Application note

Industrial

Analysis of various aromatic hydrocarbons in fuel using HPLC-RI detection as per standard ASTM 6591 D-19 method

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Keywords

Chromeleon, Aromatic Hydrocarbons, Diesel Fuel, petroleum distillates, Ultimate 3000 HPLC, ASTM 6591 D-19

Goal

The aim is to establish ASTM 6591 D-19 standard method on Ultimate 3000 HPLC for the determination of monoaromatic, di-aromatic, tri-aromatic, and polycyclic aromatic hydrocarbon contents in diesel fuels and petroleum distillates boiling in the range of 150 °C to 400 °C.

Introduction

Diesel fuel is the common term for the distillate fuel oil which is sold for use in diesel-based motor vehicles. Diesel fuel is refined from crude oil and biomass materials.[2] The aviation fuels consist of blends of over two thousand chemicals, primarily hydrocarbons (paraffin, olefins, naphthenes, and aromatics), additives such as antioxidants, metal deactivators, biocides, static reducers, icing inhibitors, corrosion inhibitors, and impurities. Iso-octane and n-heptane are the major components. Like other fuels, aviation fuel for spark-ignited piston engines is classified based on its octane rating.[3]

This test method covers a high-performance liquid chromatographic test method for the determination of mono-aromatic, di-aromatic, tri-aromatic, and polycyclic aromatic hydrocarbon contents in diesel fuels and petroleum distillates that are boiling in the range from 150 to 400 °C[4]. The total aromatic content in % m/m is calculated from the sum of the corresponding individual aromatic hydrocarbon types.

Experimental

Chemicals, apparatus, and consumables

- N-Heptane for HPLC, (approx. 99%), ACROS Organics™
- o-Xylene, 99%, pure, ACROS Organics™
- 1-Methylnapthalene, 96% pure, ACROS Organics™
- Phenanthrene 97% pure, ACROS Organics™
- Dibenzothiophene 98% pure, ACROS Organics™
- 9-Methylanthracene 99% pure ACROS Organics™
- Analytical balance
- Vortex mixer (Thermo Scientific, P/N 88880017TS, also known as 88880017)
- Variable volume micropipettes (Thermo Scientific)
- Volumetric flasks 100 mL

Analysis

The analysis was carried out using the Liquid chromatography (Thermo Scientific™ Ultimate 3000) coupled with Refractive Index (RI) detector (Thermo Scientific™ RefractoMax 521). The optimized LC conditions were given in below Table 1.

Sample Preparation

Weigh 1g (±0.05) sample, into a 10 mL volumetric flask, and makeup to the mark with heptane. Shake vigorously to mix. Allow the solution to stand for 10 min, and filter if necessary, to remove insoluble material. Inject 3 µL to HPLC.[1]

Data acquisition and processing

The data acquisition was performed by using the above-mentioned instrument conditions (Table 1). The data acquisition and processing were carried out by using Thermo Scientific™ Chromeleon 7.2.10 software. All instrument parameters were set as acceptance criteria as per ASTM 6591 D-19 method.[4]

Ultimate 3000
HPLC System

RefractoMax 521
Refractive Index Detector

Results and discussion

System performance standard (SPS)

The system performance standards (SPS) were prepared by weighing cyclohexane (1.0g), o-xylene (0.5g), dibenzothiophene (0.05g), and 9-methyl anthracene (0.05g) into a 100 mL volumetric flask and made to the mark with heptane. The symmetrical peak shape with the best chromatographic separation for all four compounds (cyclohexane, O-xylene, dibenzothiophene, and 1-methylnaphthalene) has been demonstrated in Figure 1.

