A Presentation by OI Analytical

Oxygenate Analysis on the Eclipse Purge-and-Trap Sample Concentrator

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Introduction

- Oxygen-containing compounds are frequently used as fuel additives
  - *Boost octane rating*
  - *Fuel burns more cleanly*
- Ethers (e.g., MTBE) and alcohols (e.g., TBA) are the most common oxygenate additives
- Soil and groundwater can become contaminated through leaking underground storage tanks
- UST program generated lots of oxygenate data, using multiple methods

Introduction

- Currently no validated performance-based method
- Two determinative methods are recognized as most appropriate by the USEPA
  - *Method 8260 (GC/MS)*
  - *Method 8015 (GC/FID)*
- Two preparative methods are most appropriate for low-level detection
  - *Method 5030 (P&T)*
  - *Method 5035 (closed system P&T)*

Project Objective

- Develop instrument operating conditions that produce the best performance for oxygenate compounds
  - *TBA, MTBE, DIPE, ETBE, TAME*
  - *California list*
- One change to the standard GC/MS operating conditions
  - *Add oxygenate compounds to the calibration mix*
- Minimal changes to P&T conditions so oxygenates can be included in standard Method 8260 analyses

Project Variables

- Sample size
  - *5 mL, 10 mL, and 25 mL*
- Sample temperature
  - *Ambient, 35 °C, 45 °C, and 60 °C*
- Trap selection
  - *Tenax®, silica gel, carbon molecular sieve (OI Analytical #10)*
  - *VOCARB® (OI Analytical #11)*

Test of System Performance

- Calibration
- Limit of Quantitation (LOQ)
- Statistical MDLs
- Water management
- Analyze a real-world sample

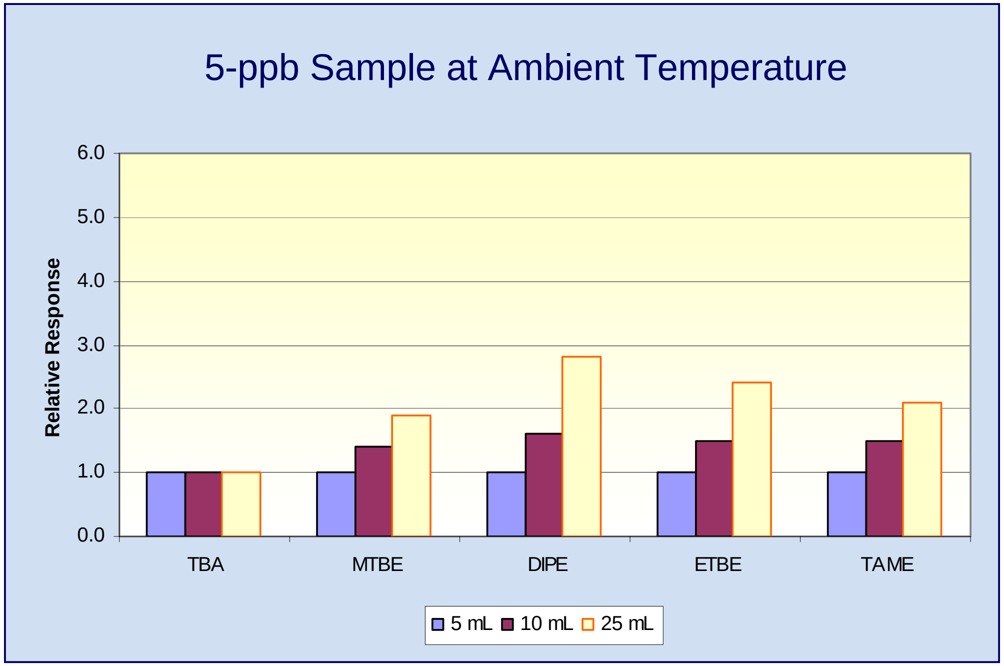
Instrumentation

Xenco Laboratories, Houston, TX

- OI Analytical Model 4660 Eclipse Purge-and-Trap Sample Concentrator
- OI Analytical Model 4552 Water/Soil Autosampler
- Agilent® 6890N GC with 5973 Inert MS

