Determination of Aromatic Hydrocarbons in Petroleum Middle Distillates with the Agilent 1260 Infinity Binary HPLC System with RID Detection According to IP391(2000)/ASTM D6591

Application Note

Energy & Chemicals - Petrochemicals

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Abstract

This Application Note shows the determination of aromatic hydrocarbons under normal phase conditions with the Agilent 1260 Infinity Binary LC system with RID detection in compliance with the IP391(2000)/ASTM D6591 methods.

Introduction

The IP391(2000)/ASTM D6591 methods cover the determination of mono-aromatic (MAH), di-aromatic (DAH), and poly-aromatic hydrocarbon (TRI+) contaminants in petroleum middle distillates and diesel fuels boiling in the range from 150 °C to 400 °C, for example gas oil[1].

The aromatic hydrocarbon content of motor diesel fuel is a factor that can affect exhaust emissions and fuel combustion characteristics, as measured by the cetane number[2].

Using this instrumental setup, it is possible to determine mono and di-aromatic hydrocarbons according[3] to IP436/ASTM D6379. It is also possible to determine the total aromatic hydrocarbons and total saturates[4] according to ASTM D7419.

This Application Note shows the possibility to determine aromatic hydrocarbons under normal phase conditions with RID detection by using the Agilent 1260 Infinity binary LC system while complying with the IP391(2000)/ASTM D6591 methods.

Experimental

Instruments

Agilent 1260 Infinity LC System

- Agilent 1260 Infinity Binary Pump (G1312B) with Agilent Infinity Standard Degasser (G1322A)
- Agilent 1260 Infinity Standard Autosampler (G1329B) with Agilent 1290 Infinity Thermostat (G1330B)
- Agilent 1260 Infinity Thermostatted Column Compartment (G1316A) with Agilent 1200 Infinity Series Quick-Change 2-postition/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

Columns

- Agilent ZORBAX NH2, 4.6 × 250 mm, 5 µm (p/n 880952-708)
- Agilent ZORBAX NH2, Guard Cartridges, 4.6 × 12.5 mm, 5 µm (p/n 820950-908)
- Agilent ZORBAX High Performance Guard Fittings Kit (p/n 820888-901)

Reagents

Mobile Phase: Heptane, HPLC Grade

Standards

- System Performance Standard (SPS) - ASTM-P-0135-PAK: cyclohexane (10 mg/mL), *o*-xylene (5 mg/mL, MAH), dibenzothiophene (5 mg/mL, DAH), 9-methylanthracene (5 mg/mL, TRI+).
- Calibration Standard: ASTM-P-0136-SET

	Std. 1 (mg/mL)	Std. 2 (mg/mL)	Std. 3 (mg/mL)	Std. 4 (mg/mL)
Cyclohexane	50	20	5	1
o-Xylene (MAH)	40	10	2.5	0.5
Debenzothiophene (DAH)	40	10	2.5	0.2
9-Methylantracene (TRI+)	4	2	0.5	0.1

LC method

RID	
Peak width	> 0.2 minutes (4 second response time) (2.28 Hz)
Temperature	35.00 °C
Column compartment	
Initial valve position	Port 1 → 6
Temperature	30.00 °C
Change valve position	7.48 minutes: Port 1 → 2
Sampler	
Injection mode	Standard injection
Injection volume	20.00 µL
Needle wash in vial with heptane	
Binary pump	
Flow	1.000 mL/min
Stop time	30.00 min
Solvent A	Heptane, isocratic

Valve operation (Figure 1)

In the OFF position, the sample is injected into the column through the autosampler. Once the DAH is eluted from the column, the valve is switched to the ON position, which reverses the flow in the column, backflushing the TRI+ aromatics to the RID detector.

The time B (seconds) for switching to backflush is calculated based on an injection of the System Performance Standard (SPS) without valve switching using the following equation:

$$B = t_A + 0.4\,(t_B - t_A)$$

Where: t_A is the retention time of dibenzothiophene (DAH), in seconds. t_B is the retention time of 9-methylanthracene (TRI+), in seconds.

