

Gas Chromatography

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Determination of Low-Level Oxygenated Compounds in Gasoline Using the Clarus 680 GC with S-Swafer Micro- Channel Flow Technology

Introduction

The existing ASTM® D4815 method is designed to monitor oxygenated compounds in gasoline at percentage concentrations. The method described in this application note is intended to enable these analytes to be monitored down to low-ppm concentrations.

There is an increased need to monitor the level of oxygenates in reformulated gasoline because of the increased risk of contamination from more abundantly available biofuels. Gasoline contamination with oxygenated compounds can lead to more toxic carbonyl emissions into the atmosphere from engines running the fuel.

Contamination of feedstocks with oxygenated compounds can cause degradation of expensive catalysts and impact the refining process.

The analytes targeted in this method are those specified in ASTM® D4815 and are given in Table 1.

Table 1. Targeted Oxygenated Compounds.

Methanol
Ethanol
Isopropanol
<i>tert</i> -Butanol
<i>n</i> -Propanol
Methyl <i>tert</i> -butyl ether (<i>MTBE</i>)
<i>sec</i> -Butanol
Diisopropyl ether (<i>DIPE</i>)
Isobutanol
Ethyl <i>tert</i> -butyl ether (<i>ETBE</i>)
<i>tert</i> -Pentanol
1,2-Dimethoxyethane
<i>n</i> -Butanol
<i>tert</i> -Amyl methyl ether (<i>TAME</i>)

Experimental

Figure 1 shows a diagram of the S-Swafer™ micro-channel flow splitting device used to perform this analysis. This two-column backflushing configuration (designated as S6 in the Swafer documentation) enables the first column to be back-flushed while the analytes are still being chromatographed on the second column. A restrictor tube is also connected

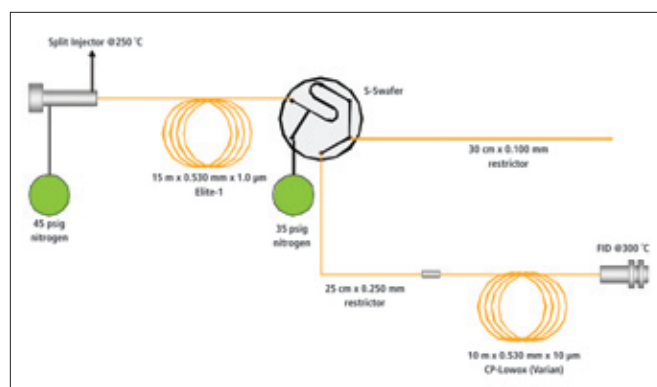


Figure 1. Diagram of the S-Swafer micro-channel flow technology used to determine trace-level oxygenated compounds in gasoline.

to one of the S-Swafer outlets to enable the carrier-gas flow rate to be increased and to allow the chromatography to be monitored on the first column by connecting the restrictor outlet to the FID. Note the use of nitrogen as the carrier gas. This carrier gas is well suited to 0.530 mm i.d. columns and is consistent with initiatives to reduce the use of the declining global stocks of helium.

The experimental details for this analysis are given in Table 2. The sample of gasoline is injected and chromatographed on the non-polar precolumn. The polar oxygenated compounds are quick to elute into the second CP-Lowox® column and will precede the bulk of the gasoline hydrocarbons. Once the oxygenated compounds are in the second column, the first column is backflushed to remove the hydrocarbons

Table 2. Analytical Conditions for the Determination of Trace-Level Oxygenated Compounds in Gasoline.

Gas Chromatograph	PerkinElmer® Clarus® 680 GC	Analytical Column	10 m x 0.530 mm x 10 µm Varian® CP-Lowox® with in-line 25 cm x 0.100 µm deactivated fused silica restrictor connected between S-Swafer and column
Oven Temperature	80 °C for 1 minute then 5 °C/min to 125 °C then 10 °C/min to 230 °C	Restrictor Tubing between S-Swafer and Detector	30 cm x 0.100 µm deactivated fused silica
Injector	Heated split/splitless	(Midpoint) Pressure at S-Swafer	35 psig
Injector Temperature	250 °C	Timed Events (see text)	Carrier gas pressure set to 45 psig at -1.00 min Carrier gas pressure set to 2 psig at 1.52 min
Carrier Gas	Nitrogen	Sample Preparation	a) AccuStandard® 4815-RT-PAK diluted ~1:1500 in washed gasoline to give 27.4 to 50 ppm w/w b) AccuStandard® 4815-RT-PAK diluted ~1:7500 in washed gasoline to give 5.5 to 10 ppm w/w
Initial Injector Pressure	2.0 psig (see text)	Sample Injection	Fast injection of 1.0 µL of prepared sample using an autosampler
Injector Split-Flow Rate	15 mL/min		
Detector	Flame Ionization (FID)		
Detector Temperature	325 °C		
Detector Combustion Gases	Air: 450 mL/min, Hydrogen: 45 mL/min		
Detector Range	x1		
Detector Attenuation	x4		
Backflush System	S-Swafer configured in S6 mode		
Precolumn	15 m x 0.530 mm x 1 µm PerkinElmer Elite™-1 with 25 cm x 0.250 mm deactivated fused silica restrictor connected between S-Swafer and column		

from the GC system. While the backflushing is in progress, the oxygenated compounds are chromatographed on the highly polar CP-Lowox® column which easily separates them from any hydrocarbons that also enter the second column.

