Determination of Ethylene Oxide at Ultra Trace Concentrations in Ambient Air Using EPA Method TO-15A: Optimization of VOC Preconcentrator and GC-MS Analytical Method Parameters

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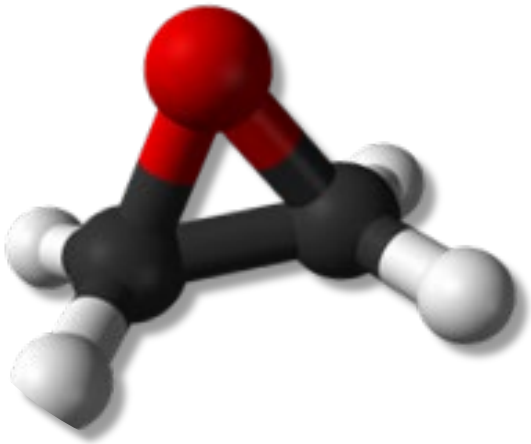
Ethylene Oxide – An EPA Priority for Air

- EPA updated IRIS assessment for ethylene oxide (EtO) in December 2016
  - Cancer risk value is now ~60x higher than previous estimate
  - Based on lifetime inhalation unit risk estimate, 100-in-million cancer risk is 11 pptv
- EtO is a hazardous air pollutant of concern for communities near sources, including communities with environmental justice concerns
- ORD and Office of Air and Radiation developing methods and guidance for monitoring
- Our team evaluating measurement using EPA Method TO-15A

EtO Analytical Challenges

- IRIS value necessitates ultra-low method detection limit (MDL) of ~10 pptv
- National Air Toxics Trends Stations (NATTS) Technical Assistance Document (TAD):
  - EtO vendor gas standards instability
  - Some cleaned canisters may exhibit growth or contamination
  - Difficulty quantitating due to coelutions and instrument sensitivity



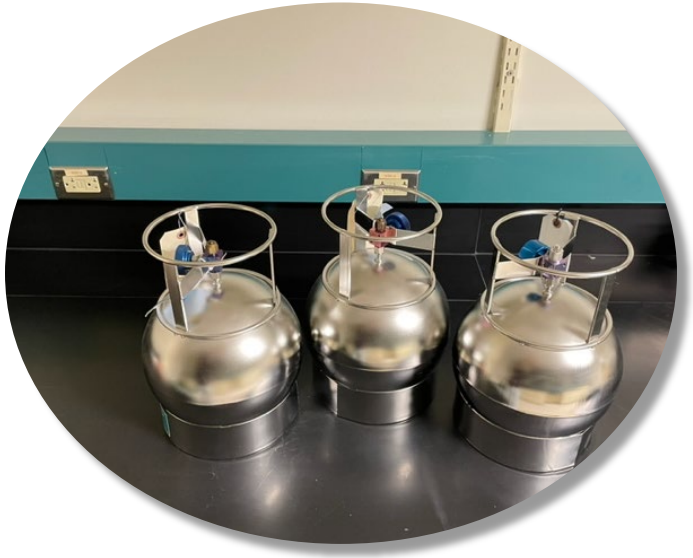
https://www.epa.gov/system/files/documents/2022-08/NATTS-TAD-Revision-4-Final-July-2022-508.pdf

Research Plan

- Evaluating state-of-the-art volatile organic compound (VOC) preconcentrator GC-MS systems
- Evaluating silico-ceramic lined canisters
- Optimizing settings to achieve robust measurements of EtO at low-pptv levels – cleanliness target for TO-15 of 200 pptv reduced to 20 pptv for TO-15A (our target EtO MDL is even lower)

Canister Cleaning

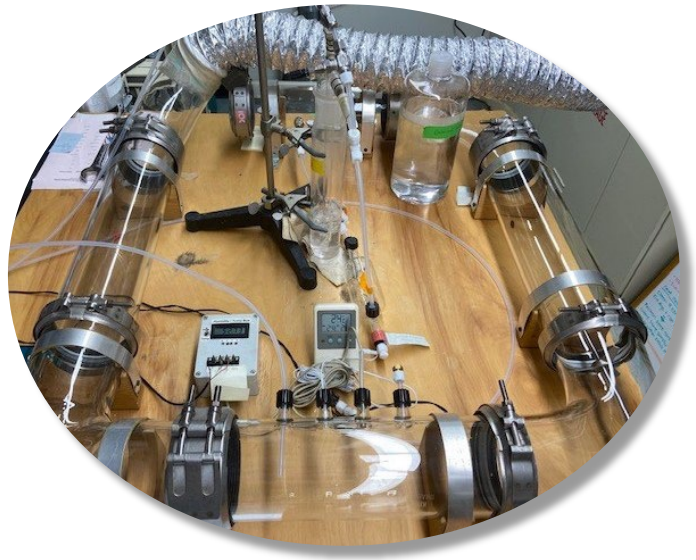
- Precleaning step with four fill/evacuation cycles using ultra-zero air and rough pump
- Xontech/Xonteck Model 960 systems
  - 4 hours total cycle time currently, may be modified
  - Research-grade nitrogen for fill gas
  - Fill gas humidified to 95% RH
  - Canisters heated to ~85 °F
  - Final high-vacuum finish (8 microns Hg)



