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ETHYLENE OXIDE BY EPA METHOD TO-15
(TOXIC ORGANIC COMPOUNDS IN AMBIENT AIR)
GAS CHROMATOGRAPHY/MASS SPECTROMETER DETECTION

Access to this SOP shall be available within the laboratory for reference purposes; the official copy of this SOP resides on the official Georgia EPD website at <https://epd.georgia.gov/about-us/epd-laboratory-operations>. Printed copies of this SOP will contain a watermark indicating the copy is an uncontrolled copy.

1. Scope and Application

- 1.1. Federal law (CFR Title 40 Part 58) requires the States to establish a network of toxic organic monitoring sites in ozone non-attainment area. As part of the ETO monitoring requirements, this lab analyzes volatile organic chemicals from ambient air sample collected in in SUMMA or Silco Steel lined 6L canisters. The target compound for this analysis is:

Compound	CAS Number
Ethylene Oxide	75-21-8

- 1.2. This SOP covers the steps used by the Ga. EPD Laboratory to clean and prepare a certified clean canister, canister pickup/mailling for sampling, and sample analysis and data reporting.
- 1.3. Air samples collected in canisters are introduced into a GC/MS via a cryogenic pre-concentrator. During analysis, water vapor is condensed on a first trap while the VOCs are transferred to a second cryogenically-cooled trap. The temperature of the traps are raised and the VOCs are finally forced into the GC column. The components are separated in the temperature programmed GC and the effluent is detected via a mass spectrometer in the SIM mode. Identification of target compound is accomplished by comparison of the retention time with known standard retention times, comparison of mass spectral target ions from standards, and with mass spectrum library searches.
- 1.4. The EPD Laboratory incorporates MQOs from the EPA Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, October 2016

2 Definitions

- 2.1 Refer to Chapter 3 of the Georgia EPD Laboratory Quality Assurance Manual for Quality Control Definitions.

3 Interferences

- 3.1 Very volatile compounds, such as Ethylene Oxide can display peak broadening and co-elution with other species if the compounds are not transferred to the GC column in the smallest volume possible. Focusing of the sample on a third cryogenically cooled trap at the head of the gas chromatographic column mitigates these problems.
- 3.2 Interferences in canister samples may result from improper use or from contamination from the following:
 - 3.2.1 The canisters contaminated due to poor manufacturing practices
 - 3.2.2 The canister cleaning apparatus
 - 3.2.3 The field sampling system.
- 3.3 Attention to the following details will help to minimize the possibility of contamination of canisters.
 - 3.3.1 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.
 - 3.3.2 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.
 - 3.3.3 As suggested by the 2016 TAD, some canisters are separated from field analysis and filled with zero air or with a known concentration of standard and held for 30 days as a bias check. The blank zero air canister and known concentration canister should pass TAD criteria listed below:
 - 3.3.3.1 Pressure: <0.1psi/day leak criteria
 - 3.3.3.2 Zero Air filled “Blank” canister: analyte <3x MDL or <0.2PPBV, whichever is lower
 - 3.3.3.3 Known Standard filled canister: all targets $\pm 30\%$ of nominal value
- 3.4 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.
- 3.5 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems.
- 3.6 The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks.
- 3.7 The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.
- 3.8 Interference from one sample to the next, with the first being a highly contaminated sample and the next being clean, has been studied by Entech, and is stated in their manual to not be a problem they have seen for ambient air samples (vs smokestack samples).
 - 3.8.1 Previous interference can be noticed easily by monitoring the daily standard and blank that follows it. With normal operation of the instrument, this is not a problem. If contamination does appear in the second blank then there is a problem with the system that must be investigated and resolved.

4 Safety

- 4.1 Refer to Laboratory Chemical Hygiene Plan
- 4.2 High pressure ETO gas cylinders must always be strapped or attached to a wall or bench
 - 4.2.1 Working ETO gas cylinder attached with regulators must be stored in vented cabinet.
- 4.3 Canister pressure cannot exceed 40 PSI Gauge.
- 4.4 All gas standards transfer to a canister must be done inside a hood
- 4.5 Used expired field canisters are vented inside a hood.

- 4.6 Any high pressure gas cylinder must be transported with the safety screw cap on the cylinder and using a cylinder cart with 4 wheels.
- 4.7 Due to cryogenic extreme cold temperatures, special gloves are available in the lab for closing liquid Nitrogen valves and handling frozen instrument components.
- 4.8 All canister heaters and/or oven must be turned off before leaving the day/shift.
- 4.9 Daily Check Routine Maintenance List
 - 4.9.1 Daily check TO-15 standard canister for pressure .
 - 4.9.2 Daily check TO-15 internal standard canister pressure at or above 100 PSI.
 - 4.9.3 Daily check column for performance by checking daily CC, replace septa if needed.
 - 4.9.4 Daily check connection ferrules by checking CC performance, replace if needed.
 - 4.9.5 Daily check that nitrogen gas pressure gauge feeding Entech is above 20 PSI.
 - 4.9.6 Daily check oil level on rough pump, refill as needed.

5 Apparatus and Equipment

- 5.1 Entech 7200 cryogenic concentrator is used for sample concentration and introduction to the GC. The system has eight ports.
 - 5.1.1 Port Number 1 is dedicated as a blindstream, to run leakchecks.
 - 5.1.2 Port Number 2 is dedicated for helium to purge the system's transfer lines.
 - 5.1.3 Port Number 3 is dedicated to the internal standard.
 - 5.1.4 Port Number 4 is dedicated to the calibration standard.
 - 5.1.5 Port Number 5 is dedicated to the autosampler that allows up to 16 6L canisters to run in a sequence.
 - 5.1.6 The Entech control software controls the canister position, cryotrap method being run.
 - 5.1.7 The Entech software is MS Windows based and run on the instrument control computer.
 - 5.1.8 The following are the system parameters of the Entech concentrator for cryogenic trapping of ETO standards and samples for introduction into the GC:

Table 5.1.8.1 Entech Trap Parameters			
Module	M1(5975)	M2(5975)	M3(5975)
	Empty Trap	Tenax	On Column Focus
Trap	-40° C	-60° C	-150° C
Preheat	-5° C	No	No
Desorb	-5° C	230° C	2.5 min
Bake	150° C	230° C	20 min

Table 5.1.8.2 Entech Bulkhead Parameters		
	Bulkhead Heater 1	Bulkhead Heater 2
Trap Sample	30° C	30° C
Desorb Sample	30° C	40° C
Bake	150° C	150° C

Table 5.1.8.3 Entech Flow Rates	
Sample Flow	100 ml/min
Minimum	10 ml/min

Table 5.1.8.2.4 Transfer from M1 to M2 to M3	
Volume M1 to M2	15 ml
Inject + Extra M2 to M3 Transfer	0.2 Min

Table 5.1.8.2.5 Entech Instrument Constant Temperatures	
Sample Transfer Line	80° C
Rotary Valve Plate	80° C
GC Transfer Line	100° C

5.2 The Entech 7016D has an autosampler with 16 canister positions and is intended for 6L canisters. The QC Cleaned Can is rotated through the positions as a check that the autosampler positions are clean of contamination.

5.3 The Gas Chromatograph and Mass Spectrometers are GCMS16 5975 (GC6890 with a 5975 Mass Spec)

5.3.1 The GC program is set with the following parameters for sample analysis:

5.3.2 GC Oven Parameters

Table 5.3.2.1 Overall Oven Parameters	
Oven Maximum	325° C
Oven	On
Cryo	On
Cryo Blast	On
Equilibration Time	0.5 Min
Column Flow Rate	1.0 ml/min

5.3.3 GC Oven Temperature Program

Table 5.3.3.1 GC Oven Temperature Program	
Initial Temperature	-50° C
Initial Time	1 Min
Rate 1	10° C/Min to 220° C
Rate 2	15° C/Min to 220° C
Final Holding Time	13.0 Min
Total Run Time	41.0 Min

5.3.4 GC column: HP-1: length 50 m; ID 0.32 mm; film thickness 1.05 µm

5.4 A computer with a minimum of 64 MB of Ram and a 2.8 GHz computer are used for instrumental control and data processing and 500GB hard drive for data storage.

