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The Application of Field-ionization and Field-desorption Mass Spectrometry to the Analysis of Coal-derived Oil

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Field-ionization (FI) and field-desorption (FD) mass-spectroscopic techniques have been applied to the analysis of ring-type fractions of coal-derived oil, obtained by liquid chromatography. These techniques produce only the molecular ion and its isotopic signals, free from fragment ions, of a molecule, consequently the exact molecular-weight-distribution profiles of chromatographic fractions. The peak intensities are reproducible within a variation coefficient ($\sigma/\bar{x}$) of about 5—8% on repeated runs. The number-average molecular weights ($\overline{Mn}$) of the ring-type fractions, as calculated from the peak intensities, are close to those obtained by means of a vapor-pressure osmometer (VPO). These techniques, on the whole, give reliable mass spectra of coal-derived oil, although the isotope-ion ratios are overestimated compared to the theoretical natural abundances. The group-type analysis of the ring-type fractions has been made on the basis of their mass spectra, and the skeletal structures corresponding to each mass z series have been proposed.

In recent yeras, the shortage in energy resources has become a serious problem all over the world. Therefore, coal has been recognized again as one of the most valuable energy resources, and the development of an economical coal liquefaction process has been attempted.

Coal-derived oil is a multicomponent mixture of aromatic and hydroaromatic hydrocarbons. To date, however, there has been very little information on the mass distribution of the individual components, and coal-derived oil has generally been characterized as having an average molecular weight. Since a large portion of the coal-derived oil consists of low-volatile fractions, such as heavy oil and asphaltene, the use of a gas chromatograph-mass spectrometer (GC-MS) equipped with an electron-impact (EI) ion source has been severely limited.

On the other hand, the FI and FD techniques[1,2] produce only molecular ions and their isotopic peaks of the components in a mixture. The FD technique especially does not require the vaporization process of the sample for ionization, in contrast to the EI and FI techniques; consequently, it permits the analysis of thermally labile or nonvolatile substances. The usefulness of these techniques has already been proved in the analysis of biochemical substances[3] and aromatic hydrocarbons.[4] They can also be expected to be useful for the compositional analysis and determination of the molecular-weight distribution of coal-derived oil.

The purposes of the present work are to perform a quantitative mass analysis of coal-derived oil and to determine the types of hydrocarbons and their distribution in the coal-derived oil based on group-type analysis. The determination of the sensitivity coefficients of the hydrocarbons is beyond the scope of this work.

Experimental

The coal sample used in the present work was obtained from Akabira, Hokkaido. The sample was hydrogenated over Adkins catalyst at 400 °C for 60 min under an initial hydrogen pressure of 100 kg/cm^2. The hydrogenated product was extracted with hexane in a Soxhlet extractor. The extracted coal-derived oil was separated into five fractions on the liquid chromatograph by means of a modification of the Bureau of Mines-API 60 method:[5] saturates(Fr-P), monocyclic aromatics(Fr-M), bicyclic aromatics(Fr-D), tri- and tetracyclic aromatics(Fr-T), and polycyclic aromatics and polar compounds(Fr-PP). The Fr-PP fraction was further subdivided into eight fractions by gel-permeation chromatography(GPC). The volatile fractions were subjected to FI analysis by the direct-inlet method; they were charged into a glass tube with active alumina powder. On the other hand, the nonvolatile fraction(Fr-PP-8) was subjected to FD analysis by loading about 1 μg of a sample on the emitter with a microsyringe. The emitter was prepared by Beckey's method.[6] The FI and FD mass spectra were measured by means of a JMS-D300 double-focusing mass spectrometer equipped with an EI/FI/FD-combination ion source(JEOL Ltd). Ions were detected through an electrical detector connected to a data-analysis system, JMA-2000. The emitter current was kept at 5 mA for the FI analysis in order to prevent any condensation of the sample on the emitter and was elevated at a rate of 4 mA/min for the FD analysis. The scan speed for the mass range of m/z 100—550 was 5 s/cycle. Scanning was repeated 300—400 times in the FI and 40—50 times in the FD. The chamber temperature was maintained at 200 °C for the FI and at 60 °C for the FD. Throughout this work, homologs are assumed to have identical sensitivity coefficients.[7]

The average molecular weight was determined by the VPO (Knauer) method. Chloroform was used as the solvent.

