Article

Determination of Low Levels of Methanol in Crude Oils by Multi-dimensional Gas Chromatography (MDGC) Using Novel Micro Channel Flow Technology

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The accurate and precise determination of methanol in crude oils at concentrations less than 10 ppm is of economic value to the petroleum industry. This report presents the optimization, results and long term performance of a flow switching device MDGC hardware, the Swafer[TM], for the rapid and precise analysis of methanol from approximately 0.4 ppm (w/w) to 1000 ppm. The use of low temperature injection and backflush technique decreases maintenance and increases sample throughput. The short term quantitative percent relative standard deviations at 1, 30 and 1000 ppm (w/w) methanol in crude oils are 5, 3 and 0.3, respectively. The MDGC procedure follows closely that described in ASTM D7059 for determination of crude oils; however, D7059 previously has not been evaluated at concentrations of less than 10 ppm. This work further extends the application of D7059 to concentrations of <10 ppm.

Introduction

The determination of methanol is important for assessing crude oil quality (1). Methanol is intentionally introduced in deepwater production to prevent the formation of gas hydrates in crude oil exposed to cold temperatures when wells are shut in or when production rates are slowed. Since methanol is miscible in water in crude distillation tower during desalting, the primary impact is on the refinery water treatment systems. As a result, there is commercial global need to measure the methanol level in the crude oil by analytical petrochemical laboratories. ASTM® D7059 (2) is a popular test method based on MDGC developed recently for the analysis of methanol in crude oils. ASTM D7059 states an applicable range of 15 to 900 ppm. During the ASTM development of this method, the perceived commercial need for such a method was for concentrations greater than 25 ppm and, therefore, lower concentrations were not evaluated extensively. However, there is a commercial need for lower level detection of methanol in crude oil. The low-level methanol detection, for example, at 1-5 ppm or less may affect refinery operations in certain cases.

One aspect of flow switching MDGC is the heartcutting of analytes of interest from a pre-column to an analytical column as demonstrated by Deans (3-5). Subsequently, MDGC has been applied to many complex petroleum, environmental and similar analyses. MDGC with flow switching involving pre-column backflushing is a highly efficient means of removing unwanted low volatility material from a GC column without employing high column temperatures. Generally, crude oils may contain low volatility components up to C100+.

In the analysis of methanol in crude oils little has been published in the open literature. The ASTM method D7059 (2) was the first consensus method describing the use of MDGC for such analysis. Other non-published methodologies reported by commercial testing laboratories and instrument vendors' literatures have included water extraction of the methanol followed

by GC/flame ionization (GC/FID) or gas chromatography/mass spectrometry (GC/MS) detection, extraction followed by colorimetric reaction detection and near-infrared (NIR). A more general colorimetric reaction detection (6) was not applied to crude oils. None of the latter methodologies have demonstrated sufficient data to be able to evaluate the feasibility of analysis at <10 ppm concentrations.

This report describes a precise and accurate analysis of methanol at concentrations <10 ppm not previously reported in detail using the MDGC technique as used in ASTM D7059. In addition, a newer micro-channel flow MDGC switching device, S-Swafer[TM], is presented and its functionality demonstrated in the determination of methanol in crude oil in the range 0.4 to 1000 ppm methanol. The combined use of the Swafer technology and low temperature injection technique to minimize heavy crude components from entering the pre- and analytical columns allows for the efficient analysis of difficult crude samples through decreased maintenance, good precision and accuracy, and fast sample throughput.

Experimental

Instrumentation

A PerkinElmer Clarus® 680 GC (Waltham, MA) fitted with a Perkin-Elmer S-Swafer micro-channel flow splitting device was used (Figure 1). The operating conditions are summarized in Table I. The two-column heart-cutting and backflushing configuration enables the pre-column to be backflushed while the heart-cutted analytes are eluted from the second analytical column.

A restrictor tube (Figure 1) is connected to one of the S-Swafer outlets and temporarily connected to the single FID to allow a rapid determination of the pre-column backflush time. Once the backflush time is determined the pre-column is disconnected from the FID and the analytical column is connected for the routine analysis of samples. Nitrogen is used as the low cost carrier gas.

Sample preparation and analysis

The crude-oil sample is diluted 50:50 with toluene that contains a 1-propanol internal standard in a concentration such that the final concentration of 1-propanol in the crude sample is 500 ppm (w/w). The diluted sample is injected at 125 °C into the programmable split/splitless (PSS) injector. At 125 °C only the light compounds of the crude oils and the methanol and internal standard enter the pre-column, leaving most of the heavier compounds in the PSS glass liner of the injector.

