cleanliness of the sampling system is determined by testing the sampler with humid zero air without an evacuated gas sampling canister, as follows.

2.1.3.2. Assemble the calibration system and manifold. Connect the sampler (without an evacuated gas canister) to the manifold and activate the zero air cylinder to generate a humid gas stream (2 L/min) to the calibration manifold.

2.1.3.3. The humid zero gas stream passes through the calibration manifold, through the sampling system (without an evacuated gas canister) to the water management system/VOC pre-concentrator of an analytical system. After the sample volume is pre-concentrated on the trap, heat the trap and the VOCs are thermally desorbed and refocused on a cold trap. This trap is heated and the VOCs are thermally desorbed onto the head of the capillary column. The VOCs are refocused prior to GC separation. Then,

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the oven temperature (programmed) increases and the VOCs begin to elute and are detected by the GC/MS. The analytical system should not detect > 0.2 ppbv of any targeted VOC in order for the sampling system to pass the humid zero air certification test. If the sampler passes, test it with humid calibration gas standards containing selected VOCs at concentration levels expected in field sampling.

2.1.4. Sampler System Certification with Humid Calibration Gas Standards from a Dynamic Calibration System:

2.1.4.1. Assemble the dynamic calibration system.

2.1.4.2. Verify that the calibration system is clean (< 0.2 ppbv of any target compounds) by sampling a humidified gas stream, without gas calibration standards, with a previously certified clean canister.

2.1.4.3. The assembled dynamic calibration is certified clean if < 0.2 ppbv of any targeted compounds is found.

2.1.4.4. For generating the humidified calibration standards, attach the calibration gas cylinder(s) (containing nominal concentrations of 10 ppmv in nitrogen of selected VOCs) to the calibration system. Open the gas cylinder(s) and pass the gas mixtures through 0 to 10 mL/min certified mass flow controllers to generate ppb levels of calibration standards.

2.1.4.5. After the appropriate equilibrium period, attach the sampling system (containing a certified evacuated cylinder) to the manifold.

2.1.4.6. Sample the dynamic calibration gas stream with the sampling stream.

2.1.4.7. Concurrent with the sampling system operation, real-time monitoring of the calibration gas stream is accomplished by the on-line GC/MS to provide reference concentrations of generated VOCs.

2.1.4.8. At the end of the sampling period (normally the same time period used for experiments), analyze the sampling system canister and compare to the reference GC/MS analytical system to determine if the concentration of the targeted VOCs was increased or decreased by the sampling system

2.1.4.9. Recovery should be between 90% and 110%.

3. Definitions:

3.1. Gauge Pressure – pressure measured with reference to the surrounding atmospheric pressure, usually expressed in units of kPa or psi. Zero gauge pressure is equal to atmospheric pressure.

3.2. Absolute Pressure – pressure measured with reference to absolute zero pressure.

3.3. Cryogen – a refrigerant used to obtain sub-ambient temperatures in the VOC concentrator and/or on front of the analytical column. Typically cyrogens are liquid nitrogen (b.p. –195.8ºC), liquid argon (b.p. –185.7ºC), and liquid CO_2 (b.p. –79.5ºC).

3.4. Dynamic Calibration – calibration of an analytical system using calibration gas standard concentrations in a form identical or very similar to the samples to be analyzed and by introducing such standards into the inlet of the samples or analytical system from a manifold through which the gas standards are flowing.

3.5. Dynamic Dilution – means of preparing calibration mixtures in which standard gas(es) from pressurized cylinders are continuously blended with humidified zero air in a manifold so that a flowing stream of calibration mixture is available at the inlet of the analytical system.

3.6. MS-SCAN – mass spectrophotomeric mode of operation in which the GC is coupled to a MS that is programmed to SCAN all ions repeatedly over a specified mass range.

3.7. MS-SIM – mass spectrophotomeric mode of operation in which the GC is coupled to a MS that is programmed to SCAN a selected number of ions repeatedly (i.e., selected ion monitory [SIM]).

3.8. Qualitative Accuracy – the degree of measurement accuracy required to correctly identify compounds with an analytical system.

3.9. Quantitative Accuracy – the degree of measurement accuracy required to correctly measure the concentration of an identified compound with an analytical system with known uncertainty.

