3M Environmental Laboratory

Standard Operating Procedure

Canister Cleaning and Certification

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Quality Assurance

1 Scope and Application

This procedure provides guidance for cleaning canisters used for ambient air and process air sampling and analysis. It also describes procedures and quality control criteria for certifying canisters for air sampling with analysis by gas chromatography mass spectrometry (GC-MS).

This procedure is suitable for all sizes of canisters that can be physically attached to the equipment. The cleaning sections of the procedure are applicable for all canisters that are used in the laboratory, both for samples and standards.

The certification sections of the procedure apply to sample canisters where quantitative results are required. The purpose of certifying sample canisters is to demonstrate that the sample canisters are representative of the standard canisters with respect to analyte recovery. Canisters which are used only for standards (typically 6-L and larger) do not require certification. Standard canisters are not typically exposed to compounds that are not readily removed by the cleaning procedures described herein. Furthermore, calibration curves routinely require multiple canisters which demonstrates consistent analyte recovery when quantitative criteria is met.

2 Summary

Fused silica lined stainless steel canisters are reusable sampling containers for collecting ambient air and process air samples. Canisters are cleaned via repeated evacuation and pressurization cycles, using humidified zero grade nitrogen, while applying heat.

The intent of the exhaustive cleaning procedure detailed within this SOP is an earnest attempt to:

1. Remove contamination that may reside in a condensed phase on the inner surfaces of a canister
2. Passivate reactive surfaces (catalytically active sites) that could be present within a canister

After cleaning, sample canisters are subjected to measures to demonstrate canister integrity such as a leak check, challenging the canister with a standard mixture, and conducting a recovery and unknowns analysis using gas chromatography mass spectrometry (GC-MS). This process is referred to as canister certification.

3 Definitions

3.1 LabWare LIMS

The laboratory information management system used by the 3M Environmental Laboratory.

3.2 Parts Per Billion by Volume (PPBv)

$$\text{PPBv} = \frac{10^{-9}\text{L of target analyte}}{1\text{ L of air}} = \frac{1\text{ nL of target analyte}}{1\text{L of air}}$$

3.3 Parts Per Million by Volume (PPMv)

$$\text{PPMv} = \frac{10^{-6}\text{L of target analyte}}{1\text{ L of air}} = \frac{1\ \mu\text{L of target analyte}}{1\text{L of air}}$$

3.4 Volatile Organic Compounds (VOCs)

Defined in USEPA Compendium Method TO-15 as organic compounds having vapor pressures greater than 10^{-1} Torr at 25°C and 760 mm Hg.

3.5 Pounds per Square Inch Gauge Pressure (psig)

Pressure measured with reference to the surrounding atmospheric pressure, expressed in units of pounds-per-square-inch-gauge (psig). Zero gauge pressure is equal to atmospheric pressure.

3.6 Pounds per Square Inch Absolute Pressure (psia)

Pressure measured with reference to absolute zero pressure, expressed in units of pounds-per-square-inch-absolute (psia).

3.7 Torr & mm Hg & mTorr

14.696 psia = 1 atm = 760 mm Hg = 760 Torr

1 mTorr = 0.001 Torr

3.8 Manifold

An array of fittings and plumbing within a canister cleaning oven that facilitates the simultaneous connection of numerous canisters to the can cleaning system's vacuum pumps and nitrogen (diluent) pressurization inlet.

3.9 High Vacuum & Rough Vacuum

For the purposes of communicating the typical operation and maintenance of canister cleaning equipment the terms high vacuum, high-vac (etc.) refer to the range of pressures only achieved through the use of a molecular drag pump or similar high vacuum pump. Typically from about 2 to less than 2000 mTorr.

During operation, exposure of the high vacuum pump to pressures above 1 psia must be avoided. In routine operation the high vacuum pump is not used above the pressure which would cause the high vacuum pump to drop below its operating speed of 27,000 RPM. This pressure is typically less than 1 psia (about 0.2 to 0.7 psia).

Rough vacuum, rough-vac (etc.) refers to the range of pressures typically achieved through the use of the online oil free diaphragm pump or similar vacuum pump. Recommended online maximum 29.4 psia (14.7 psig) down to approximately 0.1 psia.

The rough and high vacuum pressure gauges in the canister cleaning equipment are typically only factory calibrated. The pressures measured with theses gauges are approximate.