For the determination of methanol at <10 ppm, internal standard calibration was used. Several solutions of methanol were prepared in toluene with the following amounts of methanol: 0.397, 0.990, 1.98, 4.96 and 9.92 ppm.
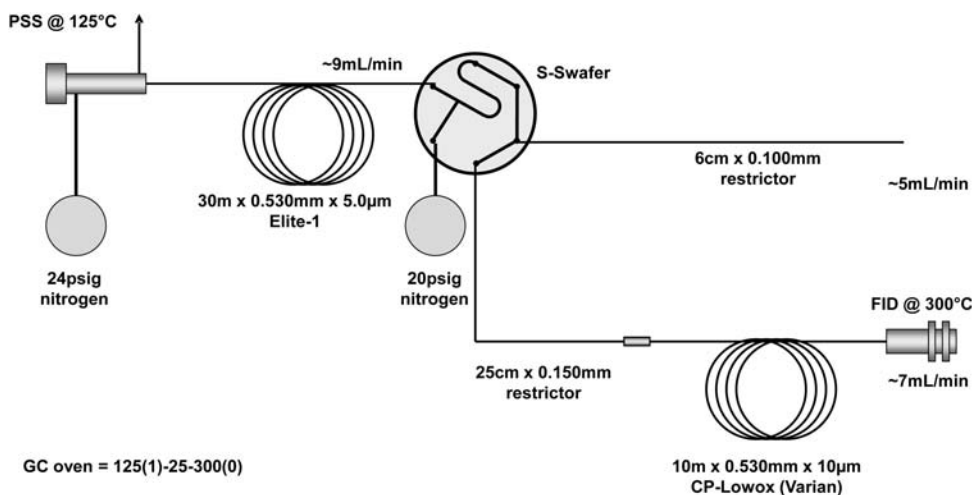
Figure 1. The S-Swafer MDGC system with single FID used to determine methanol in crude oil. Restrictor is manually connected to the FID while determining the pre-column backflush time.

For the determination of methanol at higher concentrations up to approximately 1000 ppm, an internal standard (1-propanol) calibration approach was used as described in ASTM D7059 (2). A methanol calibration curve of seven points was prepared in toluene between 5.33 ppm up to 1179 ppm. The internal standard concentration was 500ppm.

Results and Discussion

Determination of backflush time with S-Swafer

A chromatogram with the analytes eluted from the pre-column of a standard mixture obtained with the restrictor (Figure 1)

connected to the FID is shown in Figure 2. This allows for the rapid determination of the backflush time. If the column was used, instead of the pre-column, to determine backflush time, the operator would need to make several injections to optimize this time until the toluene peak was no longer detected. Figure 3 shows the response from elution through the pre-column after adding the backflush time as determined in Figure 2. In Figure 3 the toluene is not detected since it is backflushed through the injector.

Backflushing through the injector at the predetermined backflush time is accomplished by reducing the pressure to 2 psi (Table I) at the pre-column inlet such that it is less than that at the pre-column outlet. When the backflush time is invoked, the PSS is simultaneously temperature programmed to 400°C to volatilize the heavier compounds of the crude oil which had been held in the injector at 125°C prior to backflushing. This prevents the high boiling compounds from entering the columns, and they are flushed out of the inlet. The split vent flow is increased at the backflush time to expedite the removal of most of the compounds that remained in the inlet. The Lowox stationary phase used in the analytical column is a proprietary phase with a high selectivity for the methanol and the 1-propanol over light hydrocarbons.

Figure 4 presents a chromatogram of a crude oil spiked with 25 ppm methanol and 500 ppm of the internal standard 1-propanol. The components eluting ahead of the methanol are light hydrocarbons which are also heartcut to the analytical column. The pre-column is maintained in the backflush mode (i.e., 2 psi and 100ml/min split flow in injector) during cooling of the GC oven to ensure that heavy crude oil components and 'bleed' from the methylsilicone pre-column not reach the Lowox analytical column.

