Application note | 003285

Industrial

Analysis of various polyaromatic hydrocarbons in diesel fuels using an HPLC-RID system

Compliance with both the ASTM standard test method (D6591-19) and the People's Republic of China standard test method (NB/SH/T 0806-2022)

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Keywords

Diesel fuels, aromatic hydrocarbons, PAH, automated backflush, normal phase, Vanquish Core HPLC, Chromeleon CDS, refractive index detection

Goal

This work had two objectives: first, to establish the ASTM D6591-19 standard test method on a Thermo Scientific™ Vanquish™ Core HPLC system with Thermo Scientific™ Vanquish™ Refractive Index Detector (RID), and second, to evaluate this system for the determination of monoaromatic, di-aromatic, tri-aromatic, and polycyclic aromatic hydrocarbon (PAH) content in diesel fuel as described in the People's Republic of China (PRC) NB/SH/T 0806-2022 standard test method.

Introduction

Oil industry experts have reported that the PAH content in diesel fuels can directly affect particulate matter (PM) emissions. The higher the PAH content, the greater the PM emissions from diesel fuel combustion. Since PAHs are potent carcinogens, higher PAH content can also increase the toxicity of discharged pollutants. Consequently, reducing the PAH content in diesel fuels is crucial to the improvement of ambient air quality.

The original ASTM standard for diesel middle distillates was recently updated to ASTM D6591-19.[1] It describes a high-performance liquid chromatographic-refractive index detector (HPLC-RID) test method for the measurement of four compounds representing different PAH classes (mono-aromatic, di-aromatic, tri-aromatic, and polycyclic aromatic hydrocarbons) found in diesel fuels and petroleum distillates (Table 1). The PRC NB/SH/T 0806-2022 standard test method[2] extends the number of compounds measured by the ASTM standard to 7 (Table 1). Therefore, the PRC standard places a higher requirement for the separation ability of the selected chromatographic column compared to the ASTM D6591-19 standard test method. This method was reproduced on a Vanquish Core-RID system modified with the Normal-Phase (NP) kit and evaluated by measuring the aromatic hydrocarbon content in diesel fuel samples provided by a customer.

Table 1. Representative compounds measured by the ASTM and PRC standard test methods

	ASTM D6591-19	PRC NB/SH/T 0806-2022
Non-aromatic hydrocarbons	Cyclohexane	Cyclohexane
Mono-aromatic hydrocarbons (MAHs)	*o*-Xylene	Dodecylbenzene Hexa-methylbenzene *o*-Xylene
Di-aromatic hydrocarbons (DAHs)	1-Methylnaphthalene	Naphthalene
Tri-aromatic hydrocarbons (T+AHs)	Phenanthrene	9-Methylanthracene Dibenzothiophene

Experimental

Reagents, standards, and samples

- *n*-Heptane: HPLC grade
- 1-Methylnaphthalene, 9-methylanthracene, cyclohexane, dibenzothiophene, dodecylbenzene, hexamethylbenzene, naphthalene, *o*-xylene, phenanthrene: Sinopec Research Institute of Petroleum Processing Co., Ltd.

The standard performance solution (SPS) for system performance verification was purchased from the Sinopec Research Institute of Petroleum Processing Co., Ltd. and contained: cyclohexane, dodecylbenzene, *o*-xylene, hexamethylbenzene, naphthalene, dibenzothiophene, and 9-methylanthracene (Table 2A).

The working curve standard solution was purchased from the Sinopec Research Institute of Petroleum Processing Co., Ltd. and contained *o*-xylene, 1-methylnapthalene, and phenanthrene (Table 2B).

