Application Note 19960204

Analysis of Fuel Oxygenates Using The Eclipse Purge-and-Trap Sample Concentrator

Keywords
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Introduction

Fuel oxygenates are oxygen-containing compounds such as ethers or alcohols, which are added to gasoline to boost octane rating and to make fuel burn more cleanly. The two most common oxygenate additives have been methyl-*tert*-butyl ether (MTBE) and *tert*-butanol (TBA). Fuel oxygenates are being found in increasing concentrations in groundwater, and in recent years the US Environmental Protection Agency's Leaking Underground Storage Tank (LUST) program has generated a great deal of oxygenate data. Unfortunately, the lack of a single validated performance-based method for determining fuel oxygenates in environmental matrices has raised concerns about the quality of the data already collected and how they should be interpreted, as well as questions about which method should be used going forward.

The USEPA recognizes SW-846 Method 8260 using gas chromatography and mass spectrometry (GC/MS) and Method 8015 using GC/flame-ionization detection (FID) as being the two most appropriate determinative methods for oxygenates, with Methods 5030 and 5035 (purge-and-trap (P&T) and closed system P&T) cited as the most appropriate sample preparation techniques for low-level detection. Both the MS and FID detectors are capable of detecting oxygenates at low concentrations, but only the MS is capable of positive compound identification based on the mass spectrum, making Method 8260 the preferred method. Modifying the determinative GC/MS method to include analysis of fuel oxygenates is not necessary or desirable. Only the calibration and sample preparation steps need modifying, and those should be altered as little as possible so that the oxygenates can be included in the already standardized analyses without significant changes.

Fuel oxygenate compounds are highly soluble in water, difficult to purge, and can be reactive under certain conditions, making analysis by standard P&T methods challenging. One specific problem with interpreting existing data is that environmental samples have been historically preserved with acid to pH <2. If the acidic sample is then heated to ~80°C during purge, MTBE in the sample can undergo hydrolysis to TBA. This can result in an artificially low MTBE number and a high bias for TBA. To counteract this effect, the USEPA is considering a recommendation to preserve samples that will be analyzed for oxygenates to pH >11 with trisodium phosphate dodecahydrate (TSP). Purging the sample at a more moderate temperature of 40° to 45°C can also help minimize MTBE hydrolysis under acidic conditions.

This application note explores the P&T variables that can be modified to obtain optimum and reliable performance for fuel oxygenates without making fundamental or extreme changes to previously standardized P&T procedures.

Experimental

A series of experiments were designed to test the effects of three variables that could be easily modified without making any fundamental changes to the standard P&T method. The variables tested were sample size (5, 10, and 25 mL), sample temperature set point (ambient, 40°C, 60°C, and 80°C), and trap type (Tenax®/silica gel/carbon molecular sieve and VOCARB®). All analyses were performed using the OI Analytical Model 4552 Water/Soil Autosampler and the Model 4660 Eclipse Sample Concentrator (Figure 1). Operating conditions for both instruments are listed in Table 1. The analyses were performed on an Agilent® 6890 GC and 5973 Inert MS using standard GC/MS operating conditions described previously (see OI Analytical Application Note 1937 for a full description of all operating parameters).

Figure 1. OI Analytical Model 4660 Eclipse Sample Concentrator

A primary standard supplied by Restek® contained the five oxygenates commonly required for analysis by the State of California, *tert*-butanol (TBA), methyl-*tert*-butyl ether (MTBE), isopropyl ether (DIPE), ethyl-*tert*-butyl ether (ETBE), and *tert*-amyl methyl ether (TAME). TBA was present in the mix at a concentration five times that of the four ethers. A large volume of secondary standard was prepared at 5 ppb (25 ppb TBA) and used for all of the sample size and sample temperature analyses. Duplicate aliquots of each sample size (5, 10, and 25 mL) were analyzed at each of the four temperature set points (ambient, 40°, 60°, and 80°C), for a total of 24 analyses on each trap.

Once the optimum sample size and temperature set point were established, an estimated LOQ (limit of quantitation) determination was made for each trap. Standards were prepared at 5 ppb (25 ppb TBA), 1 ppb (5 ppb TBA), and 0.2 ppb (1 ppb TBA), and analyzed in triplicate using the established optimum size and temperature conditions. During the LOQ tests and the size and temperature analyses, the mass range was extended to include *m/z* 18 so the amount of water to the GC/MS system could also be monitored.

An eight-point calibration curve was run covering a range from 0.2 to 200 ppb (1–1,000 ppb TBA) and a statistical MDL study was performed by analyzing seven replicate aliquots of a 0.5 ppb standard (2.5 ppb TBA). Finally, tap water was spiked with 1-ppm unleaded gasoline and 100-ppb oxygenates and analyzed using the recommended conditions to demonstrate performance of the instrumentation on a real-world sample.

All experiments described here were designed to use the same GC and MS parameters previously optimized for detecting and quantifying all analytes in USEPA Method 8260. Other than the temporary change in mass range to include *m/z* 18, no changes were made to the GC or MS operating conditions.

Table 1. Instrument operating conditions

Parameter	Setting
Autosampler	**Model 4552 Water/Soil Autosampler**
Sample type	Soil mode
Sample volume	3 mL (volume of clean water used to transfer standards to the vial)
Number of rinses	0 (sparge tube rinses not necessary with soil analysis mode)
Standard 1	Yes (internal standard addition)
Standard 2	No
Sample preheat stirring	Yes (magnetic stir bar added to each vial)
Stir	Yes
Syringe flushes	0
Preheat	Yes
Preheat temperature set point	Ambient, 40°, 60°, and 80°C
Actual maximum sample temperature	Ambient, 37°, 46°, and 62°C (see “Results and Discussion”)
Preheat time	1 minute
Purge time	11 minutes
Desorb time	0.5 minute
Soil transfer line temperature	110°C
Sample concentrator	**Model 4660 Eclipse**
Trap	#10 (Tenax/silica gel/carbon molecular sieve) #11 (VOCARB)
Purge	11 minutes with trap at 20°C
Dry purge	Not necessary with the patented water management fitting
Desorb preheat	ON #10 trap to 180°C #11 trap to 230°C
Desorb	0.5 minute #10 trap at 190°C #11 trap at 240°C
Bake	5 minutes #10 trap at 210°C #11 trap at 250°C
Water management fitting	Factory default settings 110°C at purge, 0°C at desorb, 240°C at bake
Sparge mount temperature	40°C
Valve oven temperature	110°C
Transfer line temperature	110°C

Results and Discussion

Sample Size, Sample Temperature, and Trap Selection

The results of the sample size and temperature analyses are shown in Figure 2 and Figure 3. Each bar in the charts represents the average response from duplicate analyses. The small number above the bar is the relative percent difference (RPD) between the two runs. All responses are reported relative to the response of a 5-mL aliquot analyzed at ambient temperature.