5.5 Entech 3000SL, 3100D1, and 3100D2 canister cleaning systems.

5.6 Canister Pressure Gauge, certified once per year.

6 Reagents

- 6.1 Helium: UHP/Zero Grade - Helium is the sweep/purge gas medium for the sample going through the Entech and GC/MS instruments.
 - 6.1.1 Before the Helium travels to the instrument system, it must go through an oxygen scrubber and a hydrocarbon scrubber to ensure that the helium is free of hydrocarbons, oxygen and moisture.
- 6.2 Air: UHP/Zero Grade or House Zero Grade - Zero air is used for the MS detector and in all blank analysis. Prior to the Zero air traversing through the system, a hydrocarbon filter is utilized to minimize possible contamination and generation of false peaks in the MS detector and for the canister cleaning system.
- 6.3 Liquid Nitrogen, supplied by Air Products, is stored in a large cryogen tank outside the rear of the building
- 6.5 High pressure cylinder, Ethylene Oxide Calibration Standard Gases are ordered at a concentration of 500 PPBV, in nitrogen gas mixture, NIST traceable. Obtained from Apel-Riemer.
- 6.6 High pressure cylinder, Internal Standard Gases at a concentration of 50 PPBV in a nitrogen gas mixture, NIST traceable. Obtained from The Linde Group or Apel-Riemer.
- 6.7 High pressure cylinder, Ethylene Oxide Second Source Standard Gases ordered at a concentration of 500 PPBV in a nitrogen gas mixture, NIST traceable. Obtained from Apel-Riemer (Special allowance made by EPA for a second source from one vendor).
- 6.8 Each high pressure standard cylinder is logged into the standards logbook. Each Zero Air cylinder must be logged into the Reagent Logbook and given a unique ID Number. This number is placed prominently on the cylinder and is used for reference purposes in the Laboratory.
- 6.9 Laboratory Deionized Water

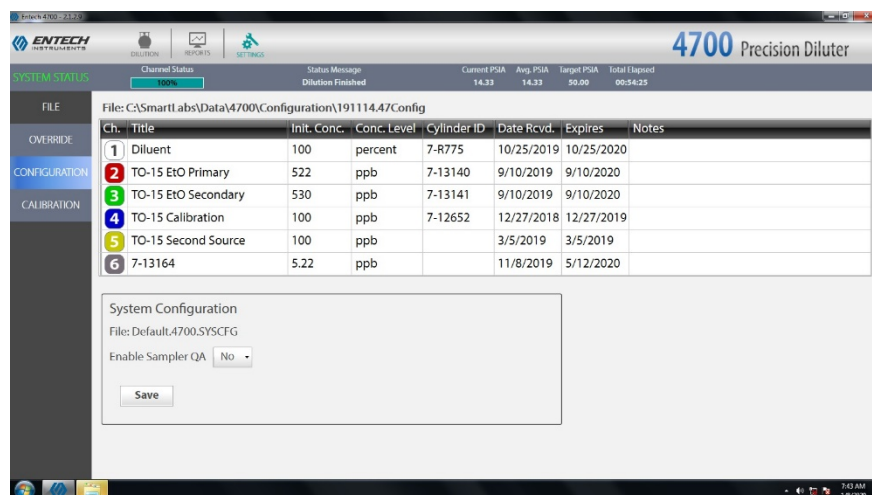
7 Sample Collection

- 7.1 Air sample collected in SUMMA or Silco lined 6 L canisters by the EPD Air Group. Holding time for air samples is 30 days from collection.

8 Calibration

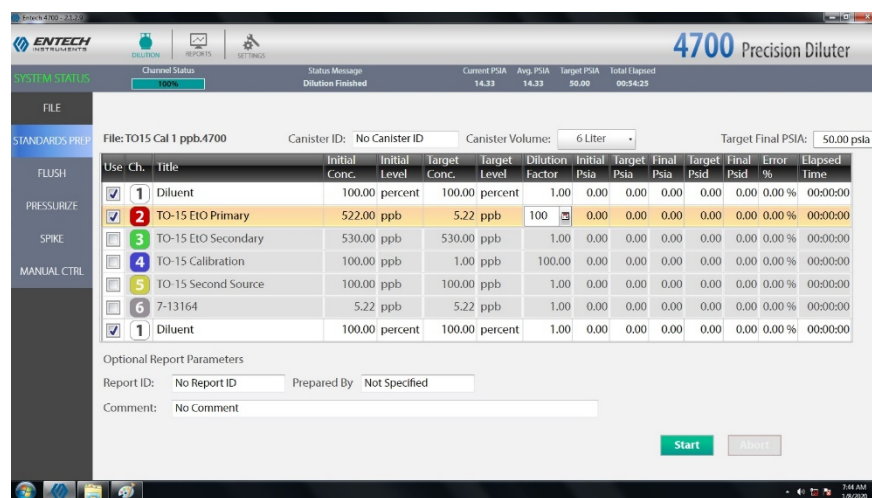
- 8.1 Ethylene Oxide standard cylinders must be diluted to single digit PPBV working levels
- 8.2 Any prepared dilution canister must sit overnight before calibration use
 - 8.2.1 Any prepared dilution canister must sit overnight before preparing a series dilution from the prepared canister into a second canister
 - 8.2.2 After all dilutions, close zero air cylinder, standard cylinders, and zero air valve.
- 8.3 Procedures for Standard Dilution (Static)
 - 8.3.1 Humidify the Standard Canister To the inside of the canister valve add DI water, 75µl for the 6L or 187µl to a 15L.
 - 8.3.2 The 4700 Static Diluter has different channel positions to use for dilutions
 - 8.3.3 Channel 1 is for the zero air cylinder
 - 8.3.4 Channel 2-5 are for standard cylinders
 - 8.3.5 Channel 6 is to take a standard canister and dilute it into a second canister.
- 8.4 Diluter control is via desktop computer... double click the 4700 diluter icon
 - 8.4.1 Load the correct configuration under settings tab (see image #1 below)

Image #1



- 8.4.2 Open zero air cylinder, zero air valve (next to the diluter), and the standard cylinder you are using for the dilution.
- 8.4.3 Select flush under dilution tab
- 8.4.4 Select channels to flush by clicking to highlight
- 8.4.5 Set Flush Configuration: Diluent flush (20 sec), standards flush (600 sec) diluent flush between (15 sec)
- 8.4.6 Click "start"
- 8.5 Select standards to prepare under the dilution tab
 - 8.5.1 Enter canister ID, select canister volume 6L or 15L, enter target final PSIA (50)
 - 8.5.2 Check "Use" box for diluent channel 1 and EtO primary or secondary channel
 - 8.5.3 Change the target concentration (5ppbv) (see image #2)
 - 8.5.4 The maximum dilution factor 100x

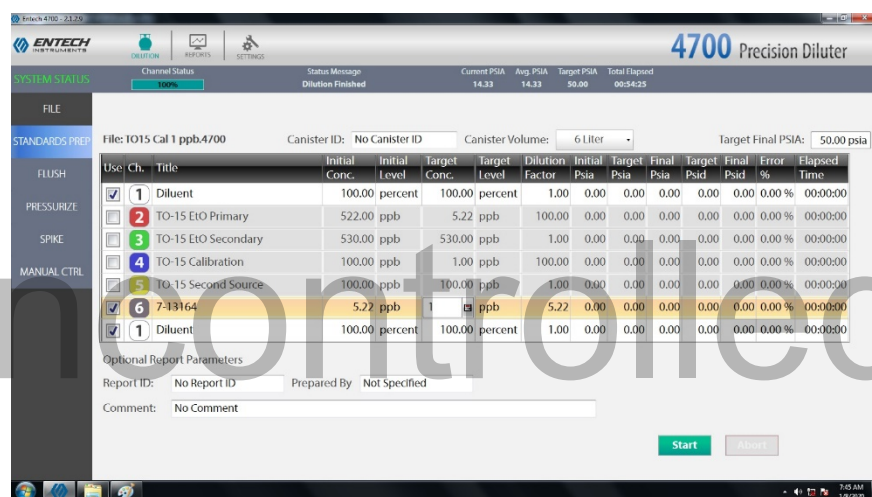
Image #2



- 8.5.6 Connect humidified can to canister output on the 4700

- 8.5.7 Leak check. Open the valve on the canister to apply vacuum to the 4700 and then close 5 the valve. Leak tight if 0.5psia/30 seconds.
- 8.5.8 Once the canister passes the leak check open the valve of the canister
- 8.5.9 Click “start”
- 8.5.10 When “Dilution Finished” status message appears, close canister and disconnect
- 8.6 To dilute a prepared canister into a second canister
- 8.6.1 Load the correct configuration under settings tab
- 8.6.2 Select standards prep under the dilution tab
- 8.6.3 Enter canister ID, select canister volume 6L or 15L, enter target final PSIA (50)
- 8.6.4 Check Use box for diluent channel 1 and channel 6 for re-dilute
- 8.6.5 Change the target concentration (1ppbv calibration standard / 0.05ppbv MDL standard), see image #3
- 8.6.6 The maximum dilution factor is 100x

Image #3



- 8.7 To dilute a previously prepared canister, connect the previously prepared standard canister to channel 6 on the front of the 4700
- 8.7.1 Connect humidified canister to canister output on the 4700
- 8.7.2 Leak check. Open the valve on the canister to apply vacuum to the 4700 and then close the valve. Leak tight if 0.5psia/30 seconds.
- 8.7.3 Once the canister passes the leak check open the valve of the canister
- 8.7.4 Open previously prepared standard canister
- 8.7.5 Click start
- 8.7.6 When “dilution finished” status message appears, close canisters and disconnect them
- 8.8 Standards concentrations and dilutions and cylinders
- 8.8.1 Standards are ordered at a nominal concentration of 500 PPBV
- 8.8.1.1 Actual certified concentration value will differ from the 500 PPBV ordered
- 8.8.1.2 Dilution factors will have to be calculated for each cylinder to obtain the target final concentration of EtO for each canister prepared.
- 8.8.2 2 high pressure cylinders are used, a primary source, and a second source.

