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Determination of Methanol in Crude Oils According to ASTM D7059-04 Using the Clarus 680 GC with S-Swafer Micro-Channel Flow Technology

Introduction

The gas chromatographic (GC) analysis of crude oil is a challenging undertaking. Samples are viscous, making them difficult to handle, and they contain hundreds of different compounds with carbon numbers up to or even above C_{120}, making a complete chromatographic separation effectively impossible.

ASTM® D7059-04 is an established method that has been well validated for the determination of methanol in crude oils. The method lists five variants of the instrumentation that have demonstrated compliance with this method. The method also allows for alternative configurations that will meet the required performance criteria.

In this application note, a method based on a PerkinElmer® Clarus® 680 GC with an S-Swafer™ micro-channel flow splitting device is described; the data presented here will demonstrate that this method complies with the requirements of ASTM® D7059-04.

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Experimental

The Clarus 680 GC used in this application note is described in Figure 1 with a diagram, and Figure 2 with a photograph 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 backflushed while the analytes are still being chromatographed on the second column. A restrictor tube is also connected 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. Nitrogen is used as the carrier gas throughout this application – it is well suited for use with 0.530 mm i.d. columns. Nitrogen, when compared to helium, is less expensive, more available, and not in limited supply. The use of nitrogen is consistent with PerkinElmer initiatives to reduce the use of the declining global stocks of helium.

The crude-oil sample is diluted 50:50 with clean toluene solvent containing 1-propanol internal standard to produce a final concentration of 500 ppm. 1.0 µL of the diluted sample is injected into the programmable split/splitless (PSS) injector which has the liner temperature set to 125 °C. At this temperature, only the volatile fraction of the sample
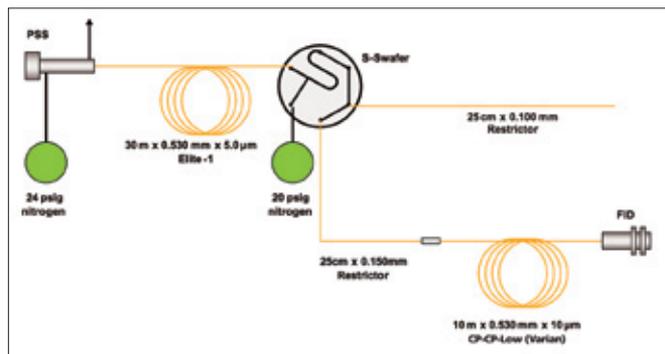

Figure 1. The S-Swafer system used to determine methanol in crude oil.

Figure 2. Photograph of installed system showing the S-Swafer connections.

will enter the first column, leaving the heavier crude-oil compounds in the liner. The two alcohols enter the first non-polar column and elute early in the chromatography. A chromatogram of a standard mixture is shown in Figure 3.
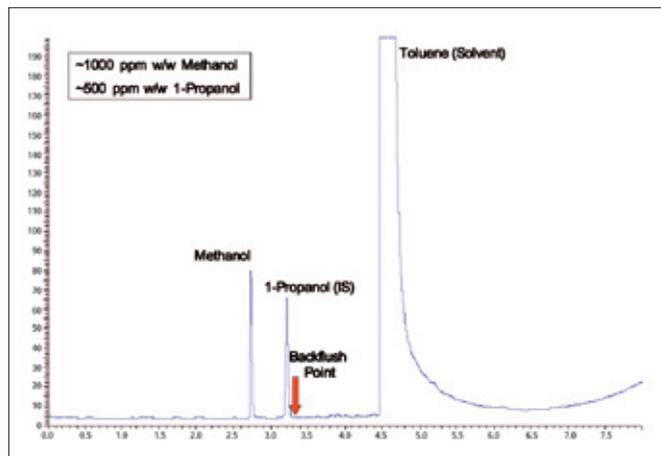

Figure 3. Chromatogram of standard mixture on first column with the restrictor tube connected to the FID.

From Figure 3, it can be seen that the last peak of interest, the 1-propanol internal standard, elutes at about 3.2 minutes. Anything that elutes later than this time is of no analytical interest and backflushing should commence soon after elution of the 1-propanol peak – in this case 3.3 minutes.

The backflushing process occurs when the pressure at the column inlet is less than that at the column outlet. This can be achieved by reducing the first-column inlet pressure at the PSS injector, increasing the (midpoint) pressure at the S-Swafer or doing both. In this analysis, we want to continue chromatography on the second column while we backflush the first column so the only option is to reduce the pressure at the injector. To enable a large backpressure to be used, the second column has an inline restrictor connected between it and the S-Swafer. This enables the midpoint pressure to be increased, yet still allows reasonable flow rates to be applied to the second column. The reduction in the inlet pressure is affected through the use of a simple GC timed event.

