Analysis of Ethylene Oxide by EPA Method TO-15 / TO-15A

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Collection and Analysis of Ethylene Oxide

- Sources and Health Risk Summary

- Ethylene Oxide Chemical Overview

- Technical Development/Evaluation

- TO-15/TO-15A Results

- Conclusions

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Common Sources

- Chemical Manufacturing
  - Antifreeze, Plastics, Detergents, Adhesives
  - Most use as a chemical intermediate
- Medical Sterilization
  - Approximately 50% of medical equipment sterilized using Ethylene Oxide
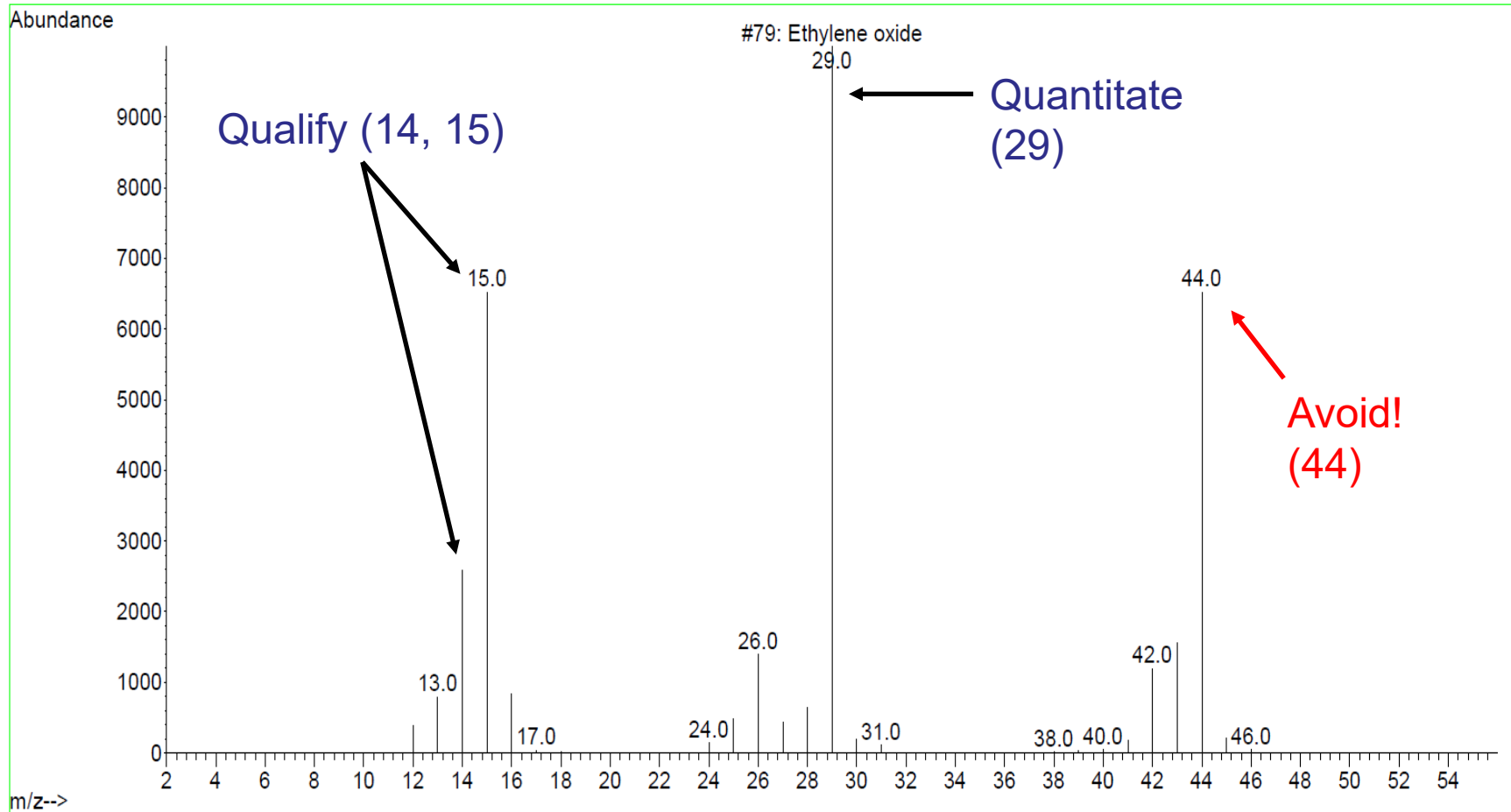
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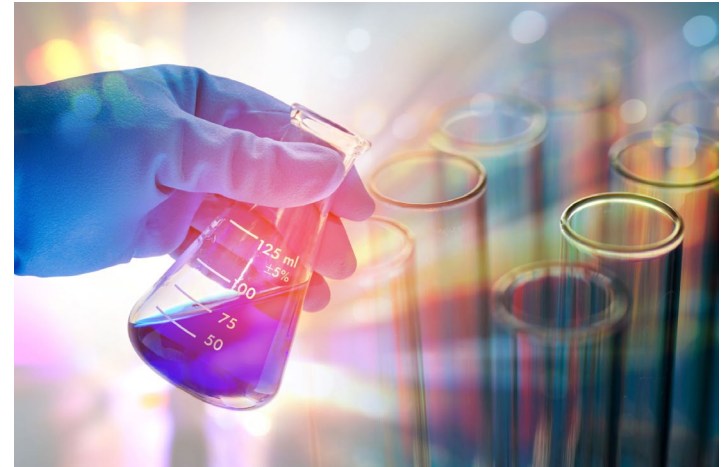
Health Risk

