

Analysis of Aromatic Hydrocarbons in Fuels by ASTM D6379 and D6591 on a Single HPLC Platform

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Introduction

Determining the aromatic content of hydrocarbon fuels is crucial to assessing their combustion characteristics and compliance with environmental regulations. One of the longest- and most commonly-used test methods for aromatics in hydrocarbon-based fuels is ASTM D1319, a column chromatography method that separates fuel components into visible bands within the column for quantitation. Recently, one of the reagents necessary for this test became unavailable and hydrocarbon processors are searching for alternatives to ASTM D1319.

Two methods that are used for quantitation of aromatic components of fuels are ASTM D6379 and D6591, for kerosene and middle distillates (e.g., jet fuel) and diesel fuel, respectively. These methods are normal-phase, liquid chromatography methods in heptane mobile phase that separate and quantitate aromatics from fuel samples by refractive index detection.

Experimental

Both ASTM D6379 and D6591 are isocratic HPLC separations that use heptane mobile phase and polar stationary phase. In the case of D6379 both an amino and cyano bonded phase in a 5 micron particle size are used in series, and for D6591 the best result was observed with a single amino column in a 3 micron particle size. The same amino guard column was used prior to the switching valve for both assays.

Table 1 summarizes column information and instrument parameters for both of the methods. A single HPLC system composed of the LC-20AD HPLC pump, DGU-20A5R degasser, SIL-20AC autosampler, CTO-20A column oven with 6-port 2-position valve, and RID-20A refractive index detector. Figure 1 illustrates the Prominence HPLC system and the valve diagram for the 2-position valve installed in the column oven. While this valve is not required for ASTM D6379, a backflush step is specified for ASTM D6591.

Parameter	Value
HPLC	Shimadzu Prominence HPLC
Analytical Columns ASTM D6379	1. Shim-pack™ GIST NH ₂ 4.6×250 mm, 5 μm (P/N 227-30302-08) 2. Shim-pack™ GIS CN 4.6×150 mm, 5 μm (P/N 227-30263-06)
Analytical Column ASTM D6591	Shim-pack™ GIST NH ₂ 4.6×250 mm, 3 μm (P/N 227-30296-07)
Guard Column (both)	Shim-pack™ GIST NH ₂ 4.0×10 mm, 5 μm (P/N 227-30315-02)
Column Oven Temperature	35° C
RID Temperature	35° C
Injection Volume ASTM D6379	1 μL
Injection Volume ASTM D6591	3 μL
Mobile Phase	Heptane, HPLC grade
Flow rate ASTM D6379	1.0 mL/min
Flow rate ASTM D6591	0.8 mL/min
Run time ASTM D6379	15 minutes
Run time ASTM D6591	28 minutes

