Interferences With Ethylene Oxide Testing in Air

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Outline

- TO-15A and ethylene oxide (EtO) method parameters
- Interferences and need for cryogenic cooling
- EtO in canister blanks – Humid air, dry air, and inert He fill
- EtO growth in blanks – Comparison between manufacturers
- EtO in used customer canisters
- Results after cleaning

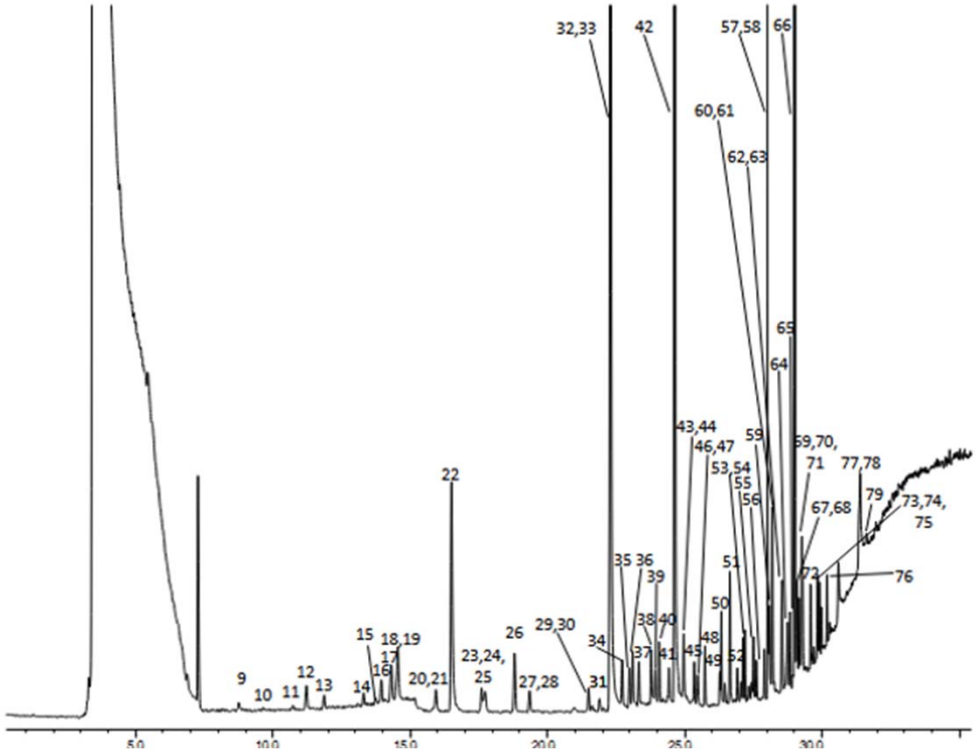
EtO and TO-15A Method

GC	Agilent 7890B
Injection type	On-column
Column	624Sil MS 60m x 0.25mm x 1.4um
Carrier gas	He , constant flow
Flow rate	2mL/min
Oven temp	0°C (hold 5 min) to 60°C at 3.5°C/min (hold 0 min) to 260°C at 24°C/min (hold 5 min)

Detector	MS Agilent 5977A
Acquisition mode	SIM/Scan
Scan parameters	
Scan range (amu)	29-226
Scan rate (scans/sec)	3.7
SIM parameters	
SIM ions	15, 29, 43, 44, 56
Dwell time	50
Transfer line	250°C
Analyzer type	Quadrupole
Source type	Extractor
Source temp	230°C
Quad temp	150°C
Electron energy	70eV
Solvent delay time	0 min
Tune type	BFB
Ionization mode	EI

