

Determination of Aromatic Hydrocarbons in Jet Fuel by LC-RID According to ASTM D6379 / IP436 using a Single Column

■ Introduction

The test method presented here is applicable to the determination of mono- and di-aromatic hydrocarbon content in aviation fuels and middle distillates with boiling points in the range of 50° C to 300° C in accordance with ASTM D6379 and IP436. This application is relevant to some of the most commonly-used aviation fuels, such as Jet A and Jet A-1. The accurate determination of the aromatic content of fuels is critical to assessing their quality and combustion characteristics. These parameters are crucial to ensuring aviation safety and compliance with environmental regulations.

This methodology presents an alternative to ASTM D1319. Though ASTM D1319 has enjoyed widespread use, it relies on the use of a fluorescent dye which was discontinued, and the replacement no longer produces reliable results, particularly for middle distillates. As such, many laboratories are exploring alternative methods, including ASTM D6379 / IP436, for determination of the total aromatics in kerosene and jet fuels.

This application news demonstrates the use of the Shimadzu Prominence™ HPLC for the determination of mono- and di-aromatic hydrocarbons in aviation fuel and other middle distillates in compliance with parameters set out in ASTM D6379 and IP436.



Prominence™ HPLC System

■ Experimental Design

Instrument

Shimadzu Prominence HPLC

- LC-20AD HPLC Pump
- DGU-20A_{3R} Degasser
- SIL-20AC Autosampler
- CTO-20A Column Oven with 6-port 2-position valve
- RID-20A Refractive Index Detector

Software

LabSolutions™ LC/GC

Column

1. Shim-pack™ GIST NH₂ 4.6×250 mm, 3 μm (P/N 227-30296-07) with guard (P/N 227-30310-02)

Reagents

Mobile Phase: Heptane, HPLC Grade

Standards

ASTM D-6379 Kit from AccuStandard®

- System Resolution Standard: cyclohexane (10 mg/mL), *o*-xylene (0.5 mg/mL), 1-methyl naphthalene (0.05 mg/mL) in *n*-heptane
- Four (4) calibration standards as shown in Table 1.

Valve Operation

This system contains a 6-port, 2-position valve within the analytical line and is operated in the 1 → 6 position (Fig. 1). The valve is not actuated for this method but is included because, with the addition of a CN column in line, other methods such as ASTM D6591 / IP391 can be run on the same system but require a valve switch for back-flushing of more retained compounds such as tri-aromatic hydrocarbons.

Analytical Conditions

- Mobile phase flow rate: 1 mL / min
- Injection volume: 1 μL
- Column temperature: 35° C
- RID temperature: 35° C

Table 1: Standard analytes and concentrations

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-Methylnaphthalene	5	1	0.2	0.05

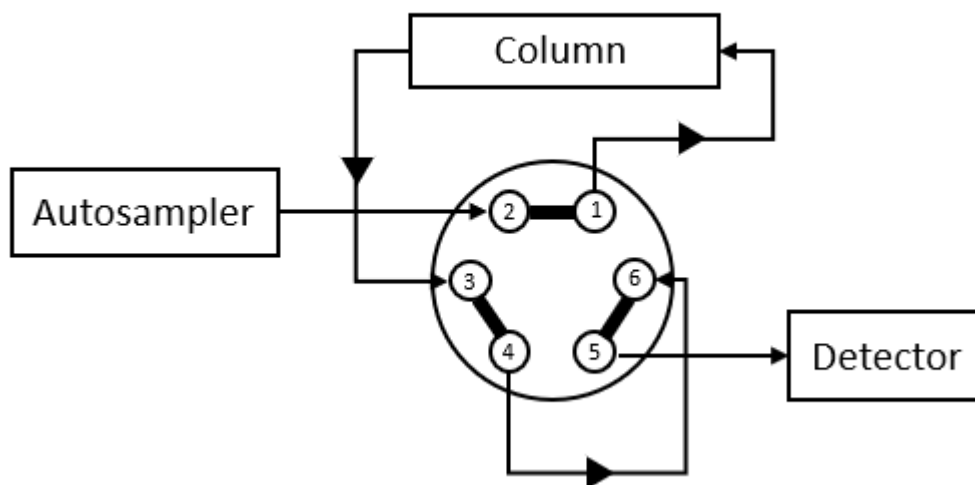


Figure 1: Simplified flow schematic of the HPLC used for this application

■ Results

An injection of the system resolution standard (SRS) demonstrated method-appropriate resolution of the three component peaks (Fig. 2). Cyclohexane, a proxy for saturated compounds of samples, eluted at 3.46 minutes, whereas *o*-Xylene, a proxy for mono-aromatic hydrocarbons (MAHs), eluted at 4.86 minutes. Finally, 1-Methylnaphthalene eluted at 6.08 minutes and serves as a proxy for di-aromatic hydrocarbons (DAHs). The resolution of cyclohexane and *o*-Xylene was 7.1, which exceeds both the ASTM and the IP standards of 5 and 5.7, respectively.