Table 1. LC-MS/MS Instrument Conditions

Liquid Chromatography Method		
Instrumentation	Ultimate 3000 HPLC (Isocratic pump ISO-3100SD) (Thermo Scientific™)	
Column	Hypersil Gold Amino column, 150 mm x 4.6 mm, 5.0 µm (Thermo Scientific™, P/N 25705-154630)	
Sample Compartment temp	20 °C (WPS-3000 Thermo Scientific™)	
Column oven temp	25 °C (TCC-3100, Thermo Scientific™)	
MSV time program	**Time (min)**	**Valve Position**
	0.0	1-2
	4.0	6-1
	15.0	1-2
Injection volume	3 µL	
Needle wash	100% n-Heptane	
Mobile Phase	A: 100% n-Heptane	
Set inline filter	350 µL	
Total run time	25.0 min	
Refractive Index detector conditions		
Instrumentation	Refractive Index-RefractoMax 521 (Thermo Scientific™)	
Intergrator range	500 µRIU/V	
Polarity	Positive	
Data collection rate	5 Hz	
Rise time	0.5 S	
Detector temperature	35 °C	

Analysis

The optimized liquid chromatographic method offered excellent separation and peak shape for monoaromatics, diaromatics, and tri-aromatics hydrocarbons. A representative chromatogram is shown below (Figure 2).

Method Performance

Linearity

The linearity was plotted in the range given in Table 2 as per the ASTM 6591-D19 method. Excellent linearity was achieved for all the target analytes with correlation coefficients greater than 0.99 with less than 20% residuals in both matrices and solvent by following the linear equation and 1/x weighting factor. The calibration curves for all the target analytes were shown in Figure 3.

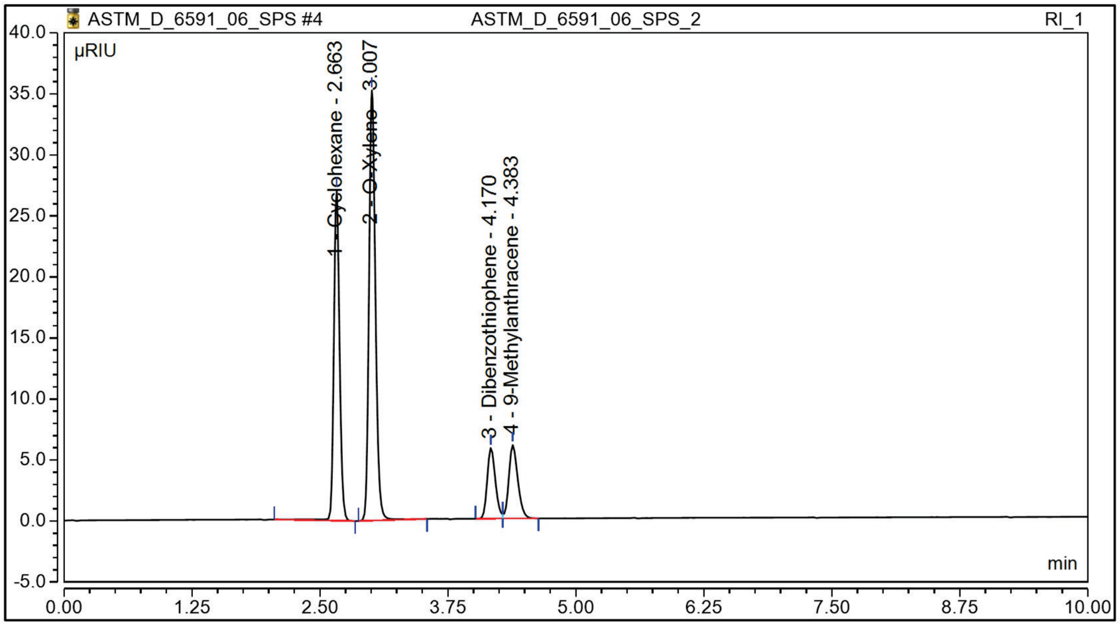

Figure 1. A representative chromatogram demonstrating separation for cyclohexane, O-xylene, dibenzothiophene, and 1-methylnaphthalene.

