Determination of Ethylene Oxide at Ultra-trace Concentrations in Ambient Air Using EPA Method TO-15A: Laboratory Experiments to Inform Development of a Guidance Document

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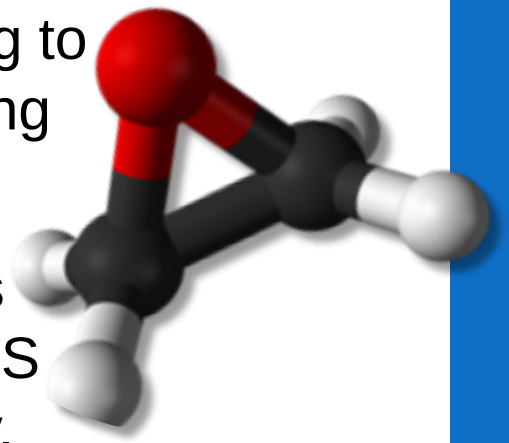
Development of Guidance Document for Ethylene Oxide Using Method TO-15A

Challenge: Determine ethylene oxide (EtO) at ultra-trace levels in ambient air using specially prepared canisters.

Approach: Adhere to Method TO-15A (from canister cleaning to preconcentration to GC-MS analysis) with the goal of achieving method detection limits (MDLs) below 10 pptv for EtO.



Results: Developed a robust analytical method that achieves preliminary MDLs of 4–23 pptv for EtO on two different GC-MS systems. Method Update Rule MDL determined to be 12 pptv.

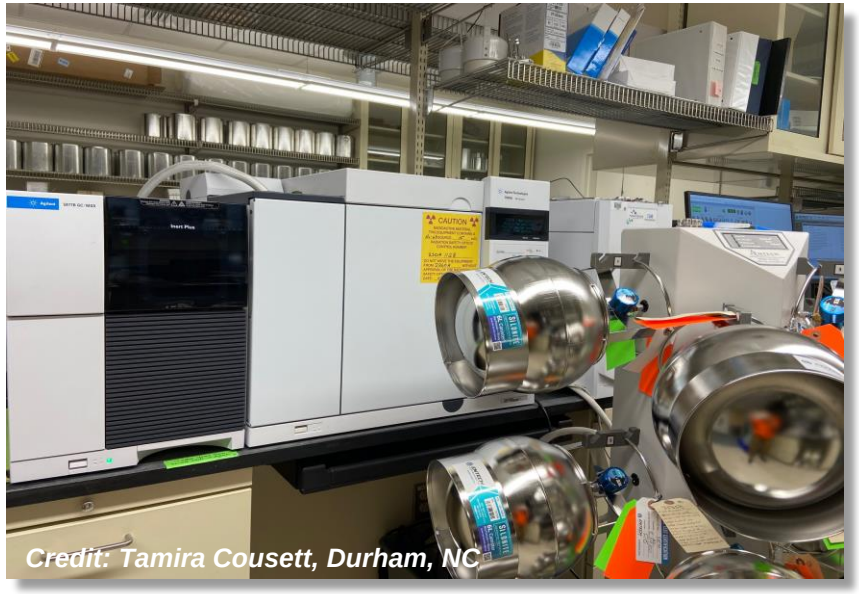
Impact: Use Method TO-15A guidelines and best practices plus lessons learned to develop EtO guidance document that ensures high-quality data for ambient air samples, even at ultra-trace concentrations.

Previous Research Efforts Presented at Air and Waste Management Conference

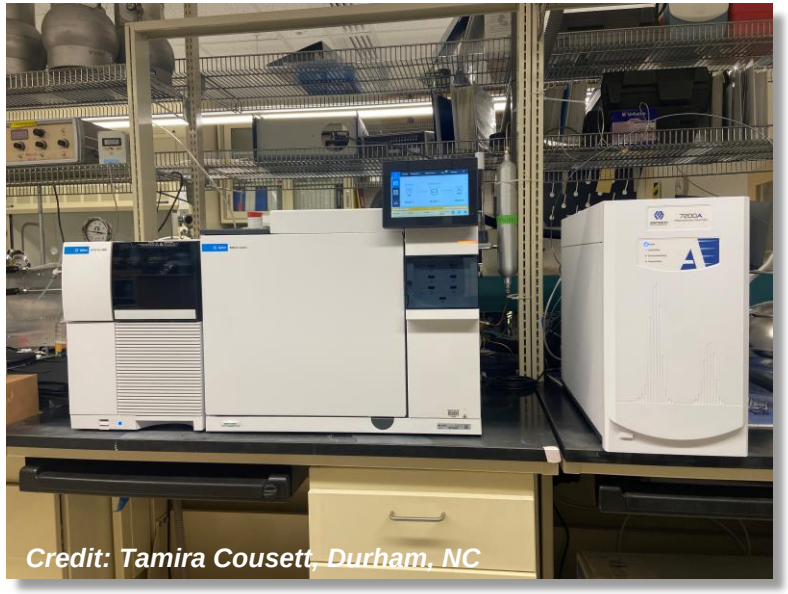
November 2023

(https://www.epa.gov/system/files/documents/2024-05/awma-presentation-final-nov-2023_508.pdf)