When the backflushing commences after a crude-oil sample has been injected, the heavier fraction of the sample will still reside within the injector liner which has been held at 125 °C. At this point, the PSS liner is temperature programmed to a high temperature to vaporize this less-volatile material. Because the column is being backflushed, none of this vapor will enter the column, but will be flushed out of the system through the split vent. In this way, removal of the heavy compounds is very efficient and doesn't expose the columns to this material, thus prolonging the column life.

Figure 4 shows a chromatogram of a standard solution on the first column with backflushing applied at 3.3 minutes. The chromatography is now very clean beyond the 1-propanol peak.
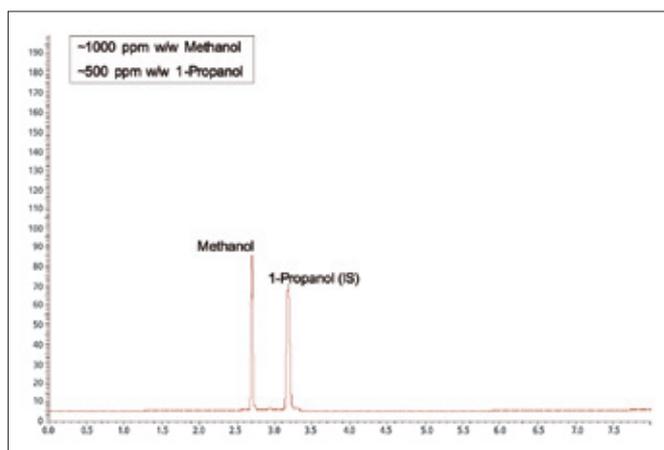

Figure 4. Chromatogram of standard mixture on first column with backflushing at 3.3 minutes with the restrictor tube connected to the FID.

Figure 5 shows chromatograms from the CP-Lowox® column of three calibration mixtures that cover the calibration range of this method. Again, the chromatography looks very clean.
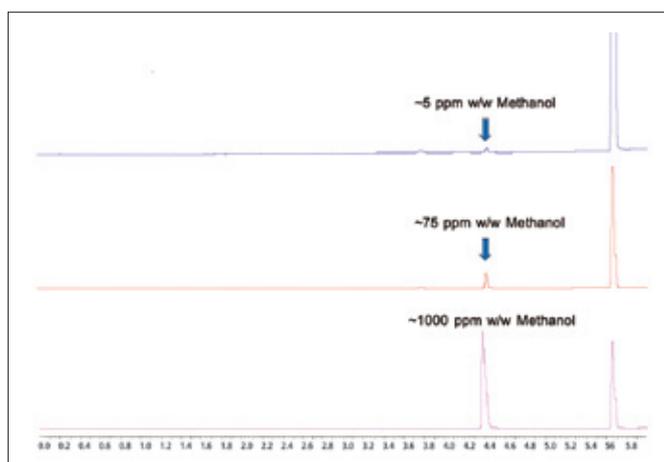

Figure 5. Chromatography of three methanol standard solutions containing ~500 ppm w/w 1-propanol internal standard.

The full method for this analysis is given in Table 1. The use of timed events in this method needs explanation. The GC oven needs to be programmed up to 250 °C in order to elute the analytes from the CP-Lowox® column. At this temperature, there is some slight stationary-phase bleed from the thick-film methyl silicone precolumn. The precolumn remains in the backflush mode during cooling to prevent any of the bleed from the precolumn at the onset of cooling from entering the CP-Lowox® column. The initial injector pressure of 2 psig and the pre-run timed event to set the pressure to 24 psig at -1.00 minutes ensures that the pre-column is

backflushed until the oven reaches its initial programmed temperature. The initial split-flow rate is set to 100 mL/min to ensure that the pre-run pressure change equilibrates quickly. The split flow is reset to 10 mL/min by a pre-run event at -0.50 minutes, which occurs once the pressure has stabilized. These split-flow changes serve only to save time.

