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# **3M Environmental Laboratory**

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## ***Standard Operating Procedure***

### ***Gas Standard Preparation***

***SOP Number: ETS-8-196.4***

***Adoption Date: 04/24/02***

Approved By:

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William Reagen  
Technical Director

Effective Date (date of Quality Assurance signature):

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Quality Assurance

## 1 Scope and Application

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This procedure provides guidance for ambient and source level gas standard preparation in stainless steel SUMMA and fused silica lined canisters used for instrument calibration. It also describes procedures and quality control parameters for standards traceability and documentation. This Standard Operating Procedure is based on EPA Compendium Method TO15.

## 2 Definitions

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### 2.1 Gauge pressure ( $P_g$ )

Pressure measured from gauge with reference to atmospheric pressure, usually expressed as psig (pounds per square inch gauge) or kPa. Zero gauge pressure is equal to ambient atmospheric pressure.

### 2.2 Absolute pressure ( $P_g + P_a$ )

Pressure measured with reference to absolute zero, usually expressed as psia (pounds per square inch absolute), kPa, or mm Hg. It is the sum of the gauge pressure in the canister ( $P_g$ ) and the barometric (atmospheric) pressure ( $P_a$ ).

### 2.3 Cryogen

A refrigerant used to obtain very low temperatures for sample concentration. A typical cryogen is liquid nitrogen (b.p. - 195.8°C).

### 2.4 Parts per Million by Volume

A concentration unit expressing a compound amount in a volume-to-volume ratio abbreviated as PPMv.

### 2.5 Parts per Billion by Volume

A concentration unit expressing a compound amount in a volume-to-volume ratio abbreviated as PPBv.

## 3 Precautions

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### 3.1 Health and safety warnings

Wear appropriate lab attire for all parts of this procedure.

Handle all solvent and chemicals in a hood for all parts of the described standard preparation procedure.

Handle syringes with care and dispose of them in the appropriate receptacle.

For potential hazards of each chemical used, refer to material safety data sheets, vendor literature, and 3M Environmental Laboratories Chemical Hazard Review.

Instrument hazards are those commonly associated with electricity, high heat generation, cryogenics, and the use of compressed gases. Refer to Operator's Manuals, the 3M Guide to Laboratory Practices, and ETS-9-4, Working with Compressed Gases, where appropriate.

Clean all regulators before and after use in a hood by pulling room air through them with a diaphragm pump.

## 4 Responsibility

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All analysts and technicians who perform canister standard preparation activities are responsible for following the procedures described in this document.

## 5 Supplies and Materials

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### 5.1 Reagents and Standards

#### 5.1.1 Certified Vendor Prepared Gas Mixture Standards

Greater than or equal to 5% analytical accuracy obtained from a reputable vendor.

#### 5.1.2 Neat Liquid Standards

Greater than or equal to 95% purity obtained from a reputable vendor.

#### 5.1.3 ASTM Type I Reagent Water

Used for humidifying canisters, also referred to as canister passivation. This simulates the conditions of an actual sample. Water from the Millipore Milli-Q Ultrapure Water System (ETS-9-9) is used.

#### 5.1.4 Liquid Nitrogen Dewar (50 or 350 psig)

Equipped with a nitrogen regulator, for a clean source of nitrogen gas as a diluent.

#### 5.1.5 Pressure Regulators

Dual stage stainless steel pressure regulator(s) for the certified mixture cylinder(s), neat gases and 50 or 350 psig nitrogen dewar.

High accuracy pressure gauge, with readout to the nearest 0.2 psig or equivalent equipped with a needle valve.

### 5.2 Equipment

#### 5.2.1 Canisters

Stainless steel SUMMA canisters in a variety of sizes (3.0-L, 6.0-L, and 15-L).

Fused silica lined canisters in a variety of sizes (0.4-L, 1.0-L, 3.0-L, 6.0-L, and 15-L).

#### 5.2.2 Syringes

Gas tight syringes in a variety of sizes (10  $\mu$ L, 25  $\mu$ L, 50  $\mu$ L, 100  $\mu$ L, 250  $\mu$ L, 500  $\mu$ L, 1000  $\mu$ L).

Disposable syringes in a variety of sizes (1 mL, 5 mL, 10 mL, 30 mL, and 60 mL).