- Acute exposure:
  - Central nervous system depression
  - Irritation of the eyes and mucous membranes
- Chronic Exposure:
  - Confirmed carcinogen and mutagen
  - Damage to the nervous system
  - Reproductive effects (miscarriage and testicular degradation)

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Ethylene Oxide Spectrum

Chemical Properties

- Overview:
  - Unstable: strained cyclic ether
  - Poor chromatographic response
  - Expected oxidation in atmosphere
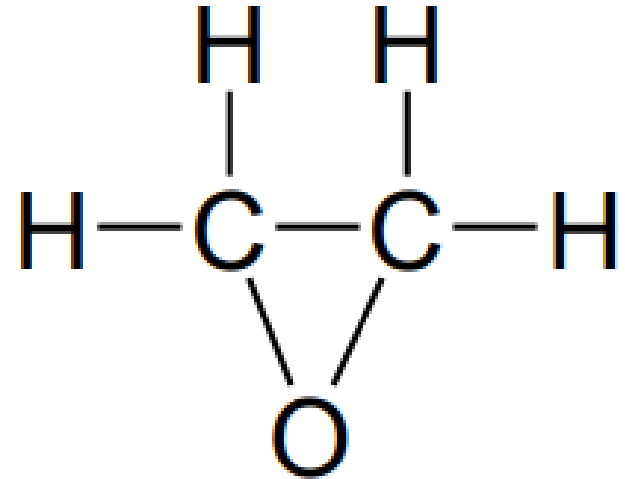 - Estimated 2-5 month half life in atmosphere

Table 4-2. Physical and Chemical Properties of Ethylene Oxide

Property	Information	Reference
Molecular weight	44.05 g/mol	WHO 2003
Color	Colorless	WHO 2003
Physical state	Gas	NIOSH 2007
Melting point	-111.7°C	HSDB 2010
Boiling point	51°F (10.6°C)	NIOSH 2016
Density at 10°C	0.8824	HSDB 2010; Weast 1985
Odor	Sweet, olefinic; ether-like	NIOSH 2007; Verschueren 1983
Odor threshold:		
Water	140 mg/L	Amoore and Hautala 1983
Air	787 mg/m³ (432.85 ppm)	Amoore and Hautala 1983

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Instrumentation

- Types of media
  - Summa and treated canister
- Instrumentation
  - Agilent 5977B MS-SIM/ 8890 GC
  - Entech 7200A Preconcentrator
- Analytical method
  - EPA Method TO-15
  - EPA Method TO-15A
- Standards material
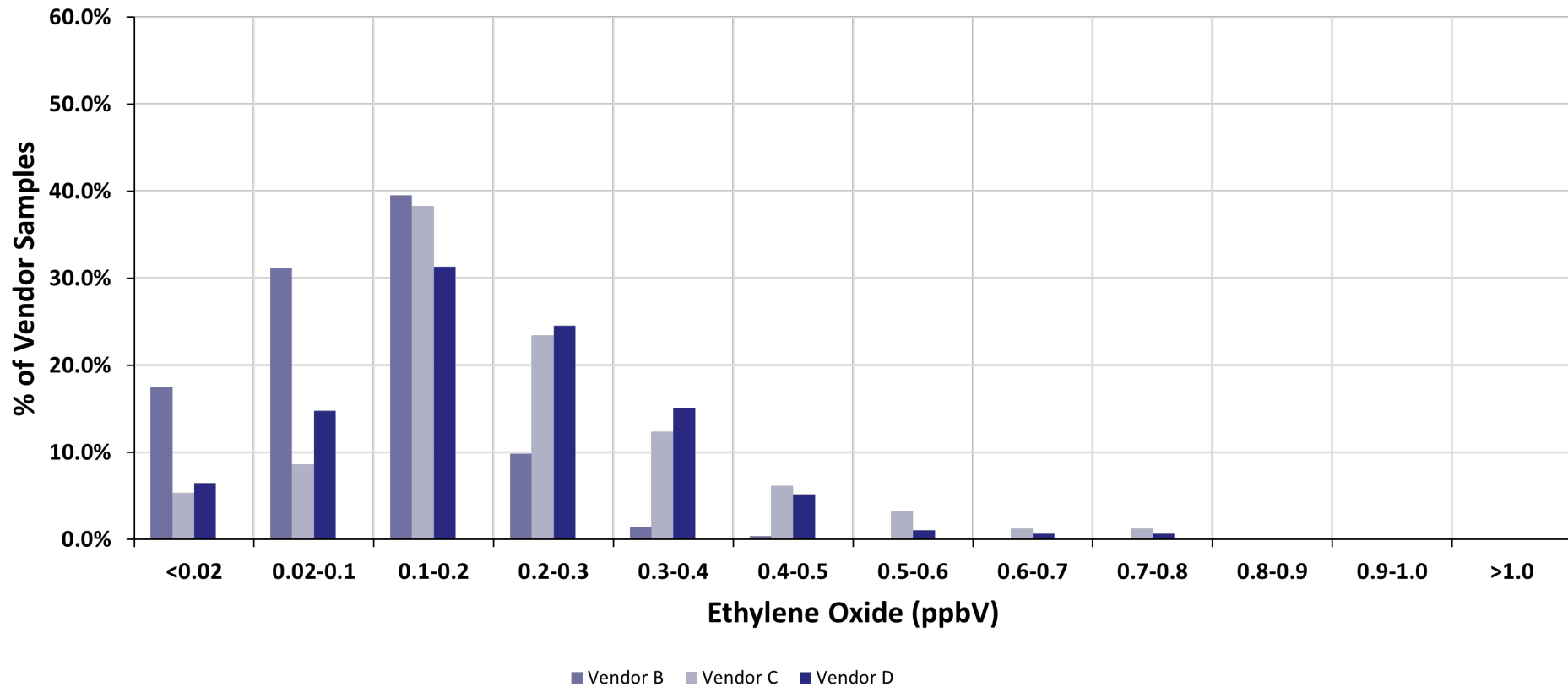 - Pressurized gas cylinder

