Enricher for Fraction of High-Pressure Liquid Chromatography

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Abstract

A device is developed for concentrating a dilute solution without losing the components with boiling points slightly higher than the solvent. The device consists of an evaporator, receptor, and approximately 100 capillaries. A dilute solution is introduced into the evaporator and heated at a lower temperature than the boiling point of the solvent with the addition of a helium gas flow. As a result, mostly only the solvent evaporates, passes through the capillaries, and enters into the receptor. The low-boiling-point components in the solute, with boiling points slightly higher than the solvent, are trapped at the inlet of the capillaries. These components are then recovered by a small amount of solvent supplied from the receptor through the capillaries, with the main components of the solute concentrated at the bottom of the evaporator. A diesel fuel is separated into aliphatic and aromatic fractions by high-pressure liquid chromatography using a silica gel column. These fractions are then analyzed by low-resolution field ionization mass spectrometry, following concentration using the described device. The analytical results show that the final composition of the fractions is almost the same as that of the aliphatic or aromatic hydrocarbons in the original fuel.

Introduction

As regulations concerning automobile exhaust emissions and the level of desulfurization in fuels have become stricter (1–3), higher-level analyses of fuels are increasingly necessary. Although, until now, diesel fuels have usually been analyzed by high-pressure liquid chromatography (HPLC) (4,5), more precise analyses that include, for instance, identification of molecular formula, have recently been required.

The only method for analyzing the composition of a diesel fuel according to molecular formula is field ionization (FI) mass spectrometry (MS) (6–8). However, a conventional MS cannot obtain accurate mass spectra of FI ions. Therefore, hydrocarbons with a double bond equivalence value (DBE) (DBE of hydrocarbon: C_nH_m is $n + 1 - m/2$) of x and those with a DBE of $x + 7$, such as nonane (C_9H_{20}, M_w = 128.156) and naphthalene ($C_{10}H_8$, M_w = 128.078), cannot be distinguished using FIMS. Accordingly, the diesel fuel must be separated into aliphatic and aromatic fractions by a separation method such as HPLC. Moreover, these fractions need to be concentrated before FIMS analysis because the concentrations of these fractions (< 1%) are too low to obtain FIMS spectra with sufficient intensity.

The mildest conditions to concentrate a solution are considered to be evaporation at room temperature under atmospheric pressure. However, even if such mild conditions are applied to a dilute solution, the loss of low-boiling-point components cannot be avoided, which is evident from consideration of Figure 1. From this background, a device was developed to concentrate a dilute solution obtained as an HPLC fraction (9). This paper describes the construction of the device and the analysis of HPLC fractions of a diesel fuel, which were concentrated by the device.

Experimental

Enricher

The design of the enricher device is shown in Figures 2 and 3. The enricher basically consists of an evaporator, capillaries, and a

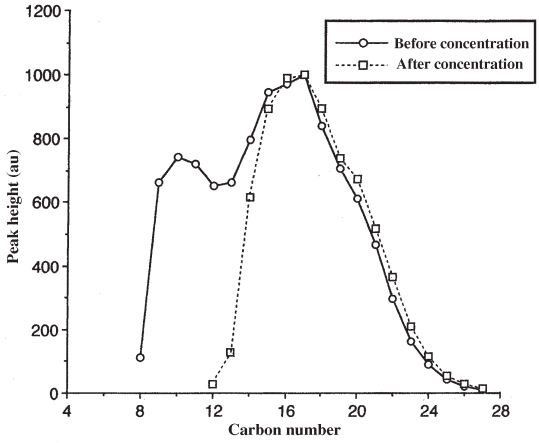

Figure 1. Carbon-number distribution of *n*-paraffins in *n*-hexane solution of diesel fuel. Before and after concentration in a beaker at 23°C. The carbon-number distributions from C_8 to C_{12} of whole fuel consists of paraffins and alkylnaphthalenes.

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receptor. The evaporator consists of a lid (A), glass cylinder (E), base plate (H), and valve (U) for recovery. The lid (A) contains a port (B) for introducing the effluent from the HPLC, a port (C) for controlling the inlet of the 104 capillaries, and a cone (D) to promote the accumulation and drip-back of low-boiling-point components condensed on the ceiling of the lid.

