

## Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates with the Alliance HPLC System and RI Detection According to ASTM D6379 (IP436)

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This is an Application Brief and does not contain a detailed Experimental section.

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## Abstract

This application brief highlights the use of the Waters Alliance HPLC System coupled to the Waters 2414 Refractive Index Detector to determine mono- and di-aromatic hydrocarbon contents in petroleum distillates and aviation fuels in compliance with the ASTM D6379 (IP436) method. This instrument system setup is demonstrated to comply with the standards set out in the method, exceeding the linearity, resolution, and precision criteria.

## Benefits

- Compatible with a wide range of solvent types to support normal-phase applications
- Tool-free maintenance for common user-replaceable parts minimizes system down times
- Utilizes one of the most widely referenced HPLC columns in scientific literature
- Centralized methods, data, electronic sign-off, and reporting via Empower Software, ensuring data integrity
- Empower is scalable for your laboratory with personal, workgroup, or enterprise versions

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## Introduction

This high performance liquid chromatography (HPLC) test method covers the determination of mono-aromatic and di-aromatic hydrocarbon contents in petroleum distillates and aviation fuels boiling in the range of 50 to 300 °C, such as Jet A or Jet A-1 fuels, in accordance with ASTM D6379.<sup>1</sup>

It is important to ascertain the total level of aromatic hydrocarbon types to determine the effects of petroleum processes on production of various finished fuels. These levels are central in understanding the quality of fuels and for assessing the relative combustion properties of finished products.<sup>1</sup> Therefore, it is essential to derive accurate quantitative information on the aromatic component levels in fuels to ensure that they perform as they should during operation.

To ensure that the finished fuel products are safe and compliant, the aromatic hydrocarbon content level must be assessed by the ASTM D6379 test method and meet the criteria within.

This application brief demonstrates that the Alliance HPLC System with refractive index detection (RID) and Empower Chromatography Data System (CDS) can determine aromatic hydrocarbons under normal phase conditions and in compliance with the ASTM D6379 method.

## Experimental

Experimental conditions outlined in ASTM D6379 were followed.

Instruments:	Alliance HPLC System 2414 Refractive Index Detector
Software:	Empower 3 Chromatography Data System
Column:	<p>Waters Spherisorb Amino (NH<sub>2</sub>) Column, 80 Å, 5 µm, 4.6 x 250 mm (p/n: PSS831115 &lt;<a href="https://www.waters.com/nextgen/global/shop/columns/pss831115-spherisorb-amino-nh2-column-80a-5--m-46-mm-x-250-mm-1-pk.html">https://www.waters.com/nextgen/global/shop/columns/pss831115-spherisorb-amino-nh2-column-80a-5--m-46-mm-x-250-mm-1-pk.html</a>&gt; )</p> <p>Waters Spherisorb Amino (NH<sub>2</sub>) Guard Cartridge, 80 Å, 5 µm, 4.6 x 10 mm (p/n: PSS830079 &lt;<a href="https://www.waters.com/nextgen/global/shop/columns/pss830079-spherisorb-amino-nh2-guard-cartridge-80a-5--m-46-mm-x-10-mm-3-pk.html">https://www.waters.com/nextgen/global/shop/columns/pss830079-spherisorb-amino-nh2-guard-cartridge-80a-5--m-46-mm-x-10-mm-3-pk.html</a>&gt; )</p> <p>Waters In-Line Guard Cartridge Holder Kit (p/n: PSS830008 &lt;<a href="https://www.waters.com/nextgen/global/shop/columns/pss830008-in-line-guard-cartridge-holder-kit-for-46-mm-x-10-mm-guards.html">https://www.waters.com/nextgen/global/shop/columns/pss830008-in-line-guard-cartridge-holder-kit-for-46-mm-x-10-mm-guards.html</a>&gt; )</p>
Reagents (mobile phase):	Heptane (HPLC-grade, Sigma-Aldrich (Dorset, UK))
Standards:	<p>Cyclohexane (Merck Biosciences Ltd (Nottingham, UK))</p> <p><i>o</i>-Xylene (Merck Biosciences Ltd (Nottingham, UK))</p>