#### 5.2.3 Flask

2.0-Liter round bottom glass volumetric dilution flask equipped with a gas tight Mininert cap.

#### 5.2.4 Septa

Thermogreen™ 11 mm septa or equivalent.

## 5.3 Canister Suitability

### 5.3.1 SUMMA Stainless Steel Canisters

Stainless steel canisters are electro polished with nickel-plating on the inner walls. This canister type is suitable for most applications. The exceptions are standards containing polar, sulfur containing, or reactive compounds. These compounds adsorb onto the canister walls. Adding moisture to the canisters prior to standard additions reduces this problem, but, over time, the polar compounds compete with the water for the active sites on the canister wall and may result in standard losses.

### 5.3.2 Fused Silica Lined Stainless Steel Canisters

Fused silica lined canisters are canisters where the inner walls and valve assembly areas are chemically treated with a thin fused silica coating. This inert coating provides an anti-adsorptive surface for polar and sulfur containing compounds. Humidifying this canister type is not critical, but is highly recommended. Any non-uniformity on the inner walls may potentially be an active site. A fused silica lined canister is recommended for most usage.

## 6 Gas Standard Preparation

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### 6.1 Summary

Gas standards are prepared in canisters in two different ways. A neat liquid standard aliquot can be added directly to an evacuated canister. The low pressure (approximately 50 mTorr) causes the liquid to go into the vapor phase upon addition to the canister. High concentration or stock standards are typically prepared in this manner. For compounds that are gases at room temperature or to dilute high-level gas standards, standards are prepared by simple gas dilution ( $C_1V_1=C_2V_2$ ) with nitrogen. For most gas standard preparation methods using canisters, it is important to humidify the canister prior to preparing the gas standard. Normally, a final humidity of approximately 0.7% v/v is desired.

### 6.2 Canister Certification

All canisters must be cleaned and evacuated prior to standard preparation (Refer to Canister Certification SOP ETS-8-190).

### 6.3 Canister Humidification

Humidification of canisters with ASTM Type I reagent water is highly recommended prior to standards introduction. Adding moisture to the canister aids in quenching any potential active sites on the canister wall. This humidification also makes the standards more representative of a typical ambient air sample having a certain percent relative humidity. The percent humidity is dependent on the final canister pressure after the standard has been prepared. The target level of humidification is approximately 0.7% v/v; however, the analyst may adjust the final percent humidity depending on the specific analysis. Typically, the targeted percent humidity is changed to reflect the humidity present in the average sample or to improve chromatographic conditions. The final canister humidity is documented in LabWare.

Cap the canister with a  $\frac{9}{16}$ " nut with a septum. Open the canister valve and inject the required volume of water with a clean syringe. After approximately one minute, close the valve. After humidification, set the canisters aside for a minimum of 3 hours for equilibration before standard spiking. Table 1 below lists the recommended water aliquots required to attain 0.7% v/v moisture.

**Table 1: Canister Humidification**

Canister Volume at Ambient Pressure and Temperature (L)	Canister Final Pressure (psig)	Water Aliquot Required for 0.7% v/v (mL)
0.4	10	0.0036
0.4	20	0.0050
0.4	30	0.0060
6	10	0.053
6	20	0.075
6	30	0.097
15	10	0.13
15	20	0.19
15	30	0.24

**Equation 1: Percent Moisture by Volume**

$$\% \text{ moisture by volume} = \frac{\left[ \frac{\left( \frac{A_w(D)}{M_w} \right) (R)(T)}{P} \right]}{V_c} (100)$$

where,

- $A_w$  = Water aliquot added to the canister (mL);
- $D$  = Water density (g/mL);
- $M_w$  = Molecular weight;
- $R$  = Gas constant (0.08206 atm-L/mol-K);
- $T$  = Temperature (K);
- $P$  = Canister final pressure (atm);
- $V_c$  = Canister volume at ambient pressure and temperature (L).

## 6.4 Mixed Standard Preparation

A mixed standard is prepared when multi-component stock standards are needed. Individual neat liquid aliquots for each compound are blended into one liquid mixture. It is important that the blended neat liquids are compatible. This mixture is then injected directly into a static dilution vessel or an evacuated canister.

