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Identification and Quantification of Poly(oxyethylene) Alkyl Ether Nonionic Surfactants in River Water at Trace Levels by Field Desorption Mass Spectrometry

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Field desorption mass spectrometry (FDMS) was applied to the identification and quantification of poly(oxyethylene) alkyl ethers in natural waters at trace levels. The FD mass spectrum of poly(oxyethylene) (POE) derivatives, which produce $(M+H)^+$, $(M+\text{cation})^+$, and cluster ions of the type $(M_1+M_2+H)^+$, was mainly affected by emitter current, amount of sample loading, and the presence of metal salts. POE alkyl ethers were extracted from water by means of XAD-4 resin adsorption or solvent extraction under nitrogen bubbling, and determined by FDMS using tetradeuterioocta(oxyethylene) dodecyl ether as an internal standard. Sample sizes from 10^{-6} to 10^{-8} g are suitable for the quantification of POE alkyl ethers. The mole ratio of POE methyl-substituted undecyl ethers to POE dodecyl ethers was estimated by comparison with the FD mass spectra of the HPLC fractions of the extract.

Although gas chromatograph-mass spectrometry (GCMS) has successfully been applied for identification and quantification of organic pollutants in natural waters, relatively high molecular weight pollutants, which could not be determined by GCMS, remain to be analyzed. Therefore, field desorption mass spectrometry (FDMS), which is one of the most useful tools for identifying and quantifying relatively high molecular weight and thermally labile organic compounds, is being applied to the analysis of environmental samples.[1]

Use of poly(oxyethylene) (POE) derivatives nonionic surfactants in place of anionic surfactants is increasing because of their high biodegradability and low toxity in aquatic environment. Though some colorimetric determinations of POE derivatives were reported,[2,3] they have rarely been applied to the analysis of environmental samples. The reasons may be limitations of the colorimetric methods, such as the lack of selectivity and the dependence of color development upon the degree of polymerization of ethylene oxide (EO). Jones and Nickless reported that the macroreticular resin Amberlite XAD-4 was a useful adsorbent for the separation of POE derivatives from water,[4] but they could not determine individual components in environmental samples by means of UV, IR, and NMR analysis even after a long clean-up procedure.[5]

In the preceding paper, we developed a method for concentration and quantification of poly(oxyethylene) alkylphenyl ethers in water by high pressure liquid chromatograph (HPLC) with UV detector; FDMS was applied to confirm the presence of these compounds in the HPLC fractions.[6] POE alkyl ethers, however, could not be determined by this method, because they have no UV absorption. This paper describes how POE alkyl ethers in water can easily be determined by FDMS using a stable isotope labeled internal standard, and shows that the ratio of POE alkyl ethers having normal alkyl groups to those having branched alkyl groups can be estimated by HPLC-FDMS.

Experimental

Apparatus. Mass spectrometry was performed on a JEOL JMS-O1SG double focusing mass spectrometer with a combined field desorption/field ionization/electron impact ion source, connected to a JMS-2000 mass data analysis system (Japan Electric and Optics Laboratory). The FD emitter used was a 10 μm tungsten wire with carbon needles grown at high temperature.[7] An anode potential of 10 kV and a cathode potential of −3 kV were applied. Emitter current was increased linearly by use of an emitter current programmer.[8] The sample was loaded on the emitter by the microsyringe technique.[9] FD mass spectra were obtained by integration of each individual FD mass spectrum, which was measured by repetitive magnet scanning at an interval of 10 s.

HPLC was performed on a Waters ALC/GPC-204 liquid chromatograph equiped with two 6000 A pumps, a model 660 solvent programmer, a U6K injector, a model 400 UV detector operating at 254 nm, and a model R-400 RI detector.

Materials. Methanol (Mallincklodt) was nanograde and pure water was prepared by passing distilled water through a Milli-Q system(Millipore). POE dodecyl ethers and monodisperse POE dodecyl ethers (degree of polymerization; $m=1$ to 8), supplied by Daiichi Seiyaku Co., Ltd. and Tokyo Kasei Co., Ltd. respectively, were used.