3.10 Tentatively Identified Compounds (TICs)

Tentatively identified compounds are detected sample components that are not identified as calibrated or target analytes. Consequently, these components do not have established calibration curves. The mass spectra of non-target sample components are searched against a mass spectral library such as NIST14 and/or an in-house library.

4 Precautions

The operator must be familiar with the canister cleaning equipment, canister autosampler and concentrator equipment and GC-MS systems and their associated hazards including, but not limited to the following: electricity, high heat generation, effluent venting, moving autosampler parts, low-pressure vacuum system, cryogens, and compressed gases. All instrument split vents, exhaust vents, and pump exhaust vents should be vented to a hood or the building exhaust ducts. Refer to 3M Environmental Laboratory document ETS-2-001 "General Laboratory Safety Practices and Procedures" and the appropriate equipment procedures, methods, SOPs, or operator manuals for additional information and cautions.

Some samples and standard canisters submitted for cleaning may contain hazardous and/or highly toxic compounds. The operator should treat all canisters as such.

5 Responsibility

All analysts and technicians who perform canister cleaning activities or certification analyses are responsible for following the procedures described in this document.

6 Reagents and Standards

6.1 Internal standards

Methylene chloride-d_2, toluene-d_8, and o-xylene-d_{10}, greater than 95% purity, obtained from a reputable vendor such as Aldrich. These are recommended internal standards; other compounds may be substituted or added. See Method ETS-8-196 for standard preparation.

6.2 ASTM Type I Reagent Water

The nitrogen (diluent gas) that is used in the course of the cleaning process is humidified as it passes through an in line reservoir attached to an Entech 3100 canister cleaning system or similar system. Water can also be added directly to evacuated canisters. Moisture aids in removing some organic compounds. Water is obtained from a Millipore Milli-Q water purification system or equivalent (ETS-9-009).

7 Supplies

7.1 Capillary Chromatographic Column

Fused silica capillary column suitable for use with the instrumentation and for separation and analysis of the volatile compounds of interest.

7.2 Nitrogen

Liquid nitrogen Dewar equipped with a nitrogen gas regulator, for a clean source of nitrogen gas as a diluent. High purity house nitrogen may be used if available.

7.3 Pressure Gauge (For Canister Pressure Checks)

Pressure gauge with analog scale divisions or digital resolution to the nearest 0.5 psig or better and 0.1 psig measurement precision or better. Capable for measuring pressures up to 30 psig.

8 Equipment

8.1 Automated Canister Cleaner

Entech 3100A or 3100D canister cleaning equipment, or equivalent.

8.2 Gas Chromatograph

Hewlett-Packard 6890/7890 gas chromatograph, equipped with a split/splitless injection port and electronic pressure control (EPC), or equivalent.

8.3 Mass Spectrometer

Agilent 5973/5975/5977 Mass Selective Detector, with MassHunter Acquisition software and MassHunter Quant, or equivalent.

8.4 Canister Autosampler and Concentrator

Entech 7032 or 7650 autosampler and Entech 7100 or 7200 concentrator, or equivalent.

9 Canister Cleaning

No sooner than one week after the report for a project has been issued, or after a standard is no longer needed, the associated canisters are submitted for cleaning. Vent canisters that are at or above 14.7 psig to ambient pressure in a hood. Refer to the corporate laboratory safety manual, "3M Guide to Laboratory Practices", and if there are any questions, contact the Lab Safety/EHS personnel.

Refer to the Entech 3100 Canister Cleaning System Operator's Manual for additional operating instructions for the cleaning system and the associated controlling software.

9.1 Water Addition

Water is added to evacuated canisters prior to full canister cleaning. Water addition is optional but has been observed to refurbish canisters that have previously persistently failed recovery criteria. It is possible that certain classes of compounds, which would otherwise 'stick' to the walls of a canister, enter the liquid water phase and then they are ultimately evacuated out with the water. It is also possible that the presence of excess water (gas phase saturation), in an evacuated canister simply out-competes active sites on the inner wall of a canister, and then passivates these sites, which would otherwise potentially remain active and lead to poor target analyte recovery.

9.1.1 Water Spike

Manually evacuate canisters, one at a time, and add about 40 µL of water per 380-cc or 450-cc canister. Allow the added water to be drawn into the evacuated canister. Do not force water though the syringe needle if the plunger on the syringe feels 'stuck' or if the syringe needle is apparently clogged for any reason.