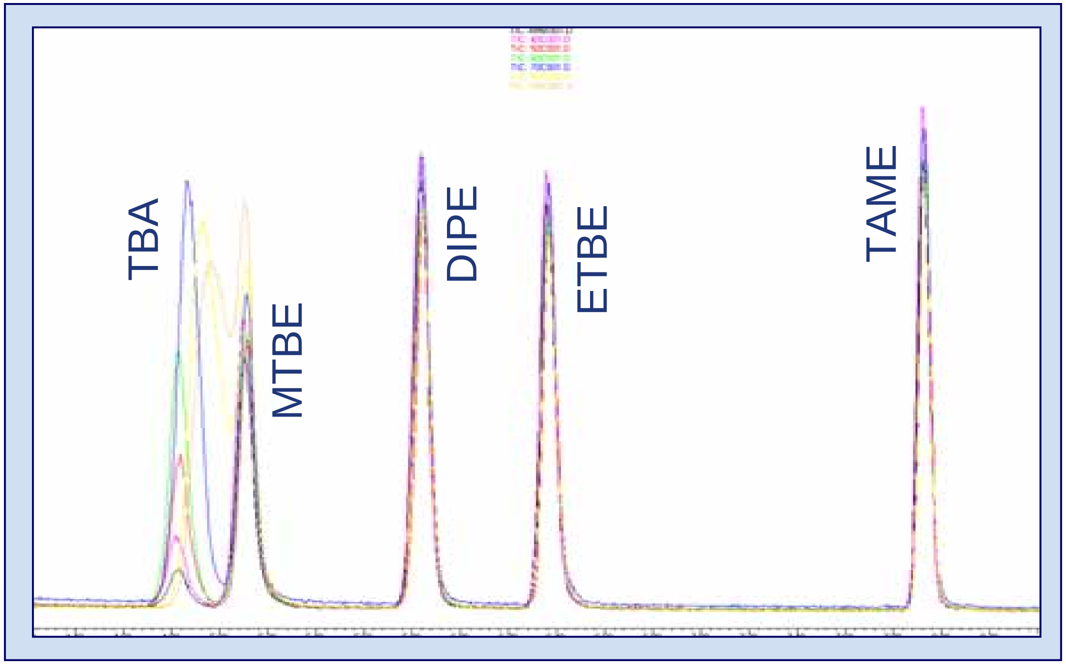
Sample Size Results

- Ether response increased with sample size
- TBA response remained steady
- Similar results at all temperatures and both traps



Sample Temperature Results

- TBA response increased with temperature
- Ether response stayed approximately the same
- Similar results at all sample sizes and both traps