- 8.8.3 Two first dilution canisters are prepared at 5.0 PPBV from the high pressure gas cylinders, a primary canister and a second source (ICV) canister.
- 8.8.4 The two first dilution canisters are then diluted into additional canisters to obtain a 1.0 PPBV working standard for building the calibration curve and for second source (ICV) of the curve.
- 8.8.5 The first dilution canister of the primary source at 5.0 PPBV is diluted into an additional canister to obtain a 0.05 PPBV MDL level standard.

Table 8.8.5.1 Cylinder Standards and Canister Standards

EtO Standard Concentration (canister or cylinder)	Concentration	Target Final PSIA	Target Concentration	Dilution Factor	Final EtO Canister Concentration
Primary Source Cylinder 500 PPBV	500 PPBV	50.0	5.0 PPBV	100X	5.0 PPBV Primary Source Canister
Second Source Cylinder 500 PPBV	500 PPBV	50.0	5.0 PPBV	100X	5.0 PPBV Second Source Canister
Primary Source Canister	5.0 PPBV	50.0	1.0 PPBV	5X	1.0 PPBV Primary Source Canister
Second Source Canister	5.0 PPBV	50.0	1.0 PPBV	5X	1.0 PPBV Second Source Canister
Primary Source Canister	5.0 PPBV	50.0	0.05 PPBV	100X	0.05 PPBV MDL Canister

8.9 Calibration Curve

- 8.9.1 TO-15 method requires a minimum 5 point calibration curve, the GC/MS Laboratory currently uses a seven-point initial calibration curve, based on a 500ml sample size.
- 8.9.2 The calibration system uses NBS traceable standards or NBS/EPA CRMs in pressurized cylinder containing Ethylene Oxide at an ordered at a nominal concentration of 500 PPBV in nitrogen as working standards to be diluted with humid zero air. The actual concentration of the cylinder must be checked against the certificate of analysis.
- 8.9.3 A 7-point calibration is performed to determine the response factors for each compound.
- 8.9.4 The calibration curve consists of the calibration standards at concentrations of 0.1, 0.25, 0.5, 0.75, 1.0, 1.5, and 2.0 PPBV. The Entech Concentrator sequence table uses the Primary Calibration Volume size to trap the selected Primary Calibration Standard and inject it into the GC/MS for that particular point of the Curve.

Table 8.9.4.1 Calibration Curve				
Primary Cal. Std.	Prim. Cal. Volume	Method Sample Size	Dilution Factor	Final Conc. Std. of the Curve
1.0 PPBV STD	50 ml	500 ml	10X	0.1 PPBV
1.0 PPBV STD	125 ml	500 ml	4X	0.25 PPBV
1.0 PPBV STD	250 ml	500 ml	2X	0.5 PPBV
1.0 PPBV STD	375 ml	500 ml	1.333X	0.75 PPBV
1.0 PPBV STD	500 ml	500 ml	1X	1.0 PPBV
1.0 PPBV STD	750 ml	500 ml	0.666X	1.5 PPBV
1.0 PPBV STD	1000 ml	500 ml	0.5X	2.0 PPBV
Curve is based on sample size of 500ml				

8.9.5 These volumes are based upon a ratio of the normal volume taken for a sample (500 mL) and the concentration of the standard (1.0 PPBV). For example, to calculate the 0.5 PPBV calibration point: 500 ml to 250 ml is a 2X dilution factor. Therefore, 1.0 PPBV diluted 2 times is 0.5 PPBV.

8.9.6 A 50 PPBV internal standard/surrogate, high pressure cylinder, (Bromochloromethane, 1,4-Difluorobenzene, and Chlorobenzene-d5) and one surrogate (Bromofluorobenzene) is used in calibration, quality control, and sample analysis. The cylinder is purchased directly from a vendor and does not undergo any dilution, it is plumbed directly into the Entech concentrator into the Internal Standard Port located on the back of the concentrator.

Table 8.9.6.1 Internal Standards and Surrogate Standard					
Standard Name	Int Std Conc	Volume Injected	Method Sample Size	Dilution Factor	Final Concentration
Bromochloromethane	50 PPBV	100 ml	500 ml	5X	10 PPBV
Chlorobenzene-d5	50 PPBV	100 ml	500 ml	5X	10 PPBV
Bromofluorobenzene (Surrogate Std)	50 PPBV	100 ml	500 ml	5X	10 PPBV

8.9.7 100 ml of the 50 PPBV Internal Standard Cylinder is injected and based on a 500 ml sample size this is a 5X dilution, 50 PPBV divided by 5 results in a 10 PPBV concentration.

8.9.8 If a RRF with %RSD fit is used, the final calibration curve average relative response factor curve fit and should result in a $RRF \leq 30\%$ RSD for each analyte. Each level of the curve must be re-quanted with the new curve and each calibration level must be within $\pm 30\%$ of nominal value.

8.9.9 If a linear regression fit is used, linear or quadratic, the $r \geq 0.995$ for each analyte. Each level of the curve must be re-quanted with the new curve and each calibration level must be within $\pm 30\%$ of nominal value.

8.9.10 If a compound fails the %RSD, or $r \geq 0.995$, or $\pm 30\%$ of nominal value, then a new calibration curve must be created, if the new curve fails then the instrument/standards/canisters must be inspected for problems. If no identifiable problems can be determined, then the failing compound must be flagged on all field

samples.

- 8.9.11 A RRT form must be generated for the new calibration curve. The unit-less RRT value must be ± 0.06 for each target compound.
- 8.9.12 The Retention Time of each internal standard in the new calibration curve must be within ± 0.33 min of its mean initial calibration retention time.
- 8.9.13 The Internal Standard Area for each internal standard in each level of the curve must not deviate more than ± 40 % from the initial calibration curve area average for that internal standard.
- 8.9.14 The second source standard will be analyzed after the calibration curve. The recovery must be $\pm 30\%$ of nominal or RRF within $\pm 30\%$ RSD of mean ICAL RRF.
- 8.9.15 The paperwork from the curve data files is stored in file cabinets under specific ETO calibration curve headings. Paperwork contains the curve date built and the calibration curve printout with the resulting RRF and % RSD for each analyte, and the RRT form report and the Internal Standard Area Report.
- 8.10 Daily Calibration Verification
- 8.10.1 Prior to any 24-hour analysis period a daily continuing calibration verification must be performed.
- 8.10.2 This calibration analysis is a quality control measure to ensure integrity of the instrument's VOC retention time and quantitation parameters. This QC sample is a sample of 500 ml from the 1.0 PPBV standard canister which is a 1.0 PPBV standard.
- 8.10.3 The continuous calibration sample is quantitated and the target peaks reviewed. A continuing calibration report is generated, each target must recover 70-130% of the nominal spiked value if fit linear or quadratic, or the RRF must be within $\pm 30\%$ of the mean Initial Calibration RRF if curve fit using %RSD.
- 8.10.4 If a compound fails the ± 30 %RSD, or 70-130% of nominal value, then a new calibration curve must be created, if the new curve fails then the instrument/standards/canisters must be inspected for problems. If no identifiable problems can be determined, then the failing compound must be flagged on all field samples.
- 8.10.5 The Internal Standard Area must not deviate more than ± 40 % from the initial calibration curve area average.
- 8.10.6 All evaluation data files for the continuous calibration are printed and filed with the sample batch folder for that 24hr period sample analysis.

9 Quality Control

- 9.1 Refer to Appendix A for PQLs, Table 13.1 for Quality Control Acceptance Criteria, and Table 13.2 for Quality Control Procedures associated with this method.
- 9.2 A Method Detection Limit Study for all analytes must be performed initially, after major instrument repairs or changes to procedures. MDL studies performed for these purposes can be done by the analysis of 7 samples and 7 blanks over 3 separate days.
- 9.2.1 The 7 MDL samples study is performed by preparing 7 spiked canisters, MDLSpike, and are spiked below the lowest point of the curve. Also prepared are an additional 7 zero air clean blank canisters, MDLBlank. These sets of spiked and blank canisters are analyzed over a period of 3 separate days, there must be a non-analysis day between each of the 3 days. A total of 14 canisters are analyzed, 7 spiked and 7 blank. This is performed once a year.
- 9.2.2 Ethylene Oxide MDL must meet 10^{-6} ug/m³ cancer risk MDL MQO at 0.11ug/m³, See Table 9.2.3.1.

