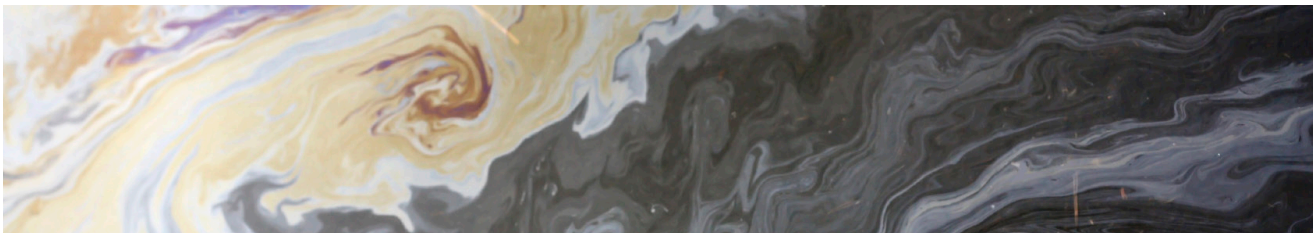


Analysis of Trace Oxygenates in Petroleum-Contaminated Wastewater, Using Purge-and-Trap GC-MS (U.S. EPA Methods 5030B & 8260)

By Chris English

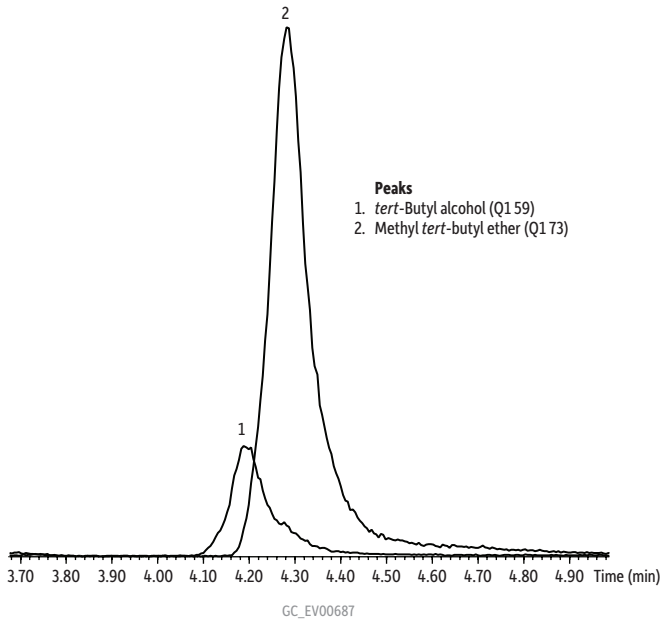
Gasoline and other petroleum-derived fossil fuels consist mainly of compounds that contain only carbon and hydrogen atoms. Oxygenates—ethers and alcohols—contain oxygen atoms in addition to carbon and hydrogen. Oxygenates are added to gasoline to enhance various aspects of its performance as a fuel. Methyl tertiary-butyl ether (MTBE) is the most common fuel oxygenate. MTBE was first introduced into gasoline in 1979, to reduce overall emissions, replace lead, and increase octane rating. In 1992, gasoline with up to 15% MTBE content by volume was used nationally to meet the first federally mandated wintertime reduction of carbon monoxide emission.

With over one million underground fuel tanks in the United States, contamination of ground and surface water with gasoline components, including oxygenates, is a major environmental concern. Storage tanks worldwide potentially will require monitoring and cleanup in the future. The U.S. EPA has not sanctioned any wastewater method specifically for analysis of oxygenates from gasoline. Consequently, environmental laboratories in the U.S. have used a variety of methods to report these analytes, including EPA Methods 8015B, 8021B, and 8260. Regulatory agencies recommend adding *tert*-butyl alcohol (TBA) to the target list for contaminated sites known to contain MTBE because it is both a breakdown product of MTBE and a gasoline additive in its own right. Identification and quantification of these fuel-derived pollutants in a gasoline-water matrix is a challenging task, because compounds such as MTBE and TBA coelute on many of the GC column stationary phases in capillary gas chromatography columns, and share ions used for identification in gas chromatography-mass spectrometry (GC-MS).

Method 8015B calls for using a flame ionization detector (FID) to match a known chromatographic pattern for gasoline to an unknown sample containing peaks that fall within the gasoline pattern range. This method can be used to identify oxygenates by retention time, but a high probability of misidentifications dictates the need for confirmation on a second column. A second analysis entails additional costs and additional time. Method 8021B was written specifically for analysis of aromatic and halogenated volatiles, and employs a photoionization detector (PID). This is the least reliable of the 3 methods: a PID is very sensitive to double bonds, but is much less sensitive to ether and hydroxy groups. In a test analysis of a gasoline composite standard conducted in our laboratories, use of Method 8021B resulted in false positive identification of a sample component as diisopropyl ether. Confirmation analysis by GC-MS correctly identified the compound as 2-methyl-1-pentene [1].