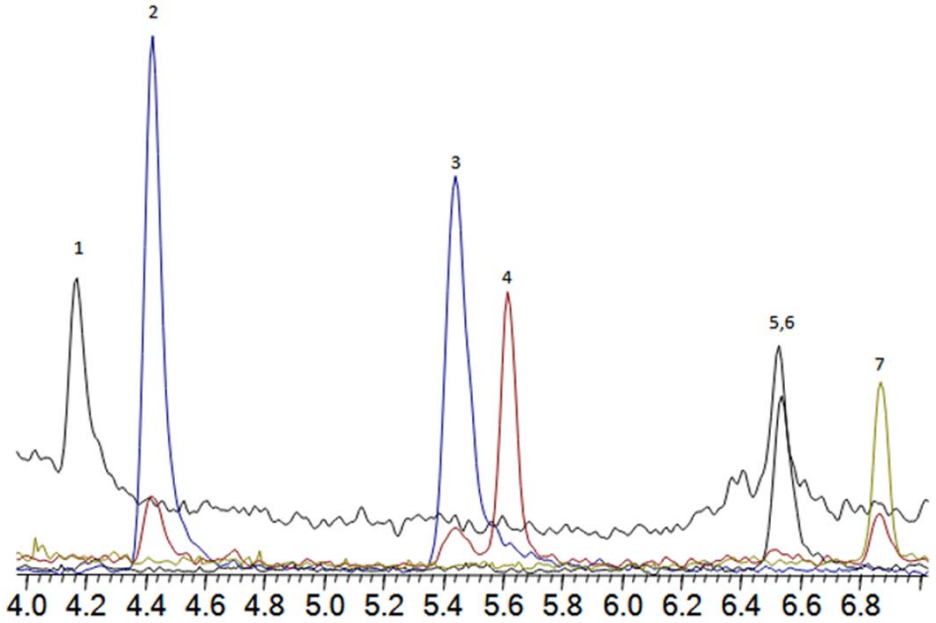
Preconcentrator	Markes Unity 1+ CIA
Trap 1 settings	
Cooling temp	5°C
Desorb temp	300°C
Desorb flow	6 mL/min
Desorb time	180 sec
Internal Standard	
Purge flow	50 mL/min
Purge time	60 sec
Volume	50mL
ISTD flow	50mL/min
Sample	
Volume	400mL
Purge flow	50mL/min
Purge time	60 sec
Sample flow	100mL/min