Poly(oxyethylene) hexadecyl ethers were prepared from hexadecyl bromide and sodium salt of polyethylene glycol 400.

Nona- and deca(oxyethylene) dodecyl ether were prepared from dodecyl bromide and sodium salt of nona- and decaethylene glycol,[10] respectively.

Octa(oxyethylene)-$\alpha,\alpha,\beta,\beta$-$d_4$ dodecyl ether was prepared from the sodium salt of ethylene-d_4 glycol (E. Merck, G. F. R.) and 1-chloro-3,6,9,12,15,18,21-heptaoxatritriacontane, which was synthesized from thionyl chloride and hepta(oxyethylene) dodecyl ether.

These POE derivatives were purified by column chromatography (silica gel/ethyl acetate:acetone:water=55:35:10) before use. Other chemicals of the highest grades from Wako Pure Chemical Ind., Ltd. were used without further purification.

HPLC Separation of POE Alkyl Ethers. *UV Detection*: To the 200 μL solution of POE alkyl ethers (1 mg/mL ethyl acetate), freshly distilled 2 mg 3,5-dinitrobenzoyl chloride and a small piece of magnesium turnings were added, and the mixture was heated at 80 °C for 15 min. After cooling, 1 μL of the reaction mixture was injected. The mobile phase was methanol–water at the flow rate 2 mL/min and stationary phase was Radialpak C_{18} (Waters). The percentage of methanol in water was increased from 50% to

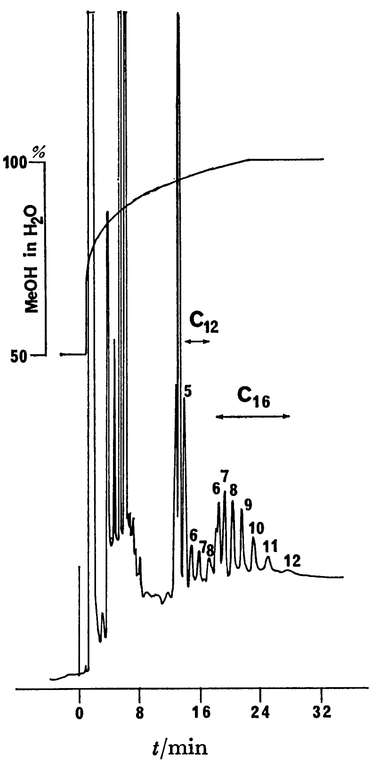

Fig. 1. Typical liquid chromatogram of the separation of POE dodecyl and hexadecyl ethers. Flow rate of 2 mL/min.

100% on the mode 2 in the Waters programmer, as shown in Fig. 1. The programming time was 20 min.

Refractive Index Detection: The Mobile phase was methanol–water (80:20) at the flow rate 1 mL/min and the stationary phase was μ-Bondapak C$_{18}$ (Waters). A sample was dissolved in methanol–water (80:20) and injected. Fractions were collected as needed. All experiments were done at ambient temperature.

Extraction from Water. XAD-4 Adsorption:[5] The resin (5 g) was mixed with acetone and the slurry was packed into the column (55 cm long × 1.1 cm I.D.). A 50 mL volume of acetone–hexane (1:1), 50 mL acetone, 100 mL ethanol, and another 50 mL acetone were passed through the column in order to wash the resin. Before use, the resin was washed with 1 L distilled water and then the water sample was passed through the column at 20 mL/min. POE derivatives were eluted by 70 mL acetone and concentrated by a rotary evaporator.

Solvent Extraction:[11] One hundred grams of sodium chloride were added to a 1 L water sample in a concentration apparatus by gas bubbling. After the sodium chloride was dissolved, 100 mL ethyl acetate was added to the sample and nitrogen saturated with ethyl acetate was bubbled through a glass filter from the bottom of the apparatus for 10 min. The upper layer was separated, and the same extraction procedure was repeated twice. The extracts were combined and concentrated by the rotary evaporator.