The glass cylinder (E) is made of quartz glass with an internal diameter (i.d.) of 49 mm and a height of 40 mm. The base plate (H) has a line (F) for introducing the carrier gas and a concave-conical shaped concentration zone (G), which has a pit (W in Figure 4) for gathering the concentrate at the bottom. The base plate also contains two cartridge heaters (V in Figure 4, 110 V, 100 W) and a thermocouple.

The recovery valve (U), which recovers the concentrate from the pit (W in Figure 4) in the base plate (H), is attached on the undersurface of the base plate (H). The sectional view and the upper and lower side views of the valve (U) are shown in Figure 4.

The capillaries (K) consist of 104 individual capillaries cut from a capillary gas chromatography (GC) column (DB-1, J&W Ltd., Folsom, CA). The inner diameter and length of each capillary were 0.25 mm and 60 cm, respectively. The inlet and outlet of the capillaries were fixed at the inlet port (C) on the lid of the evaporator and the outlet port (N) on the receptor, respectively, using an inorganic adhesive (Ceramabond, Aremco Products Inc., Valley Cottage, NY). All the capillaries (K) are contained within the oven (M, 140- × 100-mm i.d.), which is filled with ice water or air.

The receptor consists of a lid (O), metal cylinder (Q), and base plate (S). The lid (O) has a port (N) for the outlet of the capillaries. The metal cylinder (Q), which has a height of 40 mm and a 20-mm i.d., has a port (P) for the carrier gas or recovery solvent. A slide valve (R) for discharging waste solvent is placed in the lower side of the metal cylinder (Q). The base plate (S) has a port and line for waste solvent (T) located on the underside.

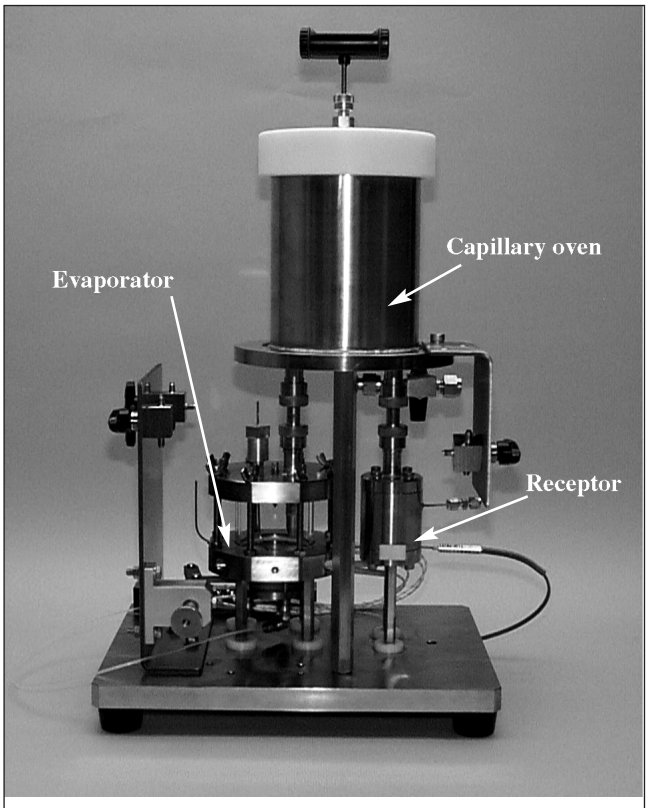

Figure 2. Enricher apparatus.

Fractionation of diesel fuel

The enricher was connected to a refractive index (RI) detector of a Gulliver semipreparative HPLC system using a Teflon tube (0.5-mm i.d.), as shown in Figure 5. The semipreparative HPLC system consisted of the following components: a JASCO DG-980-50 degasser; JASCO PU-986 pump (JASCO, Tokyo, Japan); Rheodyne injection valve with a sample loop of 50 µL (Rheodyne, Rohnert Park, CA); JASCO CO-966 column oven; JASCO Finepak SIL-5 semi-preparative column (205- × 7.5-mm i.d.) packed with 5-µm particles; JASCO MD-915 multiwavelength detector; and a Showa Denko RI-72 RI detector (Tokyo, Japan).