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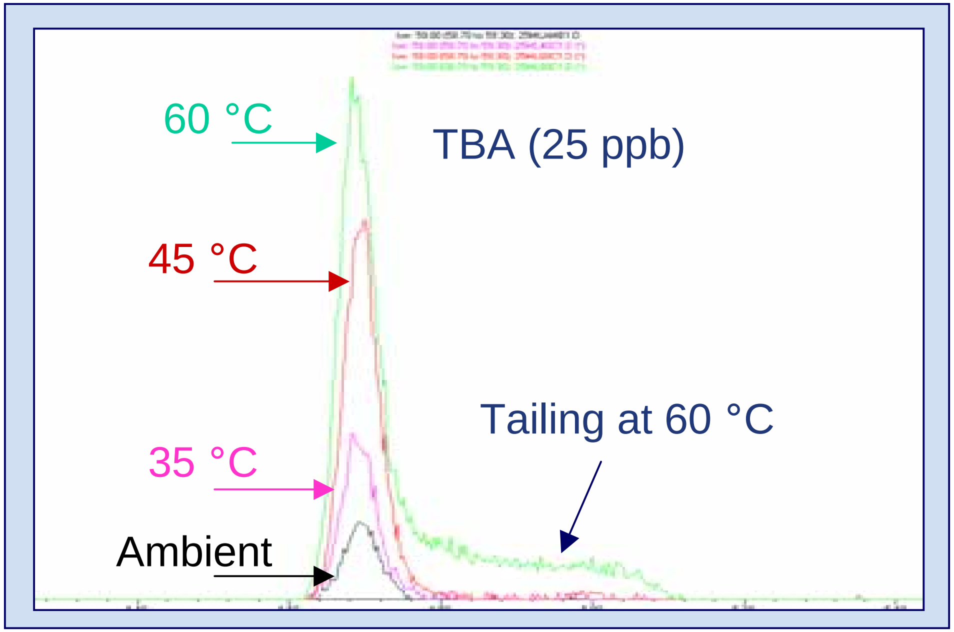
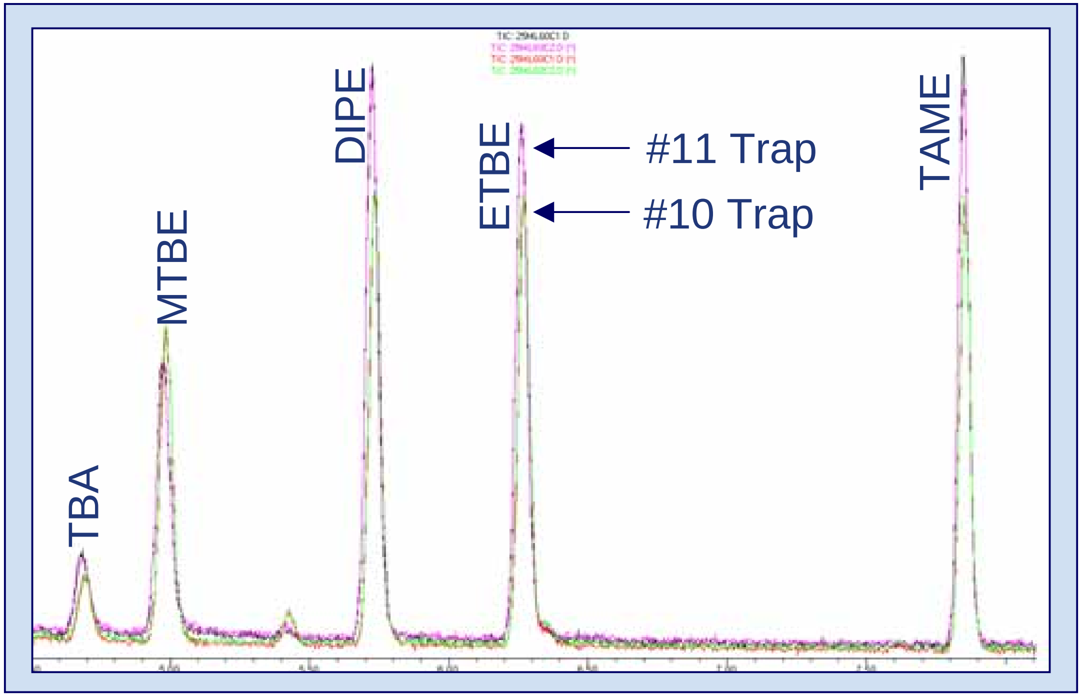
TBA Tailing at 60 °C

- TBA may tail at high temperatures
- Extra H_2O purged onto the trap at higher temperatures
  - *H_2O-soluble, difficult to focus*
  - *TBA moves with H_2O through the trap*



Trap Selection Results

- Slightly better sensitivity on the VOCARB (#11) trap, ~5%
  - *VOCARB is a more hydrophobic material*
- Both traps provide excellent chromatography



