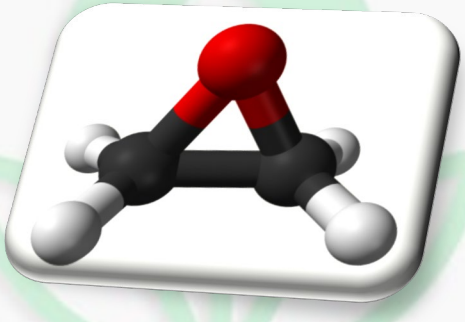
Ethylene Oxide Measurements by TO-15 Method



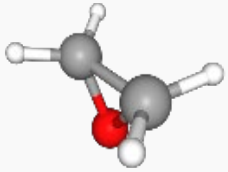
EPA/OAQPS/AQAD

Ambient Air Monitoring Group

Outline

- EtO basics and background information
- EtO analytical specifics using TO-15 method
- EtO co-elutions and issues with target ion for quantitation
- Method improvements for EtO analysis
- Summary
- Next steps

EtO physical chemical properties

- Chemical formula: C_2H_4O
- Chemical structure: 
- Molar mass:44.052 g/mol
- Vapor pressure: 1095 mmHg @20^{o}C
- Boiling point: 10.4^{o}C

EtO Methodological Challenges

- Standard Stability
  - ✓Primary and secondary source EtO standards procurement

NATTS TAD

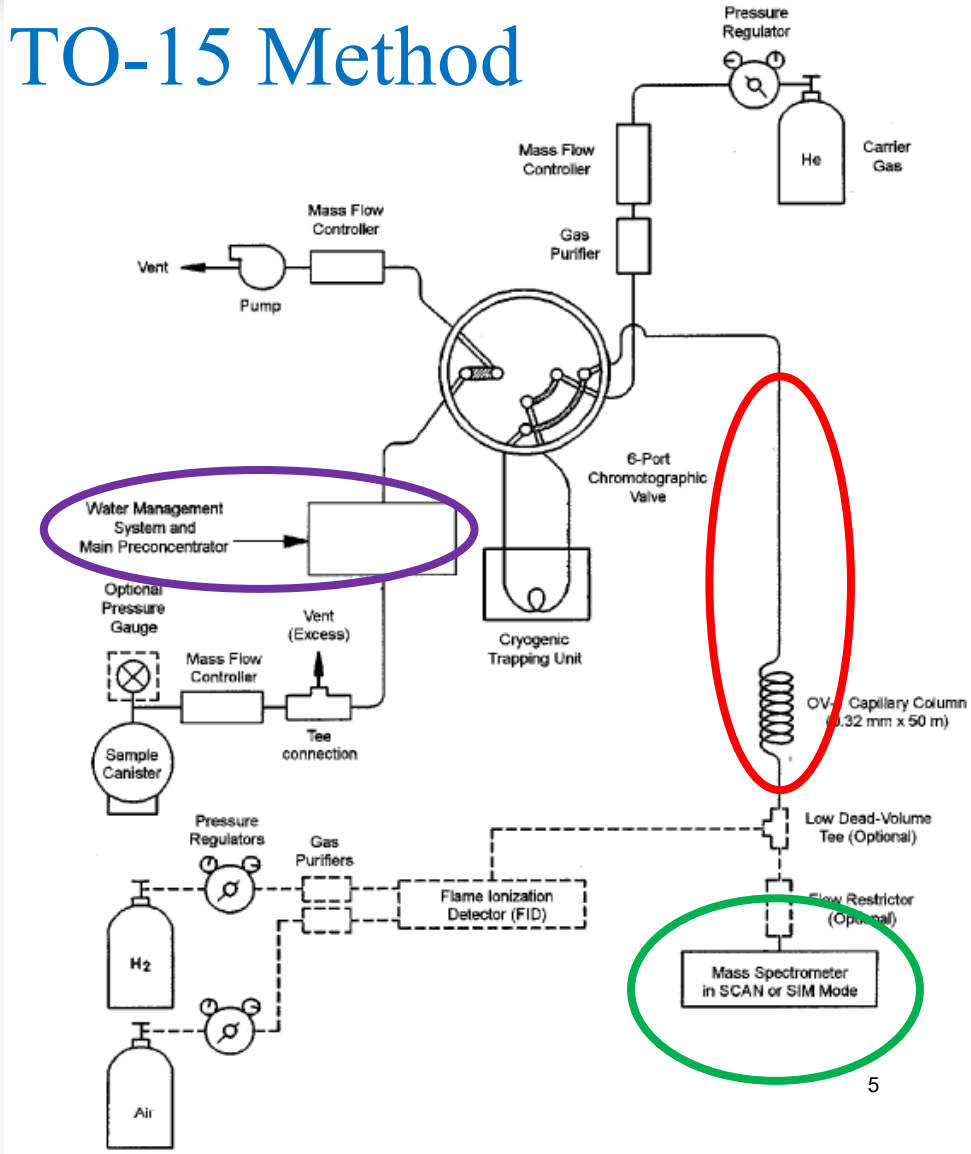
4.2.8.3.2 Secondary Source Calibration Standards. Secondary source stock calibration gases must be procured from a separate supplier and meet the criteria listed above in Section 4.2.10.3.1. A standard prepared with a different lot of source material from the same supplier as the primary calibration stock is only acceptable if it is unavailable from another supplier. As with the calibration stock gases, the secondary source stock must be recertified annually.

- Method Sensitivity
- Specificity (Co-elution)

GC/MS system

- ✓Preconcentrator
- ✓Capillary column
- ✓Mass spectrometer

TO-15 Method



EtO Measurement by GC/MS and TO-15

- Full spectrum scan
  - Lower analytical sensitivity and efficiency
  - Less uncertainty with full spectrum information collected for compound identification
- Selected ion monitoring (SIM)
  - Higher analytical sensitivity and efficiency (desired lower MDL)
  - Uncertainties and limitations due to decreased collected spectra information (possible interferant)

Example GC/MS running conditions

VOC GC/FID/MS Operating Conditions

Parameter	Operating Value
Sample Volume	250 mL
Restek R_{xi}-I_{ms} Capillary Column: Length: Inside diameter: Film thickness: Oven temperature:	 60 m 0.32 mm 1 µm -50°C for 5 minutes, 15°C/min to 0°C then 5°C/min to 150°C, then 25°C/min to 220°C for 1 minute then 25°C/min to 150°C for 4 minutes
Temperatures: FID: Injector Oven Temperature: MS Quad Temperature: MS Source Temperature:	 300°C 220°C 200°C 280°C (350°C 5975)
Gas Flow Rates: Column Carrier Gas (Helium (He)): FID Make-up (He): FID (Hydrogen (H_2)): FID (Air):	 2 mL/min 30 mL/min 30 mL/min 300 mL/min
Entech Sample Interface Conditions: Module 1 - Glass Bead/Tenax® Trap Initial Temperature: Module 2 - Tenax® Trap Initial Temperature: Module 3 - Cryofocuser Temperature:	 -150°C -50°C -196°C

