BEYOND MEASURE

Methanol in Crude Oil Analysis According to ASTM D7059-04

Application Note

AN069

INSTRUMENT TYPE

Scion Instruments GC-based Analyser

DESCRIPTION

The analysis of methanol in crude oil according to ASTM D 7059: "Standard Test Method for Determination of Methanol in Crude Oils by Multidimensional Gas Chromatography."

In the production of crude oil, methanol is often added to prevent formation of hydrates (i.e., solid water-hydrocarbon structures) that block transportation via pipelines. However, methanol, as with most oxygenated components, will poison catalysts when the crude oil is converted into other products. Catalysts are very expensive, and high methanol levels add a big cost factor. Therefore, the content of methanol in a crude oil is very important and must be measured accurately at low (ppm) concentrations. Depending on the methanol level, the crude oil can be applied straight or needs extra treatment(s) to reduce the methanol content. The determination of methanol is done via an internal standard method using 1-propanol as the internal standard. The measuring range of methanol is specified from 15 to 900 ppm (m/m).

CONFIGURATION

The system is a SCION SSL capillary split/splitless injector using a pressure point over the pre-column. The heavy components of the crude oil are backflushed over a filter to prevent blockage of the vent line. The configuration can be seen in Figure 1.

SYSTEM SETTINGS

Table 1. Analytical conditions of the GC-FID

Conditions	
S/SL Injector	325°C
Split Ratio	1:10 Helium
EFC Injector	13.6Psi (1') – 400 Psi/min 2.0Psi (14.4)
EFC Car-2	7.2Psi
Oven	150°C (3 mins), 20°C/min to 300°C (5 mins)
FID	325°C

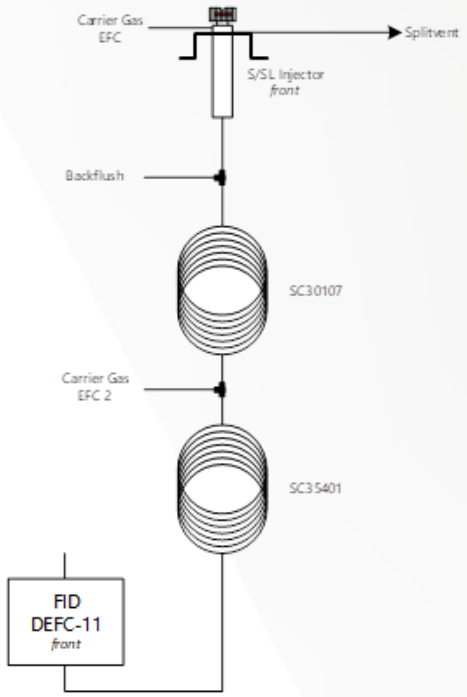

Figure 1. Schematic overview of the configuration

RESULTS

The chromatograms of methanol in toluene, at 150ppm and 6ppm, test mix can be found in Figures 2 and 3.