EtO and TO-15A Method

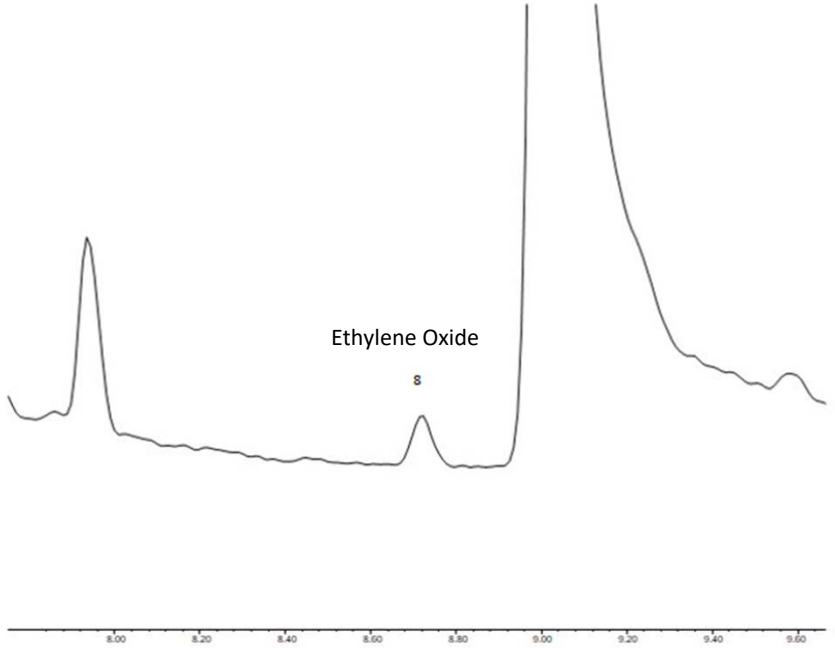


Total Ion Chromatogram - TO-15A standard 200 ppt

EtO and TO-15A Method



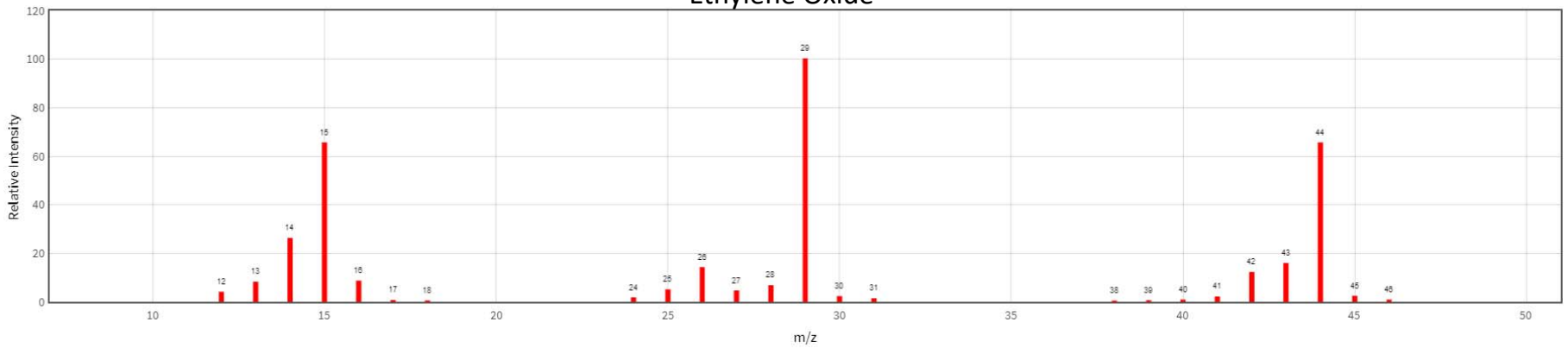
Extracted Ion Chromatogram - TO-15A standard 200 ppt



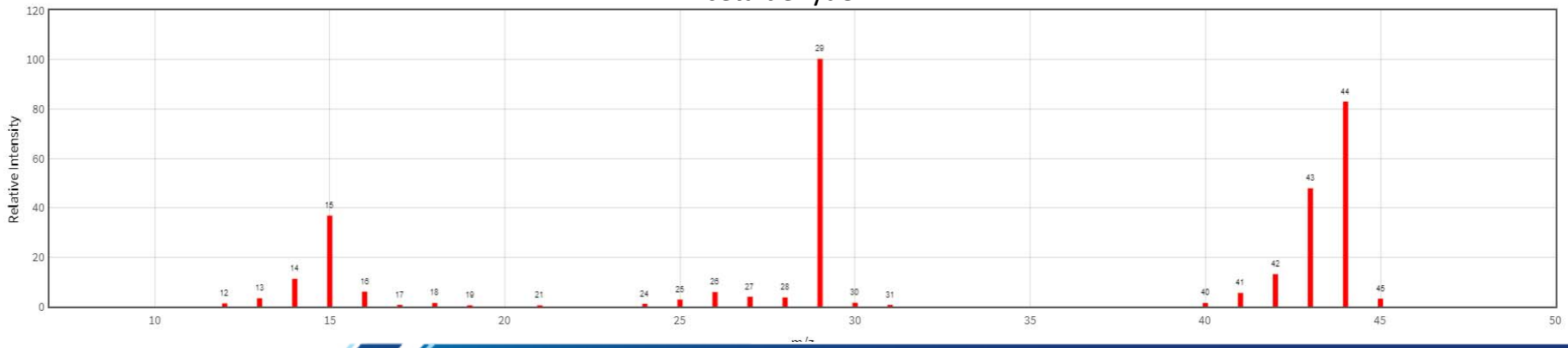
Extracted Ion Chromatogram - EtO standard 50 ppt

