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, while the number becomes lower and the amount of particulate matter in exhaust gas increases as the concentration of aromatics increases. For such reasons, the analysis of diesel fuel is becoming important in 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 2003[1].   We demonstrated the SFC with supercritical CO_2 to 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 model PU-2080-CO2 Supercritical CO2 delivery pump, a model GC-4000 Gas chromatograph with an FID (GL Science), CO-2060 Column oven, BP-2080 automatic back-pressure regulator, AS-2059-SF autosampler and ChromNAV Chromatography Data System controlling and data processing of all of above modules. All components were from JASCO except the gas chromatograph. The SFCpak SIL PA column (5μm silica gel, 4.6mmID x 250mmL) 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.
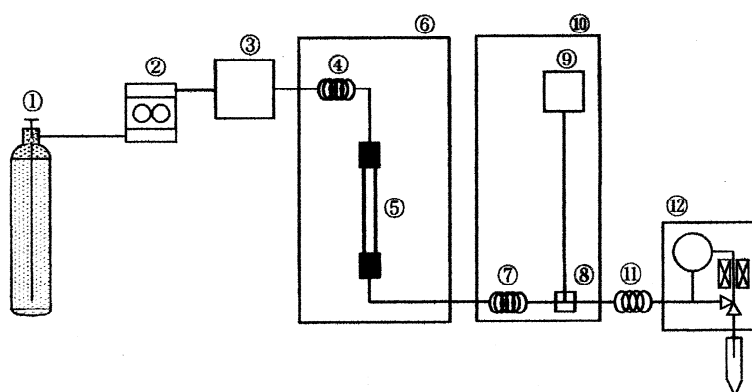

Figure 1 Schematic diagram of the supercritical chromatgram 1 = bottle of liquefied carbon dioxide, 2 = pump, 3 = amtosampler, 4 = heating coil, 5 = column, 6 = column oven, 7 = preheating coil, 8 = splitter, 9 = FID, 10 = oven for GC, 11 = cooling coil, 12 = back-pressure regulator.

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An SFC chromatogram of the standard mixture of 1-hexadecane (0.600mg), toluene (0.0245mg), tetralin (0.163mg) and naphthalene (0.0163mg) is shown in Figure 2. Excellent resolutions (Rs), 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 reproducibilities 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.
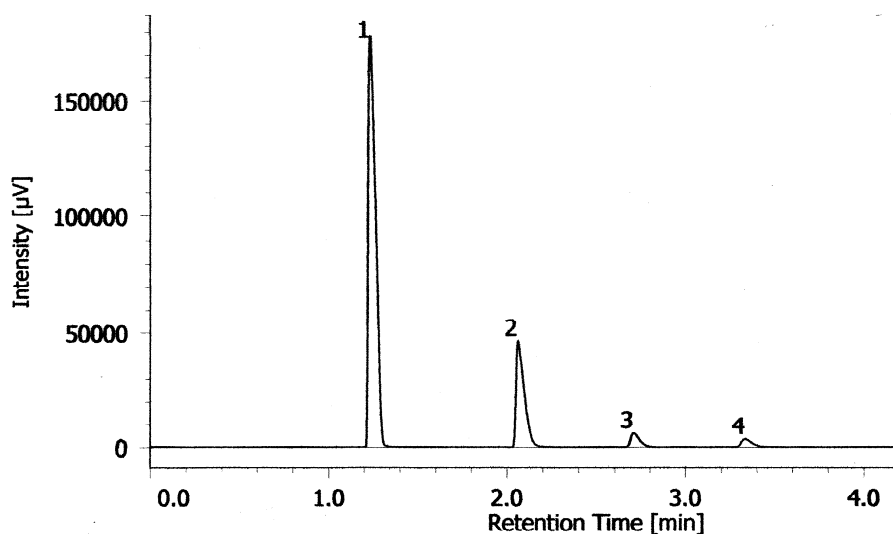

Figure 2. SFC chromatogram of the standard mixture Peaks: 1 = n-hexadecane (0.600 mg), 2 = toluene (0.0245 mg), 3 = tetralin (0.163 mg), 4 = naphthalene (0.0163 mg)) Conditions: column = SFCpak SIL PA (4.6 mm ID x 250 mm L, 5μm), flow rate = 2.0 mL/min, column temperature = 35°C, temperature of FID =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

Table 1. Repeatabillities 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 (μV sec)	510673	149556	21701	14901
standard deviation (μV 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 1μL 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.

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We injected 1µL of commercially available diesel fuel into the system and obtained chromatogram is shown in Figure 3. Four repetitive injections of the fuel quantified the contents of non-aromatic hydrocarbons to be (79.77±0.12%) and aromatic hydrocarbons to be (20.23±0.12%).
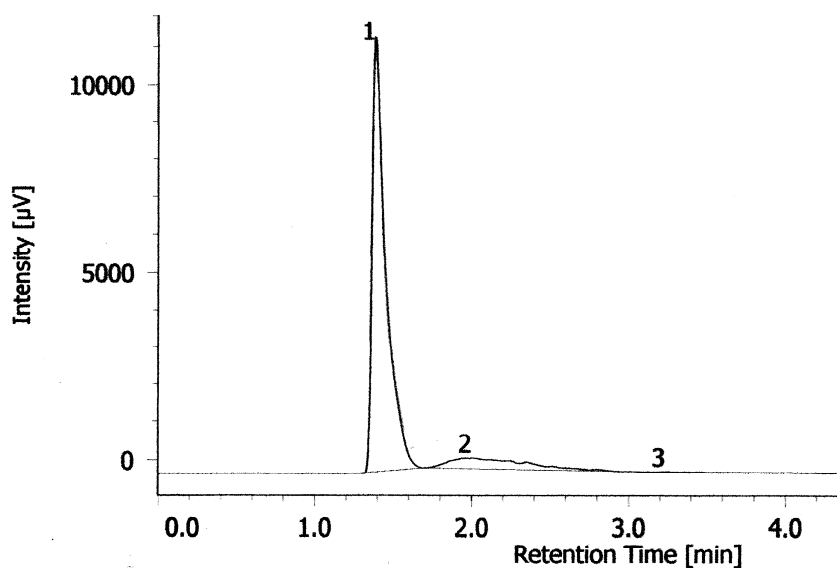

Figure 3. SFC chromatogram of diesel fuel Conditions: injection volume = 1µL. The other conditions are the same as in Figure 2. Nonaromatic and aromatic content is 79.77 and 20.23 % (standard deviation = 0.12%).

Conclusion

As we have shown, the JASCO SFC system well clears the precision and accuracy requested by ASTM.

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)"