In general, the four ethers behaved uniformly and as predicted. Responses increased with increasing sample size at all temperatures and on both traps. Average relative response of the four ethers on the #10 trap at a 60°C temperature set point were 0.9 (5 mL), 1.5 (10 mL), and 3.4 (25 mL), and on the #11 trap they were 1.0, 1.8, and 4.0, respectively, indicating a slightly higher increase in response on the #11 trap. This difference in response between the two traps is illustrated in Figure 4 and Table 2. In contrast, increasing the sample temperature had only a minor effect on the ether response, as can be seen in Table 3. For the ethers, the chromatography and RPD between duplicate runs was excellent at all sample sizes and temperatures and no significant analytical difficulties were encountered.

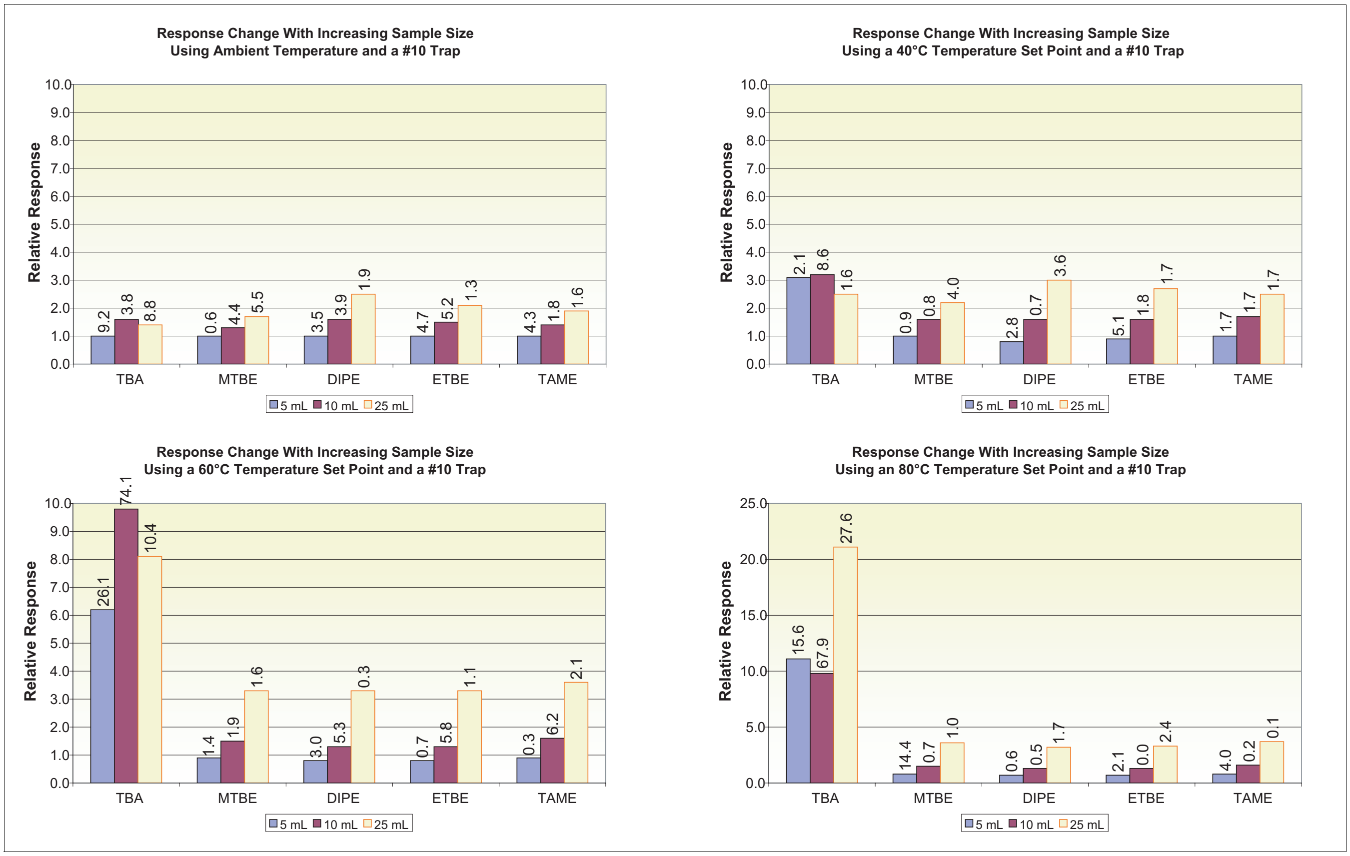
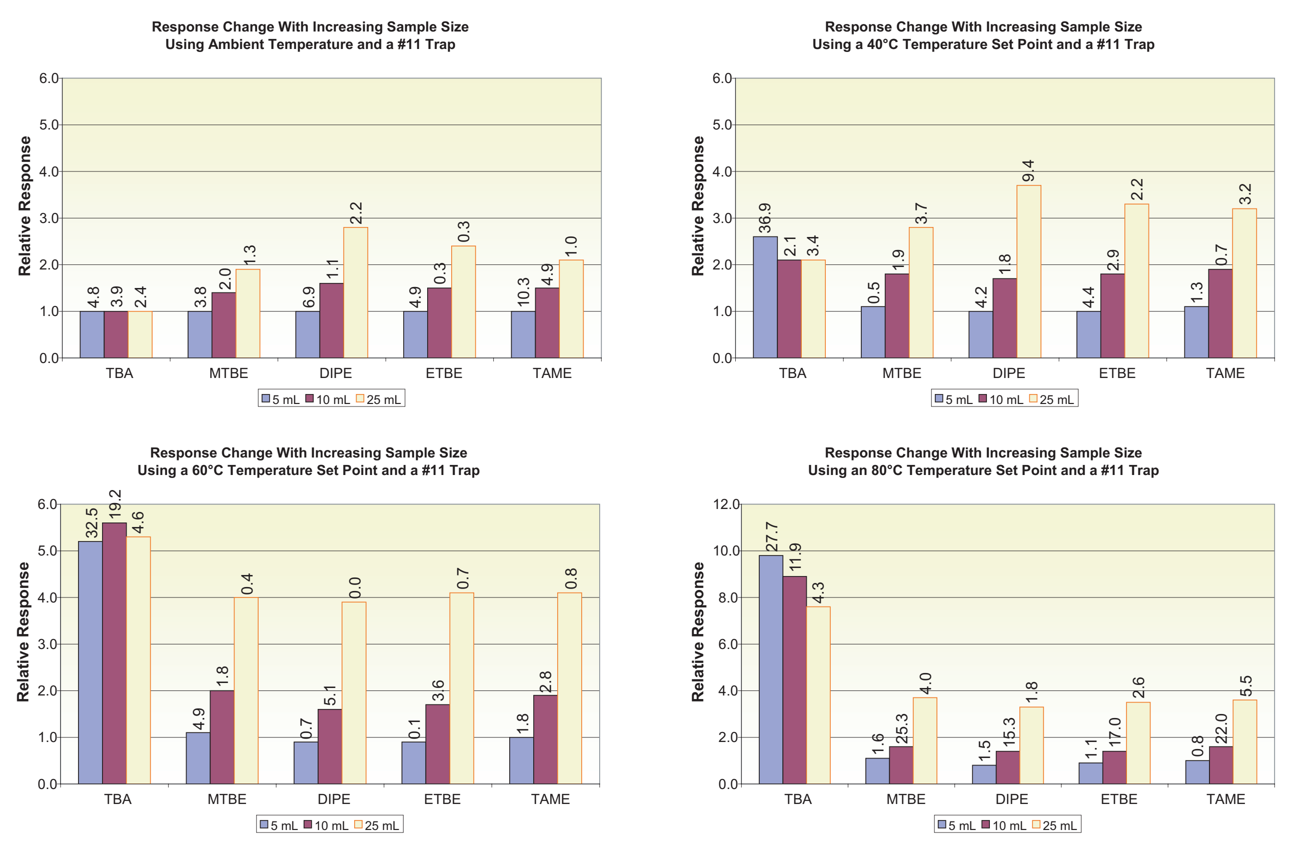