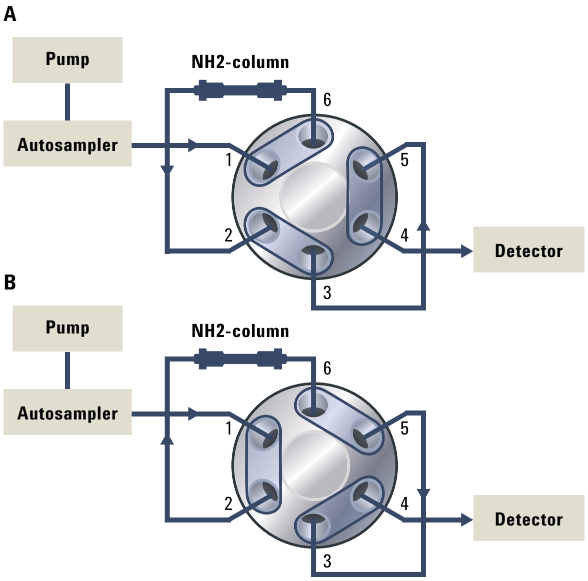

Figure 1. Valve configuration for the IP 391 method. A) OFF Position 1 → 6 is the loading position. B) After switching to ON position 1 → 2 the compounds are eluted and analyzed in backflush.

Sample preparation

Place between 0.9 g to 1.1 g of sample, to the nearest 0.001 g, into a 10-mL volumetric flask and fill to the mark with *n*-heptane. Shake thoroughly to mix, and filter the sample to remove the particulate matter.

Results and Discussion

With the final method, all four calibration standards were measured (Figure 2). The measurement showed a good separation of the inherent compounds, a clear separation of the aromatic compounds from the aliphatic cyclohexane, and a separation of the poly nuclear aromatic hydrocarbons to a much higher retention time. This is necessary for their determination in real samples.

For the non-aromatic as well as aromatic compounds (MAH, DAH, TRI+), individual calibration curves were created. They ranged from 1 to 50 mg/mL for cyclohexane, 0.5 to 40 mg/mL for MAH and DAH, and 0.1 to 4 mg/mL for TRI+ aromatics (Figure 3). All calibration curves for the aromatic hydrocarbons showed linearity coefficients better than 0.9998. To determine the limit-of-detection (LOD), the signals and the noise were measured for a 1/10 dilution of Standard 4. The typical LOD for aromatic compounds is 1 µg/mL (calculated for a signal-to-noise ratio of 3). Statistical evaluation of retention time and area for the aromatic compounds by multiple injection of calibration standard level 3 showed RSD values typically below 0.06 % and 0.16 %, respectively (Table 1).

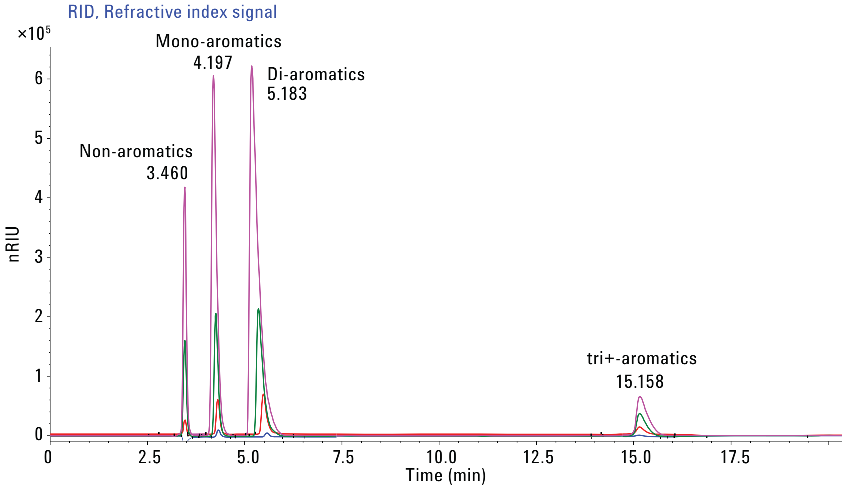

Figure 2. Overlay of IP391 Calibration standard 1–4 (ASTM-P-0136-SET), cyclohexane (non-aromatics), *o*-xylene (MAH), dibenzothiophene (DAH), 9-methylanthracene (TRI+).