A diesel fuel reference sample was purchased from Sinopec Research Institute of Petroleum Processing Co., Ltd. (Table 2C). For more details describing the sample preparation see the PRC NB/SH/T 0806-2022 standard test method.[2]

Table 2A. Standard solution preparation for SPS system performance verification

Compound	Cyclohexane	Dodecylbenzene	*o*-Xylene	Hexamethylbenzene	Naphthalene	Dibenzothiophene	9-Methylanthracene
Concentration (g/100 mL)	1.00	0.10	0.50	0.1	0.1	0.05	0.05

Table 2B. Preparation of working curve standard solution

	Name	Level 1 (g/100 mL)	Level 2 (g/100 mL)	Level 3 (g/100 mL)	Level 4 (g/100 mL)
MAHs	*o*-Xylene	0.05	0.25	1.00	4.00
DAHs	1-Methylnaphthalene	0.02	0.25	1.00	4.00
T+AHs	Phenanthrene	0.01	0.05	0.2	4.00

Table 2C. Aromatic hydrocarbons content in the diesel fuels reference sample

Compound	Monocyclic aromatic hydrocarbons	Bicyclic aromatic hydrocarbons	Tricyclic + bicyclic aromatic hydrocarbons	T+AHs
Content (%)	12.1	5.9	0.3	6.2
Reproducibility (%)	1.8	2.5	0.4	2.5

Analysis

The analysis was carried out using a Vanquish Core HPLC system with integrated Vanquish RID:

- Vanquish Core System Base (P/N VC-S01-A-02)
- Vanquish Quaternary Pump CN (P/N VC-P21-A-01) with normal phase kit (P/N 6036.3972)
- Vanquish Split Sampler CT (P/N VC-A12-A-02)
- Vanquish Column Compartment C (P/N VC-C10-A-03)
- Vanquish Refractive Index Detector C (P/N VC-D60-A01)
- Passive Pre-heater (P/N 6732.0170)
- 2-position/6-port Column Switching Valve (P/N 6230.2520)
- Optional Pulse Dampener (P/N 6042.6010) with Thermo Scientific™ Viper™ capillary 0.18 x 250 mm, SST (P/N 6040.2386)

Conditions

Table 3. HPLC-RID instrument conditions

Liquid chromatography method		
Column – analytical	Thermo Scientific™ Hypersil™ APS-2 Amino 250 × 4.6 mm, 3 µm (P/N 30703-254630)	
Column – guard	Thermo Scientific™ Hypersil™ APS-2 Amino Guard cartridge, 10 × 4.6 mm, 3 µm (P/N 30703-014001) Guard cartridge holder kit (P/N 850-00)	
Sample compartment temperature	Room temperature	
Column compartment temperature	35 °C	
Backflush MSV time program	Time (min)	Valve position
	0.0	1_2
	6.3	6_1
	15.0	1_2
Injection volume	5 µL	
Needle wash	3 s, 24 µL/s (before and after)	
Mobile phase	*n*-Heptane	
Flow rate	1.0 mL/min	
Total run time	30 min	
RID conditions		
Integrator range	500 µRIU	
Polarity	Plus	
Data collection rate	10 Hz	
Rise time	0.5 s	
Detector temperature	35 °C	

Data acquisition and processing

Data acquisition and processing were performed using Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) 7.3.2.