3.10. Replicate Precision – precision to be determined from two canisters filled from the same air mass over the same time period and determined as the absolute value of the difference between the analyses of canisters divided by their average value and expressed as a percentage.

3.11. Duplicate Precision – Precision determined from the analysis of two samples taken from the canister. The duplicate precision is determined as the absolute value of the difference between the canister analyses divided by their average value and expressed as a percentage.

3.12. Audit Accuracy – the difference between the analysis of a sample provided in an audit canister and the nominal value as determined by the audit authority, divided by the audit value and expressed as a percentage.

4. Apparatus and Materials:

4.1. Analytical Apparatus:

4.1.1. Sampling/Concentrator System:

4.1.1.1. Electronic Mass Flow Controllers: Used to maintain constant flow (for purge gas, carrier gas and sample gas) and to provide an analog output to monitor flow anomalies.

4.1.1.2. Vacuum Pump

4.1.1.3. Stainless Steel Cylinder Pressure Regulators: Standard, two-stage cylinder regulators with pressure gauges.

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4.1.1.4. Gas Purifiers: Used to remove organic impurities and moisture from gas streams.

4.1.1.5. Six-Port Gas Chromatographic Valve: For routing samples and carrier gas flows.

4.1.1.6. Mulitsorbent Concentrator: Solid adsorbent packing with various retentive properties for adsorbing trace gases.

4.1.1.7. Cryogenic Concentrator.

4.1.2. GC/MS System:

4.1.2.1. Chromatographic Columns: 100% methyl silicone or 5% phenyl, 95% methyl silicone fused silica capillary columns of 0.25 to 0.53 mm I.D. of varying lengths are recommended.

4.1.2.2. MS: Either a linear quadruple or ion trap MS can be used, as long as it is capable of scanning from 35 to 300 amu every 1 second or less, utilizing 70V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum with meets all the instrument performance criteria when 50 ng or less of BFB is analyzed.

4.2. Calibration System and Manifold Apparatus:

4.2.1. Calibration Manifold: Stainless steel, glass, or high purity quartz manifold (e.g., 1.25 cm I.D. x 66 cm) with sampling ports and internal baffles for flow disturbance to ensure proper mixing. The manifold should be heating to ~50ºC.

4.2.2. Humidifier: 500 mL impinger flask containing HPLC grade DI water.

4.2.3. Electronic Mass Flow Controllers: One 0 to 5 L/min unit and one or more 0 to 100 mL/min units for air, depending on number of cylinders used for calibration.

4.2.4. Teflon Filters: 47 mm Teflon® filter for particulate collection.

5. Reagents:

5.1. Neat Materials or Manufacturer-Certified Solutions/Mixtures.

5.2. Helium and Air: Ultra-high purity grade in gas cylinders. He s used as carrier gas in the GC.

5.3. Liquid Nitrogen or Liquid Carbon Dioxide: Used to cool secondary trap.

5.4. Deionized (DI) Water: HPLC grade, ultra-high purity (for humidifier).

6. Calibration:

6.1. Instrument Performance Check:

6.1.1. **Summary**. It is necessary to establish that a given GC/MS meets tuning and standard mass spectral abundance criteria prior to initiating any data collection. The GC/MS system is set up according to the manufacturer's specifications, and the mass calibration and resolution of the GC/MS system are then verified by the analysis of the instrument performance check standard, bromofluorobenzene (BFB).

6.1.2. **Frequency**. Prior to the analyses of any samples, blanks, or calibration standards, the Laboratory must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard containing BFB. The instrument performance check solution must be analyzed initially and once per 24-hour time period of operation. The 24-hour time period for GC/MS instrument performance check and standards calibration (initial calibration or daily calibration check criteria) begins at the injection of the BFB which the laboratory records as documentation of a compliance tune.

6.1.3. **Procedure**. The analysis of the IPC standard is performed by trapping 1ppbv of BFB under the optimized pre-concentration parameters. The BFB is introduced from a cylinder into the GC/MS via a sample loop valve injection system. The mass spectrum of BFB must be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is conducted using a single scan prior to the elution of BFB.

6.1.4. **Technical Acceptance Criteria**. Prior to the analysis of any samples, blanks, or calibration standards, the analyst must establish that the GC/MS system meets the mass spectral ion abundance criteria for the instrument performance check standard as specified in Table 3 of TO-15.