Current Analytical Instrumentation



GC: Agilent 7890A
MS: Agilent 5977B/Turbopump
Source: Inert Plus Extractor
Preconcentrator: Refurbished Entech 7200



GC: Agilent 8890
MS: Agilent 5977C/Diffusion Pump
Source: Inert Plus Extractor
Preconcentrator: Entech 7200A

Optimized Analytical Method

MS Analytical Method

Parameter	Specifications
Column*	Rxi-624Sil MS 60-m x 0.25-mm ID x 1.4-µm GC column
Source/quad	230 °C/150 °C
Drawout plate	6 mm
Tune	Atune 5977B/Etune 5977C
Acquisition	SIM, low resolution
Gain	Atune Gain 10/Etune Gain 1
Column flow	1.5 mL/min

GC Oven Program

	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	-20	3
Ramp 1	1.5	1	0
Ramp 2	18	150	0
Ramp 3	12	240	3
Post-bake		180	18

*Alternate column in use is VF-624ms.
Modified Entech 7200A preconcentrator settings specified in Entech Application Note A-3742-01 to hybrid mode.

Recent Research Efforts

Credit: Karen Oliver, Durham, NC

Credit: Tamira Cousett, Durham, NC

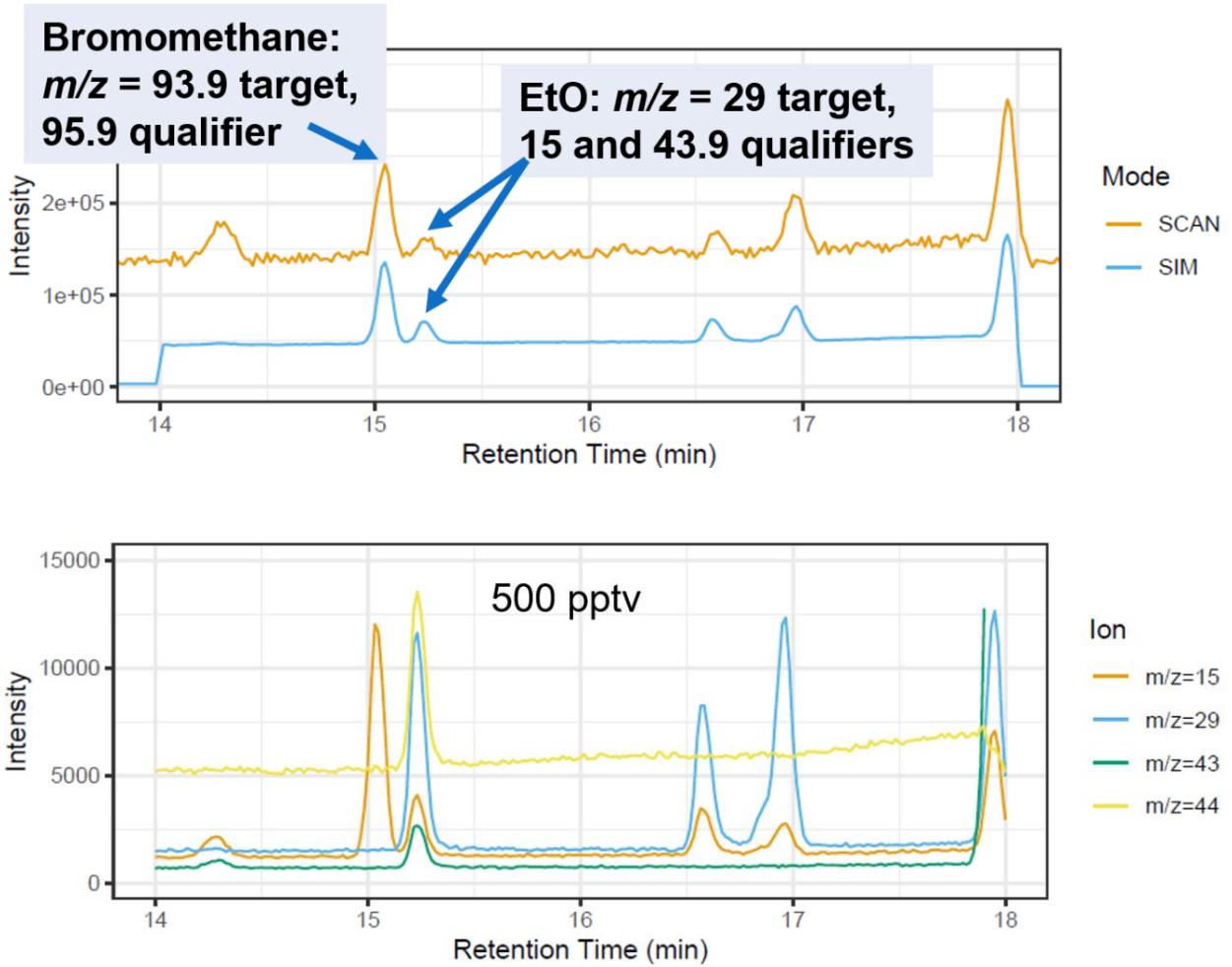
Evaluated Canister Cleaning Cycles

Pre-evacuation: Four cycles of ultra-zero air to 15 psig, room temp

Canister cleaning:

- Research-grade nitrogen
- High humidity – 95% RH
- Heating to 85 °C
- 2-h cycles in sequence
- High-vacuum finish – <20 mTorr at end of each 2-h cycle
- 4 h vs 24 h – comparable results

Verified No Coelutions
(139 Component VOC Mix)



Note: Results from 7890A GC–5977B MSD using VF-624ms column.

Canister Validation Studies

Canister Selection

- Current effort – silicon-ceramic coated canisters
- Canisters in use generally have only been exposed to low concentrations of VOCs, either standards ≤1500 pptv or ambient air, over their lifetime
- On rare occasions some canister standards were prepared at ~10 ppbv during the research effort
- Canisters are approximately 4 years old and have only been used in this current research effort

Canister Validation Studies
(continued)

Zero-Air Challenge*

Example Compounds	Concentration (pptv)
Chloromethane	<7
1,3,-Butadiene	0
Ethylene oxide	0
Benzene	<11
Toluene	<5
m,p-Xylene	<5
1,2,4-Trichlorobenzene	<22

*Ultra-zero air samples prepared using 4700 static diluter, 50% RH, 25 psia, n = 32.
Samples were analyzed on days 1, 7, 14, and 21; sample volume 250 cc.
EPA Method TO-15A criteria (Table 10.3) for 25 psia canisters: ≤12 pptv.

Canister Validation Studies
(continued)

Brought Dynamic Diluter into Operation

Diluter	EtO Mean (pptv)	Standard Deviation (pptv)	Preconcentrator Sample Volume (cc)
4700 (Static)/Can 35356*	54	3	25
4600 (Dynamic)/Can 37576*	56	6	250