Table 9.2.3.1- NATTS 10-6 ug/m³ cancer risk MDL MQO				
Analyte	Cancer Risk 10⁻⁶ ug/m³	Noncancer Risk at HQ=1 ug/m³	MDL MQO ug/m³	MDL MQO PPBV
Ethylene Oxide	0.0002	-----	0.11	0.061*

*(ETO ug/m³ / 1.8037 = ETO PPBV)

- 9.2.3 The higher value of the 2 MDLs, either MDL_{Blank} or MDL_{Spike}, will be used as the reporting MDL.
- 9.2.4 If the MDL_{Spike} is used the following must be true for the MDL to be valid:
MDL < Spike Amount < 10 x MDL
- 9.3 Sample Analysis QC Batch: Method TO-15 requires additional QC samples that are analyzed. These include the Method Blank, LCS and LCSD, and a Replicate Analysis. These QC samples are run with every batch of field sample canisters, up to a maximum of 20 field samples per batch. The group of 20 samples and the QC samples analyzed within a 24hr analysis period are defined as a batch.
- 9.4 Method Blank: The Method Blank is a certified cleaned canister filled with zero air and is used as a quality control measure for the analysis process. It is used to check the analysis results and prove no laboratory contamination of the samples in the batch has occurred. The Method Blank is a canister cleaned over multiple cycles and analyzed on the instrument to be certified clean. Method Blank results must be ≤ 3x MDL for all analytes or <0.2ppbv, whichever is lower.
- 9.4.1 If a Method Blank is found to have detected compounds that exceed MDL criteria, the samples in the batch should be re-analyzed on a new batch. If it is not possible to have a Method Blank that meets criteria, then the Blank and associated sample(s) are assigned the <LB> qualifier in the Labworks qualifier field.
- 9.5 Laboratory Surrogates:
- 9.5.1 Laboratory Surrogates, are spiked into analytical sample during analysis.
- 9.5.2 Percent recoveries of the surrogate compounds must fall within acceptable limits of 80-120%.
- 9.5.3 Samples with failed surrogates are re-run to verify the failure. If it fails again a corrective action is initiated for the sample.
- 9.6 LCS and LCSD: (LCS) consisting of a cleaned canister spiked with 1.0 PPBV ETO target standards. In addition The Ga EPD Laboratory also analyzes a LCSD for each analytical batch as part of its Quality Assurance Program.
- 9.6.1 The percent recovery for the LCS must be within 70% to 130% of the nominal spike or RRF within ±30 %RSD from the mean of ICAL. For the additional LCSD analysis, the recovery of the LCSD must also be 70-130%, and the precision between the LCS and LCSD must be ≤25%RPD. All samples associated with an LCS compound that is out of control will require data qualifiers to be attached to the analytical results for that compound if re-analysis of the sample is not possible. If the LCSD fails recovery or precision, only a comment is required, no data qualifier is added.
- 9.7 Printouts of QC and Qualifiers
- 9.7.1 Printouts of the BFB pass criteria, the daily standard quantitation report, and the continuing calibration report of the daily standard are stored with the calibration curve. The 7-point curve percent relative standard deviation report is saved along with the 7 quantitation raw data reports of the 7 concentration levels.
- 9.7.2 The results of the batch are uploaded Labworks which performs calculations between the LCS and LCSD analysis, and sample and the duplicate. The required batch calculations

- 9.8 for the method for all QC and samples are processed and stored by the LIMS system. Null Code Qualifiers to be used for ETO samples, Null qualifier flags listed in the table below are applied to samples if warranted. During result entry, an appropriate null flag is entered in the “Result” field of the affected compound(s) as one of the two letter flags from the table below unless otherwise noted for a specific flag. **Only one null flag is to be applied to a given compound.**

Table 9.8.1 – NATTS Null Qualifier Flags	
Qualifier Flags	Description
AA	Sample pressure out of limits
AB	Technician unavailable
AC	Construction repairs in the area
AD	Shelter storm damage
AE	Shelter temperature out of specification
AF	Scheduled but not collected
AG	Sample time out of limits
AH	Sample flow rate out of limits
AI	Insufficient data to make calculation
AL	Voided by operator
AM	Miscellaneous void (comment required)
AN	Machine malfunction
AO	Bad weather
AP	Vandalism
AQ	Collection Error
AR	General lab error
AS	Poor quality assurance results
AT	Calibration
AU	Monitoring waived
AV	Power failure
AW	Wildfire damage
AX	Precision check performed
AY	QC Control points (Zero / Span)
AZ	QC audit
BA	Maintenance / routine repairs
BB	Unable to reach site
BC	Multipoint calibration
BD	Auto calibration
BE	Building site repair
BF	Precision, zero or span performed
BH	Interference / co-elution
BI	Lost or damaged in transit
BJ	Operator error
BK	Site computer/data logger down
MC	Module end cap missing
TS	Holding time or transport temperature is out of specs.

- 9.8.1 Quality Control and Detection Flags to be used for ETO results. If a Null qualifier from

the Null Qualifier Flags table above is entered, no Quality Control or Detection Flags are to be entered. If no Null flags are entered, up to six Quality Control or Detection Flags may be entered for a single ETO result.

- 9.8.2 Note: The Air data exporting routine automatically combines the “Result” and “Qualifier” fields for the purposes of uploading to the EPA reporting database.

Table 9.8.2.1 - Quality Control and Detection Flags, Laboratory Generated Flags, and Field Generated Flags	
Qualifier Flags	Description
SQ	Values between SQL and MDL
MD	Values less-than or equal to MDL
ND	No value detected*
FB	Field blank value above acceptable limit
LB	Lab blank value above acceptable limit
TB	Trip blank value above acceptable limit
LJ	Identification of analyte is acceptable; reported value is an estimate
LK	Analyte identified; reported value may be biased high
LL	Analyte identified; reported value may be biased low
EH	Estimated; exceeds upper range
1	MDL does not meet the requirements or ICAL recovery does not meet QC criteria
2	Operational Deviation
3	Field issue
V	Validated value
W	Flow rate average out of spec.
HT	Sample pick-up hold time exceeded; data questionable

**Note: The ND qualifier is technically a Null qualifier. “ND” is entered into the Labworks result field (which automatically is expanded to “Not Detected” by the LIMS) and the ND qualifier is entered into the qualifier field.*

9.9 NATTS Primary and Collocated (If Required by QAPP)

- 9.9.1 For the South Dekalb site, NATTS requires precision calculation between the Primary/Collocated sample and between the Collocated sample/Collocated replicate sample 6 times per year. The EPD Laboratory performs one set per month to make sure the 6 required are met if any fail due to field sampling problems.
- 9.9.2 Precision between the Primary and Collocated sample should be $\leq 25\%$ RPD for any detect $\geq 5 \times \text{MDL}$.
- 9.9.3 Precision between the Collocated sample and its Replicate sample must be $\leq 25\%$ RPD for any detect $\geq 5 \times \text{MDL}$.
- 9.9.4 Any QC failure is re-run on the instrument to verify the failure; a failure is flagged with the appropriate qualifier flag.
- 9.9.5 Precision results for Primary/Collocated samples are printed and scanned as a PDF and placed on the export drive “Q” for review by the Air Branch.
- 9.10 Replicate Samples (non-NATTS Samples)
- 9.10.1 In each field sample analysis sequence, a replicate of a field sample must be analyzed.

9.10.2 Precision between the sample and its replicate sample should be ≤ 25 %RPD for any detect $\geq 5 \times \text{MDL}$.

9.11 Retention Time

9.11.1 Initial calibration curve has RRT study for each Target and Surrogate compound and Internal Standard. Each Target Compound must be ± 0.06 RRT units of the mean of Initial Calibration RRT. Each Int Std must be within ± 0.33 minutes of mean of Initial Calibration RT.

9.11.2 For all samples in batch, the Int Std RT must be within ± 0.33 min of most recent CCV.

9.11.3 All target compounds have retention time windows set using Chemstation EnviroQuant software when building the calibration curve.

9.12 Sample Identification Number

9.12.1 When the canisters are hooked up to the canister cleaning instrument, each canister is logged in and assigned a LIMS number. This number is used for tracking the canister through the certified clean canister process, to the field, recorded on the COC, and used for laboratory ID when returned to the lab for analysis after sample collection, and for reporting results.

9.13 Target Compound Identification

9.13.1 Refer to Figure 9.13.1.1 for an example of the qualitative identification criteria listed for the discussion of section 9.13.2 – 9.13.4, followed by required **A,B,C,D** identification parameters of a target compound in a sample.