Results and Discussion

Concentration from Water and Separation by HPLC. Sensitive determination of POE alkyl ethers by HPLC would be possible, if they can be transformed into derivatives which have UV absorption. Thus, 3,5-dinitrobenzoyl chloride was used as a UV labeling agent. Figure 1 shows a typical liquid chromatogram of the separation of POE dodecyl ethers and POE hexadecyl ethers by gradient elution. Each peak was assigned in comparison with the retention time of standard monodisperse POE dodecyl and hexadecyl ethers. Though separation was performed according to both the carbon atom number in each alkyl group and the number of EO units, POE dodecyl ethers with less than five EO units had the same retention time and those with more than nine EO units were overlapped with POE hexadecyl ethers.

XAD-4 resin adsorption[5] and solvent extraction under nitrogen bubbling,[11] reported as excellent methods for concentration of POE derivatives, were reexamined. It was found that nearly quantitative recovery was achieved at 100 μg/L levels by both methods.

FDMS of POE Derivatives. The FD mass spectrum of POE derivatives was mainly affected by the emitter current, amount of sample on emitter, and the presence of metal salts. Table 1 a) shows characteristics of typical FD mass spectrum of poly(oxyethylene) dodecyl ethers. In contrast to the case of POE alkylphenyl ethers, protonated molecular ions $(M+H)^+$ were found in every 44 mass units corresponding to an EO unit. It was observed that lower molecular weight components of the mixture were desorbed at lower emitter currents. This temperature dependence of the spectrum was identical to that of POE alkylphenyl ethers.[8] Table 1 b) shows the effect of the amount of sample loading. When a large amount (*ca.* 10 μg) was loaded on the emitter, intense cluster ions, corresponding to two molecules plus one proton $(M_1+M_2+H)^+$, were observed. Intensities of these cluster ions were also dependent on the emitter current. At higher emitter currents (*ca.* 15 mA), these cluster ions were not observed. Table 1 c) shows the effect of the presence of metal salts. When an FD mass spectrum of POE alkyl ethers was measured after several measurements of salts of sodium, another series of ions due to attachment of sodium ions to molecules was observed. The same FD mass spectrum was obtained by pretreatment of emitter or sample by salts of sodium. FD mass spectrum of POE dodecyl ethers, which was concentrated from 10% sodium chloride solution by the solvent extraction method, shows sodium-ion-attached molecular ions $(M+Na)^+$, potassium-ion-attached molecular ions $(M+K)^+$ with weaker intensity, and no $(M+H)^+$ ion (Table 1 d).

The fact that ammonium, lithium, potassium rubidium, caesium, and silver could be involved in the ionization by cation attachment (Fig. 2) suggested that ionization of POE alkylphenyl ethers by cation attachment can occur, though they formed molecular ions under usual conditions. This was confirmed by the experiment using these salts. Especially in the case of the sample extracted from natural water by solvent extraction, $(M+Na)^+$ ions were major ion species.[12] Since many kinds of cations can be involved in ionization, special care has to be taken to prevent erroneous identification. For example, $(M+H)^+$ ions of POE hexadecyl ethers and (M+

Table 1.

a) Typical FD mass spectrum of POE dodecyl ether; 1 μg was loaded on new emitter.

m/z	319	363	407	451	495	539	583	627	671	715	759	769	803	813
Rel. int.	28	59	63	77	90	100	96	92	68	60	40	13	26	15
Assignment[a)]	H3	H4	H5	H6	H7	H8	H9	H10	H11	H12	H13	C9	H14	C10

b) FD mass spectrum of POE dodecyl ether; 10 μg was loaded on emitter.

m/z	275	319	363	407	451	495	539	561	583	593	605
Rel. int.	31	71	100	86	70	61	64	14	43	19	13
Assignment[a)]	H2	H3	H4	H5	H6	H7	H8	N8	H9	C5	N9

m/z	627	637	649	671	681	693	715	725	759	769	813
Rel. int.	40	32	13	34	45	14	20	51	13	46	46
Assignment[a)]	H10	C6	N10	H11	C7	N11	H12	C8	H13	C9	C10

c) FD mass spectrum of POE dodecyl ether measured after several measurements of sodium salts.