Standards Preparation

- **Entech 4700 Static Diluter**
  - Lower-concentration cylinder standards (<1 ppm) minimize serial dilutions
  - 100 ppb TO-14/50 ppb EtO
  - 100 ppb 4-component internal standard

- **Exposure Chamber**
  - Canister-free approach to calibration



A Tale of Two Systems – “System 1”

Preconcentrator: Entech 7200A

GC: Agilent 8890

MS: 5977B Turbo EI

Source: Inert Plus Extractor

System 1 – Background Information

- Chosen to meet the low-pptv MDL and cleanliness requirements of Method TO-15A—and specifically as applicable for EtO
- Sensitive, inert, reasonably priced system
  - Preconcentrator introduced in 2020 offers improvements in both water management and system cleanliness compared to legacy 7200
  - Inert Plus MSD with extractor source offers better sensitivity and inertness than our aging Agilent systems

System 1 - Initial Method

Analytical Method

Parameter	Specifications
Column	DB1 30-m x 0.25-mm ID x 0.50-µm column
Source/quad	350°C/200°C
Draw-out plate	3 mm
Tune	Etune (10x sensitivity)
Acquisition	Selected ion monitoring (SIM), low resolution
Gain	10 (tested multiple settings)
Column flow	0.6 mL/min

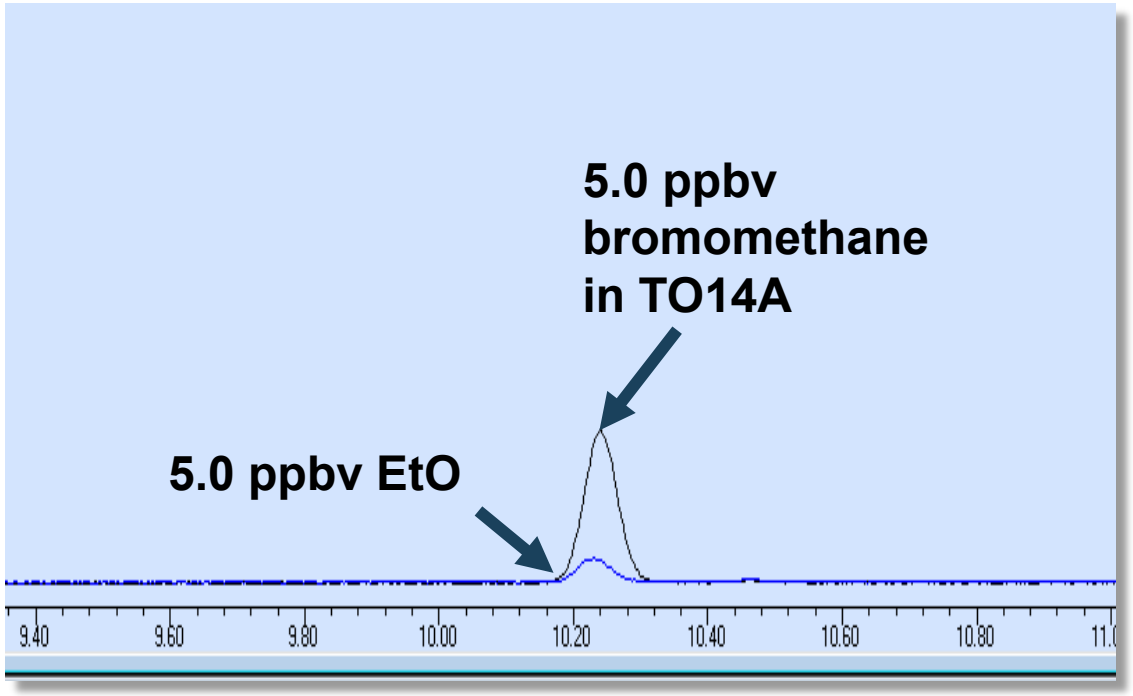
8890 GC Oven Program

	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	35	3
Ramp 1	20	80	0
Ramp 2	25	160	0
Ramp 3	40	250	1
Ramp 4	50	180	4
Post bake		35	0

Entech 7200A Preconcentrator settings specified in Entech Application Note A-3742-01

System 1 – Initial Method (cont.)

