

Determination of Olefin Content of Gasoline by Supercritical Fluid Chromatography

Introduction

Gasoline is produced by fractional distillation of petroleum at a boiling point of between 30° C and 200° C and contains hydrocarbons such as paraffin, olefin, and aromatics, carbon numbers of which are between 4 and 10. Characterization of gasoline requires determination of contents of those hydrocarbons.

American Society for Testing and Materials (ASTM) announced a method, D6550-00: Standard Test Method for Determination of Olefin Content of Gasolines by Supercritical-Fluid Chromatography.

We have established an analysis system in accordance with this method.

Experimental

JASCO HPLC 2000 series were used for the measurement. The system consisted of a PU-2080-CO₂ liquefied carbon dioxide delivery pump, an AS-2059-SF autosampler, an HV-2080-01 column switching valve (2 sets), a CO-2060 column oven, a flame ionization detector, a BP-2080 back-pressure regulator, and ChromNAV chromatography data system.

Separation columns were a SFCpak SIL PA silica gel column (4.6 mm ID x 250 mmL, 5 μm) and a SFCpak SIL AGS silver-coated silica gel column (4.6 mm ID x 50 mmL, 5 μm).

The operation for the measurement was carried out as follows:

1. Connect the silica gel and silver-coated silica gel columns, and deliver liquefied carbon dioxide.
2. Inject sample to elute paraffin first.
3. Disconnect the silver-coated silica gel column from the flow path by using the column switching valves, and elute aromatics adsorbed on the silica gel column. By using the column switching valves, disconnect the silica gel column and connect the silver-coated silica gel column again, and elute olefin adsorbed on the silver-coated silica gel column.

Results and Discussion

Figure 1 illustrates a schematic of the system. Switching the two columns allowed separation of paraffin, aromatics, and olefin. Effluent from the columns was divided by a splitter and a portion of the effluent was introduced into the FID detector.

Figure 2 shows a SFC chromatogram of a standard mixture of hexadecane, toluene, and octadecene. Hexadecane was selected as paraffin, toluene as aromatics, and octadecene as olefin.

Figure 3 shows a SFC chromatogram obtained by direct injection of commercially available gasoline. The olefin content of the gasoline was quantified to be 21.1% by comparing peak areas.

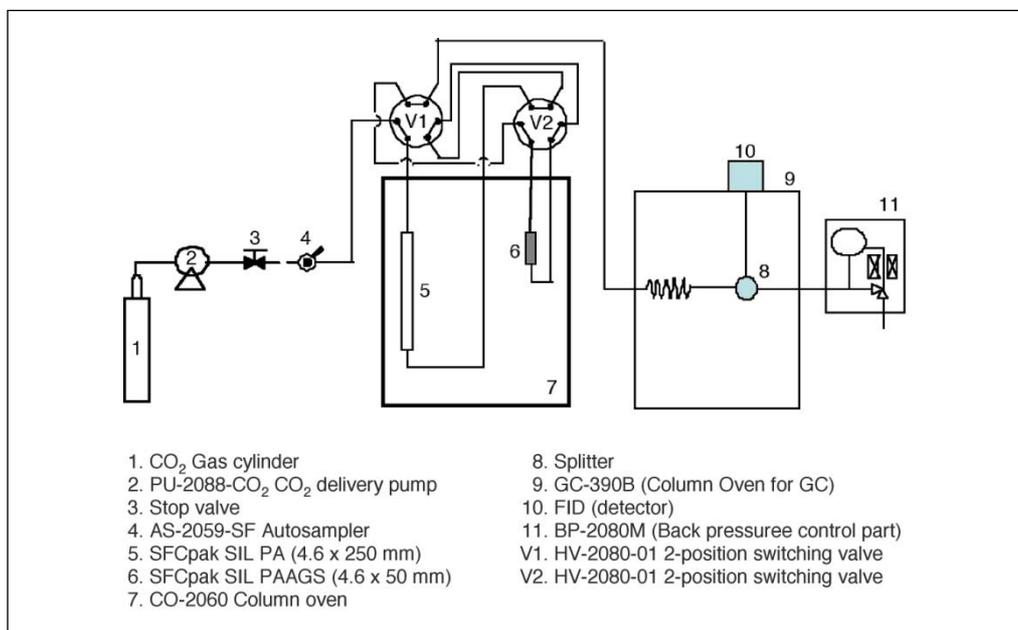


Figure 1 Schematic of the SFC system Components: 1=liquefied carbon dioxide cylinder, 2=liquefied carbon oxide delivery pump, 3=stop valve, 4=autosampler, 5=silica gel column, 6=silver-coated silica gel column, 7=column oven, 8=splitter, 9=oven for FID, 10=FID, V1 and V2=column switching valve.