Precolumn backflushing is initiated by a timed event at 1.52 minutes that reduces the pressure inside the injector to 2.0 psig so that carrier gas flows backwards. The inlet pressure is set to 2.0 psig to maintain the backflushing of the precolumn during oven cooling. A pre-run timed event sets the inlet pressure to 45 psig so that forward flow is restored prior to injection of the sample.

Figure 2 shows a chromatogram of gasoline on the pre-column with no backflushing. The oxygenated compounds would elute within the first one or two minutes of this chromatogram and would be totally obscured by the early-eluting hydrocarbons in the gasoline. The later-eluting peaks are not needed in this analysis so they will be the target of the backflushing step.

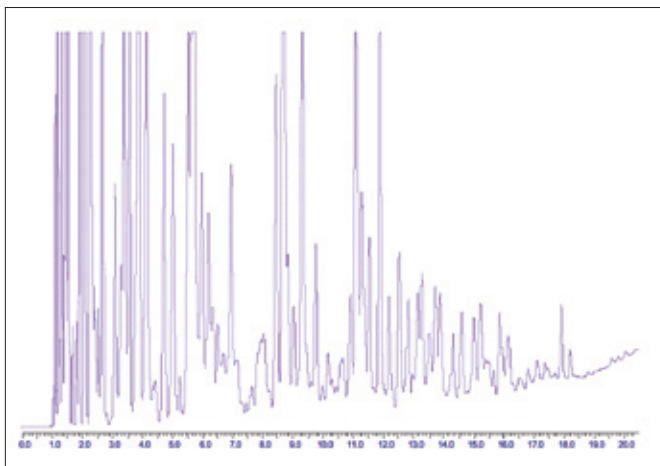


Figure 2. Chromatogram of 87-octane gasoline on the precolumn.

Figure 3 shows a chromatogram of a mixture of the oxygenated compounds (no solvent) on the precolumn and it can be seen that all the peaks of interest have eluted from this column in just less than 1.50 minutes. From this trace, the backflush point was chosen to be 1.52 minutes.

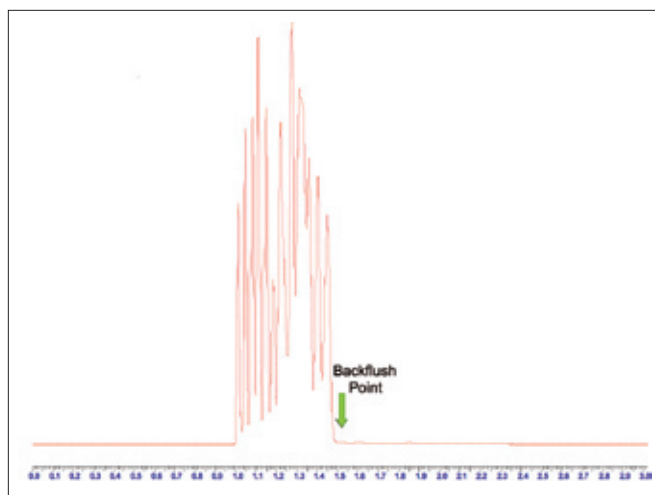


Figure 3. Precolumn chromatogram of a mixture of oxygenated compounds at 4% to 7.3% w/w concentration indicating the proposed backflush point. Injector split flow increased to 100 mL/min.

Figure 4 shows the same sample run under the same conditions as those for Figure 3 but with the detector connected to the end of the analytical column. Good peak shapes and separations of the oxygenated compounds are seen within a 20.5-minute run time. On this column, some of the alcohol isomers are not separated. The total cycle time was about 25 minutes, which included oven cooldown and equilibration and autosampler loading.

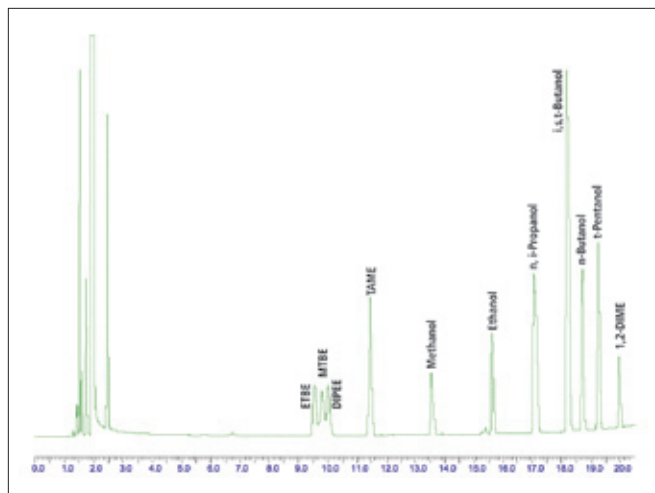


Figure 4. Analytical column chromatogram of a mixture of oxygenated compounds at 4% to 7.3% w/w concentration with precolumn backflushing at 1.52 minutes. Injector split flow increased to 100 mL/min.

