Determination of Total Aromatic Hydrocarbons and Total Saturates with the Agilent 1260 Infinity Binary LC System with RI Detection According to ASTM D7419

Application Note

Energy & Chemicals - Petrochemicals

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Abstract

This Application Note shows that the Agilent 1260 Infinity Binary LC System is able to determine aromatic hydrocarbons under normal phase conditions with RI detection, in compliance with the ASTM D7419 method.

Introduction

This Application Note describes a method that covers the determination of total aromatics and total saturates in additive-free lube base stocks using HPLC with RI detection, according to ASTM D7419. This method is applicable to samples containing total aromatics in the concentration range of 0.2 to 46 mass %, for example, lube oil[1].

The composition of lubricating oil has a large effect on the characteristics and uses of the oil. The determination of saturates, aromatics, and polar compounds is a key analysis of this composition. The characterization of the composition of lubricating oils is also important in determining, for example, their interchangeability for use in blending[1].

With the described instrumental setup, the determination of mono-, di-, and poly-aromatic hydrocarbons[2] according to IP391 (2000)/ASTM D6591 and the determination of mono- and di-aromatic hydrocarbons[3] according to IP436/ASTM D6379 are also possible.

Experimental

Instrument

Agilent 1260 Infinity LC System

- Agilent 1260 Infinity Binary Pump (G1312B) with Agilent 1260 Infinity Standard Degasser (G1322A)
- Agilent 1260 Infinity Standard Autosampler (G1329B) with Agilent 1290 Infinity Thermostat (G1330B)
- Agilent 1260 Infinity Column Compartment (G1316A) with Agilent 1200 Infinity Series Quick-Change 2-position/6-port Valve (G 4231A).
- Agilent 1260 Infinity Refractive Index Detector (G1362A)

Software

Agilent OpenLAB CDS ChemStation Edition for LC & LC/MS Systems, Rev. C.01.04

Column

- Lichrosorb Si 60-5, 4.6 × 250 mm, 5 µm (p/n LI60-5-250A) (2 columns in series)
- Agilent ZORBAX Rapid Resolution SB-CN, 4.6 × 150 mm, 5 µm (p/n 863953-905)
- Agilent ZORBAX SB-CN Guard Cartridges 4.6 × 12.5 mm (p/n 820950-916)
- Agilent High Performance ZORBAX Guard Fittings Kit (p/n 820888-901)

Reagents

Mobile Phase

Heptane, HPLC grade

Standard

Octadecylbenzene, hexadecane

LC method

RID	
Peak width	> 0.2 minutes (4-second response time) (2.28 Hz)
Temperature	35.00 °C
Column compartment	
Valve position	Port 1 → 6
Temperature	20.00 °C
8.50 minutes	Change valve position to Port 1 → 2
23.00 minutes	Change valve position to Port 1 → 6
Sampler	
Injection volume	2.00 µL
Temperature	10 °C
Binary pump	
Flow	1.000 mL/min
Stop time	25.00 minutes
Solvent A	Heptane

Valve operation to use two columns

For this method, a silica gel and a cyano column is used. The sample is injected onto the cyano column. The separation column set has little affinity for the saturated compounds, while retaining the aromatic hydrocarbons and the polar compounds. As a result of this retention, the aromatic hydrocarbons and polar compounds are separated from the saturated compounds. At a predetermined time, after the elution of the saturated compounds, the column is backflushed to elute the aromatic and polar compounds.

Calculation of the backflush time based on system performance standard:

$$B = t_1 + 0.1\,(t_2 - t_1)$$

Where:

t_1 = retention time of hexadecane, in minutes

t_2 = retention time of octadecylbenzene, in minutes

Standard preparation

System performance standard

Prepare the system performance standard (SPS) by weighing hexadecane (1.0 ± 0.1 g) and octadecylbenzene (1.0 ± 0.1 g) into a 10-mL volumetric flask and filling up to the mark with heptane.

Calibration standard

Prepare five calibration standards (A, B, C, D, and E) in accordance with the concentration given in Table 1 by weighting the appropriate material into a 10-mL volumetric flask to the nearest 0.0001 g and filling up to the mark with heptane.