Water can be safely added to any evacuated sample canister through an 11 mm septa that is seated within a quarter inch swage-lok nut. For Micro QT fitted, quick connect, canisters fit the septa & nut to a female Micro QT fitting and attach it to the canister's male Micro QT fitting.

Wait at least one day before starting a full cleaning of water spiked cans to give the added water ample time to passivate the inner surfaces of the canisters.

9.2 General Guidance on Canister Cleaning

Deep high vacuum-pressure cycling may refurbish canisters that have previously persistently failed recovery criteria. Time under high vacuum at elevated temperature (typically 100°C) allows the heaviest semi-volatile ('non-volatile') compounds that may be present in a canister to enter the gas phase so that they can be evacuated out of the canister. An in-line nitrogen humidification reservoir allows for cleaning with humidified nitrogen, which may also refurbish canisters that have previously persistently failed recovery criteria.

Entech (a canister supplier) strongly recommends against heating Silonite lined canisters over 80-85°C in the presence of air (oxygen) as it will degrade the 'inert' Silonite coating. While under high vacuum or in the presence of pure nitrogen, Entech recommends against heating Silonite canisters over 140°C. 120°C would be sufficient to volatilize the most recalcitrant residual species that could actually be evacuated out of a canister. The Viton o-rings are temperature rated from about -25 to 200°C, but can begin to dry out and lose seal above 120°C. Typically canisters are cycled several times at room temperature followed by numerous additional deep cycles at a conservative temperature of 100°C.

9.3 Canister Cleaning Procedure

1. Load water spiked cans onto the can cleaning manifold.
2. Rough-vac cans (water spike removal) to about as low as the psi pressure gauge typically reads, when there is not excess water present within the manifold.
    a. A few rough cycles and modest 50-60°C heat may be required to facilitate the bulk of the water removal.
3. High-vac cans as a preliminary leak check, and to ensure that the high-vac set point in the canister cleaning method can be achieved, allowing for vacuum-pressure cycle cleaning.
4. Thoroughly leak checking the canister cleaning manifold, can cleaning instrument, and canisters to be cleaned, allows for more effective canister cleaning as it ensures the lowest practicable high-vac set point can be achieved.
    a. Canisters that are known to have failed a leak check should not be cleaned unless the leak has been repaired.
    b. When cleaning a large volume of standard canisters, achieving this low reading at room temperature may take a few hours but it should still be possible (unless a substantive leak is present). Initially the presence of residual water within the canisters can also increase the time it takes to achieve the lowest possible reading.
5. As a precaution, before the application of 100°C heat, vacuum-pressure cycle canisters about ten times at room temperature to adequately remove the bulk of the contents of the canister.
6. Turn on 100°C heat and vacuum-pressure cycle canisters in order to remove the remaining residual contents from the canisters.
    a. Cycling is automated by running a canister cleaning instrument method. Vacuum-pressure cycle canisters under 100°C heat as many times as is practicable, or as many times as proves to be required to obtained an adequate supply of sample canisters with passing recoveries.
7. After full cleaning, evacuate all of the sample canisters under high vacuum and wait for them to cool down to room temperature. Once the sample canisters have cooled and are under vacuum, remove the canisters from the manifold.
    a. When removing manually valved canisters this is easily achieved by turning off all the canister valves and then turning off the vacuum pumps.
    b. When removing Micro QT fitted (quick connect) canisters it is best to leave the manifold under vacuum while taking the canisters off the manifold. Occasionally, when taking a QT canister off the manifold, the female fitting on the manifold will not automatically seal and a gas leak will be audible. In this instance, immediately re-connect the canister to the manifold and wait for the manifold pressure to re-stabilize to the pressure that was previously achieved. If the female fitting on the manifold is particularly poor, this course may have to be repeated several times before the female fitting on the manifold seals automatically. Mark the problematic fitting, as it must be replaced or refurbished. Spare parts (e.g. springs, o-rings, plungers) and replacement fittings can be obtained from the supplier (Entech).

9.4 Cleaning Method Examples

The following readings for the high vacuum gauge are the settings when the canister cleaning manifolds have historically been at peak performance. When these readings are not achieved through normal use of the manifold, consideration should be given if there is a substantial leak present in the manifold or due to the canister (vial, jars, or fittings). Any leaks present will extend the amount of time required to perform the number of cycles desired.