m/z	319	363	407	451	473	495	517	539	561	583
Rel. int.	19	30	41	59	10	73	23	97	49	100
Assignment[a)]	H3	H4	H5	H6	N6	H7	N7	H8	N8	H9

m/z	605	627	649	671	693	715	737	759	781	813
Rel. int.	54	70	59	67	42	49	35	32	22	22
Assignment[a)]	N9	H10	N10	H11	N11	H12	N12	H13	N13	H14

d) FD mass spectrum of POE dodecyl ether, which was extracted from the 10% sodium chloride solution.

m/z	429	477	517	561	577	605	621	649	665	693	709	737	781	825
Rel. int.	19	61	81	100	13	85	13	66	12	48	10	30	14	11
Assignment[a)]	N5	N6	N7	N8	K8	N9	K9	N10	K10	N11	K11	N12	K12	N13

[a)] Hm, Nm, Km, and Cm mean types of ions: *i.e.* $(M+H)^+$, $(M+Na)^+$, $(M+K)^+$, and $(M_1+M_2+H)^+$, respectively (m indicates total number of EO units in the ions).

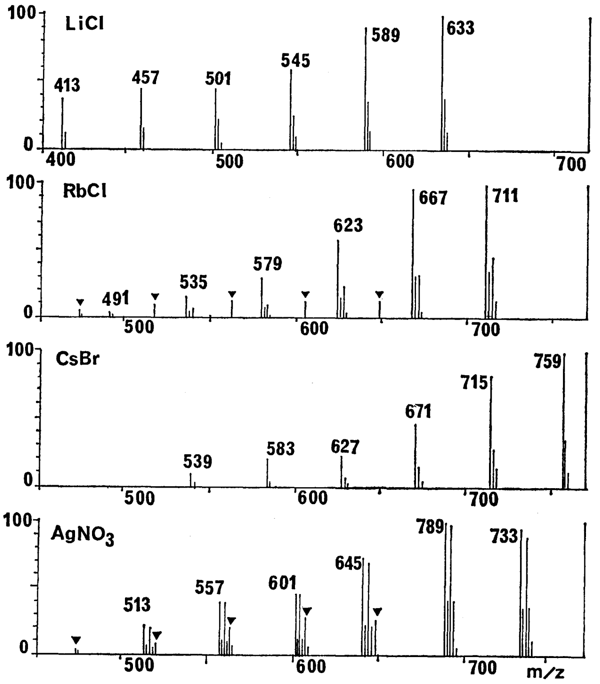

Fig. 2. FD mass spectra of equimolar mixture of monodisperse POE dodecyl ether (degree of polymerization of 5 to 10) which were measured in the presence of LiCl, RbCl, CsBr, and $AgNO_3$. ▼ indicates $(M+Na)^+$ ions of POE dodecyl ether.

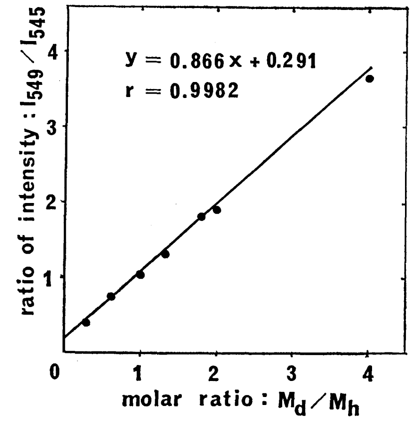

Fig. 3. Calibration curve for determination of octa(oxyethylene) dodecyl ether.

Na)$^+$ ions of POE nonylphenyl ethers gave the same m/z values. However, the two spectra could be easily differentiated by the addition of another cation source, *e.g.*, when lithium chloride was added to samples, one can observe $(M+H)^+$ ions and $(M+Na)^+$ ions to shift by 6 m/z to higher and 16 m/z to lower m/z values, respectively.