*n = 8 for each canister, analyzed on 5977C system.
Samples prepared using ultra-zero air diluent gas with source gas concentration ranges of 50–100 ppb.

Canister Validation Studies
(continued)

Known Standard Challenge – 150 pptv EtO

- Samples prepared using 4600 dynamic diluter and ultra-zero air diluent gas with EtO source gas concentration of 50 ppb; 50% RH, 25 psia
- Tested 16 cans (8 old, 8 new) at 150 pptv
- Samples were analyzed on days 0, 7, and 21 on 5977B system; sample volume 250 cc
- Between days 0 and 7, average recovery was 100% with a range of 89% to 110% (i.e., ±10%)
- Between days 0 and 21, average recovery was 100% with a range of 75% to 125% (i.e., ±25%)
- Meets EPA Method TO-15A criteria: ±30%

Tentative MDLs

Analyzed using 5977C System with Etune Gain 1

Calibration Date	MDL* (pptv)
01/24/2024	6
02/26/2024	8
03/12/2024	4
04/03/2024	23
04/10/2024	14
05/11/2024	13
06/11/2024	8
06/25/2024	11

Analyzed using 5977B System with Atune Gain 10

Calibration Date	MDL* (pptv)
01/23/2024	11
02/26/2024	11
03/11/2024	15
04/17/2024	8
05/23/2024	7
06/24/2024	11

*Tentative MDL: 40 CFR, Part 136, Appendix B, 1984 – “best case” using 7 replicates.

Method Update Rule MDL – Background

- Code of Federal Regulations (U.S. EPA, 2017; 40 CFR, Part 136, Appendix B)
- National Air Toxics Trends Stations (NATTS) Technical Assistance Document (TAD) – 2016, Photochemical Assessment Monitoring Stations (PAMS) TAD – 2019, Method TO-15A – 2019
- Accounts for the following per Method TO-15A Section 17.1:
  - Background contaminants present in the canisters
  - Contaminants introduced during canister handling, preparation, and analysis
  - Observed method variability across instruments, operators, and time

Method Update Rule MDL – Process

Method TO-15A Section 17 Procedure

- 14 separate canisters:
  - 7 spiked with humidified zero air
  - 7 spiked with 50 pptv EtO
- Prepared in 3 separate batches on 3 separate days
- Analyzed on 3 separate days
- Method Update Rule MDL is the higher of the MDLs calculated from method blanks (MDL_b) and known-standard spike samples (MDL_{sp})

Method Update Rule MDL – Blanks

- Entech 4600 dynamic diluter - sample preparation using ultra-zero air, 50% RH, 25 psia fill pressure
- 250 cc sampling volume from humidified air sample canisters
- MDL_b does not apply based on seven humidified zero air cans having no detectable EtO

Can #	35014	35357	35359	38042	38076	37998	34996
Batch	1	1	1	2	2	3	3
Measured (pptv)	ND*	ND	ND	ND	ND	ND	ND

*Not detected.

