The Determination of Aromatic and Polynuclear Aromatics in Diesel and Aviation Fuels by Supercritical Fluid Chromatography

Introduction

The combustion properties of diesel and aviation turbine fuels and the resulting emissions from their consumption are greatly affected by the percentage of aromatic hydrocarbons found therein. To assist in process and quality control, and to monitor aromatic and polynuclear aromatic (PNA) content due to environmental regulations, analytical methods for the determination of the total aromatic content of fuels have been developed. ASTM (American Society for Testing and Materials) Method D-1319 using Fluorescence Indicator Adsorption (FIA) has been used to determine the aromatic content of fuels, but it is not well suited for low polynuclear aromatic content fuels or for fuels with colored additives. HPLC and GCMS have also been used to determine the level of aromatic hydrocarbons in fuels, but the ASTM for various reasons has not accepted methods developed with these techniques.

The California Air Resources Board (CARB) has mandated that all diesel fuels sold in the state of California must be analyzed for aromatic and polynuclear aromatic content using ASTM Method D-5186. This method specifies the use of supercritical fluid chromatography (SFC) with carbon dioxide and a flame ionization detector (FID).

This note demonstrates the determination of aromatic content of diesel fuels using the protocols established in ASTM Method D-5186. The Selerity Series 3000 SFC , that was used for this study, was designed specifically for optimum performance and easy operation for the analysis of fuels. The Series 3000 features low dead volume hardware, efficient low dead volume columns and a pulse-less syringe pump as well as incorporating a temperature-controlled pressure transducer configuration for consistent pressure control. This latter innovation provides unsurpassed reproducibility in the performance of this method.

Experimental Conditions

The instrument used was a Selerity Technologies Series 3000 SFC with a flame ionization detector. A performance mix standard was prepared using hexadecane, toluene, tetrahydronaphthalene and naphthalene (75:20:3:2) and used to calibrate the system as specified by ASTM method D5186. This standard is also used to optimize the separation conditions and to set the aromatic and PNA cut points for the determination of aromatics and PNAs in fuels. The standards are injected neat and if needed, the injection duration is adjusted to prevent the unsaturated compounds from saturating the detector. See Table 1 below for run conditions.

Table 1 : SFC Conditions	
Oven Temperature	40 °C
Pump Pressure	200 atm
Column	50-cm x 1 -mm ID, silica (5-µm, 60 Å particles)
Detector	FID at 400 °C
Detector Gas Flows	Air at 600-mL/min; H2 at 90-mL/min
Restrictor	1 5-µm ID fused silica, 1 0 to 1 5-cm
Injection	Direct with timing control (0.2 sec injection time)

Results and Discussion

A typical chromatogram, which has been optimized for resolution, of the class-type separation obtained from this method is shown in Figure 1. The method specifies that the resolution between hexadecane and toluene be at lease 4 and the resolution between the other compounds be at least 2. The cut points are set between hexadecane and toluene and then between the tetrahydronaphthalene and the naphthalene at the beginning of baseline rise on the naphthalene peak as illustrated in Figure 2. Following the unsaturated peak, the mono-aromatics and polynuclear aromatics are integrated and summed for total aromatic content. Table 2 summarizes the results for the analysis of two diesel and two aviation fuels. As can be seen, the Series 3000 provides excellent reproducibility; and, in all cases, the precision, expressed as RSD, was better than 3%. This is well within the limits specified in Method D5186.

Figure 1: Chromatogram Obtained from ASTM Method D5186

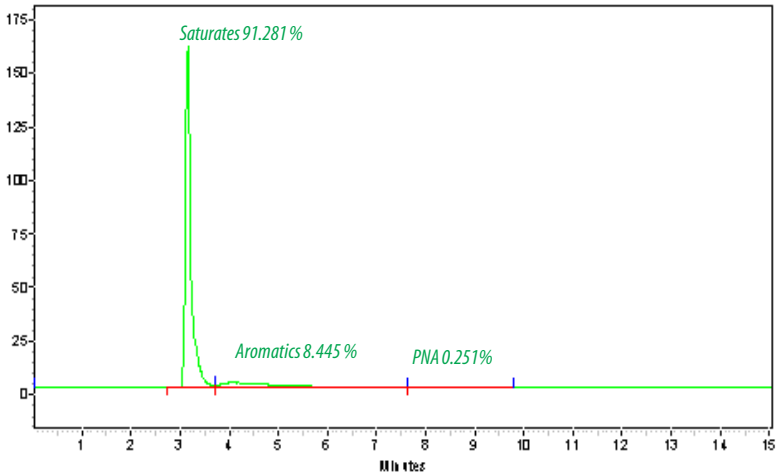

Figure 2: Overlay of Diesel and 4 Point Component mix

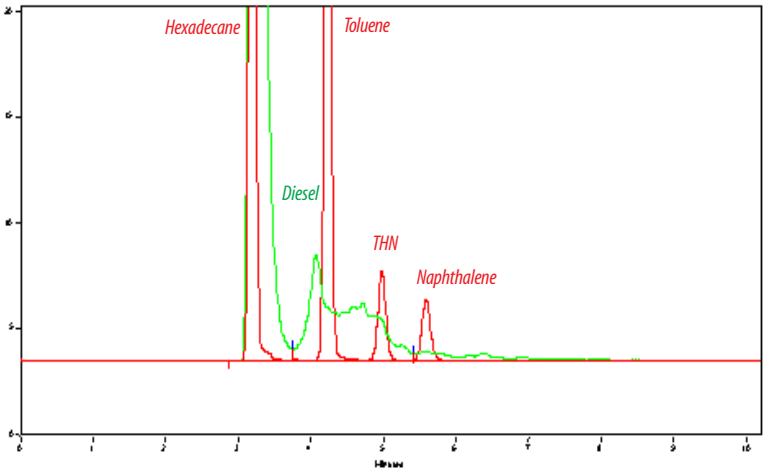

Table 2: Results of the Anlyses of Diesel and Aviation Fuels

	Run 1	Run 2	Run 3	Average Area (%)	STD	RSD (%)
Diesel A						
Saturates	67.82	67.62	67.69	67.71	0.10	**0.15**
Monoaromatics	25.03	25.14	25.12	25.10	0.05	**0.19**
Polynuclear Aromatics	7.15	7.23	7.19	7.19	0.03	**0.45**
Total Aromatics	32.18	32.38	32.31	32.29	0.08	**0.26**
Diesel B						
Saturates	65.35	65.26	65.39	65.33	0.07	**0.10**
Monoaromatics	28.08	28.16	28.03	28.09	0.05	**0.19**
Polynuclear Aromatics	6.58	6.58	6.58	6.58	0.00	**0.00**
Total Aromatics	34.65	34.74	34.61	34.67	0.05	**0.16**
Aviation Fuel A						
Saturates	83.59	83.73	83.64	83.65	0.07	**0.08**
Monoaromatics	14.32	14.30	14.28	14.30	0.02	**0.11**
Polynuclear Aromatics	2.09	1.97	2.08	2.05	0.06	**2.66**
Total Aromatics	16.41	16.27	16.36	16.35	0.06	**0.35**
Aviation Fuel B						
Saturates	77.4	77.33	77.44	77.39	0.06	**0.07**
Monoaromatics	19.82	19.87	19.89	19.86	0.03	**0.15**
Polynuclear Aromatics	2.78	2.79	2.68	2.75	0.05	**1.81**
Total Aromatics	22.60	22.67	22.56	22.61	0.05	**0.20**

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