6.1.5. **Corrective Action**. If the BFB acceptance criteria are not met, the MS must be retuned. It may be necessary to clean the ion source, or quadrupoles, or take other necessary actions to achieve the acceptance criteria.

6.1.6. **Documentation**. Results of the BFB tuning are to be recorded and maintained as part of the instrumentation log.

6.2. Initial Calibration:

6.2.1. **Summary**. Prior to the analysis of samples and blanks but after the instrument performance check standard criteria have been met, each GC/MS system must be calibrated at five concentrations that span the monitoring range of interest in an initial calibration sequence to determine instrument sensitivity and the linearity of GC/MS response for the target compounds. For example, the range of interest may be 2 to 20 ppbv, in which case the five concentrations would be 1, 2, 5, 10 and 25 ppbv. One of the calibration points from the initial calibration curve must be at the same concentration as the daily calibration standard (e.g., 10 ppbv).

6.2.2. **Frequency**. Each GC/MS system must be recalibrated following corrective action (e.g., ion source cleaning or repair, column replacement, etc.) which may change or affect the initial calibration criteria or if the daily calibration acceptance criteria have not been met. If time remains in the 24-hour time period after meeting the acceptance criteria for the initial calibration, samples may be analyzed. If time does not remain in the 24-hour period after meeting the acceptance criteria for the initial calibration, a new analytical sequence shall commence with the analysis of the instrument performance check standard followed by analysis of a daily calibration standard.

6.2.3. **Procedure**. Verify that the GC/MS system meets the instrument performance criteria in Section 9.4. The GC must be operated using temperature and flow rate parameters equivalent to those in Section 9.2.2. Calibrate the pre-concentration-GC/MS system by drawing the standard into the system. Use one of the standards preparation techniques. A minimum of five concentration levels are needed to determine the instrument sensitivity and linearity. One of the calibration levels should be near the detection level for the compounds of interest. The calibration range should be chosen so that linear results are obtained as defined in Sections 6.5.1 and 6.5.5. The primary ion should be used unless interferences are present, in which case a secondary ion is used.

6.2.4. **Calculations.**

6.2.4.1. Calculate the Relative Response Factor (RRF) for each target analyte relative to the appropriate internal standard. Calculate the mean RRF, and the Percent Relative Standard Deviation (%RSD) and Standard deviation of the RRFs.

6.2.4.2. Calculate the Relative Retention Times (RRT) for each target compound over the initial calibration range, and the mean RRT.

6.2.4.3. Tabulate the area response (Y) of the primary ions and the corresponding concentration for each compound and internal standard. Calculate the mean area response for each internal standard.

6.2.4.4. Calculate the mean of the retention time for each internal standard over the initial calibration range.

6.2.5. **Technical Acceptance Criteria for the Initial Calibration**.

6.2.5.1. The calculated %RSD for the RRF for each compound in the calibration table must be less than 30% with at most two exceptions up to a limit of 40%.

6.2.5.2. The RRT for each target compound at each calibration level must be withiin 0.06 RRT units of the mean RRT for the compound.

6.2.5.3. The area response Y of at each calibration level must be within 40% of the mean area response over the initial calibration range for each internal standard.

6.2.5.4. The retention time shift for each of the internal standards at each calibration level must be within 20 s of the mean retention time over the initial calibration range for each internal standard.

6.2.6. **Corrective Action**.

6.2.6.1. **Criteria**. If the initial calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the initial calibration technical acceptance criteria.

6.2.6.2. **Schedule**. Initial calibration acceptance criteria *must* be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed.

6.3. <u>Daily Calibration:</u>

6.3.1. **Summary**. Prior to the analysis of samples and blanks but after tuning criteria have been met, the initial calibration of each GC/MS system must be routinely checked by analyzing a daily calibration standard to ensure that the instrument continues to remain under control. The daily calibration standard is a mid-level calibration standard, should contain all the target compounds.

6.3.2. **Frequency**. A check of the calibration curve must be performed once every 24 hours on a GC/MS system that has met the tuning criteria. The daily calibration sequence starts with the injection of the BFB. If the BFB analysis meets the ion abundance criteria for BFB, then a daily calibration standard may be analyzed.

6.3.3. **Procedure**. The mid-level calibration standard is analyzed in a GC/MS system that has met the tuning and mass calibration criteria following the same procedure in Section 6.5.

