

The Analysis of Oxygenates by EPA Method 8260

Chris M. English, Frank L. Dorman &
Gary Stidsen.

(Restek Corporation, 110 Benner Circle, Bellefonte, PA 16823)

Abstract

Gasoline and other fossil fuels are derived from petroleum and consist mainly of compounds containing only carbon and hydrogen atoms. Oxygenates are compounds that contain oxygen atoms in addition to carbon and hydrogen. 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. 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. With over one million underground fuel tanks in the United States alone, contamination of ground and surface water with oxygenates and gasoline components is a major environmental concern.

Storage tanks worldwide potentially will require cleanup in the future. An equally challenging task is the identification and quantification of these fuel-derived pollutants in a gasoline matrix, since compounds such as MTBE and TBA (tert-butyl alcohol) share ions using GC/MS and coelute on many capillary column stationary phases. Regulatory agencies recommend adding 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. The US EPA has not sanctioned any method specifically for the analysis of oxygenates in gasoline. Environmental laboratories have used a variety of methods to report these analytes, such as US EPA Methods 8015, 8020, and 8260.

The analysis of oxygenates by EPA Method 8260 is a common way to increase the level of confidence in chromatographic data over GC methods. Lawrence Livermore National Laboratory has conducted studies indicating that GC/MS is the most reliable method of oxygenate detection in complex gasoline samples regardless of the concentration of the gasoline. This paper will examine the limitations of currently available columns, and will show Method 8260 applications with the addition of oxygenates to the compound list.

Introduction

Oxygen containing compounds most commonly added to gasoline are methanol, ethanol, *tert*-butanol (TBA), methyl-*tert*-butyl ether (MTBE), diisopropylether (DIPE), ethyl-*tert*-butylether (ETBE). Of these compounds MTBE is the primary additive. The ethers have not been validated in any SW-846 method. They have not been written into any EPA Method with the exception of MTBE in Method 524.2. The analytical challenge of quantitatively determining concentrations of oxygenates in the presence of gasoline has been the focus of several studies. The most commonly used wastewater tests for these compounds by Environmental laboratories are Methods, 8015, 8021 & 8260.

Method 8015 uses a flame ionization detector (FID) to match a known pattern of gasoline with an unknown sample containing peaks that fall within the gasoline pattern range. This method can be used to identify oxygenates by retention time, but the high probability of mis-identifications necessitates second column confirmation.

Method 8021 is specifically written for the analysis of aromatic and halogenated volatiles. This is the least desirable of the three methods since the photoionization detector (PID) is very sensitive to double bonds but much less sensitive to oxygenates. Our test of a gasoline composite standard resulted in a false positive for diisopropyl ether. Using GC/MS for confirmation the compound was identified as 2-methyl-1-pentene.

The most reliable methods use purge-and-trap capillary column gas chromatography/mass spectrometry (GC/MS), such as Method 8260. The GC/MS provides positive identification and overcomes the problem of false identification of unresolved constituents. Modifications to operating conditions are necessary to increase analyte response and optimize resolution between oxygenates and other target compounds of interest. One example of a required separation by GC/MS is TBA and MTBE since they share ions.

This paper presents the results of four different stationary phases evaluated in the same column dimensions for oxygenate recoveries, verifying passing criteria using modified EPA Method 5030B and Method 8260. Purge and trap conditions were changed to accommodate the addition of oxygenates. GC oven conditions were optimized for each stationary phase used to overcome coelutions of analytes that share ions. Non-oxygenated gasoline samples were spiked with low levels of oxygenates to determine if operating conditions were appropriate for separation and detection of target compounds in the presence of high concentrations of gasoline.

Experimental

The study first established that Method 8260B criteria were met. Tuning of the GC/MS was performed using 25ng standard of 4-bromofluorobenzene. All of the target compounds were added to the calibration mix along with the internal standards, the ethers and TBA (See Table 2). Methanol and ethanol were not added since these analytes are more amenable to headspace or direct injection techniques. Method 8260B does not specifically outline internal standard assignments to target compounds; therefore, Table 6 of Method 8260¹ was used. Also the internal standards and surrogates of Method 8260¹ as well as the characteristic primary ions for quantification were incorporated into our experimental design. This allowed relative response factors to be measured against established internal standards. Calibration of the curve was conducted using average response factors as outlined in section 7.6.2.1¹.