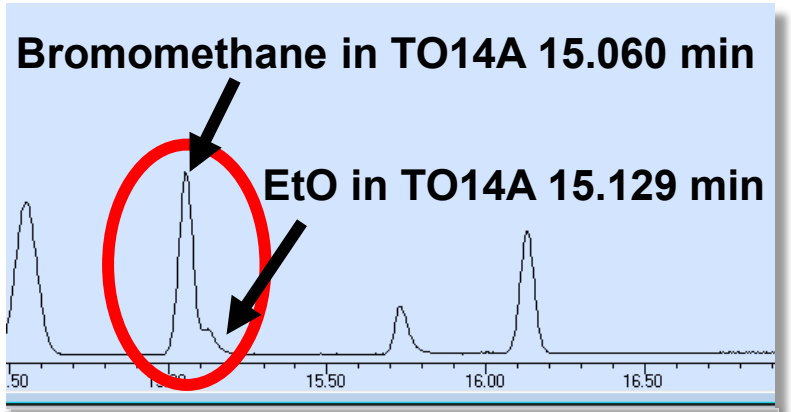
- Literature reviews/technical discussions
- Not sufficient
  - 80 pptv MDL* for EtO
  - Separation of coeluting compounds not achieved
  - GC oven program 16.35 min
- Further evaluated 12 analytical methods to reach our intermediate method



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

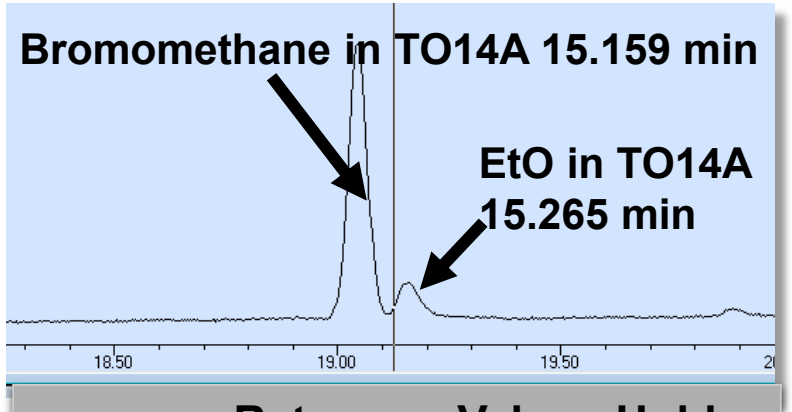
System 1 – Method Refinement Highlights

10 ppbv TO14/EtO Blend



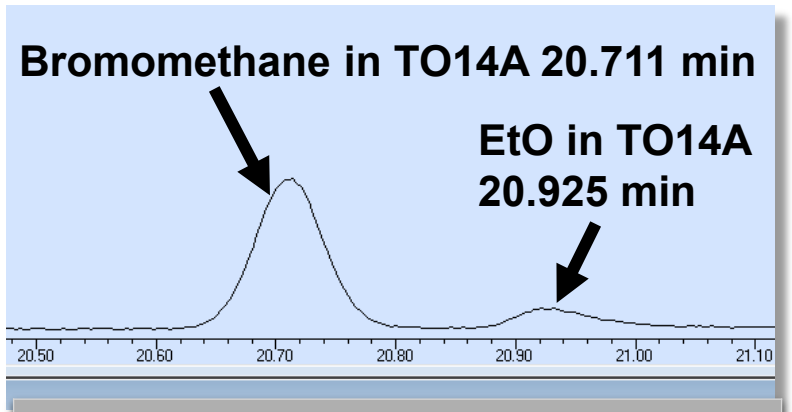
3/31/22	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	-30	5
Ramp 1	5	130	0
Ramp 2	20	220	3

5 ppbv TO14/EtO Blend



4/12/22	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	-30	2
Ramp 1	3	69	0
Ramp 2	4	141	0
Ramp 3	40	240	3.52

5 ppbv TO14/EtO Blend



4/12/22	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	-50	2
Ramp 1	3	69	0
Ramp 2	4	141	0
Ramp 3	40	240	3.52

