RESTEK environmental

Applications note

Resolving Oxygenates from Gasoline Additives Using an Rtx®-VGC GC Column

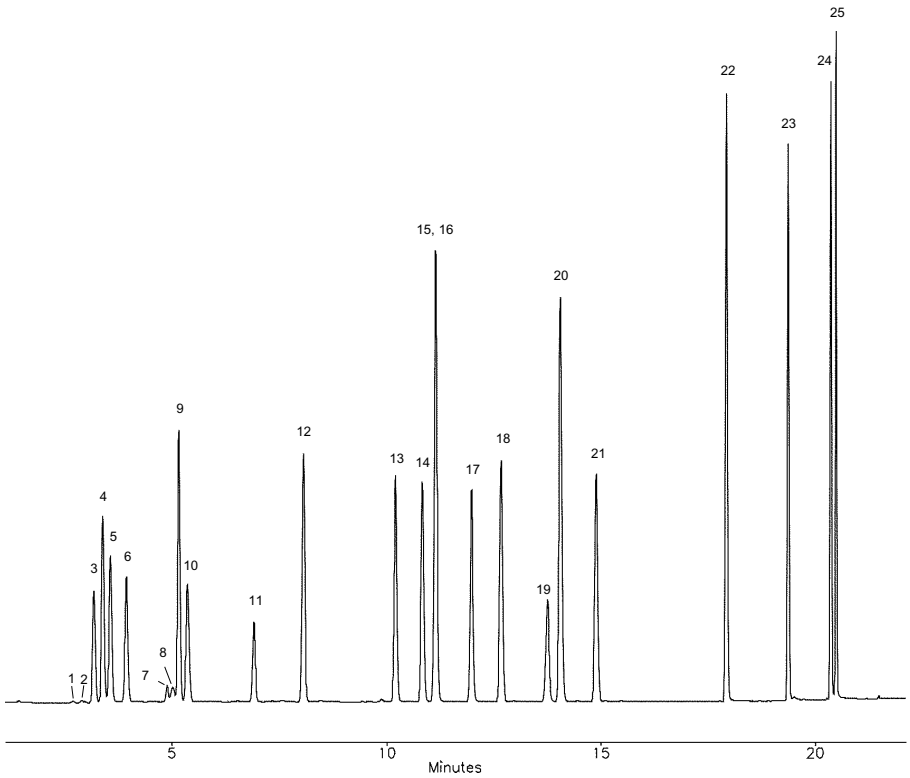
With over one million underground fuel tanks in the United States, contamination of ground and surface waters by gasoline in leaking tanks has been an environmental problem for years. Recent events have focused attention on a new class of compounds associated with gasoline leaks. These compounds, known as oxygenates—the most common of which is methyl-*tert*-butyl ether (MTBE), are added to gasoline to reduce overall emissions. Because oxygenates are polar compounds and are soluble in water, they move through aquifers easily. This poses a risk to drinking water supplies.

A variety of methods have been used by environmental laboratories to report oxygenates in gasoline, such as EPA Methods 8015, 8260, 8240, and 8020. Some of these methods recommend flame ionization (FID) or photoionization (PID) detection, while others recommend gas chromatography/mass spectrometry (GC/MS). Environmental samples contaminated with gasoline can contain both hydrocarbons and oxygenates, and to identify oxygenates it is necessary to chromatographically separate them from the hydrocarbons.

The success of these methods is based on the ability of the analytical column to resolve oxygenates from the early-eluting alkanes, alkenes, and, to a lesser extent, the alkynes. To minimize false positive results for MTBE, it is important to separate it from 2-methylpentane and 3-methylpentane. Nonpolar phases (e.g., Rtx®-1 and DB-MTBE columns) have been recommended for separating these compounds. However, these phases are incompatible with polar compounds, which can result in broader peaks and lower capacity for the alcohols. Another potential interference for MTBE is *tert*-butyl alcohol (TBA). The EPA recommends adding TBA to the target list for contaminated sites known to contain MTBE because it is a breakdown product of MTBE and an additive in gasoline. Both of these compounds respond on the photoionization detector (PID) and they share ions using mass spectrometry (MS) detection, so MTBE and TBA must be resolved regardless of which detector is used.

