

## Determination of Hydrocarbon Types in Diesel Fuel According to the JPI\* Method \*(Japan Petroleum Institute)

With the current concern regarding the environmental impact by particulate matter emitted from diesel vehicles, the testing method for evaluating the characteristics of diesel fuel is becoming increasingly important.

A testing method was developed and standardized at the Japan Petroleum Institute for the quantitation of each hydrocarbon type contained in petroleum

products, such as diesel fuel (JPI-5S-49-97)<sup>1</sup>. This method employs HPLC to separate the hydrocarbons into five categories (paraffines, olefines, mono-aromatic, di-aromatic and polycyclic aromatic hydrocarbons) and then quantitate them.

Here we will show an example of quantifying each type of hydrocarbon in a commercially marketed diesel fuel, in accordance with the JPI method.

### ■ Analytical Conditions

The analytical conditions used for this example are listed in Table 1. This method connects two types of columns in series -- a silver nitrate impregnated silica gel column, which is able to separate the paraffines and the olefines, and an amino-bonded silica column, which is able to separate the aromatic hydrocarbons into cyclic system. (Two amino-bonded silica columns are usually used, but if the retention time and separation levels satisfy the standard values, then one column may be used.)

If even a small amount of water gets in the silver nitrate impregnated column, then the retaining force will decrease, so the hexane used as the mobile phase must be dehydrated. In this case, the analysis was performed with a molecular sieve inserted into the mobile phase bottle, that had been heated to 200°C and let to cool in a desiccator.

Detection was accomplished with a refractive index detector. An ultraviolet detector is not essential, but the chromatograms by uv detector are useful for determining the boundary of each aromatic portion.

Table 1 Analytical Conditions

Column	: Senshu pak AgNO <sub>3</sub> -1071-Y (70 mm L. × 4.6 mm I.D.) Develosil NH <sub>2</sub> -5 × 2 (250 mm L. × 4.0 mm I.D., each)
Mobile phase	: <i>n</i> -Hexane
Flow rate	: 1.0 mL/min
Temperature	: 25°C
Detection	: RID-10A SPD-10AVP at 225nm

### ■ Analysis of Standard Mixture

In order to confirm the retention times for the five types of hydrocarbons, a standard mixture solution containing *n*-heptadecane, 1-heptadecene, 1,3,5-triethylbenzene, 2,6-dimethylnaphthalene, and anthracene was prepared and analyzed. The resulting chromatogram is shown in Fig. 1.

The retention time for 1-heptadecene is selectively varied depending on the degree to which the silver nitrate impregnated column is activated. According to the Japan Petroleum Institute standards, the retention time must be at least 1.15 times longer than for *n*-heptadecane.

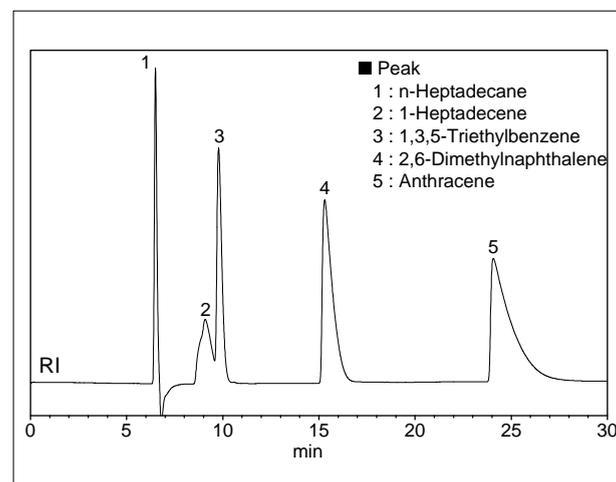


Fig. 1 Chromatogram of Standard Sample  
(1 g/L each, 10 µL Inj.).

### ■ Sensitivity Correction of Refractive Index Detector

In order to correct the sensitivity of the refractive index detector, the equivalent of 0.5 $\mu$ L 1,3,5-triethylbenzene is injected in advance and the peak area value is obtained. Fig. 2 shows an example of measurements repeated twice. The measurements are repeated until the mutual difference between peak area values is within 5% of the average value.