Purge-and-trap GC-MS methods, such as Method 8260, are favored for monitoring oxygenates in gasoline because they ensure a higher level of confidence in the data obtained, compared to GC methods, as illustrated by the 2-methyl-1-pentene example cited above. Under appropriate conditions, GC-MS circumvents the problem of false identification of unresolved constituents and provides positive identifications. Studies conducted by analysts at Lawrence Livermore National Laboratory indicate that GC-MS is the most reliable method of detecting oxygenates in complex gasoline-containing samples, regardless of the concentration of the gasoline (from neat to greatly diluted with groundwater) [2]. Although confidence in the GC-MS approach is well founded, the GC column stationary phase must be carefully chosen and tested to assure that there are no critical coelutions between target oxygenated analytes and other gasoline components, which could result in false positives for the former. Further, careful attention to operating conditions is necessary, to maximize analyte response and optimize resolution between oxygenates and other compounds of interest. TBA and MTBE, for example, must be separated, because they share ions used for identification. Figure 1 is an example of inadequate resolution of these analytes; "624"-type stationary phases are not recommended for oxygenates analysis due to this limitation. Similarly, incomplete resolution of *tert*-amyl-methyl ether (TAME) and benzene makes an Rtx®-Volatiles column inappropriate for this application.

Figure 1 "624"-type stationary phases do not resolve TBA and MTBE adequately for positive identification and reliable quantification.



Column	Rtx®-624, 30 m, 0.25 mm ID, 1.40 µm (cat.# 10968)
Sample	8260B MegaMix® calibration mix kit (cat.# 30475) California oxygenates mix (cat.# 30465) VOA calibration mix #1 (ketones) (cat.# 30006) 8260A Surrogate mix (cat.# 30240) 8260 Internal standard mix (cat.# 30074)
Injection	purge and trap split (split ratio 25:1)
Inj. Temp.:	250 °C
Purge and Trap	
Instrument:	O.I. Analytical 4560 with 4551A Autosampler
Trap Type:	#10 (Tenax®/silica gel/carbon molecular sieve)
Purge:	11 min @ 20 °C, flow 38 mL/min
Desorb Preheat Temp.:	150 °C
Desorb:	1.0 min @ 190 °C, flow 32 mL/min
Bake:	10 min @ 210 °C
Transfer Line Temp.:	110 °C
Oven	
Oven Temp:	35 °C (hold 7 min)
Carrier Gas	He, constant flow
Flow Rate:	1.3 mL/min
Dead Time:	1.47 min @ 35 °C
Detector	Agilent 5971A GC/MS
Transfer Line Temp.:	280 °C
Tune Type:	PFTBA/BFB
Scan Range:	35-260 amu
Notes	Sample size: 10 mL Sample temp: 40 °C Water Management: 110 °C purge, 0 °C desorb, 240 °C bake 6-Port Valve: 110 °C Sparge Mount: 45 °C Valve Manifold: 50 °C Other Conditions: prepurge, preheat, dry purge OFF
Acknowledgement	Purge & trap courtesy of O.I. Analytical

We evaluated the Rtx®-VMS stationary phase for analysis of oxygenates, verifying passing criteria by following EPA Method 5030B (with modification) and Method 8260. Samples of non-oxygenated gasoline, spiked with low levels of oxygenates, enabled us to determine if operating conditions were appropriate for separating and detecting these target compounds in the presence of high concentrations of other gasoline components. Purge-and-trap conditions in Method 5030B were modified to address the oxygenates in the samples: to increase responses for the oxygenates, we used a 40 °C purge temperature, rather than the ambient temperature suggested. GC oven conditions were optimized to eliminate coelutions of ion-sharing analytes.

The GC-MS system was tuned using a 25 ng standard of 4-bromofluorobenzene (BFB). Commonly analyzed compounds on the Method 8260 target list were added to the calibration mix, along with internal standards, ethers, and TBA. Methanol and ethanol were not added to these samples; these low molecular weight compounds require higher purge temperatures or are performed using static headspace techniques.

Method 8260B does not specifically assign internal standards to target compounds. Therefore, we used the internal standards and corresponding analytes listed in Table 6 of Method 8260 [3]. This allowed us to measure response factors (RF) against established internal standards. We also incorporated the Method 8260 surrogates, and the characteristic primary ions for quantification, into our experimental design. The curve was calibrated using mean response factors, as outlined in Method 8260, section 7.6.2.1. Minimum mean response factors for the volatile system performance check compounds (SPCC), as described in the method, are listed in Table I. These values confirm acceptable performance by the purge-and-trap concentrator. Note that the 40 °C purge temperature used to increase responses for the oxygenates also will increase responses for the SPCC compounds.

Table I System performance check compound (SPCC) response factor criteria for all columns under specific conditions.