The Restek Rtx®-VGC column is coated with a medium polarity phase, which makes it ideal for the analysis of both hydrocarbons and oxygenates. The unique polarity of this column improves the separation of oxygenates, which results in more accurate detection when using PID or FID. A 30m, 0.45mm ID, 2.55µm Rtx®-VGC column helps determine low concentrations of oxygenates in the presence of aliphatic compounds, resolving MTBE from 2-methylpentane, 3-methyl pentane, and TBA (Figure 1, peaks 1 to 4). These column dimensions allow for correct desorb flow rates from

Figure 1–Using purge and trap concentration, the Rtx®-VGC column resolves oxygenates and other target gasoline compounds better than other columns specifically designed to resolve MTBE.



1. 2-methylpentane
2. 3-methylpentane
3. methyl-*tert*-buyl ether
4. *tert*-butanol
5. diisopropyl ether
6. ethyl-*tert*-butyl ether
7. isooctane
8. *n*-heptane
9. benzene
10. *tert*-amyl-methyl ether
11. a,a,a-trifluorotoluene
12. toluene
13. 1-chloro-3-fluorobenzene
14. ethylbenzene
15. *m*-xylene
16. *p*-xylene
17. *o*-xylene
18. isopropylbenzene
19. ethyl-methylbenzene
20. 1,3,5-trimethylbenzene
21. 1,2,4-trimethylbenzene
22. 4-bromochlorobenzene
23. naphthalene
24. 2-methylnaphthalene
25. 1-methylnaphthalene

30m, 0.45mm, 2.55µm Rtx®-VGC (cat.# 19408); each component 100ppb in 5mL of RO water, except *tert*-butanol 5000ppb; 2/1-methynapthalene 150ppb; ethyl methyl benzene 50ppb. **GC:** Finnigan 9001; **Oven program:** 40°C (hold 2 min.) to 130°C @ 6°C/min. (hold 0 min.) to 230°C @ 30°C/min. (hold 2 min.). **Carrier gas:** helium @ ~8mL/min.; **Detector**: Finnigan PID, make up 7mL min., purge 7mL/min., set @ 0.35mV, base temperature 200°C.

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the purge and trap, faster analyses times, and better resolution of closely eluting peaks compared to traditional 0.53mm ID columns (Figure 2).

