Application Note

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Determination of Asphaltenes in Crude Oil

Using the Agilent 1260 Infinity III LC system with Agilent 1290 Infinity III evaporative light scattering detector

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Abstract

The separation of maltenes and asphaltene is readily accomplished using the Agilent 1260 Infinity III LC System with an Agilent 1290 Infinity III evaporative light scattering detector (ELSD). This system offers a rapid, robust, and accurate solution to in-process crude tests.

Introduction

The Agilent 1260 Infinity III LC system with the 1290 Infinity III evaporative light scattering detector (ELSD) was used to evaluate heptane-insoluble asphaltenes in crude oil. The separation of maltenes and asphaltenes is enabled using Agilent InfinityLab Quick Change inline filters for HPLC. The test solution was injected into a flow of heptane under normal-phase HPLC conditions using inline filters (see Figure 1). The precipitation of asphaltenes is induced as soon as the sample enters the flow of the heptane between the autosampler and inline filters. Precipitated asphaltenes are retained by the inline filters (4.6 mm id, 0.5 µm porosity), while maltenes pass through to the detector. When the mobile phase is flashed from heptane to a solvent with a high solvent power (e.g., toluene), the blend redissolves the asphaltenes. The concentration of asphaltenes is quantified using ELSD (see Figure 2). This method is fast, repeatable, and reproducible, with excellent sensitivity and detection limits.

Experimental

Table 1. Hardware and consumables.

Hardware	Part Number
Agilent 1260 Infinity III Flexible pump	G7111B
Agilent 1260 Infinity III Vialsampler	G7129A
Agilent 1260 Infinity III Multicolumn thermostat	G7116A
Agilent 1260 Infinity III Evaporative light scattering detector (ELSD)	G7102A
Agilent OpenLab CDS	MB414AA

Consumables	Part Number
Agilent InfinityLab Quick Change in-line filter assembly for HPLC	5067-1602
Agilent 5 filter discs 4.6 mm id, 0.5 µm porosity	5067-1613
Millipore Heptane, HPLC	34873
Millipore Sigma Toluene, HPLC	5190-6896
Agilent vials, screw top, clear, 20 mL, 23 × 75 mm, 100/pk (18 mm cap)	5188-2753

Mobile phase preparation

100% heptane: Transfer into HPLC mobile phase bottle A.

100% toluene: Transfer into HPLC mobile phase bottle B.

Table 2. LC conditions.

Parameter	Value
Mobile Phase	A) 100% Heptane B) 100% Toluene
Flow Rate	2.0 mL/min
Stop Time	7.0 minutes
Column Temperature	30 °C
Injection Volume	See Table 4
Autosampler Temperature	Ambient
Peak Width	> 0.0063 minutes (0.13 seconds response time) (80 Hz)
ELSD	Evaporator: 75 °C Nebulizer: 75 °C N_2 gas flow: 2.0 L/min

Figure 1. Inline filter configuration.

Table 3. LC mobile phase gradient.

Time (min)	%A	%B
0	100	0
1.99	100	0
2.00	0	100
5.00	0	100
5.01	100	0
7.00	100	0

Table 4. LC injector volume amounts.

Estimated Asphaltene Content (wt.%)	Injected Volume (mL)
< 0.1	80
0.1–0.5	80
0.5–1	40
1–10	4
> 10	2

Sample preparation for crude oil samples included adding 0.100 grams of crude oil into a 20 mL vial. Toluene (10 mL) was volumetrically added and the mixture was mixed well.

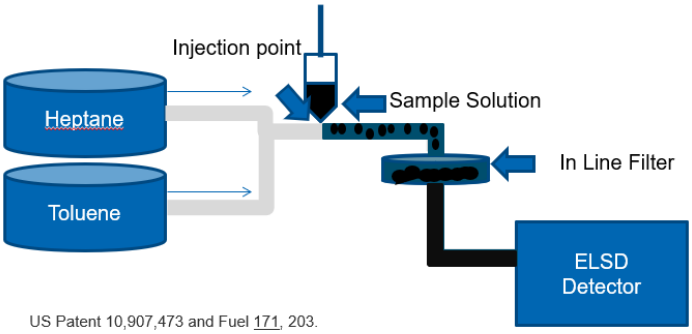

Figure 2. Flow diagram of HPLC.

Results and discussion

Calibration curves

Linearity may be determined using variable volume settings of the HPLC injector system. Seven injection levels of increasing volumes of the same crude oil standard were made. The linearity calibration is calculated from the calibration curve of the (log) peak areas versus (log) injection volume. The calculation method for quantitative analyses using an ELSD is based on the determination of the calibration curve, which correlates coefficient b and log a, the two coefficients from the equation $A = a^{mb}$ where A is the area of the chromatographic peak, m is the mass of the compound, a is the response factor, and b is the response index measured from the slope of the curve log (A) = b log (m) + log (a) that characterizes the law of the quantitative response for an ELSD. Unknown concentrations are computed from the equation of the calibration curve.