Ethylene Oxide Interferences

Ethylene Oxide

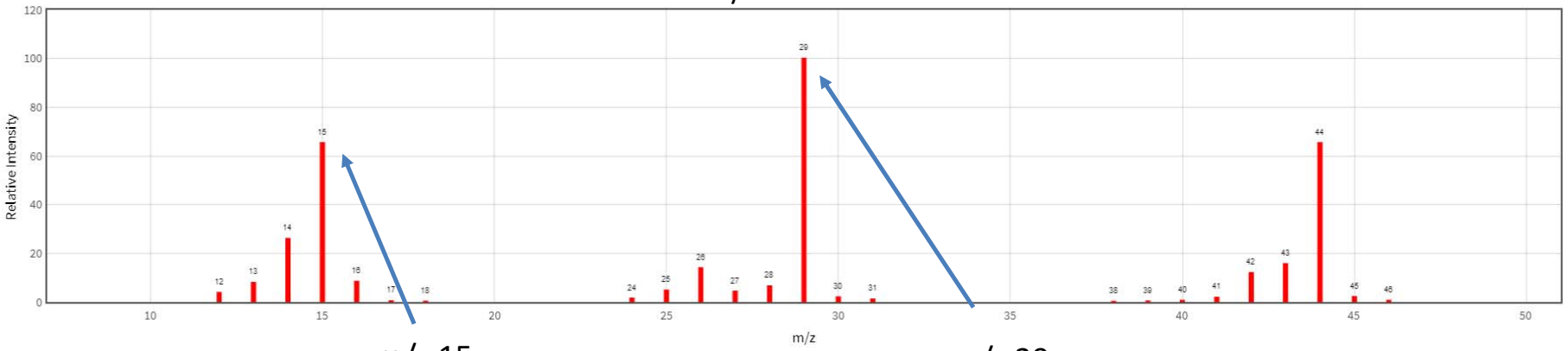


Acetaldehyde



Ethylene Oxide Interferences

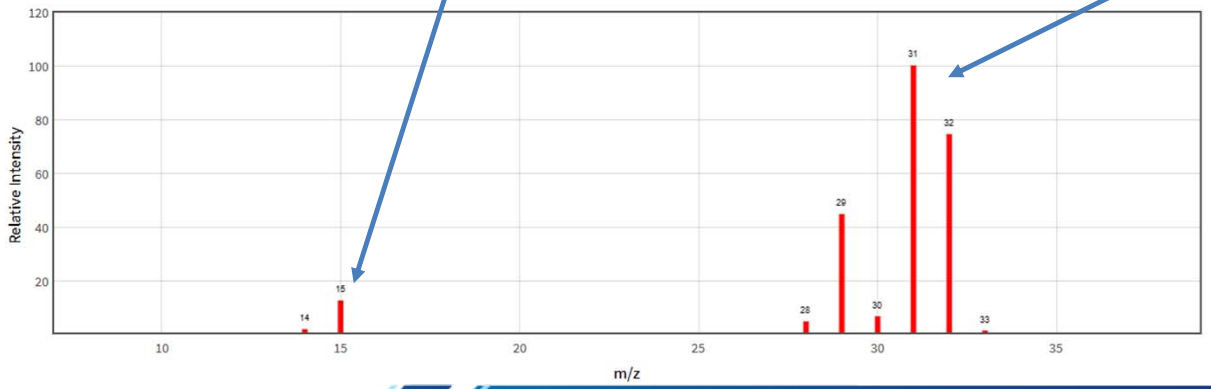
Ethylene Oxide



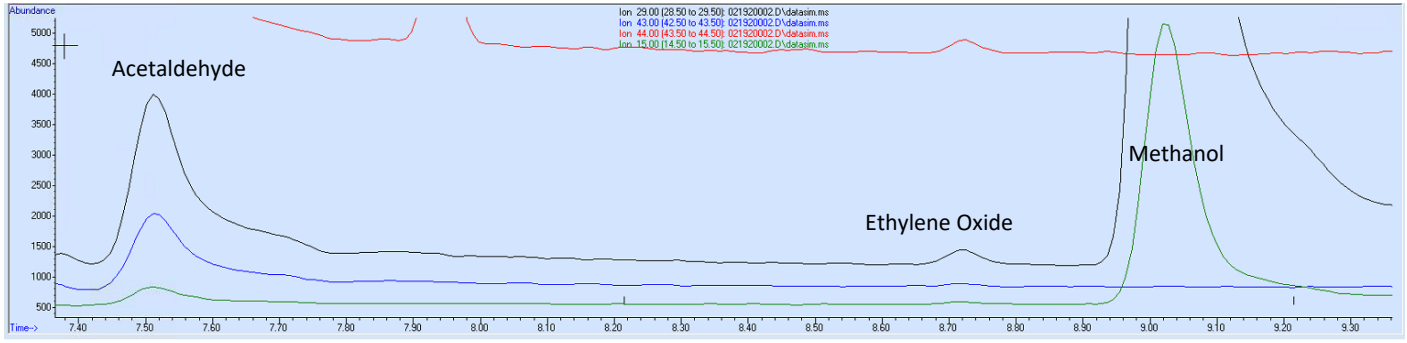
m/z 15

Methanol

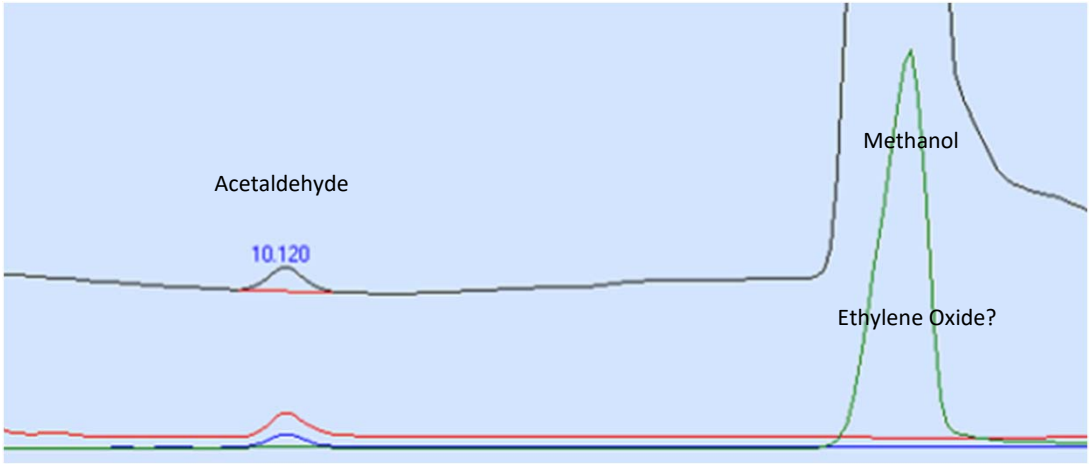
m/z 29



Ethylene Oxide Interferences



0°C start temperature