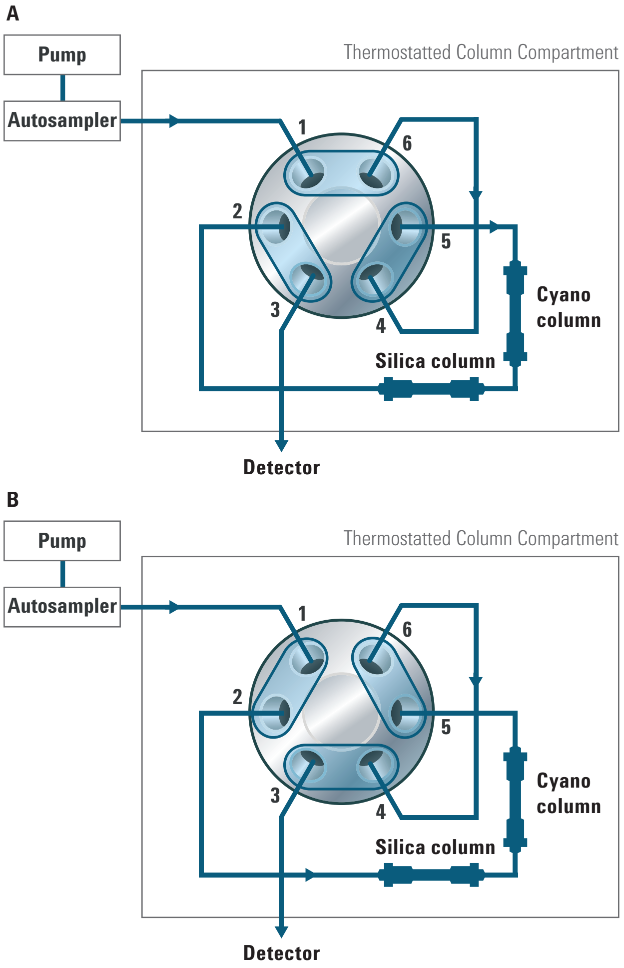

Figure 1. Valve configuration for ASTM D7419 method. A) Position 1 → 6 is the loading position. B) After switching to position 1 → 2, the compounds are eluted and analyzed in backflush.

Table 1. Calibration standards.

Calibration standard	Hexadecane (g/10 mL)	Octadecylbenzene (g/10 mL)
A	0.01	0.01
B*	0.1	0.1
C	1	0.5
D	2	1
E	5	3

* 1 g/100 mL = 1 % solution

Sample preparation

Weigh 0.5 g of the sample into a 1.5-mL autosampler vial, and add 0.5 mL of heptane. Shake thoroughly to mix. If other quantities of sample are desired, they may be prepared in a larger container with a similar ratio of sample/solvent and then transferred to the autosampler vial.

Results and Discussion

Due to the use of the valve solution to remove saturated compounds and backflushing for the elution of aromatic and polar compounds, they are eluted as single sharp band. A SPS of 10 % hexadecane and octyldecylbenzene was injected to check the system performance (Figure 2). The figure shows the compounds eluting at 8.301 and 9.797 minutes, and their detection by the RI detector. The time value for switching the columns to backflush was calculated from these retention times.

A concentration range of 0.1 % to 50 % for hexadecane and 0.1 % to 30 % for octadecylbenzene was used for calibration. The corresponding chromatograms for the lowest concentrated standard containing 0.1 % for both, and the highest concentrated standard containing 50 % and 30 % for hexadeane and otyldecylbenzene, respectively, are shown in Figure 3. Both calibration curves show good linearity and go down to a content of 0.1 % (Figure 4).

The precision performance of the system was shown for a comparable application including a valve, switching the column to backflush to separate the analyte from the matrix. Typically, the retention time RSD was below 0.1 % and the area RSD was below 0.2 %. The typical limit-of-detection (LOD) for aromatic hydrocarbons under the used method was below 1 µg/mL (calculated for a signal-to-noise ratio of 3)[3].

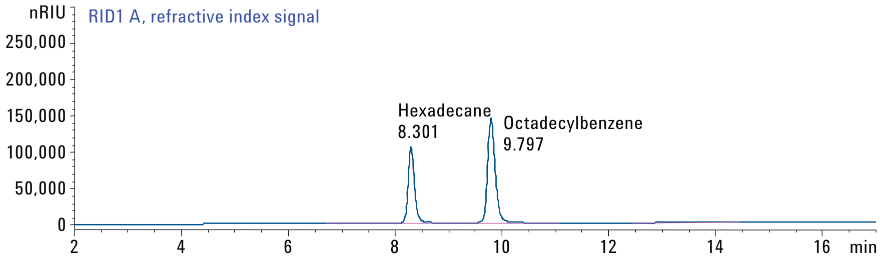

Figure 2. System performance standard (SPS) of hexadecane and octadecylbenzene.