Figure 2. Charts illustrating relative response changes on a #10 trap using different sample sizes and temperature set points. All responses are reported relative to analysis of a 5-mL aliquot at ambient temperature. Each bar represents the average response from duplicate analyses, and the small number above the bar is the relative percent difference (RPD) between the two runs. The chart for the 80°C sample temperature is shown in a different scale to accommodate the increased TBA response.


Response Change With Increasing Sample Size Using Ambient Temperature and a #11 Trap

Response Change With Increasing Sample Size Using a 40°C Temperature Set Point and a #11 Trap

Response Change With Increasing Sample Size Using a 60°C Temperature Set Point and a #11 Trap

Response Change With Increasing Sample Size Using an 80°C Temperature Set Point and a #11 Trap

Figure 3. Charts illustrating relative response changes on a #11 trap using different sample sizes and temperature set points. All responses are reported relative to analysis of a 5-mL aliquot at ambient temperature. Each bar represents the average response from duplicate analyses, and the small number above the bar is the relative percent difference (RPD) between the two runs. The chart for the 80°C sample temperature is shown in a different scale to accommodate the increased TBA response.

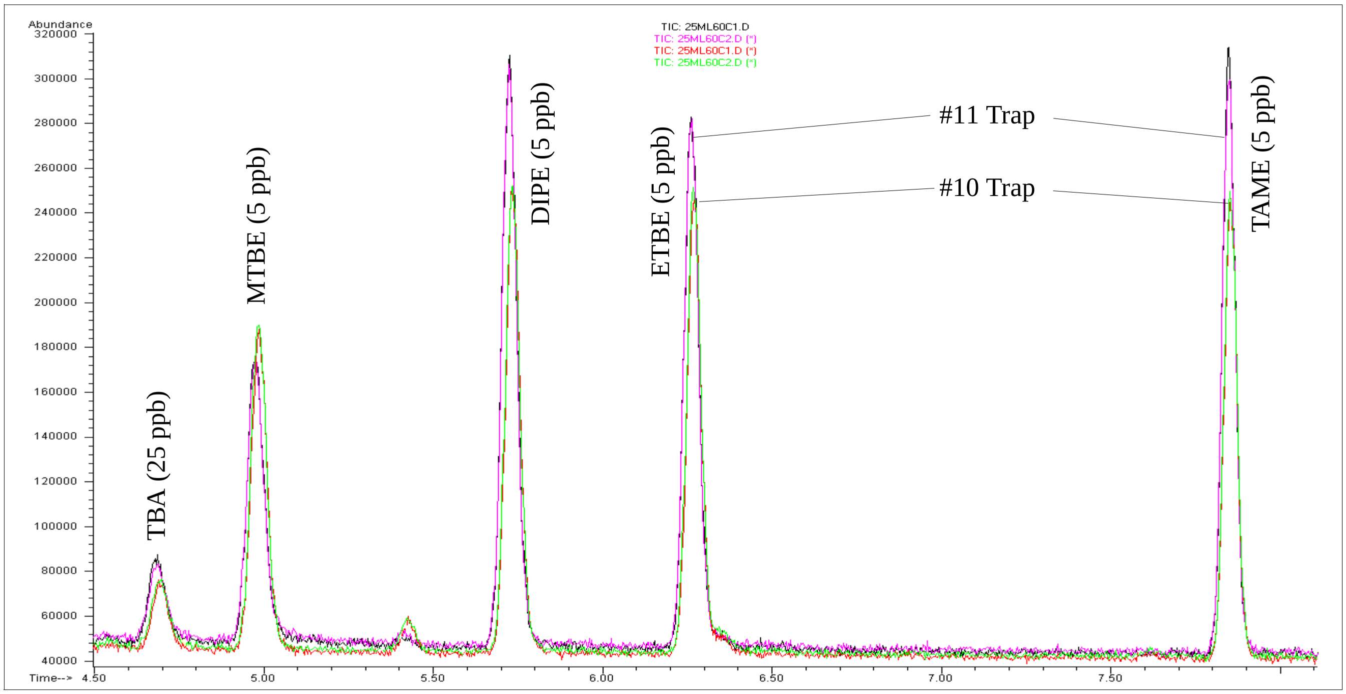


Figure 4. Overlaid chromatograms of two runs on the #10 trap and two runs on the #11 trap (25-mL sample size and 60°C set point). Chromatography on the two traps was nearly identical. However, most analytes showed a slight but distinct increase in sensitivity on the #11 trap.

Table 2. Effect of sample size on average relative response (RR) of the ethers on two different traps (60°C sample temperature set point). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Sample Size	**Ether Average RR**	
	#10 Trap	**#11 Trap**
5 mL	0.9	1.0
10 mL	1.5	1.8
25 mL	3.4	4.0

Table 3. Effect of sample temperature set point on average relative response (RR) of the ethers on two different traps (25-mL sample size). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Temperature Set Point	**Ether Average RR**	
	#10 Trap	**#11 Trap**
Ambient	2.1	2.3
40°C	2.6	3.2
60°C	3.4	4.0
80°C	3.5	3.5

TBA did not behave in the same manner as the four ethers. The TBA average relative response increased with sample temperature set point, but only a small and unpredictable change in response was observed with increases in sample size. The quantitative results are summarized in Table 4 and Table 5. Although the quantitative data suggest that the best operating temperature set point would be 80°C, chromatographic performance of TBA worsened significantly at the highest temperature, producing unacceptable tailing as shown in Figure 5. Purging at 80°C is also undesirable because of potential MTBE hydrolysis.