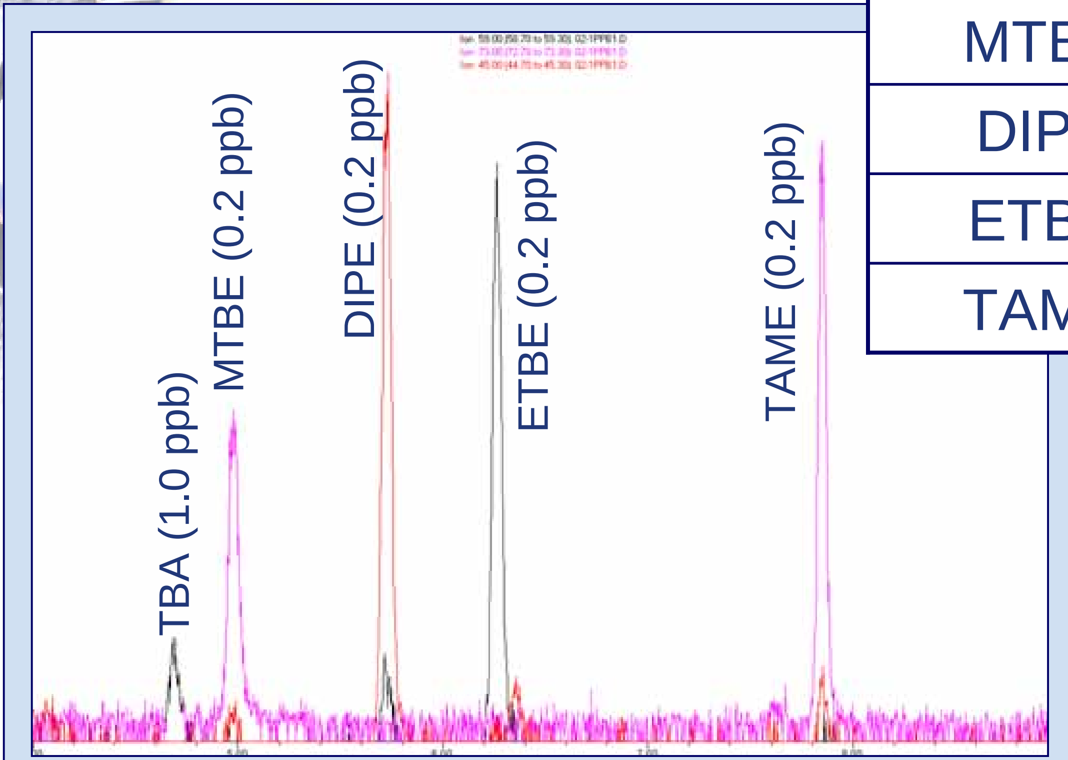
Calibration Results

- Passed all Method 8260 calibration criteria
- Not necessary to use less desirable linear calibration mode and correlation coefficient (R^2)

Calibration			
Compound	Range	Avg. RRF	%RSD
TBA	1.0–1,000	0.017	12.3
MTBE	0.2–200	0.497	7.8
DIPE	0.2–200	0.693	7.4
ETBE	0.2–200	0.606	9.4
TAME	0.2–200	0.516	9.2

LOQ and MDL Results

Compound	LOQ (ppb)	St.MDL (ppb)
TBA	1.0–2.0	1.40
MTBE	≤0.2	0.05
DIPE	≤0.2	0.04
ETBE	≤0.2	0.05
TAME	≤0.2	0.03



- 25-mL sample size
- 45 °C
- VOCARB trap

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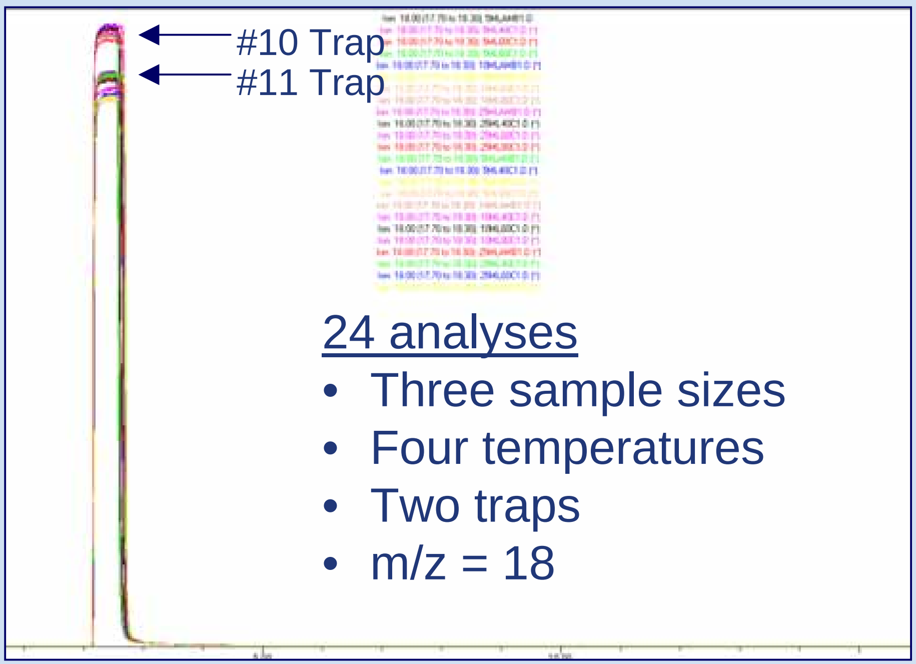
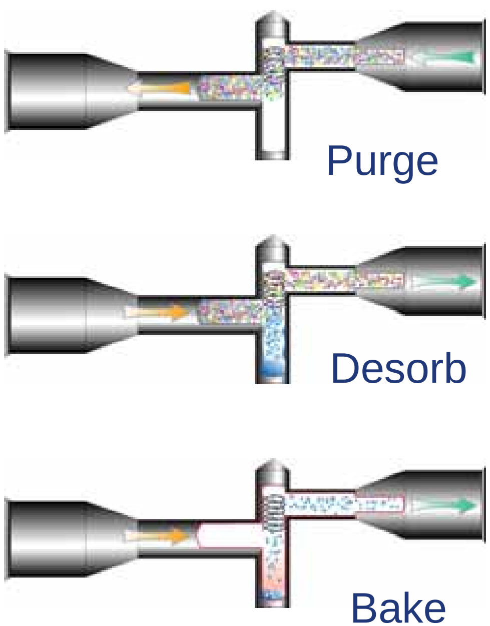
Water Management Results

