THE ANALYSIS OF GASOLINE OXYGENATES USING A NEW CAPILLARY COLUMN STATIONARY PHASE.

CHRIS M. ENGLISH, CHRISTOPHER COX,
FRANK L. DORMAN, & DINESH PATWARDHAN.

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

ABSTRACT

There are a variety of methods for the analysis of oxygenates in gasoline, such as ASTM D2887/D4815, EPA 8015, EPA 8260, and EPA 8020. Most environmental laboratories have relied on one of these methods to report gasoline and oxygenate concentrations in difficult sample matrixes. The success of these methods is based on the ability of capillary columns to resolve the oxygenates and the early-eluting alkanes such as 2-methylpentane and 3-methylpentane.

The Rtx®-VGC column is more polar than other capillary columns commonly used for gasoline range organic (GRO) analysis, which allows excellent solubility and, thus, more retention and capacity of the oxygenates. This prevents the interference of these alcohols with the alkanes and early-eluting oxygenates. The unique ability of the Rtx®-VGC column to resolve these difficult compounds prevents mis-identifications, which are common with detectors such as the photo ionization detector (PID) and flame ionization detector (FID). GC/MS column selection also is very important in preventing compounds that share ions from coeluting. Because gasoline may contain more than 500 analytes, tuned selectivity and fewer coelutions will prevent high bias. The Rtx®-VGC column has a programmable temperature limit of 260°C and exhibits exceptionally low bleed at common operating temperatures of 230°C. This paper will show applications on the Rtx®-VGC column using different methods of detection.

INTRODUCTION

The US Clean Air Act of 1990 mandated the addition of oxygenates in 30% of America's gasoline supply to improve combustion of gasoline and decrease polluting emissions. Oxygen-containing compounds most commonly added to gasoline are methanol, ethanol, *tert*-butanol, methyl-*tert*-butylether (MTBE), diisopropylether (DIPE), ethyl-*tert*-butylether (ETBE), and *tert*-amylmethylether (TAME). Of these compounds MTBE is the primary additive. The combination of its relatively low manufacturing cost and non-corrosive nature made it a clear choice for the petroleum industry. Other oxygenates are added at much lower concentrations.

These compounds have vapor pressures that range from 68mm Hg for TAME to 250mm Hg for the most volatile, MTBE. The high vapor pressure of MTBE threatens air quality at the gasoline pumps. The oxygenates are polar, which contaminates ground water. In fact, an estimated 9,000 community drinking water wells now have detectable levels of MTBE contamination. Therefore, the US EPA has moved to ban MTBE use in gasoline. Other ethers can be used as additives, but they are more expensive and pose similar health risks.

Corn-based ethanol is the proposed gasoline additive, however higher percentages of this compound (above 20%) have been shown to aid in migration of gasoline plumes from leaking underground storage tanks (LUST). Ethanol has a lower toxicity, lower volatility, and is not environmentally persistent. A variety of methods has been used for the capillary gas chromatographic (GC) analysis of oxygenates in gasoline. Success of these methods is based on the established ability of the GC capillary column to resolve oxygenates from early-eluting alkanes such as 2-methylpentane and 3-methylpentane. Because of the possibility of widespread corn-based ethanol use, the environmental chemist must address the analytical challenges associated with determining concentrations of alcohols in samples.

This new column retains the alcohols to allow quantitation of ethanol without interference from methanol. Methanol is commonly used in preparing standards and may be added to gasoline as well. The increased polarity of this column retains oxygenates and alcohols, thus, the elution order is different compared to other more non-polar stationary phases. MTBE elutes after 2-methylpentane and 3-methylpentane. These are the most commonly misidentified compounds when using PID/FID for GRO analysis (Applications #1-5).

EXPERIMENTAL

The analysis of oxygenates by EPA Method 8260B is a common way to increase the level of confidence in chromatographic data over GC methods. The first application shows the Rtx®-VGC column using a Quadrapole Mass/Spectrometer for the identification of oxygenates and alcohols. The most demanding analytes in this analysis are the alcohols since these compounds are poor purgers and can interfere with other target analytes. The methylpentanes are resolved from the oxygenates in Application #1. Although these analytes are resolved by MS detection, a slight signal on the PID from these alkanes can contribute to the quantitation of low concentrations of oxygenates that share retention times. In Application #2 all of the oxygentates are shown on an optimized column dimension, a 30m, 0.45 mm ID column. This column allows for correct desorb flows from the purge and trap, a faster analysis time, and better resolution of closely eluting peaks over regular 0.53mm ID columns. This chromatogram shows the slight response from the methylpentanes on the PID (peaks 3 & 5), and highlights the difference in retention of these analytes using the Rtx®-VGC column. Positive identification of the oxygenates and pentanes was conducted using a MS as shown in the third application. Peak shapes of all of these analytes are sharp. This is a good example of matched polarity between the analytes and the stationary phase. Using a 100% dimethyl polysiloxane (i.e., Rtx®-1) column can result in broader peaks and less capacity of the alcohols due to incompatibility between the stationary phase and the analyte.