Table 1: Instrument conditions

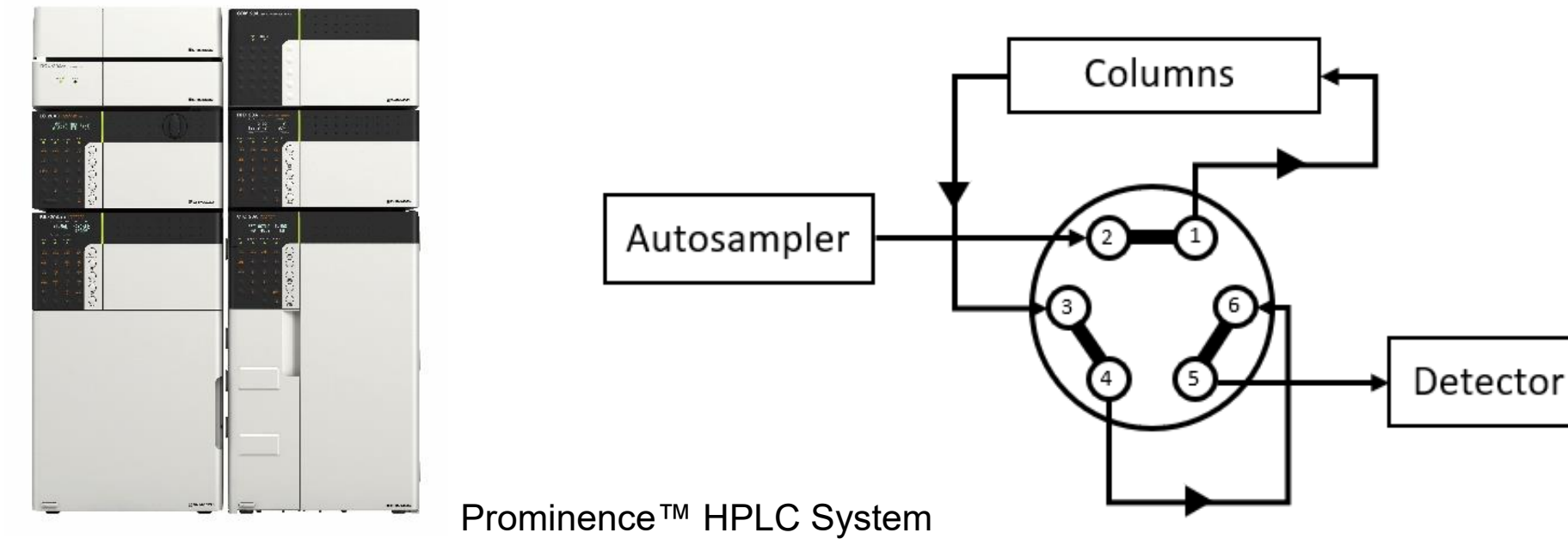


Figure 1: Modular HPLC and valve diagram

Results – ASTM D6379

An injection of the system resolution standard (SRS) demonstrated method-appropriate resolution of the three component peaks (Figure 2). Cyclohexane, a proxy for saturated compounds of samples, eluted at 5.10 minutes, whereas *o*-Xylene, a proxy for mono-aromatic hydrocarbons (MAHs), eluted at 6.56 minutes. Finally, 1-Methylnaphthalene eluted at 8.02 minutes and serves as a proxy for di-aromatic hydrocarbons (DAHs). The resolution of cyclohexane and *o*-Xylene was 8.9, which exceeds both the ASTM and the IP standards of 5 and 5.7, respectively.