VOC analytical system:

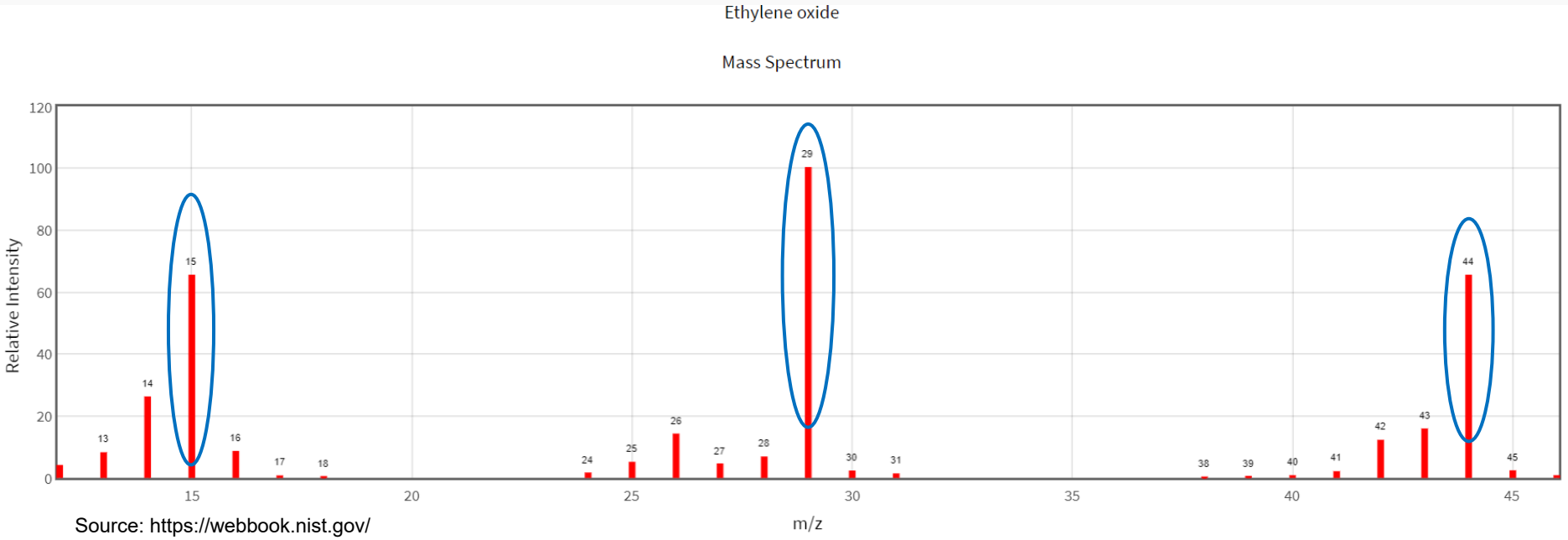
Entech 7200 Preconcentrator;

Agilent 6890 GC/FID coupled with an Agilent 5975 MS;

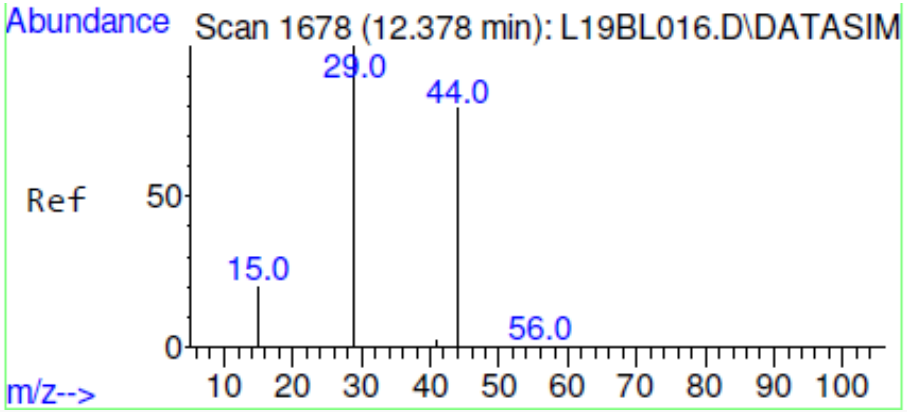
SIM mode.

https://www3.epa.gov/ttn/amtic/files/ambient/airtox/NATTS-UATMP-PAMS-SNOC-Analytical-Support-QAPP-2019.pdf

Target ion for quantitation



- Target ion 29 or 44
  - Issues discovered
- Qualifying ions: 15, 42, 43



Method Detection Limit Determination

- Over the course of three different dates
  - Prepare minimum of 7 different spiked canisters at a concentration below the calibration curve
  - Prepare minimum of 7 different method blank canisters
  - Analyze the prepared spiked and method blanks using established method
- Determine the MDL_{sp} and MDL_b
- Assign the laboratory MDL as the greater of these

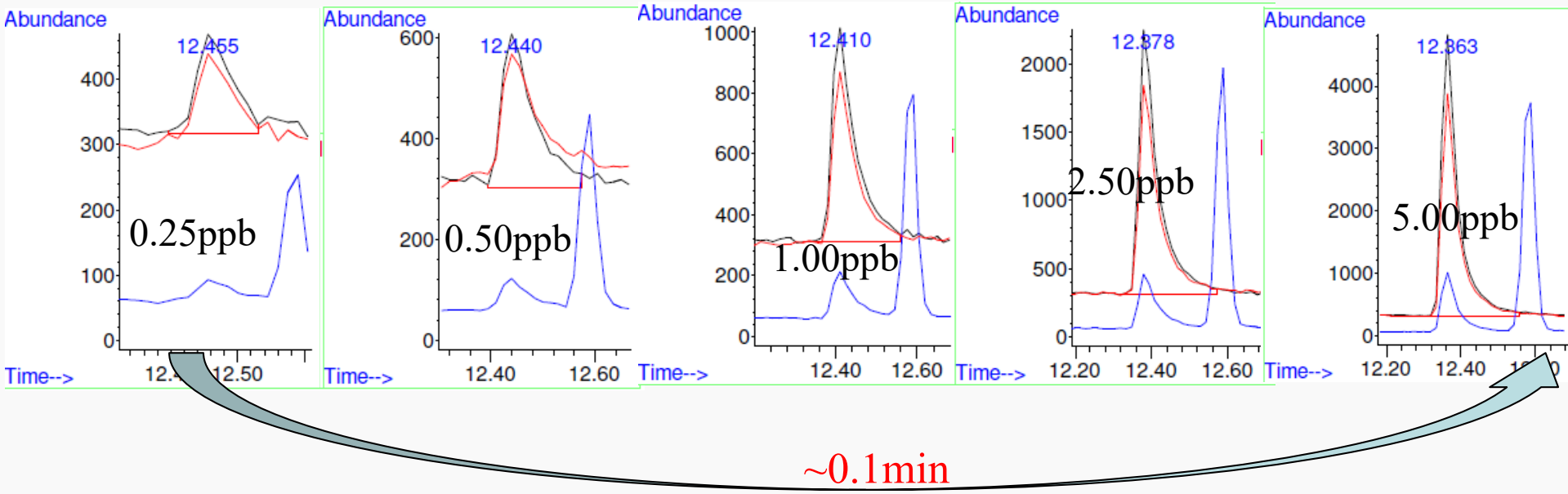
✓EPA's contract lab analyzed blank and spiked EtO canisters at 0.10ppb for MDL