Table 4. Effect of sample size on TBA average relative response (RR) on two different traps (60°C sample temperature set point). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Sample Size	**TBA Average RR**	
	#10 Trap	**#11 Trap**
5 mL	6.2	5.2
10 mL	4.2	5.6
25 mL	8.1	5.3

Table 5. Effect of sample temperature set point on average TBA relative response (RR) on two different traps (25-mL sample size). Responses are measured relative to a 5-mL sample purged at ambient temperature.

Temperature Set Point	**TBA Average RR**	
	#10 Trap	**#11 Trap**
Ambient	1.4	1.0
40°C	2.5	2.1
60°C	8.1	5.3
80°C	21.1	7.6

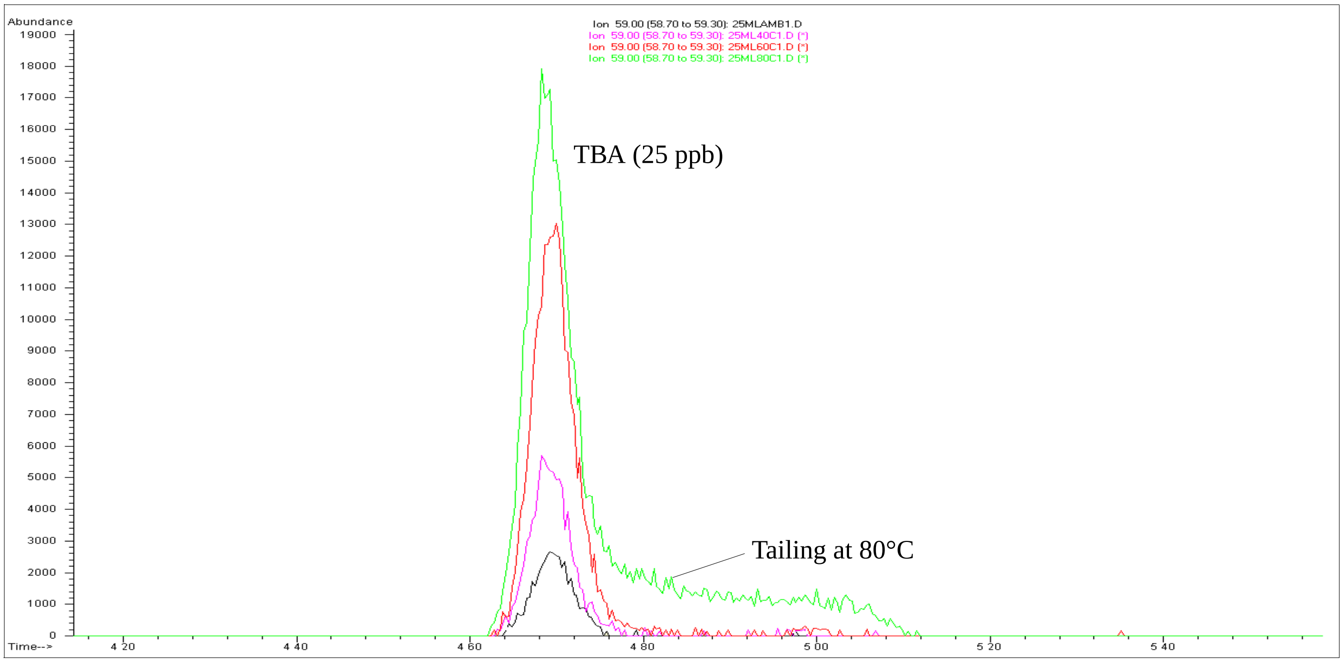


Figure 5. Overlaid chromatograms of TBA EICPs (*m/z* 59) at different temperature set points (25-mL sample size) illustrating unacceptable tailing at 80°C.

A Note About Temperature Set-Points

When the Model 4552 Autosampler operates in soil mode, the sample purges directly in the 40-mL VOA vial using a needle sparger, as described in USEPA Method 5035. Also as part of the method, a magnetic stir bar stirs the sample during purge and a heated collar around the vial brings the sample to the desired temperature, usually 40°–45°C. Using a thermocouple placed directly in the sample during preheat and purge, it was determined that the actual temperature of the sample did not reach the instrument set point when the set point was above ambient. The maximum temperatures achieved for set points of 40°, 60°, and 80°C were 37°, 46°, and 62°C, respectively. The Eclipse's patented Infra-Sparge™ sample heater is much more rapid and accurate than the collar-type heater, therefore if choosing water mode and samples purge and heat in the Eclipse sparge vessel, the sample temperature set point should be reduced to between 40° and 45°C, accordingly.

LOQ

The Limit of Quantitation (LOQ) is sometimes referred to as the practical quantitation limit. It represents the lowest compound concentration that can be accurately quantified using a given analytical method and is often used as the lowest calibration standard when developing a calibration curve. For this test, triplicate aliquots of three different low-level standards were analyzed on each trap to estimate the lowest practical LOQ for the five analytes. The results are shown in Table 6 and Figure 6.

All four of the ethers, including MTBE, showed good response on both traps at 0.2 ppb using a 25-mL sample and an actual temperature of about 45°C, and could be easily integrated and quantified at this low concentration. Chromatography and repeatability (measured as %RSD) were also excellent at this concentration for all four ether compounds. TBA had only a marginal response at 1.0 ppb. An LOQ of two-to-five times this level produced a more acceptable and quantifiable peak, as verified with the analyses at 2.0 ppb TBA in the second calibration standard. In general, repeatability was better for the ethers than for TBA and better on the #11 trap than on the #10 trap.

Table 6. Percent Relative Standard Deviation (%RSD, n=3) from triplicate analyses of three different concentrations on the two test traps (25-mL sample size, 45°C actual sample temperature)

Concentration (ppb)	**%RSD (n=3)**					
	0.2 ppb Ethers 1.0 ppb TBA		**1.0 ppb Ethers 5.0 ppb TBA**		**5.0 ppb Ethers 25.0 ppb Ethers**	
	#10 Trap	**#11 Trap**	**#10 Trap**	**#11 Trap**	**#10 Trap**	**#11 Trap**
TBA	10.9	6.0	24.3	21.0	47.9	15.3
MTBE	3.6	3.3	10.5	15.5	12.4	7.6
DIPE	2.2	2.7	2.8	4.6	5.0	3.8
ETBE	3.5	2.8	5.0	6.1	7.1	4.9
TAME	4.9	4.9	6.3	7.9	12.3	6.9