- Efficient and consistent H_2O removal using the patented Water Management Fitting (WMF)
- Regardless of sample size, temperature, or trap



<u>24 analyses</u>

- Three sample sizes
- Four temperatures
- Two traps
- m/z = 18



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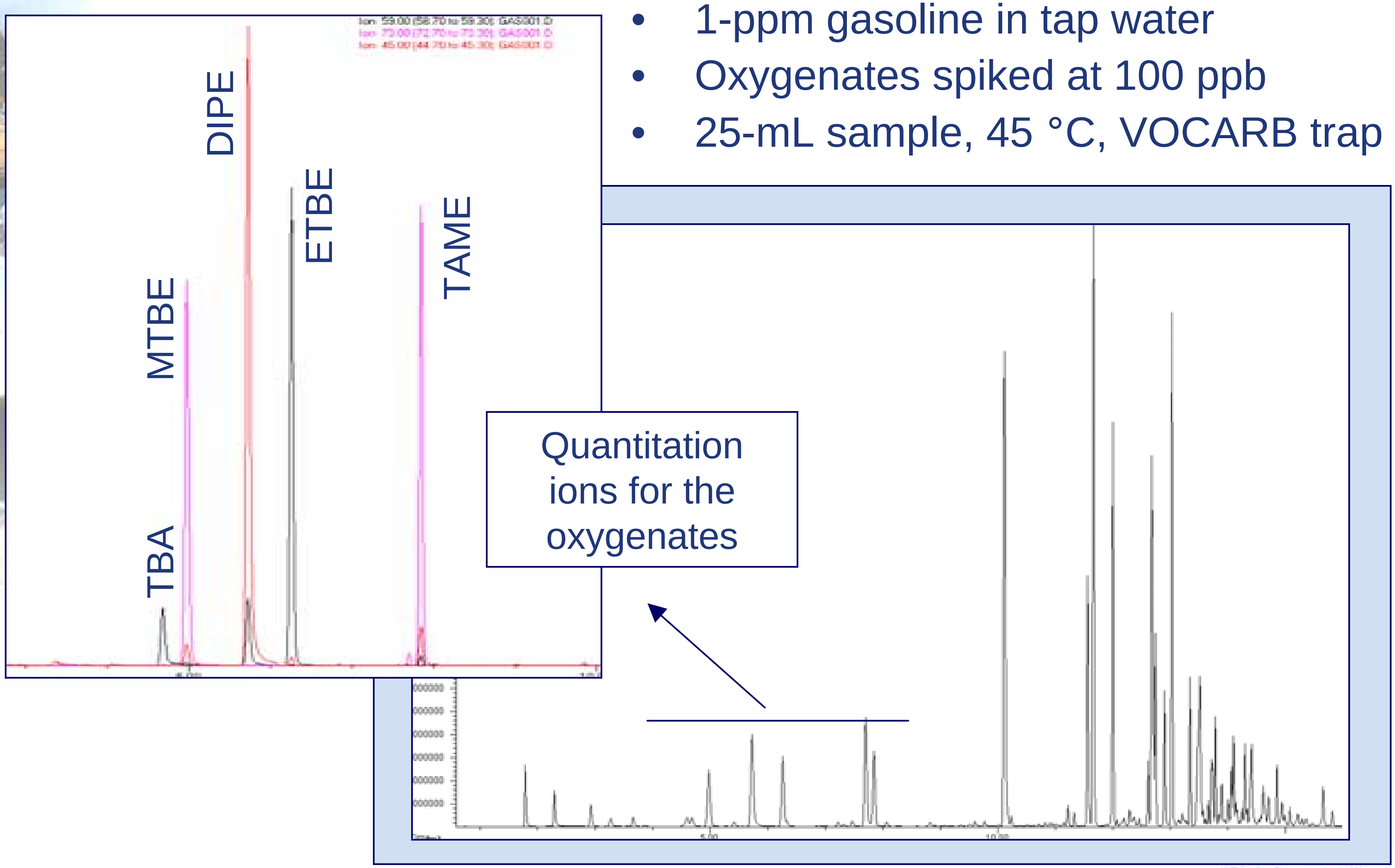
Analysis of Real-World Sample