The diesel fuel sample was separated into aliphatic and aromatic fractions. The system was operated under the following conditions: sample volume, 50 µL; sample concentration, 100%; flow rate of solvent (HPLC-grade *n*-hexane, Wako Pure Chemicals, Osaka, Japan), 2 mL/min; oven temperature, 26°C. The HPLC chromatograms were acquired using a Dell Optiplex GXMT 5133 data system (Dell, Austin, TX).

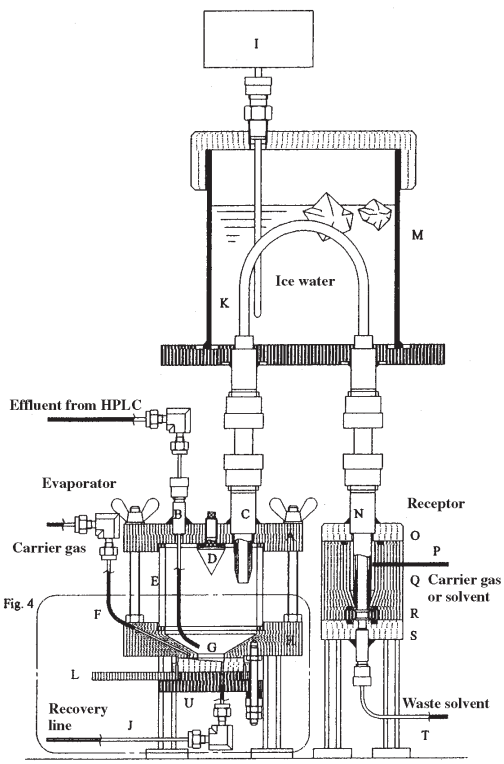

Figure 3. Detailed overview of enricher and recovery valve. For the evaporator: lid (A); port for effluent from HPLC (B); inlet port for capillaries (C); drip promoter (D); glass cylinder (E); carrier gas line (F); concentration zone (G); base plate (H); recovery line (J); and recovery valve lever (L). For the capillary: thermometer (I), capillaries (K), and capillary oven (M). For the receptor: outlet port for capillaries (N); lid of receptor (O); solvent or carrier gas line (or both) (P); body of receptor (Q); slide valve for waste solvent (R); base plate (S); waste solvent line (T); and recovery valve (U).

Concentration of the HPLC fractions

A diesel fuel sample (50 µL) was injected into the HPLC 15 times at intervals of 20 min, and the aliphatic and aromatic fractions were collected. The aliphatic fractions were directly introduced into the evaporator 15 times and concentrated in real time. During the concentration process, the base plate (H in Figure 3) of the evaporator was at 70°C and the capillaries (K in Figure 3) were at 23°C or 0°C. The concentrate in the evaporator was recovered using 1 mL of *n*-hexane.

The aromatic fractions were collected through a stainless steel tube of 1/16-inch outside diameter into 15 vials of 100 mL. The 15 aromatic fractions were concentrated off-line using the enricher, after concentration of the aliphatic fractions, under the same conditions used for the aliphatic fractions. The aromatic fraction concentrated in the evaporator was recovered using 1 mL of *n*-hexane. The other conditions for the concentration process were as follows: flow rate of the effluent from the semipreparative HPLC (= flow rate of HPLC solvent), 2 mL/min; and flow rate of helium, 1 L/min. Details of the concentration process are given in Table I.