To test the system on samples of gasoline containing known levels of oxygenated compounds, a quantity of gasoline was 'washed' with water. 5 mL of 87-octane gasoline obtained from a local filling station were shaken with 10 mL of deionized water for two minutes and then centrifuged at 5000 rpm for ten minutes. The aqueous layer was discarded and the process was repeated. 0.5 g of anhydrous sodium sulfate was added to the cleaned gasoline and shaken to remove any traces of water.

Figure 5 shows chromatography of the gasoline before and after washing. Even though the gasoline contained up to 10% ethanol, this and all other polar compounds were effectively removed by the washing procedure.

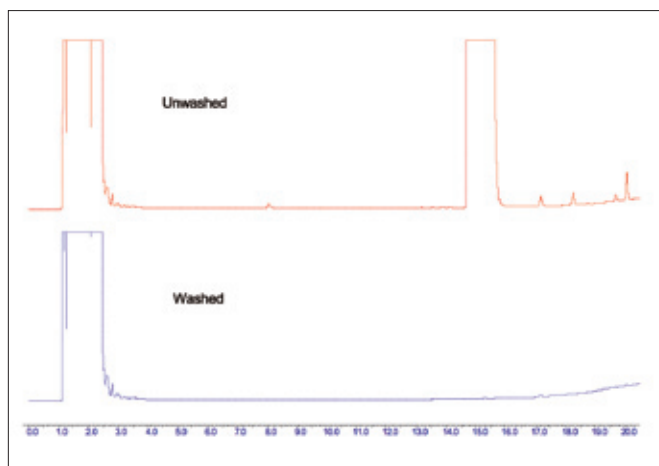


Figure 5. Efficacy of gasoline washing procedure for preparation of standard mixtures.

The standard mixture of oxygenated compounds was diluted with the washed gasoline to produce low-level mixtures. These were chromatographed using the newly developed method and the chromatogram is shown in Figure 6.

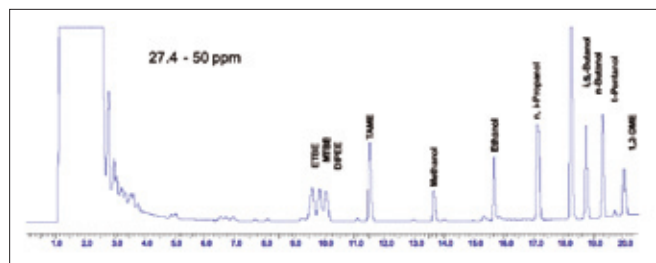


Figure 6. Chromatogram of washed gasoline spiked with low levels of oxygenated compounds.

The 27.4 – 50 ppm w/w mixture was injected repeatedly to measure the area and retention-time precisions. These are summarized in Table 3.

The area precision is around 1% relative standard deviation which is an excellent result – especially for polar compounds at low levels in a highly complex sample matrix like gasoline. The retention-time precision, which ranges from 0.013% to 0.039% relative standard deviation, is again an excellent result, considering the nature of this analysis.

Table 3. Area and Retention-Time Precision of a Standard Mixture of Oxygenated Compounds (n=9).

Compound	Conc. (ppm w/w)	Mean Area	RSD% Area	Mean R.T (min)	RSD% R.T.
Ethyl <i>tert</i> -Butylether (<i>ETBE</i>)	27.4	64807	0.69	9.580	0.028
Methyl <i>tert</i> -Butylether (<i>MTBE</i>)	27.4	58557	0.64	9.827	0.021
Diisopropylether (<i>DIPE</i>)	27.4	53993	0.80	10.044	0.039
<i>tert</i> -Amylmethylether (<i>TAME</i>)	50.0	101209	0.65	11.503	0.039
Methanol	50.0	31028	1.11	13.642	0.023
Ethanol	50.0	60104	0.96	15.663	0.015
<i>n</i> & <i>i</i> -Propanol	50.0/50.0	142362	1.10	17.109	0.016
<i>i</i> , <i>s</i> & <i>t</i> -Butanol	50.0/50.0/50.0	273656	0.72	18.233	0.009
<i>n</i> -Butanol	50.0	89299	0.76	18.740	0.013
<i>tert</i> -Pentanol	50.0	103335	0.63	19.287	0.013
1,2-Dimethoxyethane	41.1	64233	1.26	19.982	0.016

Conclusion

This method, based on the S-Swafer technology, is able to separate and quantify the ASTM® D4815 target analytes at low-ppm levels and offers the following user benefits:

- High-throughput analysis, with a complete analysis cycle time of 25 minutes
- A robust system – the analytical column is protected from most of the gasoline compounds by backflushing
- In-line restrictor with secondary column allows the primary column to be backflushed during chromatography, reducing analysis time
- Splitting restrictor enables precolumn chromatography to be monitored – facilitating system setup
- Use of nitrogen carrier gas to help preserve helium stocks and reduce operating costs
- Excellent quantitative precision.