Determination of Methanol at Low Level (<10 ppm)

Figure 5 shows a chromatogram of a 2 ppm crude sample using the method parameters listed in Table I. The methanol peak is easily detectable.
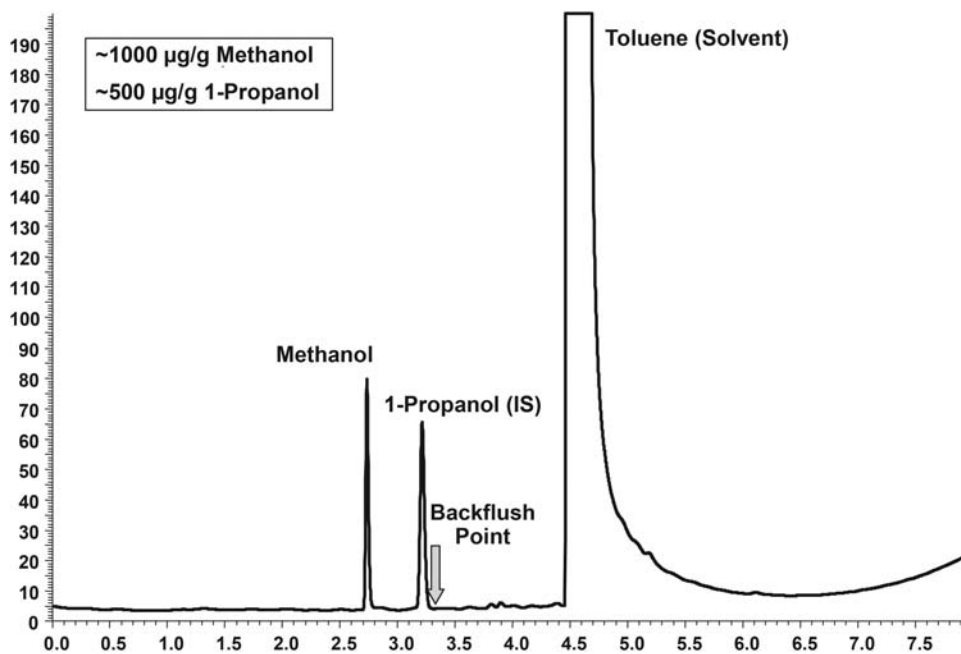
Figure 2. Chromatogram of standard mixture on pre- column with the restrictor tube connected to the FID used to determine backflush time.
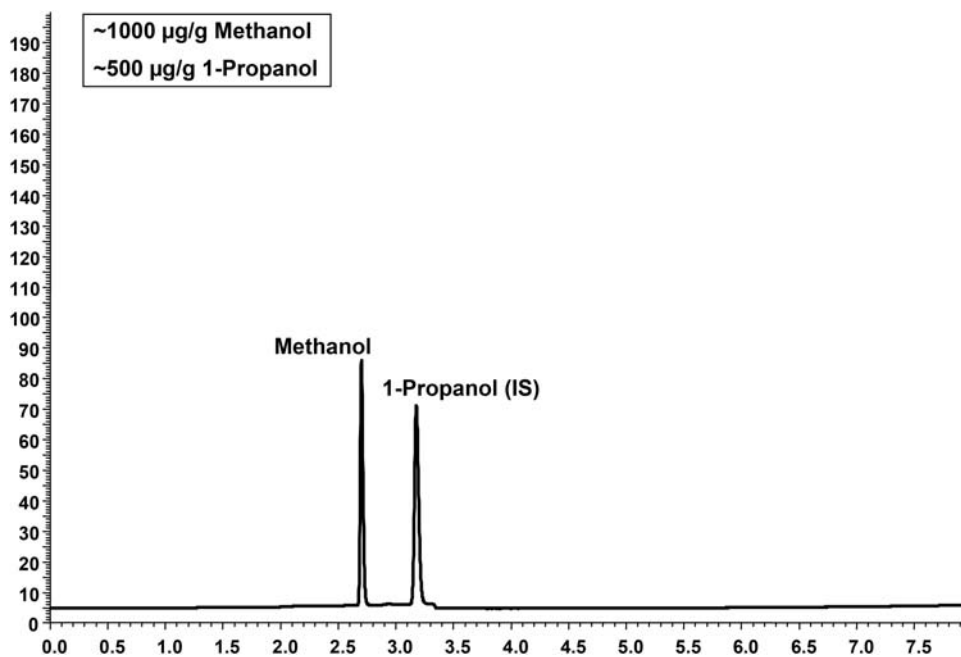

Figure 3. Chromatogram of standard mixture on pre-column with backflushing at 3.3 minutes with the restrictor tube connected to the FID. Toluene backflushed and not detected.