The minimum mean response factors (RFs) for the volatile system performance check compounds (SPCC) as described by the method are shown in Table 1 for the four different calibrations and columns. This test confirms acceptable performance of the purge and trap concentrator.

Table 1: Passing SPCC criteria for all columns under specific conditions.	Rtx-624	Rtx-Volatiles	Rtx-VRX	Rtx-VMS	EPA Response Factor (RF) Criteria
pentafluorobenzene (IS)	RF	RF	RF	RF	RF
chloromethane (spcc)	0.37	0.51	0.28	0.59	>0.10
1,1-dichloroethane (spcc)	0.68	0.19	0.59	0.64	>0.10
chlorobenzene-d5 (IS)					
chlorobenzene (spcc)	0.97	1.01	0.82	1.06	>0.30
bromoform (spcc)	0.28	0.27	0.27	0.32	>0.10
1,4-dichlorobenzene-d4 (IS)					
1,1,2,2-tetrachloroethane(spcc)	0.68	0.77	0.53	0.71	>0.30

¹ Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy (GC/MS): Capillary Column Technique Method 8260; U.S. Environmental Protection Agency. Office of Solid Waste. Washington, D.C. July 1992 Revision 0.

² Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy (GC/MS): Capillary Column Technique Method 8260B; U.S. Environmental Protection Agency. Office of Solid Waste. Washington, D.C. December 1996 Revision 2.

Table 2: Compound List for Oxygenate Study.

<u>COMPOUND</u>	#	<u>COMPOUND</u>	#	<u>COMPOUND</u>	#
1,1,1,2-tetrachloroethane	1	4-chlorotoluene	35	iodomethane	69
1,1,1-trichloroethane	2	4-methyl-2-pentanone	36	isobutyl alcohol	70
1,1,2,2-tetrachloroethane	3	acetone	37	isopropylbenzene	71
1,1,2-trichloroethane	4	acetonitrile	38	methacrylonitrile	72
1,1-dichloroethane	5	acrylonitrile	39	methyl acrylate	73
1,1-dichloroethene	6	allyl chloride	40	methyl methacrylate	74
1,1-dichloropropene	7	benzene	41	methylene chloride	75
1,2,3-trichlorobenzene	8	bromobenzene	42	methyl-tert-butyl ether	76
1,2,3-trichloropropane	9	bromochloromethane	43	methyl-d3-tert-butyl ether	77
1,2,4-trichlorobenzene	10	bromodichloromethane	44	m-xylene	78
1,2,4-trimethylbenzene	11	bromoform	45	naphthalene	79
1,2-dibromo-3-chloropropane	12	bromomethane	46	n-butylbenzene	80
1,2-dibromoethane	13	Carbon disulfide	47	nitrobenzene	81
1,2-dichlorobenzene	14	Carbon tetrachloride	48	n-propylbenzene	82
1,2-dichloroethane	15	chlorobenzene	49	o-xylene	83
1,2-dichloroethane-d4	16	chlorobenzene-D5	50	pentachloroethane	84
1,2-dichloropropane	17	chloroethane	51	pentafluorobenzene	85
1,3,5-trimethylbenzene	18	chloroform	52	p-isopropyltoluene	86
1,3-dichlorobenzene	19	chloromethane	53	propionitrile	87
1,3-dichloropropane	20	chloroprene	54	p-xylene	88
1,4-dichlorobenzene	21	cis-1,2-dichloroethene	55	sec-butylbenzene	89
1,4-dichlorobutane	22	cis-1,3-dichloropropene	56	stryrene	90
1,4-dichlorobenzene-d4	23	cis-1,4-dichloro-2-butene	57	tert-amyl-methyl ether	91
1,4-difluorobenzene	24	dibromochloromethane	58	tert-butyl alcohol	92
1,4-dioxane	25	dibromofluoromethane	59	tert-butylbenzene	93
2,2-dichloropropane	26	dibromomethane	60	tetrachloroethene	94
2-bromo-1-chloropropane	27	dichlorodifluoromethane	61	tetrahydrofuran	95
2-butanone	28	diethylether	62	toluene	96
2-chloroethanol	29	diisopropyl ether	63	toluene-d8	97
2-chloroethyl-vinyl-ether	30	ethyl methacrylate	64	trans-1,2-dichloroethene	98
2-chlorotoluene	31	ethylbenzene	65	trans-1,3-dichloropropene	99
2-hexanone	32	ethyl-tert-butyl ether	66	trans-1,4-dichloro-2-butene	100
2-nitropropane	33	Freon 113	67	trichloroethene	101
4-bromo-1-fluorobenzene (ss)	34	hexachlorobutadiene	68	trichlorofluoromethane	102
				vinyl chloride	103
Internal Standard/Surrogate		Target Analyte		Oxygenate	

Following the passing SPCC, the calibration check compounds (CCCs) were used to verify the validity of the calibration. The relative standard deviation of these compounds must be less than 15% (See Table 3).