Use of a stable-isotope-labeled internal standard is essential in quantitative FDMS, because of fluctuations of ion current. In this study, tetradeuteriaoocta(oxyethylene) dodecyl ether was systhesized and used as

Table 2. Relative intensity of quasi-molecular ions $(M+Li)^+$ in the FD mass spectrum of an equimolar mixture of monodisperse poly(oxyethylene) dodecyl ether ($m=5$—10)

m	5	6	7	8	9	10
Rel. int.	59.1	76.9	83.0	100.0	120.6	97.1
SD	11	8.3	4.6	—	5.8	10
CV %	19	11	5.6	—	4.8	10

an internal standard. The calibration curve for octa(oxyethylene) dodecyl ether was constructed by use of intensities of $(M+Li)^+$ ions (m/z 545 and 549) and a good linear relationship between the amount of sample and added internal standard was obtained (Fig. 3). The reproducibility of the relative intensity of m/z 545 to m/z 549 in each FD mass spectrum was within ±3% at 10^{-7} g levels. Optimum sample size for determination was from $3—5\times10^{-6}$ g to 10^{-8} g.

The integrated FD mass spectrum was used for determination of each component which had a different degree of polymerization of EO. The relative sensitivities of each component to octa(oxyethylene) dodecyl ether were determined by using intensities of $(M+Li)^+$ ions in the integrated FD mass spectrum of an equimolar mixture of monodisperse POE dodecyl ether, which was measured in the presence of lithium nitrate. Table 2 summarizes the realtive intensities of $(M+Li)^+$ ions, its standard deviations (SD), and variation coefficient (CV). m/z 545 (degree of polymerization; $m=8$) was chosen as a base peak in order to determine the relative sensitivities to this ion. Since the relative sensitivity may reflect the ionization efficiency of each compound by lithium ion attachment, the fact that the sensitivity increases with increase in the number of EO units suggests that the EO unit plays an important role in ionization.

Application. Figure 4 shows FD mass spectrum of mixture extracted from urban stream water by XAD-4 resin adsorption. Since lithium chloride was loaded on the emitter together with the extract, $(M+Li)^+$ ions of POE compounds should be observed. The peak at m/z 549 is due to the added internal standard. Seven series of the ion peaks with differences of 44 mass units were found. The series of the peaks at m/z 1) 415, 459, 503, 547, 591; 2) 443, 487, 531, 575, 619, 663, 707; 3) 413, 457, 501, 545, 589, 633, 677, 721; 4) 427, 471, 515, 559, 603, 647, 691, 735, 779; 5) 441, 485, 529, 573, 617, 661, 705, 749; 6) 469, 513, 557, 601, 645, 689, 733, and 7) 447, 491, 535, 579, 623, 667, 711, 755 may be due to POE 1) nonyl, 2) undecyl, 3) dodecyl, 4) tridecyl, 5) tetradecyl, 6) hexadecyl, and 7) nonylphenyl ethers, respectively. Another series of peaks with difference of 58 mass units at m/z 489, 547, 605, 663, 721, and 779 may be due to $(M+Li)^+$ ions of polypropylene glycol. These identifications were confirmed from the shift of each peak in the FD mass spectrum of the same sample, which was measured in the presence of sodium citrate.