Results and Discussion

Aspects of FI and FD Mass Spectra of Coal-derived Oil. Since any ring-type fraction of coal-derived oil is a multicomponent mixture, a sample must be introduced into an ion source without changing the composition of the mixture. However, the boiling points of these fractions cover a wide temperature range; therefore, a special technique is needed to effect simultaneous evaporation.

Figure 1 compares the total ion-current profiles (TICP) with the mass spectra of the Fr-P fraction as obtained by means of the FI and FD techniques. The TICP in FI with a direct-inlet probe suggests that the

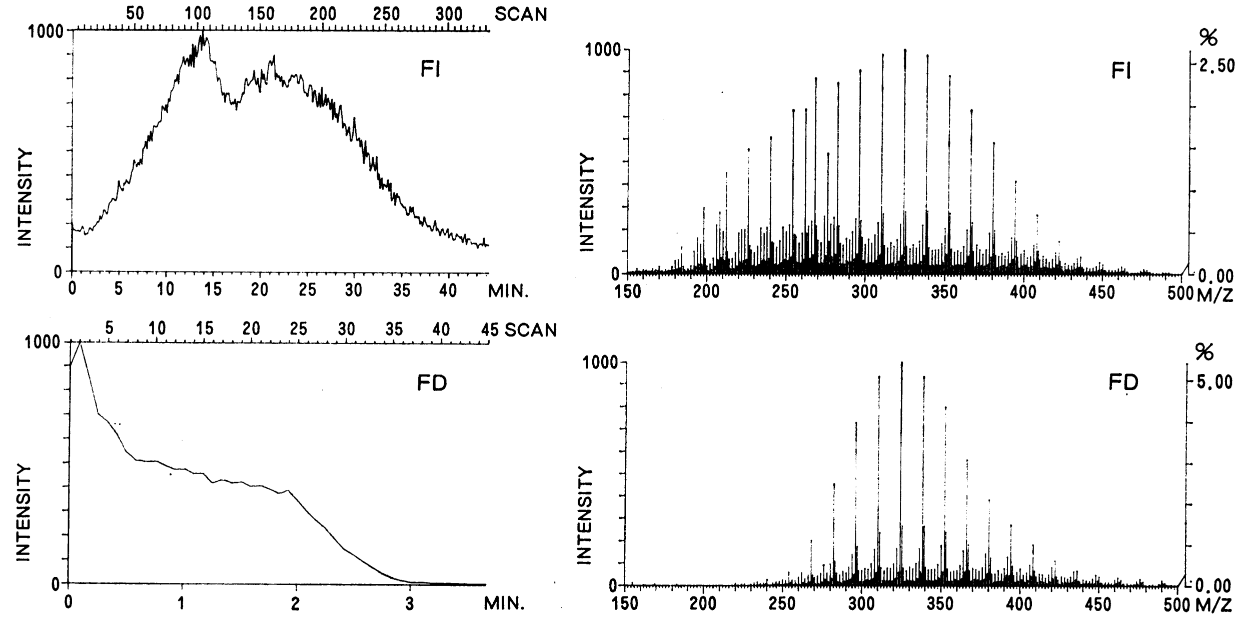

Fig. 1. Comparison of total ion current profiles with mass spectra of Fr-P for FI and FD techniques.

