



Determination of Aromatic Hydrocarbons in Aviation Fuel with the Agilent 1260 Infinity Binary LC System with RI Detection According to IP436/ASTM D6379

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 in jet fuel under normal phase conditions with RI detection, and complies with the IP436/ASTM D6379 method.



Introduction

This test method covers the determination of mono-aromatic and di-aromatic hydrocarbon content in aviation kerosene and petroleum distillates of boiling range 50 to 300 °C, according to IP436/ASTM D6379, such as Jet A or Jet A-1 fuels and kerosene¹.

Accurate quantitative information on aromatic hydrocarbon types can be useful in determining the effects of petroleum processes on the production of various finished fuels. This information can also be useful for indicating the quality of fuels, and for assessing the relative combustion properties of finished fuels¹.

With the described instrumental setup, the determination of mono-, di-, and poly-aromatic hydrocarbons² according to IP391 (2000)/ASTM D6591 and the determination of total aromatic hydrocarbons and total saturates³ according to ASTM D7419 are also possible.

This Application Note shows that the Agilent 1260 Infinity Binary LC system is able to determine aromatic hydrocarbons in jet fuel under normal phase conditions with RI detection, and complies with the IP436/ASTM D6379 method.

Experimental

Instrument

Agilent 1260 Infinity Binary 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 (G4231A).
- Agilent 1260 Infinity Refractive Index Detector (G1362A)

Software

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

Column

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

Reagents

Mobile Phase: Heptane, HPLC grade

Standard

- System Performance Standard (SPS) D-6379-SRS-PAK: cyclohexane (10 mg/mL), *o*-xylene (0.5 mg/mL), 1-methyl naphthalene (0.05 mg/mL) in *n*-heptane
- Calibration Standard D-6379-SET-PAK comprising standard 1 to standard 4 see table below

Analyte	Standard 1 (mg/mL)	Standard 2 (mg/mL)	Standard 3 (mg/mL)	Standard 4 (mg/mL)
Cyclohexane	5	2	0.5	0.1
<i>o</i> -Xylene	15	5	1	0.1
1-Methyl naphthalene	5	1.0	0.2	0.05

LC method

Agilent 1260 Infinity Refractive Index Detector	
Peak width	> 0.2 minutes (4-second response time) (2.28 Hz)
Temperature	35.00 °C
Agilent 1260 Infinity Column Compartment	
Valve position	Port 1 → 6
Temperature	35.00 °C
Agilent 1260 Infinity Standard Autosampler	
Injection volume	10.00 µL
Temperature	10 °C
Agilent 1260 Infinity Binary Pump	
Flow	1.000 mL/min
Stop time	15.00 minutes
Solvent A	Heptane

Valve operation

In the 1 → 6 position, the sample is injected onto the column through the autosampler. The compounds *o*-xylene (mono-aromatic hydrocarbons, MAH) and 1-methyl naphthalene (di-aromatic hydrocarbons, DAH) are separated and detected. The valve can be used for the determination of MAH, DAB, and TRI+ (tri-aromatic hydrocarbons) according to IP391/ASTM D6591³.

Sample preparation

Insert between 4.9 and 5.1 g, to the nearest 0.001 g, of sample into a 10-mL volumetric flask, and fill up to the mark with heptane. Shake thoroughly to mix. Allow the solution to stand for 10 minutes and filter to remove the insoluble material.

Results and Discussion

An initial experiment with the System Performance Standard (SPS) containing cyclohexane (10 mg/mL), *o*-xylene (0.5 mg/mL), and 1-methyl naphthalene (0.05 mg/mL) showed the separation of the saturated compound from the mono- and di-aromatic compound (Figure 2). Cyclohexane, as a model for the saturated compounds, eluted at 3.55 minutes, xylene, as a mono-aromatic compound, at 4.87 minutes, and the naphthalene derivative, as a di-aromatic compound, at 6.78 minutes.

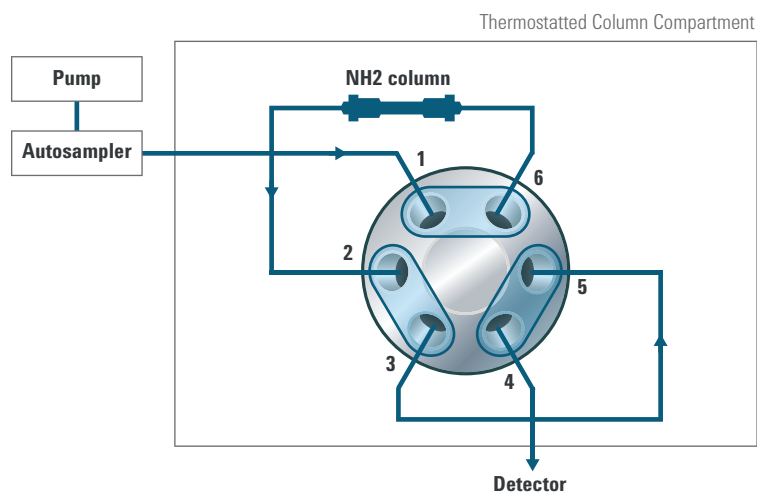


Figure 1. Valve configuration for IP 436 method. A) Position 1 → 6 is the position for loading the sample on the column and for separation in forward flush.