9.4.1 Rough Cycles

3 room temp cycles and 3 cycles as needed at 50-60°C

Rough-vac to: 0.1 psia

High-vac to: 1999 mTorr

Pressurize to: 15 psia

After the final cycle: rough-vac to 0.1 psia, high-vac to <50 mTorr.

9.4.2 Full Canister Cleaning

10 room temp cycles, 100 heated cycles at 100°C

Rough-vac to: 0.2 to 0.5 psia

High-vac to: ideally <50 mTorr

When the controlling software being used allows: hold at high-vac on each cycle (after achieving the high-vac set point) for 3 to 5 minutes or more.

Pressurize to 15 psia

After the final cycle: rough-vac to 0.2 to 0.5 psia, high-vac to <50 mTorr, then hold at high-vac.

9.5 Micro QT fittings

Canister cleaning methods are also applied to the cleaning of the lab's stock of spare Micro QT (quick connect) fittings. The o-rings contained within these fittings are made of Viton which has some marginal capacity to absorb gas phase analytes, and it may become a potential source of cross contamination if the fittings are not regularly cleaned. Glass vials and jars are also sealed with Viton o-rings. Used Micro QT fittings are routinely plugged and connected directly to the canister cleaner or they are cleaned in a sealed glass vial or other vessel that can be attached to the canister cleaner.

Micro QT fittings are also routinely pressure leak checked in both the closed (automatically sealed) state and in the open state (while connected to a plugged male or female counter part). Micro QT fitting spare parts (e.g. springs, o-rings, and plungers) and replacement fittings can be obtained from the supplier. Pressure checks can be performed by connecting the fittings to one of the lab's high resolution gauges at approximately 30 PSIG and then monitoring for pressure loss in real time.

10 Canister Certification

Canister certification is the process by which a canister's integrity and inertness is tested. Canisters are filled with a certification mixture to approximately 30 psig. After at least 36 hours the pressures of individual canisters are measured for integrity. Canisters are then vented to a pressure appropriate for analysis and are certified according to cleanliness and recovery of the certification mixture. The purpose of certifying sample canisters is to demonstrate that the sample canisters are representative of the standard canisters with respect to analyte recovery, keeping in mind that each canister is essentially a standard. Typically larger canisters are used as standard canisters and are not released as sample canisters so as to not expose the canister to conditions which may degrade the Silonite lining. Larger canisters are also considered more robust in terms of analyte recovery due to the surface-area-to-volume-ratio advantage that they provide.

10.1 Certification Mixture Cylinders

Gas cylinders containing a canister certification mixture (e.g. formaldehyde, ethylene oxide, acetone-d_6, bromobenzene-d_5, and 1,3,5-trimethylbenzene-d_{12}) are maintained by the lab and these cylinders are the routine choice for the gas certification mixture that is used in the course of the certification analysis of

sample canisters. When a new gas cylinder certification mixture is obtained, care should be taken to determine the following:

1. That it is free of contamination which might interfere with the recovery analysis of the desirable components, or be suspected of causing accelerated degradation of the desirable components.
2. That the new cylinder actually contains meaningful levels of the desired components, which are suitable for measuring recovery.
3. That any contamination present in the cylinder would not be suspected as being difficult to clean out of the canisters.

The actual concentration of each of the components in a certification mixture is not relevant to determining component recoveries since it is always compared against itself. Any expiration date assigned to a certification mixture is arbitrary. All that is required to be known about a certification mixture is that the concentration of each of the recovery analytes at any given time is low enough to meaningfully evaluate PPBv level analyte recovery.

A certification mixture may be prepared by direct introduction of standards of each of the components into the evacuated sample canisters. Addition of standard aliquots should be targeted such that, after nitrogen pressurization to approximately 30 PSIG, the resulting approximate concentrations are suitable for measuring recovery. For detail on standard preparation techniques refer to ETS-8-196.

10.2 Water Spike

Canisters that have been cleaned according to section 9 are ready for water addition prior to being filled with certification mixture. Manually fill each canister, one at a time, with about 5 µL of water per 380-cc or 450-cc canister. This equates to about 0.5% v/v per canister. The actual volume used should be consistent for each batch and volume of canister. Allow the added water to be drawn into the evacuated canister. Do not force water though the syringe needle if the plunger on the syringe feels ‘stuck’ or if the syringe needle is apparently clogged for any reason.