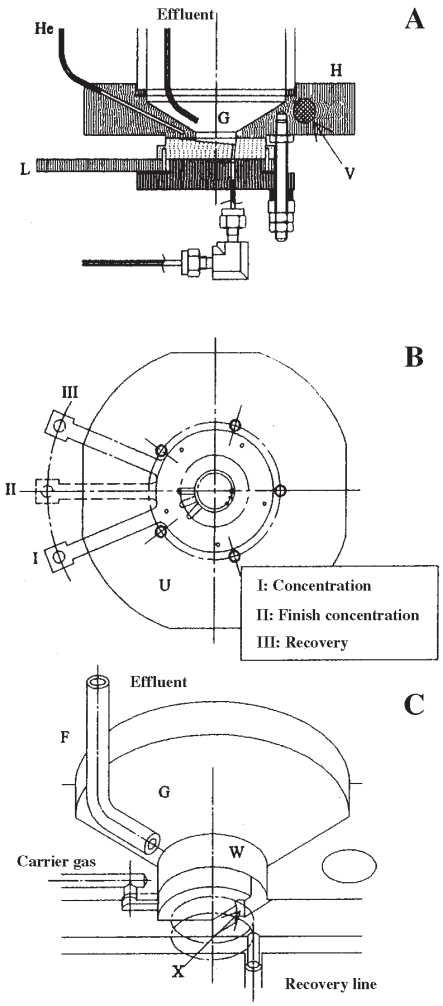

Figure 4. Recovery valve: a sectional view (A), upper side view (B), and lower side view (C). Figure labels: carrier gas line (F); concentration zone (G); recovery valve lever (L); recovery valve (U); cartridge heater (V); pit for concentrate (W); and recovery outlet (X).

Capillary GC of aliphatic fractions

The aliphatic fractions concentrated by the enricher were analyzed by an HP 5890 capillary GC (Hewlett-Packard, Palo

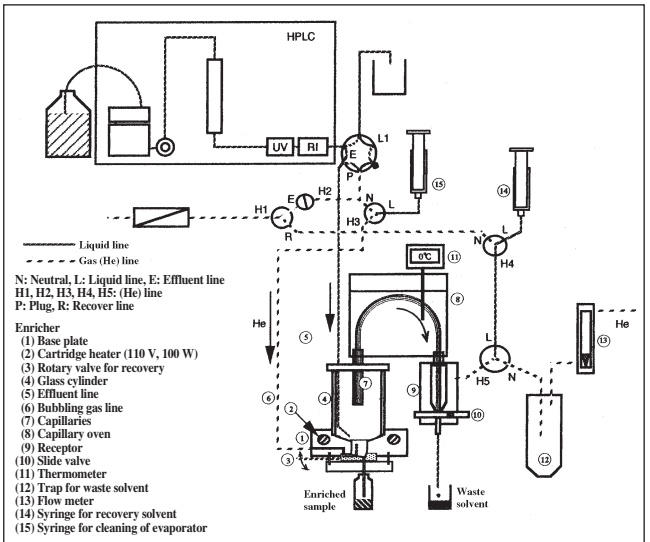

Figure 5. Schematic diagram of the HPLC and enricher.

Table I. Concentration Using the Enricher

Order	Determined operation and results
Op.* 1	Set the temperature of the base plate (H) at 70°C.
Op. 2	Set the temperature of the capillaries (K) at 0°C by pouring ice water into the capillary oven.
Op. 3	Set the lever (L) at position-I, shown in Figure 4B.
Op. 4	Open the slide valve (R).
Op. 5	Introduce the HPLC fraction into the evaporator through port B. Solvent (*n*-hexane) in the evaporator will evaporate and pass through the capillaries (K). The components with boiling points slightly higher than the solvent will evaporate and be trapped at the inlet of the capillaries. The concentrate will gather in the hollow (W) of the baseplate.
Op. 6	After evaporation of the solvent from the sample in the evaporator is completed, set the lever (L) to position-II, shown in Figure 4B. The flow of helium gas will be stopped by the above operation.
Op. 7	Monitor the pressure gauge of the evaporator until the gauge indicates 0 kg/cm^2.
Op. 8	Close the slide valve (R).
Op. 9	Pour a small amount (ca. 1 mL) of solvent into the receptor through port (P).
Op. 10	Connect a vial to the recovery line (J).
Op. 11	Set the lever (L) at position-III, shown in Figure 4B.
Op. 12	Collect the concentrate from the evaporator.

* Op. = operation.

Alto, CA) with a flame ionization detector (FID) to determine whether *n*-octane or *n*-nonane remained in the fraction after concentration.

The operating conditions of the GC were as follows: column, HP-1 (0.25-mm × 30-m i.d., 0.25-µm thickness); sample volume, 0.1 µL; injection mode, split (90/1); injector temperature, 300°C; column temperature, initially 30°C for 2 min, increased at a rate of 10°C/min up to 300°C and maintained at 300°C for 8 min; and FID temperature, 300°C.