System 1 – Intermediate Method

Analytical Method

Parameter	Specifications
Column	Rxi-624Sil MS 60-m x 0.25-mm ID x 1.4-µm GC column
Source/quad	300°C/180°C
Draw-out plate	3 mm
Tune	Etune (10x sensitivity)
Acquisition	SIM, low resolution
Gain	10/25; time segmented gain
Column flow	1.5 mL/min

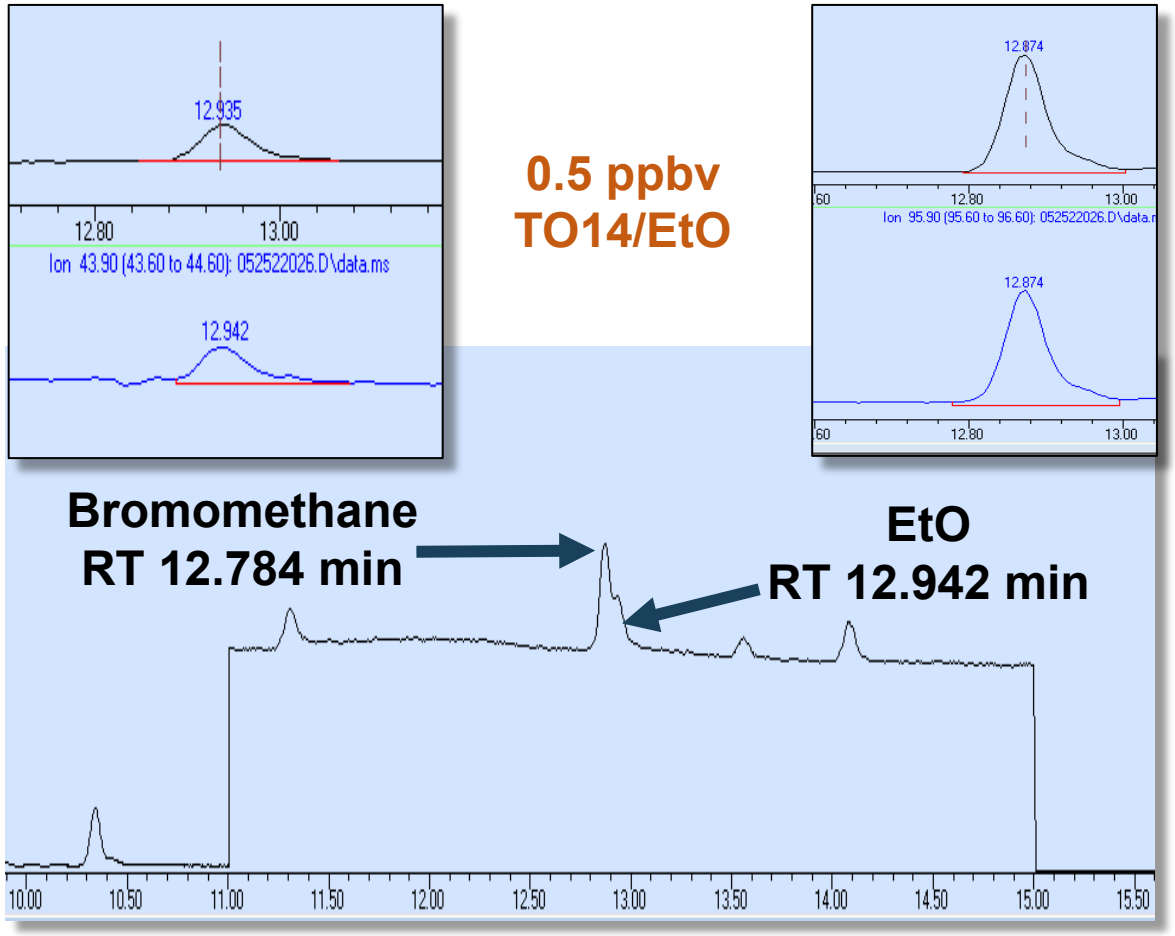
8890 GC Oven Program

	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	-20	2
Ramp 1	3	69	0
Ramp 2	4	141	0
Ramp 3	40	240	3.52
Post bake		180	6

Modified Entech 7200A Preconcentrator settings specified in Entech Application Note A-3742-01

System 1 – Intermediate Method (cont.)