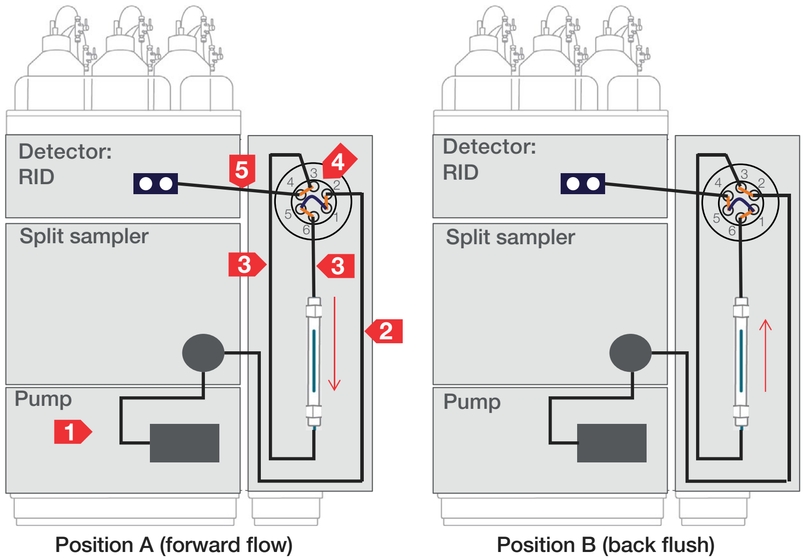
Results and discussion

Backflush

The Hypersil APS-2 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 (i.e., MAHs, DAHs, and T+AHs). At a predetermined time after the elution of the DAHs, the column is backflushed (Figure 1) to elute the T+AHs as a single sharp band.[2] See Application Note IP391 for details about calculating backflush time.[3] SPS experiments do not require backflushing, but it is necessary when generating standard curves and when measuring samples.

System performance verification experiment

The SPS-based performance verification using a non-backflush analytical method fully complied with the PRC NB/SH/T 0806-2022 standard test method. Specifically, cyclohexane, dodecylbenzene, *o*-xylene, hexamethylbenzene, naphthalene, dibenzothiophene, and 9-methylanthracene were eluted in sequence with complete baseline separation; dibenzothiophene and 9-methylanthracene peaks had signal-to-noise ratios above 1,000 (the standard requirement cannot be less than 3.0); and cyclohexane and *o*-xylene had resolution values of 6.45 (the standard requirement is no less than 5.0). Figure 2 shows an overlay of six consecutive SPS solution injections. See Table 4 for the reproducibility data.



No.	P/N	Description	Comment
1	6040.2375	Viper capillary 0.18 × 350 mmm, SST	Pump to sampler
2	6040.2395	Viper capillary 0.18 × 650 mm, SST	Sampler to Valve P2
3	6040.2245	Viper capillary, 0.10 × 450 mm, SST (or optional passive pre-heater, 0.18 × 530 mm, SST P/N 6732.0170)	To and from column
4	6040.2360	Viper capillary 0.18 × 150 mm, SST	Valve P1 to P5; Guard to column
5	6040.2245	Viper capillary 0.10 × 450 mm, SST	Valve P4 to RID

Figure 1. Flow path showing back flushing (reverse flow) and location of Viper capillaries

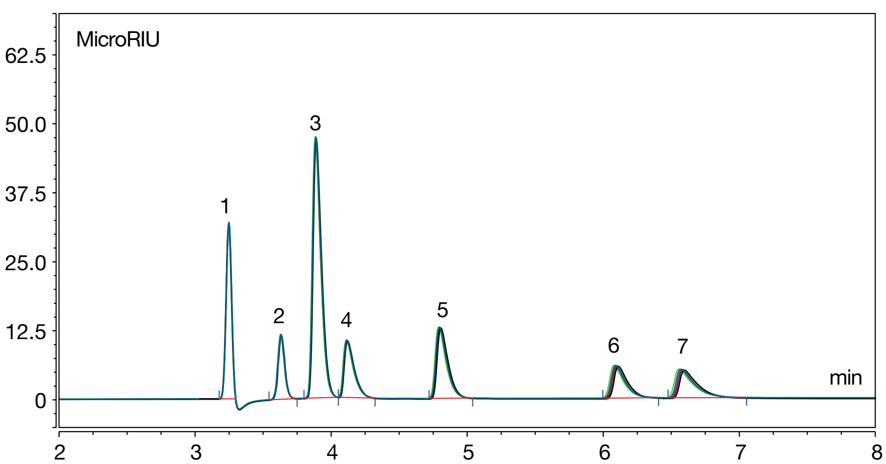


Figure 2. Overlay of six replicate SPS solution injections

Table 4. Reproducibility data of six SPS solution injections

Peak	Compound	RSD% of retention time	RSD% of peak area
1	Cyclohexane	0.06	0.66
2	Dodecylbenzene	0.09	0.51
3	*o*-Xylene	0.09	0.42
4	Hexamethylbenzene	0.11	0.54
5	Naphthalene	0.13	0.61
6	Dibenzothiophene	0.21	0.89
7	9-Methylanthracene	0.23	0.46

Table 5. Linear ranges, linearly dependent coefficients, etc. of standard working curves (see Table 2B)