FIMS of HPLC fractions

FI mass spectra of the HPLC fractions concentrated by the enricher were obtained using a Micromass ZAB-SE double focusing MS (Micromass, Manchester, U.K.) equipped with an FI with electron ionization (EI) source. The analytical conditions were as follows: sample volume, 30 µL; reservoir temperature, 200°C; ion source temperature, 140°C; ion accelerating voltage, 8 kV; and cathode voltage, –3 kV.

Masses from 90 to 450 amu were scanned every 20 s for at least 30 scans. Ion data were acquired under continuum mode using a DEC α Station 200 4/166 (Digital Equipment Corp., Cambridge, MA).

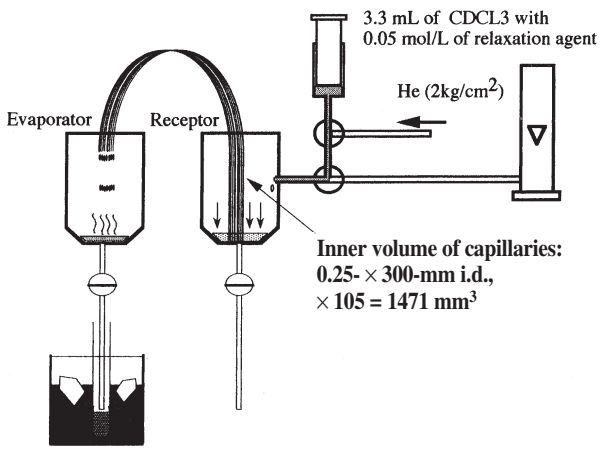

Figure 6. Recovery of sample for ^{13}C NMR.

NMR spectrometry

The diesel fuel sample was separated three times by HPLC, and the three aliphatic fractions were transferred into the evaporator of the enricher and concentrated. The concentrated aliphatic fraction was measured using ^{13}C NMR.

It is known that *n*-hexane yields peaks at chemical shifts of approximately 14, 23, and 32 ppm in the ^{13}C NMR spectrum. Therefore, these peaks overlap the aliphatic carbon peaks of the other hydrocarbons in the sample. Thus, the HPLC fraction was first concentrated completely, and the flow of helium gas introduced into the evaporator was stopped. After the inner pressure of the evaporator was reduced to 0 kg/cm^2, 3.3 mL of deuterochloroform with 0.05 mol/L of a relaxation agent was poured into the receptor. A flow of helium gas, at 2 kg/cm^2, into the receptor transferred the deuterochloroform in the receptor through the capillaries to the evaporator, where it was poured onto the aliphatic fraction (as shown in Figure 6). After the aliphatic fraction dissolved in the deuterochloroform, the deuterochloroform solution was recovered into a vial cooled by ice water.

^{13}C NMR spectra were obtained using a JEOL Lambda-500 Fourier transform NMR spectrometer (Tokyo, Japan) under the

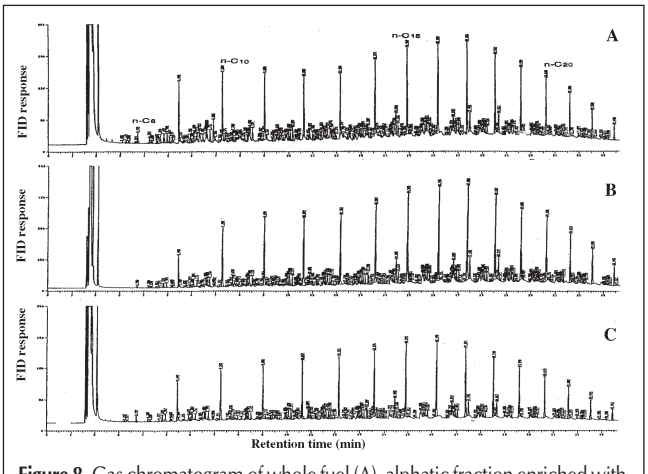

Figure 8. Gas chromatogram of whole fuel (A), alphatic fraction enriched with capillaries at 23°C (B), and 0°C (C).