	<p>1-Methylnaphthalene (Sigma-Aldrich (Dorset, UK))</p> <p>A system resolution standard (SRS) and four calibration standards were made as shown in Table 1.</p>
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## Analytical Conditions

Mobile phase flow rate:	1 mL/min
Injection volume:	10 $\mu$ L
Column temp.:	30 $^{\circ}$ C
RID temp.:	30 $^{\circ}$ C
Stop time:	15 min

## Calibration Standards

Analyte	SRS (g/100 mL)	Standard 1 (g/100 mL)	Standard 2 (g/100 mL)	Standard 3 (g/100 mL)	Standard 4 (g/100 mL)
Cyclohexane	1	5	2	0.5	0.1
<i>o</i> -Xylene	0.5	15	5	1	0.1
1-Methylnaphthalene	0.05	5	1	0.2	0.05

Table 1. Analyte concentrations in the SRS and calibration standards.

## Results and Discussion

The system resolution standard (SRS) was injected to validate the method in line with ASTM D6379 criteria. Baseline separation of the saturated compound (cyclohexane, 3.35 minutes) from the mono and di-aromatic

compounds (*o*-xylene, 5.82 minutes and 1-methylnaphthalene, 8.24 minutes) was achieved (Figure 1). The resolution between *o*-xylene and cyclohexane and *o*-xylene and 1-methylnaphthalene both greatly exceeded the ASTM standard level.

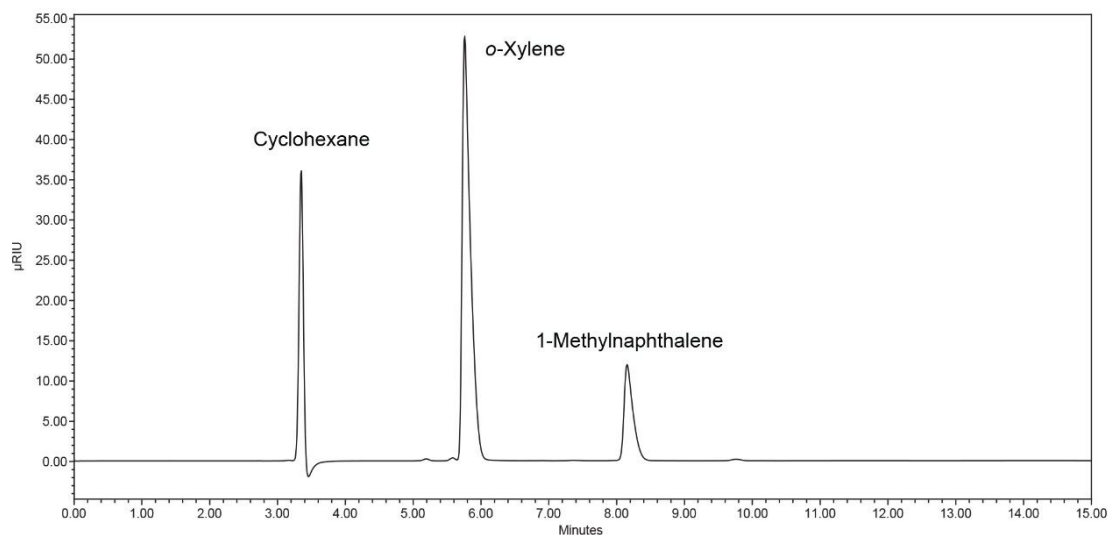


Figure 1. System resolution standard (SRS) chromatogram in heptane.

Calibration curves for the calibrant standards showed good linearity for quantification with  $r^2$  values greater than 0.999 for both *o*-xylene and 1-methylnaphthalene (Figures 2 and 3).

