Nota de aplicación

Determination of Aromatic Hydrocarbon Types in Middle Distillates with the Alliance HPLC System and RI Detection According to ASTM D6591 (IP548)

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

Abstract

This application brief highlights the use of the Waters Alliance HPLC System coupled to the Waters 2414 Refractive Index Detector to determine mono-, di-, tri+-, and polycyclic aromatic hydrocarbon contents in diesel fuels and petroleum distillates in compliance with the ASTM D6591 (IP548) method. This instrument system set up 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 time
- Utilizes one of the most widely referenced HPLC columns in scientific literature
- Centralized methods, data, electronic sign-off, and reporting via Empower 3 Chromatography Data System, ensuring data integrity
- Empower is scalable for your laboratory with personal, workgroup, or enterprise versions

Introduction

This high performance liquid chromatography (HPLC) test method covers the determination of mono-aromatic, di-aromatic, tri+-aromatic, and polycyclic hydrocarbon contents in diesel fuels and petroleum distillates boiling in the range of 150 to 400 °C, in accordance with ASTM D6591.[1]

It is important to ascertain the total level of aromatic hydrocarbon types in motor diesel fuel as it is a factor that can affect exhaust emissions and fuel combustion characteristics, as measured by cetane number. Due to limits on total aromatics content and polynuclear aromatic hydrocarbon content of motor diesel fuel by environmental regulation agencies, it is required to show compliance with appropriate analytical determination.[1]

To ensure that the finished fuel products are safe and compliant, the aromatic hydrocarbon content level must be assessed by the ASTM D6591 test method and meet the criteria within.

This application brief demonstrates that the Alliance HPLC System, with the Waters Two-Position Six-Port

Switching Valve, refractive index detection (RID), and Empower 3 Chromatography Data System can determine aromatic hydrocarbons under normal phase conditions and in compliance with the ASTM D6591 method. Using this instrument setup, it is also possible to determine mono- and di-aromatic hydrocarbons in petroleum distillates and aviation fuels according to ASTM D6379 (IP436).[2]

Experimental

Experimental conditions outlined in ASTM D6591 were followed.

Instruments:	Waters Alliance HPLC System Waters 2414 Refractive Index Detector Waters Two-Position Six-Port Switching Valve
Software:	Empower 3 Chromatography Data System
Column:	Waters Spherisorb Amino (NH_2) Column, 80 Å, 5 µm, 4.6 x 250 mm (P/N PSS83115) Waters Spherisorb Amino (NH_2) Guard Cartridge, 80 Å, 5 µm, 4.6 x 10 mm (P/N PSS830079) Waters In-Line Guard Cartridge Holder Kit (P/N PSS830008)
Reagents:	Mobile phase: Heptane (HPLC Grade, Sigma-Aldrich (Dorset, UK))
Standards:	1-Methylnaphthalene (Sigma-Aldrich (Dorset, UK)) Cyclohexane *o*-Xylene

Phenanthrene

Dibenzothiophene

9-Methylanthracene (Merck Biosciences Ltd (Nottingham, UK))

System performance standard (SPS): cyclohexane (1 g/100 mL, *o*-xylene (0.5 g/100 mL), dibenzothiophene (0.05 g/100 mL), and 9-methylanthracene (0.05 g/100 ml) in heptane

Four calibration standards were made as shown in Table 1.

Analytical Conditions

Mobile phase flow rate:	1 mL/min
Injection volume:	10 µL
Column temperature:	30 °C
RID temperature:	30 °C
Backflush time B:	11.73 min
Stop time:	30 min

Calibration Standards

Analyte	Standard 1 (g/100 mL)	Standard 2 (g/100 mL)	Standard 3 (g/100 mL)	Standard 4 (g/100 mL)
Cyclohexane	5.0	2.0	0.5	0.1
o-Xylene	4.0	1.0	0.25	0.05
1-Methylnaphthalene	4.0	1.0	0.25	0.02
Phenanthrene	0.4	0.2	0.05	0.01

Table 1. Analyte concentrations in the calibration standards.