✓Determined MDLs on 3 systems: 0.025-0.061ppb

✓EtO 100-in-1-million cancer risk level: 0.011ppb

Retention time shift

Gradual retention time shift as concentrations increase



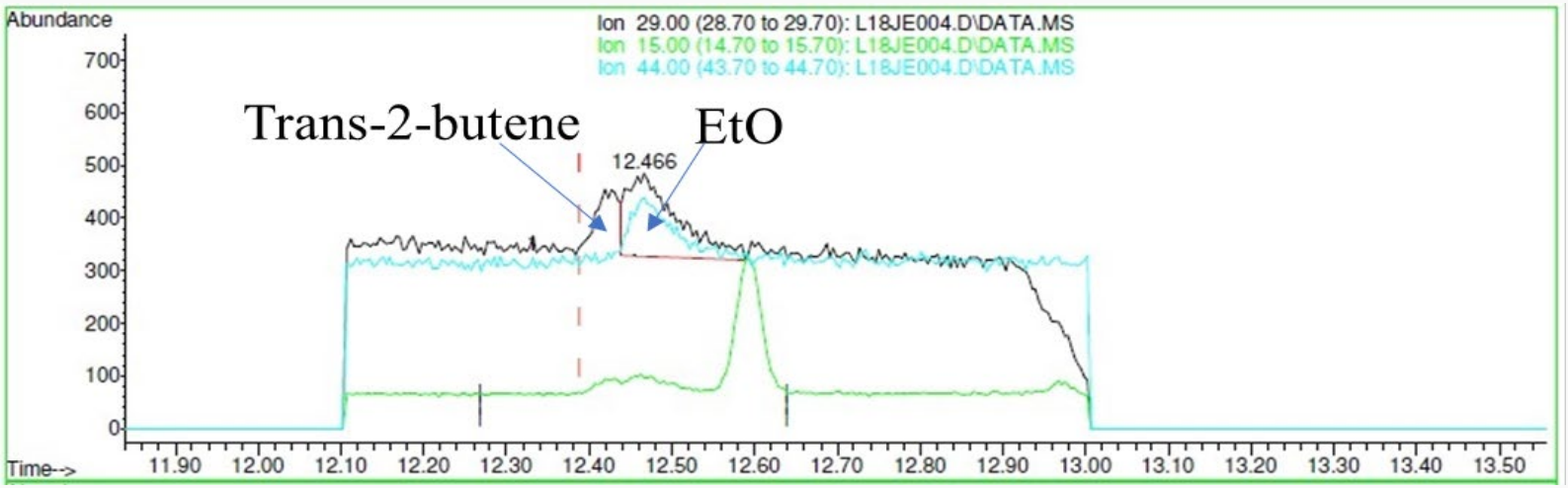
Peak retention time shift and tailing effect:

✓ Polar analyte by a nonpolar column

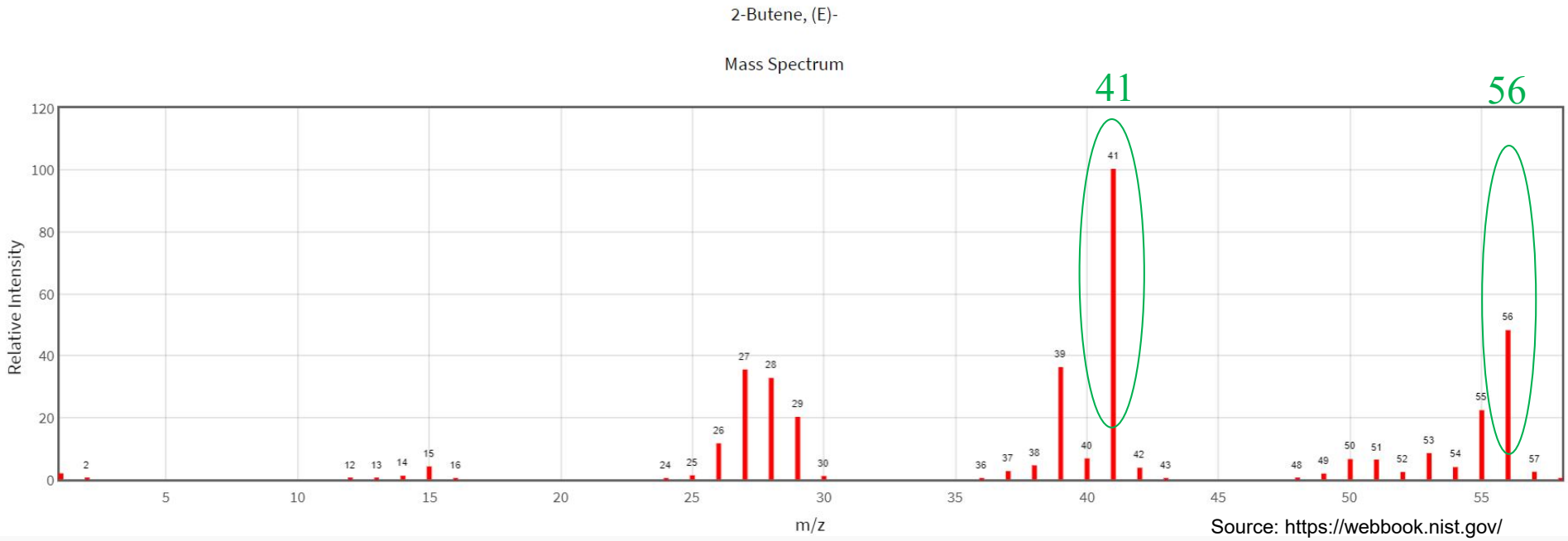
Co-elution evaluations

Potential interference analytes:

- Acetaldehyde
- Methanol
- Trans-2-butene



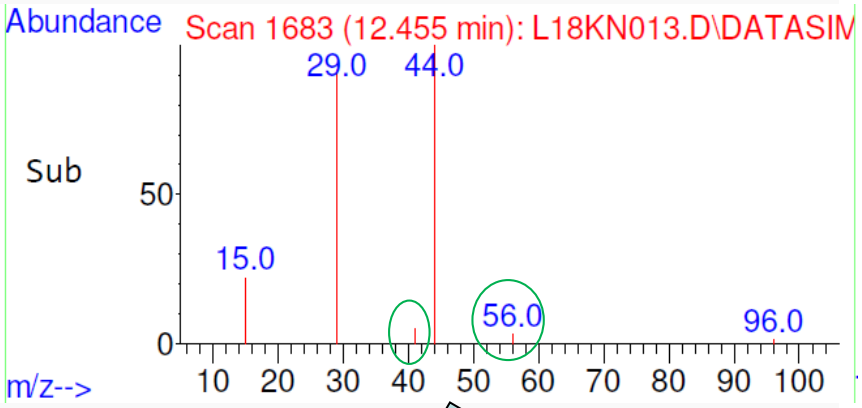
Trans-2-butene mass spectrum



Shared common fragment ions which are major/minor ions for EtO: 15, 29; 42, 43

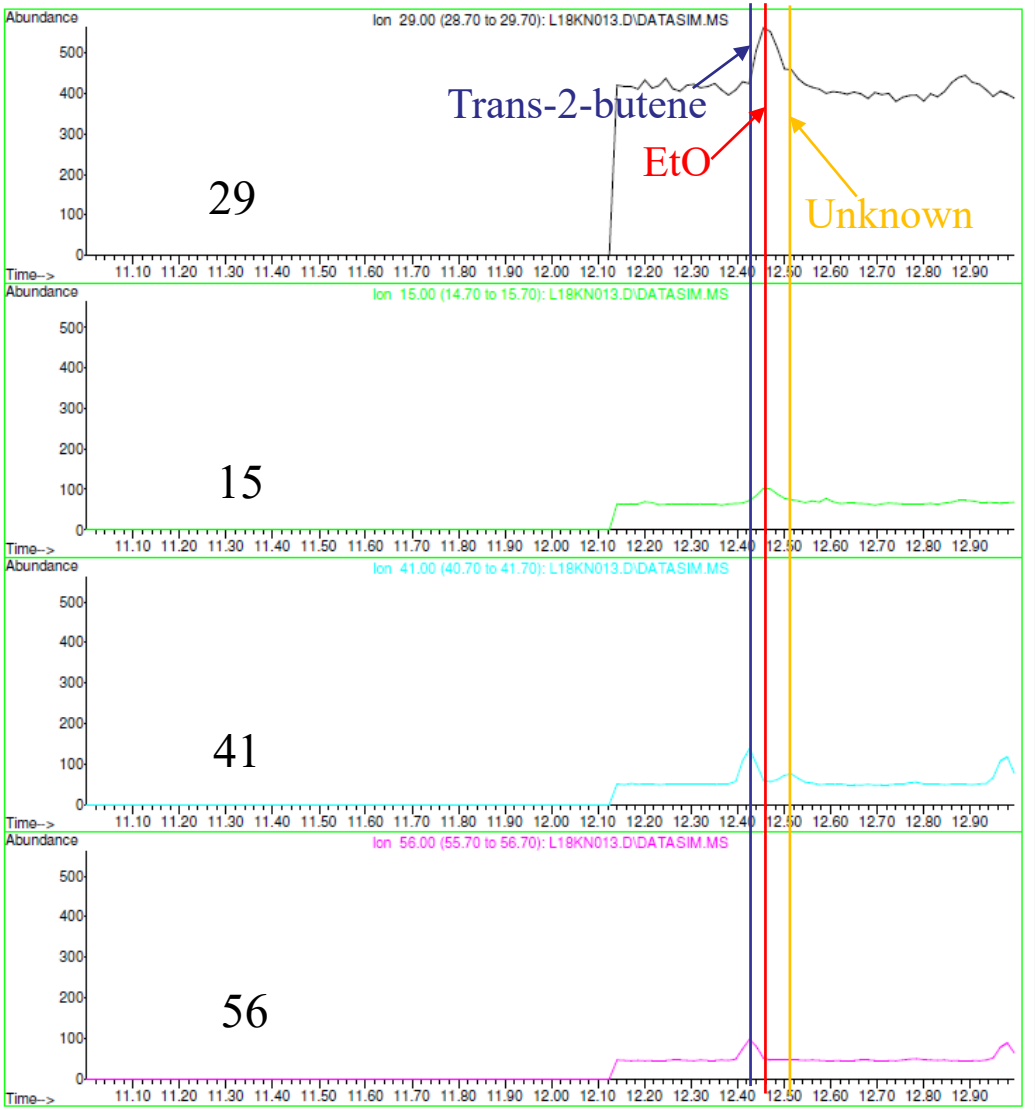
Issues with ion 29 for quantitation

EtO Measurement Technical Difficulties



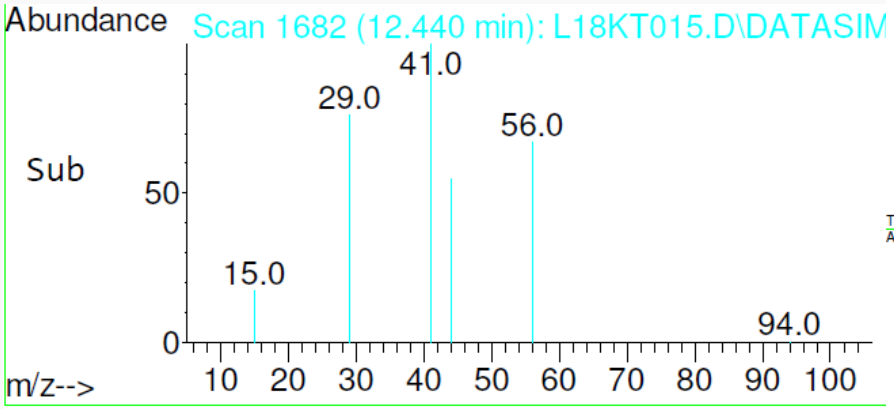
41 56

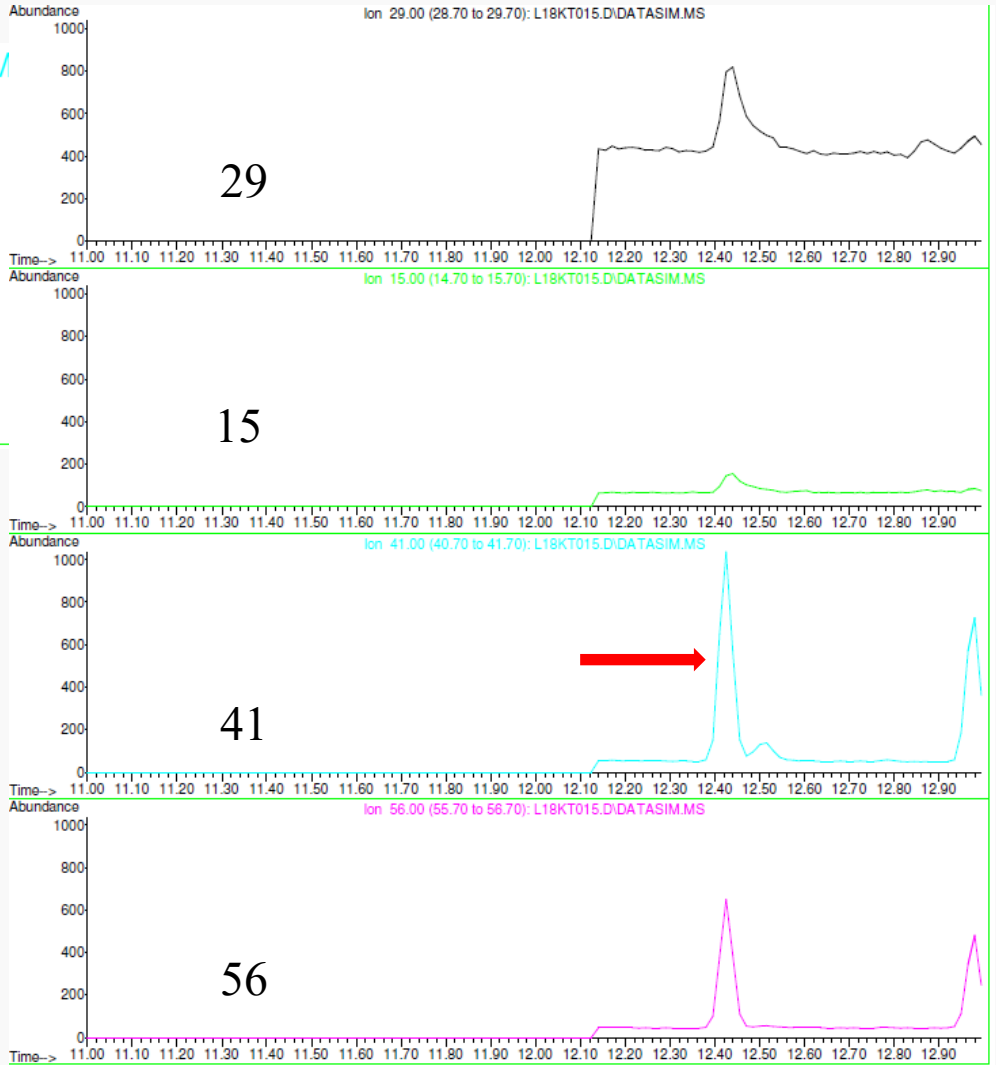
Co-elution indicators



- Retention times difference within 0.1min
- Biased high flag--LK

Unresolved peaks/beyond separation

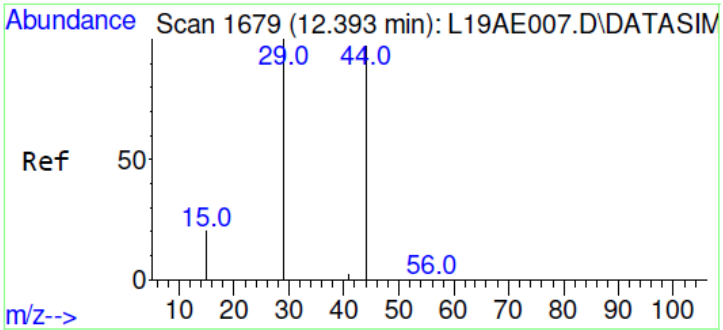




- Unresolved peaks
- Non-negligible Contribution to ion 29 from Trans-2-butene
- No clear inflection to split peaks