6.3.4. **Calculations**. Perform the following calculations:

6.3.4.1. Calculate a relative response factor (RRF) for each target compound.

6.3.4.2. Calculate the percent difference in the RRF of the daily RRF (24-hour) compared to the mean RRF in the most recent initial calibration. Calculate the %D for each target compound.

6.3.5. **Technical Acceptance Criteria**. The daily calibration standard must be analyzed at the concentration level and frequency described in this Section 6.6 and on a GC/MS system meeting the BFB instrument performance check criteria . The %D for each target compound in a daily calibration sequence must be within ±30 percent in order to proceed with the analysis of samples and blanks. A control chart showing %D values should be maintained.

6.3.6. **Corrective Action**. If the daily calibration technical acceptance criteria are not met, inspect the system for problems. It may be necessary to clean the ion source, change the column, or take other corrective actions to meet the daily calibration technical acceptance criteria. Daily calibration acceptance criteria must be met before any field samples, performance evaluation (PE) samples, or blanks are analyzed. If the % D criteria are not met, it will be necessary to rerun the daily calibration sample.

7. Quality Control:

7.1. Method Detection Limit:

7.1.1. Make seven replicate measurements of the compound of interest at a concentration near (within a factor of five) the expected detection limit. Compute the standard deviation and multiply by 3.14 (the Student's t value for 99% confidence for seven values). The MDL must be ≤ 0.5 ppbv.

7.2. Replicate Precision:

7.2.1. Calculate the percent difference between replicates. Replicate precision must be within 25%. Several factors, including target molecular weight, solubility, polarizability, and especially concentration level affect the precision. For example, styrene, classified as a polar VOC, shows poorer precision

than most nonpolar VOCs. Concentration level is a primary influence: the precision degrades as the concentration approaches the detection limit.

7.3. Audit Accuracy:

7.3.1. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measured value divided by the audit value, expressed as a percentage:

Audit Accuracy: = [(Spiked Value – Observed Value) / Spiked Value] x 100

7.3.2. Audit accuracy must be within 30% for concentrations normally expected in contaminated ambient air (0.5 to 25 ppbv).

7.4. Blank Analyses:

7.4.1. **Summary**. Laboratory method blanks are analyzed at least once in a 24-hour analytical sequence. All steps in the analytical procedure are performed on the blank using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis. A laboratory method blank (LMB) is an unused, certified canister that has not left the laboratory. The blank canister is pressurized with humidified, ultra-pure zero air and carried through the same analytical procedure as a field sample. The injected aliquot of the blank must contain the same amount of internal standards that are added to each sample.

7.4.2. **Frequency**. The laboratory method blank must be analyzed after the calibration standard(s) and before any samples are analyzed. Whenever a high concentration sample is encountered (i.e., outside the calibration range), a blank analysis should be performed immediately after the sample is completed to check for carryover effects. If there is no blank after a high concentration sample, the following samples may experience carry over and must be re-analyzed for confirmation

7.4.3. **Procedure**. Fill a cleaned and evacuated canister with humidified zero air (RH >20 percent, at 25ºC). Pressurize the contents to 2 atm. The blank sample should be analyzed using the procedure outlined under Section 10.

7.4.4. **Technical Acceptance Criteria**. A blank canister should be analyzed daily. The area response for each internal standard (IS) in the blank must be within ±40 percent of the mean area response of the IS in the most recent valid calibration. The retention time for each of the internal standards must be within ±0.33 minutes between the blank and the most recent valid calibration. The blank should not contain any target analyte at a concentration greater than its quantitation level (three times the MDL) and should not contain additional compounds with elution characteristics and mass spectral features that would interfere with identification and measurement of a method analyte.

7.4.5. **Corrective Action**. If the blanks do not meet acceptance criteria, the analyst should consider the analytical system to be out of control. Eliminate contaminants in solvents, reagents, glassware, and other sample storage and processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. If contamination is a problem, the source of the contamination must be investigated, corrected and documented before further sample analysis proceeds. If an analyte in the

blank is found to be out of control (i.e., contaminated) and the analyte is also found in associated samples, those sample results should be "flagged" as possibly contaminated.

8. Preparation of Standards:

8.1. Introduction:

8.1.1. When available, standard mixtures of target gases in high pressure cylinders must be certified traceable to a NIST Standard Reference Material (SRM) or to a NIST/EPA approved Certified Reference Material (CRM).