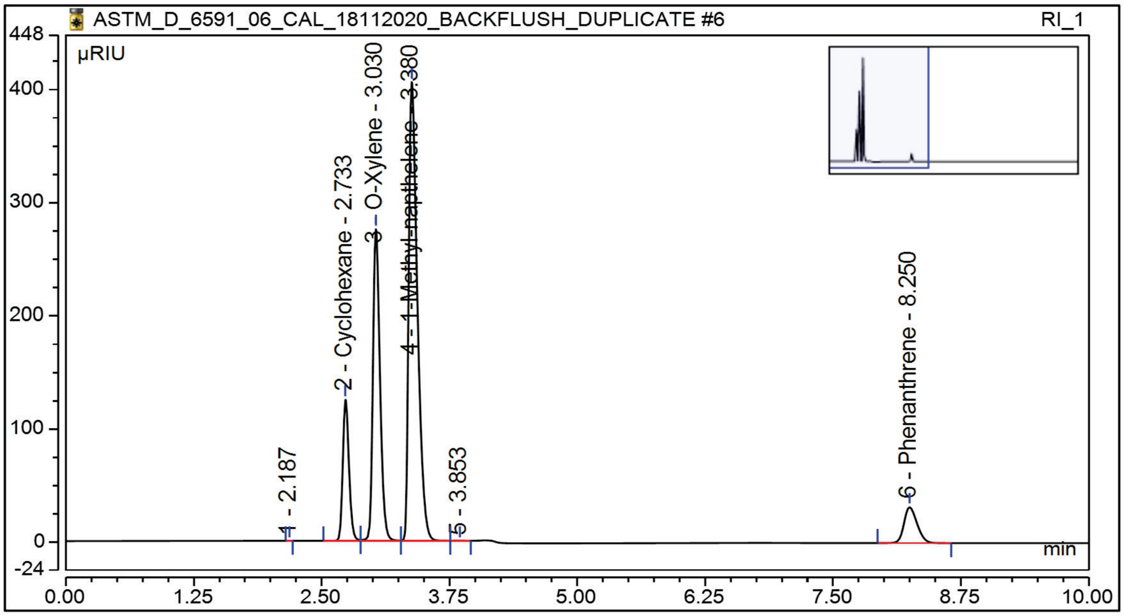

Figure 2. A representative chromatogram demonstrating separation for cyclohexane, O-xylene, 1-methyl naphthalene, and phenanthrene.

Need of Backflush

Amino column has little affinity for the non-aromatic hydrocarbons while exhibiting a pronounced selectivity for aromatic hydrocarbons. As a result of this selectivity, the aromatic hydrocarbons are separated from the non-aromatic hydrocarbons into distinct bands in accordance with their ring structure, that is, MAHs, DAHs, and T+AHs. At a predetermined time, after the elution of the DAHs, the column is backflushed to elute the T+AHs as a single sharp band

Calculated the backflush time, B, in seconds, using the following equation:

$B = tA + 0.4(tB - tA)$

where:

tA = retention time of dibenzothiophene in seconds, and

tB = retention time of 9-methyl anthracene in seconds.

NOTE: The backflush time is the time after injection at which the backflush valve will be activated to elute T+AHs as a single sharp peak

Table 2. Concentrations of Calibration Components

Calibration Standard	Cyclohexane g/100 mL	o-Xylene g/100 mL	1-Methyl-napthalene g/100 mL	Phenanthrene g/100 mL
A	5.0	4.0	4.0	0.4
B	2.0	1.0	1.0	0.2
C	0.5	0.25	0.25	0.05
D	0.1	0.05	0.02	0.01