Once the standard was analyzed by MS and identification of the target compounds was complete, it was then run by purge and trap using a photoionization detector (PID). This standard contains common gasoline components that are compared to a composite gasoline standard (Application # 4). The composite gasoline standard was also analyzed by MS to confirm the presence of oxygenates. Our gasoline sample had no matches in retention time except one peak that shares the retention time of diisopropylether. Using the MS for confirmation, we believe the compound to be 2-methyl-1-pentene. Although this analyte is found at low concentrations relative to the methylpentanes, it responds well on the PID. Using this gasoline composite, no other peaks matched within the 0.10 minute retention time window, making identification of the oxygenates possible using the PID. The use of a confirmation column is strongly suggested because alkenes can interfere with identification of oxygen-containing compounds as discussed above.

Chlorobenzene was added in Application #5 because it is commonly analyzed in addition to gasoline using purge and trap with PID detection. Action limits for this compound are similar to benzene or lower. The Rtx®-VGC column resolves chlorobenzene allowing for quantitation using the PID.

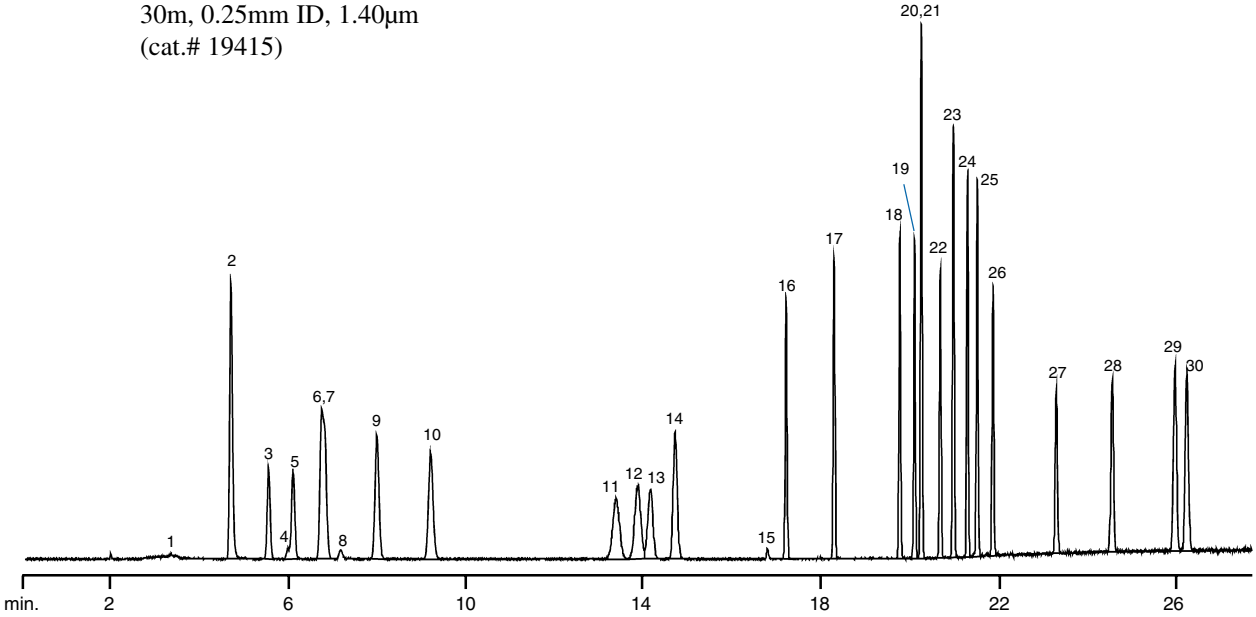
CONCLUSION

The Rtx®-VGC column is an excellent choice for GRO analysis because the most commonly found oxygen-containing compounds are resolved from alkanes & alkenes that normally coelute using other stationary phases. These polar target compounds have excellent solubility in the stationary phase, which increases retention and capacity. This column can be used for either GC or MS methods.