- Co-elution flag--BH

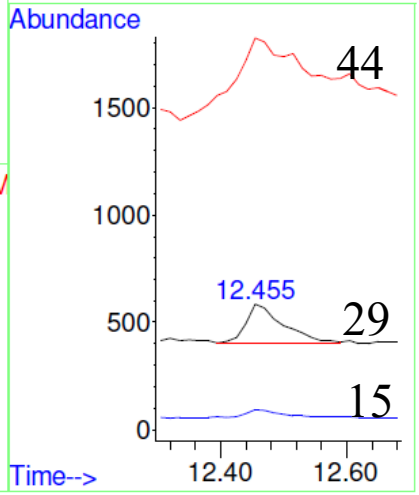
Issues with ion 44 for quantitation

Issues with ion 44-Example 1




```
#9
Ethylene oxide
Concen:    0.297 ppbv
RT:  12.455 min  Scan# 1683
Delta R.T.  0.062 min
Lab File:   L19AX016.D
Acq: 25 Jan 2019   1:29 am

Tgt Ion: 29 Resp:     748
Ion  Ratio  Lower  Upper
 29  100
 15   19.8   15.4   23.0
 44  402.7   77.4  116.2#
```



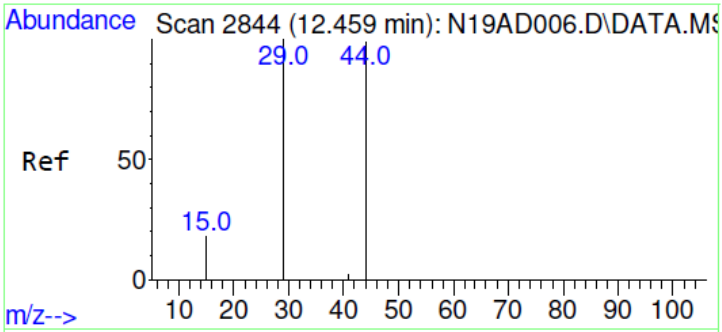
- Example sample spectra and chromatograms

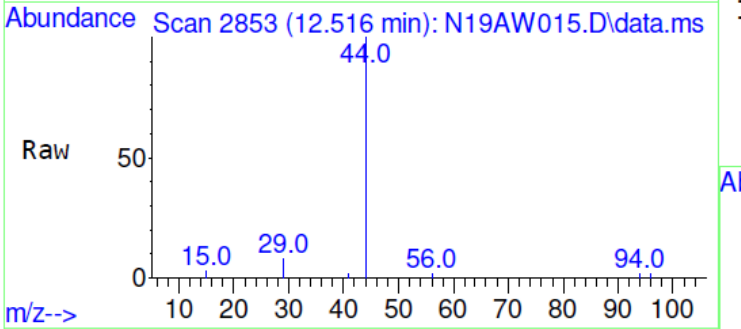
Ion 44 not ideal for quantitation

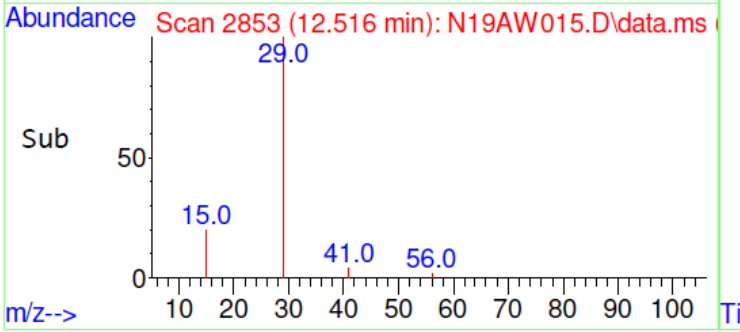
- Ion 44 – a lump and unresolved peak
- Ion 44 Abundance ratio to ion 29 extremely high