Results and Discussion

Valve Operation (Figure 1)

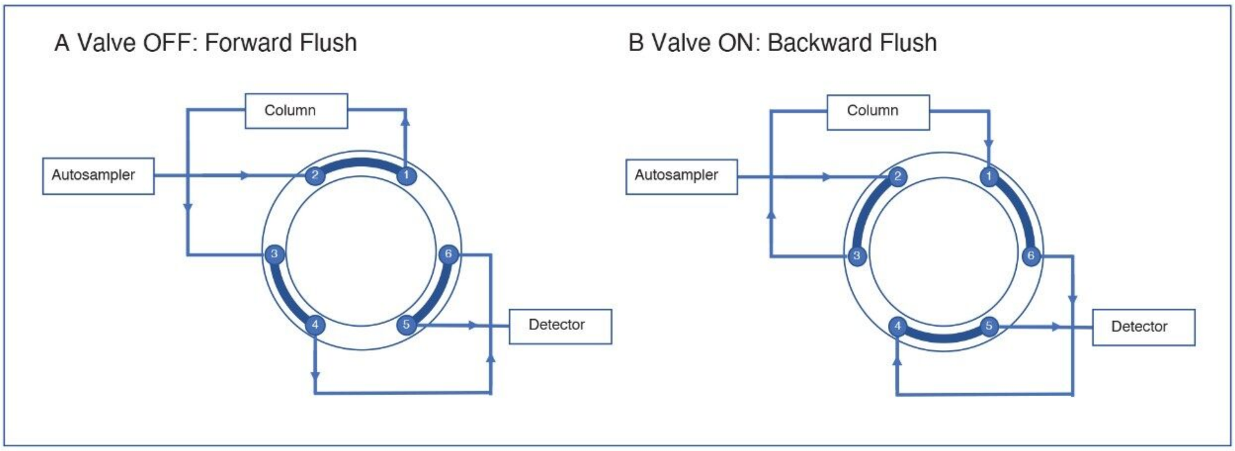

Figure 1. Simplified valve schematic demonstrating the configuration of the Waters Two-Position Six-Port Switching Valve in A) forward flush mode and in B) backward flush mode.

The system performance standard (SPS) is injected only in forward flush mode to validate the method in line with ASTM D6591 criteria. Baseline separation between all compounds in the SPS was achieved (Figure 2) with the resolution between *o*-xylene and cyclohexane greatly exceeding the ASTM standard level.

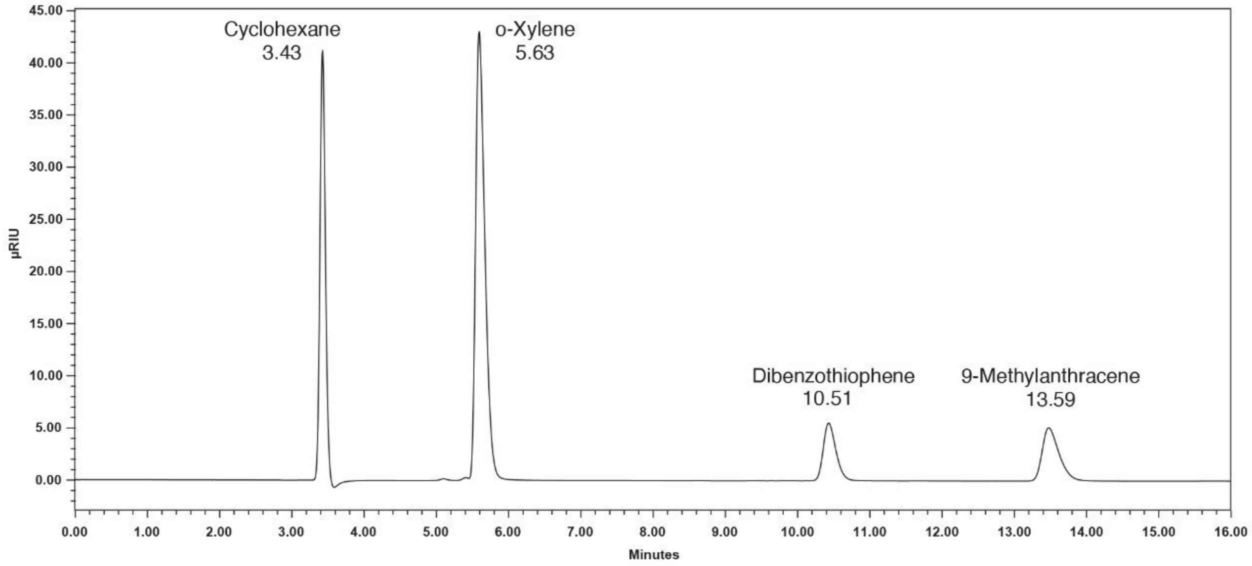

Figure 2. System performance standard (SPS) chromatogram in heptane.