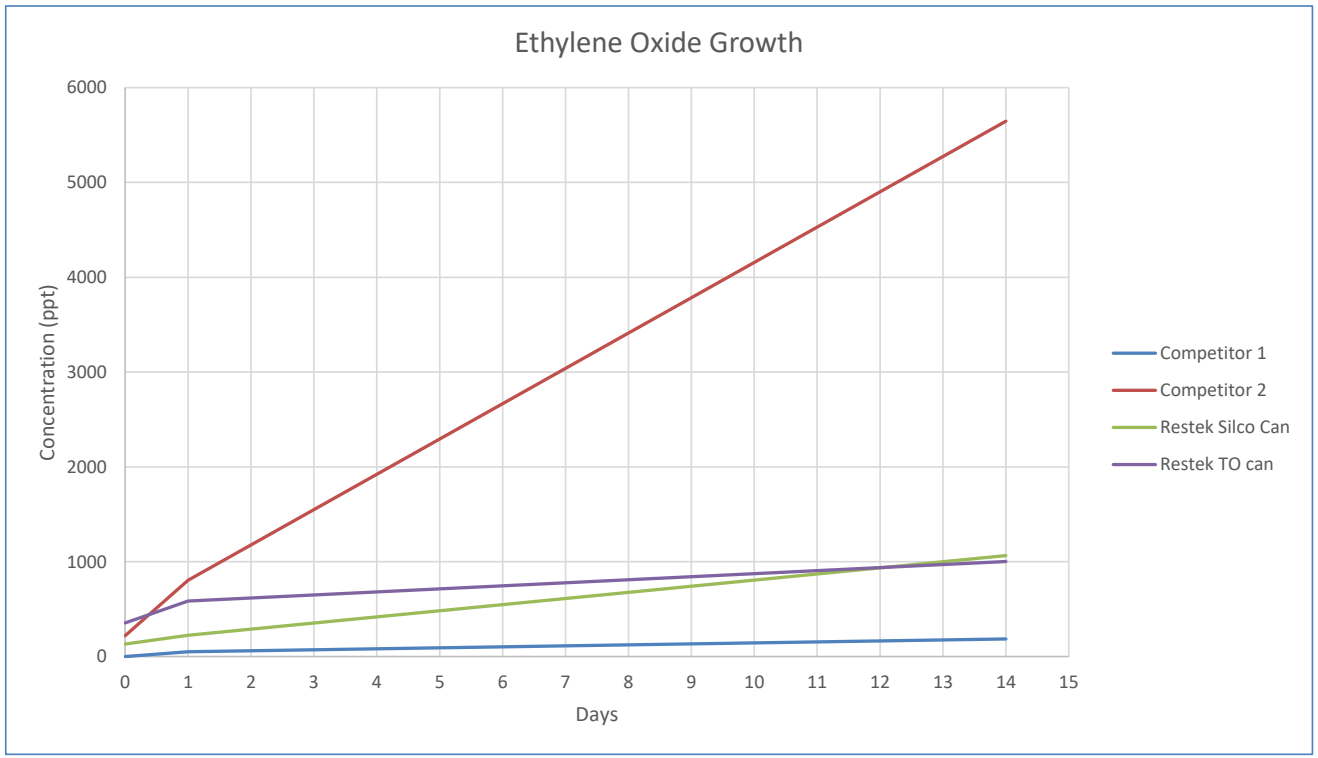
10°C start temperature

Ethylene Oxide Blanks – Fill gas

Humid Lab Air (ppt)	Dry Lab air (ppt)	Dry He (ppt)
132	ND	ND

- Each data set is an average of 3 different Restek canisters at different times.
- Humidity seems to play a key role in blank contamination for EtO

Ethylene Oxide Blanks – Growth Over Time