Technical Evaluation

1. Long Term Data Collection – monitor ambient levels over time

2. Known Addition – ambient samples spiked and then held

3. Continuing certifications of canisters – passing 3x MDL criteria on EVERY canister
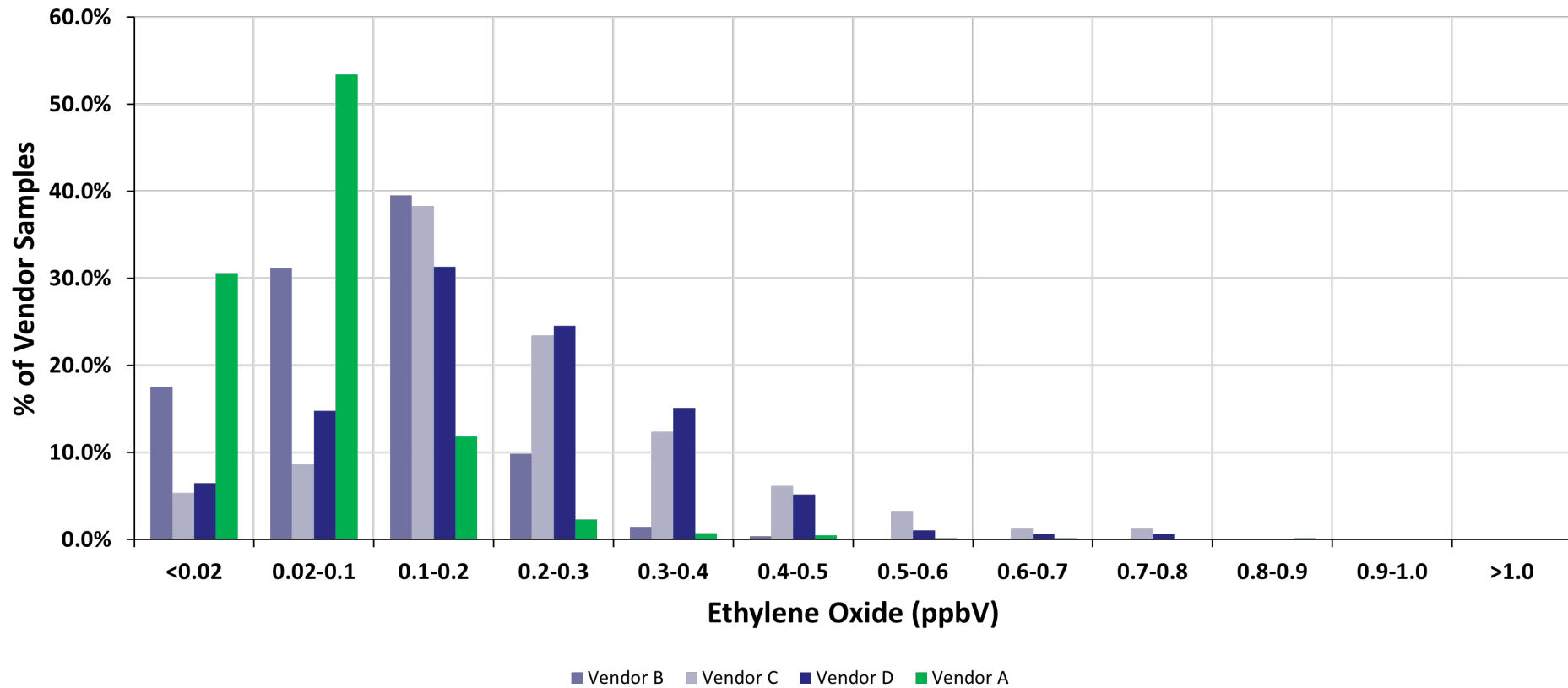
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Long Term Data Collection