Figure 6 chromatogram displays the response of the lowest methanol standard analyzed at 0.4 ppm, which approaches the detection limit of the operating conditions with a signal to noise of 28:1. The chromatogram is overlaid with a toluene blank demonstrating an interference-free background. The injection split flow was reduced to 5mL/min to attain this detection limit.

After achieving the required detection limit and separation, linearity was established by internal standard. The low concentration (i.e., <10ppm) calibration response curve was forced through the zero-intercept (i.e., y-intercept = 0) and yielded an acceptable regression coefficient of $r^2 = 0.9989$.

Table II demonstrates the precision of the methanol at a concentration of 0.99 ppm for six replicate injections. The RSD of
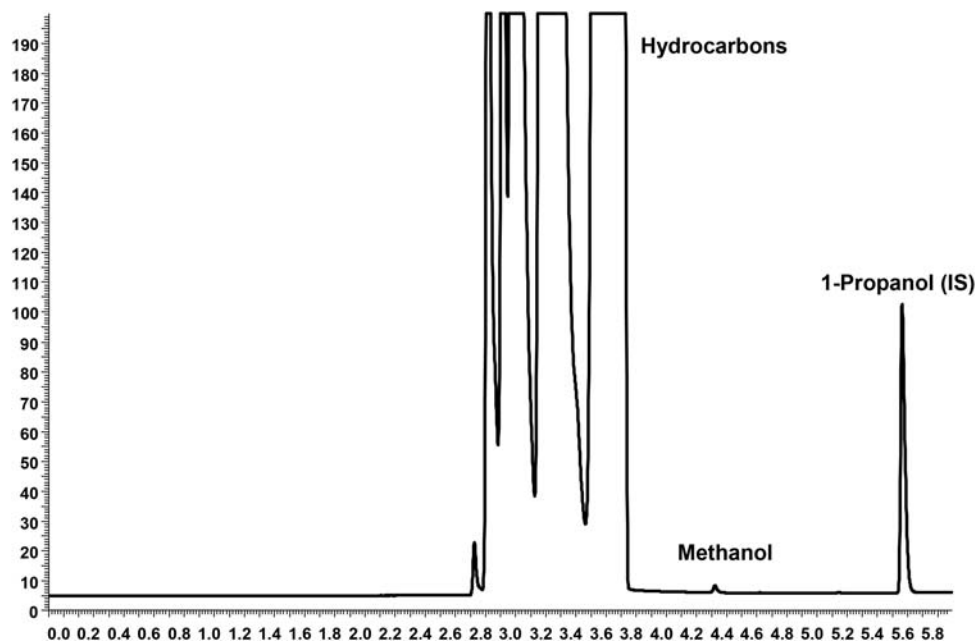
Figure 4. Chromatogram of 25 ppm methanol check standard prepared in a sample of light crude oil.
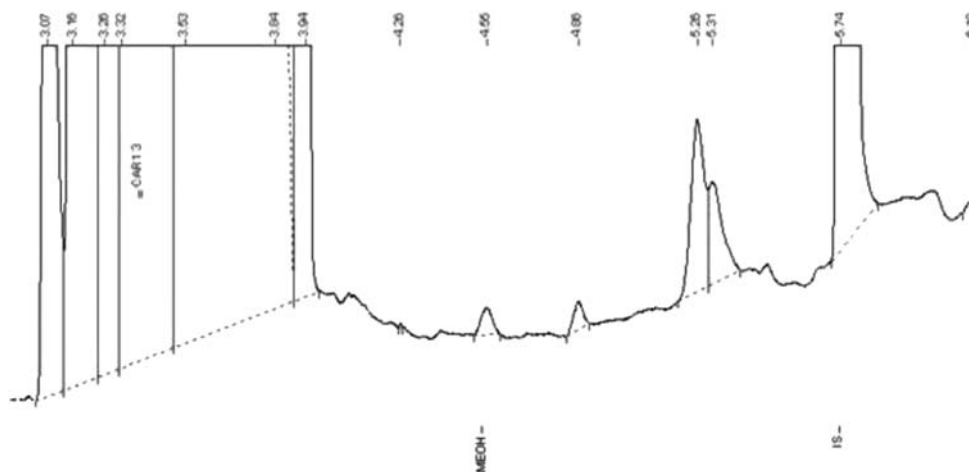

Figure 5. Chromatogram of a 2 ppm methanol crude oil sample.