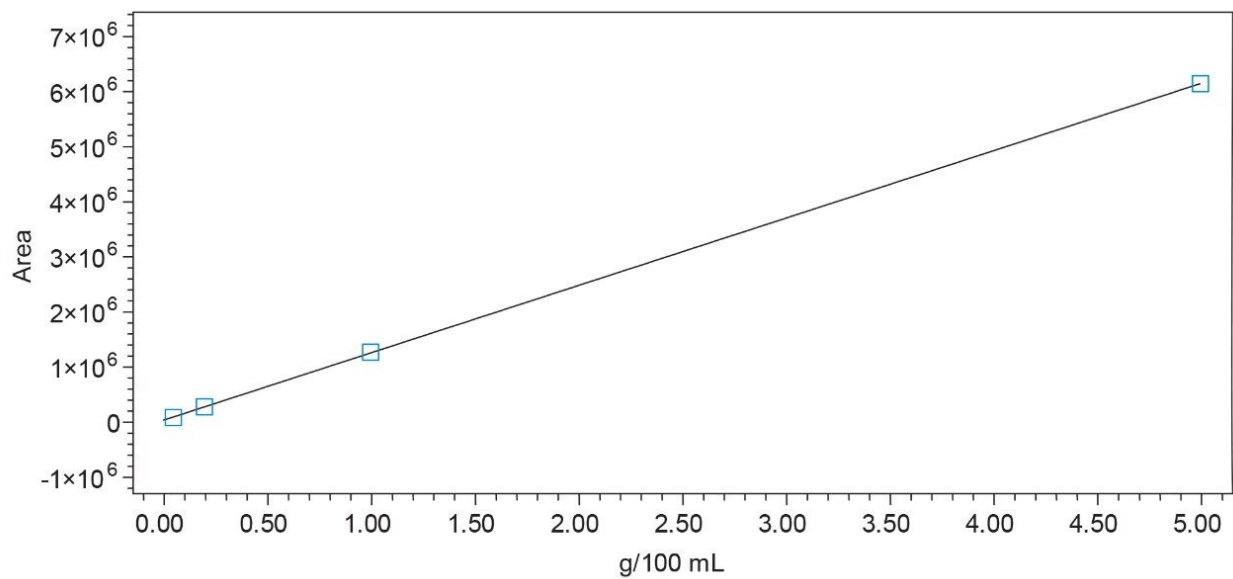


Figure 2. Calibration curve of o-xylene.