Table 3: Passing CCC criteria for all columns under specific conditions.	Rtx-624	Rtx-Volatiles	Rtx-VRX	Rtx-VMS	EPA Relative Standard Deviation Criteria
pentafluorobenzene (IS)	%RSD	%RSD	%RSD	%RSD	%RSD
1,1-dichloroethene (ccc)	13.6%	5.7%	9.5%	11.4%	< 15%
chloroform (ccc)	11.2%	6.0%	9.8%	5.5%	< 15%
1,4-difluorobenzene (IS)					
1,2-dichloropropane (ccc)	10.7%	7.9%	10.0%	4.9%	< 15%
toluene (ccc)	13.8%	6.7%	11.0%	3.0%	< 15%
chlorobenzene-d5 (IS)					
ethylbenzene (ccc)	10.1%	6.6%	8.4%	5.5%	< 15%
1,4-dichlorobenzene-d4 (IS)					< 15%
1,1,2,2-tetrachloroethane(spcc)	11.7%	3.2%	8.5%	8.6%	< 15%

Oxygenates were calculated off of the internal standard methyl-d3-tert-butyl ether to account for differences in purging efficiency specific to the ethers. The internal standards (red) in table 4 were used for calculating the RFs, RSDs and %recoveries of the target analytes shown.

Table 4: Internal standards (red) with corresponding analytes assigned for quantitation.	
methyl-D3 tert-butyl ether (IS)	1,4-difluorobenzene (IS)
methyl-tert-butylether	1,2-dichloroethane-d4 (ss)
tert-butyl alcohol (x5)	1,2-dichloropropane (ccc)
diisopropyl ether	toluene-d8 (ss)
ethyl-tert-butyl ether	toluene (ccc)
tert-amyl-methyl ether	bromofluorobenzene (ss)
pentafluorobenzene (IS)	chlorobenzene-d5 (IS)
chloromethane (spcc)	chlorobenzene (spcc)
1,1-dichloroethene (ccc)	ethylbenzene (ccc)
acetone (x2.5)	bromoform (spcc)
1,1-dichloroethane (spcc)	1,4-dichlorobenzene-d4 (IS)
chloroform (ccc)	1,1,2,2-tetrachloroethane(spcc)
dibromofluoromethane (ss)	naphthalene

Purge and Trap Procedures: Purge and trap conditions were not varied between column changes, tuning and calibrations. Below is a table detailing the purge and trap conditions common to the four columns tested for oxygenate recoveries from gasoline. Samples were heated using the Infra-Sparge™ sample heater on the O.I. 4560 concentrator. A heated purge of 40°C was the minimum temperature that would allow TBA to be detected at a concentration of 25 ppb in 10ml of water. Purge flow rate was carefully measured at 38 ml/min since lower flows dramatically effect the brominated compounds and higher flows contribute to trap breakthrough and excessive water retention.

Table 5: O.I. 4560 Purge and Trap Concentrator Conditions.

Trap	#10 trap (Tenax/Silica Gel/Carbon Molecular Sieve)
Trap Temperatures	20°C During Purge, 190°C During Desorb, 210°C During Bake.
Purge Time	11 minutes
Purge Flowrate	38ml/min
Desorb Flowrate	32ml/min
Desorb Time	1.0 minutes
Bake Time	10 minutes
6-Port Valve	110°C
Transfer Line	110°C
Sample	40°C
Sample Size	10ml
Water Management	110°C During Purge, 0°C During Desorb, 240°C during Bake
Sparge Mount	45°C
Desorb Preheat	150°C
Valve Manifold	50°C
Split Ratio	1:25
Others	Pre-Purge, Pre-Heat & Dry Purge: OFF

Conditions Suggested by O.I. Analytical see acknowledgments.

Choice of trap was based upon the recommendation of the instrument manufacturer. Future studies will examine different trap packing materials and their effects on oxygenate recoveries.