Prepare mixtures by using a clean syringe to add an aliquot of each compound to a 2 ml septum-capped and labeled amber vial. It is recommended that a fresh mixture be prepared each time. If this is not practical, the mixture can be stored in a refrigerator at 4°C. Mixture storage requirements will be left up to the analyst's discretion. Mixture stability is based on compatibility between compounds in the mix. The long-term storage stability should be based on the most reactive or unstable component in the mixture. The recommended storage time for most mixtures is six months when stored at 4°C ± 2°C. Determine each compound's mixture concentration using Equation 2.

## Equation 2: Compound Mixture Concentration

$$C_c = \frac{(A_a)(D_a)}{V_f}$$

where,

$C_c$  = Compound concentration in mixture (g/mL);

$A_a$  = Compound A aliquot (mL);

$D_a$  = Compound A density (g/mL);

$V_f$  = Mixture final volume (mL).

For example, the table below represents a mixture containing four compounds (A, B, C, & D). The mixture final volume ( $V_f$ ) in this case would 0.044 mL (0.01 + 0.008 + 0.014 + 0.012). Multiplying compound A's density (0.98 g/mL) times the mixture aliquot used (0.01 mL) gives the number of grams for compound A (0.0098 g). The final mixture concentration for compound A is calculated by dividing the gram amount by the mixture final volume which in this case is 0.0098 g/ 0.044 mL for a final concentration of 0.22 g/mL.

**Table 2: Purity Correction (example)**

Compound	Molecular Wt. (g/mole)	Density (g/mL)	Aliquot (mL)
A	100	0.98	0.010
B	98	0.93	0.008
C	106	0.91	0.014
D	110	0.95	0.012

The use of chemical standards with unknown purity should be avoided; however, the purity may be determined by GC/MS, LC/MS or NMR analysis. The equation below demonstrates how Compound A from the above table would be purity corrected if the listed purity was 80%.

$$\text{Puritycorrectedamount(g)} = \text{Volumeadded(0.01 mL)} * \text{Density} \left(0.98 \frac{\text{g}}{\text{mL}}\right) * \text{Purity}(0.80) = 0.00784\text{g}$$

### 6.4.1 Mixed Standard Storage

Mixed standards can be stored at 4°C ± 2°C for up to six months (see ETS-4-27, section 7.4).

### 6.5 Stock Gas Standard Preparation from Mixtures

A mixture aliquot is spiked into an evacuated, humidified canister. The low canister pressure causes the compounds to go into the vapor phase upon injection. The gas standard concentration is determined using Equation 3 through Equation 6.

The first step is to determine the grams added for each compound.

### Equation 3

$$C_a = (A_c)(C_c)$$

where,

$C_a$  = Compound amount in grams;

$A_c$  = Mixture aliquot injected into the canister (mL);

$C_c$  = Compound's mixture concentration (g/mL).

Continuing the example from above for compound A, injecting 0.010 mL of the mixture, the number of grams would be:

$$C_a = (0.010\text{mL})(0.22\text{g/mL}) = 0.0022\text{g}$$

Next, calculate the number of moles ( $n$ ).

### Equation 4

$$n = \frac{C_a}{W_m}$$

where,

$n$  = Moles;

$C_a$  = Compound amount in grams;

$W_m$  = Molecular weight (g/mole).

The number of moles for compound A would be:

$$n = \frac{0.00220\text{ g}}{100\text{ g/mole}} = 0.0000220\text{ moles}$$

Next, calculate the compound's gas volume using  $PV=nRT$ .

### Equation 5

$$V = \frac{nRT}{P}$$

where,

$V$  = Compound gas volume (L);

$n$  = Moles;

$R$  = Gas constant (0.08206 atm-L/mol-K);

$T$  = Temperature (K);

$P$  = Canister final pressure (atm).

The gaseous volume for compound A in a canister with a 3 atm final pressure at 25°C would be:

$$V = \frac{(0.0000220\text{moles})(0.08206\text{atmL/moleK})(273\text{K} + 25)}{3.00\text{atm}} = 0.000179\text{L}$$

The final volume-to-volume concentration is determined next.

### Equation 6

$$\text{ppmv} = \frac{V}{V_c} (1,000,000)$$

where,

ppmv	=	Parts per million by volume;
V	=	Compound gaseous volume (L);
V <sub>c</sub>	=	Canister volume at one atmosphere (L).