Water can be safely added to any evacuated sample canister through an 11 mm septa that is seated within a quarter inch swage-lok nut. For Micro QT fitted, quick connect, canisters fit the septa & nut to a female Micro QT fitting and attach it to the canister’s male Micro QT fitting.

10.3 Procedure for Certification Mixture Filling (Spiking)

Sample canisters are individually spiked with the certification mixture directly from the certification mixture cylinder. Attach, as required, any fittings to be used to the regulator in order to fill the sample canisters and adjust the regulator on the cylinder to approximately 30 psig (44.7 psia). Attach the water spiked evacuated canisters individually to the regulator and allow the sample canister to pressurize to approximately 30 psig (this may take a few minutes).

10.4 Canister Pressure Check & Pressure Check Criteria (Leak Check)

After filling the cleaned canisters to approximately 30 psig with a certification mixture, wait at least one and one half days (at least 36 hours, typically 48 hours or longer) before checking the pressure of each canister. The exact pressure to which the canisters were filled, need not be known. All that must be clear is that all of the canisters were at the same pressure when they were spiked. Approximately 30 psig is high enough to evaluate the leak-tight integrity of the canisters. Do not cap manually valved canisters during the waiting period, as it is the integrity of the canister and the valve that is being checked.

In a spreadsheet, record each canister number and the measured pressure of each canister utilizing a pressure gauge with at least 0.5 psi divisions. Record the measured pressures in psig to an accuracy of one place after the decimal. Putting the leak check data and canister numbers in a spreadsheet facilitates creation of a LIMS canister cleaning batch. Use of a bar code reader is desirable for easily scanning the canister numbers into the spreadsheet. Vent the pressure gauge to atmospheric pressure between each reading. It is advantageous to check the canisters in an order that groups canisters of the same size together.

For each canister size (volume) in the cleaning batch, identify the maximum pressure reading recorded for that canister size. For each of the canisters of the same size record the maximum pressure for that canister size as the assumed initial pressure. The measured pressures are the final pressure. Due to the canister size differences and the volume of the pressure gauge itself, it is not correct to compare canisters of different sizes to each other.

1. Canisters which exhibit a difference of 1.0 psi or greater between their assumed initial pressure and measured final pressure (over a period of at least 1.5 days) fail the pressure check.
2. Canisters which exhibit a difference of less than 1.0 psi between their assumed initial pressure and measured final pressure (over a period of at least 1.5 days) pass the pressure check.

A canister which failed the pressure check can still be analyzed for analyte recovery. If the leak can be repaired, the canister can be checked again (after completing a recovery analysis) utilizing 30 psig nitrogen. In this circumstance, it is likely that recording actual initial and actual final pressures would be most direct. The updated pressure check data could then ultimately be recorded in the LIMS system and if the canister passed recovery and cleanliness criteria, it could be issued for sample collection.

After conducting the pressure check of a cleaned batch of sample canisters, a LIMS batch is created by logging a sample for each of the sample canisters to a CAN_CLEAN batch. Batches are about 20 to 70 canisters - all of which were cleaned and spiked with a certification mixture. Batches of 30 canisters or greater are desirable for enhanced statistical validity.

10.5 Canister Recovery Analysis

After completing the pressure check and prior to conducting recovery analysis, each sample canister should be vented in a fume hood to approximately 10 to 15 psig.

Sample canisters are analyzed using a GC-MS instrument and a cold trap dehydration (CTD) sample delivery system, equipped with a canister auto-sampler. The GC-MS and CTD methods utilized are similar to the example methods depicted in ETS 8-016. At the analyst's discretion the methods can be modified to accelerate the analysis of the certification samples. For example the GC-MS temperature program may ramp more quickly, or certain steps in the CTD method may be shorter, when compared to the methods used for project sample analysis.

Sample canisters are analyzed for recovery via 200-cc injection. For each batch a calibration curve for each recovery analyte is established using at least three sample canisters that exhibit a response ratio near the median response ratio for the certification mixture analytes. These canisters are set at 100% recovery and all canisters are then compared to these canisters. Other methodology may be used at the analyst's discretion.

The analysis of blanks or calibration check samples in the course of a recovery analysis is not necessary, nor is there any criteria associated with internal standard response. The analysis of each of the sample canisters implicitly serves as a dedicated calibration and blank check.