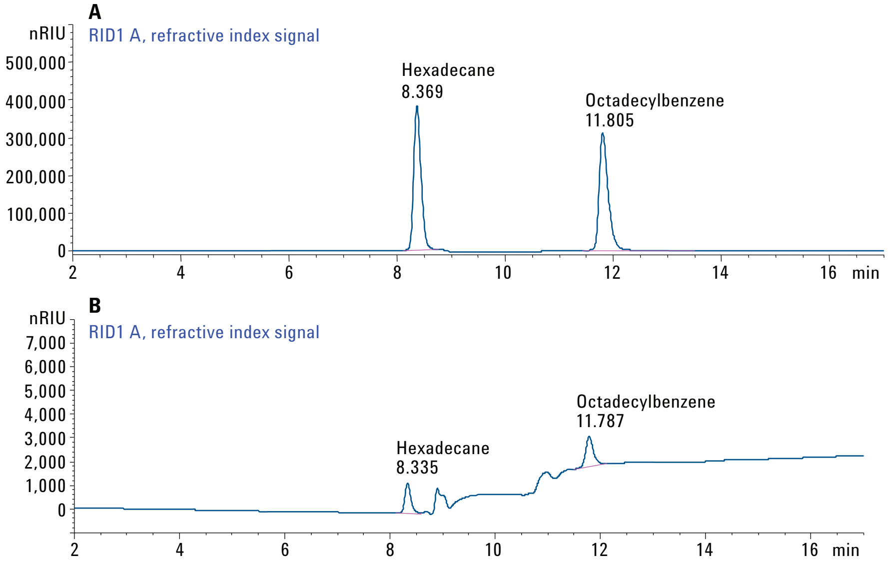

Figure 3. Calibration standards of highest (A) and lowest (B) concentration of hexadecane and octyldecylbenzene.

Conclusion

This Application Note demonstrates the use of the Agilent 1260 Infinity Binary LC System in combination with the Agilent RID detector for the determination of total aromatics and total saturates in additive-free lube base stocks according to ASTM D7419. The calibration of the RID showed good linearity for the range of 0.1 % to 50 % of saturates and 0.1 % to 30 % aromatics.

References

1. American Society for Testing and Materials (ASTM): ASTM D7419-07, Standard Test Method for Determination of Total Aromatics and Total Saturates in Lube Basestocks by High Performance Liquid Chromatography (HPLC) with Refractive Index Detection, URL: http://www.astm.org/Standards/D7419.htm.

2. Determination of Aromatic Hydrocarbons in Petroleum Middle Distillates with the Agilent 1260 Infinity Binary HPLC System with RID Detection According to IP391(2000)/ASTM D659, *Agilent Technologies Application Note*, publication number 5991-3170EN, **2013**.

3. Determination of Aromatic Hydrocarbons in Aviation Fuel with the Agilent 1260 Infinity Binary LC System with RI Detection According to IP436/ASTM D6379, *Agilent Technologies Application Note*, publication number 5991-3172EN, **2014**.

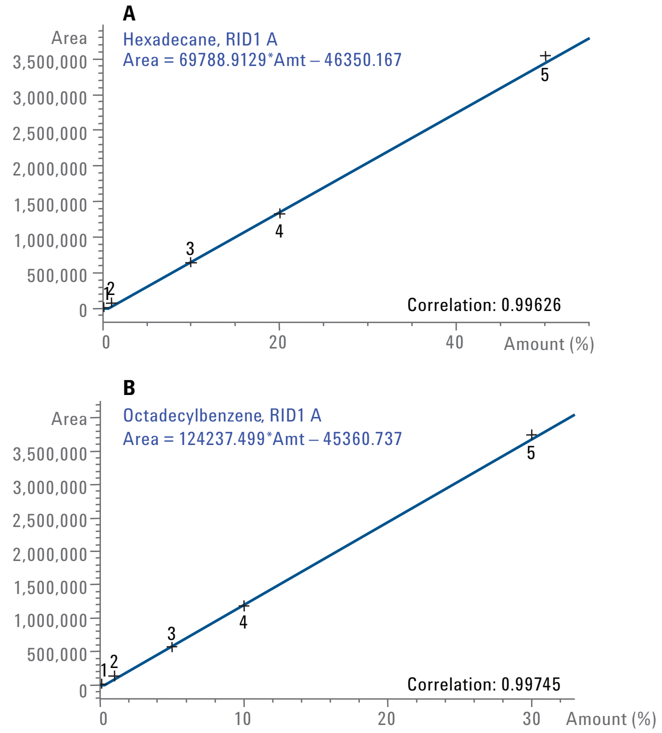

Figure 4. Calibration curves of A) hexadecane from 0.1 % to 50 % and B) for octyldecylbenzene from 0.1 % to 30 %.

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