5.4% for the amount of methanol was slightly higher for the low concentration methanol analysis versus that of the high concentration analysis (see below) but well within acceptable limits for the intended commercial use.

Determination of Methanol at High Level (>10 ppm)

Table III summarizes the precision obtained from ten replicate injections of two methanol spiked crude oil samples. Considering the complexity of the sample matrix, these results, combined with the precision results attained at 0.99ppm, demonstrate the efficacy of the Swafer and the low temperature injection methodology.

The high concentration calibration response curve was forced through the zero-intercept (i.e., y-intercept = 0) as dictated by ASTM D7059 and yielded a D7059 acceptable regression coefficient of $r^2 = 0.999$.

The 'accuracy' was validated using a partial set of samples used in the ASTM D7059 interlaboratory 'round robin' study. The samples were obtained in glass sealed vials to safeguard their quantitative integrity. Table IV summarizes the experimental results versus the average values obtained from the inter-laboratory study consisting of six laboratories. All of the results obtained are within the ASTM® D7059 statistically determined reproducibility "R" limit values.

System Long Term Stability

To verify the chromatographic system long term inertness and stability for methanol, a number of consecutive analyses were carried out and results compared. Figure 7 shows the chromatography of a crude-oil sample soon after a new liner and septum was installed compared against the chromatography after over 150 crude-oil injections into the
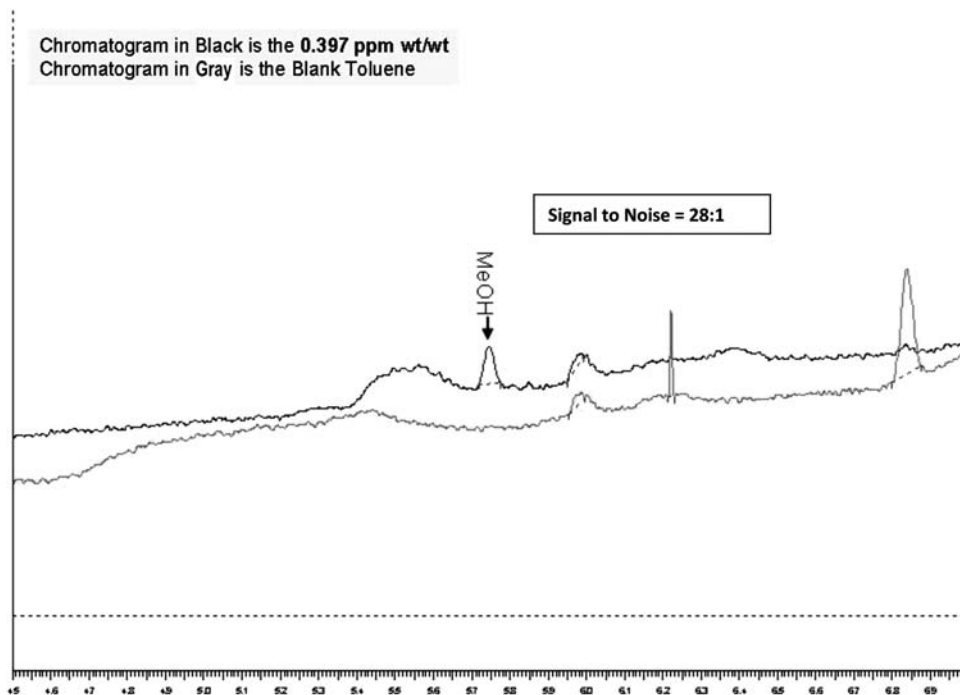
Chromatogram in Black is the **0.397 ppm wt/wt**
Chromatogram in Gray is the Blank Toluene

Signal to Noise = 28:1

MeOH→

Figure 6. Low level 0.397 ppm methanol injection.

