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Application News

No. HPLC-033

High Performance Liquid Chromatography

Determination of Aromatic Hydrocarbons in Diesel Fuel by LC-RID According to ASTM D6591

■ Introduction

The test method presented here is applicable to the determination of mono-, di-, and tri-plus aromatic hydrocarbon (MAH, DAH, and T+AH, respectively) content in diesel fuels and middle distillates with boiling points in the range of 150 °C to 400 °C in accordance with ASTM D6591. The accurate determination of the aromatic content of fuels is critical to assessing their quality and combustion characteristics. These parameters are also crucial to ensuring compliance with environmental regulations.

This method presents an alternative to ASTM D1319, which is the EPA standard method for quantification of aromatics in diesel fuel. Though ASTM D1319 has enjoyed widespread use, it relies on the use of a fluorescent dye which was discontinued and its replacement no longer produces reliable results, particularly for middle distillates. As such, many laboratories are exploring alternative methods for determination of the total aromatics in diesel fuels, such as ASTM D6591, until a replacement dye is available.

This application news demonstrates the use of the Shimadzu Prominence™ HPLC for the determination of MAHs, DAHs, and T+AHs in diesel fuel and other middle distillates in compliance with parameters set out in ASTM D6591. Due to the use of a 3 micrometer packing analytical column, the instrument is also in compliance with ASTM D6379 for jet fuel, kerosene, and middle distillates with boiling points in the range of 50 °C to 300 °C without change to the instrument configuration.

■ Experimental Design

Instrument Configuration (as tested)
Shimadzu Prominence HPLC

- LC-20AD HPLC Pump
- DGU-20A$_{3R}$ Degassing Unit
- SIL-20AC Autosampler
- CTO-20A Column Oven with 6-port 2-position valve (FCV12)
- RID-20A Refractive Index Detector

Software
LabSolutions™ LC/GC

Columns

1. Shim-pack™ GIST NH_2 250 mm x 4.6 mm I.D., 3 µm (P/N 227-30302-08)
2. Guard column – Shim-pack GIST NH_2 10 mm x 4.0 mm I.D., 5 µm (P/N 227-30315-02)

Reagents
Mobile Phase: *n*-heptane, HPLC Grade

Standards
ASTM D-6591 Kit from AccuStandard®

- System Resolution Standard: cyclohexane (10 mg/mL), *o*-xylene (5 mg/mL), dibenzothiophene (0.5 mg/mL), and 9-methylanthracene (0.5 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 (Fig. 1). The valve is actuated after the elution of di-aromatics, which back-flushes more retained compounds, such as T+AHs, off of the column and to the detector.

Analytical Conditions

- Mobile phase flow rate – 0.8 mL / min
- Injection volume – 3 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	50	20	5	1
o-Xylene	40	10	2.5	0.5
1-Methylnaphthalene	40	10	2.5	0.2
Phenanthrene	4	2	0.5	0.1

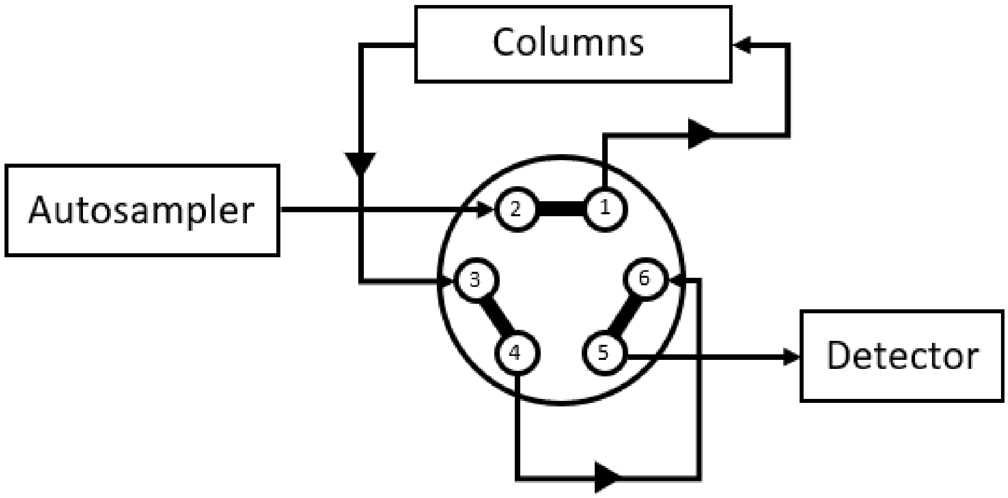

Figure 1: Simplified flow schematic of the HPLC used for this application.

■ Results

An injection of the system performance standard (SPS) demonstrated method-appropriate resolution of the four component peaks (Fig. 2). Cyclohexane, a proxy for saturated compounds of samples, eluted at 4.35 minutes, whereas *o*-xylene, a proxy for MAHs, eluted at 5.88 minutes. Dibenzothiophene, representing DAHs, eluted at 8.89 minutes and lastly, 9-methylanthracene eluted at 9.81 minutes and serves as a proxy for T+AHs. The resolution of cyclohexane and *o*-xylene was 8.9, which exceeds the ASTM standard of 5.