	EPA Criterion (Minimum Mean RF)	Rtx®-VMS Column (RF)
Pentafluorobenzene (IS)		
Chloromethane (SPCC)	>0.10	0.59
1,1-Dichloroethane (SPCC)	>0.10	0.64
Chlorobenzene-d5 (IS)		
Chlorobenzene (SPCC)	>0.30	1.06
Bromoform (SPCC)	>0.10	0.32
1,4-Dichlorobenzene-d4 (IS)		
1,1,2,2-Tetrachloroethane (SPCC)	>0.30	0.71

After the system passed the SPCC evaluation, the calibration check compounds (CCC) were used to verify the validity of the calibration. Relative standard deviations (%RSD) for these compounds must be less than 15% (Table II). The internal standards in Table III were used for calculating RFs, %RSDs, and % recoveries (%Recov.) of target analytes, as shown. Oxygenates were calculated relative to internal standard methyl-d3-*tert*-butyl ether, to account for differences in purging efficiency specific to the ethers.

Table II Calibration check compound (CCC) relative standard deviation criteria for all columns under specific conditions.

	EPA Criterion (%RSD)	Rtx®-VMS Column (%RSD)
Pentafluorobenzene (IS)		
1,1-Dichlorothene (CCC)	<15	11.4
Chloroform (CCC)	<15	5.5
1,4-Difluorobenzene (IS)		
1,2-Dichloropropane (CCC)	<15	4.9
Toluene (CCC)	<15	3.0
Chlorobenzene-d5 (IS)		
Ethylbenzene (CCC)	<15	5.5
1,4-Dichlorobenzene-d4 (IS)		
1,1,2,2-Tetrachloroethane (SPCC)	<15	8.6

Table III Internal standards with corresponding analytes assigned for quantification.

Methyl-d3-*tert*-butyl ether (IS)	Pentafluorobenzene (IS)	1,4-Difluorobenzene (IS)	Chlorobenzene-d5 (IS)	1,4-Dichlorobenzene-d4 (IS)
methyl-*tert*-butyl ether	chloromethane (SPCC)	1,2-dichloroethane-d4 (SS)	chlorobenzene (SPCC)	1,1,2,2-tetrachloroethane (SPCC)
tert-butyl alcohol (x5)*	1,1-dichlorothene (CCC)	1,2-dichloropropane (CCC)	ethylbenzene (CCC)	naphthalene
diisopropyl ether	acetone (x2.5)*	toluene-d8 (SS)	bromoform (SPCC)	
ethyl-*tert*-butyl ether	1,1-dichloroethane (SPCC)	toluene (CCC)		
tert-amyl-methyl ether	chloroform (CCC)	bromofluorobenzene (SS)		
	dibromofluoro-methane (SS)			

*Compound added at 5 times or 2.5 times the concentration of other target analytes.

Purge-and-Trap Procedures

Table IV summarizes the purge-and-trap conditions used for recovering oxygenates from gasoline. Samples were heated using the Infra-Sparge sample heater on an O.I. 4560 concentrator. The minimum purge temperature effective for detecting TBA at a concentration of 25 ppb in 10 mL of water was 40 °C. Purge flow rate was carefully adjusted to 38 mL/min; lower flows dramatically affect recovery of the brominated compounds, higher flows contribute to analyte breakthrough and excessive water retention on the trap.

Table IV Purge-and-trap conditions for recovering oxygenates from gasoline (O.I. 4560 concentrator).

Trap:	#10 (Tenax®/silica gel/carbon molecular sieve)
Purge time:	11 min
Purge flow rate:	38 mL/min
Desorb flow rate:	32 mL/min
Desorb time:	1.0 min
Bake time:	10 min
Sample size:	10 mL
Water management:	110 °C purge, 0 °C desorb, 240 °C bake
Split ratio:	1:25
Temperatures:	
Sample:	40 °C
Trap:	20 °C purge, 190 °C desorb, 210 °C bake
6-Port valve:	110 °C
Transfer line:	110 °C
Sparge mount:	45 °C
Desorb preheat:	150 °C
Valve manifold:	50 °C
Other conditions:	Pre-purge, pre-heat, dry purge OFF
Conditions suggested by O.I. Analytical.	