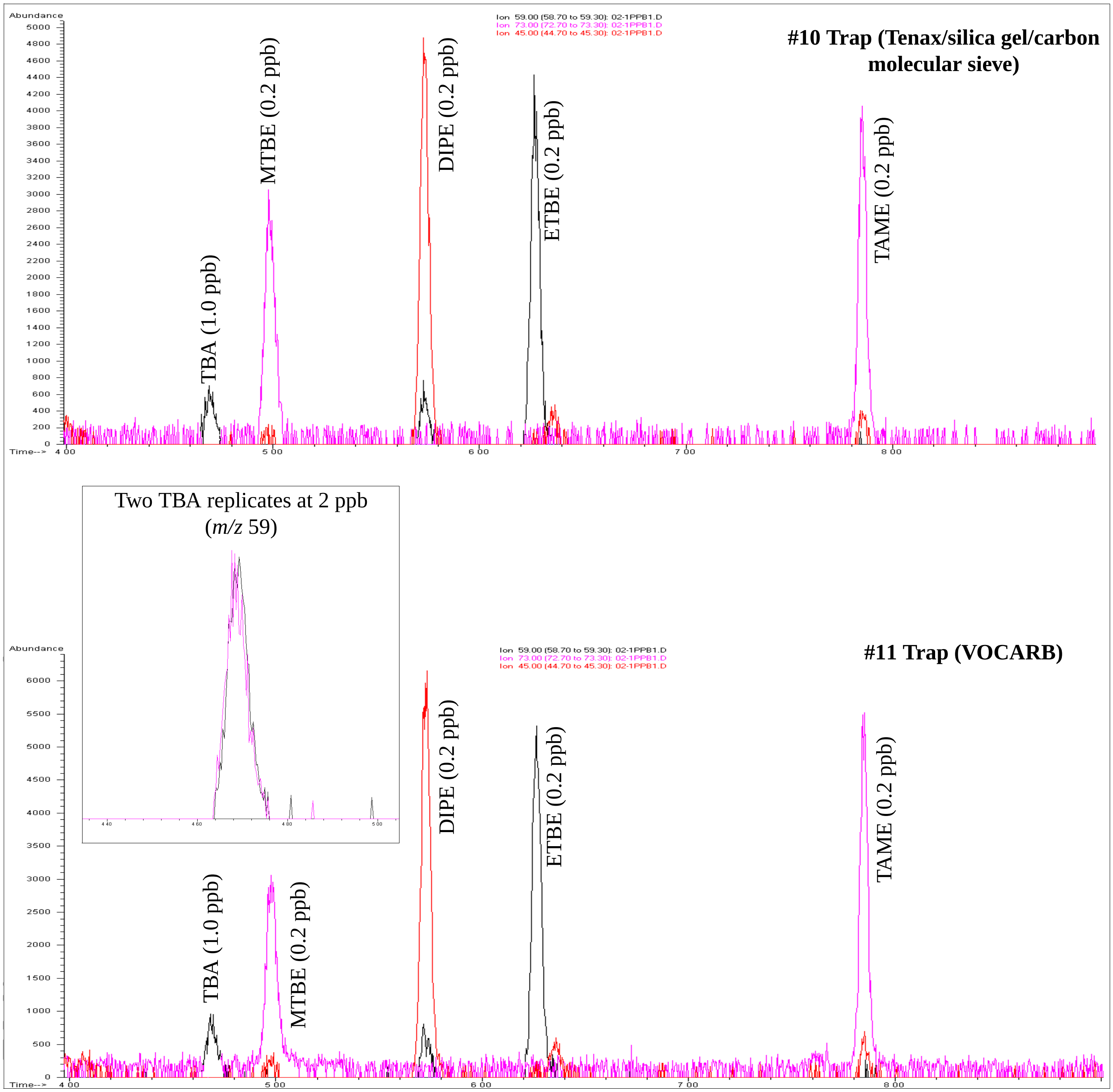


Figure 6. EICPs of TBA and the four ethers at the lowest LOQ test concentration of 0.2 ppb (1.0 ppb TBA) for the two traps tested. Chromatography for all compounds was excellent, and sensitivity of the ethers allowed easy integration and quantitation at this low concentration. The insert shows overlaid EICPs of TBA at 2.0 ppb from duplicate calibration runs.

Calibration and Statistical MDL Results

An eight-point calibration curve was prepared with the ether concentrations at 0.2, 0.4, 1.0, 5.0, 10, 20, 100, and 200 ppb. TBA concentrations were five times the concentration of the ethers and ranged from 1 to 1,000 ppb. The calibration curve and MDL study were both acquired using a 25-mL sample size, an actual sample temperature of about 45°C, and the #11 (VOCARB) trap. Each concentration level was analyzed in duplicate. A response factor (RF) was calculated for each analyte at each concentration level using fluorobenzene (80 ppb) as an internal standard. The calibration %RSD for all five compounds in the mix were below 15% and easily met the calibration criteria specified in USEPA Method 8260 and Method 524.2, Rev. 4. Using the less desirable linear calibration mode and coefficient of determination (R^2) was unnecessary for any of the compounds.

A statistical MDL determination was made by analyzing seven replicates of a standard at a concentration 0.5 ppb (2.5 ppb TBA). The MDL was calculated using the standard deviation of the seven measured concentrations and the Student's t-test. The statistically calculated MDL for TBA was 1.40 ppb and ranged from 0.03 to 0.05 ppb for the four ethers. The Initial Calibration and statistical MDL results are listed in Table 7.

Table 7. Results from the Initial Calibration and statistical MDL determination

Compound	Calibration			MDL		
	Range (ppb)	Avg. RRF	%RSD	Spike Amt.(ppb)	Std. Dev.(ppb)	Statistical MDL (ppb)
TBA	1.0–1,000	0.017	12.3	2.5	0.44	1.40
MTBE	0.2–200	0.497	7.8	0.5	0.02	0.05
DIPE	0.2–200	0.693	7.4	0.5	0.01	0.04
ETBE	0.2–200	0.606	9.4	0.5	0.02	0.05
TAME	0.2–200	0.516	9.2	0.5	0.01	0.03

Water Results

Because of the extreme water solubility of the oxygenate compounds, how well the P&T sample concentrator handles water removal becomes critical. For part of this experiment the MS mass range was extended to include *m/z* 18 to monitor the amount of water going to the GC from the P&T. As can be seen in Figure 7, the Eclipse's patented water management fitting (WMF) consistently removed all but a very minimal water amount from the sample stream as it transferred to the GC, regardless of sample size or temperature. The #11 VOCARB trap transferred slightly less water (approximately 5–10%) to the GC, probably because of its more hydrophobic character. In all cases, the water was baseline resolved from TBA and MTBE and did not interfere chromatographically with any of the compounds. The patented WMF operated using factory-default settings, and any modification to accommodate water-soluble compounds was unnecessary.