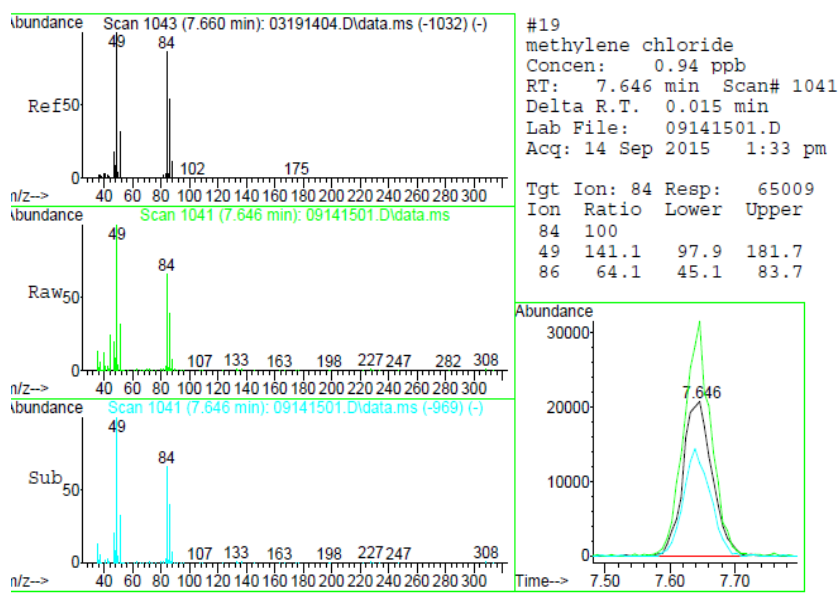
9.13.2 RT: Delta R.T. is within the retention time window defined by the method.

9.13.3 Ratios: the abundance ratios of the qualifier ions are within 30% of the ICAL average ratio: Fig. 9.18.2 “Ion” 49 and 86 have “Ratio” within “Lower” and “Upper” limits.

9.13.4 Signal-to-noise ratio: the large abundance Gaussian peak is shown to be greater than 5:1 (largest peak signal is well above noise levels at baseline just before peak begins)

9.13.5 Target and qualifier ion abundance peaks are co-maximized (largest peak and smaller peaks within the large peak so that all are within 1 scan of each other).

Figure 9.13.1.1



9.13.6 **A.** ---Signal to noise ratio of the target and qualifier ions $> 3:1$, preferable $> 5:1$

- 9.13.7 **B.** ---Target and qualifier ions co-maximized (peak apexes within 1 scan of each other)
- 9.13.8 **C.** ---RT of compound must be within acceptable RT from ICAL average
- 9.13.9 **D.** ---Abundance ratio of qualifier ion response to target ion response for at least 1 qualifier ion must be within $\pm 30\%$ of the average ratio from the ICAL.
- 9.13.10 If criteria **A-D** not met, compound is not positively identified.
- 9.13.11 An exception to **A-D** is allowed if experienced analyst opinion the compound is identified. Rationale must be documented on the instrument quantitation printed out paperwork.
- 9.14 Qualifiers are recorded in the qualifier field of result entry. The result and qualifier are automatically combined into the format during data export. Qualifiers for quantitation limit/detection limits are as follows:

Table 9.14.1 Qualifiers		
Target Concentration	Value to Report	Flag Applied
$\geq \text{SQL(PQL)}$	Value	None
$\geq \text{MDL} < \text{SQL(PQL)}$	Value	SQ
$< \text{MDL}$	Value	MD
Not Detected	0	ND

- 9.15 Every Sequence that analyzes field samples must include a Method Blank, and field replicate sample.
- 9.16 Control Charting for Trend Monitoring
- 9.16.1 Surrogate recovery, LCS and LCSDup Recovery, LCS/LCSDup Precision, Sample/Sample Duplicate Precision are charted annually for trend monitoring purposes. Limits are static, see Table 13.1.

Procedure

- 10.1 All sample canisters must be allowed to equilibrate to room temperature prior to sample preparation and/or analysis if brought in from outside extreme heat or cold.
- 10.2 When necessary, an Air (m/z 28 and 32) and Water (m/z 18) check can be performed to quickly diagnose possible mass spec problems.
- 10.2.1 Scan from 10 to 70 m/z , the ion mass of 18 (water), 28 (N_2), and 32 (O_2) should be in decreasing amounts, respectively. If an air leak is present, the ratio of m/z 28 to m/z 32 will be much larger than the water 18 m/z peak, m/z 44 is typically CO_2 .
- 10.3 Sample and QC data collection using the Entech and GC/MS
- 10.3.1 Connect sample and QC canisters to Entech autosampler rack.
- 10.3.2 Make sure the connections are secure and not over tight, keep the valves on the canisters closed.
- 10.3.3 A leak check must be performed to ensure the canister connection is leak free.
- 10.3.3.1 Click on the leak check in the sequence window.
- 10.3.3.2 The autosampler ports listed in the sequence will be checked automatically.
- 10.3.3.3 To perform a manual check first update to the port to be leak checked. Vacuum down to 1 psi and isolate, then check for ± 0.2 psi over 30 seconds.
- 10.3.3.4 When the auto leak check method is finished, a report will be printed to show if the autosampler ports pass the leak check of ± 0.2 psi over 30 seconds.
- 10.3.3.5 If any autosampler port did not pass the leak test, re-tighten the connections and re-

- run the leak check method for that port, or connect the canister to a different port.
- 10.3.4 Once the canisters pass the automatic leak check, open the valve of each canister.
- 10.3.5 Verify the sample amount and port numbers in the sequence; also verify the internal standard amounts to be added to each sample.
- 10.3.6 Save the sequence, use that day's numbers as the name: 180204 (2018, Feb, 4th).
- 10.3.7 Once the sample sequence is built click start.
- 10.3.8 The sequence begins on the line that is highlighted in the sequence, double check this.
- 10.3.9 The autosampler will perform the sample concentration and introduction process.
- 10.3.10 The progress of Entech controller can be monitored by selecting "view" from the control menu.
- 10.3.11 Changes to the sequence can be made during the post injection delay of any sample. Make sure after making changes that the highlighter is once again on the sample being run at present.
- 10.3.12 Sequence in Agilent GC/MS ChemStation,
- 10.3.13 This sequence must match exactly the sequence that was built using Entech since the HP is doing the data collection for the sample that the Entech is transferring over to the GC.
- 10.3.14 Simulate the sequence. If nothing is wrong, you are ready to run.
- 10.3.15 Start the GC/MS sequence on the same sample as the Entech sample and press "Run Sequence". The Entech will generate a start signal to the GC and the MS systems.
- 10.4 BFB
- 10.4.1 Running the GC/MS system for a calibration curve, continuous calibration verification, or for sample analysis cannot begin until the required BFB mass ion fractions and ion abundance criteria are met.
- 10.4.2 The Mass Spec software Chemstation has a BFB auto tune program that will tune the mass spec and automatically adjust the voltages in the ion source.
- 10.4.3 After the auto BFB tune program has completed, save the tune file to BFB.U.
- 10.4.4 The daily 24hr shift BFB tune check is accomplished by using the BFB in the method blank from the 100ml of internal standard mixture (50 PPBV/0.05 PPMV) from the internal standard cylinder.
- 10.4.5 The amount of Bromofluorobenzene in the traceable certified internal gas standard is injected at a volume of 100ml into the MS will be at the amount of 35.6 ng. See calculations below:

$$\text{Equation 10.4.5.1} \quad mg/m^3 = ppmv \left[\frac{M}{(.08205 \cdot T)} \right]$$

Where:

mg/m³ = milligrams of pollutant per cubic meter of air at sea level atmospheric pressure and T

ppmv = air pollutant concentration, in parts per million by volume

T = ambient temperature in K = 273. + °C

0.08205 = Universal gas constant in atm·m³/(kmol·K)

M = molecular mass (or molecular weight) of the air pollutant

m³ = 1,000 Liters

$$\text{Equation 10.4.5.2} \quad 0.356 \text{ mg/m}^3 = .05 \left[\frac{175}{(.08205 \cdot 299)} \right]$$

- 10.4.6 Conversion of BFB to units that meet injected amount required by TO-15 method

$$0.356 \text{ mg/m}^3 = 0.356 \text{ mg/1000L} = 0.000356 \text{ mg/L} = 0.356 \text{ } \mu\text{g/L} = 356 \text{ ng/L} = 35.6 \text{ ng/100ml}$$

10.4.7 BFB m/z ion fragmentation must meet criteria on Table 10.4.7.1

Table 10.4.7.1 Mass Spec Tune Criteria	
Mass	Ion Abundance Criteria
50	8.0 to 40.0 percent of m/e 95
75	30.0 to 66.0 percent of m/e 95
95	base peak, 100 percent relative abundance
96	5.0 to 9.0 percent of m/e 95
173	less than 2.0 percent of m/e 174
174	50.0 to 120.0 percent of m/e 95
175	4.0 to 9.0 percent of m/e 174
176	93.0 to 101.0 percent of m/e 174
177	5.0 to 9.0 percent of m/e 176

10.4.8 Print the passing tune criteria and file in batch folder.

10.4.9 If the BFB tune fails, attempt the BFB again. If it fails again attempt to re-tune the Mass Spec, this will mandate a new calibration curve. If the tune still fails then the Mass Spec ion source is dirty and the instrument must be red-tagged and the source cleaned.

10.5 Continuing Calibration Verification

10.5.1 After the BFB passes for any 24 hr. analysis period, a continuing calibration ETO standard at 1.0 PPBV must be run to evaluate the continuing calibration.