Additionally, the SPS serves as the basis for method calculations to determine the timing for valve actuation to backflush T+AHs from the column. Based on the SPS injection, backflush timing was set to 9.24 minutes.

The mobile phase flowrate was optimized to 0.8 mL/min, which enables maximum resolution between 9-methylanthracene and dibenzothiophene while also reducing solvent consumption and analysis time from typical methods (1.0 mL/min and 30 minutes, respectively).

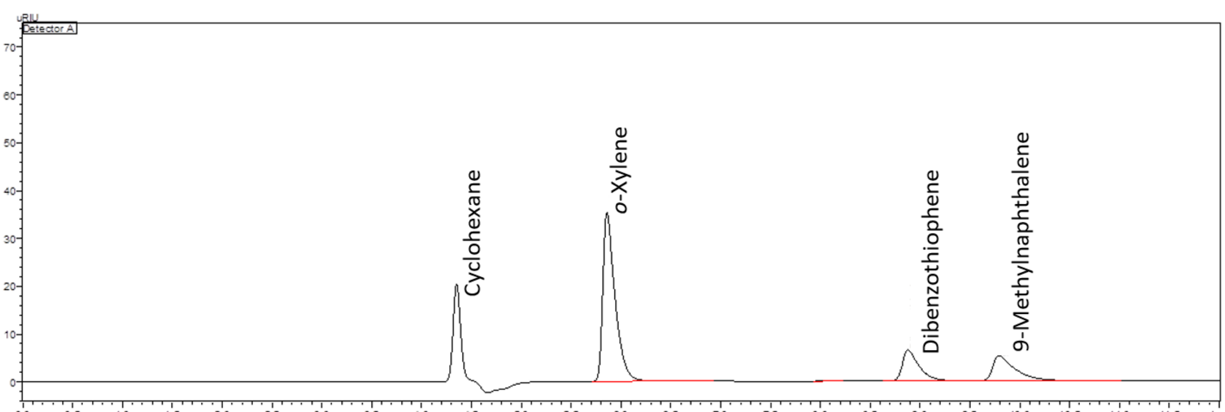

Figure 2: Chromatogram resulting from injection of the System Resolution Standard

Calibration curves generated for the compounds and at concentrations outlined in Table 1 were linear, with r^2 values of 0.99999 for *o*-xylene, and 1-methylnaphthalene, and phenanthrene (Figs. 3 - 5).

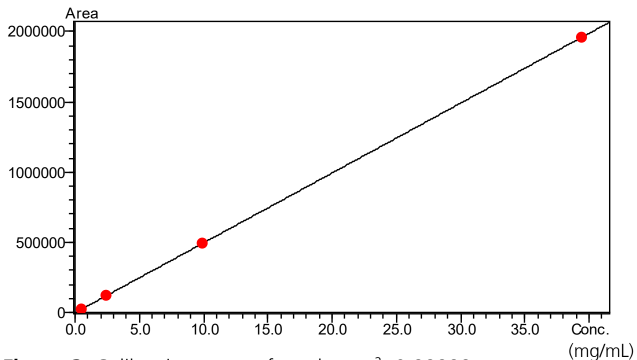

Figure 3: Calibration curve of *o*-xylene; r^2=0.99999

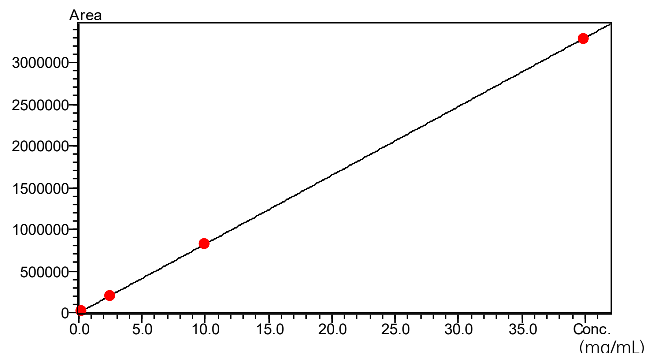

Figure 4: Calibration curve of 1-methylnaphthlene; r^2=0.99999

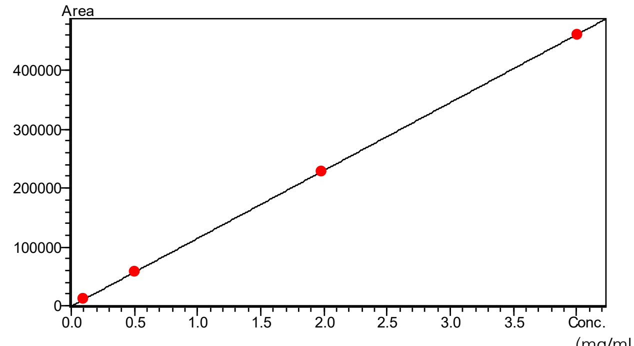

Figure 5. Calibration curve of phenanthrene; r^2=0.99999

To assess precision, three replicate injections were made of Standard 2. The RSDs for retention times of the peaks and peak areas were MAH RT = 0.127%, area = 0.124%; DAH RT = 0.128%, area = 0.104%; and T+AH RT = 0.058%, area = 1.49%, respectively.