8.1.2. The neat standards that are used for making trace gas standards must be of high purity.

8.1.3. Cylinder(s) containing ~1.0 ppmv of each of the target compounds are typically used as primary stock standards. The components may be purchased in one cylinder or in separate cylinders depending on compatibility of the compounds and the pressure of the mixture in the cylinder.

8.2. Preparing Working Standards:

8.2.1. Instrument Performance Check Standard: Prepare a standard BFB solution in humidified zero air at a concentration which will allow collection of 1ppbv of BFB under the optimized concentration parameters.

8.2.2. Calibration Standards: Three working calibration standards are prepared from a 1ppm gas standard mix. 50ppbv, 2.5ppbv and 0.25ppbv in humidified zero air. The three standards are used to perform the calibration. The following table shows the concentration in nL vs. the volume in L introduced on to the trap.

	From 0.25nL/L		From 2.5nL/L standard			From 50nL/L standard			
nL	0.05nL	0.1nL	0.25nL	0.5 nL	1 nL	2.5nL	5nL	10nL	20nL
L	0.2L	0.4L	0.1L	0.2L	0.4L	0.05L	0.1L	0.2L	0.4L

The typical calibration may range from 0.05nL to 20nL for each component under optimized parameters.

8.2.3. Internal Standard Spiking Mixture: From a 1ppmv gas standard containing bromochloromethane, chlrobenzene-d_5, and 1,4-difluorobenzene prepare a 50 ppbv standard in humidified zero air to be added to the sample or calibration standard. The volume of internal standard spiking mixture added for each analysis must be the same from run to run.

8.3. Standard Preparation by Dynamic Dilution Technique

8.3.1. Standards may be prepared by dynamic dilution of the gaseous contents of a cylinder(s) containing the gas calibration stock standards with humidified zero air using mass flow controllers and a calibration manifold. The working standard may be delivered from the manifold to a clean, evacuated canister using a pump and mass flow controller.

8.3.2. Alternatively, the analytical system may be calibrated by sampling directly from the manifold if the flow rates are optimized to provide the desired amount of calibration standards. However, the use of the canister as a reservoir prior to introduction into the concentration system resembles the procedure

normally used to collect samples and is preferred. Flow rates of the dilution air and cylinder standards (all expressed in the same units) are measured using a bubble meter or calibrated electronic flow measuring device, and the concentrations of target compounds in the manifold are then calculated using the dilution ratio and the original concentration of each compound.

Manifold Conc. = (Original Conc. x Std Gas Flowrate) / (Air Flowrate + Std Gas Flowrate)

8.3.3. Consider the example of 1 mL/min flow of 10 ppmv standard diluted with 1,000 mL/min of humid air provides a nominal 10 ppbv mixture, as calculated below:

Manifold Conc. = (10 ppm x 1 mL/min x 1,000 ppb/1 ppm) / (1,000 mL/min + 1 mL/min) = 10 ppb

8.4. Standard Preparation by Static Dilution Bottle Technique:

8.4.1. The volume of a clean 2 L round-bottom flask, modified with a threaded glass neck to accept a Mininert septum cap, is determined by weighing the amount of water required to completely fill up the flask. Assuming a density for the water of 1 g/mL, the weight of the water in grams is taken as the volume of the flask in mL.

8.4.2. The flask is flushed with helium by attaching a tubing into the glass neck to deliver the helium. After a few minutes, the tubing is removed and the glass neck is immediately closed with a Mininert septum cap.

8.4.3. The flask is placed in a 60ºC oven and allowed to equilibrate at that temperature for about 15 minutes. Predetermined aliquots of liquid standards are injected into the flask making sure to keep the flask temperature constant at 60ºC.

8.4.4. The contents are allowed to equilibrate in the oven for at least 30 minutes. To avoid condensation, syringes must be preheated in the oven at the same temperature prior to withdrawal of aliquots to avoid condensation.

8.4.5. Sample aliquots may then be taken for introduction into the analytical system or for further dilution. An aliquot or aliquots totaling greater than 1 percent of the flask volume should be avoided.

Standards prepared by this method are stable for one week. The septum must be replaced with each freshly prepared standard.