Calibration curves generated for the compounds and at concentrations outlined in Table 1 were linear, with r^2 values of 0.9999 for both *o*-Xylene and 1-Methylnaphthalene (Figs. 3 and 4).

To assess precision, three replicate injections were made of Standard 2. The RSDs for retention times of the peaks and peak areas were less than 0.2% and 0.2%, respectively.

A sample of Jet A fuel, obtained from the fuel depot at a local airport, was diluted 1:10 in heptane and injected to assess the efficacy of this instrument on real samples. An example chromatogram is provided in Figure 5. The separation of the saturates, MAHs, and DAHs is sufficient for quantitation per ASTM D6379.

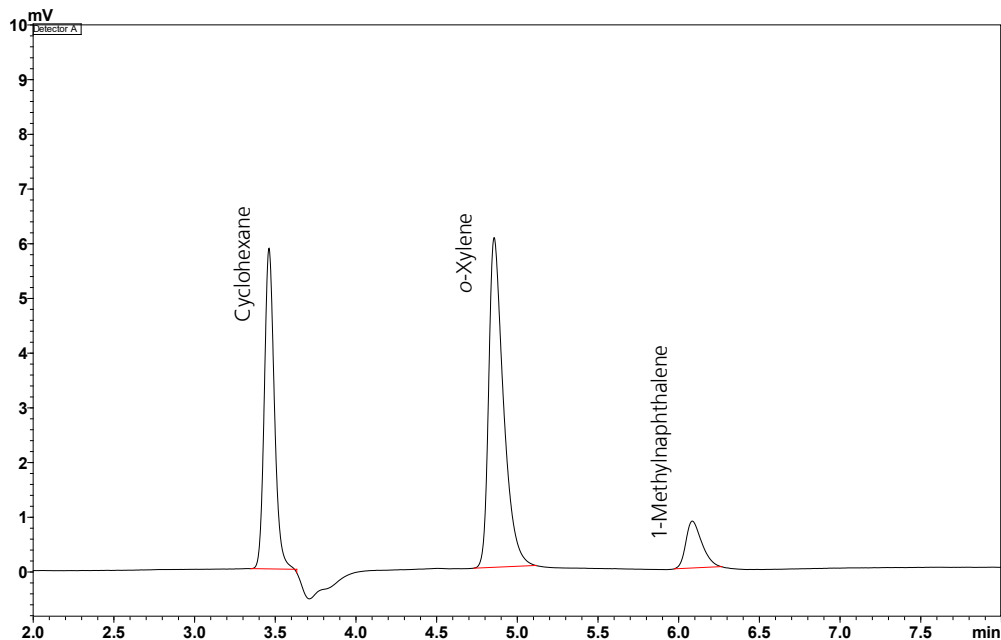


Figure 2: Chromatogram resulting from injection of the System Resolution Standard