  ~ 4x ICAL

Issues with ion 44-Example 2

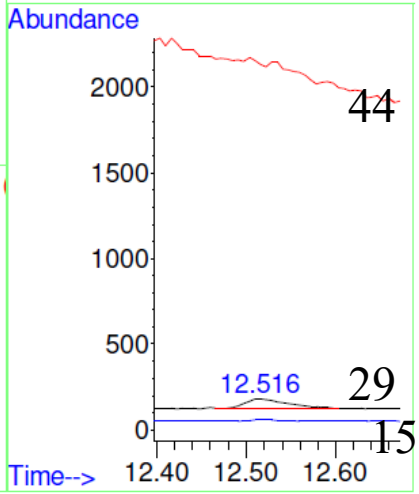







```
#9
Ethylene Oxide
Concen:    0.136 ppbv
RT:  12.516 min  Scan# 2853
Delta R.T.  0.057 min
Lab File:   N19AW015.D
Acq: 24 Jan 2019   4:28 am

Tgt Ion: 29 Resp:     191
Ion  Ratio  Lower  Upper
 29  100
 15   19.9   14.0   21.0
 44    0.0   79.2  118.8#
```



- Ion 44 not ideal for quantitation
- Baseline for ion 44 noisy and not on a reasonable flat base
- Difficult for software to accurately integrate
- Suspected leaks or CO_2 management issues

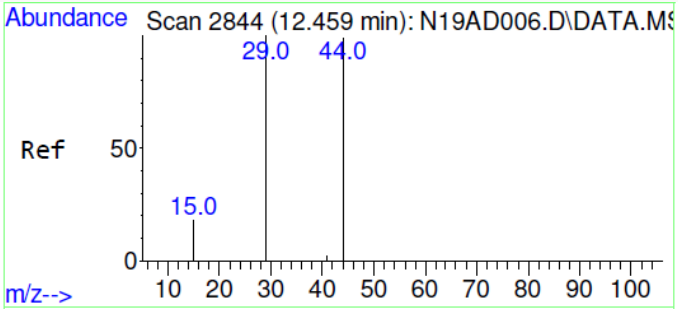
EtO Identification criteria

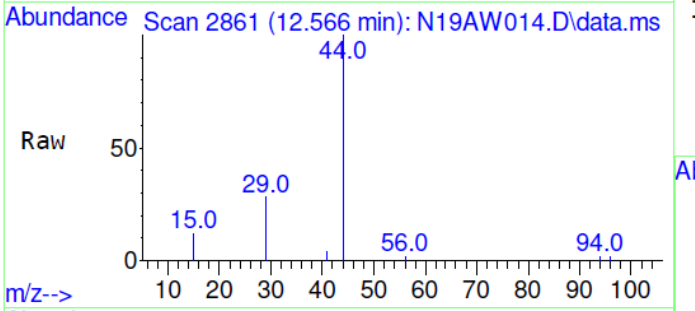
NATTS TAD

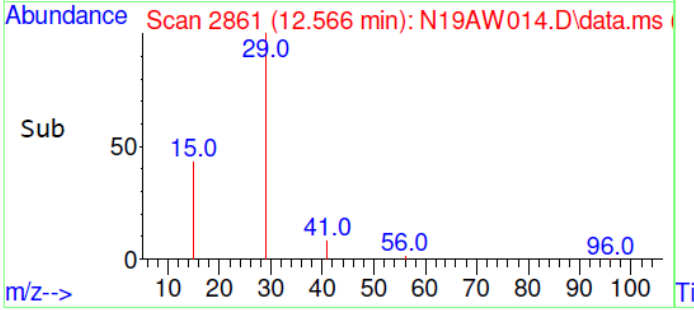
4.2.8.5.3 ***Compound Identification.*** Four criteria must be met in order to positively qualitatively identify a target compound:

1. The signal-to-noise ratio of the target and qualifier ions must be > 3:1, preferably > 5:1.
2. The target and qualifier ion peaks must be co-maximized (peak apexes within one scan of each other).[9]
3. The RT of the compound must be within the RT window as determined from the ICAL average.
4. The abundance ratio of the qualifier ion response to target ion response for at least one qualifier ion must be within ± 30% of the average ratio from the ICAL.

EtO Identification issues

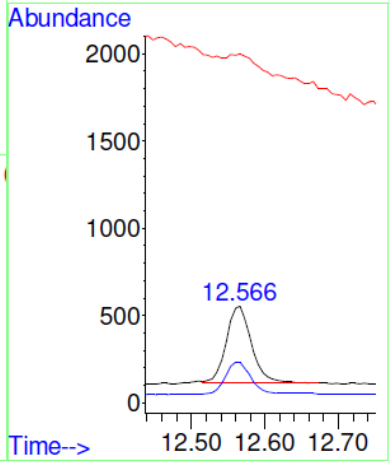






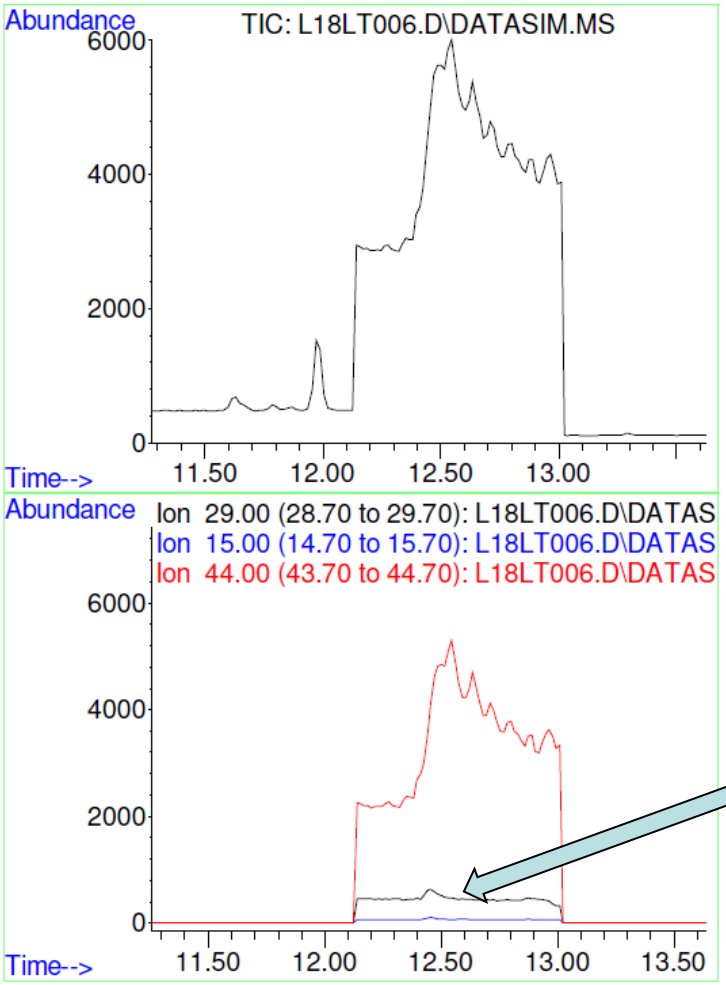

```
#9
Ethylene Oxide
Concen:    0.751 ppbv
RT:  12.566 min  Scan# 2861
Delta R.T.  0.107 min
Lab File:   N19AW014.D
Acq: 24 Jan 2019   3:26 am

Tgt Ion: 29 Resp:    1058
Ion  Ratio  Lower  Upper
 29  100
 15  42.2   14.0   21.0#
 44   0.0   79.2  118.8#
```