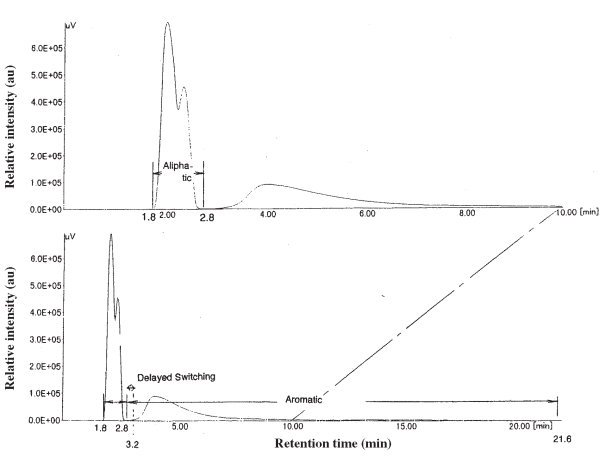

Figure 7. RI chromatogram and timing for collection of aliphatic fraction and aromatic fraction. Retention time 0–10 min (A) and 0–21.6 min (B).

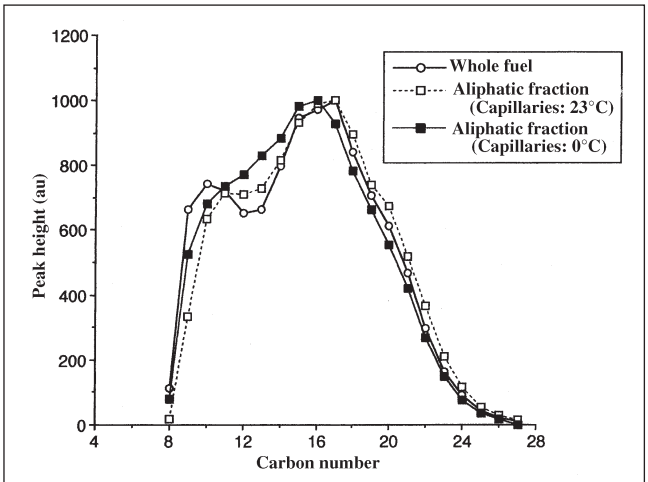

Figure 9. Carbon number distribution of *n*-paraffins in diesel fuel and its aliphatic fractions concentrated at 0°C or 23°C.

following conditions: sample size, 50 mg; relaxation agent, tris(acetylacetonate) chrome, 0.05 mol/L; solvent, deuterochloroform, 3.3 mL; observed frequency, 125.65 MHz; pulse width, 10 µs (45 pulses); recycle delay, 5 s; and scan number, 10,000. The ^{13}C NMR spectra were obtained under decoupling without nuclear Overhauser effect mode.

Results and Discussion

Fractionation of diesel fuel

Figure 7 shows one of the RI chromatograms. As shown in Figure 7, the diesel fuel was resolved into a sharp peak of aliphatic hydrocarbons, which appeared from 1.8 to 2.8 min and a broad peak of aromatic hydrocarbons, which appeared from 2.8 to 15 min.

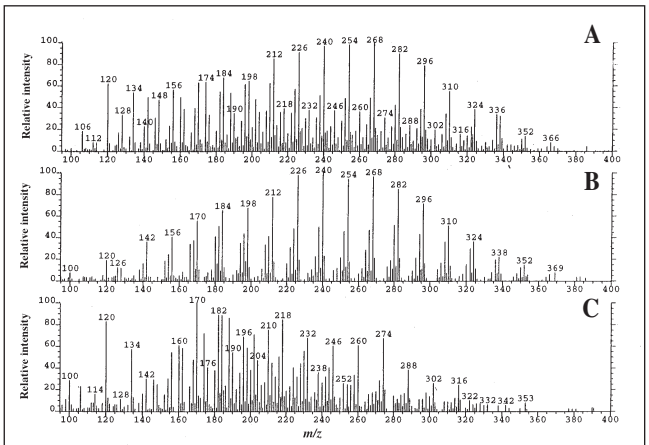

Figure 10. FI mass spectra of whole fuel (A), aliphatic fraction (B), and aromatic fraction (C).