TABLE 1. REPRODUCIBILITY OF PEAK INTENSITIES IN THE FI AND FD MASS SPECTRA OF Fr-P AND T

Sample : Fr-P
FI

m/z	(1)	(2)	(3)	$\sigma/\bar{x}(\%)$
196	270.1	286.1	269.5	3.4
212	631.3	751.3	735.8	9.2
226	742.9	831.5	830.2	6.5
240	759.8	820.7	854.5	5.9
254	857.5	925.0	965.0	5.9
268	1000.0	1000.0	1000.0	0
282	983.3	914.3	986.6	4.2
296	977.6	903.7	983.8	4.7
310	983.3	930.5	994.7	3.5
324	955.3	906.4	986.6	4.3
338	932.9	879.6	897.6	3.0
352	877.1	836.8	816.7	3.6
366	684.4	716.6	652.3	4.7
380	580.1	596.2	525.5	6.5
394	488.8	454.5	396.2	10.5

Sample : Fr-T
FD

m/z	(1)	(2)	(3)	$\sigma/\bar{x}(\%)$
192	523.0	544.0	503.2	3.9
206	742.1	820.3	772.7	5.1
220	665.6	712.1	704.0	3.6
232	1000.0	1000.0	1000.0	0
246	951.2	952.4	951.1	0.1
256	696.5	708.5	716.4	1.4
258	916.9	904.6	918.7	0.8
270	669.9	677.5	681.4	0.8
282	384.8	391.1	389.0	0.8
284	589.0	607.3	624.5	2.9
298	515.4	521.2	558.6	4.4
312	428.4	445.3	475.8	5.3
324	350.1	373.2	367.0	3.3
336	269.6	266.0	305.1	7.7
350	250.6	243.6	263.9	4.1

sample in a glass tube was not vaporized until the probe was heated enough. No residue was found in the tube after measurement. In contrast, the TICP in FD indicates that the majority of the sample molecules had vaporized *in vacuo* before the mass measurements started. The resulting FD mass spectrum reveals the absence of volatile components in the low-mass range. Thus, the FI technique with the direct-inlet probe was found to be suitable for the measurements of the volatile fractions,[8] which comprise about 30 wt% of coal-derived oil (hexane extract), while the FD technique was found to be suitable for the measurements of nonvolatile fractions and polar substances containing phenolic OH and nitrogen atoms.

Few quantitative studies of the FI and FD mass spectra of multicomponent mixtures have been reported.[9–12] The components of coal-derived oil have larger and more complex chemical structures than the model compounds, and the preparation of a multicomponent "model mixture" for coal-derived oil is practically impossible. Therefore, we abandoned our attempts to estimate the sensitivity coefficients of the components and to perform quantitative FI and FD mass analysis using the "model mixture." For this reason, the ring-type fractions of coal-derived oil, which have their own structural characteristics, were used as samples in the present work. Since the compositions of the ring-type fractions used are unknown, the reproducibility of the peak intensities, the isotope-ion ratios, and the number-average molecular weights, as calculated from the intensities of the peaks, were studied.

The reproducibility of the peak intensities in the FI and FD mass spectra of the Fr-P and T fractions is shown in Table 1. The reproducibility is expressed by the variation coefficient ($\sigma/\bar{x}$), defined by the following equation:

$$\sigma/\bar{x}(\%) = \frac{100}{\bar{x}}\sqrt{\frac{\Sigma(x-x_i)^2}{N-1}},$$

where $\bar{x}$ is the arithmetic mean value calculated from N

measured values of x_i. The variation coefficients of the peaks with high ion intensities are approximately 8% for FI and approximately 5% for FD. In both spectra, the variation coefficients increased with the decrease in the peak intensity. On the whole, the reproducibility of the FD mass spectra is better than that of the FI mass spectra. Both mass spectra generally tended to improve the reproducibility of the peak intensity with an increase in the amount of ions detected.