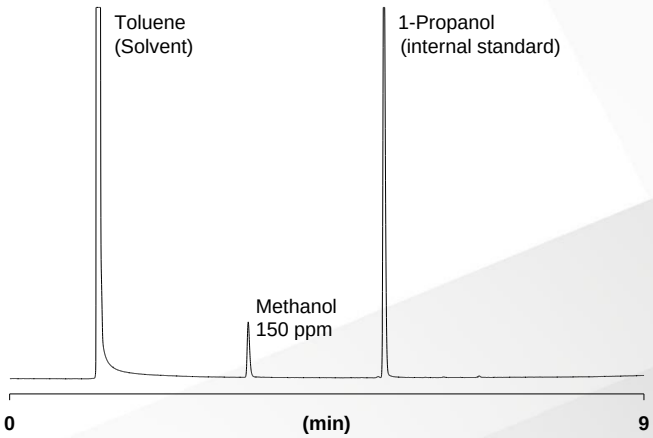

Figure 2. Test mixture of 150ppm methanol in toluene

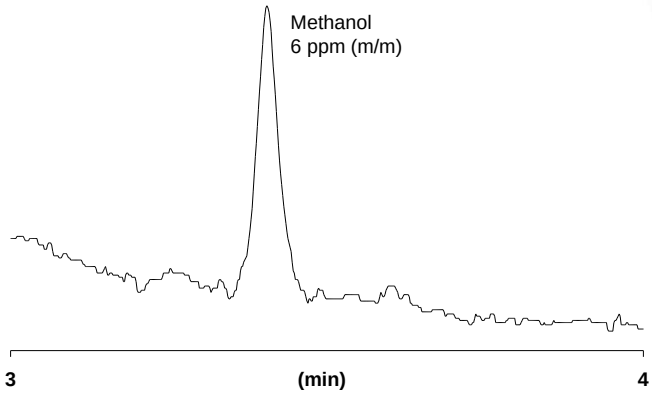

Figure 3. Test mixture of 6ppm methanol in toluene

SYSTEM LINEARITY

The linearity of the system was determined by a series of samples in toluene where the methanol concentration ranged between 1 and 1000 ppm. The internal standard concentration is set at a constant level. The linearity is shown by plotting the response ratio of the methanol and internal standard against the amount ratio of both components, as shown in Figure 4. The correlation R^2 should 0.99 or better.

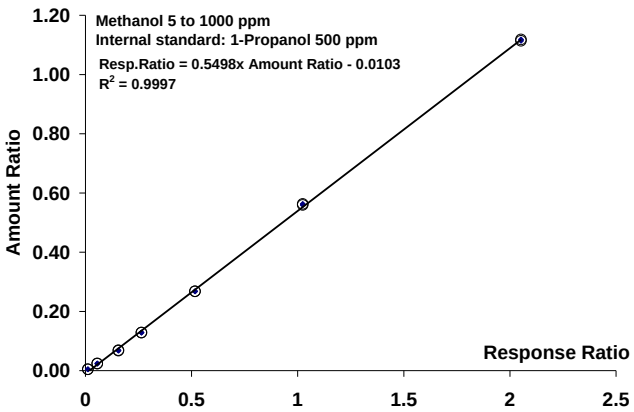

Figure 4. Multipoint calibration curve of methanol in toluene

LOQ

The limit of quantification (LOQ) specified as two times the signal noise (i.e. 10 times the standard deviation of the noise) is determined using a 6-ppm methanol standard. The LOQ measured is 1 ppm.

SAMPLE ANALYSIS

A crude oil sample was doped with low and high concentrations of methanol. Ten sequential analyses were performed for both methanol cconcentrations with data shown in Table 2. The chromatogram for the low-level and high-level methanol in crude oil is shown in Figures 5 and 6.

Table 2. Repeatability data of low and high spiked methanol in crude oil

Analysis #	Methanol (low ppm)	Methanol (high ppm)
1	24.5	1375
2	22.4	1366
3	24.5	1366
4	23.9	1367
5	23.9	1367
6	24.2	1375
7	24.1	1355
8	24.1	1374
9	23.7	1383
10	24.0	1368
Mean	23.9	1370
Std Dev	0.6	7.5
Rel Std Dev	2.4%	0.6%
Mean/SD	41	182
Repeatability*	1.6	21
ASTM Rep.	5	60

* Repeatability = 2.8 * Standard deviation

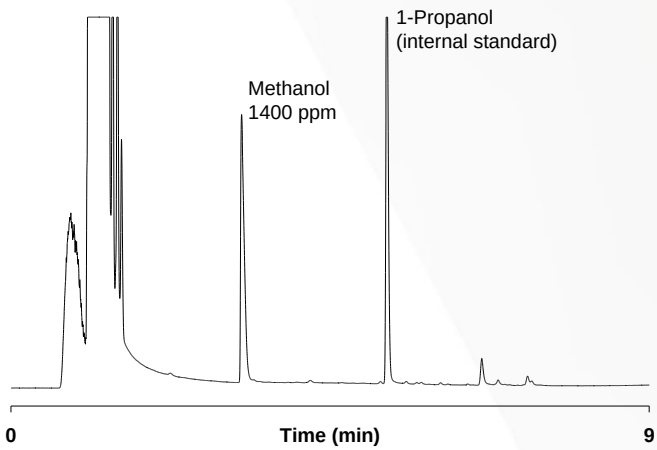

Figure 5. High-level methanol in crude oil (doped)