The final ppmv concentration in a 6 L canister for compound A at 3 atm pressure would be (12 L of 29.8 ppmv A delivered to atmospheric pressure [assume STP] from a 6 L canister pressurized to 3 atm with nitrogen):

$$\text{ppmv} = \frac{0.000179\text{L}}{6\text{L}} (1000000) = 29.8\text{ppmv}$$

### 6.5.1 Estimation of Saturation

The maximum amount of a liquid reference standard can be estimated using the following formula.

### Equation 7

$$\text{PPMv}_{(\text{max})} = (\text{VP}_{\text{atm}})(1000000)/(\text{VP}_{\text{final}})$$

Where,

PPMv <sub>(max)</sub>	=	The estimated maximum concentration before saturation is reached.
VP <sub>atm</sub>	=	The vapor pressure of the standard in atmospheres.
VP <sub>final</sub>	=	The final canister pressure in atmospheres.

A factor of 0.5 is then applied to this equation for an addition safety margin.

### 6.5.2 Canister Spiking Procedure

Humidify the canister (see 6.3).

Cap the canister with a 9/16" open-ended nut with a GC inlet grade septum inserted (injection liner septum works well).

The syringe needle volume must be accounted for during spiking; therefore, a bubble-to-bubble syringe reading technique is required. The analyst must partially draw the dry syringe plunger prior to drawing the liquid. Once the required mixture aliquot is drawn, remove the syringe and draw the plunger until the top and bottom menisci are readable. The difference between the two menisci readings is the actual delivery volume. Alternatively, a high accuracy digital syringe may be used, which eliminates the need to account for needle volume.

Heat the canister valve with a heat gun for several minutes so that when the mixture is introduced it vaporizes immediately and doesn't remain trapped in the valve as a liquid.

Open the canister valve, and spike the canister with the appropriate volume of mixture.

Close the canister valve, and set aside for a 4 hour minimum or overnight.

Pressurize to the required pressure with nitrogen.



## 6.6 Stock Gas Standard Preparation from Neat Gases

Stock gas standards for compounds that are gases at room temperature are prepared by simple gas dilution. A neat gas aliquot is added to an evacuated canister and the canister is pressurized to a final known pressure. The use of neat gases with unknown purity should be avoided; however, the purity may be estimated by another type of chemical analysis. Purity correction may be addressed on a compound per compound basis. If the general guidelines listed above are not followed, a brief comment addressing the issue should be included in the final Labware documentation.

### 6.6.1 Canister Spiking Procedure

Humidify the canister (see 6.3).

Cap the canister with a  $\frac{9}{16}$ " nut and septum. Open the canister valve.

Working in a hood, attach the appropriate dual stage stainless steel regulator to the neat gas cylinder. Before opening the high-pressure cylinder, close the regulator outlet and turn down (counterclockwise) the pressure diaphragm so that very little or no pressure will build in the regulator's second stage. With the regulator outlet end capped with a  $\frac{9}{16}$ " nut and septum, open the cylinder valve to pressurize the regulator and then close it. Turn the pressure diaphragm clockwise to build pressure in the second stage. Insert a disposable syringe needle through the septum, and slowly open the regulator outlet valve to vent the regulator into the hood. Repeat two more times and remove the disposable syringe needle. This step insures that the regulator is void of any gas other than the cylinder gas.

Open the gas cylinder and adjust the diaphragm pressure to approximately 10 psig. Fill and flush a clean gas-tight syringe three times. A gas-tight syringe equipped with a shut off valve is recommended. Fill the syringe past the target mark and depress the plunger to the exact required transfer volume and allow the syringe to equilibrate to atmospheric pressure (2 to 4 seconds is sufficient, depending on the syringe size). Inject the neat gas into a capped, evacuated canister allowing the canister vacuum to pull the syringe contents into the canister.

Flush and fill the syringe multiple times with room air in the hood. If toxic gases are being prepared, disassemble the syringe and leave it in the hood overnight.

For non-flammable gases, remove the regulator and attach a diaphragm pump on the regulator exit end. Pump room air through the regulator, venting the exhaust to the hood. This will clean the regulator making it ready for subsequent usage.

For flammable gases, pressurize the regulator with clean nitrogen, exhausting the effluent in a hood for 15 minutes.

Pressurize the canister with zero grade nitrogen to a predetermined pressure. Allow the canister to equilibrate for a four-hour minimum prior to use.