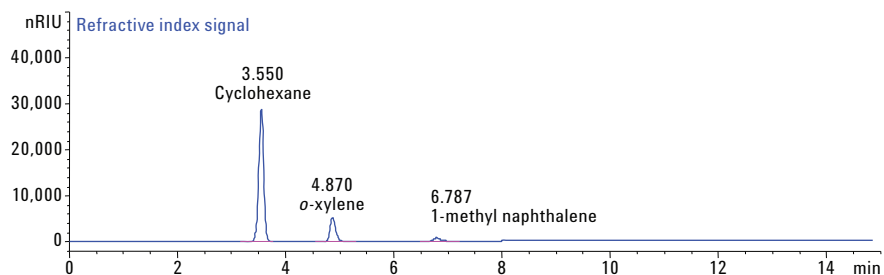


Figure 2. System performance standard (SPS) IP436/ASTM D6379, cyclohexane (10 mg/mL), *o*-xylene (0.5 mg/mL), and 1-methyl naphthalene (0.05 mg/mL) in *n*-heptane.

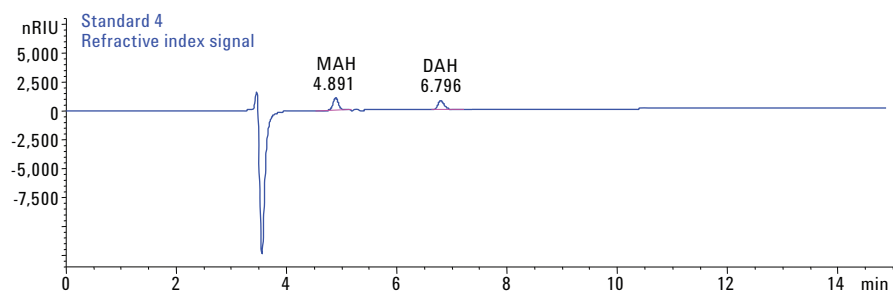


Figure 3. Standard 4, IP436/ASTM D6379, *o*-xylene (MAH, 0.1 mg/mL), 1-methyl naphthalene (DAH, 0.05 mg/mL).

The separation of the lowest level calibration standard containing 0.1 mg/mL *o*-xylene (MAH) and 0.05 mg/mL 1-methyl naphthalene (DAH) showed their clear detection by RID at the lowest concentration level (Figure 3). The calibration curves of *o*-xylene (MAH) and 1-methyl naphthalene (DAH) by RID detection demonstrated good linearity for quantification (Figure 4). For *o*-xylene, the linearity coefficient was 0.99990, and for 1-methyl naphthalene the linearity coefficient was 0.99997.

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 is below 1 µg/mL (calculated for a signal-to-noise ratio of 3)².

Conclusion

This Application Note demonstrates the use of the Agilent 1260 Infinity Binary LC System in combination with the Agilent 1260 Infinity Refractive Index Detector for the determination of MAH and DAH contaminants in aviation kerosene and petroleum distillates boiling in the range of 50 to 300 °C, according to IP436/ASTM D6379. The calibration of the RID showed excellent linearity for the range of 0.01 % to 1.5 % MAH and 0.005 % to 0.5 % DAH.

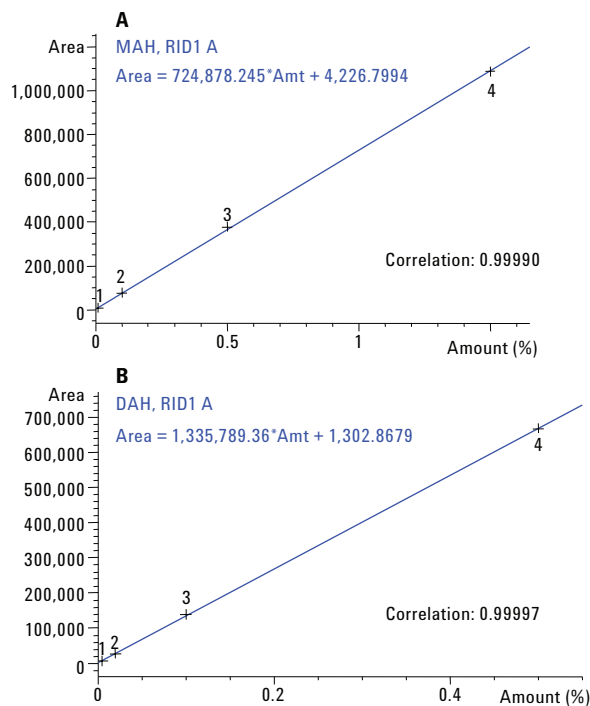


Figure 4. Calibration curves for A) MAH, *o*-xylene, and B) DAH, 1-methyl naphthalene by RID detection.

References

1. American Society for Testing and Materials (ASTM): ASTM D6379 – 11, Standard Test Method for Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection, <http://www.astm.org/Standards/D6379.htm>
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3. Determination of Total Aromatic Hydrocarbons and Total Saturates with the Agilent 1260 Infinity Binary LC System with RI Detection According to ASTM D7419, *Agilent Technologies Application Note*, publication number 5991-3171EN, **2014**.

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Published in the USA, September 1, 2016
5991-3172EN



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