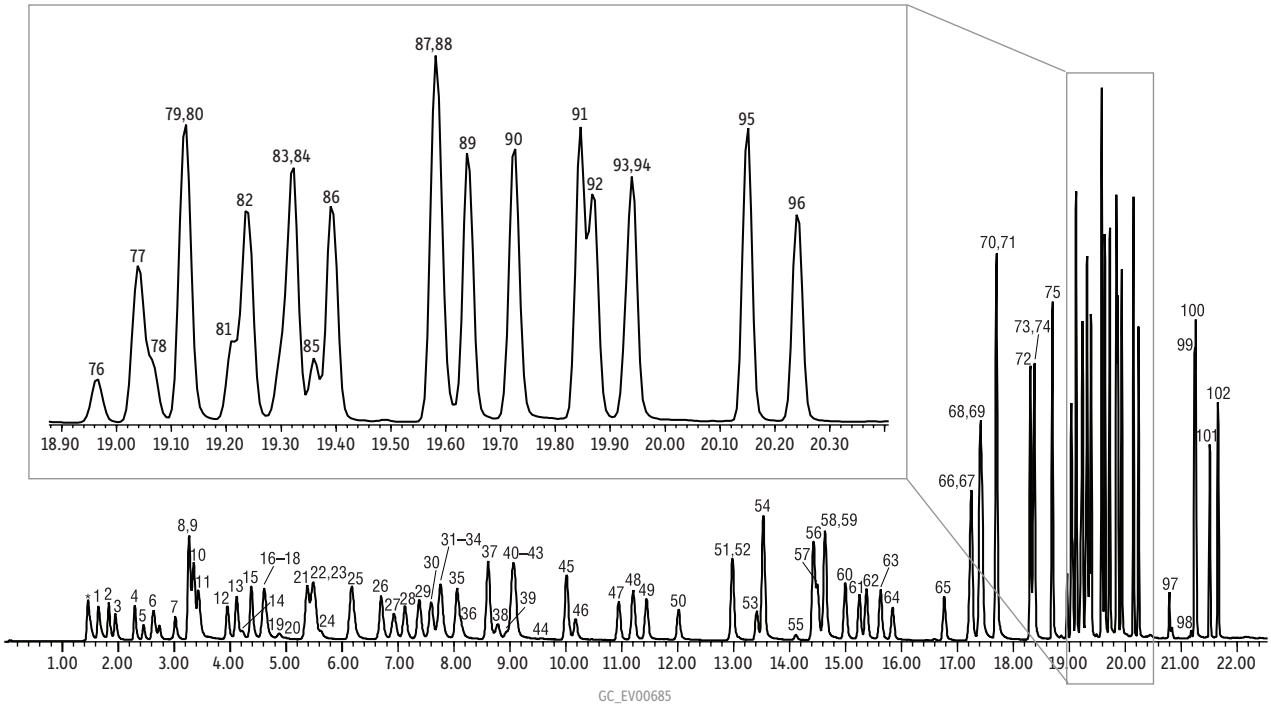
Analytical Procedures

An Agilent 5890 Series II GC coupled with an Agilent 5971A GC-MS detector fitted with a K&M electron multiplier was used for the analysis. Helium carrier gas was adjusted to 1.3 mL/min constant flow. The oven temperature program was optimized as follows: 35 °C (hold 7 min) to 90 °C @ 4 °C/min (hold 0 min), to 220 °C @ 45 °C/min (hold 1 min). Analysis time was 25 minutes; cycle time was 30 minutes. The MS was set for full scan from 35 amu to 260 amu and was initially tuned with or PFTBA calibration gas, followed by a BFB tune check. A 30 m x 0.25 mm x 1.4 µm Rtx®-VMS column (cat.# 19915) was used for the separations.

Standards

The five points of the calibration were 5, 10, 20, 40, and 80 ppb, with internal standards (IS) and surrogate standards (SS) added to each calibration standard at 20 ppb. Intermediate standards were made separately for each calibration point, to maintain equal amounts of methanol added to the 10 mL volume of water. Samples were spiked and were transferred to the concentrator by hand. Calibration was performed using the analyte list in Table III, but all compounds shown in Figure 2 were added in order to check for critical coelutions between oxygenates and Method 8260B target compounds. Calibration verification standards (CVS) were added at 10 ppb; recoveries were within 20% of expected values. Two blanks were analyzed, followed by a 5 ppb QC standard to verify recoveries at the low point of the curve [4]. Reference materials used are listed in Table V.

Figure 2 Detecting oxygenates in gasoline-water samples: 80 ppb each analyte.