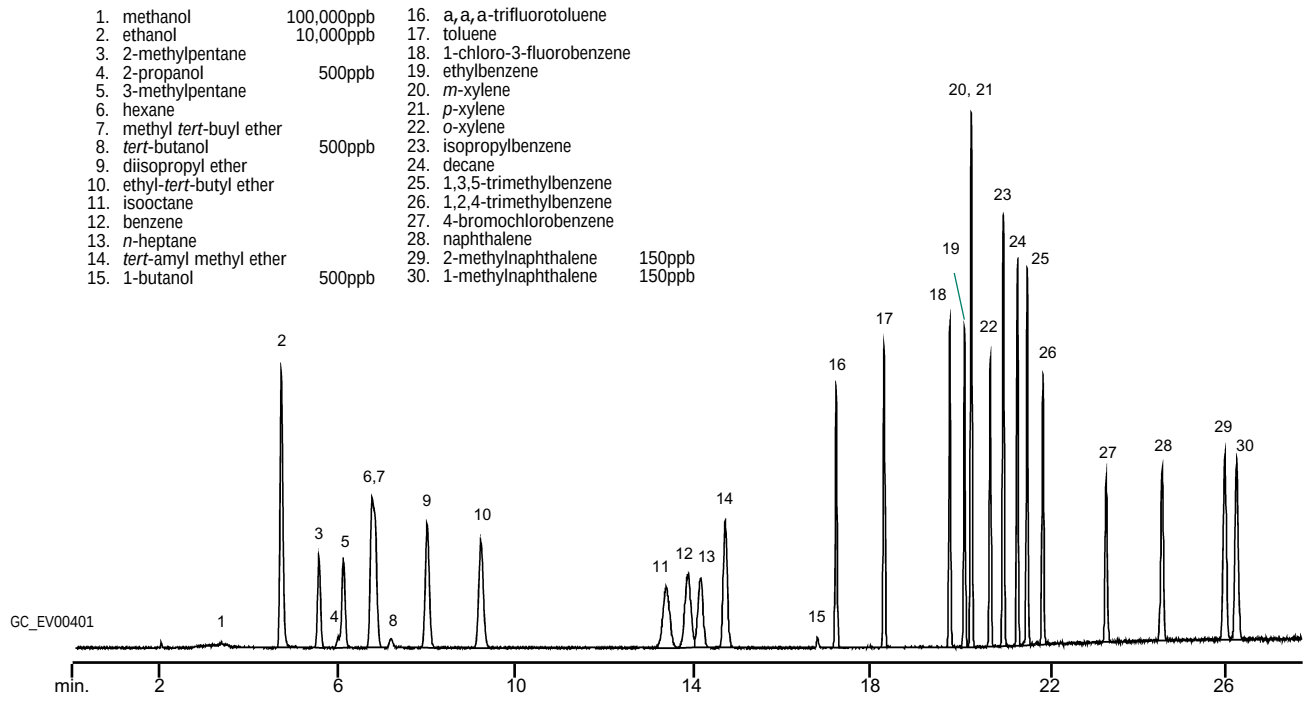
Oxygenates also can be analyzed by GC/MS following the protocol defined in US EPA Method 8260B. GC/MS is a common way to increase the level of confidence in chromatographic data over the GC methods. Using a 30m, 0.25mm ID, 1.4µm Rtx®-VGC column with a quadrapole MS can identify oxygenates and alcohols with a high degree of certainty because the compounds that share ions are well resolved using this column (Figure 2). The MS was used to positively identify oxygenates and pentanes from their spectra (Figure 3). Peak shapes are symmetrical for all these compounds using the Rtx®-VGC column, regardless of detector.

Purge and trap conditions such as purge time and temperature must be optimized to achieve good purging efficiency of oxygenates and hydrocarbons. You can review optimized conditions in the figures shown in this Applications Note. The selection of the trap adsorbent material also is critical to achieving accurate quantitative results. The most demanding compounds to analyze are the alcohols because they purge poorly and can interfere with other target analytes. A 'J' trap (e.g., BTEXTRAP™ trap) can handle a heavy sample load with percent levels of methanol, but has a lowered ability to retain the more polar analytes like ethers and alcohols. So, if the majority of your samples are highly contaminated soils requiring methanol extract and you are analyzing for MTBE, it is best to use a 'J' trap. For cleaner samples where sensitivity is an issue, then you will achieve better results with a 'K' trap (e.g., VOCARB 3000™ trap). Additionally, GC analysis conditions such as temperature program rate and flow rate are critical for achieving good separation of oxygenates from hydrocarbons.

To confirm the ability of the Rtx®-VGC to provide accurate quantitative results, a composite gasoline standard was analyzed using both PID and GC/MS. The GC/MS analysis was used to confirm the identity of the analytes that matched target compound retention times on the PID. Any compound that was found within 0.10 minute of a target compound could be identified as a possible oxygenate. The GC/MS confirmed that only one target compound, diisopropyl ether, gave a false positive retention time match with 2-methyl-1-pentene. Although 2-methyl-1-pentene is found at low concentrations relative to the methylpentanes, it responds well on the PID. Using the composite gasoline standard, no other oxygenates matched within the 0.10 minute retention time window, thereby making positive identification for most of the oxygenates possible using the PID (Figure 4). Because gasoline composition can vary from state to state, the use of a confirmation column or MS detection is strongly recommended because alkenes such as 2-methyl-1-pentene can interfere with positive identification of oxygen-containing compounds.