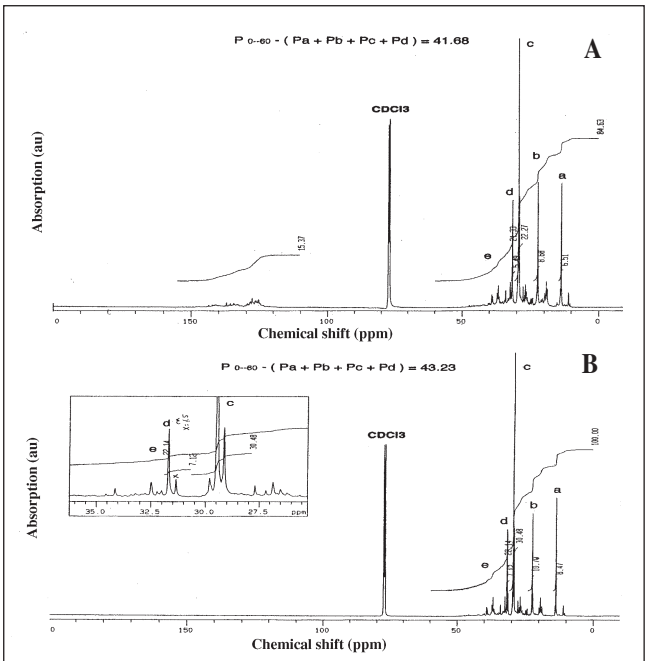

Figure 11. ^{13}C NMR spectra of whole fuel (A) and aliphatic fraction (B).

GC–FID of aliphatic fractions

The aliphatic fraction concentrated in the enricher with the capillaries at 23°C was analyzed by GC–FID, and the GC is provided in Figure 8B. The strong peaks in the GC were assigned to *n*-paraffins by comparison with the data obtained by GC–EI-MS, which is not described here. The numbers noted above the peaks indicate the carbon numbers of the *n*-paraffins. Through comparison of the GC (Figure 8B) with that of the original fuel (Figure 8A), it was found that the carbon-number distribution of *n*-paraffins in the two GCs was nearly the same. However, it was revealed that *n*-octane and *n*-nonane, in the aliphatic fraction concentrated by the enricher, were slightly decreased. The reason for the decrease was considered to be that a capillary temperature of 23°C was too high to trap the low-carbon-number hydrocarbons such as *n*-octane and *n*-nonane.

The temperature of the capillaries was therefore lowered to 0°C. The same aliphatic fraction was then concentrated again under the same conditions (Figure 8C shows the resulting GC). The peak intensities of the *n*-paraffins in the three chromatograms of Figure 8 were plotted against the carbon number in Figure 9. Figure 9 shows that the aliphatic fraction concentrated by the enricher with the capillaries at 0°C has the same carbon-number distribution of *n*-paraffins as the whole fuel, including the amounts of *n*-octane and *n*-nonane.

FIMS of HPLC fractions

The aliphatic and aromatic fractions of diesel fuel concentrated in the enricher with capillaries at 0°C and a solution of the whole fuel were analyzed by FIMS. Figure 10 shows the FIMS spectra from which the following observations were made: (*i*) The carbon-number distribution of *n*-paraffins in the aliphatic fraction (Figure 10B) is almost the same as that in the whole fuel (Figure 10A). (*ii*) The carbon-number distribution of alkylbenzenes in the aromatic fraction (Figure 10C) is nearly the same as that in the whole fuel (Figure 10A). The signal-to-noise ratio (s/n) of the aromatic fraction spectrum was poor because the amount of aromatic fraction was not sufficient for FIMS analysis. If a sufficient amount of aromatic fraction were obtained by preparative HPLC, FIMS spectrum with higher s/n would be obtained. (*iii*) Although the aliphatic fraction (Figure 10B) mainly consists of aliphatic hydrocarbons, the aliphatic fraction includes a small amount of propylbenzene and its isomers (*m/z* = 120). This indi-

Table II. ^{13}C NMR Results of Whole Fuel and Aliphatic Fraction – Atomic %

	Aliphatic-C						
	Straight-C				Branch-C		St.+Br.
Sample	a	b	c	d	a + b + c + d	e	F*
Whole	6.51	8.68	22.27	5.49	42.95	21.33	20.35
Fuel	7.69	10.26	26.31	6.49	50.75	25.20	24.05
Aliphatic fraction	8.47	10.70	30.48	7.12	56.77	22.14	21.09

* F = $P_{0–60}$ – (a + b + c + d). Where, $P_{0–60}$ is the total peal area with a chemical shift in the range of 0 to 60 ppm.

cates that HPLC using a silica gel column cannot perfectly separate the diesel fuel into an aliphatic and aromatic fraction. (*iv*) The aromatic fraction does not contain aliphatic hydrocarbons. Although the ions of *m/z* 100 and 114 are seen in the spectrum of the aromatic fraction (Figure 10C), these ions were assigned as ions because of impurities in the solvent (*n*-hexane) by GC–EI-MS.