- 1-ppm gasoline in tap water
- Oxygenates spiked at 100 ppb
- 25-mL sample, 45 °C, VOCARB trap



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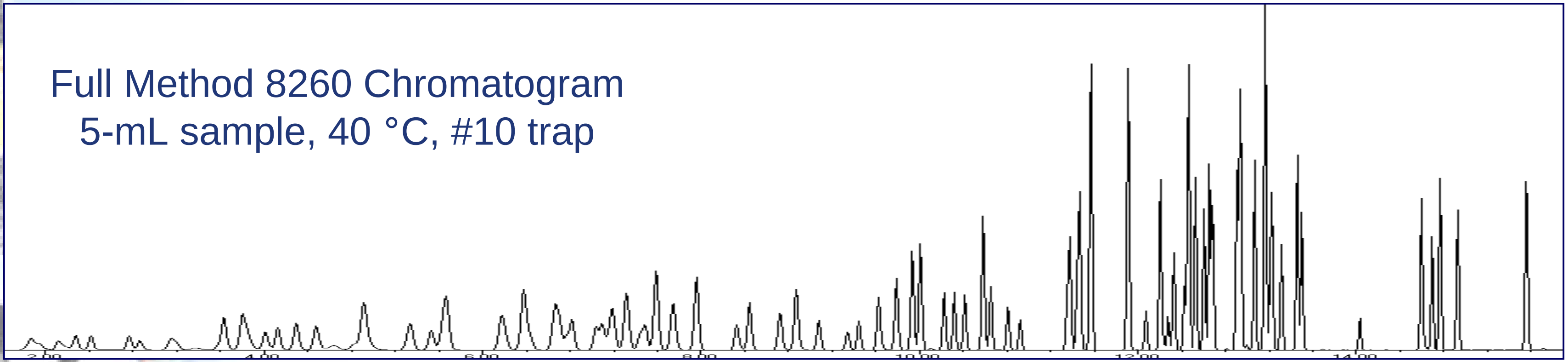
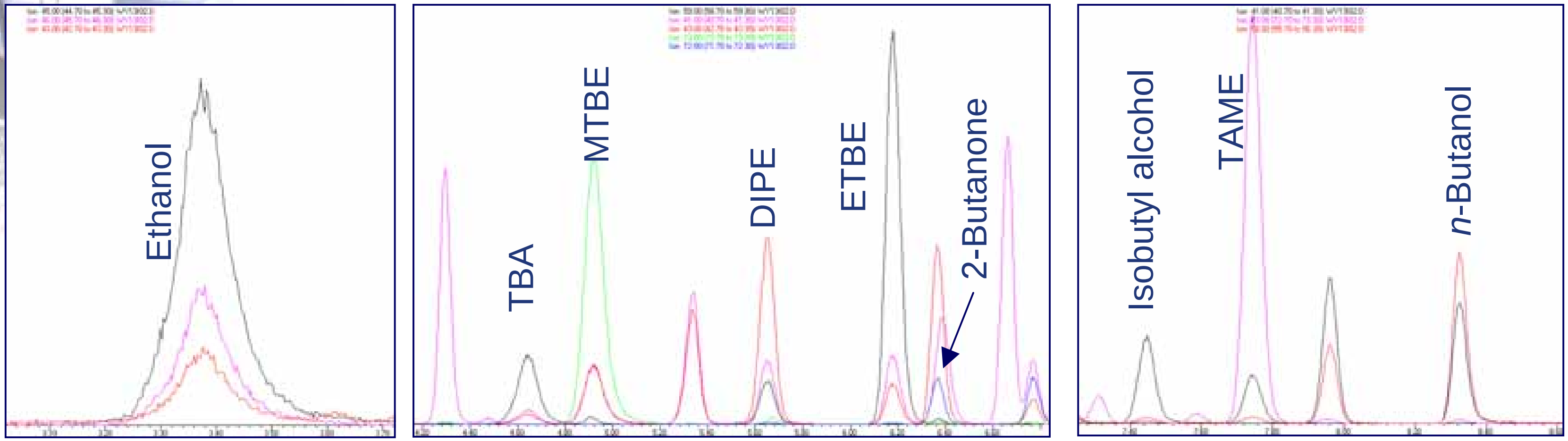
Included in Method 8260