	Peak name	Retention time (min)	Calibration type	Evaluation type	Data points	Coefficient of determination	CO intercept	C1 slope
MAHs	*o*-Xylene	3.867	Lin, WithOffset	Peak area	4	0.99999	-0.006	7.045
DAHs	1-Methylnapthalene	4.747	Lin, WithOffset	Peak area	4	0.99999	0.009	11.599
T+AHs	Phenanthrene	12.687	Lin, WithOffset	Peak area	4	0.99997	-0.010	14.857

Linear range test

A linear range test was performed for *o*-xylene (representative of monocyclic aromatic hydrocarbons), 1-methylnapthalene (representative of bicyclic aromatic hydrocarbons), and phenanthrene (representative of aromatic hydrocarbons with three or more rings). The three compounds all had linearly dependent coefficient $r^2 > 0.9999$, showing good linear relationships (Table 5). See Figure 3 for the chromatogram overlay of standard working curves.

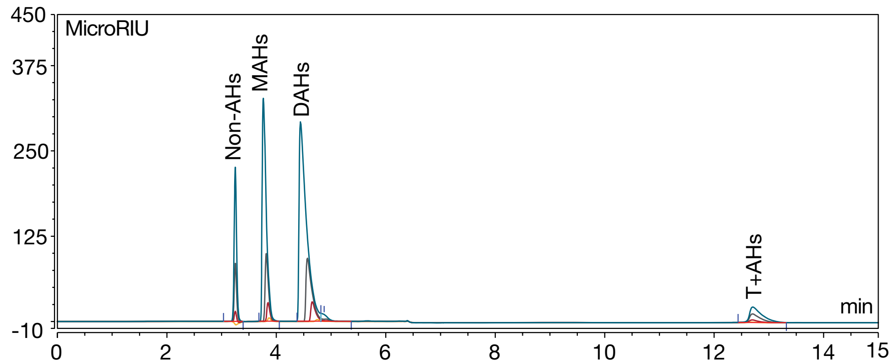


Figure 3. Chromatogram overlay of standard working curves (four concentration points as described in Table 2B)

Analysis of samples

The sample used to evaluate the method is a commercially available diesel fuel reference sample from Sinopec Research Institute of Petroleum Processing Co., Ltd. See Figure 4 for the chromatogram of the reference sample. Table 6 shows that the reproducibility exceeds the quality control sample requirements.

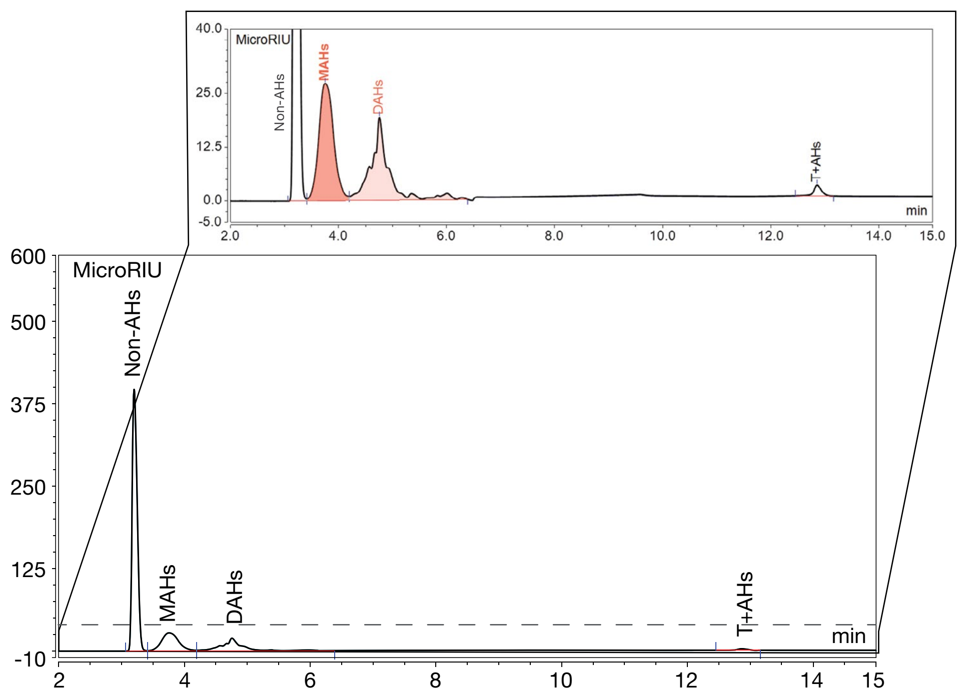


Figure 4. Analysis of diesel fuels reference sample showing zoomed-in chromatogram