Application #1

Oxygenates & BTEX Rtx®-VGC

Rtx®-VGC
30m, 0.25mm ID, 1.40µm
(cat.# 19415)



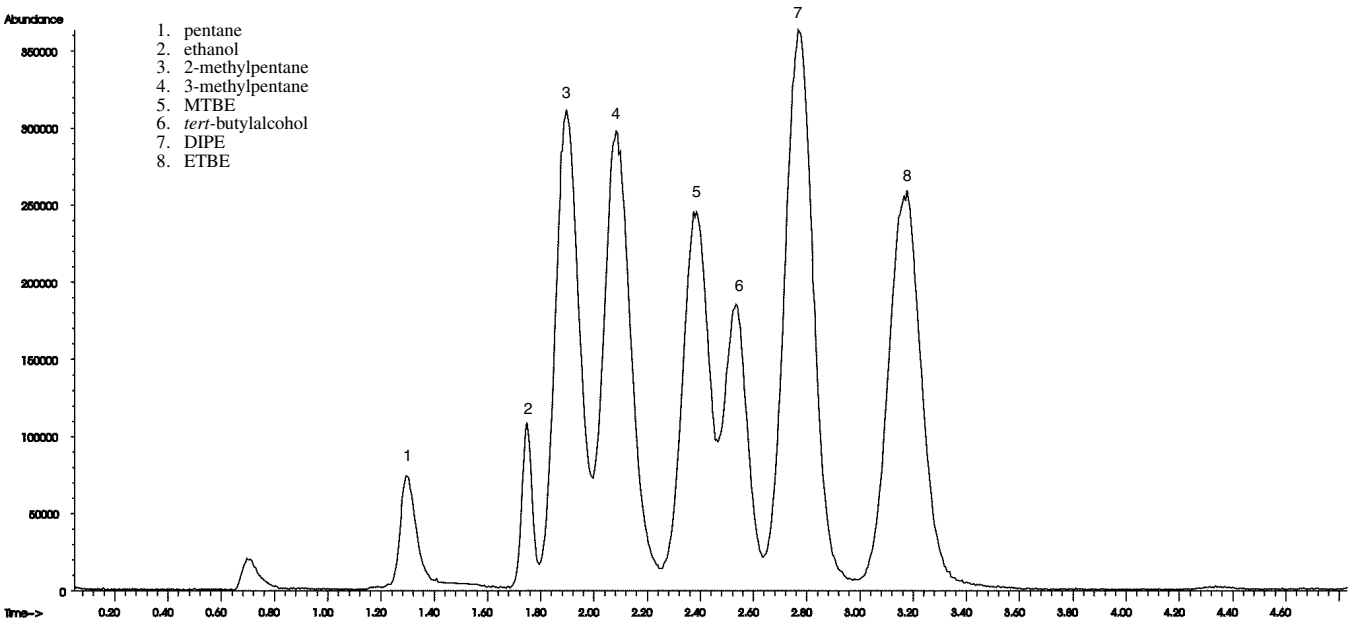
30m, 0.25mm, 1.40µm Rtx®-VGC (cat.# 19415)
1:10 split at injection port; 1mm ID sleeve
Compounds at 100ppb in 5mL of RO water (unless otherwise noted);
Oven program: 35°C (hold 14 min.) to 220°C @ 24°C/min. (hold 6 min.);
Carrier gas: He @ ~1mL/min. constant;
Concentrator: Tekmar LSC-3100 Purge and Trap;
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.

1. methanol 100,000ppb
2. ethanol 10,000ppb
3. 2-methylpentane
4. 2-propanol 500ppb
5. 3-methylpentane
6. hexane
7. methyl *tert*-buyl ether
8. *tert*-butanol 500ppb
9. diisopropyl ether
10. ethyl-*tert*-butyl ether
11. isooctane
12. benzene
13. *n*-heptane
14. *tert*-amyl methyl ether
15. 1-butanol 500ppb
16. α,α,α-trifluorotoluene
17. toluene
18. 1-chloro-3-fluorobenzene
19. ethylbenzene
20. *m*-xylene
21. *p*-xylene
22. *o*-xylene
23. isopropylbenzene
24. decane
25. 1,3,5-trimethylbenzene
26. 1,2,4-trimethylbenzene
27. 4-bromochlorobenzene
28. naphthalene
29. 2-methylnaphthalene 150ppb
30. 1-methylnaphthalene 150ppb