Traditional Technology

Long Term Data Collection

New Technology

Technical Evaluation

1. Long Term Data Collection – monitor ambient levels over time

2. Known Addition – ambient samples spiked and then held

3. Continuing certifications of canisters – passing 3x MDL criteria on EVERY canister

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Known Addition - Winter
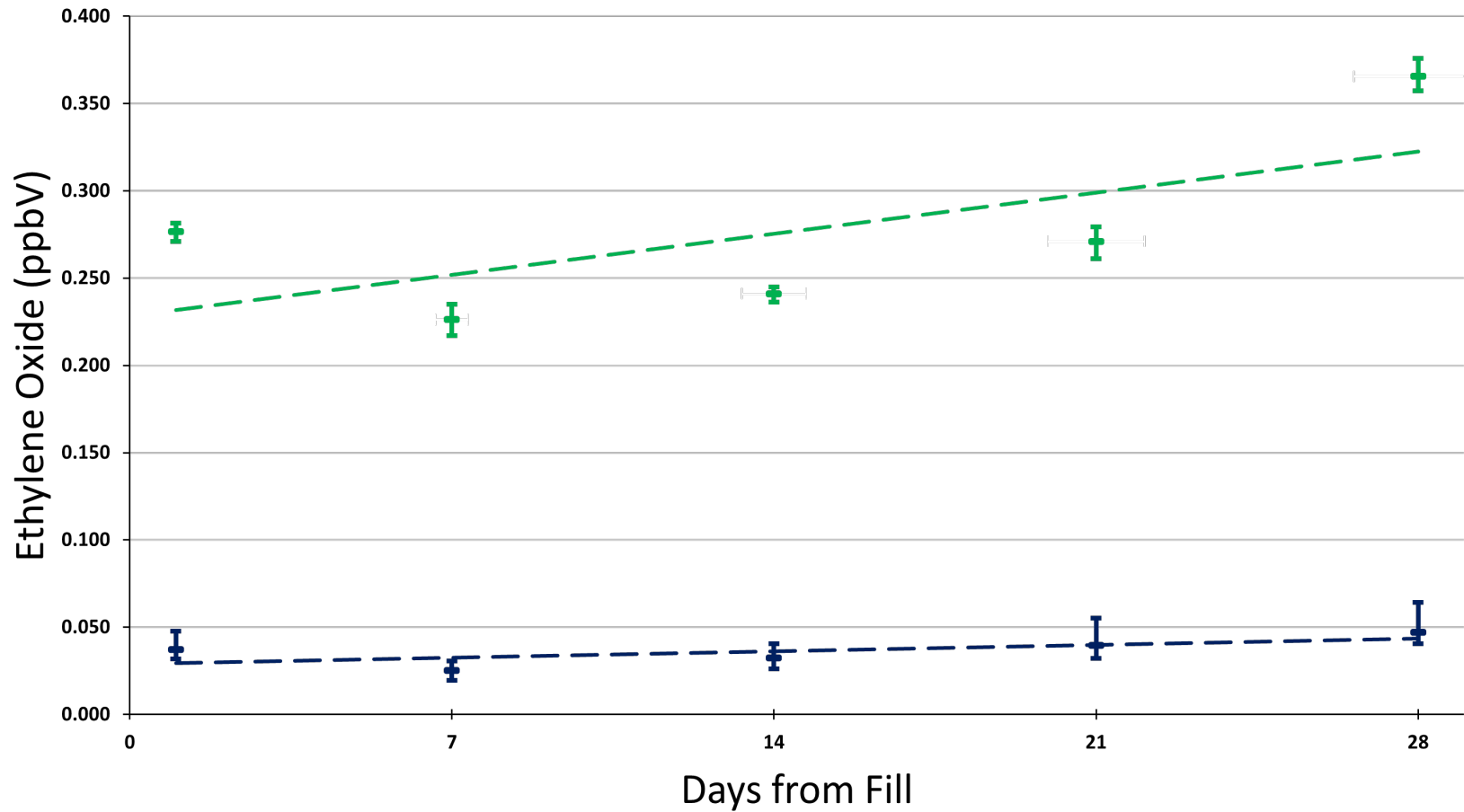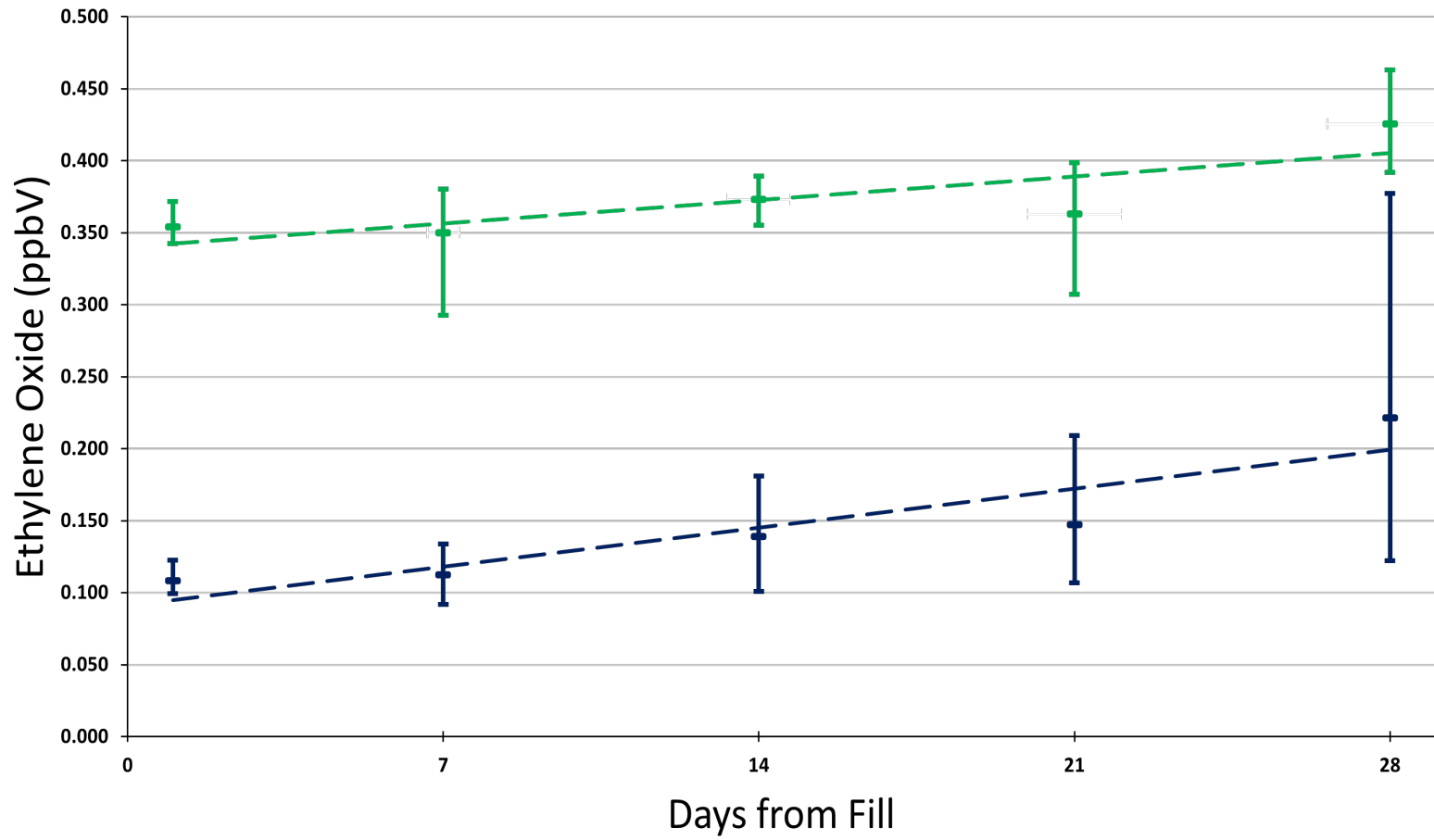
Known Addition - Summer