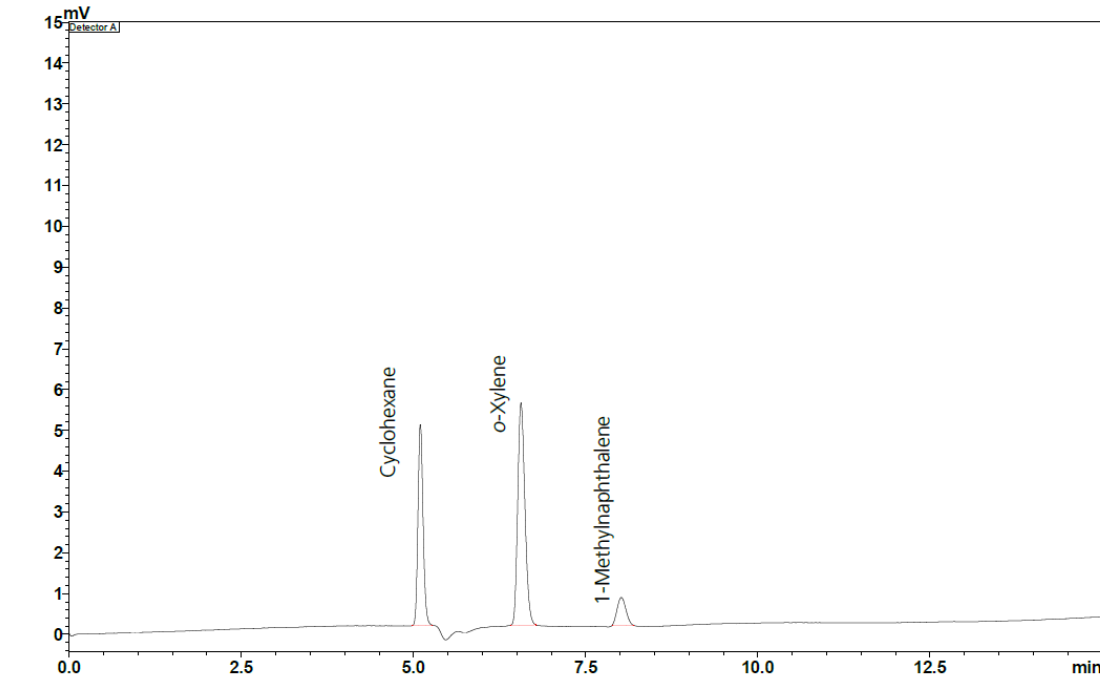


Figure 2: ASTM D6379 system resolution standard chromatogram

Calibration curves generated for the standard compounds were linear, with r^2 values of 0.9999 for both *o*-Xylene and 1-Methylnaphthalene (Figures 3 and 4). To assess precision, three replicate injections were made of Standard 2. The RSDs for retention times of the peaks and peak areas were less than 0.5% and 0.3%, respectively. A sample of Jet A fuel, obtained from the fuel depot at a local airport, was diluted 1:10 in heptane and injected to assess the efficacy of this instrument on real samples. An example chromatogram is provided in Figure 5. The separation of the saturates, MAHs, and DAHs is sufficient for quantitation per ASTM D6379.