Method Update Rule MDL – Spikes

- Entech 4600 dynamic diluter – sample preparation using ultra-zero air diluent gas to fill 50 pptv EtO-spiked canisters at 50% RH and 25 psia
- 250 cc sampling volume
- MDL_{sp} is 12 pptv based on seven spiked EtO cans with 52 pptv mean and 4 standard deviation
- Method Update Rule MDL is 12 pptv

Can #	37790	37918	38090	38042	38076	37551	37937
Batch	1	1	1	2	2	3	3
Measured (pptv)	49	53	57	57	46	51	50

NATTS 2024 Quarter 1 Proficiency Test Results for EtO*

Our Lab Reported Value (ppbv)	OAQPS†/Battelle Nominal Spike Value		Mean of Participating NATTS Laboratories	
	(ppbv)	% difference	(ppbv)	% difference
5977C system:				
0.224	0.19	17.90	0.16	40.00
5977B system (ancillary results not reported to NATTS):				
0.170	0.19	10.50	0.16	6.25

†Office of Air Quality Planning and Standards.
*TO-15A ±30% criteria; other than EtO, all NATTS compounds reported by our lab were in the range -9.1 to 9.0 % difference from mean of participating NATTS laboratories.

Ambient Samples – Precision

Credit: Tamira Cousett, Durham, NC

Metric	RPD (7 Paired Samples)
Collocated precision*	0.2–21.5%
Replicate precision*	0.1–24.3%

*Relative percent difference (RPD) = absolute value of (diff/mean)*100 per TO-15A; TO-15A specifies ≤ to 25%.

Ambient Samples – Day 1 and Day 7 Comparison

Mean concentration of EtO and carbon tetrachloride (CCl_4) in collocated ambient samples, n = 6 (two canisters each analyzed three times)

5977B system analysis of grab samples in backyard at Chapel Hill, NC, residence (previous slide photo) collected May 2024

Analysis	EtO (pptv)	EtO Standard Deviation (pptv)	CCl_4 (pptv)	CCl_4 Standard Deviation (pptv)
Day 1	42	3	66	1
Day 7	43	4	66	1

Ambient Samples – Day 1 and Day 7 Comparison

Mean concentration of EtO and CCl4 in collocated ambient samples, n = 6 (two canisters each analyzed three times)

5977B system analysis of grab samples at Cedar Falls Park, Chapel Hill, NC, collected May 2024

Analysis	EtO (pptv)	EtO Standard Deviation (pptv)	CCl_4 (pptv)	CCl_4 Standard Deviation (pptv)
Day 1	60	6	66	1
Day 7	58	4	65	0

EtO Background in Ambient Air April/May 2024 Grab Samples

Location*	System	EtO Concentration (pptv)	Standard Deviation (pptv)
Emerald Isle, NC	5977C	22	2
EPA RTP, NC, Discovery Lake	5977C	61	2
Chapel Hill, NC, Backyard (April)	5977B	31	4
Chapel Hill, NC, Cedar Falls Park	5977B	60	6
Chapel Hill, NC, Backyard (May)	5977B	42	3
Olympia, WA, Backyard	5977C	25	2
Olympia, WA, State Capitol Park	5977C	33	4

*n = 6, two canisters per site analyzed three times each except Olympia where n = 4, two canisters per site analyzed two times each.

Summary of Research Results

- Canister cleaning 4 h vs 24 h comparable for TO-14A VOCs plus EtO
- No coelutions for EtO in 139-component VOC mix
- TO-15A criteria met:
  - Zero-air challenge of canisters
  - Known standard challenge of canisters
  - Replicate/collocated precision for ambient grab samples
- Ambient air background of EtO – 22 to 61 pptv
- Day 1 and Day 7 analyses of EtO in canisters compare well (*limited measurements were made*)
- Tentative MDLs of 4–23 pptv (*used to guide method optimization*)
- Method Update Rule MDL is 12 pptv

Guidance Document Timeline

- EPA ORD guidance document on schedule for completion in September 2024
- EPA OAQPS will coordinate external review and posting of document
- Canister cleaning experiments with additional canisters will continue this fall and will be reported in approximately 6 months

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