Peaks

1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. Diethyl ether
8. 1,1-Dichloroethene
9. Carbon disulfide
10. 1,1,2-Trichloro-1,2,2-trifluoroethane
11. Iodomethane
12. Allyl chloride
13. Methylene chloride
14. Acetone
15. *trans*-1,2-Dichloroethene
16. Methyl-d3-*tert*-butyl-ether
17. Methyl acetate
18. Methyl *tert*-butyl ether
19. *tert*-Butyl alcohol
20. Acetonitrile
21. Diisopropyl ether
22. Chloroprene
23. 1,1-Dichloroethane
24. Acrylonitrile
25. Ethyl *tert*-butyl ether
26. *cis*-1,2-Dichloroethene
27. 2,2-Dichloropropane
28. Bromochloromethane
29. Chloroform
30. Carbon tetrachloride
31. Tetrahydrofuran
32. Methyl acrylate
33. 1,1,1-Trichloroethane
34. Dibromofluoromethane
35. 1,1-Dichloropropene
36. 2-Butanone
37. Benzene
38. Propionitrile
39. Methacrylonitrile
40. 1,2-Dichloroethane-d4
41. Pentafluorobenzene
42. *tert*-Amyl methyl ether
43. 1,2-Dichloroethane
44. Isobutyl alcohol
45. Trichloroethene
46. 1,4-Difluorobenzene
47. Dibromomethane
48. 1,2-Dichloropropane
49. Bromodichloromethane
50. Methyl methacrylate
51. *cis*-1,3-Dichloropropene
52. 2-Chloroethyl vinyl ether
53. Toluene-d8
54. Toluene
55. 2-Nitropropane
56. Tetrachloroethene
57. 2-Bromo-1-chloropropane
58. 4-Methyl-2-pentanone
59. *trans*-1,3-Dichloropropene
60. 1,1,2-Trichloroethane
61. Ethyl methacrylate
62. Dibromochloromethane
63. 1,3-Dichloropropane
64. 1,2-Dibromoethane
65. 2-Hexanone
66. Chlorobenzene-d5
67. Chlorobenzene
68. Ethylbenzene
69. 1,1,1,2-Tetrachloroethane
70. *m*-Xylene
71. *p*-Xylene
72. *o*-Xylene
73. Bromoform
74. Styrene
75. Isopropylbenzene
76. 4-bromo-1-fluorobenzene (SS)
77. Bromobenzene
78. *cis*-1,4-Dichloro-2-butene
79. 1,4-Dichlorobutane
80. *n*-Propylbenzene
81. 1,1,2,2-Tetrachloroethane
82. 2-Chlorotoluene
83. 1,2,3-Trichloropropane
84. 1,3,5-Trimethylbenzene
85. *trans*-1,4-Dichloro-2-butene
86. 4-Chlorotoluene
87. *tert*-Butylbenzene
88. Pentachloroethane
89. 1,2,4-Trimethylbenzene
90. *sec*-Butylbenzene
91. *p*-Isopropyltoluene
92. 1,3-Dichlorobenzene
93. 1,4-Dichlorobenzene-D4
94. 1,4-Dichlorobenzene
95. *n*-Butylbenzene
96. 1,2-Dichlorobenzene
97. 1,2-Dibromo-3-chloropropane
98. Nitrobenzene
99. Hexachlorobutadiene
100. 1,2,4-Trichlorobenzene
101. Naphthalene
102. 1,2,3-Trichlorobenzene

*carbon dioxide

Column	Rtx®-VMS, 30 m, 0.25 mm ID, 1.4 µm (cat.# 19915)
Sample	8260B MegaMix Calibration Mix Kit (cat.# 30475) California Oxygenates Mix (cat.# 30465) VOA Calibration Mix #1 (ketones) (cat.# 30006) 8260A Surrogate Mix (cat.# 30240) 8260 Internal Standard Mix (cat.# 30074)
Injection	purge and trap split (split ratio 25:1)
Inj. Temp.:	250 °C
Purge and Trap	
Instrument:	O.I. Analytical 4560 with 4551A Autosampler
Trap Type:	#10 (Tenax®/silica gel/carbon molecular sieve)
Purge:	11 min. @ 20 °C, flow 38 ml/min.
Desorb Preheat Temp.:	150 °C
Desorb:	1.0 min. @ 190 °C, flow 32 ml/min.
Bake:	10 min. @ 210 °C
Transfer Line Temp.:	110 °C

Oven	
Oven Temp:	35 °C (hold 7 min.) to 90 °C at 4 °C/min. to 220 °C at 45 °C/min. (hold 1 min.)
Carrier Gas	He, constant flow
Flow Rate:	1.3 mL/min.
Dead Time:	1.47 min. @ 35 °C
Detector	Agilent 5971A GC/MS
Transfer Line Temp.:	280 °C
Tune Type:	PFTBA/BFB
Scan Range:	35-260 amu
Notes	Sample size: 10 mL Sample temp: 40 °C Water Management: 110 °C purge, 0 °C desorb, 240 °C bake 6-Port Valve: 110 °C Sparge Mount: 45 °C Valve Manifold: 50 °C Other Conditions: prepurge, preheat, dry purge OFF
Acknowledgement	Purge & trap courtesy of O.I. Analytical

Table V Calibration mixes and other reference materials for oxygenates analysis.