10.5.2 The continuous calibration sample is quantitated and the target peaks reviewed. A continuing calibration report is generated, each target must recover 70-130% of the nominal spiked value if the fit is linear or quadratic, if RRF is used it must be within 30% of the mean Initial Calibration RRF if fit using %RSD.

10.5.3 The same instrument data collection and analysis methods is used for the CCV as for the samples and all QC samples.

10.6 Method Blank

10.6.1 After the CCV, run 500 ml of Zero Air using the Blank Canister as the Method Blank.

10.6.2 The Method Blank must have all target VOC's < 3x MDL or < 0.2 PPBV (whichever is lower) for the system to be considered clean enough for analysis.

10.6.3 If the blank fails and the system is contaminated with target VOC's try to fix the problem by re-running another blank; bakeout the column; check for leaks in lines; run three consecutive blanks to clean out the instrument. If the blank is still contaminated, further inspection of the system is required and no samples should be run until a clean blank has been confirmed.

10.7 Sample Data Review using Agilent Chemstation EnviroQuant

10.7.1 All sample and QC target compounds must be reviewed and a detailed report on all 7 targeted compounds must be printed out after the review is completed.

10.7.2 Open QEdit (Quick Edit) to review the sample data, each target compound will be examined for peak shape and integration, retention time window, baseline noise, and most importantly comparison against a known mass spectrum for the instrument for that particular target compound.

- 10.7.3 After QEdit, print a detailed report of the sample, this will include a TIC and triple plots.
- 10.8 Target Compound Peak Identification for reporting into LIMS follows the procedures outlined in the Quality Control section of this SOP.
- 10.9 If the initial analysis of a sample has a higher concentration than the upper limit of the calibration curve the sample must be reanalyzed at a dilution so that the results will fall within the calibration curve.
- 10.10.1 For a dilution analysis, you can apply a multiplier to the Chemstation Report to perform the multiplication dilution factor automatically to all detected compounds.
- 10.11 All data results are entered into the laboratory LIMS network.
- 10.11.1 A copy of the detailed sample report is kept in a file folder batch QC and filed.
- 10.11.2 The data stored on disk is backed up periodically on a DVD.
- 10.11.3 Each sample should appear in the next screen with 'pending' by it. Use right side of mouse to load results for the test code '\$ETO'. Click 'Load results' and select the corresponding result file
- 10.11.4 Review and assure and double check that the analysis date and time and the reporting concentration numbers match your results in the printed out reviewed paperwork.
- 10.12 LIMS test codes for uploading results into Labworks

ETO Batch Test Codes

\$B_ETO (Method blank)

\$ETO (Sample results)

\$ETO-UGM3 (Sample results ug/m3)

\$D_ETO (Sample replicate analysis)

\$LDETO (LCS Duplicate)

\$LSETO (Daily LCS/CC Standard– 1.0 PPBV)

\$LAETO (amount of the Daily Standard spiked – 1.0 PPBV)

\$L2ETO (LCS Duplicate recovery)

\$LRETO (LCS recovery)

\$P_ETO (Precision sample and sample duplicate)

\$LPETO (Precision LCS and LCSDup)

VAL_AIR (Validation by GCMS Laboratory)

\$MLETO (MDL results)

\$MAETO (Amount used to spike the MDL canister)

INSTR-ETO (Instrument used to perform MDL analysis)

NATTS Primary/QA Collocated Samples

\$CollocatedQAETO (Collocated results)

\$XQETO (Precision between Primary and Collocated)

\$XXETO (Collocated Replicate results)

\$XPETO (Precision between Collocated and its Replicate)

ETO Certified Clean Canister Batch Test Codes

\$BETOC (QC Canister Results)

\$B_ETOC (Method Blank)

\$LDETOC (LCS Duplicate)

\$LSETOC (Daily LCS/CC Standard- 1.0 PPBV)

\$LAETOC (Amount of the Daily Standard spiked – 1.0 PPBV)

\$L2ETOC (LCS Duplicate recovery)

\$LRETOC (LCS recovery)
\$LPETOC (Precision LCS and LCSDup)
RCLNCAN(Validation Reviewed of QC Clean Canister Results)

- 10.13 Canister Cleaning
- 10.13.1 Start the system vacuum pumps, rough first, then the turbo pump.
- 10.13.2 Open all zero air gas supply valves on humidifiers and high pressure cylinders
- 10.13.2.1 If the zero air high pressure cylinder must be changed, be sure to close off the humidified air canister valves so that no water back flows into the lines and wets the hydrocarbon filter.
- 10.13.3 Attach the dirty cans to the manifold and tighten the connections. Hold the valves with your other hand or wrench when tightening so the valves do not twist.
- 10.13.4 Tightly cap off any unused manifold connections.
- 10.13.5 Remove all tags from the canisters.
- 10.13.6 DO NOT OPEN any of the valves until leak check is done.
- 10.13.7 Open the canister cleaner icon.
- 10.13.8 Running Leak Check on the System
- 10.13.9 Make sure all manifold connections are tight and the can valves are closed, press the Rough Pump button, this will open the manifold to the rough pump. After the pressure has dropped to below 1 psi, press the H.V. button, this will open the turbo pump to the manifold. The "mtorr" readings should begin to drop and go down to "0". For 3100D can cleaners "mtorr" readings should be less than "50".
- 10.13.9.1 If the pressure has dropped to "0" mtorr, the system is considered sealed by Entech and ready for canister cleaning. If the pressure in the system does not go down to "0", then re-check the canister connections and make sure all canister valves are closed.
- 10.13.10 The maximum temperature of the oven should be about 80° C.
- 10.13.11 Load and run the "Clean" program from the top, it will run 8+ cleaning cycles.
- 10.13.12 Press the rough pump button to start the rough pump.
- 10.13.13 Go to all the canisters and open the valves. The pressure will rise in the manifold, and the pump will make noise, press the 'GO' button, this will start the cleaning cycles.
- 10.13.14 When the cleaning cycle has ended, the vacuum should show 00 mtorr and the screen will display 'run complete'.
- 10.13.14.1 Close off 1 canister which will be the QC canister used for certification of the batch.
- 10.13.14.2 Press the 'all off' button, then press the 'diluent' button to allow zero air to fill the other 5 canisters until the pressure reaches 30 psia. When the 30 psia pressure is reached press the 'all off' button again, open QC canister for about 3 minutes to fill it using the other 5 canisters. Then close QC canister and evacuate the other 5 canisters back to "0" mtorr, hold at this vacuum for 5 minutes, then close the valves of the 5 canisters.
- 10.13.15 The QC canister is then analyzed on the instrument, all targets should be < 3x MDL or < 0.20 PPBV, whichever is lower, for a valid QC canister. If a target is detected the entire batch must be re-cleaned. If the Air Branch group cannot wait for re-cleaning of the canisters, then the canisters are released but the failing target compound will be flagged on the final report after the Air Branch group has returned the sampled canisters for analysis.

- 10.13.16 After the QC can has passed on the GC/MS analysis instrument, hook it back up to the manifold, perform a leak check, and evacuate it down to 00 mtorr and wait about 5 minutes then close the canister valve.
- 10.13.17 LOGIN of cleaned canisters
- 10.13.17.1 Make sure the Epson printer is selected as the default printer on your computer for the label printer to work at login.
- 10.13.17.2 In Labworks, choose multisample login.
- 10.13.17.3 An Excel type looking sheet will come up.
- 10.13.17.4 At the top will be the Source ID, DNR Lab Reference, Date Last Used, DNR Project, and Entry Point. Each of these fields must be filled in.
- 10.13.17.5 Listed below are the parameters used to fill in the rows for logging in the certified cleaned canisters.

Table 10.13.17.5.1 Canister Login LIMS Parameter	
Source ID	This will be "CANETO" for ETO canisters
DNR LAB Reference	This will be the Canister Number on the Canister
Date Last Used	This will be the cleaning date of the canister, entered as month/date/year
DNR Project	This will be "AIR"
Entry Point	Designate the canister(s) that are QCCAN(s)

- 10.13.17.6 After the canister information is filled in for all canisters, press the "LOGIN" button, and this will log them in. The labels should be printed out at the same time. (If they do not print-go under 'Modify', type the login numbers, press 'OK', then 'labels')
- 10.13.18 Batching the cleaned canisters of QC cans analysis after LOGIN by themselves (QC Canister run by itself on GC/MS instrument)
- 10.13.18.1 Open the QA/QC batch program in Labworks and select 'QA Batch', 'New Batch', then 'batch by sample'.
- 10.13.18.2 Type the previously generated Labworks Login numbers. Select 'Unbatched Pending' and 'completed', select "Find Samples", then 'ok'. Highlight Val_Air
- 10.13.18.3 At the next window should be the canisters you just logged in. Click the batch button off (the red check will disappear) and this should turn off all the buttons for the samples. Turn the batch button back on, then click on the buttons to the canisters that you want to batch together. Select O.K when prompted.
- 10.13.18.4 The next window is the result search, so press 'OK'
- 10.13.18.5 Remember to pick the QC canister as the one that was used for the certification of the batch, and add the analysis code to load the results:ETO--select #CNOETO
- 10.13.18.6 Be sure at this point to write down the name of the batch because it may be used to print out the worksheet for the QC login. Select "Print", "Newest Batch", and then scan and select report type "Cancert". The report is filed in the canister cleaning log sheet for that particular batch.
- 10.13.19 Batching the cleaned canisters of QC cans analyzed with sample canisters (QC Canister run with field samples on the GC/MS instrument)
- 10.13.19.1 Open the QA/QC batch program in Labworks and select 'QA Batch', 'New Batch', then 'batch by sample'.