- Retention time deviation
- Qualifier ion abundance ratio outside of ±30%
- Misidentified as EtO by Chemstation

EtO Identification issues-ND



#9
Ethylene oxide
Concen: N.D.
Expected RT: 12.38 min

Lab File: L18LT006.D
Acq: 20 Dec 2018 9:34 am

Tgt Ion: 29

Sig	Exp Ratio
29	100
15	20.3
44	90.0

- Obvious ion 29 peak;
- S/N>3;
- When manually integrated, EtO~0.23ppb

❖Software inappropriately assign sample as non-detect; peak not recognized

✓Peak rejection threshold set too high

✓Adopt S/N tool

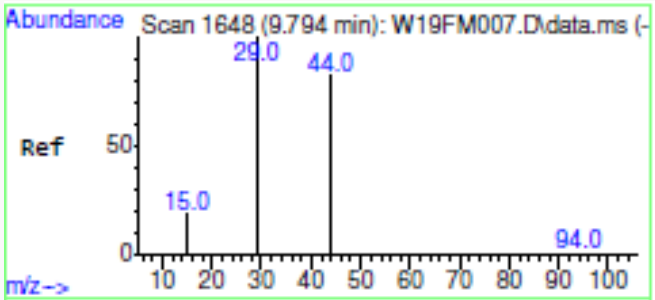
✓Need to review chromatograms and spectra by analyst

Method improvements for EtO measurements by TO-15

Method Improvement for EtO Co-elutions

- ❖ Adjust chromatographic parameters
  - ✓ Choose different target ion for quantitation and identification
  - ✓ Change oven temperature program
    - ➢ Ramp more slowly
    - ➢ Begin at sub-ambient temperature
    - ➢ Increase temperature around EtO elution window– might make peak shape sharper
- ❖ Change column
  - ✓ Increase polarity of stationary phase (e.g., DB-624 column)
- ❖ https://www.restek.com/ezgc

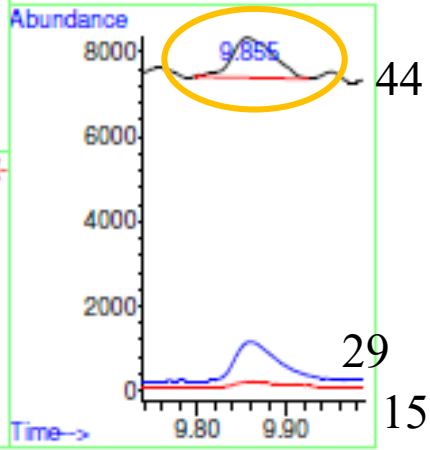
Improved CO_2/water management and ion 44 peaks



#9
Ethylene oxide
Concen: 0.341 ppbv m
RT: 9.855 min Scan# 1662
Delta R.T. 0.061 min
Lab File: W19GC007.D
Acq: 03 Jul 2019 05:23 pm

Tgt Ion: 44 Resp: 3094

Ion	Ratio	Lower	Upper
44	100		
29	110.5	85.3	158.3
15	19.6	14.6	27.0

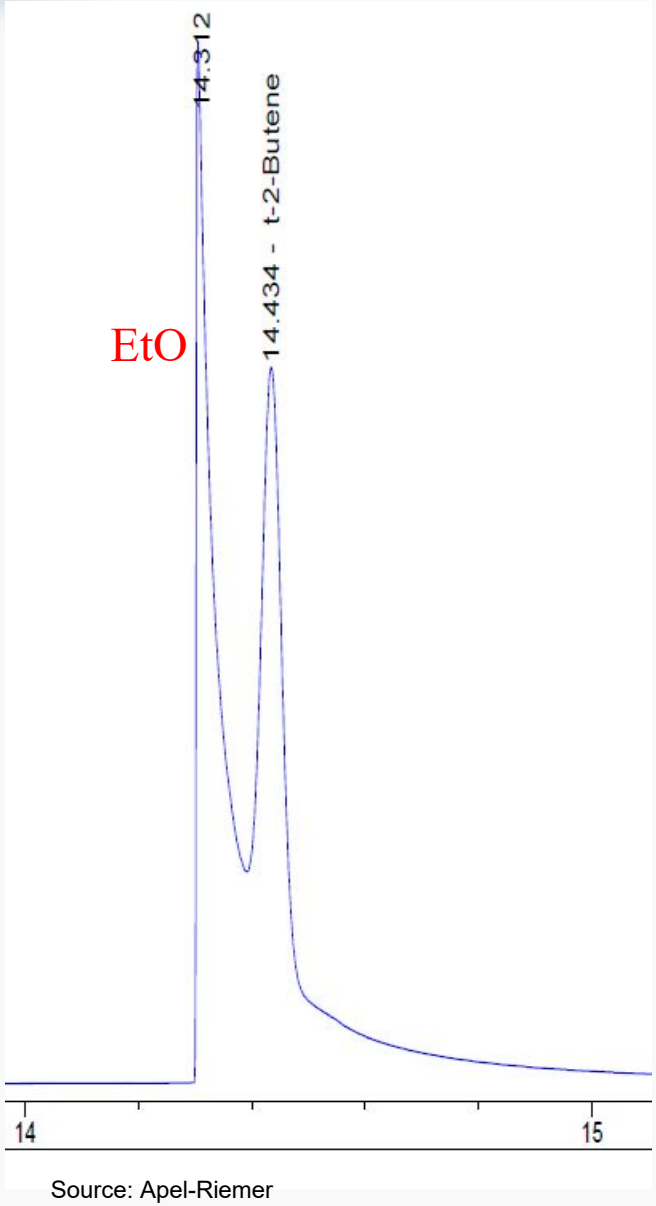


- ❖Ion 44 as target ion
- ✓Baseline for ion 44 improved
- ✓EtO ion 44 peak distinct and clear shaped
- ✓Ion 44 absent from trans-2-butene

EtO Co-elution Improvement

Longer non-polar column—DB-1 100m

- ❖Better separation for EtO and co-elutions
- ❖May alter retention order
- ❖Longer running time per sample