Instrumental Procedures: The study was conducted using an Agilent 5890 Series II GC coupled with an Agilent 5971A GC/MS detector with an after-market K&M electron multiplier. Helium carrier gas was adjusted for all columns to be at 1.3-ml/min constant flow. The GC/MS was set for full scan from 35amu to 260amu and was initially tuned with calibration gas (FC-43 or PFTBA), followed by BFB.

Standards: Separate intermediate standards were made for each calibration point to maintain equal amounts of methanol added to the 10ml volume of water. Sample transfer to the concentrator and sample spiking were done by hand. Calibration was performed using the analyte list in table 4, but all of the compounds in table 2 were added to check for critical coelutions between oxygenates and the regular Method 8260B target compounds. The five points of the calibration were; 5, 10, 20, 40 and 80ppb with internal standards (IS) and surrogate standards (SS) spiked at 20ppb. Calibration verification standards (CVS) were spiked at 10ppb with recoveries within 20% of the expected values. Two blanks were analyzed followed by a 5ppb standard to verify recoveries at the low point of the curve. The standards are listed below in table 6.

Table 6: Volatile Standards	Restek Part #s
Internal Standard & Surrogate Standard Mix	Cat# 30240 Lot# A025538 Custom Lot#03010401s Cat# 30074 Lot# A022472
Calibration Mix	Cat# 30475B Lot# A021105 Cat# 30465 Lot# A024826 Cat# 30006 Lot# A024175 Cat# 30042 Lot# A024616
QC Second Source Calibration Mix	Cat# 553595 Lot# A025888
Unleaded Gasoline (Unweathered)	Cat# 30096 Lot# A022384
Non-Oxygenated Unleaded Gasoline (Unweathered)	Custom Lot# OFR-TK253

Gasoline Spiked Samples: After the 5 ppb QC standard was analyzed a 1 ppm non-oxygenated gasoline standard was run. The non-oxygenated standard was analyzed a second time with 5ppb of the target compounds spiked. Calculations determined the % recoveries of a 5 ppb oxygenates standard from a high concentration gasoline matrix (1ppm). The final standard was a 1 ppm unleaded gasoline (unweathered) sample. All of the above samples were spiked with the appropriate IS and SS.

Results and Discussion

Calibration curves for the four columns evaluated passed EPA 8260 criteria for response factors and relative standard deviations. Two compounds in the test set showed poor response, acetone and TBA. The Rtx-624, Rtx-Volatiles, Rtx-VRX and Rtx-VMS were tested in the 30m x 0.25mm x 1.4df column dimensions.

Rtx-624 Results: The 30m x 0.25mm ID column was unable to adequately resolve TBA from MTBE. Extracted ion chromatograms illustrate that a minor ion of MTBE (59) contributed to the area of TBA (fig. 1).