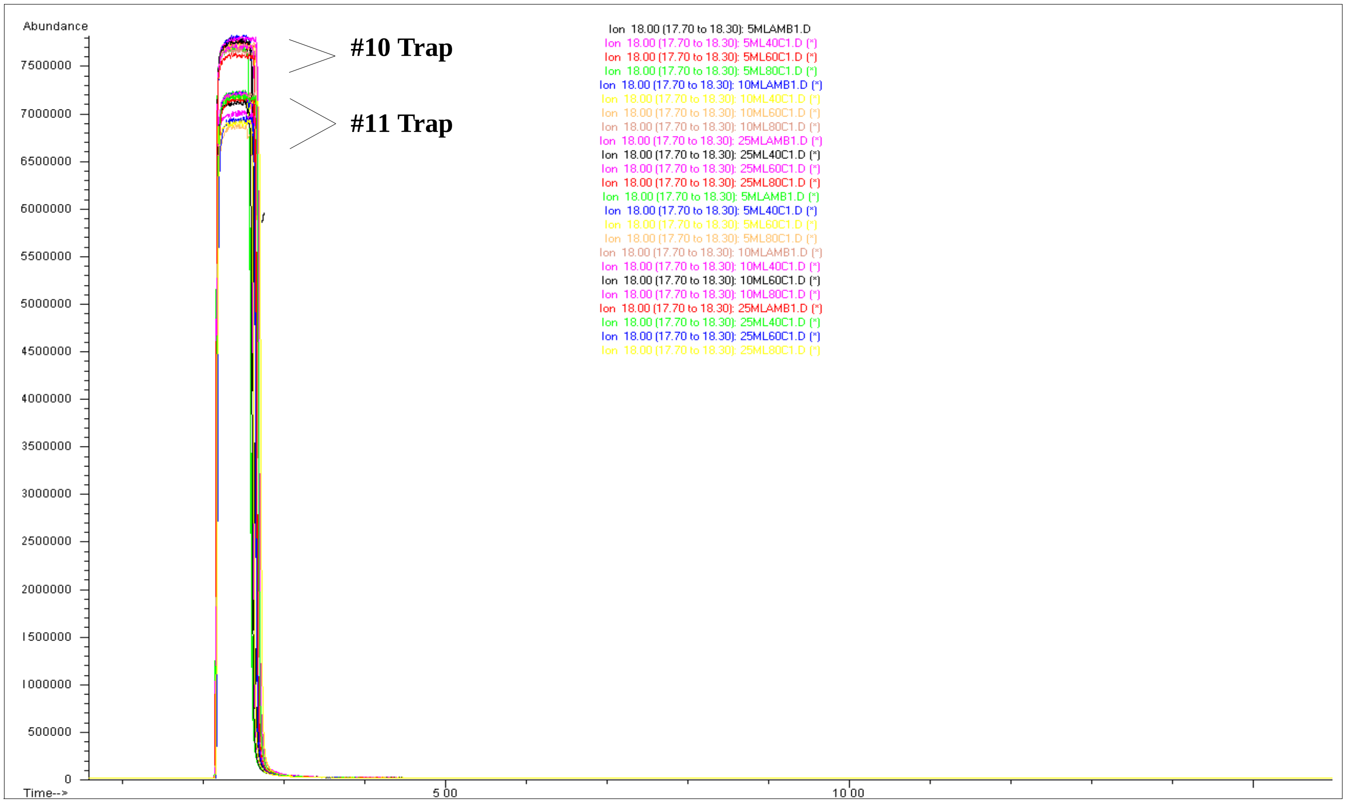


Figure 7. Overlaid EICPs (*m/z* 18) from 24 analyses illustrating the efficient and consistent water removal of the patented water management fitting, regardless of sample size, sample temperature, or trap type. The WMF operated using factory default settings.

Real-World Sample

Groundwater and wastewater samples encountered in laboratories often contain volatile gasoline components that can complicate the analysis. To simulate this real-world situation, a sample was prepared by spiking tap water with 1-ppm gasoline and 100-ppb oxygenates, and analyzed using the prescribed conditions (#11 trap, 25-mL sample size, 45°C actual sample temperature). Figure 8 shows the total ion chromatogram (TIC) from this analysis with the oxygenate EICPs overlaid. Chromatography was excellent and peak identification in this simulated “dirty” matrix was unambiguous using the MS.

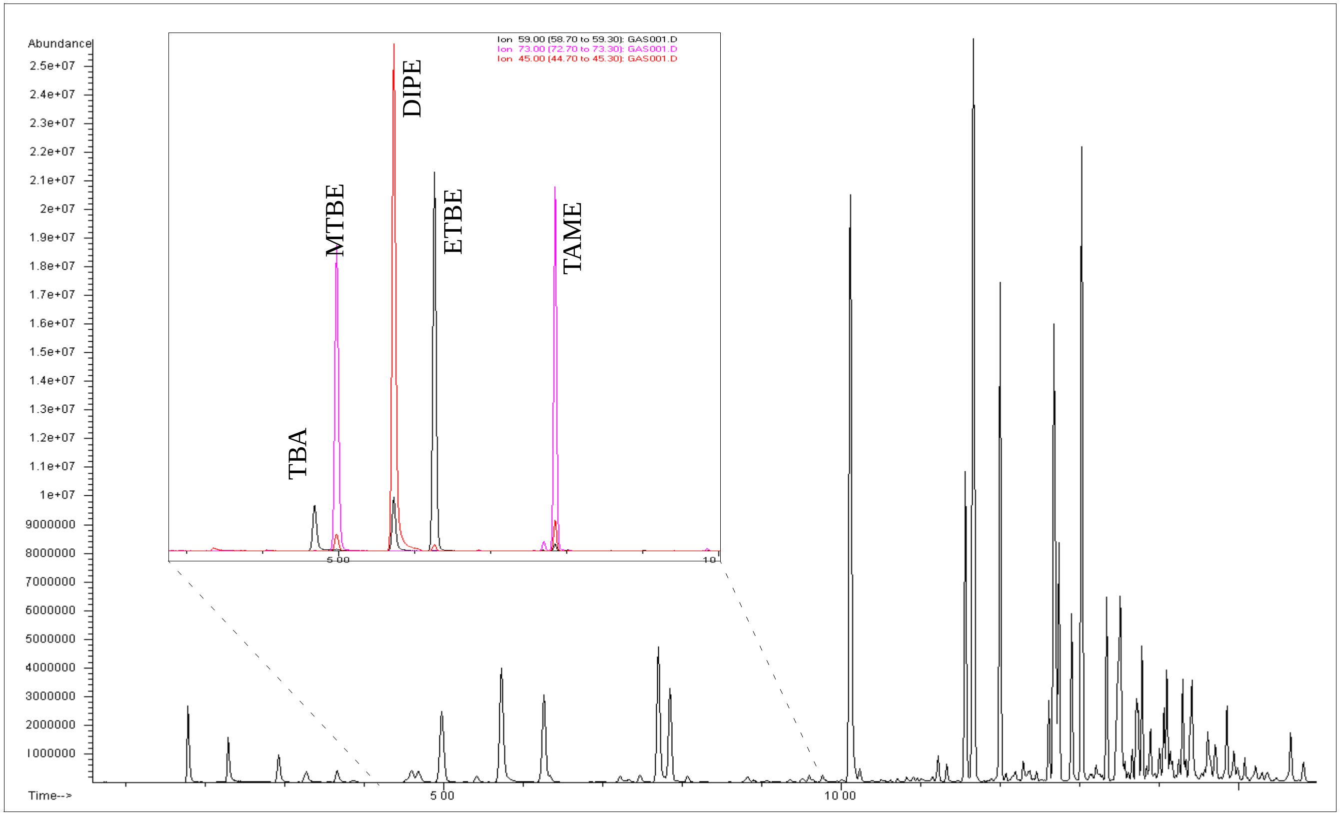


Figure 8. Chromatogram of water spiked with 1-ppm gasoline and 100-ppb oxygenates and analyzed using the Eclipse Sample Concentrator. The overlaid EIPCs show the MS ions used for quantitation of the oxygenate compounds.