Reference Material	Restek cat.#	Lot#
Internal standard and surrogate standard mix	cat.# 30240	lot# A025538
	custom	lot# 03010401s
	cat.# 30074	lot# A022472
Calibration mix	cat.# 30475	lot# A020908
	cat.# 30465	lot# A024826
	cat.# 30006	lot# A024175
	cat.# 30042	lot# A024616
QC second source calibration mix	custom	lot# A025888
Unleaded gasoline (unweathered)	cat.# 30096	lot# A022384
Non-oxygenated unleaded gasoline (unweathered)	custom	lot# OFR-TK253

Gasoline-Spiked Samples

Analysis of the 5 ppb QC standard was followed by analysis of a 1 ppm non-oxygenated gasoline standard, then by analysis of the non-oxygenated standard with 5 ppb of each target compound added. Recoveries for the 5 ppb oxygenate standards were calculated from this high concentration gasoline matrix. The final standard analyzed was 1 ppm (unweathered) gasoline. All samples were spiked with the appropriate IS and SS. The calibration curve passed EPA 8260 criteria for response factors and relative standard deviations. Only two compounds in the test set showed poor response: acetone and TBA.

Results

Table VI summarizes results. All oxygenates were resolved from other target compounds and potentially interfering gasoline components. TBA and MTBE were well resolved using the 35 °C GC oven starting temperature. Figure 3 represents a TIC of 1 ppm non-oxygenated unleaded gasoline spiked with 5 ppb of oxygenates. The inset is an extracted ion chromatogram showing oxygenates are recovered without interference from the gasoline matrix.

Table VI Efficient recovery of ppb oxygenates, using an Rtx®-VMS column.

Compound	5-Point Curve (RF)	5-Point Curve (RSD)	Method Blank (%Recovery)	5 ppb Standard (%Recovery)	1 ppm Non-oxygenated Standard (%Recovery)	1 ppm Non-oxygenated Standard 5 ppb Spike (%Recovery)	1 ppm Gasoline Composite Standard (% Recovery)
methyl-d3-*tert*-butyl ether (IS)	-	-	-	-	-	-	-
tert-butyl alcohol (x5)*	0.13	17	-	93	-	90	-
methyl-*tert*-butyl ether	0.91	7	-	99	-	92	6.2 ppb
diisopropyl ether	1.08	7	-	100	-	94	-
ethyl-*tert*-butyl ether	1.21	8	-	98	-	90	-
tert-amyl-methyl ether	1.15	5	-	105	-	98	< LOD
pentafluorobenzene (IS)	-	-	-	-	-	-	-
acetone (x2.5)*	0.05	12	-	62	< LOD	> ND	-
dibromofluoromethane (SS)	0.43	3	102	89	106	97	98
1,4-difluorobenzene (IS)	-	-	-	-	-	-	-
1,2-dichloroethane-d4 (SS)	0.22	6	103	111	102	100	102
toluene-d8 (SS)	1.02	4	101	108	98	97	98
toluene (CCC)	0.78	3	-	106	94.4 ppb	89.6 ppb	81.9 ppb
bromofluorobenzene (SS)	0.45	2	91	103	90	90	95
chlorobenzene-d5 (IS)	-	-	-	-	-	-	-
chlorobenzene (SPCC)	1.06	6	-	108	-	-	-
ethylbenzene (CCC)	1.71	5	-	110	21.4 ppb	24.9 ppb	23.9 ppb
1,4-dichlorobenzene-d4 (IS)	-	-	-	-	-	-	-
naphthalene	2.08	3	-	93	4.7 ppb	8.8 ppb	5.0 ppb