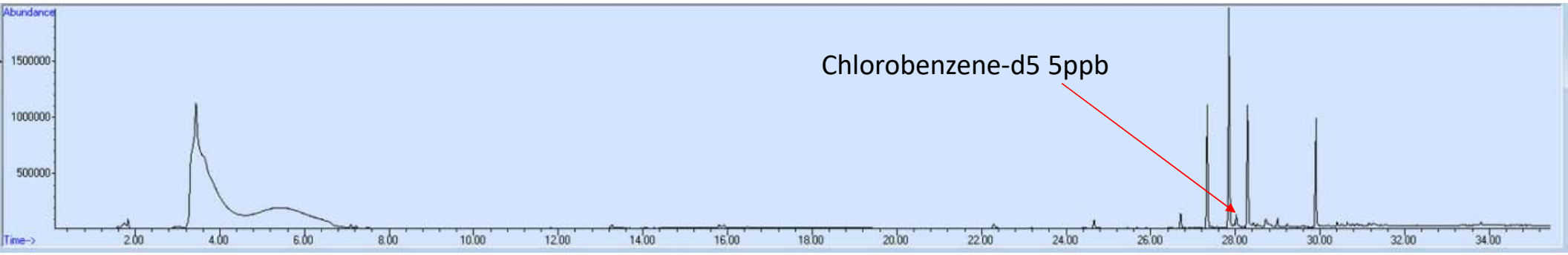


- N=3 for all data sets
- All canisters filled with 50% humid air to 30psi

Ethylene Oxide Blanks – Customer Canisters

	Humid Air (ppt)	Dry He (ppt)
Customer 1 Canister 1	242	ND
Customer 1 Canister 2	145	ND

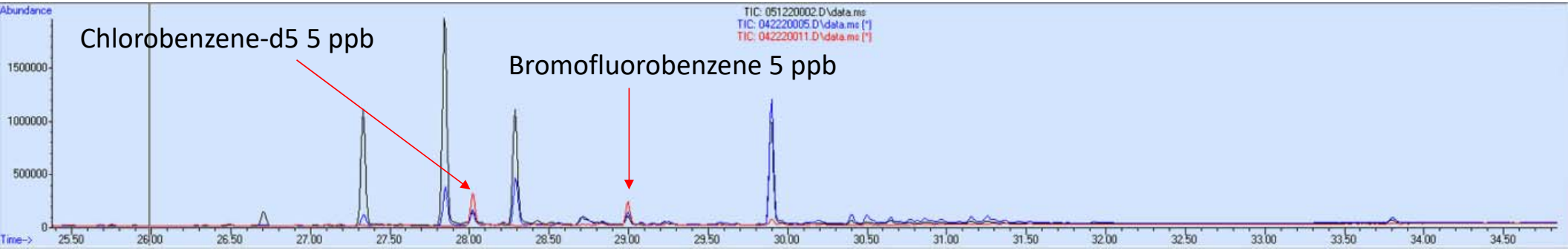
Ethylene Oxide Blanks – Customer Canisters