A sample of on-highway diesel fuel, obtained from a local gas station, was diluted per method specifications, 1.0586 g into 10 mL *n*-heptane, and injected to assess the efficacy of this instrument on actual diesel fuel samples. An example chromatogram is provided in Figure 6. The separation of the saturated compounds, MAHs, DAHs, and TAHs, is sufficient for quantification per ASTM D6591.

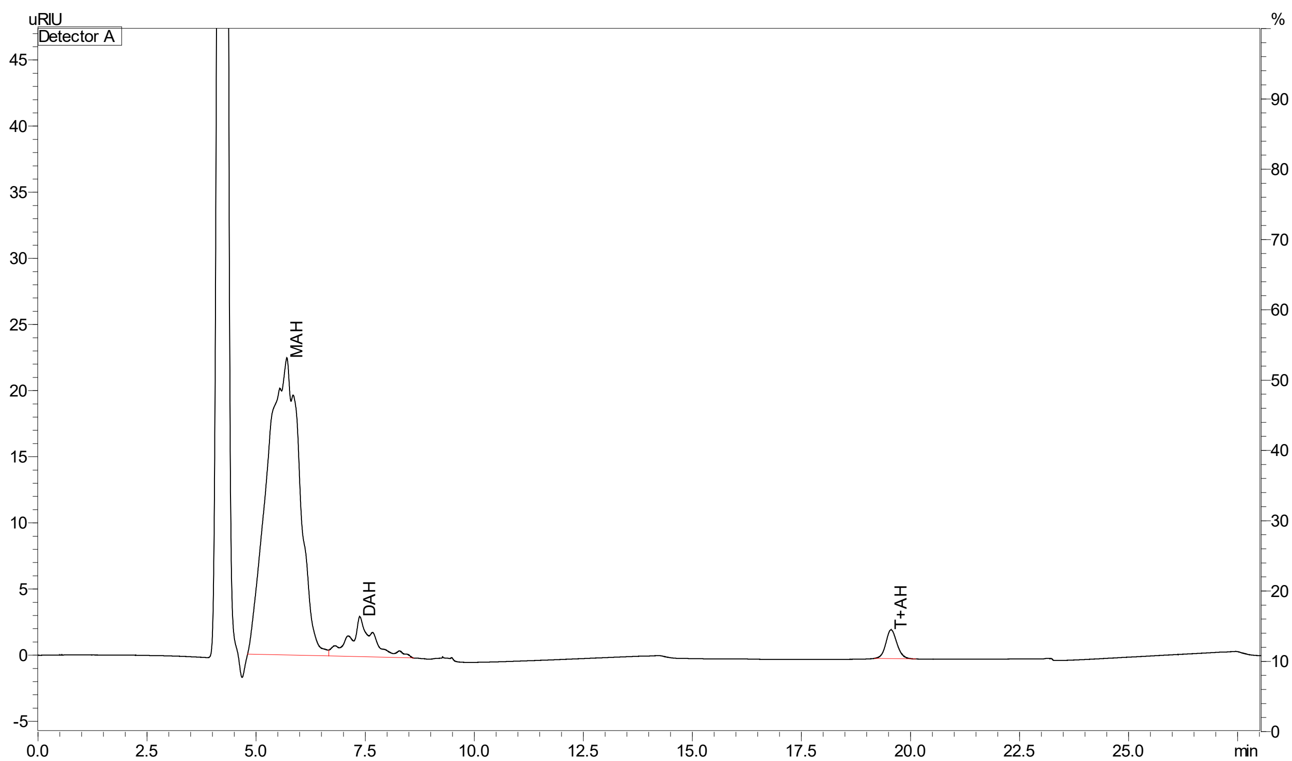

Figure 6: Injection of on-highway diesel prepared at 1.0586 g/10 mL in *n*-heptane.

■ Discussion and Conclusions

This application news demonstrates the detection and quantification of MAHs, DAHs, and T+AHs using a Prominence HPLC, as well as method-compliance for ASTM D6591. Coefficients for the calibration curves with r^2 values of 0.99999 indicate a strong linear response of these compounds and exceeds the requirements of the method.

The column set used in this application maintains minimal analysis times and ensures compliance with resolution standards set by ASTM D6591 of 5.0 between cyclohexane and *o*-xylene. Additionally, the column set provides a solution that minimizes column reconditioning or replacement. Finally, the set is also in compliance with ASTM D6379, allowing a single instrument to be used for both methods without modification.

■ 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 D6591-18, Standard Test Method for Determination of Aromatic Hydrocarbon Types in Middle Distillates—High Performance Liquid Chromatography Method with Refractive Index Detection, 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

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