Using the retention times, in seconds, of the di-aromatic hydrocarbon (DAH), dibenzothiophene (t_A), and the tri+-aromatic hydrocarbon (T+AH), 9-methylanthracene (t_B), the time to switch to backflush mode (time B) can be calculated using the equation:

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

The calibration standards were injected in forward flush mode to elute the non-aromatic, mono-aromatic (MAH), and DAH compounds, then the valve is turned ON to switch to backward flush mode at time B to elute the T+AH standard as a single sharp peak. Calibration curves for the calibrant standards showed excellent linearity for quantification with r^2 values greater than 0.999 for *o*-xylene, 1-methlynaphthalene, and phenanthrene (Figure 3).

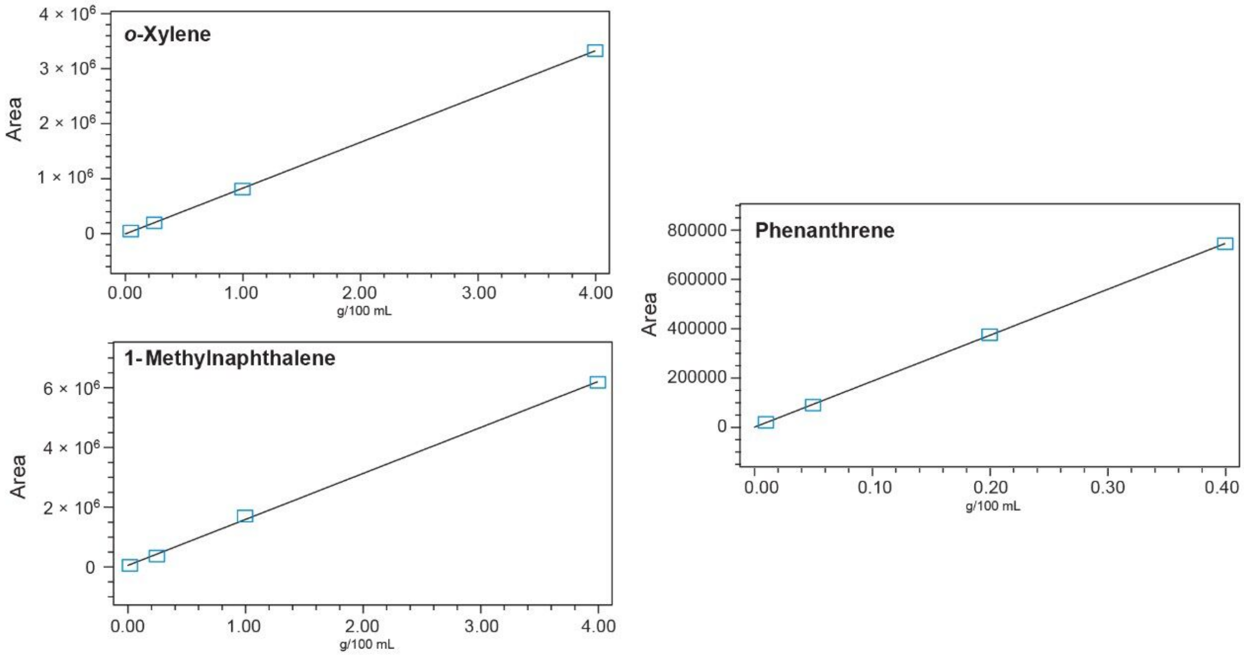

Figure 3. Calibration curves of o-xylene, 1-methylnaphthalene, and phenanthrene.

Replicate injections of calibration standard 2 were undertaken to assess precision. For each compound, the RSDs for the peak retention times and the peak areas, respectively, were less than 0.03% and 0.5% (MAH), 0.04% and 0.2% (DAH), 0.01% and 0.4% (T+AH).