- Customer 1 canister 1 at 30 psig 50% RH air
- All TO-15A compounds detected at 500 ppt or less
- Large peaks from 27-30 minutes without good library match

- Customer 1 uses SIM for EtO analysis – possibly not seeing the large unknowns
- Customer 1 uses humid nitrogen as a blank, not humid air

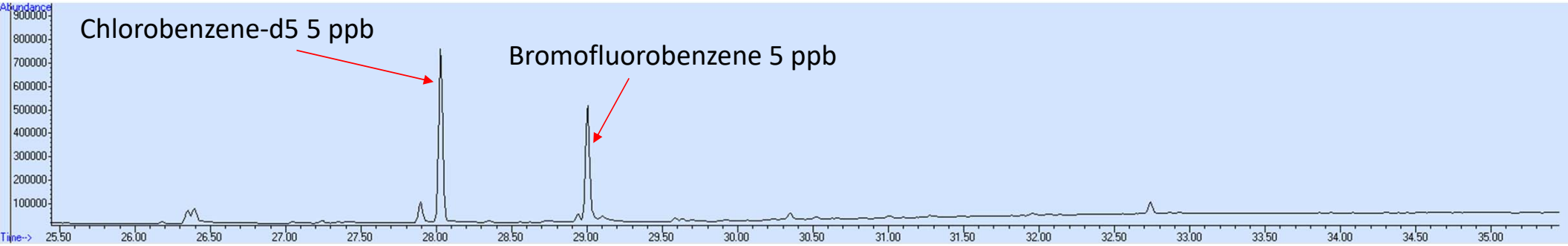
Ethylene Oxide Blanks – Customer Canisters



- Black- Customer 1 canister 1
- Blue – Competitor 2 canister
- Red – Restek TO canister

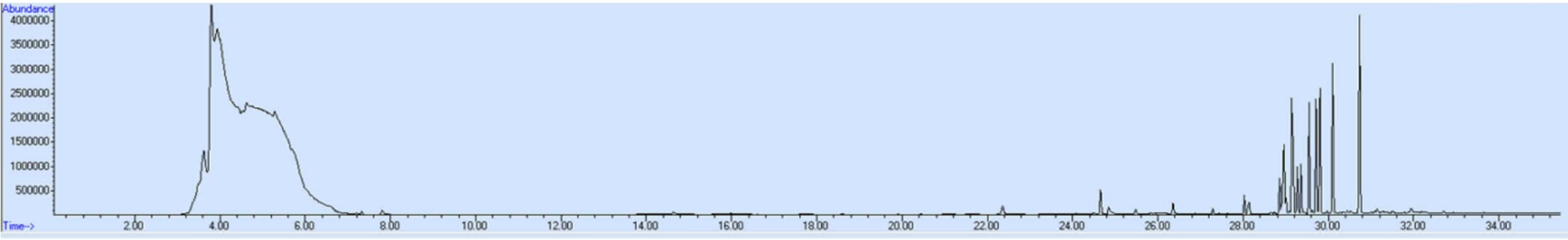
- Customer 1 canisters and Competitor 2 canisters show similar contamination and EtO growth