- **Refinements to reach intermediate method:**
  - Optimized Entech/GC-MS settings
- **Achievements:**
  - Desired chromatographic separation
  - Identified potential interferents
  - MDL* range of 12–20 pptv

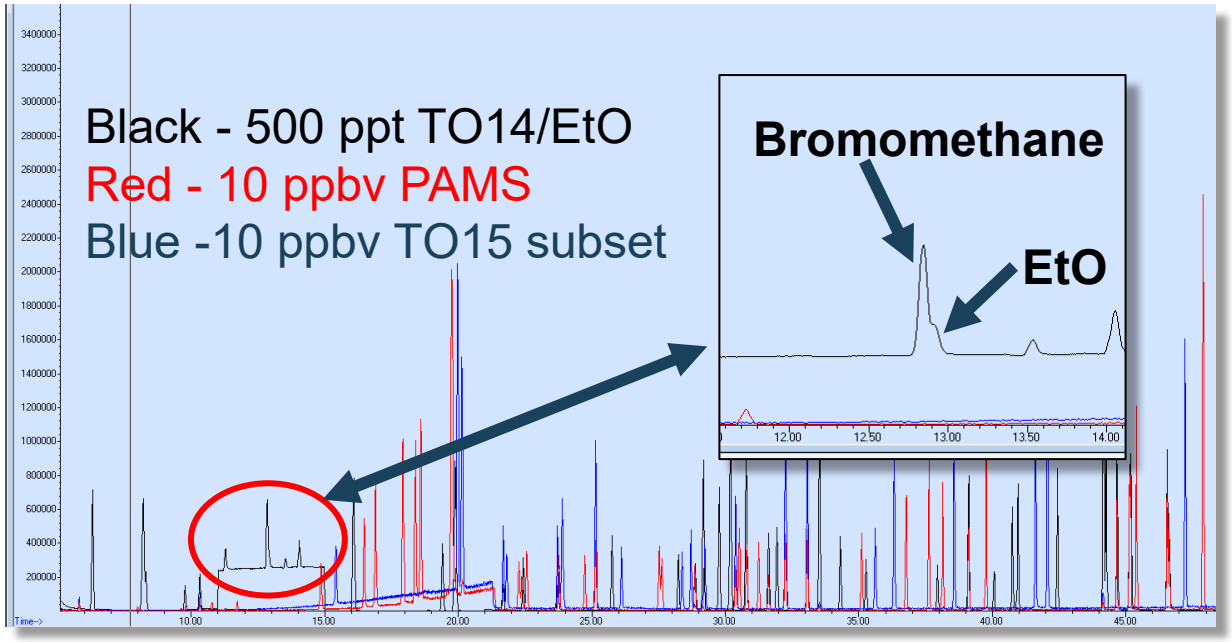


*Tentative MDL: 40 CFR, Part 136, Appendix B, 1984 – “best-case” using 7 replicates

System 1 – Intermediate Method (cont.)

- **Caveat:**
  - Oven program 55+ min
- **Continued method refinements:**
  - Checked coelutions: TO-15 subset, TO-14/EtO blend, and Photo-chemical Assessment Monitoring Stations (PAMS) VOCs
  - Further adjust preconcentrator/ MS settings/GC oven programs

Co-elutions with PAMS, TO14, EtO, and TO15 subset



System 1 – Optimized Method

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
Draw-out plate	6 mm
Tune	Atune/Etune evaluations
Acquisition	SIM, low resolution
Gain	Testing overall and segmented
Column flow	1.5 mL/min