A canister passes recovery analysis if it meets the following criteria:

1. All three of the VOC surrogate recovery analytes (e.g. acetone-d_6, bromobenzene-d_5, and 1,3,5-trimethylbenzene-d_{12}) are within ±30% recovery.
    a. If any of the VOC surrogate analytes do not pass the recovery analysis criteria, the canister will not be certified for quantitative (i.e. ±30% accuracy) analysis and will be labeled as such. This canister may repeat the cleaning and certification process if deemed appropriate for that canister.
2. Additional analytes (e.g. formaldehyde and ethylene oxide) are within ±30% recovery, provided that the VOC surrogate recoveries also meet ±30%. The canister will then be certified for VOCs and any additional analyte that passes.

It is critical that any outliers be identified within the certification batch and be excluded from passing. The analyst may fail a canister even though it passes the recovery criteria at their own discretion.

Upon completion of the recovery analysis, the results are uploaded into LIMS. Certification labels are printed from LIMS that will indicate the certification status of the individual canister (e.g. leak check and recovery results) and attached to the tag on the canister.

Despite most exhaustive and repeated cleaning, if a canister repeatability fails recovery criteria, it is possible that the interior surfaces of the canister have become corroded or an interfering solid phase (or particularly non-volatile liquid phase) is contained within the canister. Canisters which persistently fail recovery criteria despite the best attempts to clean them should be removed from service as certified canisters.

Apart from the most exceptional circumstance of a aggressively corrosive sample matrix, it is still advisable that canisters at least demonstrate a passing recovery for bromobenzene-d_5 or 1,3,5-trimethylbenzene-d_{12}. These recovery analytes are more resistant to degradation than acetone-d_6.

10.6 Canister Background Acceptance

Canisters available for certification are also analyzed using the Agilent MassHunter Unknown's Analysis program or a similar GC-MS data reduction software tailored towards tentative identification of unknown chemical compounds. Canister background contaminants are estimated as tentatively identified compounds (TICs) by comparison to an internal standard response, typically toluene-d8.

1. Contamination that is present in all canisters that can be attributed to the certification mixture or as a known degradation product of the certification mixture is disregarded.
2. Any other remaining residual contamination that is not known to be attributable to the analytical instrument itself, is attributed to the canister. If present in the canister at an estimated level of greater than 0.004 PPMv, it is clearly hand written on the canister's certification label. It is then determined if the canister should be resubmitted for cleaning or if the contaminant has a low enough concentration to not affect typical sample analysis to be passed for certification.

11 Final Canister Evacuation

Prior to sample collection, the certification mixture must be cleaned out of the canisters, and the canisters need to be evacuated. The steps related to water spike removal are skipped and the number of vacuum-pressure cycles can be reduced substantially.

The presence of any of the deuterated components of a certification mixture, in a project sample would be an indication that additional cycles or deeper high-vac is required during final cleaning. After final cleaning canisters are routinely evacuated to the lowest pressure reading that can be achieved on the can cleaning manifold at 100°C (e.g. 10 mTorr). As it should be indicated on all canister tags, canisters issued for sample collection are guaranteed to be at a pressure of less than 50 mTorr at the time of final evacuation.

If a canister has not been used in four months since its final evacuation, the pressure of the canister should be checked and the final evacuation procedure should be repeated if a pressure greater than 50 mTorr (i.e -28" Hg) is measured.

11.1.1 Recommended Canister Final Evacuation

10 room temp cycles and 40 heated cycles at 100°C

Rough-vac to: 0.2 to 0.5 psia

High-vac to: ideally 50 mTorr

Pressurize to 15 psia

After the final cycle: rough-vac to 0.2 to 0.5 psia, high-vac to <50 mTorr, then hold at high-vac.

12 Sample Two Sided Canister Tags

A two sided (lab and field use) form label is affixed to each canisters card stock tag. The passing LIMS Certification Label must also be affixed to each VOC certified canister tag. Sample form labels are depicted here. VOC certified canisters receive yellow tags. In exceptional circumstances where corrosive samples are to be collected in canisters with failing VOC recoveries these canisters are green tagged and the failing LIMS certification label should also be affixed to the canister tag. Canister numbers appear on the LIMS Certification Labels so they do not necessarily need to appear on the lab and field use form labels.

12.1.1 VOC Certified Canisters (Yellow Tagged)

Unpressurized Ambient Air Sample

3M Environmental Laboratory

Sample ID: _____

Date: _____ Tech: _____
Start:_____ End:_____use 24 hr time

Controller #E000000_____(if applicable)

Final Pressure_____

Use by:
Return promptly. Samples must be analyzed within 30 days of collection.