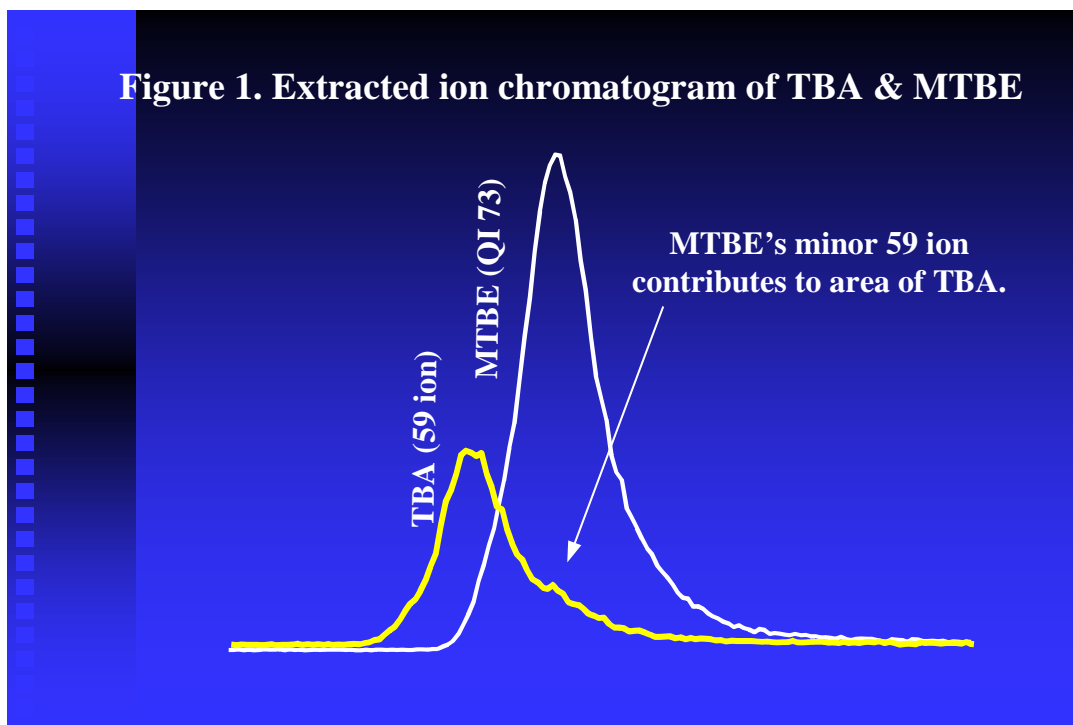


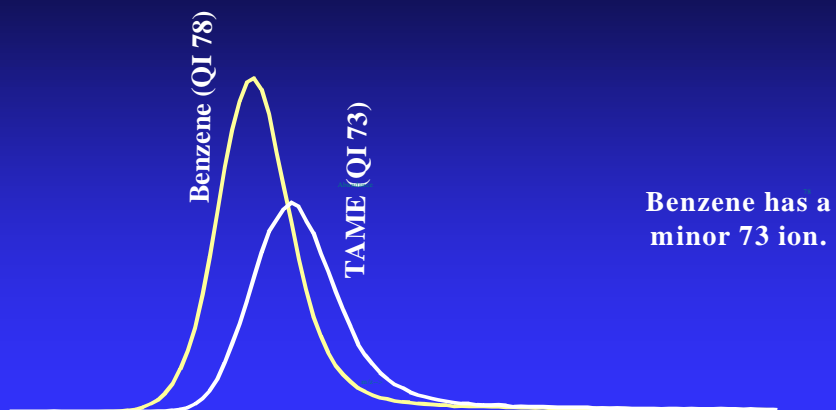
Table 7 is a summary of the results of the Rtx-624 column evaluation. The optimized oven conditions were as follows: 35°C (hold 6 min.) to 90°C @ 8°C/min. (hold 1 min.) to 220°C @ 16°C/min. (hold 2 min.). The GC runtime was 24 minutes with a cycle time of 30 minutes. This column is capable of resolving the ethers from a 1ppm standard of unleaded gasoline. Since TBA is a breakdown component of MTBE and is also a gasoline additive these column dimensions and conditions are not recommended for the analysis of TBA.

Table 7: Rtx-624 30m x 0.25mm x 1.4df Results		5 pointcurve		Method Blank	5 ppb Standard	1 ppm non-oxygenated Std.	1 ppm non-oxygenated w/ 5 ppb spike	1 ppm gasoline composite standard
		RF	RSD	REC	REC	REC	REC	REC
methyl-D3 tert-butyl ether (IS)								
tert-butyl alcohol (x5)		0.19	7%		77%		81%	< D.L.
methyl-tert-butylether		0.95	7%		102%		101%	6.0 ppb
diisopropyl ether		1.14	8%		110%		97%	
ethyl-tert-butyl ether		1.19	6%		107%		99%	
tert-amyl-methyl ether		1.14	8%		103%		95%	< D.L.
pentafluorobenzene (IS)								
acetone (x2.5)		0.06	22%		55%		J 7.2ppb	< D.L.
dibromofluoromethane (ss)		0.49	4%	103%	104%	102%	103%	105%
1,4-difluorobenzene (IS)								
1,2-dichloroethane-d4 (ss)		0.25	4%	100%	104%	103%	102%	104%
toluene-d8 (ss)		0.90	7%	108%	104%	108%	108%	110%
toluene (ccc)		0.66	14%		106%	102 ppb	106 ppb	90.1 ppb
bromofluorobenzene (ss)		0.34	17%	118%	87%	121%	122%	123%
chlorobenzene-d5 (IS)								
chlorobenzene (spcc)		0.97	8%		104%		103%	
ethylbenzene (ccc)		1.47	10%		104%	24.6 ppb	28.9 ppb	24.9 ppb
1,4-dichlorobenzene-d4 (IS)								
naphthalene		2.28	5%		141%	4.4 ppb	8.6 ppb	5.1 ppb