8890 GC Oven Program

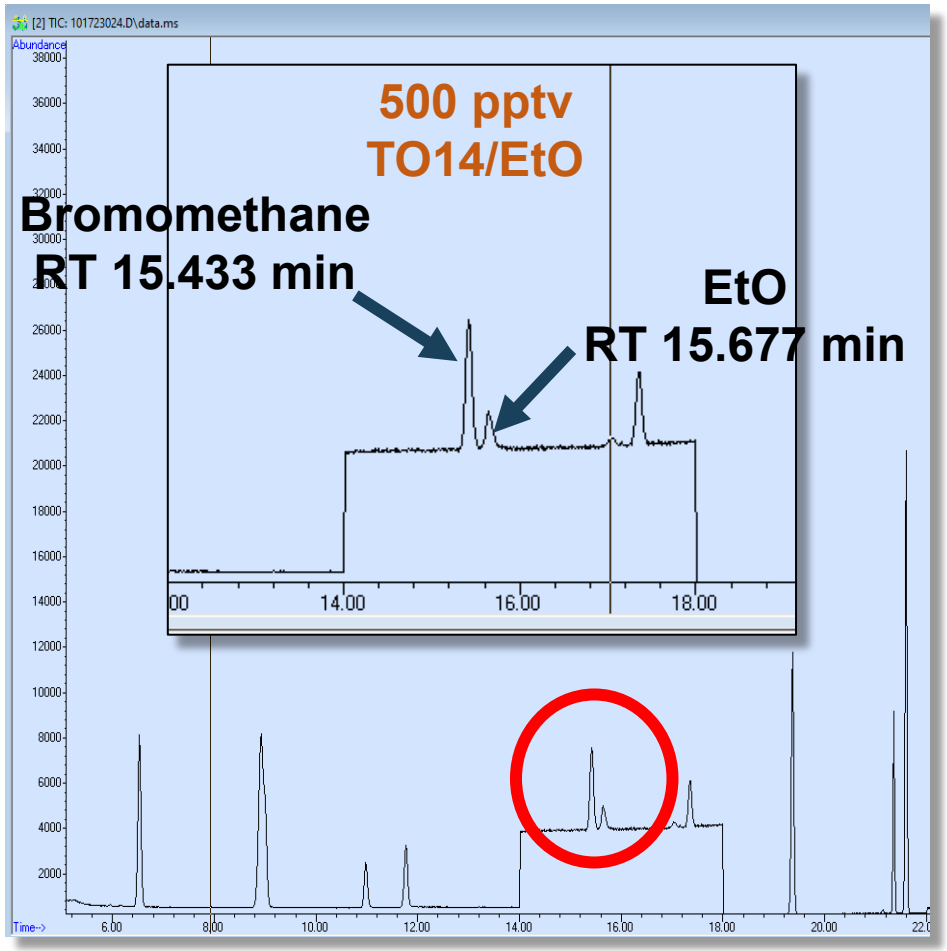
	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	-20	3
Ramp 1	1.5	1	0
Ramp 2	18	150	0
Ramp 3	12	240	3
Post bake		180	18

Modified Entech 7200A Preconcentrator settings specified in Entech Application Note A-3742-01 to hybrid mode

System 1 – Optimized Method (cont.)

Method refinements to reach optimized method:

- Varied temperatures, ramps, hold times:
  - Dichlorotetrafluoroethane (F-114) and chloromethane
  - Styrene and *o*-xylene
  - Bromomethane and EtO
  - All compounds separated in the quantitation software
- Optimized oven program to 35.1 min



System 1 – Optimized Method (cont.)

- Implemented standard source and quad temperatures (230°C/150°C)
- 6 mm draw-out plate and new column (same phase) installed
- Evaluated Atune vs Etune
- Tentative MDLs* of 5–11 and 7–18 pptv were calculated for Atune and Etune, respectively
- Analyzed ambient air samples – data reduction in progress

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

System 1 – Tentative MDLs*

MDL Studies - Entech 7200A/8890A GC - 5977B MS						
Study	**Tune**	**Source/Quad, °C**	**Lens (mm)**	**Gain**	**EtO MDL (pptv)**	**Timeline**
03/07/22	Etune	350/200	3	10	79	initial
05/04/22	Etune	350/200	3	10	24	initial
05/25/22	Etune	350/200	3	10	9	initial
08/08/22	Etune	350/200	3	10	17	intermediate
10/25/22	Etune	350/200	3	10	20	intermediate
03/07/23	Etune	300/180	3	10	12	intermediate
03/30/23	Etune	300/180	3	10	19	intermediate
05/23/23	Etune	300/180	6	25	7	optimized
06/05/23	Etune	300/180	6	25	10	optimized
06/08/23	Etune	300/180	6	25	8	optimized
06/15/23	Etune	300/180	6	25	11	optimized
08/17/23	Atune	230/150	6	default	10	optimized
08/23/23	Etune	230/150	6	default	18	optimized
08/30/23	Etune	230/150	6	25	8	optimized
09/13/23	Atune	230/150	6	default	10	optimized
10/17/23	Atune	230/150	6	default	5	optimized
10/30/23	Atune	230/150	6	25	11	optimized

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

System 1 – NATTS PT Results

- Solid NATTS CY2023 Q2 results – met TO-15A ±30% criteria – our goal
- Analytical parameters:
  - Etune
  - SIM mode
  - 230°C/150°C
  - Default gain factor of 1
  - MDL* for EtO: 18 pptv

*Tentative MDL: 40 CFR, Part 136, Appendix B, 1984 – "best-case" using 7 replicates