Once the area value is obtained, calculate the correction factor ( $f$ ) using the formula given in the Japan Petroleum Institute Standard. The purpose of this factor is to match the sensitivity to the sensitivity of the refractive index detector that was used for the standard.

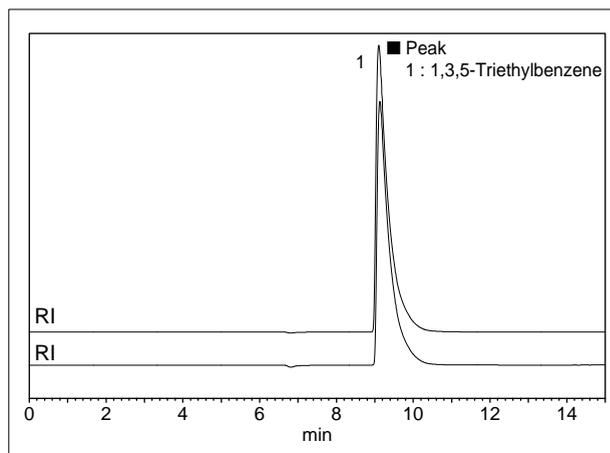


Fig. 2 Chromatogram of 1,3,5-Triethylbenzene (10%(vol/vol), Injection volume 5  $\mu$ L).

### ■ Analysis of Diesel Fuel

Fig. 3 is an example of using the method to analyze commercially marketed diesel fuel. Similarly, Fig. 4 is an example of analyzing low-sulfur diesel fuel.

Based on the chromatogram from the refractive index detector, the peaks are separated into five hydrocarbon types, and each area value is calculated. These respective values, the correction factor ( $f$ ) explained above, the sample density  $D$  and kinetic viscosity  $V$ , are plugged into the formula included in the Japan Petroleum Institute Standard and the volume percent for each hydrocarbon type is calculated.

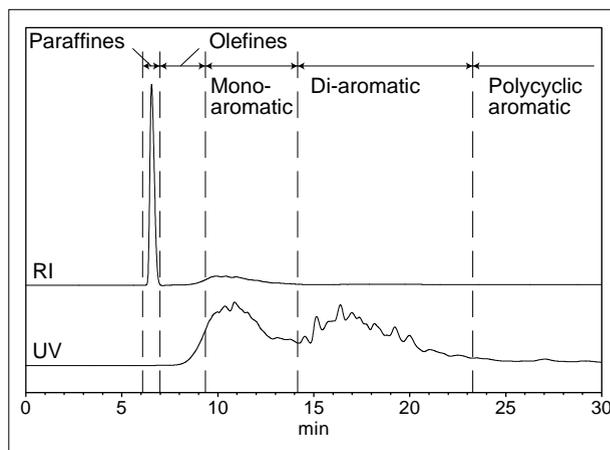


Fig. 3 Chromatogram of Diesel Fuel (10%(vol/vol), Injection volume 5  $\mu$ L).

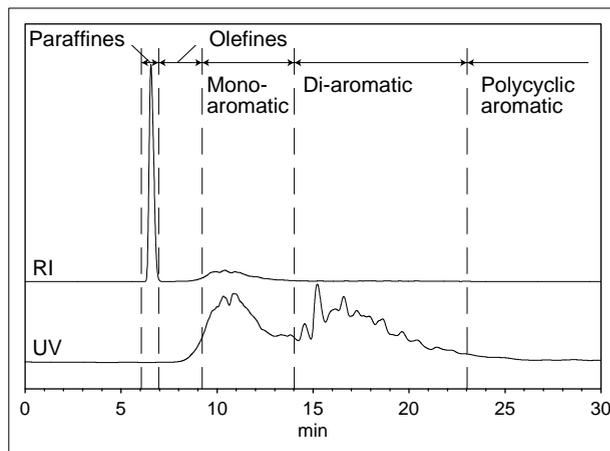


Fig. 4 Chromatogram of Low-Sulfur Diesel Fuel (10%(vol/vol), Injection volume 5  $\mu$ L).

#### Reference:

- 1) Japan Petroleum Institute Standard "Hydrocarbon Type Testing Method for Petroleum Products using High Performance Liquid Chromatography" JPI-5S-49-97



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