Application #3

Oxygenates Rtx®-VGC

Rtx®-VGC
30m, 0.45mm ID, 2.55µm
(cat.# 19408)



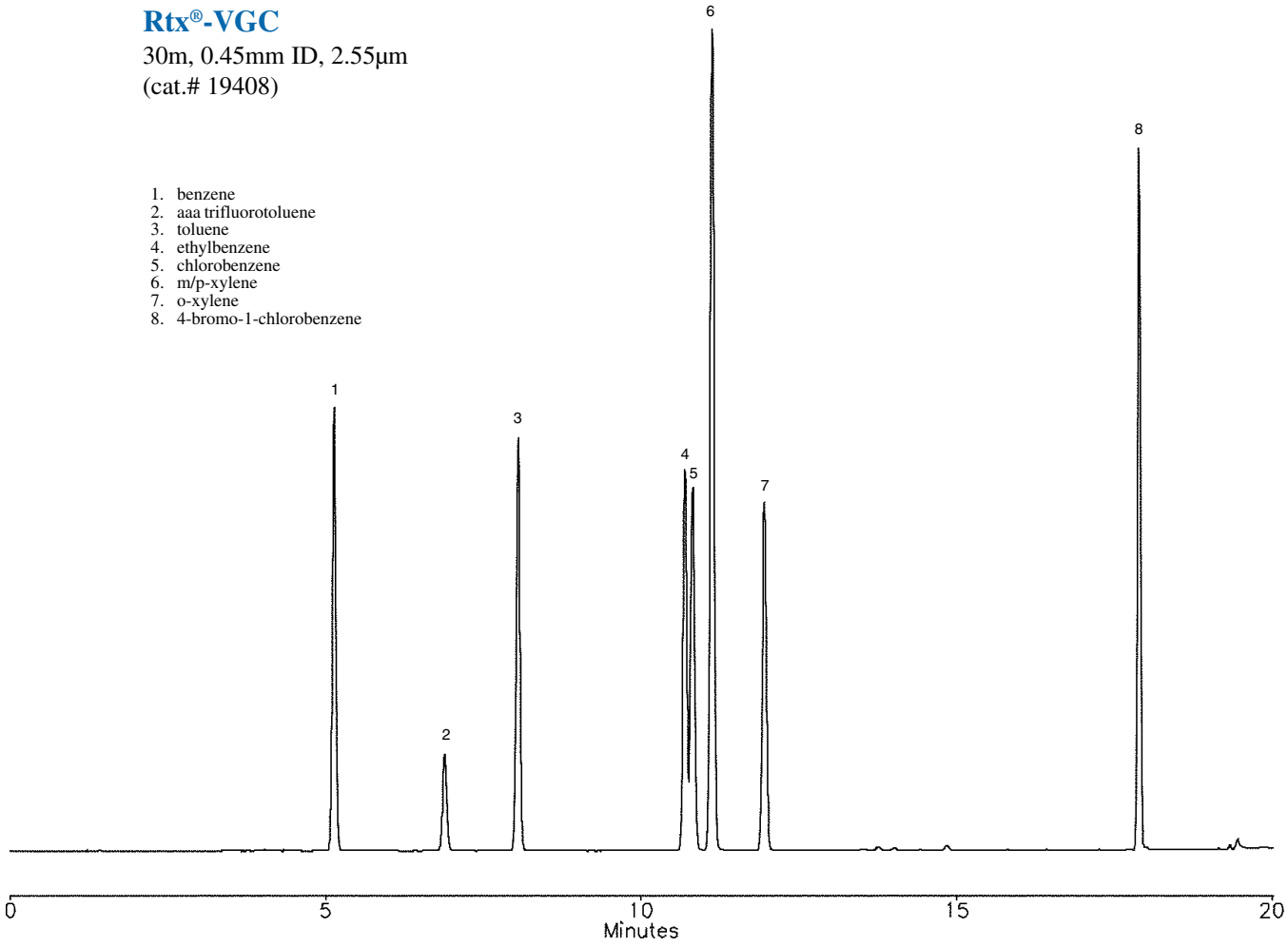
30m, 0.45mm, 2.55µm Rtx®-VGC (cat.# 19408)
splitless injection w/ 0.5 min. purge off
Compounds in at 100ppm
Oven program: 35°C (hold 5 min.);
Carrier gas: helium @ ~8mL/min.;
Detector: Agilent 5971A;
Scan range: 35 to 200 AMU.