3M Environmental Laboratory

(This Side for Laboratory Use Only)

Date Evacuated:
Final Pressure: <50 mTORR
Surrogate Spike: _____
Initial / Final Pressure: _____/_____
Spiked By / Date: _____

12.1.2 Project Specific – Certified for Use and Re-Use (Yellow Tagged)

Unpressurized Ambient Air Sample

3M ECAN0611

Sample ID: _____

Date: _____ Tech: _____
Start:_____ End:_____use 24 hr time

Controller #E000000_____(if applicable)

Final Pressure_____

Use by:
Return promptly. Samples must be analyzed within 30 days of collection.

3M BIODEG HEADSPACE ONLY

(This Side for Laboratory Use Only)

Date Evacuated:
Final Pressure: <50 mTORR
Surrogate Spike: _____
Initial / Final Pressure: _____/_____
Spiked By / Date: _____

12.1.3 Failing VOC Recovery – Corrosive Sample Matrix (Green Tagged)

Not Certified for PPBv Recovery

3M Environmental Laboratory

Sample ID: _____

Date: _____ Tech: _____
Start:_____ End:_____use 24 hr time

Controller #E000000_____(if applicable)

Final Pressure_____

Use by:
Return promptly. Samples must be analyzed within 30 days of collection.

3M Source Level Sampling Only

(This Side for Laboratory Use Only)

Date Evacuated:
Final Pressure: <50 mTORR
Surrogate Spike: _____
Initial / Final Pressure: _____/_____
Spiked By / Date: _____

13 References

US EPA Compendium Method TO15, January 1999.

ETS-8-016 Sample analysis SOP

ETS-8-196 Standard prep/dynamic diluter SOP

Entech 3100 Canister Cleaning System Operator's Manual

14 Affected Documents

None

15 Revisions

Revision Number	Summary of Changes
1	1. Added clarification of the certification requirements for canisters used only for standards; Section 1. 2. Added information on formaldehyde certification; Sections 1.1, 4.1.5, and 8. 3. Changed certification and pressure check holding times; Sections 1.1 and 7. 4. Added reference to ETS-9-004, Section 2.1. 5. Deleted path to ETS Inventory Tracking database, Section 6 6. Deleted references to Canister Lot Cleaning Logbook and added descriptions of cleaning records in LabWare; Sections 6, 8.2, and 10. 7. Added notes on connecting manifolds in series and the auxiliary humidification chamber, Section 6. 8. Changed analysis pressure requirement to <20 psig, Section 8. 9. Added a note on outlier removal, Section 8.1. 10. Added an alternative procedure for background acceptance, mild acid cleaning as an alternative aggressive cleaning procedure, and Figure 1, a control chart example, Section 8.2. 11. Modified the canister tag labels in Figure 2 and added storage of old canister tags, Section 9. 12. Removed attachments of Logbook examples, Section 11.
Revision Number	Summary of Changes
2	1.1 Added an alternate spiking technique. 1.2.5 New definition added. 1.2.6 New definition added. 2.1 Added cryogenics to the last paragraph. 4.1.5 Addressed the formaldehyde spike concentration for the alternate spiking technique. 4.2.27.2 Removed reference to the LN2 pressure. 6 Reduced the waiting period in between report issuance and canister cleaning from two weeks to one week. Corrected pressurization pressure from 35 psig to 35 psia. Replaced reference to ETS-2-004 with "3M Guide to Laboratory Practices" and attached a link the appropriate section of the "3M Guide to Laboratory Practices" Changed scan location from Lotus Notes to LIMS. 7 Added an alternate spiking technique (paragraph 2), and added a note referencing different valve styles. Added detail to how the pressurization is conducted. 8 Added an optional Entech concentration technique suitable for all spiked compounds. 8.1 Added an option to evaluate inertness based on percent recovery. 9.3 Modified the number of cleaning cycles.

9.7 Updated canister tag.

Revision Number	Summary of Changes
3	Extensive revisions throughout the whole document. Sections were revamped to be more consistent with other laboratory method SOP documents. Major revisions include: • More detailed information was added including water addition procedures and more details about the parameters for the can cleaning manifold (Section 9). • Addition of information regarding Micro QT quick connect fittings throughout the document.