Rtx-Volatiles Results: Table 8 is a summary of the results collected using the Rtx-Volatiles column. The optimized oven conditions were as follows: 35°C (hold 6 min.) to 140°C @ 10°C/min. (hold 0 min.) to 220°C @ 20°C/min. (hold 2 min.). The GC runtime was 22.5 minutes with a cycle time of less than 30 minutes. Distance between TBA and MTBE was 0.8 minutes on this stationary phase. 1,1-dichloroethene has a minor 59 ion but is nearly resolved from TBA (QI 59). The column in table 8 labeled, “1 ppm non-oxygenated Std” appears to have trace amounts of TAME present. Upon further investigation there is a contribution of ion 73 from benzene (fig. 2). TAME and Benzene elute at nearly the same time. These column dimensions and conditions would be unsuitable for the analysis of higher concentrations of benzene in the presence of TAME.

Table 8: Rtx-Volatiles 30m x 0.25mm x 1.4df Results	5 pointcurve	5 pointcurve	Method Blank	5 ppb Standard	1 ppm non-oxygenated Std.	1 ppm non-oxygenated w/ 5 ppb spike	1ppm gasoline composite standard
methyl-D3 tert-butyl ether (IS)	RF	%RSD	REC	REC	REC	REC	REC
tert-butyl alcohol (x5)	0.15	6%		73%		50%	< D.L.
methyl-tert-butylether	0.97	6%		96%		98%	5.8 ppb
diisopropyl ether	1.21	9%		94%		98%	
ethyl-tert-butyl ether	1.21	8%		96%		98%	
tert-amyl-methyl ether	1.15	7%		98%	< D.L.	107%	< D.L.
pentafluorobenzene (IS)							
acetone (x2.5)	0.08	11%		50%		64%	< D.L.
dibromofluoromethane (ss)	0.49	1%	102%	103%	99%	102%	99%
1,4-difluorobenzene (IS)							
1,2-dichloroethane-d4 (ss)	0.21	2%	104%	106%	109%	109%	106%
toluene-d8 (ss)	1.01	2%	102%	102%	100%	98%	99%
toluene (ccc)	0.76	7%		105%	94.3 ppb	100 ppb	84.3 ppb
bromofluorobenzene (ss)	0.43	6%	103%	103%	99%	99%	99%
chlorobenzene-d5 (IS)							
chlorobenzene (spcc)	1.01	6%		103%		110%	
ethylbenzene (ccc)	1.62	7%		100%	21.5 ppb	28.0 ppb	23.9 ppb
1,4-dichlorobenzene-d4 (IS)							
naphthalene	1.96	9%		111%	4.9 ppb	11.0 ppb	5.94 ppb

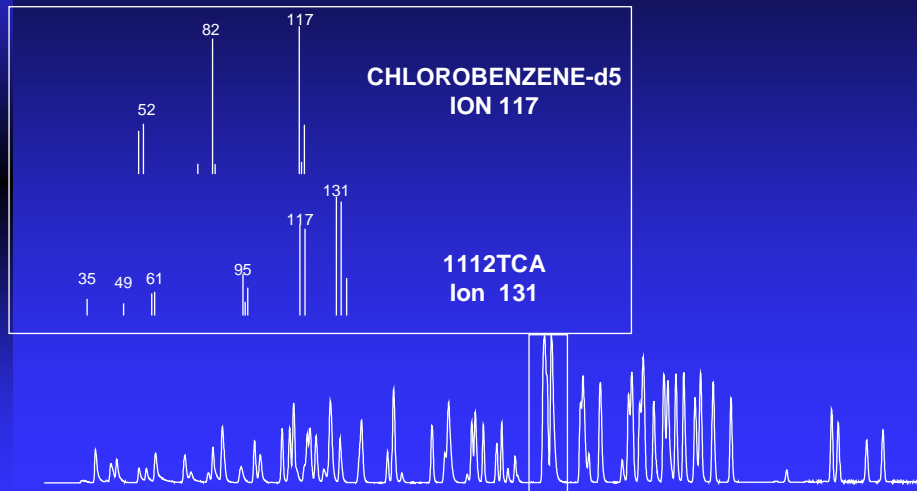
Figure 2. Extracted ion chromatogram of Benzene & TAME



Rtx-VRX Results: The optimized oven conditions were as follows: 40°C (hold 1min.) to 75°C @ 2°C/min. (hold 1 min.) to 220°C @ 22°C/min. (hold 2 min.). The GC runtime was 26 minutes with a cycle time of just over 30 minutes. The Rtx-VRX has the same close elution of 1,1-dichloroethene / TBA as the Rtx-Volatiles phase. These target analytes share ion 59. A lower starting temperature or a longer initial hold time will easily resolve these analytes. On this stationary phase the internal standard chlorobenzene-d5 and 1,1,1,2-tetrachloroethane, which share ion 117, coelute which requires either changing the internal standard choice or changing the quantification ion to 82 (fig. 3). The Rtx-VRX is a good choice for analyzing oxygenates in gasoline (Table).