Technical Evaluation

1. Long Term Data Collection – monitor ambient levels over time

2. Known Addition – ambient samples spiked and then held

3. Continuing certifications of canisters – passing 3x MDL criteria on EVERY canister

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Canister Certification

- Leak Test – 7 Days

- Fill – UHP N_2

- Hold – 10 Days

- GC/MS Analysis

  - TO-15 Analytes <3x MDL or 0.200ppbV
  - Total Hydrocarbon <20 ppbC
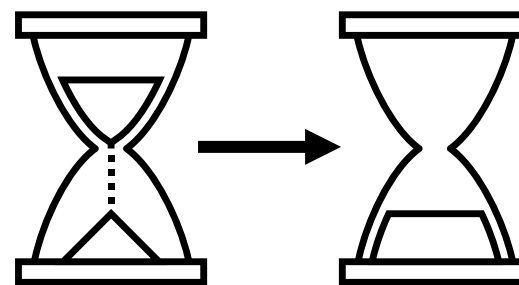
>3 Weeks for **EVERY** Canister!

Total Cans	Passed Leak Test	TO-15 Certified	EtOx Certified	Hydrocarbon Certified
1118	1038	796	818	707

Method Detection Limit

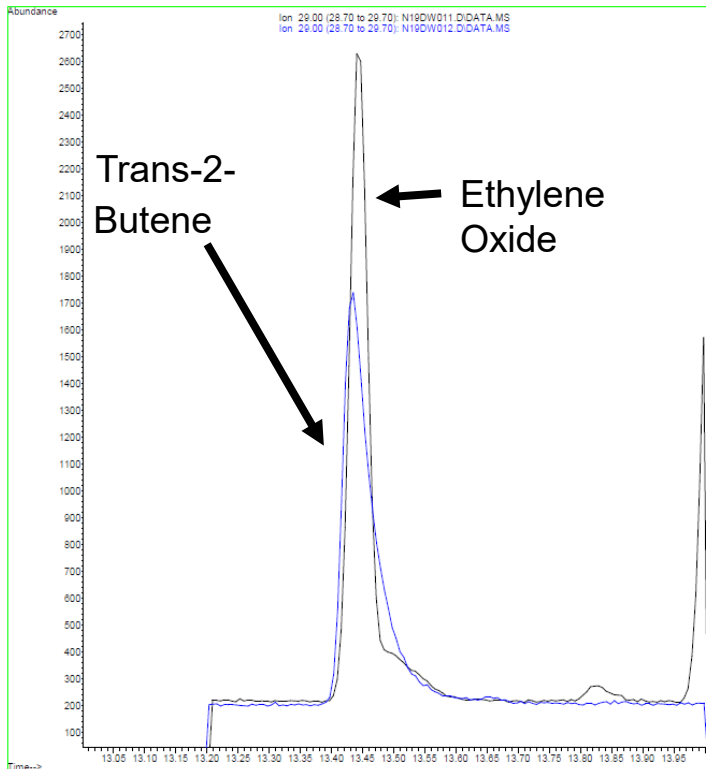| MDL Data 2018-2022 (pptV)				
	MS-1	MS-4	MS-6	MS-8
2018	45.3			
2019	61.4	48.5	**25.0**	
2020	85.7	**23.2**	**28.5**	
2021	21.9	**22.0**	**26.1**	**20.9**
2022	48.0	-	**3.7**	**42.8**