To assess the instrument system for real samples, a sample of diesel was collected from a UK petrol station and diluted 1:10 in heptane and injected. An example chromatogram of a diesel injection, Figure 4, shows the separation of non-aromatics, MAHs, DAHs, and T+AHs to be sufficient for quantitation per ASTM D6591.

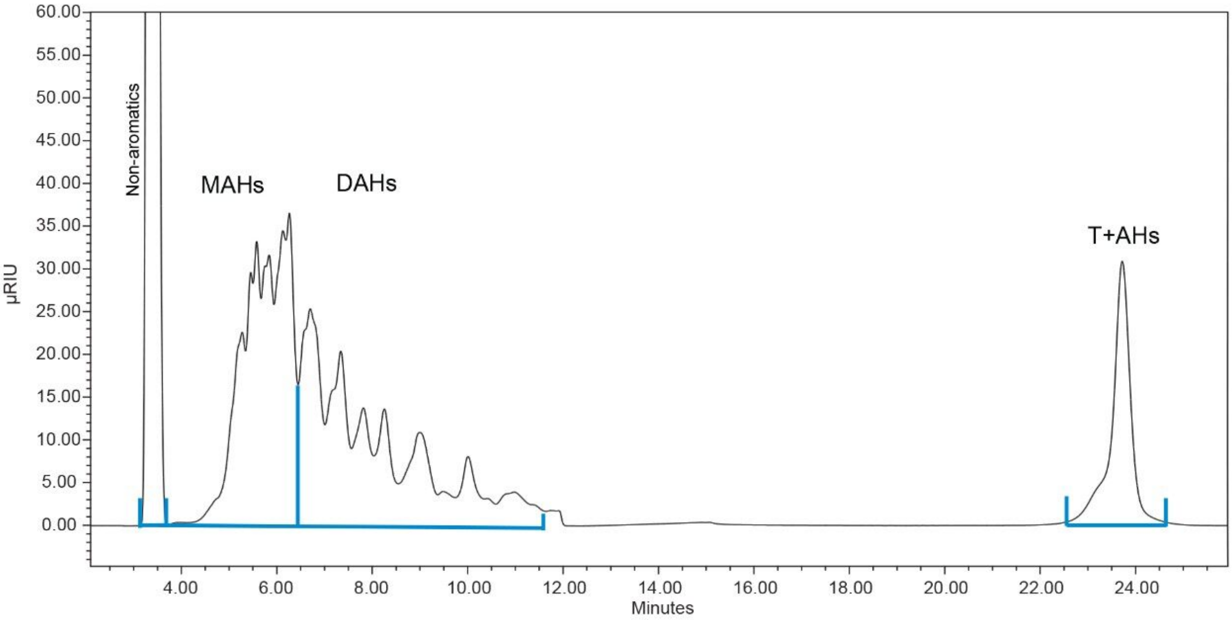

Figure 4. Injection of a UK sourced diesel sample showing integration points of predicted aromatic hydrocarbon type groups using the calibration standards and the ASTM standard method as a reference.

Conclusion

The Waters Alliance HPLC System, with the Waters Two-Position Six-Port Switching Valve, coupled to the Waters 2414 Refractive Index Detector, is shown to greatly exceed the performance requirements for the application of the ASTM D6591 (IP548) standard method for the determination of aromatic hydrocarbons in middle distillates. The instrument set up demonstrates compliance with the ASTM standard method, meeting the linearity, resolution, and precision criteria, with calibration coefficients that demonstrate an excellent linear response for quantification of aromatic hydrocarbons.

References

1. American Society for Testing and Materials (ASTM): ASTM D6591–19, Standard Test Method for

Determination of Aromatic Hydrocarbon Types in Middle Distillates – High Performance Liquid Chromatography Method with Refractive Index Detection, https://www.astm.org/Standards/D6591.htm < https://www.astm.org/Standards/D6591.htm> .

2. Determination of Aromatic Hydrocarbon Types in Aviation Fuels and Petroleum Distillates with the Alliance HPLC System and RI Detection According to ASTM D6379 (IP436), Waters Application Note 720006977EN <https://www.waters.com/nextgen/us/en/library/application-notes/2020/determination-of-aromatic-hydrocarbon-types-in-aviation-fuels-and-petroleum-distillates-with-the-alliance-hplc-system-and-ri-detection-according-to-astm-d6379-ip436.html> , 2020.

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