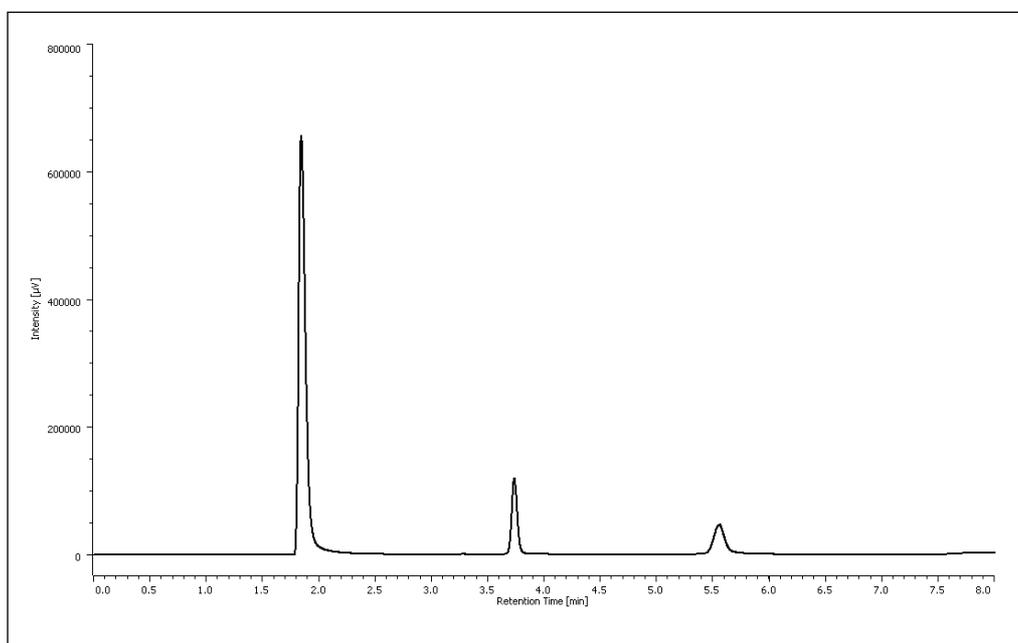


Figure 2 SFC chromatogram of standard mixture. Peaks: 1=hexadecane, 2=toluene, 3=octadecene. Conditions: separation column=SFCpak SIL-PA (4.6 mmID x 250 mmL, 5 μm) and SFCpak SIL PA-AGS (4.6 mmID x 50 mmL, 5 μm), flow rate of liquefied carbon dioxide=2 mL/min, injection volume=1 μL

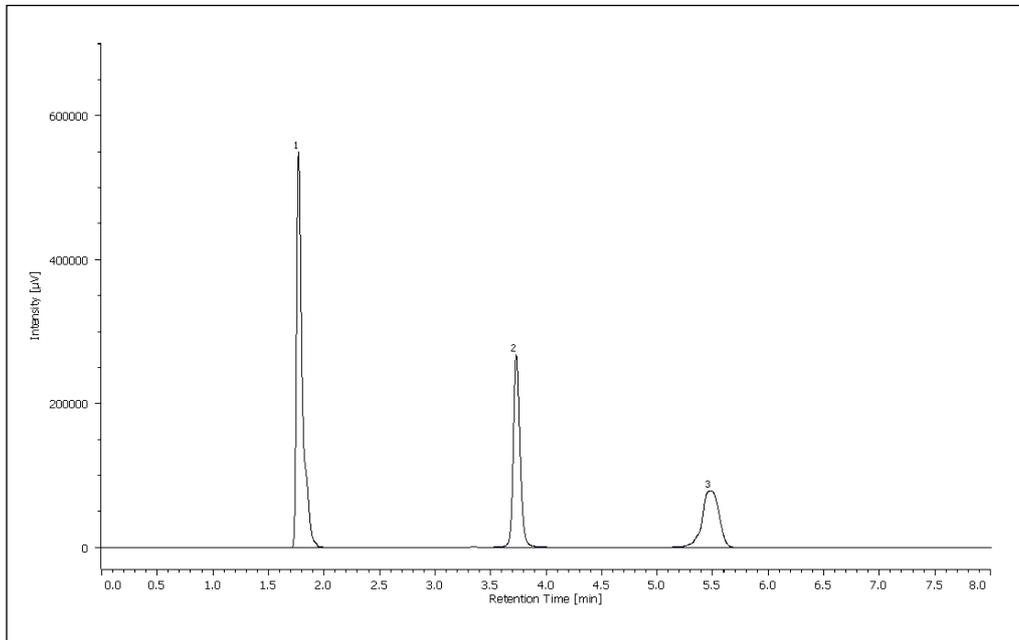


Figure 3 SFC chromatogram of commercially available gasoline.
The other conditions are the same as in Figure 2.