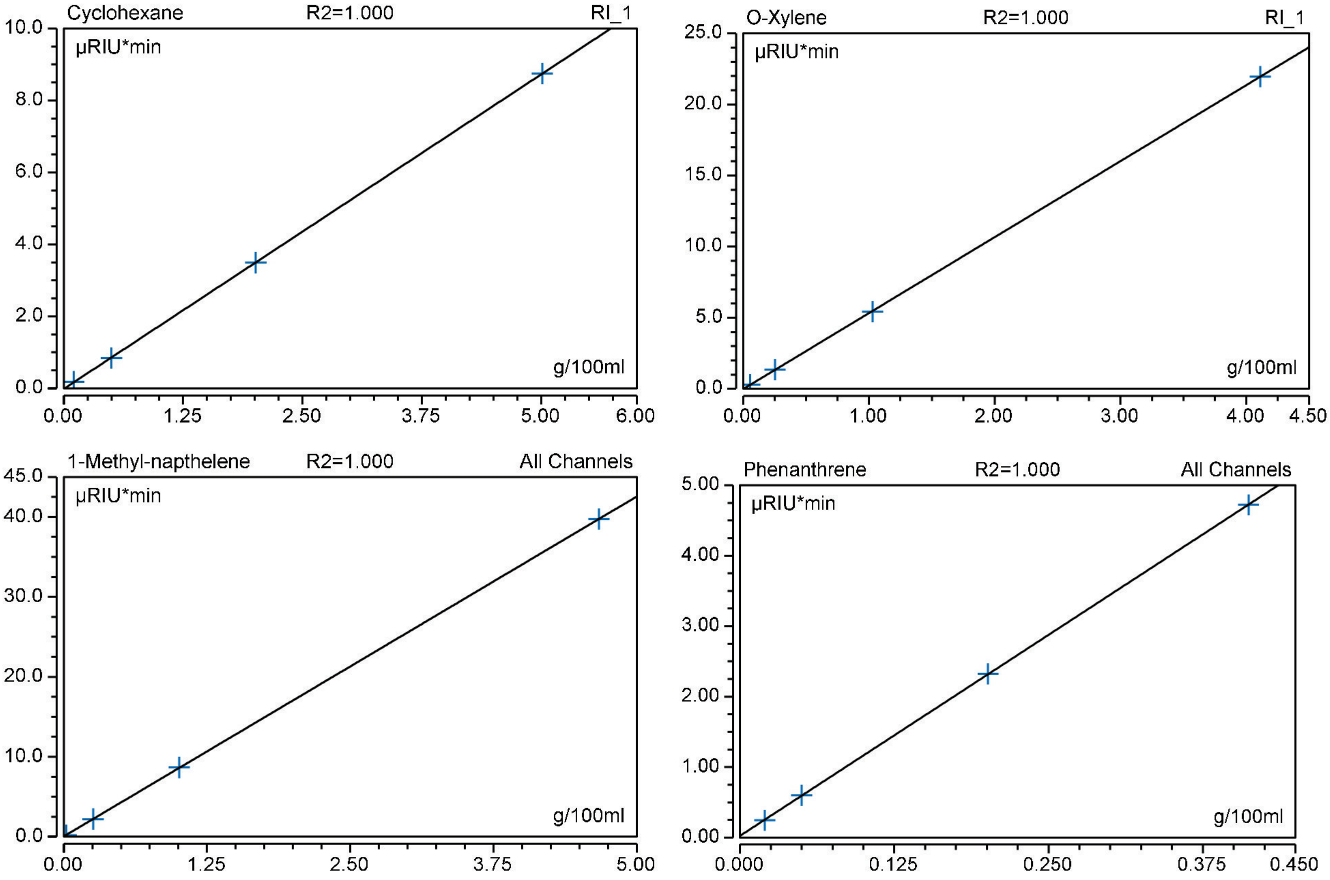

Figure 3. Calibration curves for cyclohexane, O-xylene, 1-methylnaphthalene, and phenanthrene.