Ethylene Oxide Blanks – Customer Canisters

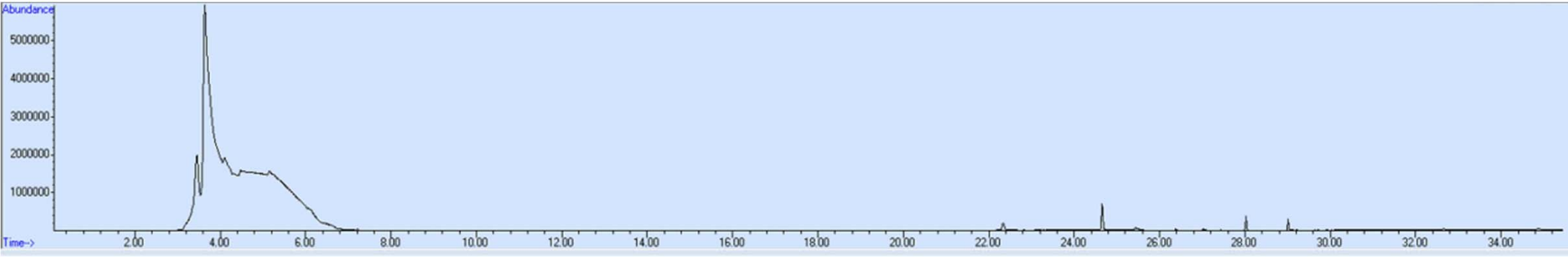


- Customer 1 canister post proprietary Restek cleaning
- EtO level from 242 ppt pre cleaning to ND post cleaning (tested after 7 days)

Ethylene Oxide Blanks – Customer Canisters

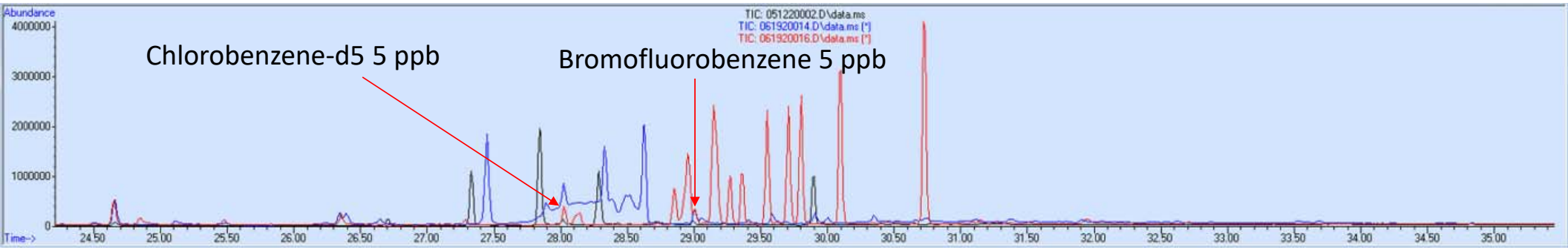


- Customer 2 Canister 1 pre-proprietary cleaning – EtO 5.9 ppb



- Customer 2 Canister 1 post-proprietary cleaning – EtO ND

Ethylene Oxide Blanks – Customer Canisters



- Black- Customer 1 canister 1
- Blue – Customer 2 canister 1
- Red – Customer 2 canister 2

- No consistent pattern to contamination peaks between canisters yet, but EtO contamination seems to be related to SVOC contamination.

Conclusions

- Simultaneous analysis of EtO with TO-15A compounds down to 50 ppt is possible using cryogenic cooling to resolve methanol and acetaldehyde interferences
- Dry, inert gas masks potential EtO contamination and growth that may be present in canisters
- EtO levels in humid air canisters increases over time
- All canister types appear to grow EtO with time. Not a new story for canister sampling (hint hint… acrolein)
- Greatest EtO increase comes from customer and competitor canisters with most SVOC contamination, possible link between cleanliness and EtO growth

Additional Considerations

- Customer 1 reported lab blanks were free of EtO

- Customer 1 cleans with nitrogen and fills blanks with nitrogen, which is an inert gas
  - Their humidity is probably 25% RH or less
  - We know this, as Restek OEMs the canister cleaning ovens customer 1 uses

- Previous results have demonstrated nitrogen results in artificially biased low canister blanks (Herrington et al., AWMA 2016)
  - This phenomenon has now been officially addressed in TO-15A (section 9.4.2)

Additional Considerations (cont'd)

- Air contains oxygen, which helps oxidize compounds (sometimes for the better and sometimes for the worse)
- All of the aforementioned ties in nicely with the observation that Customer 1 reported the introduction of ambient air (with humidity and oxygen) resulted in an increase in EtO
- Possibly the result of reactions with unknown higher molecular weight compounds shown before
- NOTE: These canisters should probably have never been deployed to the field based on those high (i.e., ~5 ppbv) hits of unknown compounds