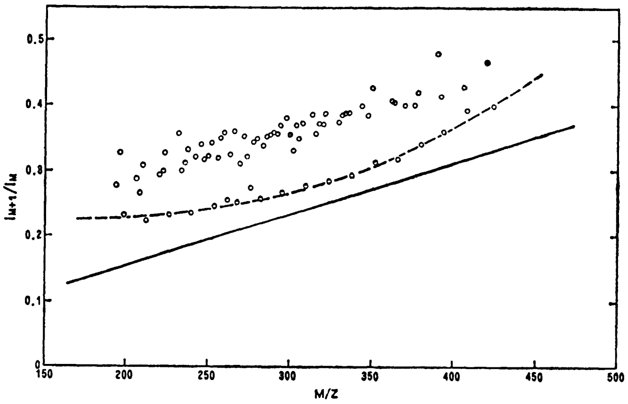

Fig. 2. Comparison of observed and calculated isotope ion ratios.

The reliability of the peak intensity was investigated by comparing the observed and calculated isotope-ion ratios. The isotope ratios in the FI mass spectrum of the Fr-P fraction are compared with the natural abundance (straight line) in Fig. 2. The observed isotope ratios are close to natural abundance when the peak intensities are high (broken line), but they tended to increase with the decrease in the peak intensity. The isotope ratios of peaks with small ion intensities are overestimated. These tendencies were observed in the FI and FD mass spectra of every ring-type fraction. Further studies are needed to elucidate the phenomenon. As a whole, the intensities of the peaks in the FI and FD mass spectra were well reproduced, although the isotope ratios deviated slightly from their natural abundances.

The FI and FD techniques give the molecular-weight-distribution profiles of mixtures. The reliability of the profiles was tested in terms of the number-average molecular weight, as calculated from the intensities of the mass peaks. The number-average molecular weight obtained from the mass spectrum is defined by the following equation:

$$Mn = \frac{\Sigma M_i I_i}{\Sigma I_i},$$

where M_i is the mass of the i th peak and where I_i is the intensity of the i th peak. The number-average molecular weights calculated from the FI and FD mass spectra of the Fr-P and T fractions are shown in Table 2. The molecular weight, like the peak intensity, is reproduced better in the FD mass spectra than in the FI mass spectra.

Furthermore, the calculated number-average molecular weights were compared with those measured by the VPO method in order to check whether or not the spectral patterns of mixtures corresponded to their real molecular-weight distributions. The number-average molecular weights of the ring-type fractions (Fr-P, -M, -D, -T, and -PP-8) were calculated from the FI and FD mass spectra in Figure 3 and are summarized in Table 3. The volatile fractions (Fr-P, -M, -D, and -T) were measured by FI, and the nonvolatile fraction (Fr-PP-8), by FD. In all the mass spectra of the ring-type fractions, ions were scarcely detected in the mass range below m/z 150, where the appearance of fragment ions was anticipated. Table 3 shows that the calculated molecular weights of all fractions but Fr-PP-8 are slightly greater than the VPO values. The overestimation is probably caused by an increase in the sensitivity coefficient with the number of carbon atoms in the molecule.[7] The great overestimation of the Fr-PP-8 fraction must be caused by the increase in the sensitivity coefficient and by the vaporization of the volatile components in this fraction. Table 3 suggests that most of the peaks in the mass spectra can be assigned to molecular and isotopic ions alone. Thus, the FI and FD mass spectra are suitable for the compositional analysis and for the determination of the molecular-weight distribution of coal-derived oil.

Table 2. Number-average molecular weights as calculated from FI and FD mass spectra of Fr-P and T

Sample :	Fr-P FI	Fr-T FD
1st	301	277
2nd	297	277
3rd	313	288
4th	293	278
5th	301	284
Mean	301	281

Table 3. Comparison of number-average molecular weights of ring-type fractions obtained by FI/FD-MS and VPO

Fr	Yield		$\overline{Mn}$	
	%		MS	VPO
P	8.2	FI	301	270
M	6.4	FI	273	240
D	10.1	FI	231	220
T	7.2	FI	283	270
PP-8	7.7	FD	332	270

In conclusion, we advise that the FI technique is applied to the analyses of volatile fractions, and the FD technique, to the analyses of nonvolatile fractions, of coal-derived oil. These techniques provide more precise and useful data than those obtained by conventional analytical methods, such as GPC and VPO, and may be one of the most powerful tools for elucidating the components of coal-derived oil, although several problems must be solved before we can obtain fully quantitative FI and FD mass spectra.

