

Determination of Non-Aromatic and Aromatic Hydrocarbon Contents of Diesel Fuels by Supercritical Fluid Chromatography

Introduction

Diesel fuel is a complex mixture of hydrocarbons including non-aromatic, mono-aromatic and poly-aromatic hydrocarbons. It is well known that the composition of these compounds is closely related to the cetane number of fuel in the way that the cetane number becomes higher as the concentration of non-aromatics increases. The number becomes lower and the amount of particulate matter in exhaust gas increases as the concentration of aromatics increases. The analysis of diesel fuel is taking an important role in the automobile and fuel industries.

ASTM (American Society for Testing and Materials) published the "Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels By Supercritical Fluid Chromatography (D 5186 – 03)" using a Flame Ionization Detector (FID) in 2003¹⁾. This application note demonstrates that SFC with supercritical CO₂ can determine the non-aromatic and aromatic contents in commercially available diesel fuel in accordance with the ASTM method.

Experimental

The SFC system we used consisted of a JASCO model PU-2080-CO₂ Supercritical CO₂ delivery pump, a GC-4000 Gas chromatograph with an FID (GL Science), JASCO's CO-2060 Column oven, a BP-2080 automatic back-pressure regulator, and a JASCO AS-2059-SF autosampler with a Chromatography Data System controlling and data processing data from all of above modules. The SFCpak SIL PA column (5 μm silica gel, 4.6 mm I.D. x 250 mmL) was used for the sample separation. The column effluent was split upstream of the back-pressure regulator and a certain amount of the fluid was introduced into the FID as shown in Figure 1.

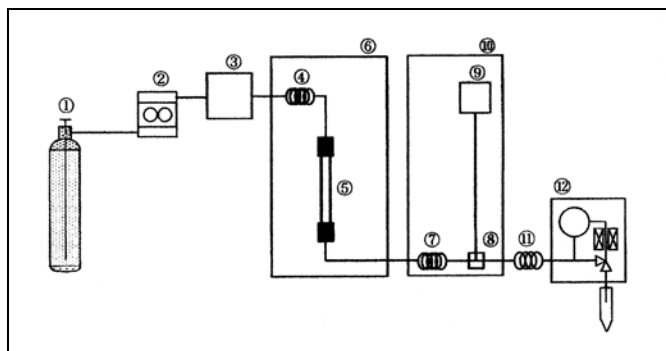


Figure 1 Schematic diagram of the supercritical chromatograph
 1 = bottle of liquefied carbon dioxide, 2 = pump, 3 = autosampler, 4 = heating coil, 5 = column, 6 = column oven, 7 = preheating coil, 8 = splitter, 9 = FID, 10 = oven for GC, 11 = cooling coil, 12 = back-pressure regulator.

Results and Discussion

An SFC chromatogram of the standard mixture of 1-hexadecane (0.600 mg), toluene (0.0245 mg), tetralin (0.163 mg) and naphthalene (0.0163 mg) is shown in Figure 2. Excellent resolutions (*R_s*), 10.56 ± 0.04 and 6.27 ± 0.03 were obtained in the separation between 1-hexadecane and toluene peaks, and tetralin and naphthalene peaks, respectively. Also excellent reproducibility of retention times (0.12 to 0.17% RSD, n=10) and peak areas (1.37 to 1.73% RSD, n=10) were obtained as listed in Table 1.

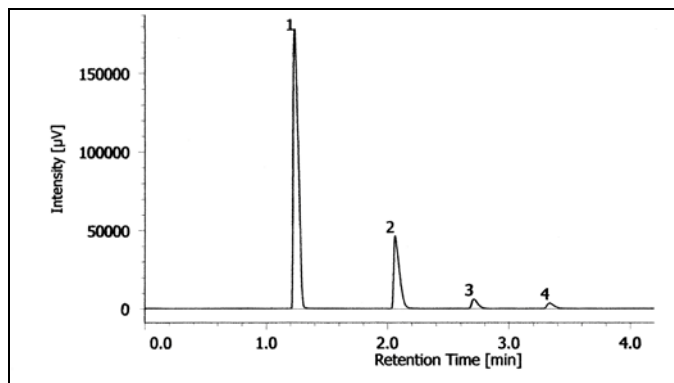


Figure 2 SFC chromatogram of the standard mixture
 Peaks: 1 = n-hexadecane (0.600 mg), 2 = toluene (0.0245 mg), 3 = tetralin (0.163 mg), 4 = naphthalene (0.0163 mg)) Conditions: column = SFCpak SIL PA (4.6 mm ID x 250 mm L, 5 μm), flow rate = 2.0 mL/min, column temperature = 35°C, temperature of FID = 350°C, back pressure = 20 MPa, injection volume = 1 μL, GC oven temperature = 200°C

Table 1 Reproducibility of retention time and peak area

Analyte	n-hexadecane	toluene	tetralin	naphthalene
average of retention time (min)	1.2240	2.0602	2.7068	3.3290
standard deviation (min)	0.0021	0.0027	0.0032	0.0043
relative standard deviation (%)	0.17	0.13	0.12	0.13
average of peak area ($\mu\text{V sec}$)	510673	149556	21701	14901
standard deviation ($\mu\text{V sec}$)	6983	2472	347	258
relative standard deviation (%)	1.37	1.65	1.60	1.73

We evaluated the linearity of peak response by injecting $1\mu\text{L}$ each of standard mixtures with several different concentrations that were made up by diluting 2, 3 and 4 times with n-hexadecane and observed good linearity.

We injected $1\mu\text{L}$ of commercially available diesel fuel into the system and obtained the chromatogram which is shown in Figure 3. Four repetitive injections of the fuel quantified the contents of non-aromatic hydrocarbons to be $(79.77\pm 0.12\%)$ and aromatic hydrocarbons to be $(20.23\pm 0.12\%)$.

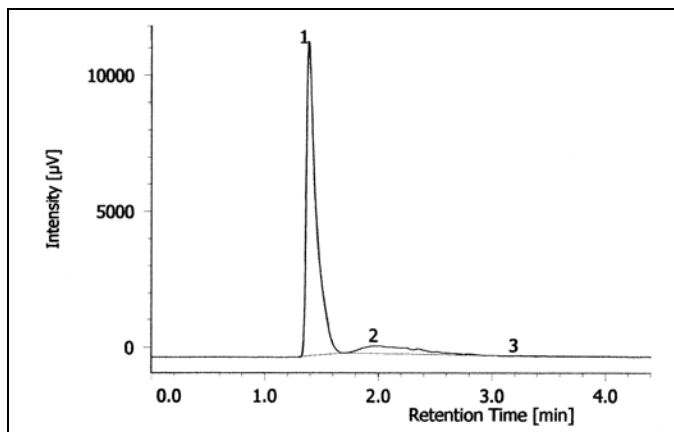


Figure 3 SFC chromatogram of diesel fuel
 Conditions: injection volume = $1\mu\text{L}$. The other conditions are the same as in Figure 2. Nonaromatic and aromatic content is 79.77 and 20.23% (standard deviation = 0.12%)

We have shown the JASCO SFC system can easily perform the analysis requirements of the ASTM with precision and accuracy.

Reference

- 1) “Standard Test Method for Determination of the Aromatic Content and Polynuclear Aromatic Content of Diesel Fuels and Aviation Turbine Fuels By Supercritical Fluid Chromatography (D 5186 - 03)”