If the canister gas standard is to be used for instrument calibration, vent the canister to 15 psig. For intermediate gas standards prepared in canisters, leave the canisters under high pressure.

## 6.7 Low Level (PPBv) Calibration Gas Standard Preparation from Custom Made Stock Standard Gases by Dilution

Ambient air sample analysis requires low-level calibration gas standards typically ranging from 2 to 200 ppbv. These standards are prepared by diluting stock standards. Often more than one stock standard will be combined to make calibration standards. Use Equation 8 to calculate standard concentration.

**Equation 8: Calibration Gas Standard by Dilution**

$$C_c = \frac{(A_s)(C_s)}{\left(\frac{V_c(P_f)}{P_a}\right)}$$

where,

$C_c$  = Calibration standard concentration (ppbv) (where  $C_c$  is the concentration of the gas delivered from the pressurized canister ( $P_i$ ) to atmosphere (14.7 psia) and assuming 298K);

$A_s$  = Stock standard aliquot (L);

$C_s$  = Stock standard concentration (ppbv);

$V_c$  = Canister volume at ambient temperature and pressure (L);

$P_a$  = Absolute pressure (14.7 psia);

$P_f$  = Final canister pressure (psia).

### 6.7.1 Procedure

Humidify the canister (see 6.3).

With the canister(s) capped with a  $\frac{9}{16}$ " nut and septum, open the canister valve. Fill and flush the syringe three times with the stock standard. Fill the syringe past the target mark and depress the plunger to the exact required transfer volume and allow the syringe to equilibrate to atmospheric pressure (2 to 4 seconds is sufficient, depending on the syringe size). Inject into the capped evacuated canister. The canister vacuum will aid in drawing the gas out of the syringe into the canister.

Pressurize the canister with zero grade nitrogen to the desired final pressure using a high accuracy pressure gauge. Allow the canister(s) to equilibrate for a minimum of four hours prior to use. If the final canister pressure is greater than 20 psig, adjust to less than 20 psig prior to analysis.

### 6.8 Gas Standard Canister Pressurization

Prior to pressurizing the canister, purge the lines with nitrogen. Set the second stage regulator on the liquid nitrogen dewar to approximately 2 psig greater than the target canister pressure. Connect the high accuracy pressure gauge/needle valve assembly to the canister. Open the needle valve and pressurize the closed system. In order to avoid contaminating the pressure gauge, slowly open the canister to allow the nitrogen to flow in, yet not too open as to allow a vacuum on the pressure gauge. Adjust the needle valve to slow the flow rate for the last 5 psig. This will help in controlling the flow when the canister approaches the final pressure.

Allow equilibration for a four-hour minimum prior to use. For canisters with high molecular weight and/or low vapor pressure compounds, equilibrate over night before use.

If the gas standard prepared in a canister is for instrument calibration, vent the canister to 15 psig before analysis. For intermediate standard canisters, hold the canister under high pressure.

### 6.9 Gas Standard Storage and Expiration Dates

#### 6.9.1 Calibration Standards

Gas phase volatile organic compound stability in specially treated canisters has been well documented (see References 7, 8, and 9). Compound stability is dependent upon the following major factors: canister type, compound type, canister pressure, moisture, and compound concentration. Most losses occur due to interactions with the canister wall. This canister wall interaction loss is more evident at lower concentrations (<1 ppmv). For this reason, gas standards prepared in canisters storage requirements are based on concentration. Gas standards containing volatile organic compounds <1 ppmv can be stored under ambient conditions for up to 30 days. Gas standards prepared at  $\geq 1$  ppmv can be stored under ambient conditions for up to 180 days.

Exceptions, i.e. extended storage times, to these storage requirements can be made on a compound-by-compound basis if literature can be cited or data referenced to support the extended storage period. This literature or data must be referenced in the standard preparation documentation. For a mixture, the storage requirement must be based on the least stable

compound (i.e. the compound with the shortest documented stability period). The table below lists how expiration dates are typically assigned to gas calibration standards.