Percent Difference against the NATTS Lab Average, per laboratory (%)		
Analyte	**Target Conc. (ppbv)**	**AMCD AAB**
1,1,2,2-Tetrachloroeth	0.034	-2.9%
1,2-Dibromoethane	0.29	-3.1%
1,2-Dichloroethane	0.22	-3.6%
1,2-Dichloropropane	0.20	0.5%
1,3-Butadiene	0.16	-25.6%
1,3-Dichloropropene -	0.16	7.5%
1,3-Dichloropropene -	0.15	8.0%
Acrolein	0.16	NR
Benzene	0.17	-6.5%
Carbon Tetrachloride	0.056	-26.8%
Chloroform	0.26	-6.2%
Dichloromethane	0.23	-9.6%
Ethylene Oxide	0.11	16.4%
Tetrachloroethylene	0.12	7.5%
Trichloroethylene	0.14	-0.7%
Vinyl Chloride	0.15	-8.7%
overall average		-3.6%

System 1 - Challenges

- Residual water may be impacting MS internal components
- Instrument stability issues potentially due to temperature stress on source/quad
- Etune vs. Atune operational issues
- Poor Etunes are a first indicator of system beginning to fail; need to check voltages; source cleanings not necessarily sufficient
- Considerable downtime over last year

System 1 - Conclusions

- Excellent collaborations on optimization of instruments and methods
- Thoroughly evaluated/optimized method parameters, completed SOP
- Etune with gain plus SIM mode provides optimal sensitivity
- Settled on standard 230°C/150°C source/quad temperatures
- 6 mm draw-out plate is viable option vs 3 mm draw-out plate
- Tentative MDLs in 5-18 pptv range (combined Atune and Etune results)
- Solid audit results for EtO

A Tale of Two Systems – “System 2”

Preconcentrator: Entech 7200 (refurbished)

GC: Agilent 7890A

MS: 5975C with diffusion pump

Source: Inert with triple-axis detector

System 2 – Background Information

- Evaluating legacy system viability for determination of ultra-low EtO concentrations
- Refurbishment of 9-year-old Entech 7200 completed
- Diffusion pump rather than turbopump system for MS

System 2 – Current Method

Analytical Method

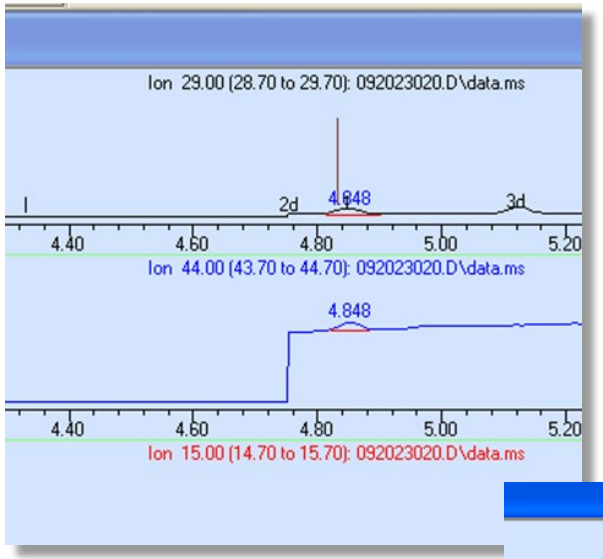
Parameter	Specifications
Column	Rxi-1ms 60-m x 0.32-mm x 1-µm column
Source/quad	230°C/150°C
Draw-out plate	Standard
Tune	HiSense/Atune
Acquisition	SIM, low resolution
Gain	Various settings tested
Oven program	Ambient starting temp

7890A GC Oven Program

	Rate (°C/min)	Value (°C)	Hold (min)
Initial	–	35	5
Ramp 1	5	130	0
Ramp 2	20	220	3
Post bake		220	7

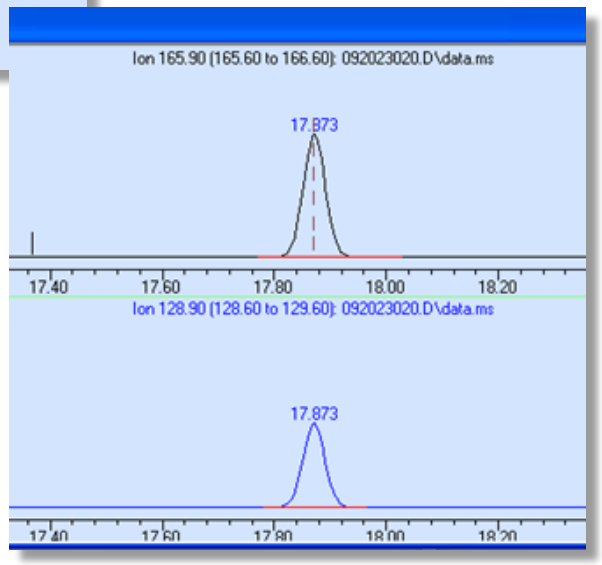
System 2 – Current Method (cont.)