As shown in Figure 3, the linearity of the calibration curve (log mass versus log area) for the asphaltene standard was checked over the injection volume ranges of 0.5 to 10 µL. The plotted curve was linear over these concentration ranges (n = 7). The resultant curve was subjected to a linear regression analysis. The correlation coefficient (R^2) (n = 7) was 0.9974.

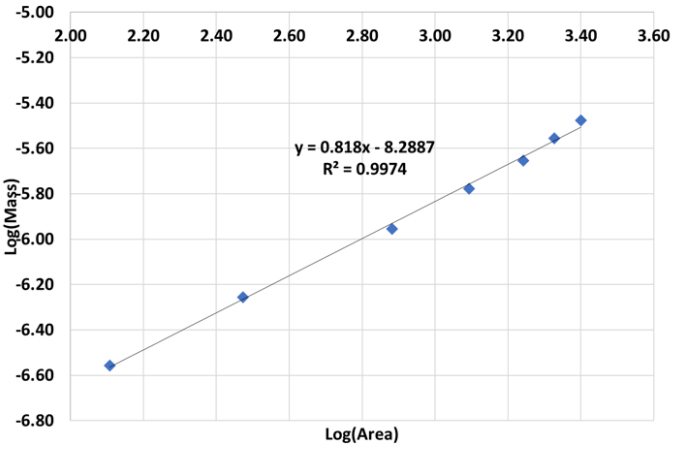

Figure 3. Calibration curve for asphaltene determination.

A typical LC trace is shown in Figure 4. The first peak corresponds to the maltenes, and the second signal corresponds to the asphaltenes. The limit of detection (LOD) and limit of quantitation (LOQ) of asphaltenes were determined by analyzing different solutions until asphaltenes could not be measured or detected. A concentration of 0.02% asphaltenes was determined to be the lowest concentration in a sample that could be detected from background.

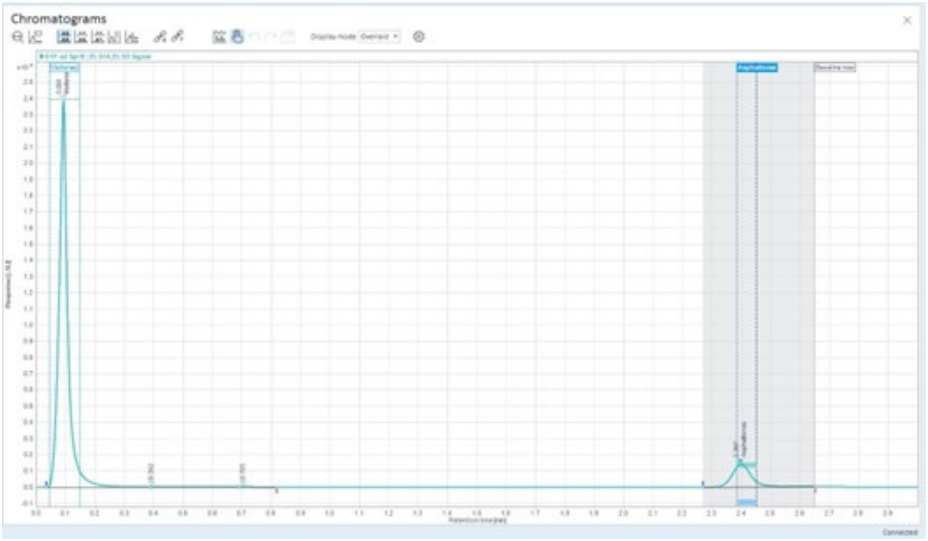

Figure 4. Typical LC-trace for asphaltene determination.

Table 5. Asphaltene sample results (in percent).

Time (min)	% Asphaltene (wt.%)
Sample A	0.039 ± 0.004
Sample B	0.030 ± 0.003
Sample C	0.041 ± 0.005
Sample D	0.14 ± 0.01
Sample E	1.10 ± 0.03
Sample F	1.63 ± 0.04
Sample H	3.6 ± 0.1
Sample I	4.2 ± 0.2
Sample J	10.5 ± 0.07
Sample K	20.4 ± 0.3

Values show an average of eight days of testing. Each test consists of the average of two duplicates. A new calibration was performed every day.

In the low range, samples containing between 300 and 1,400 ppm were tested. Samples include crude oils and processed samples (products). The results are the average of the same sample test on eight consecutive days. Each point was calculated as the average of two duplicates. Errors in the low range varied between 10 and 12%.

Conclusion

An improved analytical method was developed to determine asphaltene content in crude oils and petroleum samples. The inline filtration method takes just under 10 minutes and has a repeatability equivalent to or better than conventional gravimetric methods. Among other advantages, filters are inexpensive and can be easily replaced, as they are commercially produced and readily available, and their characteristics are less variable than handmade columns. The Agilent 1260 Infinity III LC system with the Agilent 1290 Infinity III evaporative light scattering detector was used to evaluate heptane-insoluble asphaltenes in crude oil. This solution is fast, more repeatable, and reproducible with better sensitivity and detection limits than traditional gravimetric methods.

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