8.4.6. The concentration of each component in the flask is calculated using the following equation:

$$\text{Concentration, mg/L} = (V_a)(d)/V_f$$

where :

V_a = Volume of liquid neat standard injected into flask, µL.

d = Density of liquid neat standard, mg/µL.

V_f = Volume of flask, L.

8.5. Standard Preparation Procedure in High Pressure Cylinders:

8.5.1. The standard compounds are obtained as gases or neat liquids (> 98 percent purity).

8.5.2. An aluminum cylinder is flushed with high-purity nitrogen gas and then evacuated to better than 25 in. Hg.

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8.5.3. Predetermined amounts of each neat standard compound are measured using a µL or gastight syringe and injected into the cylinder. The cylinder is equipped with a heated injection port and nitrogen flow to facilitate sample transfer.

8.5.4. The cylinder is pressurized to 30 psig with zero nitrogen.

8.5.5. The contents of the cylinder are allowed to equilibrate (-24 hrs) prior to withdrawal of aliquots into the GC system.

8.5.6. If the neat standard is a gas, the cylinder concentration is determined using the following equation:

$$\text{Concentration, ppbv} = (\text{Standard Volume} / \text{Dilution Gas Volume}) \times 10^9$$

8.5.7. If the neat standard is a liquid, the gaseous concentration can be determined using the following equation:

$$V = nRT / P \qquad \text{and} \qquad n = (mL \times d) / MW$$

where:

V = Gaseous volume of injected compound at EPA standard temperature (25ºC) and pressure (760 mm Hg), L.

n = Moles.

R = Gas constant, 0.08206 L-atm/mole EK.

T = 298 K (standard temperature).

P = 1 standard pressure, 760 mm Hg (1 atm).

mL = Volume of liquid injected, mL.

d = Density of the neat standard, g/mL.

MW = Molecular weight of the neat standard expressed, g/g-mole.

8.6. Standard Preparation by Water Methods:

8.6.1. A previously cleaned and evacuated canister is pressurized to 760 mm Hg absolute (1 atm) with zero grade air.

8.6.2. The air gauge is removed from the canister and the sparging vessel is connected to the canister with the short length of 1/16 in. stainless steel tubing.

8.6.3. A measured amount of the stock standard solution and the internal standard solution is spiked into 5 mL of water.

8.6.4. This water is transferred into the sparge vessel and purged with nitrogen for 10 minutes at 100 mL/min. The sparging vessel is maintained at 40ºC.

8.6.5. At the end of 10 mins, the sparge vessel is removed and the air gauge is re-installed, to further pressurize the canister with pure nitrogen to 1500 mm Hg absolute pressure (~ 29 psia).

8.6.6. The canister is allowed to equilibrate overnight before use.

8.7. Preparation of Standards by Permeation Tubes:

8.7.1. Permeation tubes can be used to provide standard concentration of a trace gas or gases. The permeation of the gas can occur from inside a permeation tube containing the trace species of interest to an air stream outside. Permeation can also occur from outside a permeable membrane tube to an air stream passing through the tube (e.g., a tube of permeable material immersed in a liquid).

8.7.2. The permeation system is usually held at a constant temperature to generate a constant concentration of trace gas. Commercial suppliers provide systems for generation and dilution of over 250 compounds.

8.8. Storage of Standards:

8.8.1. Working standards prepared in canisters may be stored for thirty days in an atmosphere free of potential contaminants.

9. GC/MS Operating Conditions:

9.1. Pre-concentrator: The following are typical cryogenic and adsorbent preconcentrator analytical conditions which, however, depend on the specific combination of solid sorbent and must be selected carefully by the operator. The reader is referred to Tables 1 and 2 of Compendium Method TO-17 for guidance on selection of sorbents.. Oven temperature programming starts above ambient.

9.1.1. Sample Collection Conditions

Cyrogenic Trap	Adsorbent Trap
Set Point: 150ºC	Set Point: 27ºC
Sample Volume: up to 100 mL	Sample Volume: up to 1,000 mL
Carrier gas purge flow: none	Carrier gas purge flow: selectable

9.1.2. Desorption Conditions

Cyrogenic Trap	Adsorbent Trap
Desorb Temp: 120ºC	Desorb Temp: Variable
Desorb Flow Rate: 3 mL/min He	Desorb Flow Rate: 3 mL/min He
Desorb Time: < 60 s	Desorb Time: < 60 s

The adsorbent trap conditions depend on the specific solid adsorbents chosen.