Table 9: Rtx-VRX 30m x 0.25mm x 1.4df Results	5 pointcurve	5 pointcurve	Method Blank	5 ppb Standard	1 ppm non-oxygenated Std.	1 ppm non-oxygenated w/ 5 ppb spike	1 ppm gasoline composite standard
	RF	%RSD	REC	REC	REC	REC	REC
methyl-D3 tert-butyl ether (IS)							
tert-butyl alcohol (x5)	0.18	13%		98%		121%	
methyl-tert-butylether	0.94	6%		105%		106%	5.7 ppb
diisopropyl ether	0.85	6%		100%		110%	
ethyl-tert-butyl ether	1.07	5%		104%		107%	
tert-amyl-methyl ether	1.06	5%		104%		103%	< D.L.
pentafluorobenzene (IS)							
acetone (x2.5)	0.06	18%		123%	< D.L.	144%	< D.L.
dibromofluoromethane (ss)	0.48	3%	97%	97%	98%	97%	96%
1,4-difluorobenzene (IS)							
1,2-dichloroethane-d4 (ss)	0.27	11%	100%	103%	100%	100%	99%
toluene-d8 (ss)	0.98	4%	96%	100%	96%	99%	97%
toluene (ccc)	0.70	11%		104%	94.8 ppb	99.2 ppb	82.1 ppb
bromofluorobenzene (ss)	0.44	12%	85%	98%	90%	94%	93%
chlorobenzene-d5 (IS)							
chlorobenzene (spcc)	0.82	15%		115%		111%	
ethylbenzene (ccc)	1.36	8%		113%	25.6 ppb	28.3 ppb	26.5 ppb
1,4-dichlorobenzene-d4 (IS)							
naphthalene	1.96	9%		111%	5.0 ppb	9.7 ppb	5.6 ppb

Figure 3: Rtx-VRX: Ion 82 can be used as the primary ion for Chlorobenzene-d5, allowing these two compounds to coelute



Rtx-VMS Results: Table 10 is a summary of the results gathered using the Rtx-VMS column. The optimized oven conditions were 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.). The GC runtime was 25 minutes with a cycle time of 30 minutes. All of the oxygenates are resolved from target compounds and interfering gasoline components. TBA and MTBE are well resolved using the 35°C starting temperature. Figure 4 represents a TIC of 1-ppm non-oxygenated unleaded gasoline spiked with 5 ppb of oxygenates. The inset in this figure is an extracted ion chromatogram showing the recovery of oxygenates without interference from the gasoline matrix.

Figure 4: Rtx-VMS 1 ppm Non-Oxygenated Gasoline Standard Spiked with 5 ppb Oxygenates.