Chlorobenzene also is a common contaminant in drinking water and is commonly analyzed in addition to gasoline using purge and trap with PID detection. Because the boiling point and retention time of chlorobenzene are similar to ethylbenzene, *m*-xylene, and

Figure 2–Optimized Rtx®-VGC column dimensions (30m x 0.45mm ID) allow for correct desorb flow rates from the purge and trap, faster analyses times, and better resolution of closely eluting peaks compared to traditional 0.53mm ID columns.



30m, 0.25mm, 1.40µm Rtx®-VGC (cat.# 19415); 1:10 split at injection port; 1mm ID liner; Compounds at 100ppb in 5mL of RO water (unless otherwise noted); **Oven program:** 35°C (hold 14 min.) to 220°C @ 24°C/min. (hold 6 min.); **Carrier gas:** He @ ~1mL/min. constant; **Concentrator:** Tekmar LSC-3100 Purge and Trap; **Trap:** Vocarb™ 3000; **Purge:** 11 min. @ 40mL/min. @ ambient temperature; **Dry Purge:** 1 min. @ 40mL/min. (MCS bypassed using Silcosteel® tubing); **Desorb Preheat:** 245°C; **Desorb:** 250°C for 2 min., Flow 10mL/min.; **Bake:** 260°C for 8 min.;**Interface:** transfer line 0.32mm ID Siltek™ fused silica; **Detector:** HP 5973 MS; **Scan range:** 25 to 300 AMU.

p-xylene on many capillary columns, it is difficult to separate from the aromatic compounds found in gasoline. The Rtx®-VGC column resolves chlorobenzene from the other aromatic compounds, allowing quantitation by PID (Figure 5).

The excellent resolution achieved by the Rtx®-VGC column prevents misidentifications common with PID and FID. GC/MS methods provide positive identification of coeluting analytes, but the right column can avoid coelutions of compounds that share quantitation ions. The Rtx®-VGC column is selective, has a programmable temperature limit of 260°C, and exhibits exceptional low bleed at common operating temperatures of 230°C. It is an ideal choice for analyzing gasoline additives in GRO samples.

Figure 3–MS detection of a flash splitless 2µL injection positively identifies the oxygenates and pentanes.

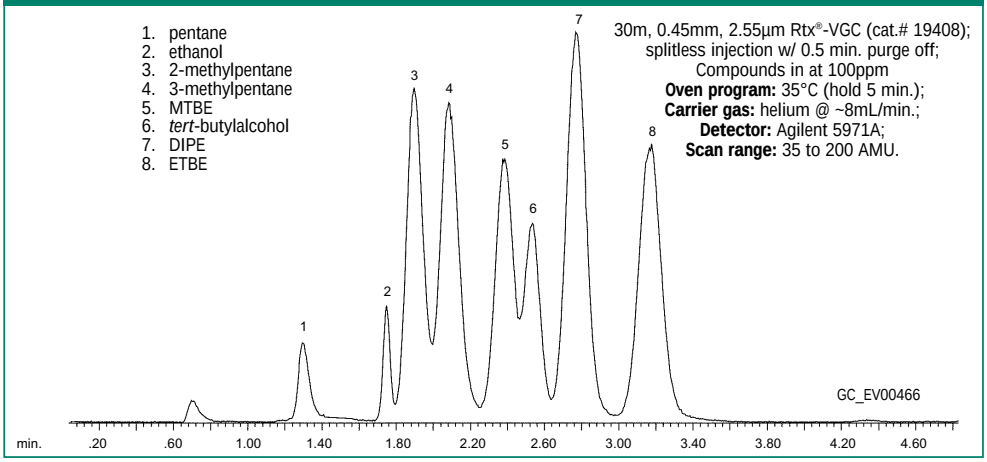


Figure 4–Using the Rtx-VGC column and a PID makes possible the identification of most oxygenates in a gasoline standard.