**Table 3. Expiration Assignments.**

<b>Stock Type</b>	<b>Analyte Concentration in Final Gas Standard</b>	<b>Expiration Date</b>
Mixture	PPMv	<sup>(1)</sup> 180 days post gas standard preparation
Gas (neat or vendor prepared dilution)	PPMv	180 days post standard preparation
Gas (neat or vendor prepared dilution)	PPBv	30 days post gas standard preparation
Mixture and Gas	PPMv or PPBv	<sup>(2)</sup> Component in mixture with shortest expiration date as described above.

(1) Expiration date on the gas standard may exceed mixture expiration. Compounds are generally considered more stable after they have undergone a phase change from the condensed state (neat liquid) to the gas phase. Therefore, the expiration date of a gas standard prepared from a mixture is assigned from the date of the phase change.

(2) Exception: Intermediate mixture (1000-2000 PPMv) of the following fluorochemicals prepared from neat gases: octafluoro-2-butene, chlorotrifluoroethylene, 1,1-difluoroethylene, perfluoroethane sulfonyl fluoride, perfluoromethane sulfonyl fluoride, sulfuryl fluoride, and 1,1,1,2,2,2-pentafluoropropane. When this mixture is used as part of the standard fluorochemical mix routinely analyzed, the expiration date of the final calibration standard will not be based off the date the initial mixture was prepared. Due to the demonstrated inertness of FCs, it is believed that these compounds are stable in canisters for much longer than 180 days. Therefore, the final expiration date of the calibration standard will be based off either of the two following conditions: (1) the date the mixture was combined with the other components to form the final standard or (2) the shortest expiration date of another component added. Note: a stock cylinder of other FC compounds at approximately the same level (3000 PPMv) has shown no signs of degradation for years (see Reference 5).

## 6.9.2 Internal Standards

Low-level ambient internal standards prepared in canisters can be stored under ambient conditions for up to 180 days. High-level source standards prepared in canisters for loop analyses can be stored under ambient conditions for up to 2 years. Since the internal standard is added to every method blank, any potential degradation by-products would be detected in the method blanks. If any internal standard breakdown components are detected in the method blank, the internal standard should be discarded and new standard prepared.

## 6.9.3 4-Bromofluorobenze Performance Check Standard (BFB Tune)

Gas standards for 4-bromofluorobenzene (BFB) prepared in canisters can be used until the standard has been exhausted. Since the requirement for a BFB tune is to analyze 50 ng or less every 24-hour period during sample or standard analyses, any significant standard degradation would be apparent in this routine analysis. If degradation is evident (i.e. poor response, contamination), a new BFB tuning gas standard must be prepared. This BFB tuning standard has no expiration date.

## 6.9.4 Expired Vendor Prepared Gas Cylinders

Vendor prepared gas cylinders are routinely used as stock standards to prepare calibration standards for ETS-8-16. In most circumstances, the vendor will certify the cylinder concentration for up to 6 months past the preparation date. Because of the time and costs associated with acquiring these specialty standards, it is not practical to dispose of the cylinder after only 6 months of use. Consequently, several gas cylinders have been and will continue to be used beyond the vendor listed expiration date. One way to verify that the cylinder concentration is still valid after the expiration date is to monitor the relative response factor(s) (RRF) of the cylinder components. Ideally, multiple RRF data points generated before the cylinder expiration date will be used to establish a baseline value. As the cylinder is used beyond the expiration date, the average RRF and the resulting percent relative standard deviation (RSD) will be recorded. As long as the analytes average RRF exhibits minimal degradation after the expiration date, the cylinder will

continue to be used with the vendor-listed concentration. A guideline for acceptable before/after expiration percent difference is  $\pm 30\%$ ; however, the data points should be carefully analyzed for any trends (fluctuation about the mean vs. slow degradation). Depending on the characteristics of the analyte, the cylinder expiration dates will be extended by an arbitrary time frame. For inert fluorochemicals, the expiration date is extended in one-year increments. For other compounds, the time increment assigned will depend on known stability factors and the amount of historical data available.

The equation used to calculate the RRF is given below.

$$\text{RRF}(\text{analyte}) = \frac{(\text{peak area analyte quantity}) * (\text{Conc. of Internal Standard})}{(\text{peak area Internal Standard quantity}) * (\text{Conc. of analyte})}$$

$$\text{Percent Difference} = \frac{(\text{Average RRF after expiration} - \text{Average RRF before expiration})}{\text{Average RRF before expiration}} * 100\%$$

When appropriate, the concentration of expired cylinders may be verified using gas-phase Fourier transform infrared (FTIR) spectroscopy.