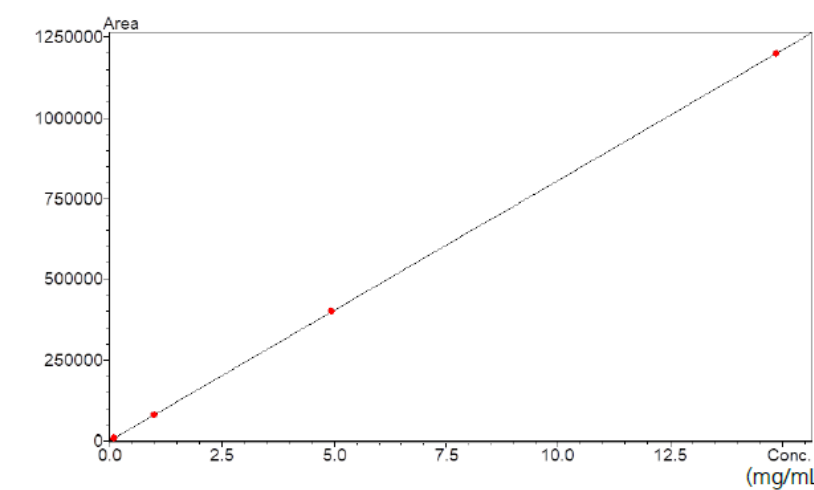


Figure 3: ASTM D6379 Calibration curve of *o*-Xylene $r^2=0.9999$

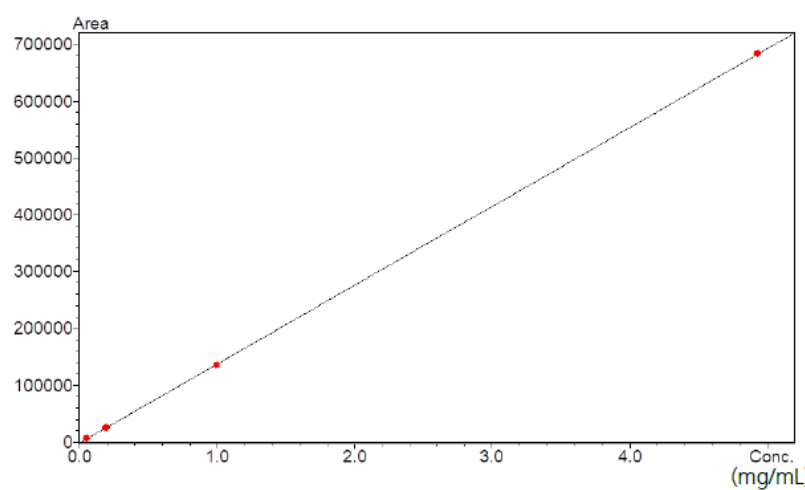


Figure 4: ASTM D6379 Calibration curve of 1-Methylnaphthalene $r^2=0.9999$

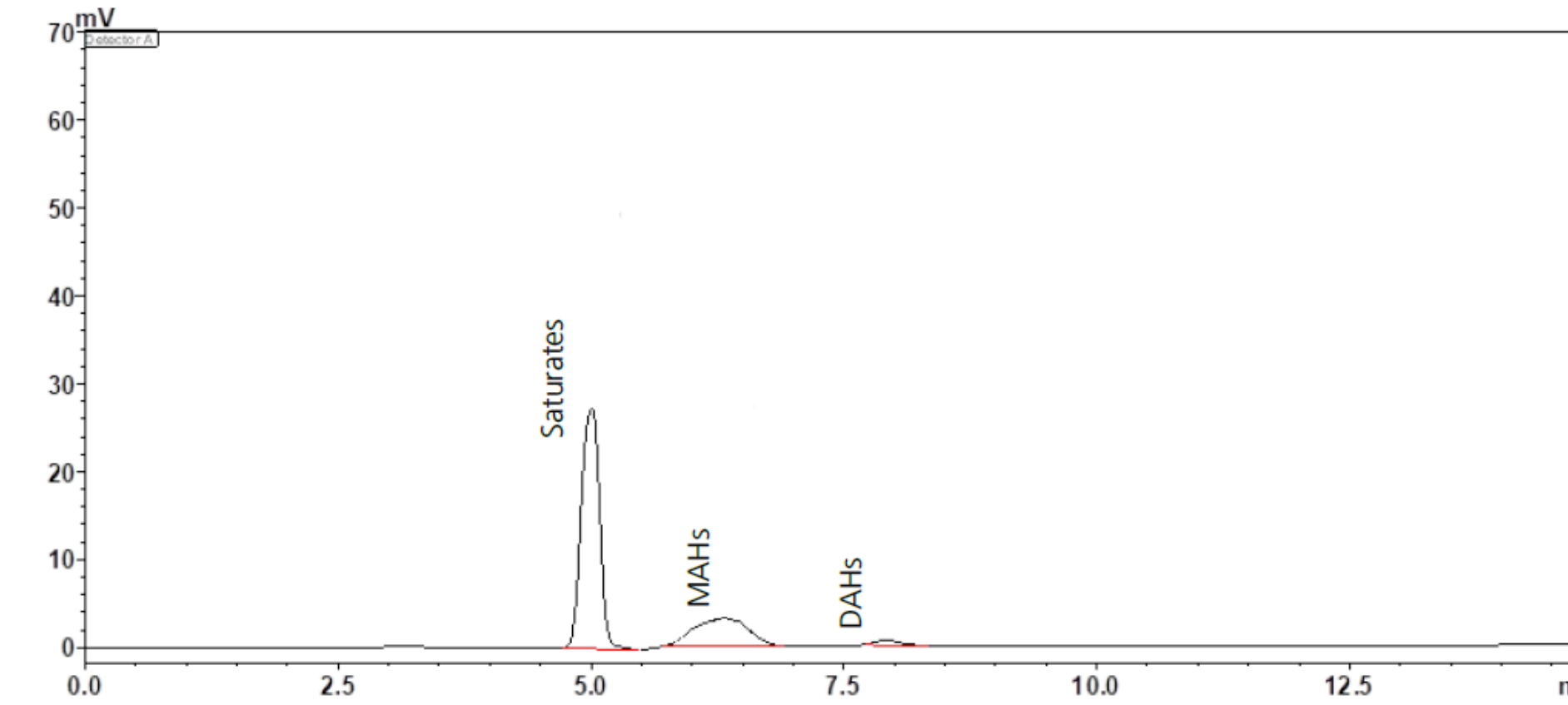


Figure 5: Injection of Jet A diluted 1:10 in heptane conforming to ASTM D6379

Results – ASTM D6591

As with method D6379, D6591 requires the injection of a system calibration standard that is to establish minimum resolution between saturates and MAHs and to establish the back-flush time that allows the elution of tri+ aromatics from the system (T+AH). Using the calculation provided by the method and the result obtained, the back-flush time was set to 9.24 minutes. A flow rate of 0.8 mL/min allowed for the greatest resolution of 9-methylantracene and dibenzothiophene, and was selected to reduce solvent consumption while still allowing run time to be slightly reduced versus other published methods (28 min. versus 30 min.). Figure 6 illustrates the system calibration standard chromatogram.