Results From Other Laboratories

Immediately after introducing the Eclipse, it was run in a high-throughput production laboratory that routinely includes an extensive list of oxygenate compounds in its Method 8260 analyses. That laboratory used equipment identical to the instrumentation described here, but ran their Model 4552 Autosampler in water mode rather than soil mode. They also used a #10 trap and a 5-mL sample instead of a 25-mL sample. The samples transferred to the Eclipse fritted sparge vessel, where they heated during purge to 40°C with the patented Infra-Sparge sample heater. (Note that the Infra-Sparge sample heater raised the sample temperature to the actual set point of 40°C in less than one minute, where the collar heater in the Model 4552 Autosampler required a set point of 60°C to reach approximately the same temperature after six minutes.) Selected results from those analyses are shown in Figure 9 and Figure 10, and Table 8.

The calibration produced single-digit %RSDs for all oxygenates on the extended list, and the same initial calibration curve was used for over three months. All ongoing quality control (QC) check standards (CCV, LCS, IS responses, etc.) met the method and laboratory QC criteria during the same three-month period. Other than including the oxygenate standards in the calibration mixtures, modifying any of instrument operating conditions to accommodate the additional compounds was unnecessary.

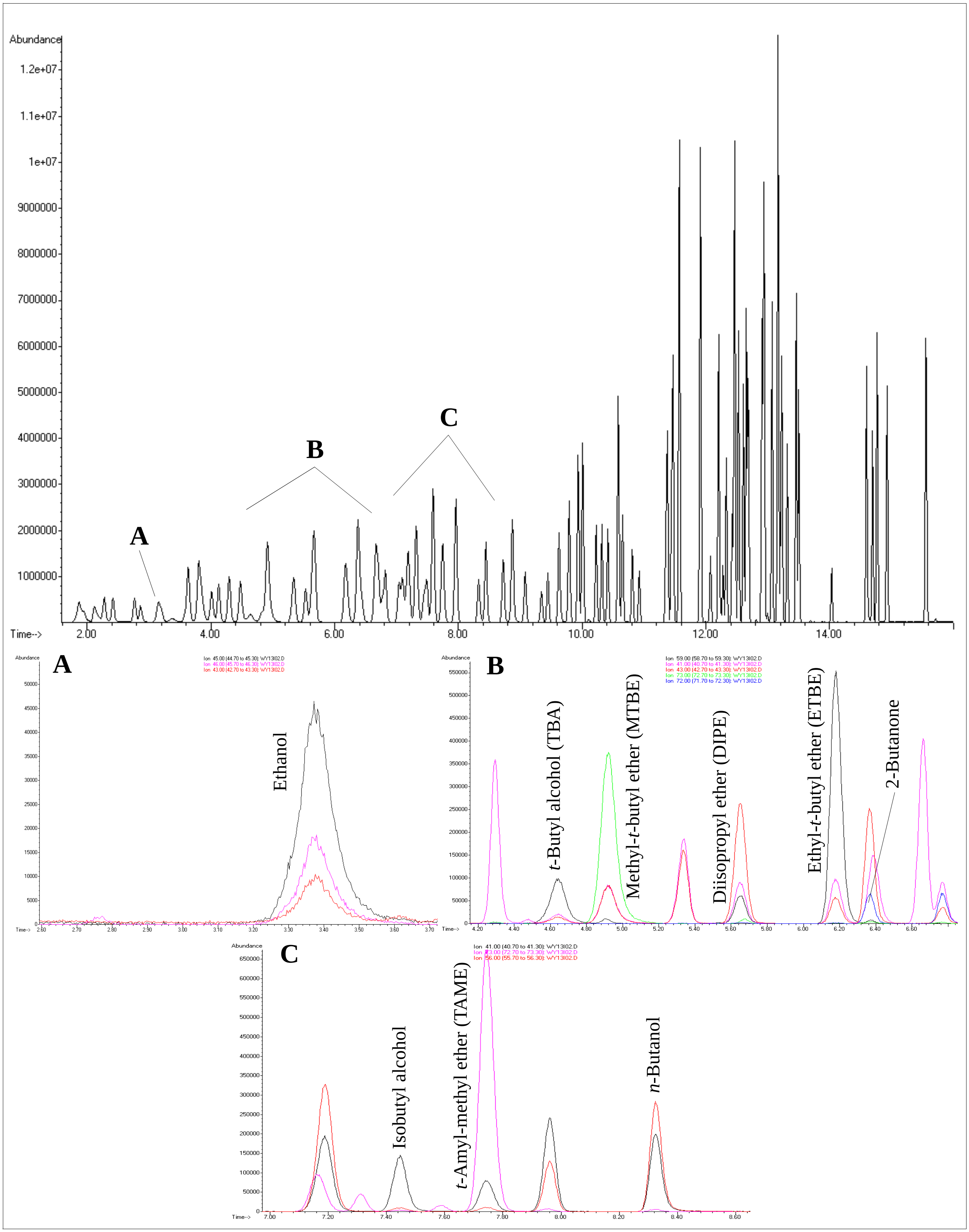


Figure 9. Chromatogram from a calibration standard run on the Eclipse at a commercial production laboratory using standard conditions optimized for Method 8260. The inserts show the chromatography of some of the more difficult oxygenates. See OI Analytical Application Note 1937 for complete analytical details.