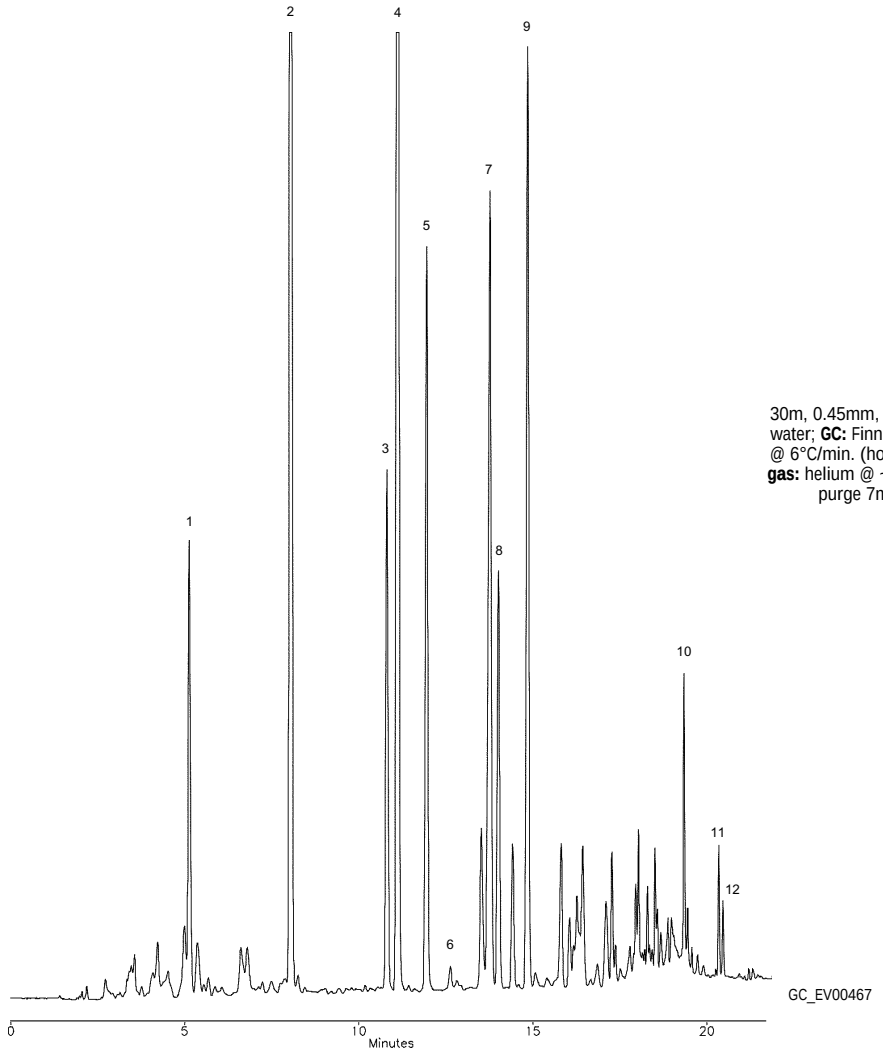
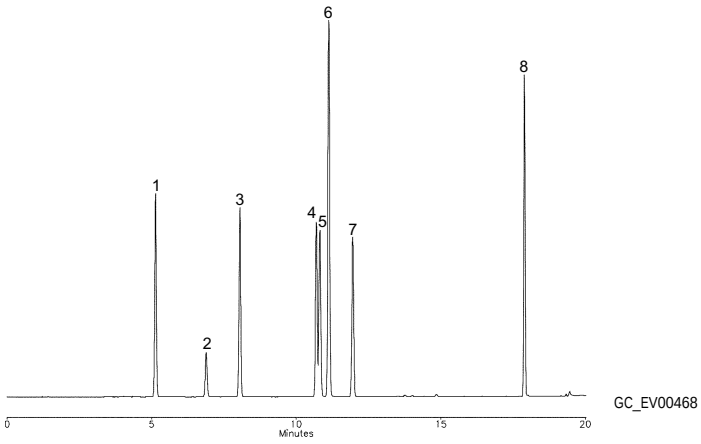


Figure 5–The Rtx®-VGC column successfully resolves chlorobenzene, allowing quantitation by PID.