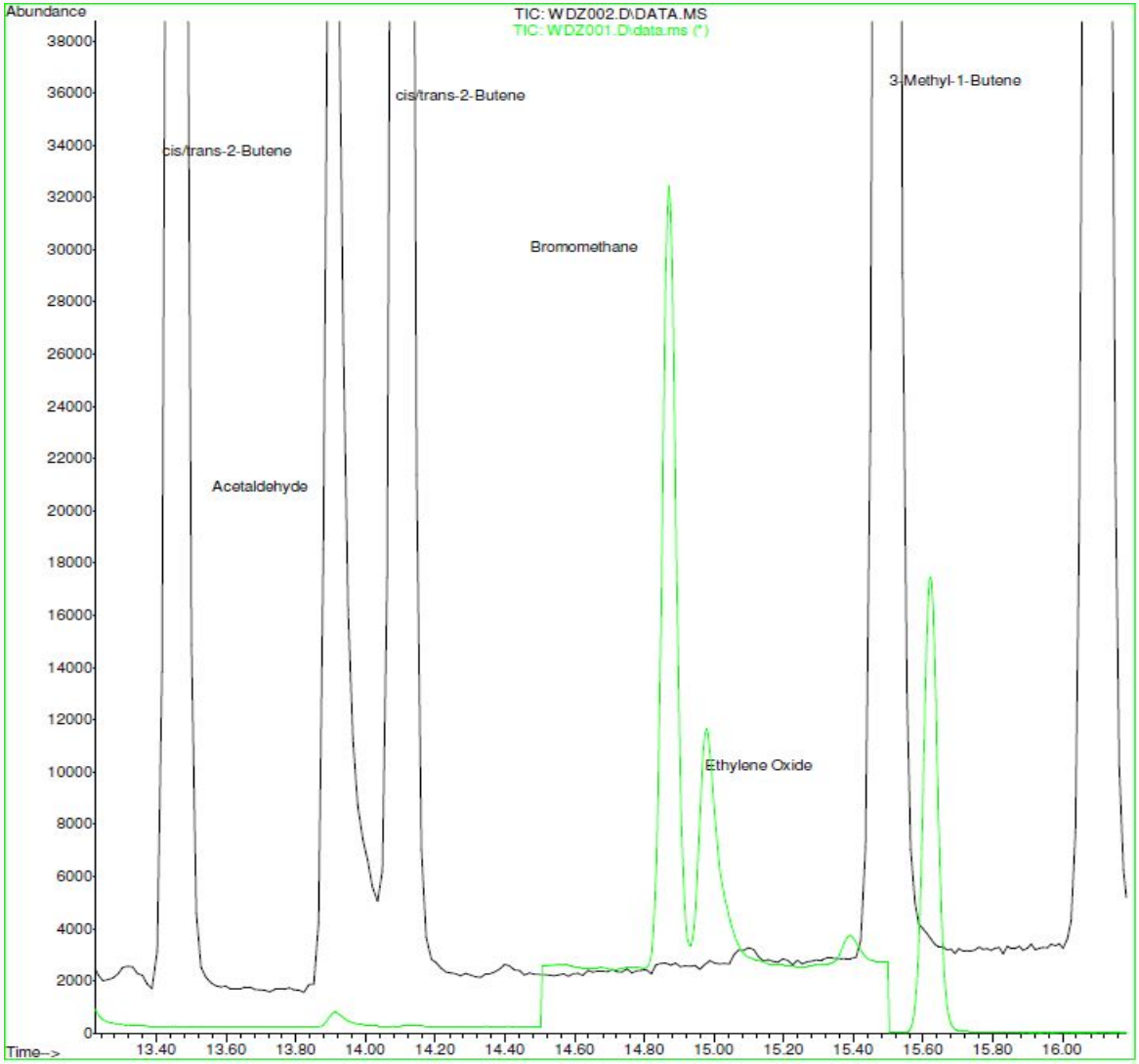


Source: Apel-Riemer

EtO Co-elution Improvement

Slightly polar column- DB-624

- ❖Better separation for EtO and co-elutions
- ❖Altered retention order
- ❖May reduce performance for other target analytes



EtO TO-15 Method Evaluations

- Determine method detection limit (MDL)
  - ✓ Determine the MDL_{spike} and MDL_{blank}
- Verify canister cleanliness
- Evaluate EtO stability in canisters
  - ✓Canister zero stability checks
  - ✓Canister known standard stability checks
- Verify sampling unit cleanliness
  - ✓Zero air challenge
  - ✓Known standard challenge

Summary

- ❖EtO measurements can achieved by typical TO-15 method setup, however with limitations
  - ➢MDL not as low as desired even with SIM
  - ➢Slight retention time shift and observed tailing on typical nonpolar column used
  - ➢Lower MDL and consistent retention time could be achieved by a polar column, but performance of a few low MW analytes reduced

Summary

- Issues with the most abundant ions for quantitation
  - Ion 29—co-elutions (one identified as trans-2-butene)
    - ✓ Monitor additional ions 41 and 56 to aid EtO identification and quantitation, however may reduce sensitivity
    - ✓ Co-elution indicator—shoulder peak or inflection
    - ✓ Appropriate data qualifiers(e.g., LK and BH)
  - Ion 44—CO_2 or water management issues
    - ✓ Leak checks
    - ✓ Optimize pre-concentrator settings
- Assess appropriate peak rejection threshold
- Review chromatograms and spectra for proper identification

Next steps—EtO research

- EPA ORD started study on EtO stability in cylinders
  - EtO calibration standards from vendors who supply EtO, concentration from 100ppb to 100ppm range
  - A blend of EtO with stable SF_6 to monitor concentration ratios over time by FTIR
- EPA ORD lab will further investigate co-elutions with EtO
  - Two GC systems set up with TO-15 capability
    - ✓Typical GC/MS coupled with nonpolar column
    - ✓GC/TOF-MS coupled with slightly polar DB-624 column
  - Analyze samples from subset of NATTS/UATMP sites with observed EtO co-elution to identify interferants

Next Steps—Proficiency Tests

EtO Implementation Plan[4]

Task	Responsible agency	Expected timeline	Note
Obtain EtO standards	NATTS labs	July-September 2019	OAQPS to provide a list of vendors and recommended standard concentrations
Provide training and assistance to NATTS labs	OAQPS	July-August 2019	OAQPS to provide technical details for EtO analysis through webinars, schedule TBD
Revise QAPP to add EtO to TO-15 compound list	NATTS labs	July-September 2019	
Conduct initial method setup and MDL study	NATTS labs	July-December 2019	
Evaluate EtO for PT procedures (method demonstration)	Battelle	August-September 2019	
Spike first PT VOC samples including EtO	Battelle	August-September 2019	
Analyze quarterly PT samples and report data back*	NATTS labs	September 2019-August 2020	Increased VOC PT frequency to accommodate NATTS labs progress
Analyze canister samples from NATTS sites	NATTS labs	Once analytical method setup and evaluations completed (preferably by January 2020)	
Report EtO data to AQS	NATTS labs	Preferably by July 2020	

* PT VOC test frequency will be increased to once per quarter for the first year starting September 2019.

- ✓Battelle to conduct EtO method demonstration by evaluating spiked canisters with EtO and 15 other VOCs
- ✓First PT VOC samples expected – 3rdQ 2019
- ✓VOC PT anticipated to increase to every quarter
- ✓Non-NATTS labs can opt in

Thanks!

Questions?