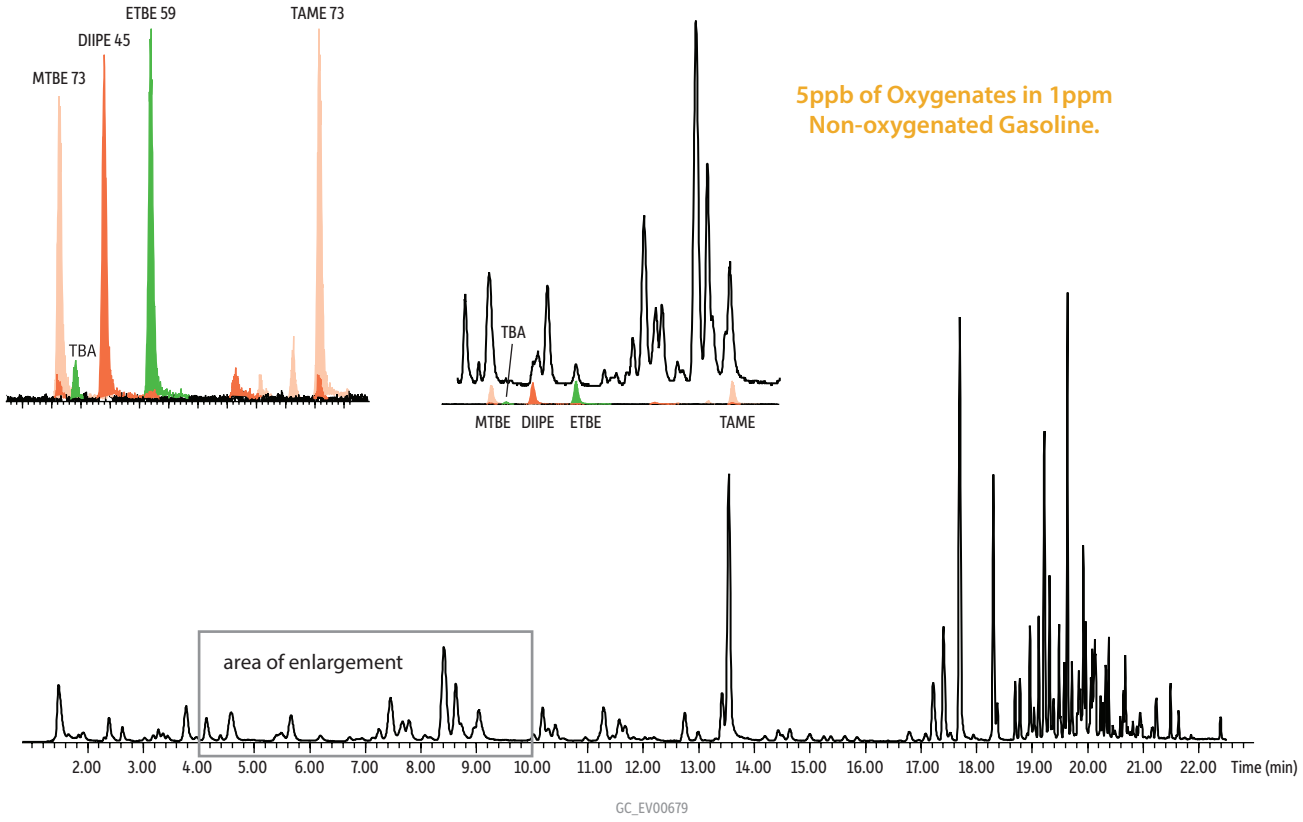
*Compound added at 5 times or 2.5 times the concentration of other target analytes.

< LOD = below limit of detection limit; ND = not detected.

Column: Rtx®-VMS, 30 m x 0.25 mm x 1.4 µm (cat.# 19915)

Conditions: given in text

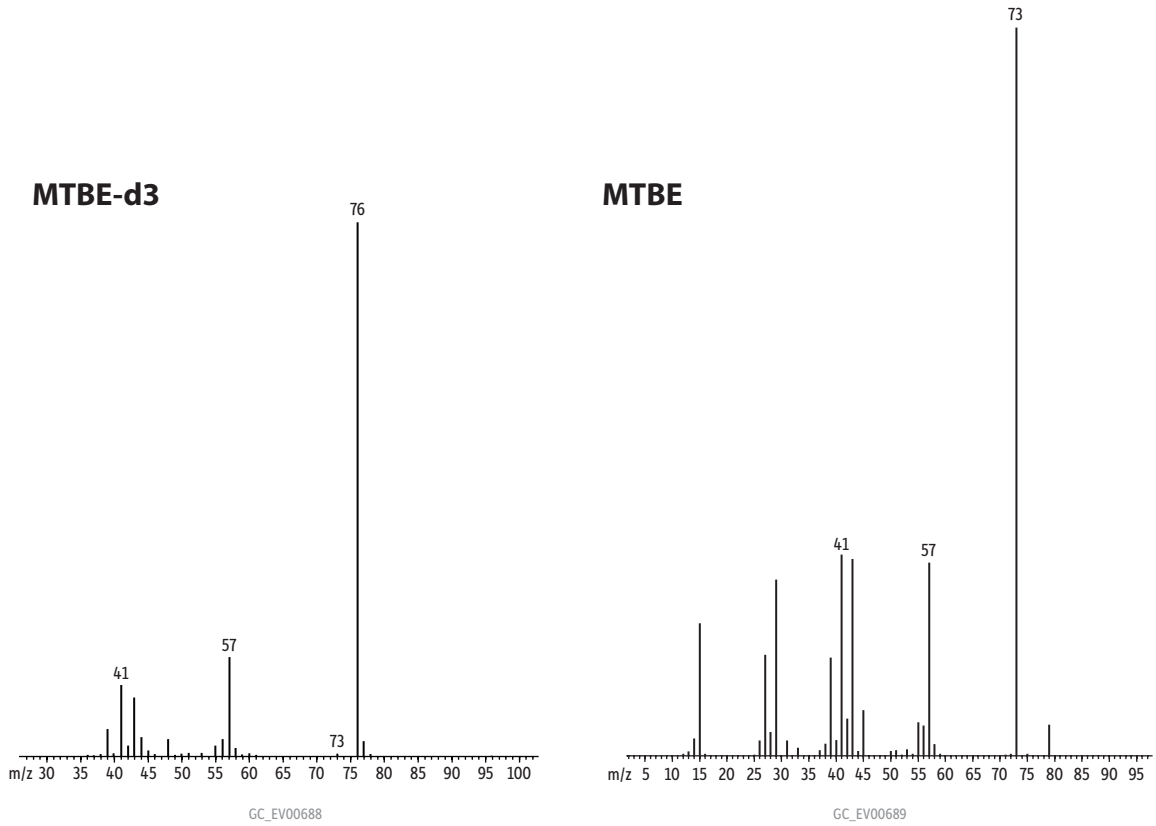
Figure 3 GC/MS with an Rtx-VMS® column allows reliable identification of 5 ppb oxygenates added to 1 ppm gasoline.