Table 1. **Analytical Conditions for the Determination of Methanol in Crude Oil.**

Gas Chromatograph	PerkinElmer Clarus 680 GC
Oven Temperature	125 °C for 1 minute, then 25 °C/min to 250 °C
Injector	Programmable Split/Splitless (PSS)
Injector Temperature	125 °C for 3.3 minutes, then 200 °C/min to 400 °C and hold until the end of the run
Carrier Gas	Nitrogen
Initial Injector Pressure Setpoint	2 psig (see text)
Initial Injector Split Flow Rate	100 mL/min (see text)
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	30 m x 0.530 mm x 5 µm PerkinElmer Elite™ 1 with 25 cm x 0.250 mm deactivated fused silica restrictor connected between S-Swafer and column
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
Restrictor Tubing between S-Swafer and Detector	30 cm x 0.100 µm deactivated fused silica
(Midpoint) Pressure at S-Swafer	20 psig
Timed Events (see text)	PSS pressure set to 24 psig at -1.00 min
	PSS split flow set to 10 mL/min at -0.50 min
	PSS pressure set to 2 psig at 3.30 min
	PSS split flow set to 100 mL/min at 3.31 min
Sample Preparation	5 g of crude-oil sample mixed with 5 g of toluene containing 1-propanol internal standard to deliver a final concentration of 500 ppm w/w
Sample Injection	Normal injection of 1.0 µL of prepared sample using an autosampler

Discussion

The calibration plot obtained for the mixtures of methanol and 1-propanol in toluene are shown in Figure 6. This plot demonstrates good linearity which is in compliance with ASTM® D7059.
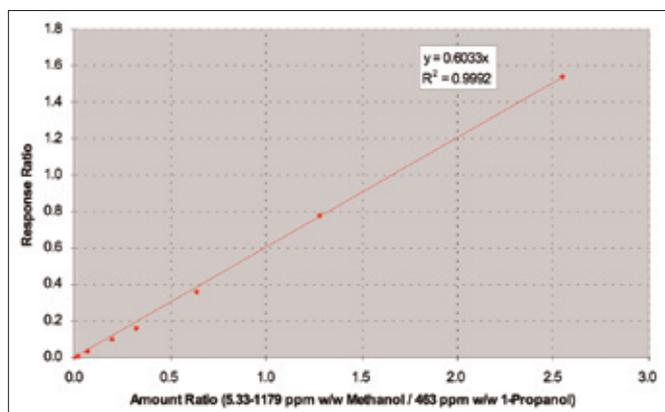

Figure 6. Calibration plot showing response ratio vs. amount ratio for methanol:1-propanol internal standard.

Figure 7 shows a chromatogram of a low-level check standard prepared from a sample of light crude oil. The hydrocarbons that elute with the alcohols into the second column before backflushing is initiated are lightly retained on the CP-Lowox® column and so quickly elute in the chromatography. The alcohols are much more strongly retained and require an extended temperature program to elute and are well separated from the light hydrocarbons in the crude oil. Note the clean baseline around the alcohols, which facilitates precise quantification.
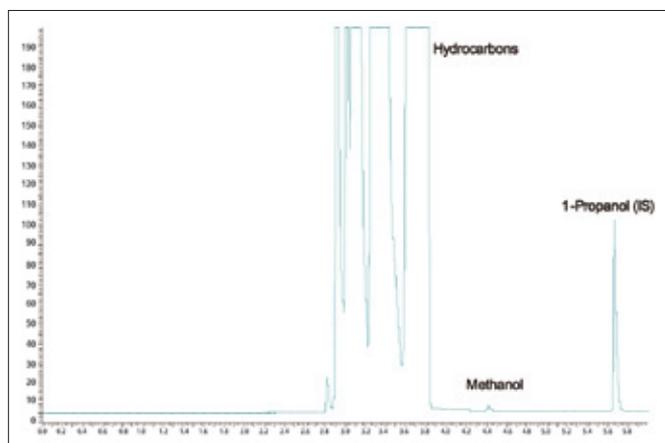

Figure 7. Chromatogram of 25 ppm w/w check standard prepared in a sample of light crude oil.

What should also be noted is that the total chromatography time is just six minutes. For most of this time, the injector liner is being heated at a high temperature and the precolumn is being backflushed at a very high flow rate, while the oven is being temperature programmed. This means that, at the end of the run, all of the less-volatile sample compounds have been flushed from the system. All that is then necessary is to cool the oven, reset the inlet pressure and inject the next sample. The Clarus 680 GC used for this analysis has rapid oven cooling and starts to load the autosampler with sample prior to the GC coming ready and so sample throughput exceeds six samples per hour.

Table 2 shows the quantitative precision obtained from ten replicate injections of a high-level and a low-level check standard. Considering the complexity of the sample matrix, these results demonstrate the efficacy of the Swafer technology for this type of application. These results greatly exceed the requirements of ASTM® D7059.