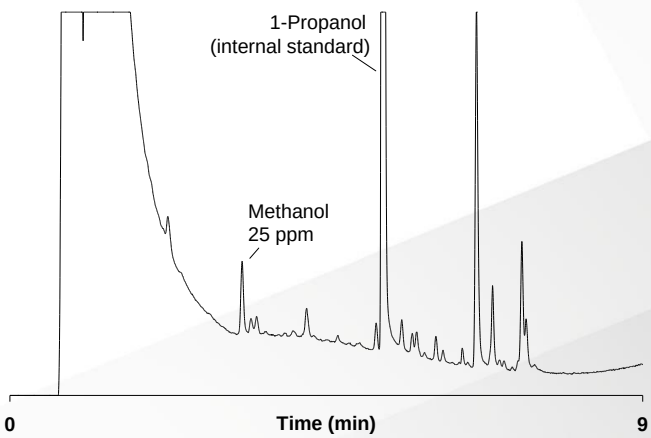

Figure 6. Low-level methanol in crude oil (doped)

REPEATABILITY

The ASTM method subscribes repeatability that is dependent on the methanol concentration. For 25ppm methanol in crude oil, the maximum repeatability is 5ppm (m/m) and for 900ppm the maximum repeatability is 60ppm (m./m). Figures 7-8 highlight the repeatability of both low and high-level methanol in crude oil according to ASTM specifications.

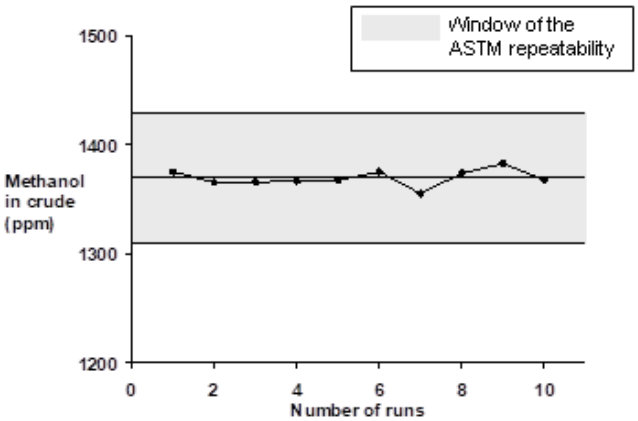

Figure 7. Repeatability of high-level methanol in crude oil.

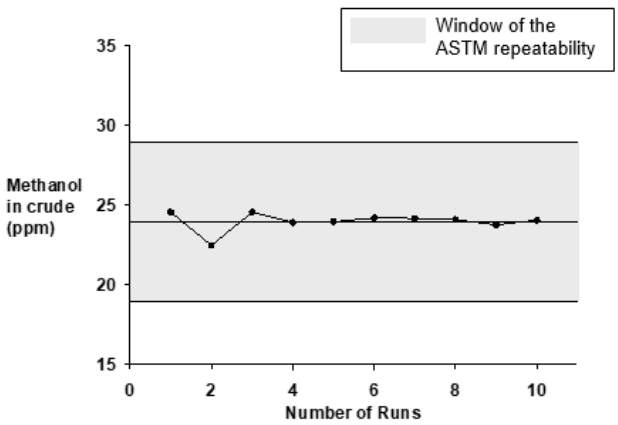

Figure 8. Repeatability of low-level methanol in crude oil.

PLOQ

The pooled limit of quantitation (PLOQ) is calculated from the ratio of the mean methanol concentration an its standard deviation for a series of measurements. PLOQ is the concentration where the ratio equals 10. At 25ppm level, the measure value is 41. This means that the PLOQ is below 25ppm. Figure 9 shows the PLOQ.

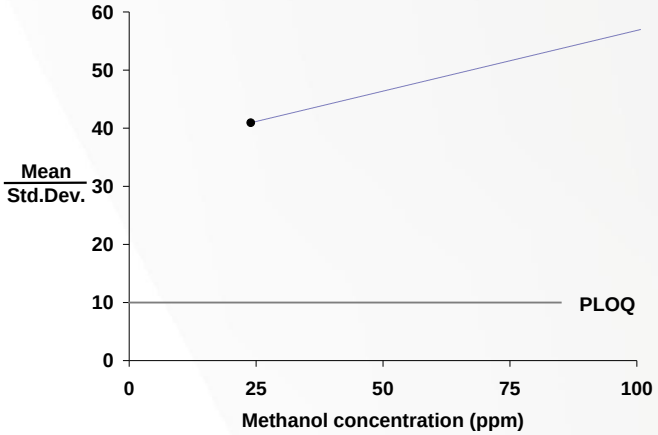

Figure 9. Determination of the PLOQ – below 25ppm.

CONCLUSION

The analysis of methanol in crude oil using a SCION Split/splitless injector and a pressure point for a back-flush configurations gives analytical results that are well within the ASTM D7059 subscribed specifications.

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