Table II
Quantitative Precision of Low-Level (0.99 µg/g) Check Standard Prepared Using a Sample of Medium Crude Oil

Sample Name	Methanol Time [min]	Amount µg/g	% Difference	Internal Standard Time [min]	Area [µV·s]
0.99 µg/g	5.75	0.91	−8.08	7.78	91102.49
0.99 µg/g	5.74	0.91	−8.08	7.78	89695.42
0.99 µg/g	5.74	0.81	−18.18	7.78	91212.78
0.99 µg/g	5.75	0.87	−12.12	7.78	91347.37
0.99 µg/g	5.75	0.81	−18.18	7.79	91160.65
0.99 µg/g	5.75	0.89	−10.10	7.79	91471.91
%RSD	**0.05**	**5.4**		**0.04**	**0.72**

Table III
Quantitative Precision of High-Level Check Standards Prepared Using a Sample of Light Crude Oil

Run	Results for Check Standard A 28 µg/g	Results for Check Standard B 1096 µg/g
1	33	1063
2	32	1063
3	33	1065
4	33	1059
5	33	1059
6	36	1062
7	33	1065
8	34	1068
9	34	1061
10	34	1064
Relative Std Dev	2.8	0.3

Table IV
Results from Analysis of Round Robin Validation Samples

Experimental	ASTM	Difference	D7059 Reproducibility 'R'
11	15	4	8
8	13	5	8
30	35	5	10
24	28	4	9
31	36	5	10
58	66	8	14
60	67	7	14
70	75	5	14
106	113	8	19
113	133	20	21
265	285	20	37
394	405	11	50
543	593	50	70
873	912	39	104
740	827	87	95
710	735	25	85

Note: ASTM value is the average value from results from six laboratories participating in a round robin for D7059

compounds out of the columns. Sample residue will accumulate as the number of injections is increased further and eventually the liner and the septum will need to be replaced. Quality control samples may be used to determine when such maintenance is required.

Conclusions

The new Swafer flow switching device combined with thermal control of the injection allows detection of methanol to as low as 0.4 ppm with excellent precision and ruggedness. The
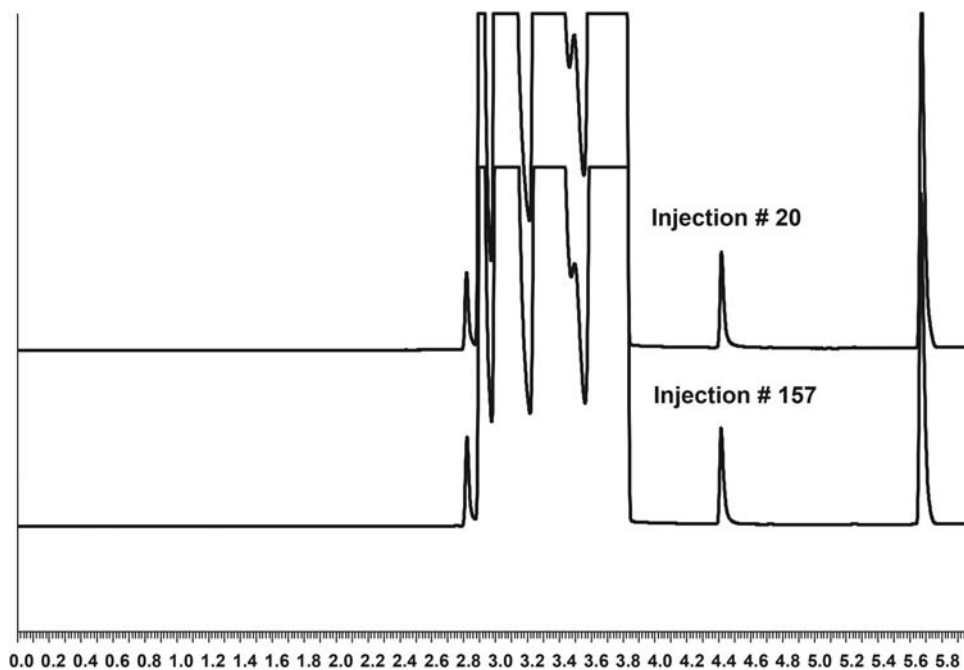
same liner and septum. The data indicates that even after more than 150 injections the system continues to perform well. The combination of low injection temperature and column backflushing maintains most of heavier sample

Figure 7. Chromatograms of crude-oil sample spiked with 400 ppm methanol produced using a single injector liner showing no significant degradation in chromatography after over 150 runs.

demonstration of performance related to improved precision, particularly at concentrations <10 ppm methanol, extends the applicability of ASTM D7059 to the wide range analysis of approximately 0.4-1000 ppm methanol in crude oils. The data will be presented to ASTM committee for its consideration as an alternative configuration for extending the D7059 test method to lower concentrations.

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