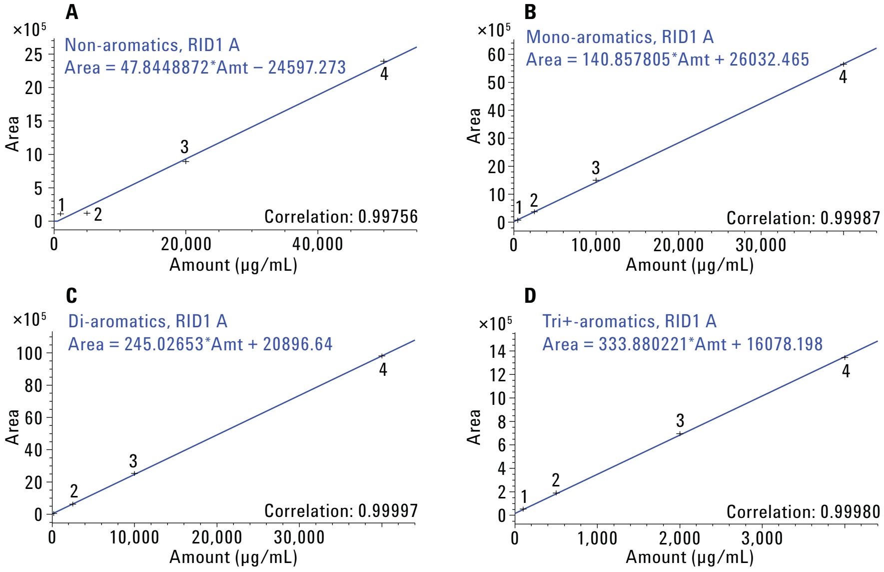

Figure 3. Calibration curves for the four compounds tested.

Table 1. Statistical evaluation of retention time and area for the aromatic compounds by multiple injection (n = 5) of calibration standard level 3.

	Mono-aromatics	Di-aromatics	Tri+-aromatics
RT (min)	4.27	5.36	15.15
RT RSD (%)	0.06	0.06	0.02
Area RSD (%)	0.12	0.16	0.15
LOD (µg/mL)	1	0.7	1

Figure 4 displays a RI chromatogram of a real sample. This sample shows approximately 4.3 mg/mL of tri+aromatic compounds.

Conclusion

This Application Note demonstrates the use of the Agilent 1260 Infinity Binary LC in combination with the Agilent 1260 Infinity RI Detector for the determination mono-aromatic (MAH), di-aromatic (DAH), and tri+-aromatic (TRI+) contaminants in petroleum middle distillates and diesel fuels according to IP 391(2000)/ASTM D6591. The calibration of the RID showed excellent linearity for MAH, DAH, and TRI+ aromatics. The retention time RSD is typically below 0.06 % and the area RSD is typically below 0.16 %.

References

1. IP391(2000)/ASTM D6591–11, Standard Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection.

2. http://www.astm.org/Standards/D6591.htm

3. Agilent Application Note, Publication number 5991-3171EN

4. Agilent Application note, Publication number 5991-3172EN

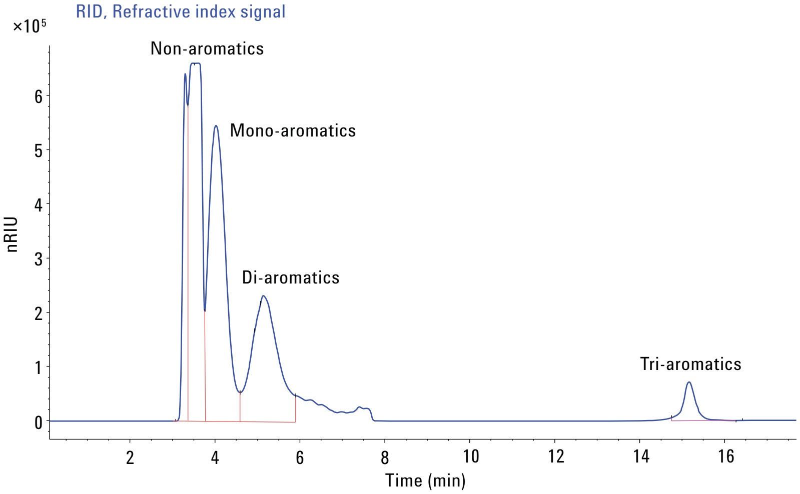

Figure 4. Real diesel oil sample showing aromatic compounds.

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