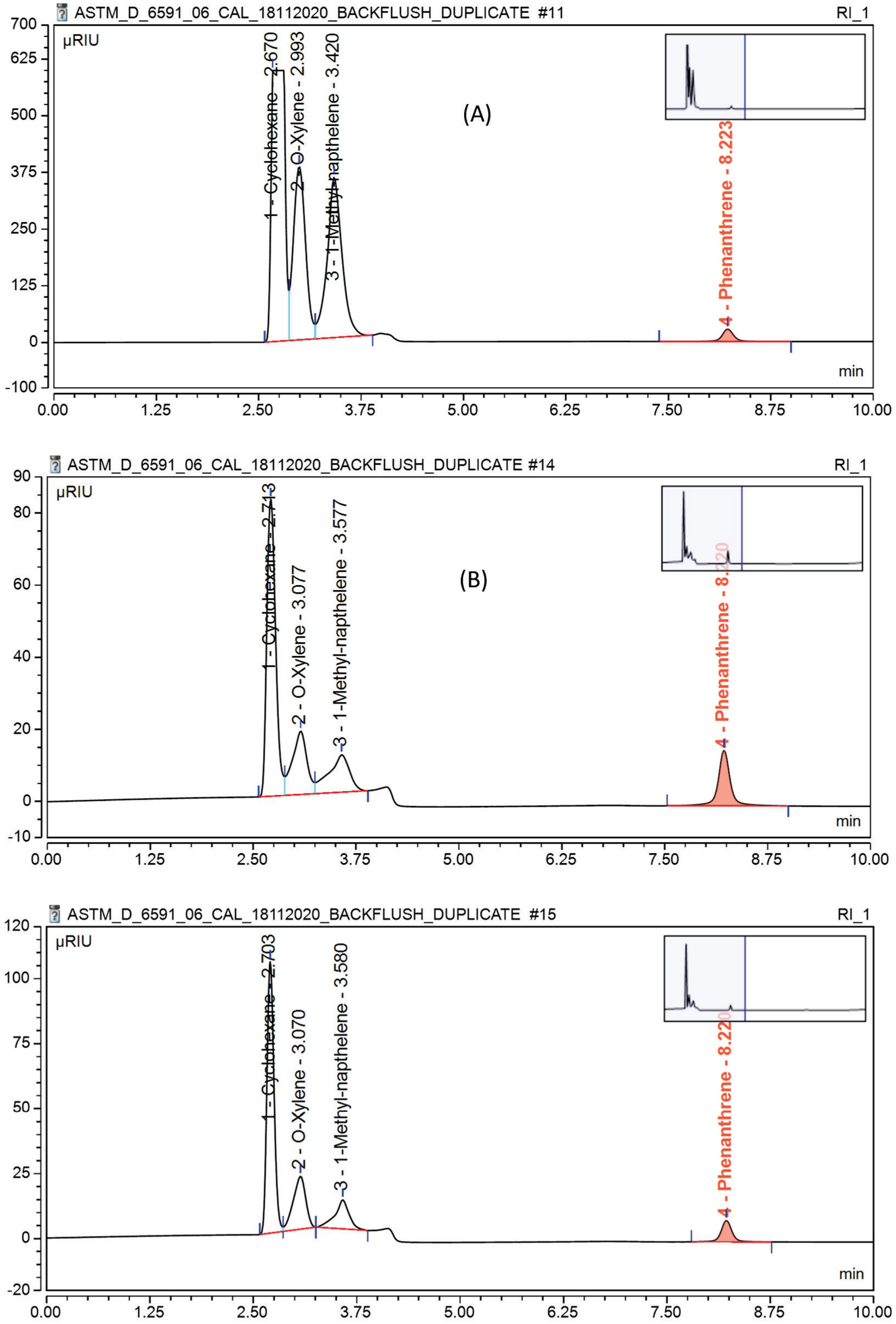

Figure 4. Chromatogram of real (commercial) samples i.e. DHDT feed Diesel (A), Crack feed Diesel (B), and combined feed diesel (C).

Results

Sample Name	Group Name	Amount (g/100 mL)	Acceptable range[4]
DHDT feed Diesel	MAH (O-Xylene)	12.39	4-40
	DAH (1-Methyl-napthelene	8.78	0-20
	T+AH (Phenanthrene)	0.39	0-6
Crack feed Diesel	MAH (O-Xylene)	13.76	4-40
	DAH (1-Methyl-napthelene	7.13	0-20
	T+AH (Phenanthrene)	4.52	0-6
Combined feed Diesel	MAH (O-Xylene)	13.60	4-40
	DAH (1-Methyl-napthelene	5.17	0-20
	T+AH (Phenanthrene)	2.10	0-6

Application to real samples

The optimized method was applied to the real (commercial) samples i.e. DHDT feed Diesel, Crack feed Diesel, and combined feed diesel (Figure 4). The results observed for all three samples were within the prescribed limit of the ASTM 6591-D19 method.[4]

Conclusion

The HPLC-RI detector offered an excellent separation with symmetrical peaks for all the target analytes. The combination of Ultimate 3000 HPLC (Isocratic pump ISO-3100SD) along with the RI detector was found satisfactory to meet the criteria of the ASTM 6591- D19 method. The results of three real samples (MAH's, DAH's, and T+AH's) were within the acceptable range given in the ASTM-6591-D19. This reveals that the total workflow optimized using the HPLC-RI detector offered excellent results.

References

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