1. benzene
2. a,a,a-trifluorotoluene
3. toluene
4. ethylbenzene
5. chlorobenzene
6. *m/p*-xylene
7. *o*-xylene
8. 4-bromo-1-chlorobenzene

30m, 0.45mm, 2.55µm Rtx®-VGC (cat.# 19408); 100ppb in 5mL of RO water; **GC:** Finnigan 9001; **Oven program:** 40°C (hold 2 min.) to 130°C @ 6°C/min. (hold 0 min.) to 230°C @ 30°C/min. (hold 2 min.); **Carrier gas:** helium @ ~8mL/min.; **Detector:** Finnigan PID, make up 7mL min., purge 7mL/min., set @ 0.35mV, base temperature 200°C

Rtx®-VGC Columns

(-40 to 240/260°C)

RESTEK Exclusive!

ID	df (µm)	30-Meter	60-Meter	75-Meter	105-Meter
0.25mm	1.40	19415	19416	—	—
0.32mm	1.80	19419	19420	—	—
0.45mm	2.55	19408	—	19409	—
0.53mm	3.00	19485	19488	19474	19489
ID	**df (µm)**	**20-Meter**	**40-Meter**		
0.18	1.00	49414	49415		

California Oxygenates Mix in P&T Methanol

diisopropyl ether	2,000µg/mL	*tert*-butyl alcohol	10,000µg/mL
ethyl-*tert*-butyl ether	2,000	methyl-*tert*-butyl ether	2,000
tert-amyl methyl ether	2,000		

1mL/ampul

	Each	5-pk.	10-pk.
	30465	**30465-510**	—
w/data pack	**30465-500**	**30465-520**	**30565**

Methanol Mix in DI Water

10,000µg/mL, 1mL/ampul

	Each	5-pk.	10-pk.
	30467	**30467-510**	—
w/data pack	**30467-500**	**30467-520**	**30567**

Ethanol Mix

10,000µg/mL in DI water, 1mL/ampul

	Each	5-pk.	10-pk.
	30466	**30466-510**	—
w/data pack	**30466-500**	**30466-520**	**30566**

Inlet Liners

For Agilent GCs

1mm Split Liner	*(1.0mm ID, 6.3mm OD, 78.5mm length)*
20972 (ea.)	20973 (5-pk.)

Siltek™ 1mm Uniliner®	*(1.0mm ID, 6.3mm OD, 78.5mm length)*
21052-214.1 (ea.)	21053-214.5 (5-pk.)

Unleaded Gasoline Component Standard

2,500µg/mL each in P&T methanol, 1mL/ampul

	Each	5-pk.	10-pk.
	30081	**30081-510**	—
w/data pack	**30081-500**	**30081-520**	**30181**

US EPA Method 8020A Calibration Mix

benzene	ethylbenzene
chlorobenzene	toluene
1,2-dichlorobenzene	*m*-xylene
1,3-dichlorobenzene	*o*-xylene
1,4-dichlorobenzene	*p*-xylene

2,000µg/mL each in P&T methanol, 1mL/ampul

	Each	5-pk.	10-pk.
	30222	**30222-510**	—
w/data pack	**30222-500**	**30222-520**	**30322**

aaa-trifluorotoluene

2,000µg/mL each in P&T methanol, 1mL/ampul

	Each	5-pk.	10-pk.
	30048	**30048-510**	—
w/data pack	**30048-500**	**30048-520**	**30148**

1-methylnapthalene

1,000µg/mL each in methanol, 1mL/ampul

	Each	5-pk.	10-pk.
	31283	**31283-510**	—
w/data pack	**31283-500**	**31283-520**	**31383**

PID Lamps

From Scientific Services Co.—"The Pioneers of the PID Lamp"

PID lamp model number	cat.#	PID lamp model number	cat.#
103C	20676	107-8.4	23022
108-10.0/10.6	20675	109-11.8	23023
108BTEX	23020	polishing kit	20674
108-9.6	23021		

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