<u>Red:</u> Switch to 624 column

Coelution – Column Choice

- ## DB-1 (Nonpolar) type analytical column
  - 100% Dimethylpolysiloxane
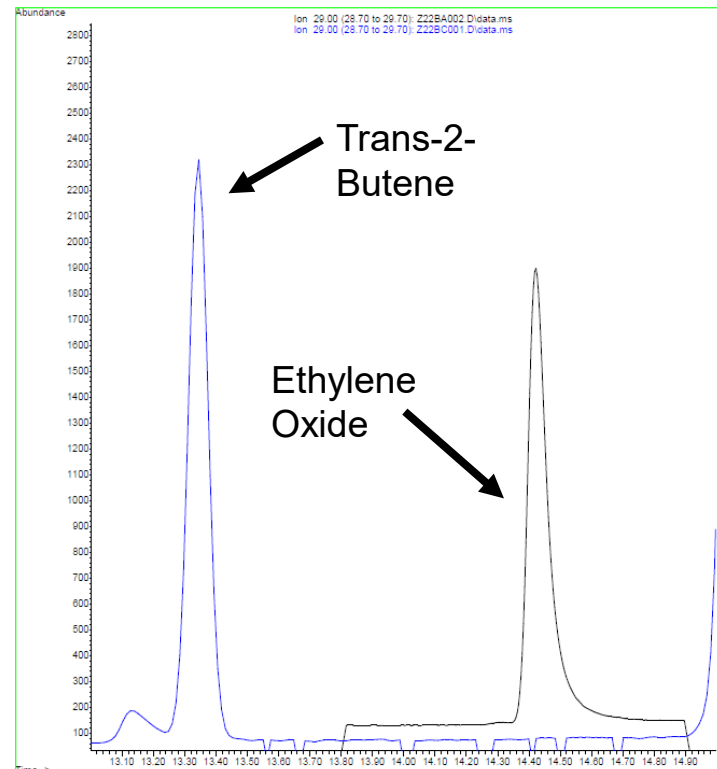 - Coelution issues with ethylene oxide

- ## DB-624 (Mid-polar) type analytical column
  - 6% cyanopropyl/phenyl, 94% Dimethylpolysiloxane
  - Resolves coelution issues with ethylene oxide
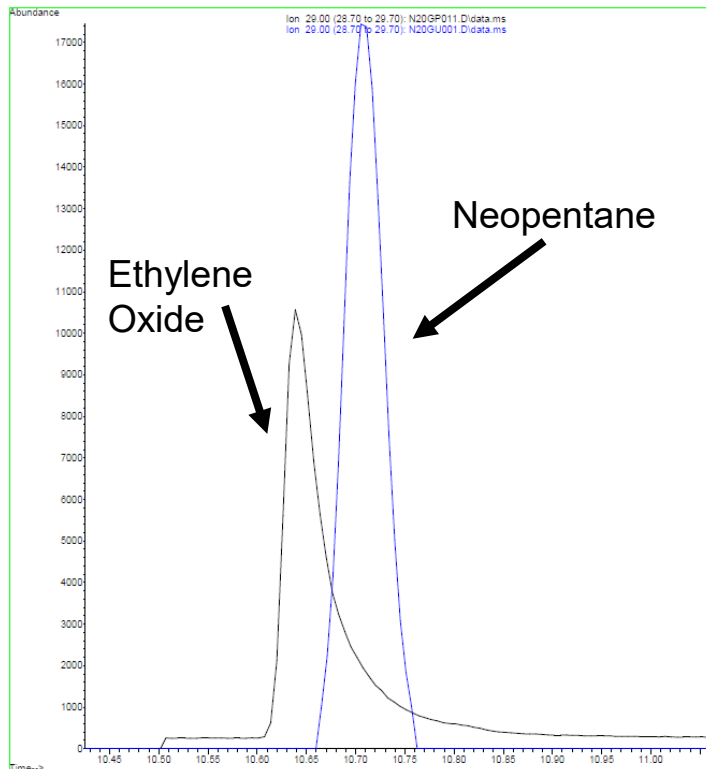
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Trans-2-Butene [Ion 29]

DB-1

DB-624

Neopentane [Full Scan]