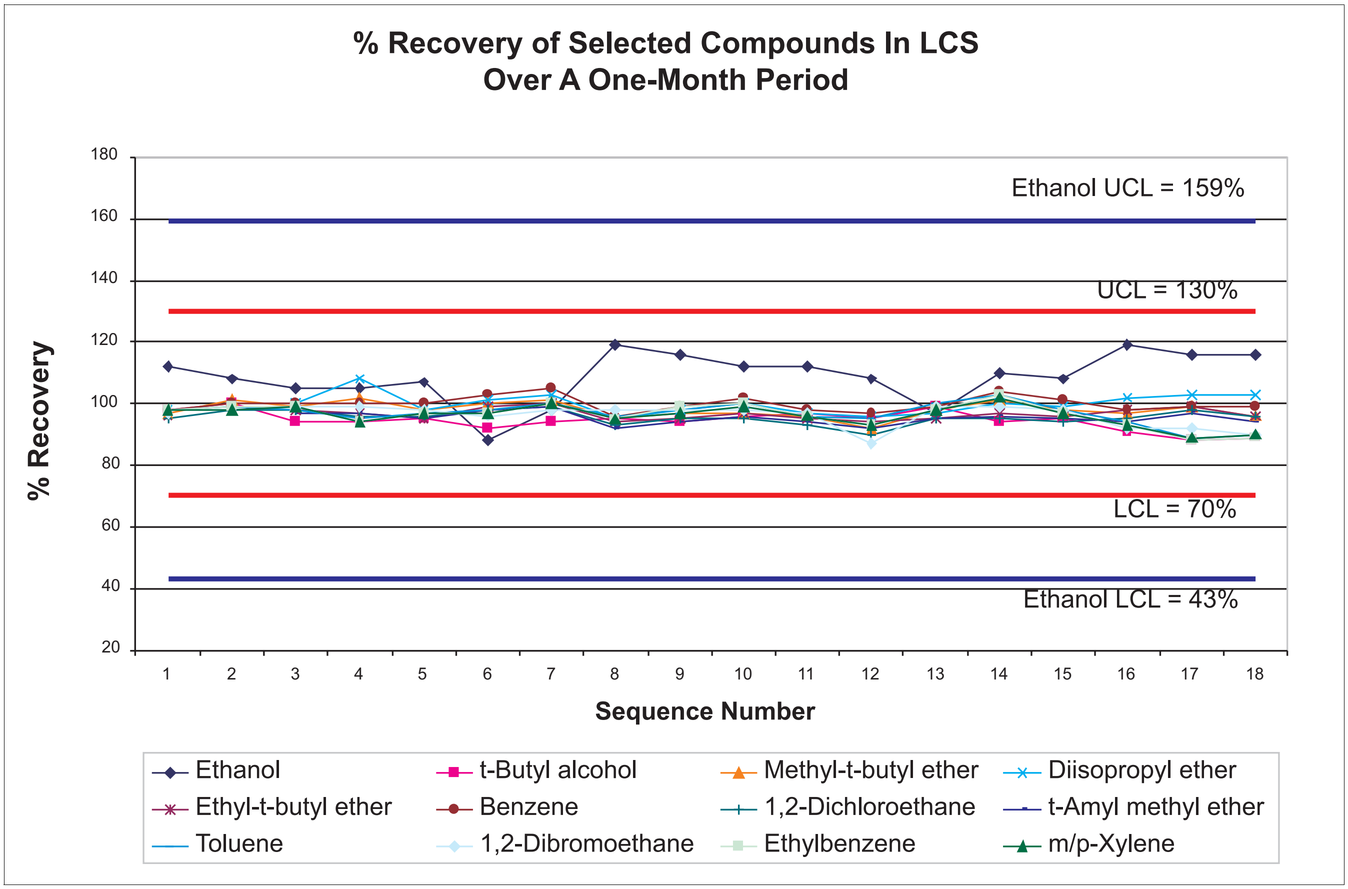


Figure 10. Percent recovery of 12 selected compounds in the Laboratory Control Sample (LCS) analyzed on the Eclipse during a one-month period. The six oxygenate compounds performed as well as the BTEX. All recoveries met the QC acceptance criteria without difficulty.

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Table 8. Selected results for fuel oxygenates from a high-throughput production laboratory. The laboratory routinely includes an extensive list of oxygenate compounds in its Method 8260 analyses and does not modify their instrument operating conditions to accommodate additional compounds. See OI Analytical Application Note 1937 for full results.

Compound	**Calibration**			**MDL**		**Initial Demonstration (n=4)**			
	Range (ppb)	**Avg. RRF**	**%RSD**	**Spike Amt. (ppb)**	**MDL (ppb)**	**Spike Amt. (ppb)**	**Measured (ppb)**	**Std. Dev (ppb)**	**Pass?**
Ethanol	50–7,500	0.132	6	50	14.5	500	544.7	8.4	Yes
TBA	20–1,500	1.312	4	10	1.01	200	194.4	0.9	Yes
MTBE	1–300	0.861	3	0.5	0.05	20	19.8	0.1	Yes
DIPE	1–300	0.924	2	0.5	0.23	20	20.0	0.2	Yes
ETBE	1–300	0.897	2	0.5	0.07	20	19.5	0.2	Yes
2-Butanone	2–600	0.045	3	1.0	0.62	150	128.9	0.5	Yes
Isobutyl alcohol	50–3,750	0.015	4	25	16.8	500	491.5	2.1	Yes
TAME	1–300	0.853	1	0.5	0.05	20	19.4	0.1	Yes
n-Butanol	100–7,500	0.013	7	50	22.3	1000	946.9	13.4	Yes

Salting Techniques

Another commonly discussed technique for enhancing oxygenate performance is modifying the matrix by salt addition to increase the ion content of the solution. This technique has been shown to work, however, most high-throughput laboratories do not want to add the labor-intensive step of modifying the sample matrix prior to analysis. In addition, salting can add significantly to routine instrument maintenance, causing additional instrument downtime and lost revenue.

Conclusions and Recommendations

In general, response of the four ethers increased with increasing sample size, and the more polar TBA responded better when the sample temperature was raised. The best performance for all compounds was achieved by using a large sample volume (25 mL) and heating the sample to 40° to 45°C during purge. Higher sample temperatures were not necessary, and the more moderate temperature of 40°–45°C will minimize the possibility of MTBE hydrolysis. The patented WMF provided excellent water management using factory default settings. Both traps gave approximately equivalent results with slightly higher response seen on the #11 trap. Either trap should be expected to perform favorably under these temperature and sample size conditions.

Using the conditions described here, the four ethers were accurately quantified at 0.2 ppb, and TBA at 1.0 to 2.0 ppb. Statistical MDLs were 0.03 to 0.05 ppb and 1.40 ppb, respectively, with single-digit %RSDs for calibration of most compounds.

Many laboratories routinely include the fuel oxygenates in the Method 8260 analyte list. They achieve excellent and consistent results using the Eclipse, meeting all QC criteria and low detection limits without making any significant changes to their P&T or GC/MS methods.

Acknowledgement

OI Analytical thanks Trent Sprenkle, Group Leader, GC/MS Volatiles at Lancaster Laboratories in Lancaster, PA, for providing data from his laboratory, which illustrates how fuel oxygenates can be added to Method 8260 without making significant changes to the methodology.

OI Analytical thanks Restek Corporation for supplying the oxygenate analytical standard (PN 30465-510) and capillary GC column (Rtx-624, 30 meter x 0.25 mm I.D. x 1.4-µm film) used in this project.

References

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5. OI Analytical Application Note 1937, *The Eclipse Purge-and-Trap Sample Concentrator Initial Laboratory Test Results, Part II.*

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