- 10.13.19.2 Type the previously generated Labworks login numbers, plus the login number of the QC (duplicate field sample) run that day. Select 'Unbatched Pending', 'completed' and 'Pending-Batched', select "Find Samples", then 'ok'. Highlight 'Val_Air'
- 10.13.19.3 At the next window should be the canisters you just logged in. Click the batch button off (the red check will disappear) and this should turn off all the buttons for the samples. Turn the batch button back on, then click on the buttons to the canisters that you want to batch together. Select O.K when prompted.
- 10.13.19.4 The next window is the result search, so press 'OK'.
- 10.13.19.5 Remember to pick the QC canister as the one that was used for the certification of the batch, and add the analysis code to load the result ETO--select #CBAETO
- 10.13.19.6 Be sure at this point to write down the name of the batch because it may be used to print out the worksheet for the QC login. Select "Print", "Newest Batch", then scan and select report type "Cancert". The report is filed in the canister cleaning log sheet for that particular batch.
- 10.13.20 Paperwork for the QC Clean Can Batch
- 10.13.20.1 The QC Clean Can Batch page is printed in duplicate, one is placed in the batch clean logbook and the other goes into the GC/MS analysis batch folder.
- 10.13.20.2 The analyst's name and certification date are filled out in the logbook page.
- 10.14 Certified Cleaned Canister storage.
- 10.14.1 Take the QC can to be certified to the program analyst for analysis on the instrument. The remainder of the canisters are placed at the "to be certified" location until the QC canister is certified clean.
- 10.14.2 After the QC canister is certified clean and evacuated, the batch of tagged clean canisters are placed on the clean canister rack, with the newest cans being moved to the bottom, and the old ones placed on the top (to be used first).
- 10.14.3 On the clean field sampling ready rack, any canisters that are past the 30 day limit must be removed from the rack, and be re-cleaned and re-certified.
- 10.15 Canisters picked up by Field Sampling Personnel
- 10.15.1 Sampling personnel should call the lab 3 days before wanting to pick up canisters to be sure clean canisters are ready. The air analyst monitors the sampling dates throughout the year to be sure to have the number required for sampling for pickup in addition to 2 extra clean canisters as backup.
- 10.15.2 The oldest cleaning date canisters are removed from the canister ready tree and this cleaning date checked. This date is reviewed with the personnel to be sure that the sampling date will be within 30 days of this cleaning date.
- 10.15.3 The canister is then pressure checked to ensure it is still under a vacuum, between 28 and 30 inches Hg. If the gauge reads between 28 and 30 inches Hg, the canister can be released for use. If the vacuum is not less than 28 inches Hg, then the canister must be set aside for further investigation and cannot be used for sampling until the pressure problem is determined.
- 10.15.4 The canister pickup/shipping logbook is filled out with the canister LIMS number and the canister serial number. Also recorded is the person picking up the canister and to what sampling location it is going to.
- 10.15.5 Canisters for Mailing
- 10.15.6 Canisters are mailed to remote sampling sites 10 days before the sampling date by a contracted company. This allows for lost shipment or canister problems to be resolved before the sampling date passes. They are shipped second day air via UPS as this service offers package tracking in case they are lost. The cost of a

- lost canister and shipper more than makes up for this expense.
- 10.15.7 Canisters to be mailed are removed from the canister ready tree and the cleaning date checked. The cleaning date is compared to the sampling date being prepared for to be sure that this cleaning date will be within 30 days of the sampling date.
- 10.16 Canister Receipt back into the Lab and then GC/MS Department
- 10.16.1 Samples are logged in through the receiving department and are delivered to the GC/MS lab by receiving personnel.
- 10.16.2 Once accepted, the canister is logged into the Chain of Custody for Canisters book.
- 10.16.3 The sampling site, date received, and pressure are recorded in the appropriate columns adjacent to the corresponding canister number.
- 10.16.4 The pressure of the canister is measured with a certified gauge and is recorded on the chain of custody as well as in the shipping logbook.
- 10.17 Safety during Canister Cleaning
- 10.17.1 Heaters must be turned off when done
- 10.17.2 Do not leave the lab unattended with the heaters turned on. If the cycles are running overnight, the heaters must be turned off before the last person leaves.
- 10.17.3 Check the temperature after the heaters have been on about 10 minutes to make sure the cans are not above 80° C.
- 10.17.4 Do not forget to turn the heaters off when finished running.
- 10.17.5 Pumps must be turned off when done
- 10.17.6 The pumps get hot, do not touch them.
- 10.17.7 The turbo pump can overload if a problem develops, and the temperature light will go on and shut the pump off.

Calculations

11.1 Relative Response Factor (*RRF*)

Relative Response Factor: Calculate the relative response factors (*RRF*) for each target compound relative to the appropriate internal standard (i.e., standard with the nearest retention time) using the following equation:

$$\text{Equation 11.1.1 } RRF = \frac{A_x C_{is}}{A_{is} C_x}$$

Where:

RRF = Relative response factor

A_x = Area of the primary ion for the compound to be measured

A_{is} = Area of the primary ion for the internal standard

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

C_x = Concentration of the compound in the calibration standard, PPBV

NOTE: The equation above is valid under the condition that the volume (500 ul) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume of field and QC sample introduced into the trap is the same for each analysis. *C_{is}* and *C_x* must be in the same units.

11.2 Mean Relative Response Factor (\overline{RRF})

Mean Relative Response Factor: Calculate the mean RRF (\overline{RRF}) for each compound by averaging the values obtained at the five concentrations using the following equation:

Equation 11.2.1
$$\overline{RRF} = \sum_{i=1}^n \frac{x_i}{n}$$

where:

\overline{RRF} = Mean relative response factor

x_i = RRF of the compound

n = Number of values

- 11.3 Linearity through the origin is not assumed in a least squares fit. The instrument responses versus the concentration of the standards for the calibration points are evaluated using the instrument data analysis software. The regression will produce the slope and intercept terms for a linear equation. The regression calculation will regenerate a correlation, r , a measure of goodness of fit of the regression line to the data. A value of 1.0 is a perfect fit. An acceptable correlation of coefficient should be $r \geq 0.995$ (or $r^2 \geq 0.990$). See calculations 11.3.4.1

11.3.1 First Order Linear Regression Response Equation

$$Y = ax + b$$

This rearranges to:

$$x = Y - b/a$$

Where:

Y = Instrument response

a = Slope of the line

b = Intercept

x = Concentration in the extract or standard

- 11.4 Alternatively, second order quadratic fit may be used with an acceptable correlation of coefficient of $r \geq 0.995$ (or $r^2 \geq 0.990$). Note: quadratic fit will be calculated by chromatographic software. See calculation 11.3.5.1.

11.4.1 Second Order Quadratic Fit Equation

$$Y = ax^2 + bx + c$$

Where:

Y = Instrument response

a = Slope of the line

b = Intercept

c = constant

x = Concentration in the extract or standard

11.4.2 Subtract Y from c to get modified equation $0 = ax^2 + bx + c$

11.4.3 Solve for x using the quadratic formula:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

A positive and negative value will be generated. Use positive value.

11.5 Percent Relative Standard Deviation (%RSD)

Using the RRFs from the initial calibration, calculate the %RSD for all target compounds using the following equations:

$$\text{Equation 11.5.1} \quad \%RSD = \frac{SD_{RRF}}{RRF} \times 100$$

and

$$\text{Equation 11.5.2} \quad SD_{RRF} = \sqrt{\frac{\sum_{i=1}^n (RRF_i - \overline{RRF})^2}{n-1}}$$

where:

SD_{RRF} = Standard deviation of initial response factors (per compound)

RRF_i = Relative response factor at a concentration level

\overline{RRF} = Mean of initial relative response factors (per compound).

n = Number of values

11.6 Relative Retention Times (RRT)

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. Calculate the RRTs for each target compound over the initial calibration range using the following equation

$$\text{Equation 11.6.1} \quad RRT = \frac{RT_c}{RT_{IS}}$$

where:

Rt_c = Retention time of the target compound

RT_{IS} = Retention time of the internal standard.