Column	Rtx®-VMS, 30 m, 0.25 mm ID, 1.40 µm (cat.# 19915)
Sample	8260B MegaMix® calibration mix kit (cat.# 30475) California oxygenates mix (cat.# 30465) VOA calibration mix #1 (ketones) (cat.# 30006) 502.2 Calibration mix #1 (gases) (cat.# 30042) Unleaded gasoline: unweathered (cat.# 30096) 8260A Surrogate mix (cat.# 30240) 8260 Internal standard mix (cat.# 30074) Non-oxygenated unleaded gasoline (cat.# custom)
Injection	purge and trap split (split ratio 25:1)
Inj. Temp.:	250 °C
Purge and Trap	
Instrument:	O.I. 4560 Purge and Trap Concentrator
Trap Type:	#10 Tenax®/silica gel/carbon molecular sieve
Purge:	11 min @ 20 °C, flow 38 mL/min
Desorb:	1.0 min @ 190 °C, flow 32 mL/min
Bake:	10 min @ 210 °C
Oven	
Oven Temp:	35 °C (hold 7 min) to 90 °C at 4 °C/min to 220 °C at 45 °C/min (hold 1 min)
Carrier Gas	He, constant flow
Flow Rate:	1.3 mL/min
Dead Time:	1.47 min @ 35 °C
Detector	MS
Mode:	Scan
Tune Type:	PFTBA/BFB
Scan Range:	35-260 amu
Instrument	Aglient 5971A GC/MS
Notes	10 mL sample @ 40°C
Acknowledgement	Purge and Trap courtesy of O.I. Analytical.

The internal standard methyl-d3 *tert*-butyl ether was added to compensate for variations in purging efficiency specific to the ethers. After the data were acquired we observed a small ion 73 component as part of the IS mass spectrum (Figure 4). MTBE and the IS share retention time and MTBE produces ion 73. Our initial thought was to discard the data, but we determined the distribution of the relative abundance of ion 73 to ion 76 for the IS was between 0.3% and 0.5%. This would affect calculated concentrations of MTBE by no more than 2%. Analysts in environmental laboratories can decide if this is an acceptable degree of error. Some laboratories use TBA-d9 instead, which accounts for variations common to alcohols, but not to ethers.

Figure 4 MTBE and internal standard methyl-d3-*tert*-butyl ether share identification ion 73.



Column	Rtx®-VMS, 30 m, 0.25 mm ID, 1.4 µm (cat.# 19915)
Sample	Custom
Injection	purge and trap split (split ratio 25:1)
Inj. Temp.:	250 °C
Purge and Trap	
Instrument:	O.I. Analytical 4560 with 4551A Autosampler
Trap Type:	#10 (Tenax®/silica gel/carbon molecular sieve)
Purge:	11 min @ 20 °C, flow 38 mL/min
Desorb Preheat Temp.:	150 °C
Desorb:	1.0 min @ 190 °C, flow 32 mL/min
Bake:	10 min @ 210 °C
Transfer Line Temp.:	110 °C
Oven	
Oven Temp:	35 °C (hold 7 min) to 90 °C at 4 °C/min to 220 °C at 45 °C/min (hold 1 min)
Carrier Gas	He, constant flow
Flow Rate:	1.3 mL/min
Dead Time:	1.47 min @ 35 °C
Detector	Agilent 5971A GC/MS
Transfer Line Temp.:	280 °C
Tune Type:	PFTBA/BFB
Scan Range:	35-260 amu
Notes	Sample size: 10 mL Sample temp: 40 °C Water management: 110 °C purge, 0 °C desorb, 240 °C bake 6-Port valve: 110 °C Sparge mount: 45 °C Valve manifold: 50 °C Other Conditions: prepurge, preheat, dry purge OFF
Acknowledgement	Purge & trap courtesy of O.I. Analytical

Conclusion

With an expanding target list and difficult sample matrixes, such as petroleum distillates, extreme care must be taken, even with GC-MS, to assure correct identification of oxygenates in the presence of interfering analytes. Under the conditions used here, an Rtx®-VMS column is suitable for analyzing low levels of oxygenates in the presence of other gasoline components. For additional information, view our presentation [5].

References

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[2] A.M. Happel, E.H. Beckenbach, R.U. Halden, An Evaluation of MTBE Impacts to California Groundwater Resources, UCRL-AR-130897, Lawrence Livermore National Laboratory, 1988.
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