Group-type Analysis of Ring-type Fraction. As discussed in the preceding section, ring-type fractions

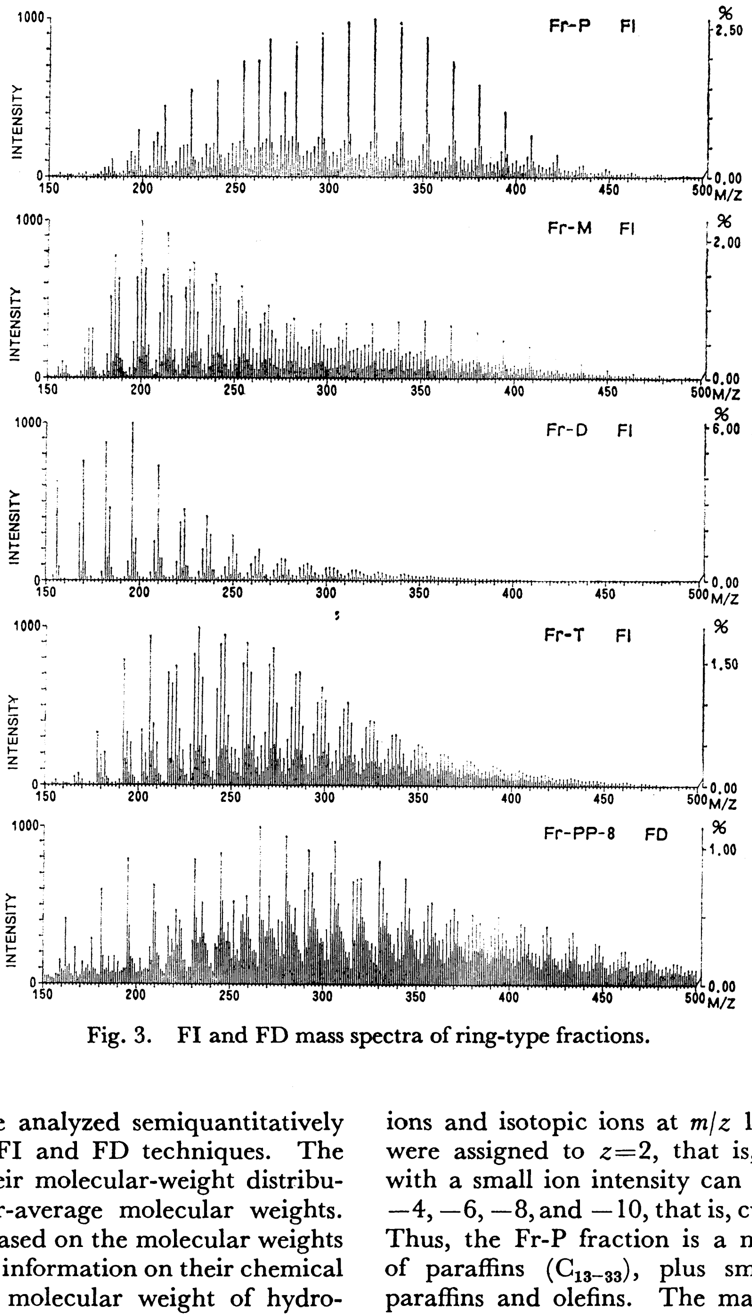

Fig. 3. FI and FD mass spectra of ring-type fractions.

of coal-derived oil can be analyzed semiquantitatively by the combined use of FI and FD techniques. The resulting spectra show their molecular-weight distribution profiles and number-average molecular weights. The group-type analysis based on the molecular weights of components should give information on their chemical structures. That is, the molecular weight of hydrocarbon is expressed by the following equation: $M = 12C_n + H_{2n+z}$, and the components in coal-derived oil can be assigned to several group types by the use of the value of z.