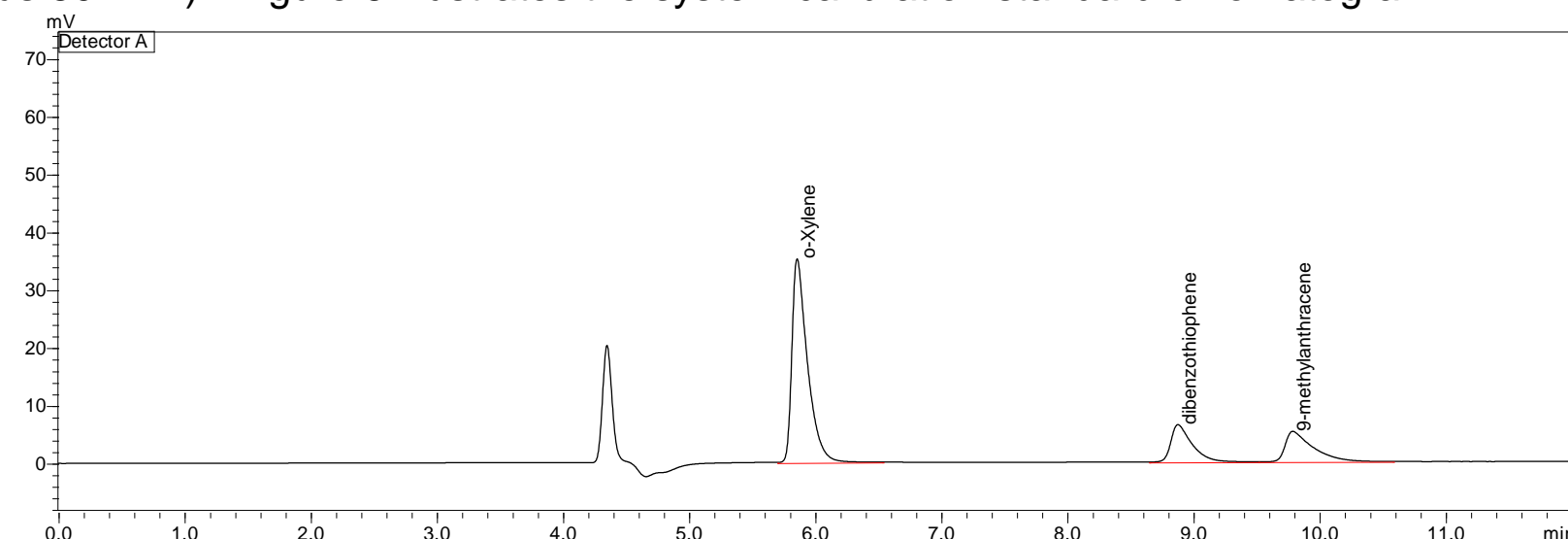


Figure 6: ASTM D6591 system calibration standard chromatogram

Figure 7 represents the calibration results for the 3-component standard for D6591. Excellent linearity was observed for the 4-level calibration, results are based on triplicate injection of standards.