DB-1

Neopentane

Ethylene Oxide

DB-624

Ethylene Oxide + Bromomethane

Neopentane
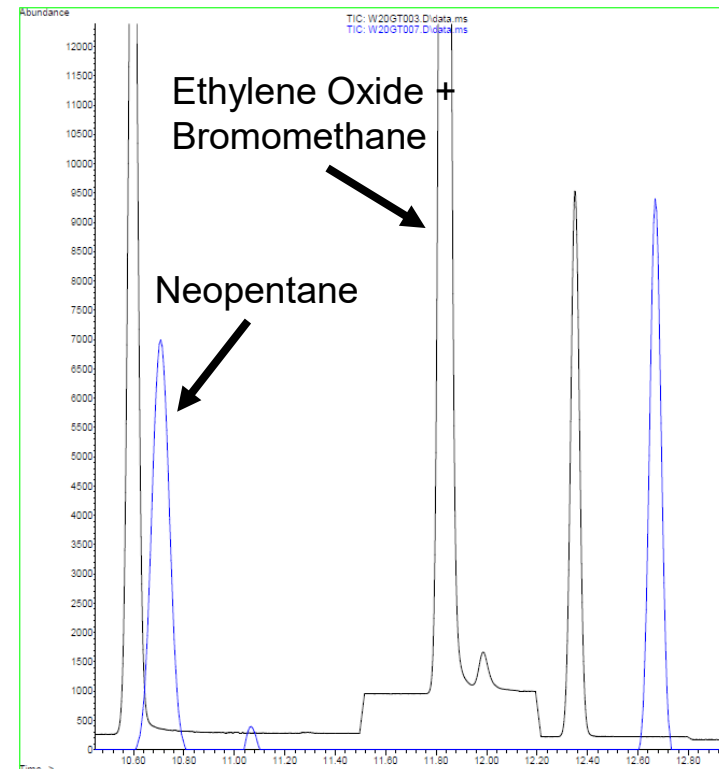
Bromomethane [SIM]
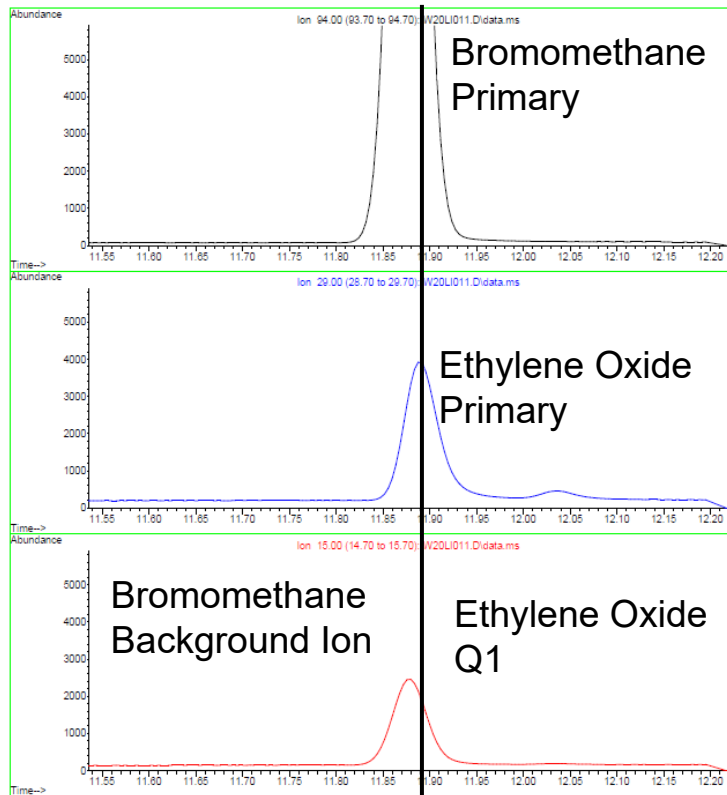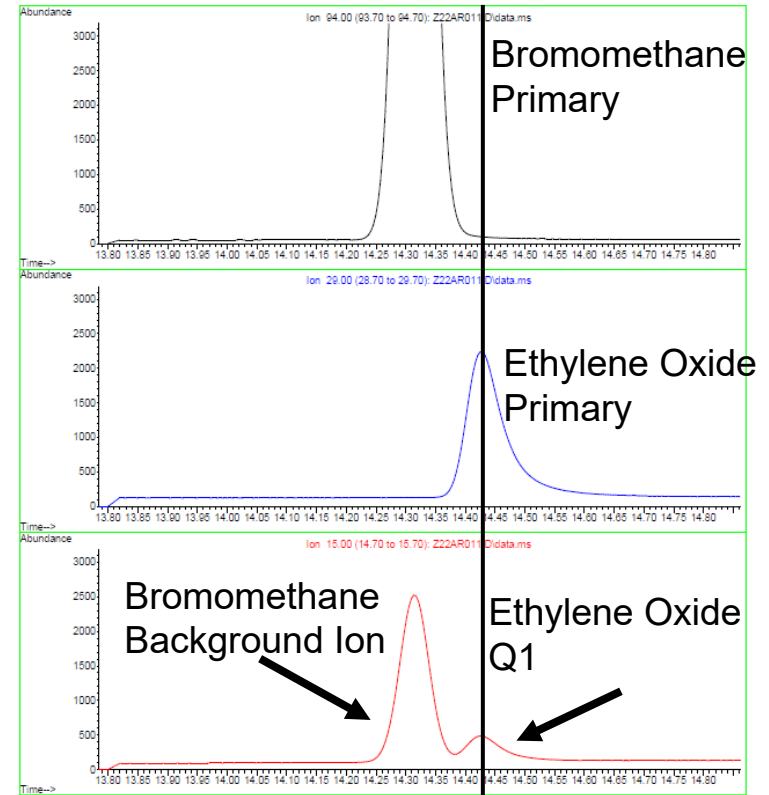
Other Possible Co-elution

Acetaldehyde

Ethylene Oxide

Methanol

- Continuing need to verify possible co-eluting compounds
- Low GC/MS response can make Full-Scan difficult
- Column type and oven conditions are critical considerations

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NATTS Performance

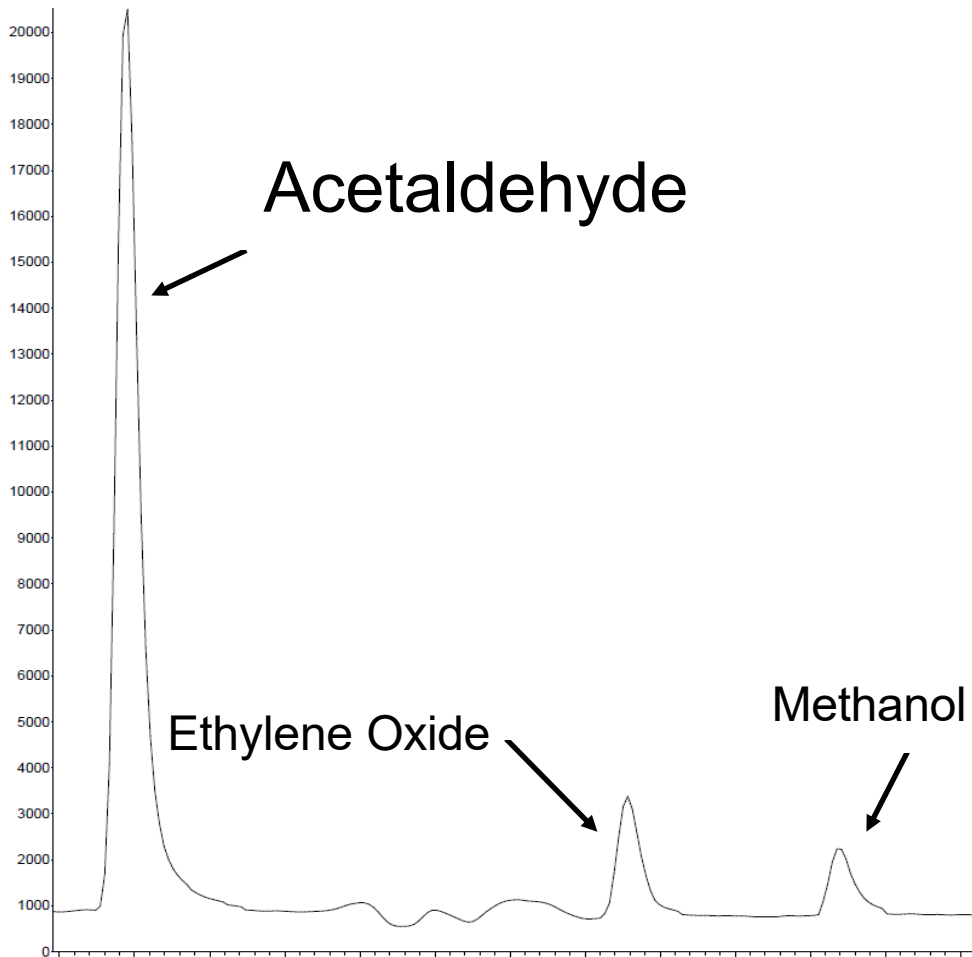- ERG is required to analyze a PT twice a year
- Results are compared to the average of all laboratories in the network