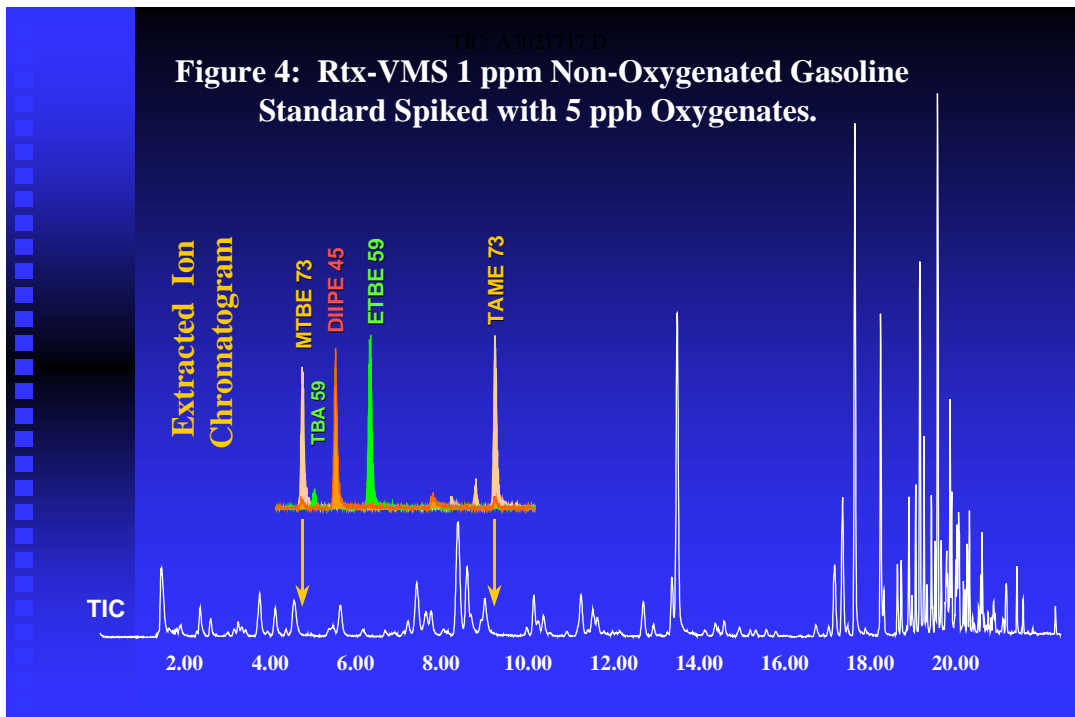


Table 10: Rtx-VMS 30m x 0.25mm x 1.4df Results	5 pointcurve	5 pointcurve	Method Blank	5 ppb Standard	1 ppm non-oxygenated Std.	1 ppm non-oxygenated w/ 5 ppb spike	1ppm gasoline composite standard
methyl-D3 tert-butyl ether (IS)	RF	%RSD	REC	REC	REC	REC	REC
tert-butyl alcohol (x5)	0.13	17%		93%		90%	
methyl-tert-butylether	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%	< D.L.
pentafluorobenzene (IS)							
acetone (x2.5)	0.05	12%		62%	< D.L.	N.D.	
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

Results: Table 11 provides results of an unleaded gasoline composite sample tested for the presence of oxygenates down to 5ppb. Trace amounts of TAME below the detection limit were observed using several ions for identification. MTBE results were very consistent from column to column.

Figure 11: Recoveries of MTBE in 1 ppm of unleaded gasoline composite sample.

methyl-D3 tert-butyl ether (IS)	Rtx-624	Rtx-Volatiles	Rtx-VRX	Rtx-VMS
methyl-tert-butylether	6.0 ppb	5.8 ppb	5.7 ppb	6.2 ppb

Future Studies

The next paper will calculate detection limits, enlarge the calibration curve, and calibrate the entire 8260B compound list shown in table 2. The focus will be on optimizing performance of oxygenates without sacrificing the 8260B target list. Response for TBA and acetone were a problem during this study. Steps will be taken to get better response for these compounds, i.e. testing new trap packing materials. Auto samplers will be incorporated into our next round of purge and trap studies to prove that these results can be duplicated in a production laboratory.

The internal standard M-d3-TBE was added to allow for variations in purging efficiency specific to the ethers. After the data was acquired we observed a small 73-ion fragment as part of the IS spectra. The IS and MTBE share retention time and MTBE uses ion 73. Our initial thoughts were to discard all of the data, but the distribution of the relative abundance of ion 73 to 76 was measured at between 0.3% and 0.5%. This may have effected calculated concentrations of MTBE by 2%. Future studies will replace this IS to eliminate the possibility of inaccuracy.

Conclusions

The Rtx-VRX and Rtx-VMS under the given conditions are suitable for analyzing low levels of oxygenates in the presence of gasoline. Incomplete resolution of TAME and benzene make the Rtx-Volatiles a poor choice for this application. The Rtx-624 also suffers from a coelution of TBA/MTBE. With an expanding target list and difficult sample matrixes, such as petroleum distillates, extreme care must be taken to assure correct compound identification in the presence of interfering analytes.

Acknowledgments

We would like to thank the following people for their technical contributions to this paper:

Laura Chambers, Applications Chemist, OI Corporation.
Jeff Gindstaff, GC/MS Manager, Columbia Analytical.
Barry Lesnik, Organic Methods Manager, USEPA OSW.
Hal White, Hydrogeologist, USEPA OUST.