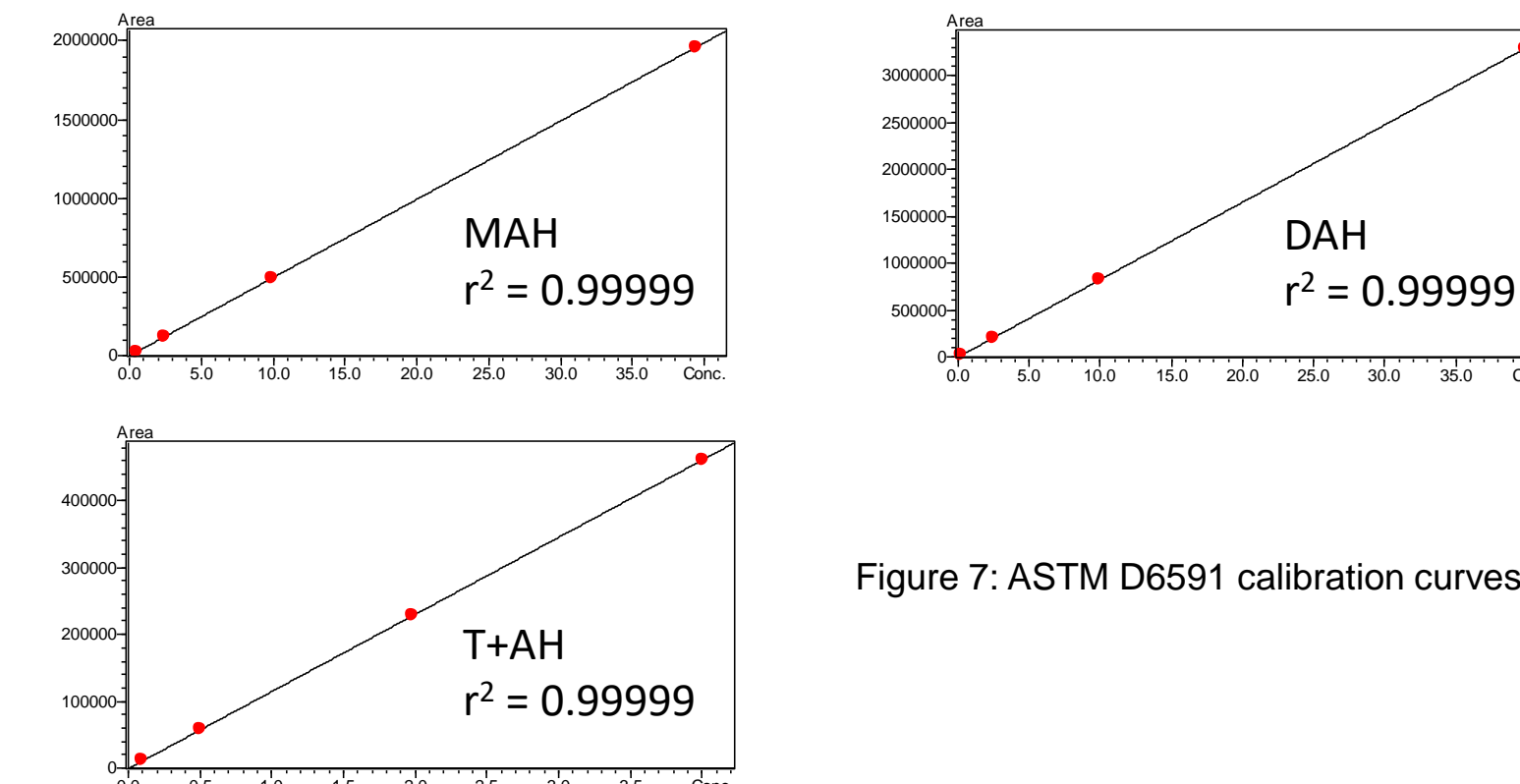


Figure 7: ASTM D6591 calibration curves

A sample of diesel fuel from the pump was diluted to method specifications, 1.0586 g in 10 mL heptane, and the resulting chromatogram obtained. Note the separation achieved among the DAHs, as the 3 micron column provides increased resolution versus 5 micron packing.