^{13}C NMR of aliphatic fraction

Figure 11 shows the ^{13}C NMR spectra of the aliphatic fraction concentrated in the enricher and of the whole fuel. The peaks in these spectra were assigned as shown in Table II. By comparison of these spectra, the following observations were made: (*i*) The aliphatic fraction has fewer branched carbon atoms (tertiary or quaternary carbon atoms) than the whole fuel. This means that the concentration of branched carbon atoms in the aromatic fraction was higher than that in the aliphatic fraction. (*ii*) The concentration of methylene carbon atoms (peaks b and c in Figure 11 and Table II) in the aliphatic fraction is higher than that in the aromatic fraction. This is easily understood by comparison of the aromatic and aliphatic hydrocarbon structures. (*iii*) The aliphatic fraction includes few aromatic carbon atoms.

Conclusion

A device was developed for concentrating a dilute solution eluted from HPLC, in which the solution is heated at a lower temperature than the solvent boiling point and only the solvent is removed from solution through capillaries using a helium gas flow.

An aliphatic and aromatic fraction of a diesel fuel was concentrated using the mentioned device, and these fractions were analyzed by GC, FIMS, and ^{13}C NMR. The results of GC analysis revealed that the carbon-number distribution of the paraffins in the aliphatic fraction was almost the same as that of the whole fuel. In other words, it was found that there was no difference between the amounts of *n*-octane and *n*-nonane in the aliphatic fraction and whole fuel.

The results of FIMS analysis revealed that the compositions of the aliphatic and aromatic fractions were the same as for the aliphatic or aromatic hydrocarbons in the diesel fuel. The results of ^{13}C NMR analysis revealed that the concentration of the branched carbons in the aliphatic fraction was lower than that in the diesel fuel. In other words, it was found that the aromatic fraction was richer in branched carbons than the aliphatic fraction.

Thus, the enricher device was found to be useful for concentration of dilute solutions such as HPLC fractions that contain components with boiling points slightly higher than the solvent.

Acknowledgments

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References

1. S. Kobayashi, T. Nakajima, and M. Hori. *Effect of Fuel Sulfur and Aromatics on Diesel Exhaust Emissions*. JSAE Technical Paper 9304428, The Society of Automotive Engineers, Tokyo, Japan, 1993.
2. T. Kaneko and M. Akiyama. Desulfurization of diesel fuel. *Nisseki Tech. Rev.* **39:** 169–92 (1997).
3. T. Fujikawa. Ultra-deep HDS technology of diesel fuels: A review of the recent approaches in europe and U.S.A. *J. Jpn. Inst. Energy* **78(5):** 305–14 (1999).
4. The Japan Petroleum Institute. "Determination of hydrocarbon types – high pressure liquid chromatography". JPI-5S-49-97. *JPI Standard and Manuals Testing Method for Petroleum Producers.* JPI, Tokyo, Japan, 1997.
5. Institute of Petroleum. *Aromatic Hydrocarbon Types in Diesel Fuels and Petroleum Distillates by High Performance Liquid Chromatography with Refractive Index Detection.* IP Method 391/90. IP, London, U.K., 1990.
6. H. D. Beckey. *Field Ionization Mass Spectrometry*. Pergamon Press, Oxford, U.K., 1971.
7. M. Kuras and M. Ryska. Analysis of saturated hydrocarbons by field ionzation mass spectrometry. *Anal. Chem.* **48:** 196–98 (1976).
8. K. Kasamatsu and M. Noda. Determination of hydrocarbon types in low olefinic naphthas by field ionization mass spectrometry. *J. Jpn. Pet. Inst.* **26:** 369–76 (1983).
9. T. Ogawa, T. Mizuno, M. Matsui, and M. Inoue. Method for concentrating solution and device for the same. *U.S. Patent* 6,152,989, November 28, 2000.

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