9.1.3. Trap Reconditioning Conditions

Cyrogenic Trap	Adsorbent Trap
Initial Bakeout: 120ºC (24 h)	Initial Bakeout: Variable (24 h)
After each run: 120ºC (5 min)	After each run: Variable (5 min)

9.2. GC/MS System:

9.2.1. Optimize GC conditions for compound separation and sensitivity. Baseline separation of benzene and carbon tetrachloride on a 100% methyl polysiloxane stationary phase is an indication of acceptable chromatographic performance.

9.2.2. The following are the recommended gas chromatographic analytical conditions when using a 50-meter by 0.3-mm I.D., 1 µm film thickness fused silica column with refocusing on the column:

Item	Condition
Carrier Gas:	Helium
Flow Rate:	Generally 1-3 mL/min

Temperature Program:	Initial Temp: -50ºC
	Initial Hold Time: 2 min
	Ramp Rate: 8ºC/min
	Final Temp: 200ºC
	Final Hold Time: Until all targets elute

9.2.3. The following are the recommended mass spectrometer conditions:

Item	Condition
Electron Energy	70 Volts (nominal)
Mass Range:	35-300 amu [35 amu excludes the detection of some target analytes such as methanol and formaldehyde, and the quantitation of other such as ethylene oxide, ethyl carbamate, etc. lowering the mass range will be necessary in these cases.]

Scan Time: To give at least 10 scans per peak, not to exceed 1 second per scan.

10. Sample Analysis:

10.1. The recommended GC/MS analytical sequence for samples during each 24-hour time period is as follows:

10.1.1. Perform instrument performance check using bromofluorobenzene (BFB).

10.1.2. Initiate multi-point calibration or daily calibration checks.

10.1.3. Perform a laboratory method blank.

10.1.4. Complete this sequence for analysis of ≤ 20 field samples.

10.2. **Summary**. An aliquot of the air sample from a canister (e.g., 500 mL) is pre-concentrated and analyzed by GC/MS. If using the multi-sorbent/dry purge approach, adjust the dry purge volume to reduce water effects in the analytical system to manageable levels.

10.3. **Frequency**. If time remains in the 24-hour period in which an initial calibration is performed, samples may be analyzed without analysis of a daily calibration standard. If time does not remain in the 24-hour period since the injection of the instrument performance check standard in which an initial calibration is performed, both the instrument performance check standard and the daily calibration standard should be analyzed before sample analysis may begin.

10.4. **Procedure for Instrumental Analysis:**

10.4.1. All canister samples should be at temperature equilibrium with the laboratory.

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

10.4.3. Connect the sample canister to the inlet of the GC/MS analytical system. The desired sample flow is established through the six-port chromatographic valve and the pre-concentrator to the downstream

flow controller. The absolute volume of sample being pulled through the trap must be consistent from run to run.

10.4.4. Heat/cool the GC oven and cryogenic or adsorbent trap to their set points. Assuming a six-port value is being used, as soon as the trap reaches its lower set point, the six-port chromatographic valve is cycled to the trap position to begin sample collection. Utilize the sample collection time which has been optimized by the analyst.

10.4.5. Introduce an internal standard during the sample collection period. Add sufficient internal standard equivalent to 25 ppbv in the sample. For example, a 100 mL volume of a 50ppbv mixture of internal standard compounds, added to a sample volume of 200 mL, will result in 25 ppbv of each internal standard in the sample. (50nl/L X 0.1L)/0.200L(samp) = 25nL/L or 25ppbv.

10.4.6. After the sample and internal standards are pre-concentrated on the trap, the GC sampling valve is cycled to the inject position and the trap is swept with helium and heated. Assuming a focusing trap is being used, the trapped analytes are thermally desorbed onto a focusing trap and then onto the head of the capillary column and are separated on the column using the GC oven temperature program. The canister valve is closed and the canister is disconnected from the mass flow controller and capped. The trap is maintained at elevated temperature until the beginning of the next analysis.

10.4.7. Upon sample injection onto the column, the GC/MS system is operated so that the MS scans the atomic mass range from 35 to 300 amu. At least ten scans per eluting chromatographic peak should be acquired. Scanning also allows identification of unknown compounds in the sample through searching of library spectra.