Table 2. **Quantitative precision of low-level and high-level check standards prepared using a sample of light crude oil.**

Run	Results for Check Standard A 28.2 ppm w/w	Results for Check Standard B 1096 ppm w/w
1	33.2	1063
2	32.2	1063
3	32.7	1065
4	32.6	1059
5	32.9	1059
6	35.6	1062
7	33.4	1065
8	33.9	1068
9	33.6	1061
10	33.8	1064
Relative Std Dev %	**2.88**	**0.26**

The analytical system was validated using a set of 20 'round-robin' samples prepared by Spectrum Analytical Standards, Sugarland, Texas. These are shown in Figure 8. These samples were prepared five years ago to validate the published ASTM® D7059-04 method. It is believed that these samples are stable and would provide a good basis for validating this Swafer system for compliance with the ASTM® method.

Figure 8. ASTM® D7059 round-robin validation samples.

Table 3 summarizes the results from the round-robin sample set. All are within the ASTM® D7059 limits except the result for Sample 19, which is just outside the accepted range. Given the age of these samples, these results are considered acceptable, and the method does tolerate one result deviation out of twenty.

Table 3. Results obtained for ASTM® D7059 round-robin validation samples.

Sample	Experimental	Expected
1	2.0	2.7
2	4.3	5.8
3	7.4	11.7
4	11.4	14.9
5	7.8	12.9
6	29.8	35.1
7	23.8	27.6
8	31.2	35.7
9	58.1	66.3
10	60.4	67.0
11	69.5	74.5
12	105.5	113.4
13	113.4	133.2
14	265.3	285.2
15	393.8	404.7
16	542.8	592.9
17	596.3	524.2
18	873.2	912.2
19	739.8	826.5
20	709.9	734.7

One of the concerns regarding the GC analysis of crude oil is that non-volatile sample residue will accumulate in the system giving rise to adsorption, thermolysis or carryover effects. This method uses a combination of low injection temperature and column backflushing to keep heavier sample compounds out of the columns. Figure 9 shows the chromatography of crude-oil samples soon after a new liner and septum have been installed compared against the chromatography after over 150 crude-oil injections have been made into the same liner and septum. Clearly, sample residue will accumulate as the number of injections increases (particularly with heavy crude oils) and eventually the liner and the septum will need to be changed. Figure 9 shows that after 150 injections, this method continues to perform.
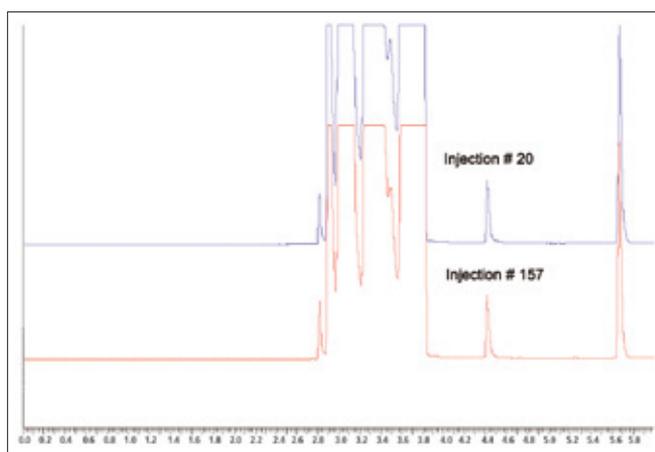

Figure 9. Chromatograms of the same crude-oil sample spiked with 400 ppm w/w methanol produced using a single injector liner showing no significant degradation in chromatography after over 150 runs.

Conclusion

This method, based on the S-Swafer technology, fully complies with the requirements of ASTM® D7059-04 and offers the user a number of unique benefits:

- The method presented here will provide very high throughput and fast delivery of results; with a complete analysis cycle time less than ten minutes per sample (more than six samples/hour throughput)

- Reduced instrument maintenance as a result of temperature-programmed injection which prevents heavy sample compounds from entering and degrading columns

- Additional protection of the analytical columns and reduction of run time with the use of backflushing

- Single-detector configuration simplifies and reduces the cost of the system

- Splitting restrictor enables precolumn chromatography to be monitored, facilitating the setup of backflush timing

- Nitrogen carrier gas reduces costs associated with carrier gas and serves to help preserve helium stocks

- Quantitative performance exceeding the method specification delivers results that will meet laboratory quality-control specifications.

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