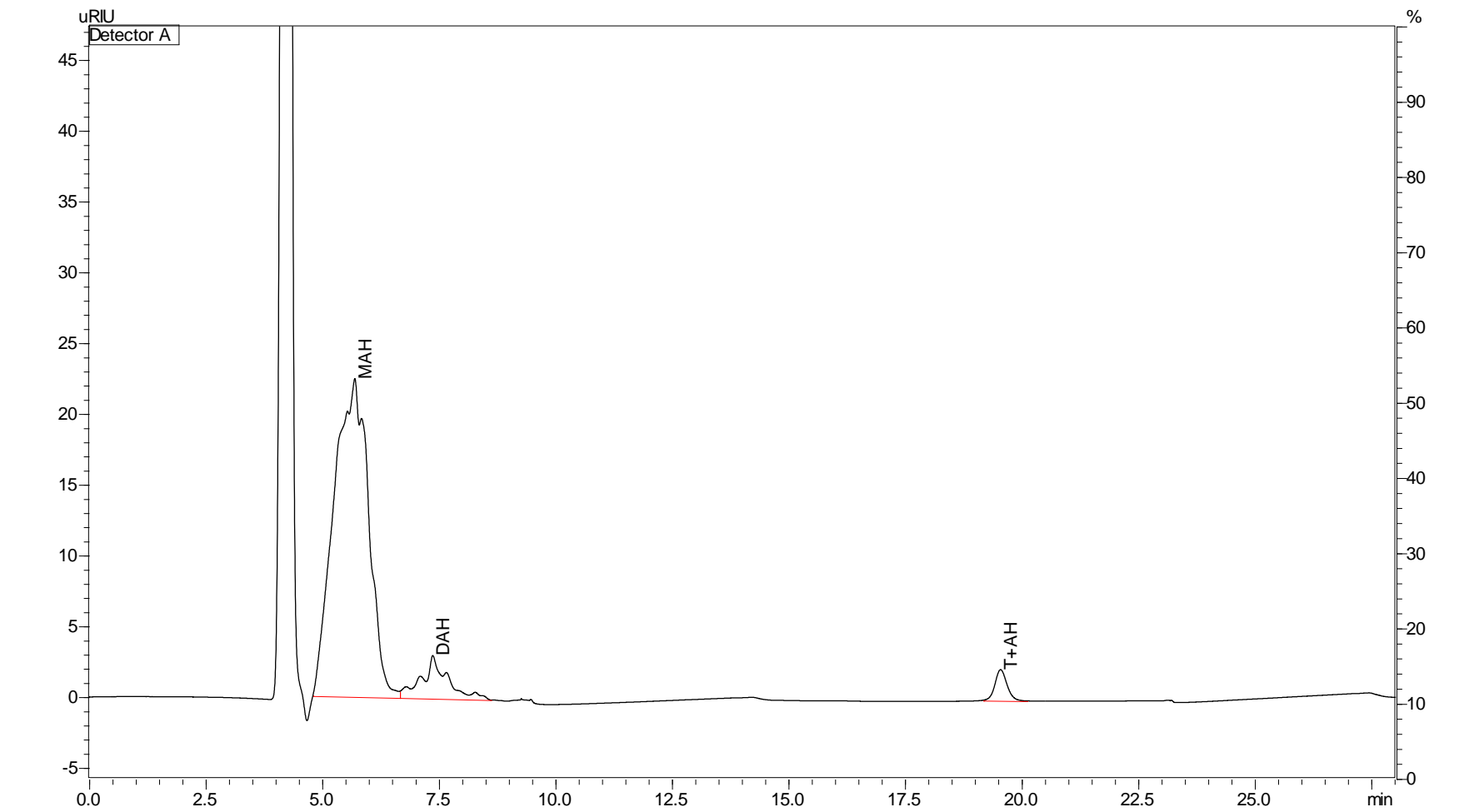


Figure 8: Injection of pump diesel prepared at 1.0586 g/10 mL

Conclusion

This poster demonstrates the detection and quantitation of MAH and DAH by ASTM D6379, as well as detection and quantitation of MAH, DAH, and T+AH by ASTM D6591 using a single Prominence HPLC. Coefficients for the calibration curves with correlation coefficient values greater than 0.9999 indicate a strong linear response of these compounds and exceed the requirements of the method. Replicate injections of standards and samples show that retention times are stable beyond the repeatability standards set forth by the methods. For ASTM D6591, retention time RSDs for real samples vary by less than 0.035%, while peak area varies by only 1% RSD for the difficult to integrate DAHs.

Using Shimadzu HPLC hardware and column technology allows for the easy modernization of assays formerly using ASTM D1319, providing the ability to more quickly and accurately quantitate aromatics in middle distillates.

References

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- 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
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