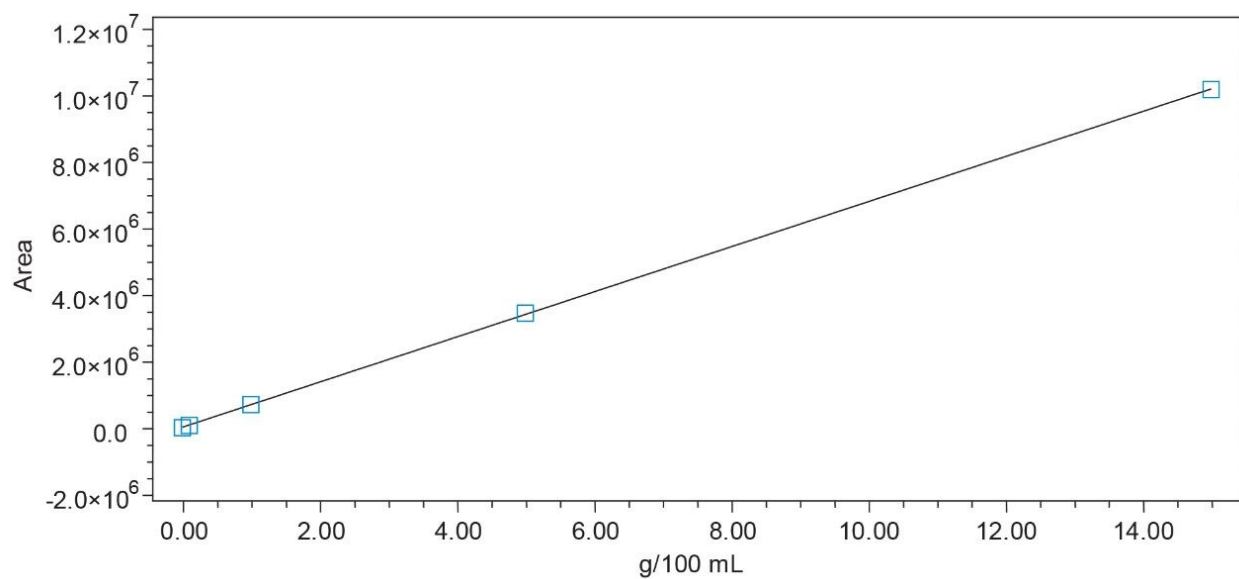


Figure 3. Calibration curve of 1-methylnaphthalene.

Replicate injections of the SRS were undertaken to assess precision. For each compound, the RSDs for the peak retention times and the peak areas were less than 0.1% and 0.6% respectively.

To assess the instrument system for real samples, a sample of Jet-A fuel (supplied by an academic

collaborator) was diluted 1:10 in heptane and injected. An example chromatogram of a Jet-A fuel injection, Figure 4, shows the separation of saturates and mono-aromatic and di-aromatic hydrocarbons to be sufficient for quantitation per ASTM D6379.

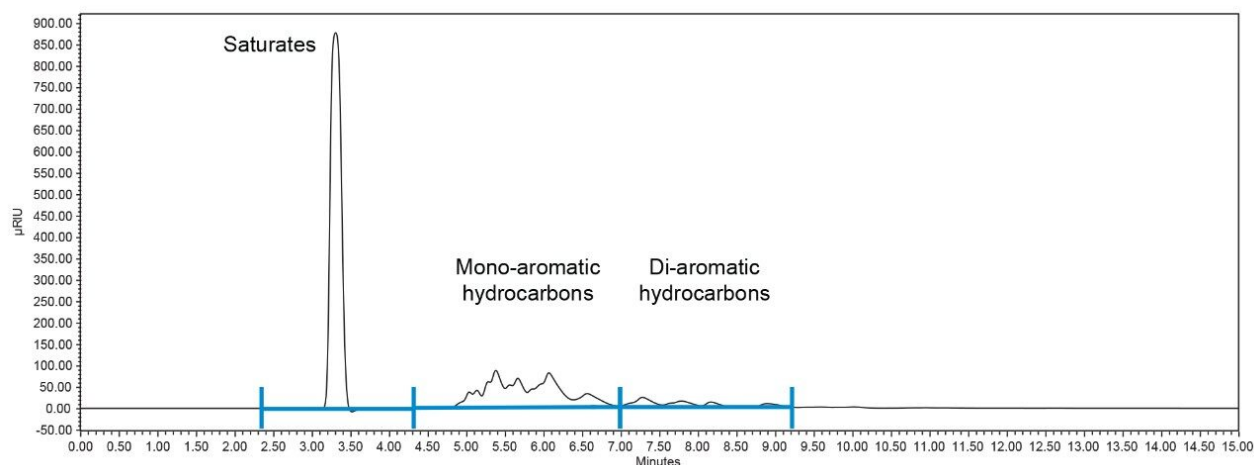


Figure 4. Injection of a Jet A-1 sample showing integration points of predicted aromatic hydrocarbon type groups.

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## Conclusion

The Waters Alliance HPLC System coupled to a Waters 2414 Refractive Index Detector is shown to be fit for purpose for the application of the ASTM D6379 (IP 436) standard method for the determination of aromatic hydrocarbons in aviation fuels and petroleum distillates. The instrument set up demonstrates compliance with the ASTM standard method, meeting the linearity, resolution, and precision criteria, with calibration coefficients that demonstrate a good linear response for quantification of aromatic hydrocarbons.

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## 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,  
<https://www.astm.org/Standards/D6379.htm> <<https://www.astm.org/Standards/D6379.htm>> .

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2414 Refractive Index (RI) Detector <<https://www.waters.com/514425>>

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