Application #5

BTEX Rtx®-VGC

Rtx®-VGC
30m, 0.45mm ID, 2.55µm
(cat.# 19408)

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



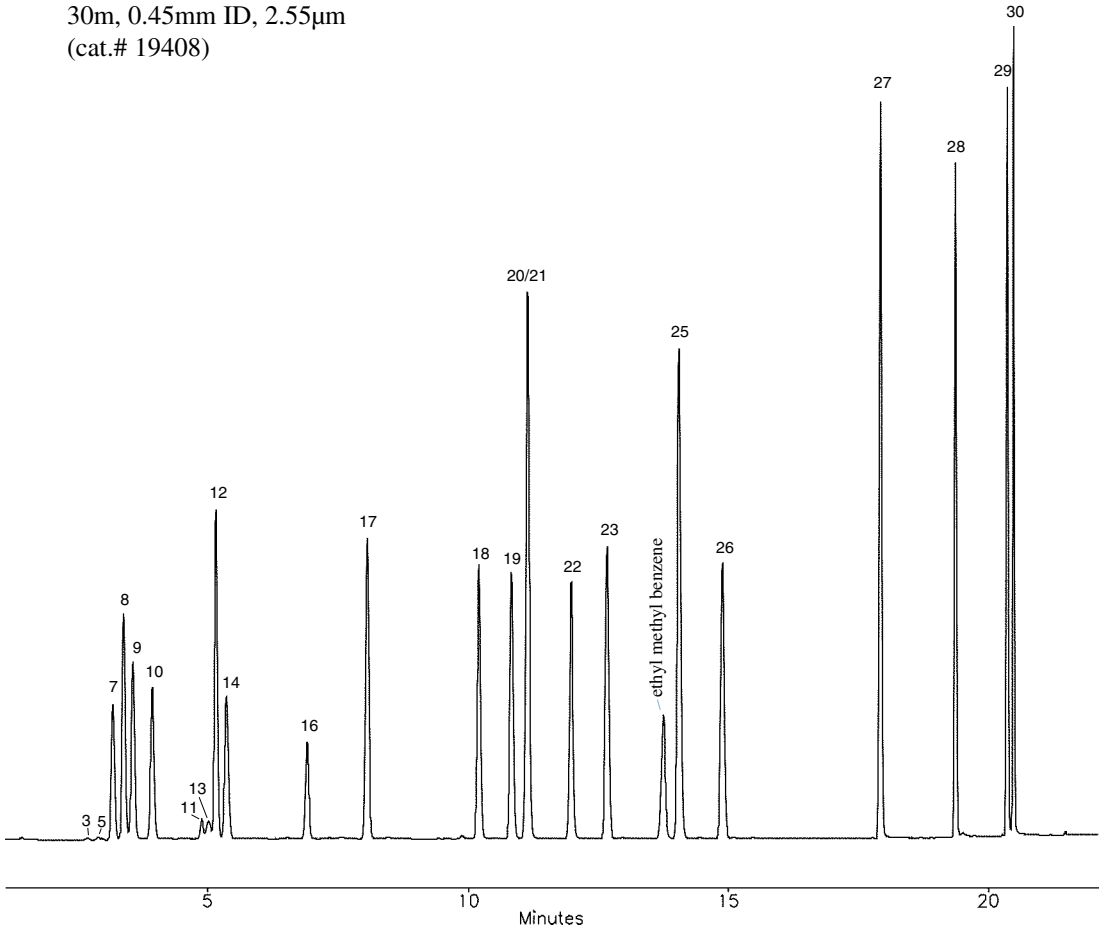
30m, 0.45mm, 2.55µm Rtx®-VGC (cat.# 19408)
100ppb in 5mL of RO water, except:
tert-butanol 5000ppb
2/1-methynapthalene 150ppb
ethyl methyl benzene 50ppb

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.

Application #2

Oxygenates and BTEX Rtx®-VGC

Rtx®-VGC
30m, 0.45mm ID, 2.55µm
(cat.# 19408)



30m, 0.45mm, 2.55µm Rtx®-VGC (cat.# 19408)
100ppb in 5mL of RO water, except:
tert-butanol 5000ppb
2/1-methynapthalene 150ppb
ethyl methyl benzene 50ppb