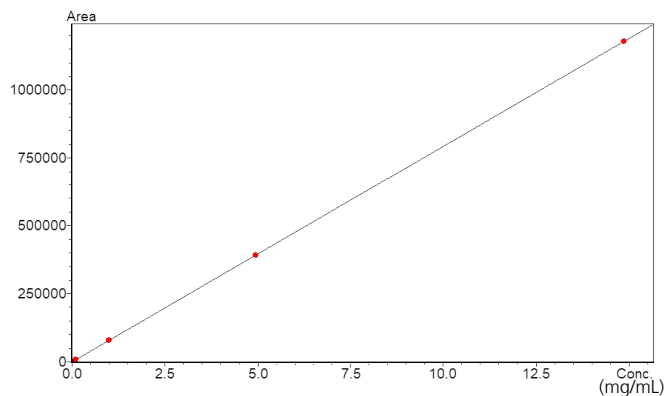


Figure 3: Calibration curve of o-Xylene. $r^2=0.9999$

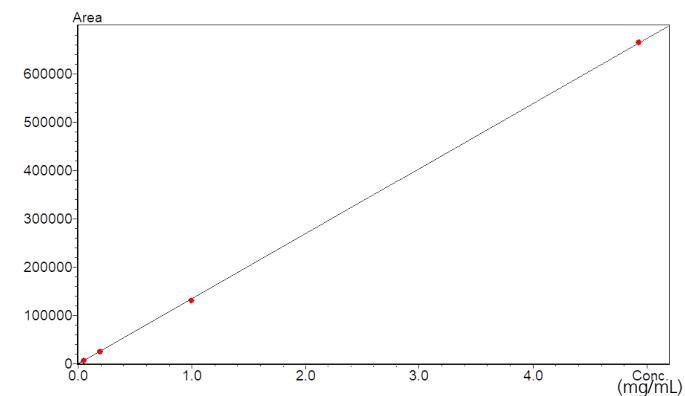


Figure 4: Calibration curve of 1-Methylnaphthalene. $r^2=0.9999$

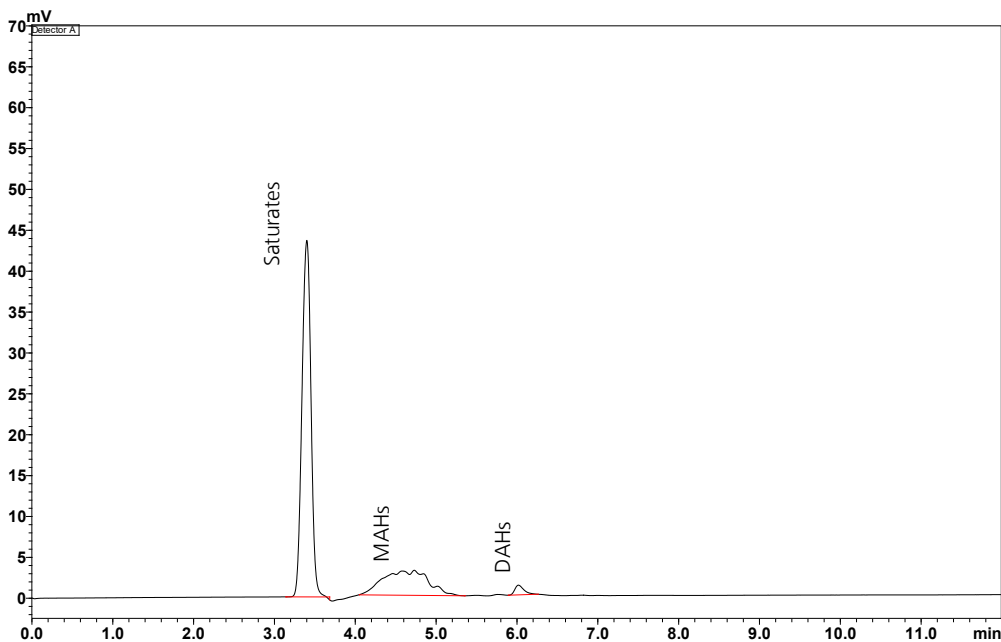


Figure 5: Injection of Jet A diluted 1:10 in heptane

■ Discussion and Conclusions

This application news demonstrates the detection and quantitation of MAH and DAH using a Prominence HPLC equipped with a single column and guard, as well as method compliance for ASTM D6379 / IP436. Coefficients for the calibration curves with r^2 values greater than 0.9999 indicate a strong linear response of these compounds and exceed the requirements of the method.

The single column used in this application maintains system simplicity and minimal analysis times, and ensures compliance with resolution standards set by ASTM D6379 and IP 436 of 5 and 5.7, respectively. With the use of the guard column inline, column reconditioning or replacement will be minimized, ensuring longevity of the analytical column. Finally, with the addition of a CN column, this instrument configuration will also comply with ASTM D6591 using the 6-port valve for backflushing.

Results generated by this method on both system check standards and real samples demonstrate its acceptability as an alternative to ASTM D1319, which has become difficult to apply to middle distillates due to the unsuitability of the fluorescent dye used in the method.

■ References

- ASTM D1319-18, Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption, ASTM International, West Conshohocken, PA, 2018, www.astm.org
- 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, ASTM International, West Conshohocken, PA, 2011, www.astm.org

Prominence, LabSolutions and Shim-pack are trademarks of Shimadzu Corporation in Japan and/or other countries. AccuStandard is a registered trademark of AccuStandard, Inc.



SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
www.ssi.shimadzu.com

For Research Use Only. Not for use in diagnostic procedure.
This publication may contain references to products that are not available in your country. Please contact us to check the availability of these products in your country.

The content of this publication shall not be reproduced, altered or sold for any commercial purpose without the written approval of Shimadzu. Shimadzu disclaims any proprietary interest in trademarks and trade names used in this publication other than its own. See <http://www.shimadzu.com/about/trademarks/index.html> for details.

The information contained herein is provided to you "as is" without warranty of any kind including without limitation warranties as to its accuracy or completeness. Shimadzu does not assume any responsibility or liability for any damage, whether direct or indirect, relating to the use of this publication. This publication is based upon the information available to Shimadzu on or before the date of publication, and subject

First Edition: July 2019