10.4.8. Each analytical run must be checked for saturation. The level at which an individual compound will saturate the detection system is a function of the overall system sensitivity and the mass spectral characteristics of that compound.

10.4.9. Secondary ion quantitation is allowed only when there are sample matrix interferences with the primary ion. If secondary ion quantitation is performed, document the reasons in the laboratory record book.

10.5. **Calculation:**

$$C_x = (A_x C_{is} DF)/(A_{is} RRF_{mean})$$

where:

C_x = Compound concentration, ppbv

A_x = Area of characteristic ion for the compound to be measured, counts

C_{is} = Concentration of the internal standard spiking mixture, ppbv

DF = Dilution factor

A_{is} = Area of the characteristic ion for the specific internal standard, counts

RRF_{mean} = mean relative response factor from the initial calibration

10.6. **Technical Acceptance Criteria**

10.6.1. The field sample must be analyzed on a GC/MS system meeting the BFB tuning, initial calibration, and continuing calibration technical acceptance criteria.

10.6.2. The field samples must be analyzed along with a laboratory method blank that met the blank technical acceptance criteria.

10.6.3. All of the target analyte peaks should be within the initial calibration range.

10.6.4. The retention time for each internal standard must be within ±0.33 minutes of the retention time of the internal standard in the most recent valid calibration.

10.7. **Corrective Action**. If the on-column concentration of any compound in any sample exceeds the initial calibration range, an aliquot of the original sample must be diluted and reanalyzed. Guidance in performing dilutions and exceptions to this requirement are given below.

10.7.1. Use the results of the original analysis to determine the approximate dilution factor required to get the largest analyte peak within the initial calibration range.

10.7.2. The dilution factor chosen should keep the response of the largest analyte peak for a target compound in the upper half of the initial calibration range of the instrument.

10.7.3. Internal standard responses and retention times must be evaluated during or immediately after data acquisition. If the retention time for any internal standard changes by more than 20 sec from the latest daily (24-hour) calibration standard (or mean retention time over the initial calibration range), the GC/MS system must be inspected for malfunctions, and corrections made as required.

10.7.4. If the area response for any internal standard changes by more than ±40 percent between the sample and the most recent valid calibration, the GC/MS system must be inspected for malfunction and corrections made as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is necessary.

10.7.5. If, after reanalysis, the area responses or the RTs for all internal standards are inside the control limits, then the problem with the first analysis is considered to have been within the control of the Laboratory. Therefore, submit only data from the analysis with SICPs within the limits. This is considered the initial analysis and should be reported as such on all data deliverables.

11. Interferences:

11.1. The method applies under most conditions encountered in sample of ambient air into canisters. However, the composition of a gas mixture in canister, under unique or unusual conditions, will change so that the sample is known not to be a true representation of the ambient air from which it was taken. For example,

11.1.1. Low humidity in the sample may lead to the losses of certain VOCs on the canister walls.

11.1.2. If the canister is pressurized, then condensation of water from high humidity samples may cause fractional losses of water-soluble compounds.

11.1.3. Since the canister surface area is limited, all gases are in competition for the available active sites. Hence an absolute storage stability cannot be assigned to a specific gas. Under conditions of usage, most VOCs can be recovered from canisters near their original concentrations after storage times of up to 30 days.

11.2. Very volatile compounds (chloromethane, vinyl chloride) can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separating focusing trap or at the head of the GC column, mitigates this problem

11.3. Interferences in canister samples may result from improper use or from contamination of: 1) the canisters due to poor manufacturing practices, 2) the canister cleaning apparatus, and 3) the sample or analytical system. The following will help minimize contamination of canisters:

11.3.1. Canisters should be manufactured using high quality welding and cleaning techniques, and new canisters should be filled with humidified zero air and then analyzed, after "aging" for 24 hours, to determine cleanliness. The cleaning apparatus, sampling system, and analytical system should be assembled of clean, high quality components and each system should be shown to be free of contamination.

11.3.2. Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

11.3.3. Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing form the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE lined thread sealants, or flow controllers with Buna-N rubber components must be avoided.

11.3.4. Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. When a high concentration (>25 ppbv of a trace species) sample is encountered, it should be followed by an analysis of humid zero air to check for carry-over contamination.

11.3.5. In cases when solid sorbents are used to concentration the sample prior to analysis, the sorbents should be tested to identify artifact formation.