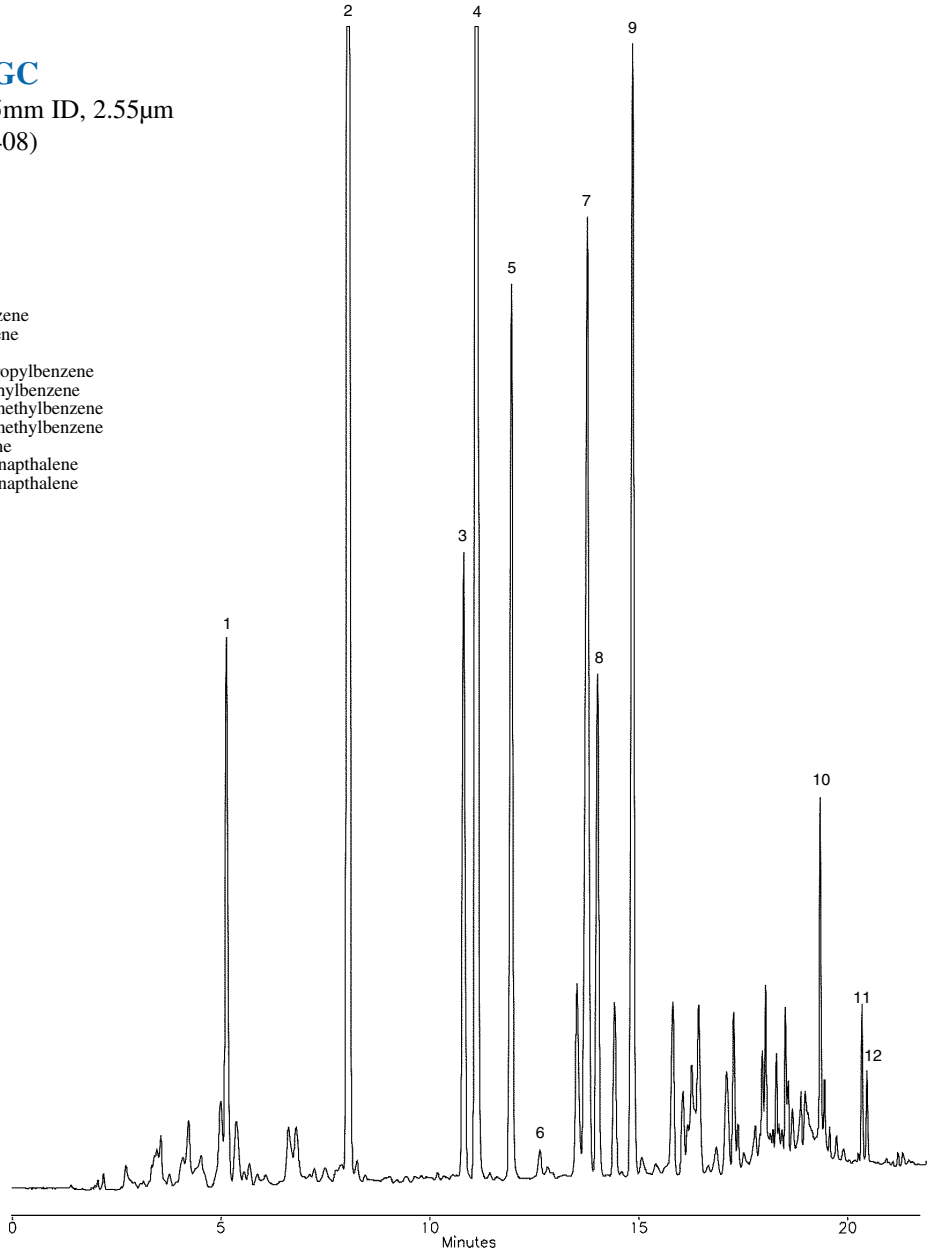
GC:	Finnigan 9001
Oven program:	40°C (hold 2 min.) to 130°C @ 6°C/min. (hold 0 min.) to 230°C @ 30°C/min. (hold 2 min.).
Carrier gas:	helium @ ~8mL/min.;
Detector:	Finnigan PID, make up 7mL min., purge 7mL/min., set @ 0.35mV, base temperature 200°C.

Application #4

Gasoline, Unleaded Rtx®-VGC

Rtx®-VGC
30m, 0.45mm ID, 2.55µm
(cat.# 19408)

1. benzene
2. toluene
3. ethylbenzene
4. M/P-xylene
5. o-xylene
6. IP0-isopropylbenzene
7. ethylmethylbenzene
8. 1,2,3-trimethylbenzene
9. 1,2,4-trimethylbenzene
10. napthalene
11. 2-methylnapthalene
11. 1-methylnapthalene



30m, 0.45mm, 2.55µm Rtx®-VGC (cat.# 19408)
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.