ERG's NATTS Proficiency Testing Results (Ethylene Oxide)					
	Q1, 2020	**Q3, 2020**	**Q1, 2021**	**Q2, 2021**	**Q3, 2021**
%Dif from Mean of Participating NATTS Labs:	-10.2%	-3.0%	-19.2%	-21.4%	-23.4%
Spike Level (ppbV):	0.450	0.470	0.193	0.374	0.120

TO-15A Feasibility - Calibration

Considerations:

- Low Pollutant Levels
- Background effects
- Curve Fit Type
  - Linear/Quadratic/RF

EtOx Response Factor Calibration			
Level	Nominal (ppbV)	Recovered (ppbV)	Nominal Difference
1	0.0000	N.D.	N/A
2	0.0193	0.0166	-14.2%
3	0.0484	0.0494	2.1%
4	0.0967	0.1044	8.0%
5	0.2418	0.2777	14.9%
6	0.9670	0.8735	-9.7%
7	1.9340	1.8794	-2.8%
8	4.8350	4.9173	1.7%

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TO-15A Feasibility - Calibration

Quadratic (Force-Zero) EtOx Calibration

Level	Nominal (ppbV)	Recovered (ppbV)	Nominal Difference
1	0.0000	N.D.	N/A
2	0.0193	0.0179	-7.6%
3	0.0484	0.0532	9.9%
4	0.0967	0.1123	16.1%
5	0.2418	0.2975	23.0%
6	0.9670	0.9243	-4.4%
7	1.9340	1.9497	0.8%
8	4.8350	4.8341	0.0%

$y = 0.0145x^2 + 0.1445x$
$R^2 = 0.9998$
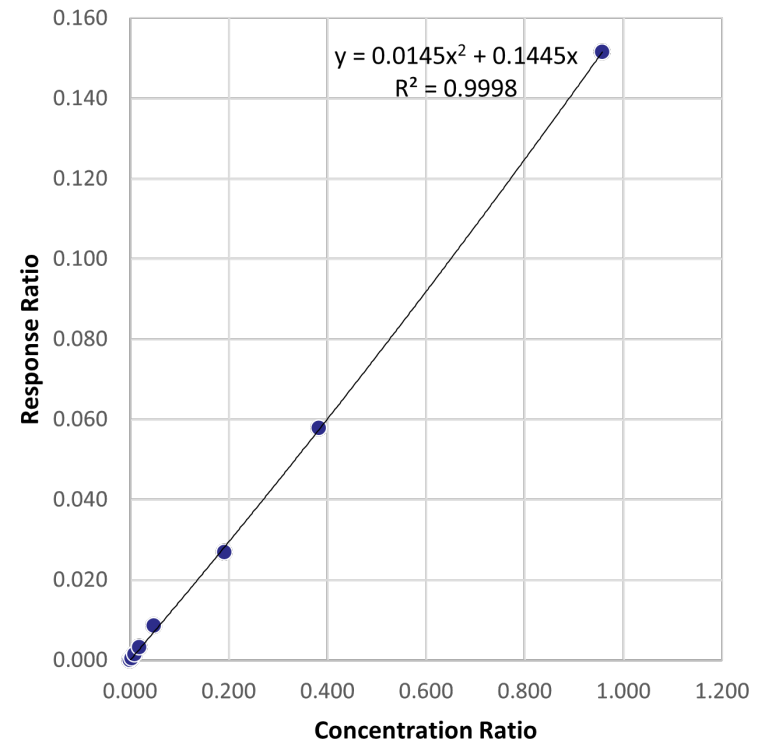
Conclusions

- Canister types – Careful scrutiny of canister inventory is **REQUIRED**!

- Column choice – Coelution effects and oven ramp make all the difference!

- Instrumentation – Advances in sensitivity will continue to help decrease MDLs and increase data reliability!

- TO-15/TO-15A – Low levels are possible, but difficult to achieve!

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Questions

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References

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- https://www.agilent.com/en/product/gas-chromatography/gc-systems/8890-gc-system?gclid=EAIaIQobChMI576TjKOy-QIVwT2tBh0C6AeNEAAYASAAEgLU4PD_BwE&gclsrc=aw.ds#zoomELIBRARY_681317