Exception: Two separate vendor prepared cylinders containing benzene-d6 (surrogate) near 0.15 and 25 PPMv respectively do not require routine recertification analyses for the monitoring of their concentrations. Degradation is monitored through routine analyses of samples and method blanks (with acceptance criteria ranging from 70% to 130% recovery), since the benzene-d6 in the calibration standards are prepared from a neat liquid. Once a decreasing trend is noted through the degradation of the sample and method blank surrogate recoveries, the cylinder must undergo recertification analysis against an initial calibration prepared from a neat liquid. A new concentration will be assigned to the cylinder. The spike purity check is accomplished through the routine analysis of surrogate spiked instrument and method blanks.

## 7 Documentation

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### 7.1 Standard Preparation Documentation

LabWare LIMS is used to track gas standard preparation. Mixtures, intermediates, and final calibration standards will be uniquely identified and documented using the "Air Standards and Reagents" template. The final LabWare report(s) will contain all pertinent traceability information for every compound in the standard.

## 8 Attachments

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None.

## 9 References

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- 1) Entech Standards Preparations user's manual.
- 2) USEPA Compendium Method TO15.
- 3) Canister Certification, SOP ETS-8-190.
- 4) Whole Air Sample Analysis by GC/MS, Method ETS-8-16.
- 5) Recertification of a 3000-PPMv fluorochemical gas mixture (cylinder no. CC45991), LIMS project numbers E08-0091, E10-0118, and E12-0149.
- 6) Operation and Maintenance of the Millipore Milli-Q Water System for ASTM Type I Reagent Water, EP ETS-9-009
- 7) "32-Week Holding Time Study of SUMMA Polished Canisters and Triple Sorbent Traps Used to Sample Organic Constituents in Radioactive Waste Tank Vapor Headspace," J. C. Evens et al, Environmental Science and Technology, 1998, 32, 3410-3417.
- 8) "Theoretical Evaluation of Stability of Volatile Organic Chemicals and Polar Volatile Organic Chemicals in Canisters," R. W. Coutant (Batelle), Atmospheric Research and Exposure Assessment Laboratory U.S. Environmental Protection Agency, February 18, 1992.
- 9) "Viability of Using SUMMA Polished Canisters for the Collection and Storage of Parts per Billion by volume Level Volatile Organics," D. A. Betmer et al, Environmental Science and Technology, 1996, 30, 188-195.

## 10 Affected Documents

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None.

## 11 Revisions

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<u>Revision Number</u>	<u>Revision</u>
1	Section 6.4 addresses cocktail storage requirements. ETS-8-196.0 stated that cocktails expired after 6 months. This was not practical and not current practice. The wording was changed to reflect current practices where cocktails can be stored up to one year before expiration.
2	6.4: Added comment on purity correction of cocktail components. 6.9.1: Section updated to include more specific information on the assignment of gas standard expiration dates. 6.9.2: Section updated to extend the expiration date of the loop level internal standards. 6.9.4: Exceptions were added to the expiration/recertification of the surrogate spike cylinders. The surrogate is self-certifying via the normal analyses and control charting. 7.1: All standard preparation is now documented in LabWare. All information regarding Excel spreadsheets was removed.
3	6.5.1: Added step indicating valve is heated. 6.9.4: Added an alternate means to monitor the stability of the vendor prepared 25-PPMv benzene-d6 surrogate gas. 7.1: Added commentary as to where the standard printouts are located and dating/initialing procedures. Changed cocktail to mixture.

- 4
- 3.1, and 6.6.1: Removed references to ETS-2-4 Workers on the Roof.
  - 5.1.3: Removed references to the Entech 4600 Dynamic Dilution System.
  - 6.3: Modified the humidification procedure to reflect actual practices. Modified Table 1, to use the same number of significant figures throughout.
  - 6.4: Removed statements inferring the use of non-purity corrected compounds.
  - 6.5.1: Included the formula for estimation of saturation.
  - 6.9.4: Replaced reference to cross-certification in between the two benzene-d6 (surrogate) cylinders with reference to a benzene-d6 calibration prepared from a neat liquid.
  - 7.1: Removed commentary as to the standard printouts dating/initialing procedures.
- Minor formatting corrections throughout.