11.7 Mean of the Relative Retention Times (\overline{RRT}):

Calculate the mean of the relative retention times (\overline{RRT}) for each analyte target compound over the initial calibration range using the following equation:

$$\text{Equation 11.7.1 } \overline{RRT} = \sum_{i=1}^n \frac{RRT}{n}$$

where:

\overline{RRT} = Mean relative retention time for the target compound for each initial calibration standard

RRT = Relative retention time for the target compound at each calibration level

n = Number of values

11.8 Tabulate the area response (Y) of the primary ion and the corresponding concentration for each compound and internal standard.11.9 Mean Area Response (\bar{Y}) for Internal Standard:

Calculate the mean area response (\bar{Y}) for each internal standard compound over the initial calibration range using the following equation:

$$\text{Equation 11.9.1 } \bar{Y} = \sum_{i=1}^n \frac{Y_i}{n}$$

where:

\bar{Y} = Mean area response

Y = Area response for the primary quantitation ion for the internal standard for each initial calibration standard.

11.10 Mean of the Retention Times (\overline{RT}) For Internal Standard:

Calculate the mean of the retention times (\overline{RT}) for each internal standard over the initial calibration range using the following equation:

$$\text{Equation 11.10.1 } \overline{RT} = \sum_{i=1}^n \frac{RT_i}{n}$$

where:

\overline{RT} = Mean retention time

RT = Retention time for the internal standard for each initial calibration standard.

n = Number of values

11.11 Percent Difference (%D):

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 using the following equation:

$$\text{Equation 11.11.1 } \%D = \frac{RRF_c - \overline{RRF_i}}{\overline{RRF_i}} \times 100$$

where:

RRF_c = RRF of the compound in the continuing calibration standard

$\overline{RRF_i}$ = Mean RRF of the compound in the most recent initial calibration.

11.12 Audit Accuracy

A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the relative difference between the measurement result and the nominal concentration of the audit compound:

$$\text{Audit Accuracy, \%} = \frac{\text{Spike Value} - \text{Observed Value}}{\text{Spike Value}} \times 100$$

11.13 Sample Concentration Calculation.

$$\text{Equation 11.13.1 } C_x = \frac{A_x C_{is} DF}{A_{is} RRF}$$

where:

C_x = Compound concentration, PPBV

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

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

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

RRF = Relative response factor from the analysis of the continuing calibration standard or the mid level standard of the initial calibration

DF = Dilution factor calculated as described in section 2. If no dilution is performed, $DF = 1$

NOTE: The equation above is valid under the condition that the volume (500 µl) of internal standard spiking mixture added in all field and QC analyses is the same from run to run, and that the volume (500 cm³) of field and QC sample introduced into the trap is the same for each analysis.

11.14 Dilution of samples

11.14.1 If a sample has a higher concentration than that of the calibration curve limit, a dilution must be done. For a dilution analysis, you must multiply the initial concentration by the dilution factor that will fall within the calibration curve. Here is an example : a 500 ml sample analyzed and a peak of 250 PPBV was recorded. You wish to dilute the sample within the 20 PPBV range the calculation is :

$$(250 \text{ PPBV}/500 \text{ ml}) \times Y = 10 \text{ PPBV}$$

$$Y = 10 \text{ PPBV} \times (500 \text{ ml}/250 \text{ PPBV})$$

$$Y = 20 \text{ ml of sample}$$

12 References

- 12.1 Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air. Center for Environmental Research Information office of Research and Development U.S. Environmental Protection Agency. Cincinnati, OH 45268, January 1999, EPA/625/R-96/010b.
- 12.2 Technical Assistance Document for the National Air Toxics Trends Stations Program, Rev. 3, October 2016 or later.
- 12.3 National Air Toxics Trends Station Work Plan, March 2015 or later.
- 12.4 GA EPD Laboratory SOPs – Initial Demonstration of Capability SOP 6-001, online revision and Continuing Demonstration of Capability SOP 6-002, online revision.
- 12.5 GA EPD Laboratory SOP – EPD Laboratory Waste Management SOP, SOP 6-015, online revision.
- 12.6 GA EPD Laboratory SOP – Determination of Method Detection Limit, SOP 6-007, online revision.
- 12.7 GA EPD Laboratory SOP – EPD Laboratory Procedures for Control Charting and Control Limits, SOP 6-025, online revision.
- 12.8 GA EPD Laboratory Quality Assurance Plan, online revision.
- 12.9 GA EPD Laboratory Safety/Chemical Hygiene Plan & Fire Safety Plan, online revision.

13 Reporting Limits (RLs) (See Appendix A), Precision and Accuracy Criteria, and Quality Control Approach

Table 13.1 Acceptance Criteria for Method EPA ETO

Method	Analyte	Accuracy (%R)	Precision (RPD)
EPA TO-15	Ethylene Oxide	70-130	<25

Table 13.2 Summary of Calibration and QC Procedures for Method EPA TO-15

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
TO-15	Volatile Organics ETO	Seven-point initial calibration for all analytes (5 point minimum)	Initial calibration prior to sample analysis	%RSD for all calibration analytes $\leq 30\%$ If fit is Linear or Quadratic the Coef of Det (R) ≥ 0.995 . Requant each level, must be $\pm 30\%$ of nominal	Correct problem then repeat initial calibration	

Table 13.2 Summary of Calibration and QC Procedures for Method EPA TO-15

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
TO-15	Volatile Organics ETO	Calibration verification	Daily, before sample analysis, every 24 hours of analysis time	RRF must be $\pm 30\%$ RSD of mean of ICAL RRF Linear fit must be in $\pm 30\%$ of nominal value. If fail high and not detected in batch do CA. If CCV fails low, re-run CCV.	Correct problem then repeat initial calibration	
		Initial Demonstration: Demonstrate ability to generate acceptable accuracy and precision using four replicate analyzes of a QC check sample	Twice/year per analyst	QC acceptance criteria, Table 2	Recalculate results; locate and fix problem with system and then rerun demonstration for those analytes that did not meet criteria	
		Check of mass spectral ion intensities using BFB	Prior to initial calibration and calibration verification	Refer to criteria listed in the method description	Retune instrument and verify	
		Int Std QC for Blanks and Daily QC and Samples	Immediately after or during data acquisition of calibration check standard	Intl Std area each level of ICAL $\pm 40\%$ of ICAL int std area mean average. Int Std each sample $\pm 40\%$ of ICAL int std area mean average.	Inspect mass spectrometry or GC for malfunctions; mandatory reanalysis of samples analyzed while system was malfunctioning	
		Method Blank	One per analytical batch	No analytes detected $>3 \times \text{MDL}$ or $>0.2 \text{ ppbv}$, (whichever is lower)	Ensure no contamination then reanalyze method blank and all samples processed with the contaminated blank	Any detects are flagged per NATTS guidelines. Any target compound in the blank will also be flagged with LB in any sample in the batch.
		LCS/LCSD for all analytes	One LCS/LCSD per analytical batch	QC acceptance criteria Table 13.1	Inspect mass spectrometry or GC for malfunctions, rerun LCS/LCSDup	Flag if LCS fails recovery Do not flag if LCSDup recovery or LCS/LCSDup precision fails.
		Surrogate spike	Every sample, spiked sample, standard, and method blank	Recovery must be from 80%-120%		
		MDL study	Minimum is once per year or after major instrument or method modification	The MDL for Tier 1 compounds must be below TAD cancer levels, MDL must be less than MDL spike level, $10 \times \text{MDL}$ must be greater than spike level.	Check calculation, redo MDL analysis and redo results, prepare higher or lower conc, as needed.	
		Estimated amount for analytes above the 7-pt calibration curve	None	All analytes $< 2.0 \text{ ppbv}$.	Sample must be diluted and reanalyzed.	Apply "EH" to all analytes out of range that cannot be diluted.

Table 13.2 Summary of Calibration and QC Procedures for Method EPA TO-15

Method	Applicable Parameter	QC Check	Minimum Frequency	Acceptance Criteria	Corrective Action	Flagging Criteria
		Precision between sample and sample replicate, or Primary and Collocated	One per analytical batch	≤ 25 RPD if amount detected ≥ 5 xMDL	Noted in comment field and correction action logbook which analyte failed precision QC	
		QC can for certifying cleaning batch	One per cleaning batch	No analytes > 3 xMDL or > 0.2 ppbv (whichever is greater)	Re-clean the entire canister cleaning batch or flag sampled canisters on final report if re-cleaning was not possible.	Flag final report for any detect > 0.20 PPBV found in all canisters in cleaning batch with "CC" for clean canister residue

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**Appendix A - Practical Quantitation Limits (PQLs) for Ethylene Oxide by EPA Method
TO-15 GC/MS Detection**

Table A.1 RLs for Method Ethylene Oxide				
Parameter/Method	Analyte	MDL	Matrix (AIR)	
			RL	Unit
Ethylene Oxide/ TO15	Ethylene Oxide	0.016	0.051	ppbv

MDL data collected 12/18/20-12/23/20

Reporting Limits = 3.18 x MDL

Updates:

Updated for online revision. Appendix A and ICN to SOP Rev. 0 added.

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