In the present work, the ring-type fractions of coal-derived oil separated beforehand by liquid chromatography were used as samples in order to get more detailed structural information. As is shown in Fig. 3, the molecular-weight distributions of all the ring-type fractions but Fr-PP-8 cover the mass range between m/z 150 and 450, with the dominant components of the Fr-M, -D, and -T fractions being distributed in the low-mass range of m/z 200—250. In the Fr-PP-8 fraction, the high-mass ions of nonvolatile components were detected; this proves that the FD technique is suitable for the measurement of nonvolatile components.

The FI mass spectrum of the Fr-P fraction was characterized by the regular occurrence of molecular ions and isotopic ions at m/z 14 intervals. These ions were assigned to $z=2$, that is, paraffins. Other ions with a small ion intensity can be assigned to $z=0$, -2, -4, -6, -8, and -10, that is, cycloparaffins and olefins. Thus, the Fr-P fraction is a mixture of various types of paraffins (C_{13-33}), plus small amounts of cycloparaffins and olefins. The mass spectra of the Fr-M, -D, -T, and -PP-8 fractions were more complicated than Fr-P. The Fr-M fraction consists predominantly of alkyl-substituted monocyclic aromatics, such as 1,2,3,4,4a,9,9a,10-octahydroanthracene ($z=-10$) and 1,2,3,4,5,9,10,11,12,15-decahydropyrene ($z=-12$), and is contaminated by small amounts of the components in the Fr-P fraction. Judging from the values of z, most of the peaks beyond m/z 280 must be paraffins and cycloparaffins. The FI mass spectrum of the Fr-D fraction is comparatively simple, and the dominant components are alkyl-substituted biphenyl ($z=-14$) and alkyl-substituted bicyclic aromatics such as 1,2,3,4-tetrahydrophenanthrene ($z=-14$). The components of the Fr-T fraction have more complicated skeletal structures than Fr-M and -D. The ^{1}H-NMR spectrum of the Fr-T fraction indicates that the average skeletal structure of Fr-T is not a cata type such as anthracene, but a phenanthrene type.[13] Since the Fr-PP-8 fraction

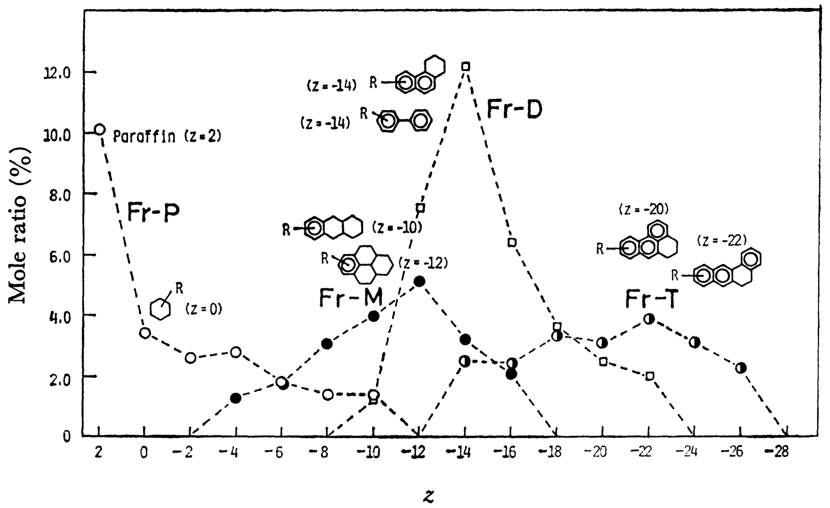

Fig. 4. Distribution of mass z series and an example of probable chemical structures for each z value.

contains the hetero atoms (oxygen and nitrogen), the assignments of the peaks must be made by using a high-resolution mass spectrometer. The distribution of the mass z series and an example of a probable chemical structure for each z value are illustrated in Fig. 4.

The FI and FD mass analysis of coal-derived oil made it possible not only to determine the molecular-weight-distribution profile, but also to speculate on the skeletal structures of components by means of group-type analysis.

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