- Legacy ambient GC oven program and MS method in place, GC oven program allowed solid separations
- Evaluated Trace Ion Detection (TID) and HiSense modes
- Challenges with peak integration for EtO below 125 pptv
- Length of oven program 31.5 min



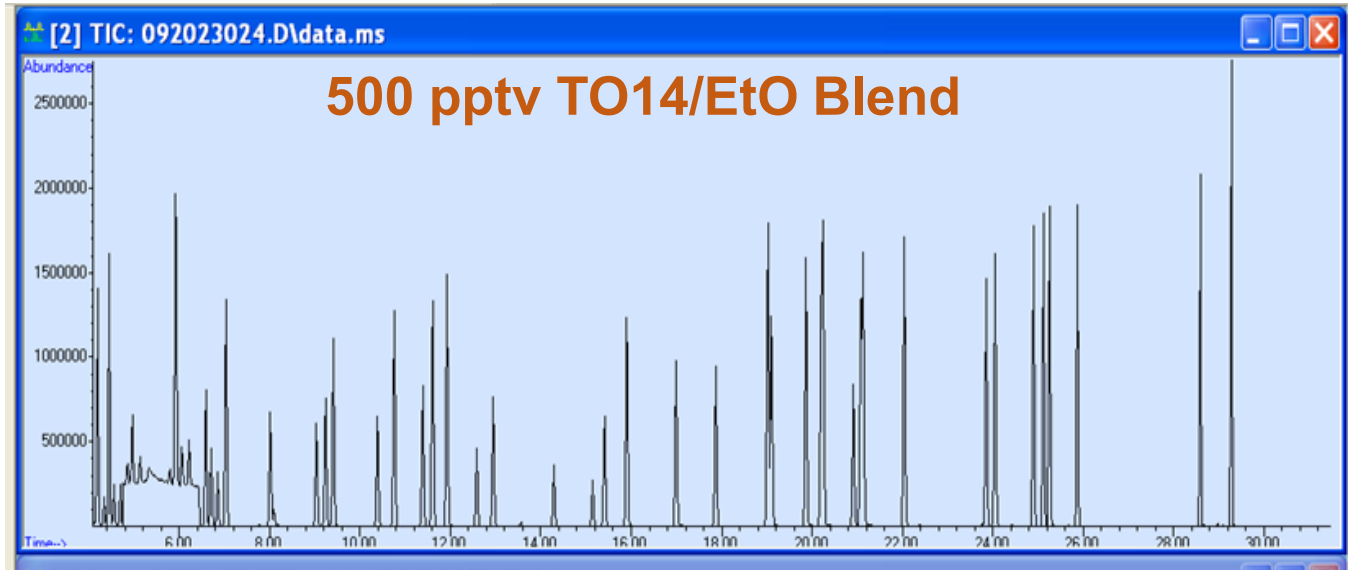
125 pptv EtO

125 pptv Perc



System 2 - Conclusions

- EtO viable on Rxi-1MS column; <0.25 ppbv difficult to integrate; may try 624 phase column
- HiSense tune improved sensitivity but not sufficiently
- EtO tentative MDLs*:
  - Atune – 96 pptv
  - Atune TID – 60 pptv
  - HiSense – 27 pptv



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“System 3”

Preconcentrator: Markes CIA Advantage/Kori-xr/Unity-xr

Agilent GC: 7890B

MS/source: Bench-TOF Select time-of-flight MS (TOF MS)

System 3 – Background Information

- GC-TOF MS system – research-grade instrument fully operational in lab
- Different preconcentration/water management system and MS
- As time allows, implement optimized method (modified as appropriate) using TO-15A sorbent traps
- Technical Note “Advances in ultra-trace air toxics analysis: Cryogen-free canister pre-concentration and GC–MS for US EPA Method” available (https://markes.com/content-hub/application-notes/application-note-169)

Next Steps

- Installation and evaluation of 5977C diffusion pump MS
- Continue analysis of ambient air samples
- Continue sample integrity studies
- Move to Method Update Rule MDL procedure
- Purchase new canisters
- Evaluate and optimize canister cleaning processes
- GC-TOF MS system experiments and methods development
- Conduct interlaboratory comparison

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