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Table 6. Test results from the diesel fuels reference sample

Sample name	Retention time (min)			Sample content (%)		
	Monocyclic aromatic hydrocarbons	Bicyclic aromatic hydrocarbons	Aromatic hydrocarbons with 3 or more rings	Monocyclic aromatic hydrocarbons	Bicyclic aromatic hydrocarbons	Aromatic hydrocarbons with 3 or more rings
#1	3.753	4.757	12.86	12.273	5.978	0.288
#2	3.753	4.76	12.857	12.246	5.938	0.289
#3	Theoretical content in reference sample (%)			12.1	5.9	0.3
Average of results between #1 and #3				12.1865	5.939	0.294
Difference between #1 and #3				0.17	0.08	-0.01
Average of results between #2 and #3				12.173	5.919	0.2945
Difference between #2 and #3				0.15	0.04	-0.01
Average of results between #1 and #2				12.2595	5.958	0.2885
Difference between #1 and #2				0.03	0.04	0.00
Reproducibility calculation formula				0.063(X2+17.3)	0.32(X2+1.8)	0.64(X2+0.3)
Reproducibility #1 and #3				1.86	2.48	0.38
				0.17<1.86, Qualified pass	0.08<2.48, Qualified pass	0.01<0.38, Qualified pass
Reproducibility #2 and #3				1.86	2.47	0.38
				0.15<1.86, Qualified pass	0.04<2.48, Qualified pass	0.01<0.38, Qualified pass
Repeatability calculation formula				0.026(X1+14.7)	0.1(X1+2.6)	0.12(X1+0.6)
Repeatability #1 and #2				0.70	0.86	0.11
				0.03<0.7, Qualified pass	0.04<0.86, Qualified pass	0<0.11, Qualified pass

Notes: X1 is the average of the results of two repeated experiments; X2 is the average of two single, independent experimental results.
#1 and #3, #2 and #3, Different operators, in different laboratories, using different instruments, and using the same method, measure the same sample separately.
The difference between two single and independent test results should not exceed the reproducibility limit of the method in Table 6.
#1 and #2, The same operator, in the same laboratory, using the same instrument, and following the same method, continuously measures the same sample.
The difference between the two test results should not exceed the repeatability limit of the method in Table 6.

Conclusions

The Vanquish Core HPLC system as a general-purpose normal and reverse phase liquid chromatography platform combined with the Vanquish Refractive Index Detector readily met the requirements of the petrochemical industry standard of the PRC NB/SH/T 0806-2022 "Determination of aromatic hydrocarbon types in middle distillates—High performance liquid chromatography method with refractive index detector".

- The SPS experiment showed resolution and peak shape superior to those provided by standard chromatograms.
- The standard working curve linearity and intercept were in full compliance with the standard.
- Due to the improved performance of the Hypersil APS-2 Amino column, the actual sample analysis time was half of the 30 minutes set forth in the PRC standard test method, while still meeting the standard requirements. This results in cost reduction, increased efficiency, and enhanced data quality.
- Lastly, the processing of sample test data required no manual integration. Convenient and fast automated integration delivered excellent, reliable, and efficient experimental results.

References

1. ASTM D6591-19: Standard Test Method For Determination Of Aromatic Hydrocarbon Types In Middle Distillates—High Performance Liquid Chromatography Method With Refractive Index Detection
2. NB/SH/T 0806-2022. Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detector
3. IP391. Analysis of various aromatic hydrocarbons in fuel using HPLC-RI detection as per standard ASTM 6591 D-19 method

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