Chromatogram courtesy of Lancaster Laboratories, Lancaster, PA

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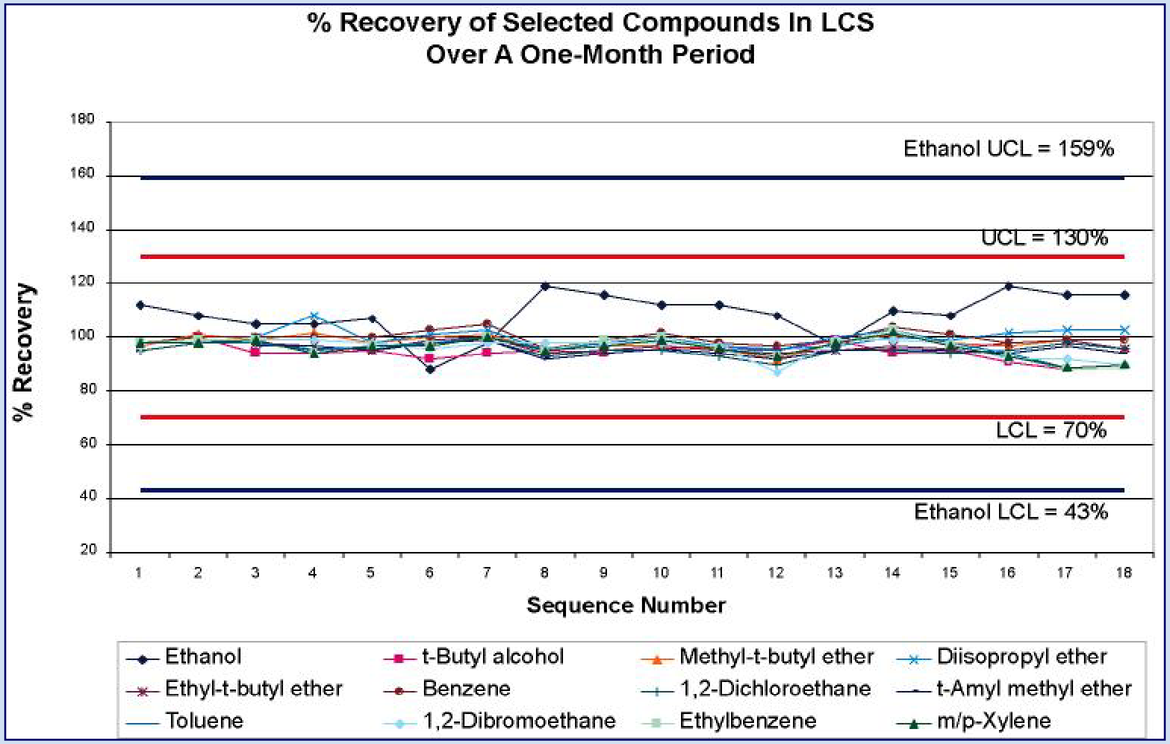
Recovery of BTEX and Oxygenates



Percent recovery of 12 selected compounds in the LCS during a one-month period analyzed on the Eclipse. Oxygenates met the criteria as easily as the BTEX compounds.

Data courtesy of Lancaster Laboratories, Lancaster, PA

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Conclusion

- Oxygenates can be included in Method 8260 analyses with only very minor changes
- Best conditions
  - *Use largest sample size possible (25 mL)*
  - *Mild heating to 40–45 °C improves purge efficiency*
  - *Either trap gives excellent results*
- Met all method calibration RF criteria
- LOQs ≤0.2 ppb for the ethers
  - *TBA LOQ at 1.0–2.0 ppb*
- No problems with H_2O when using the Eclipse patented Water Management Fitting

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Application Note 1996

For full details on this and other P&T applications, visit our website at: www.oico.com

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