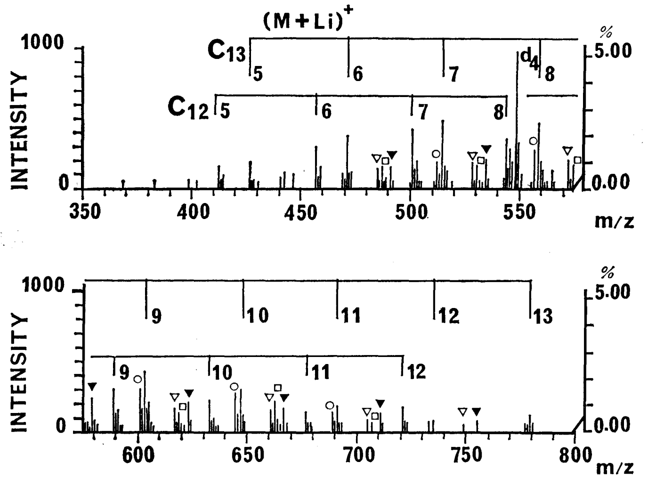

Fig. 4. FD mass spectrum of the extracted organic compounds from 1L polluted stream water. Tetradeuterioocta(oxyethylene) dodecyl ether (16.8 μg) was added as an internal standard. □, ▽, ○, and ▼ indicate $(M+Li)^+$ ions of POE undecyl, tetradecyl, hexadecyl, and nonylphenyl ethers, respectively.

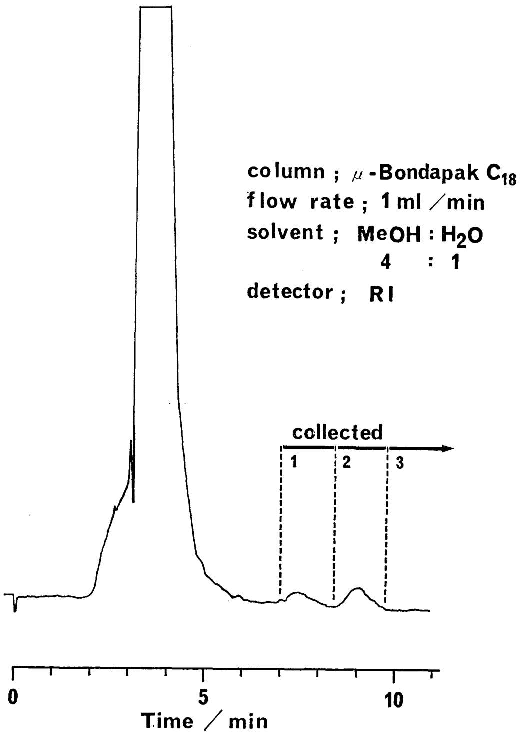

Fig. 5. Liquid chromatogram of the organic compounds extracted from polluted urban stream water.

Further confirmation was tried by HPLC fractionation followed by FDMS. Figure 5 shows the liquid chromatogram of the extract containing tetradeuterioocta(oxyethylene) dodecyl ether as the internal standard. After the large peak of unidentified compounds was eluted, fractions containing POE alkyl ethers were collected. Although POE alkyl ethers could hardly be detected by the RI detector, the presence of POE alkyl ethers was confirmed by FDMS. Figures 6 and 7 show the FD mass spectra of the fraction 1 and 3, respectively. From the analysis of the FD mass spectra, we could determine that fraction 1 contained POE nonylphenyl, dodecyl, and small amount of un-

Table 3. Concentration (μg/L) of POE-alkyl and alkylphenyl ethers in the polluted stream water

n	m 5	6	7	8	9	10	11	12	13	Total
8				1.3						1.3
9		1.7	2.7	3.1	3.6	2.9	2.1			16.1
10						4.0				4.0
11		2.1	3.1	2.9	2.6	2.4	4.5	1.5		19.2
12	3.4	5.5	7.8	6.2	4.6	4.6	2.9	3.9		39.9
13	4.2	7.2	9.2	7.3	6.6	6.4	4.0	1.8	2.8	49.5
14	2.0	2.9	3.9	3.7	2.7	3.1	2.0			20.4
16	2.7	4.0	5.8	5.7	4.6	3.1	1.7			27.5
Nonyl	2.5	3.1	4.3	4.3	3.3	3.6	2.7	1.9		25.5
Total	14.8	26.5	36.8	34.4	28.0	30.1	19.9	9.1	2.8	202.4

n and *m* indicate carbon numbers of alkyl group and numbers of EO units, respectively. Nonyl indicates POE nonylphenyl ether.

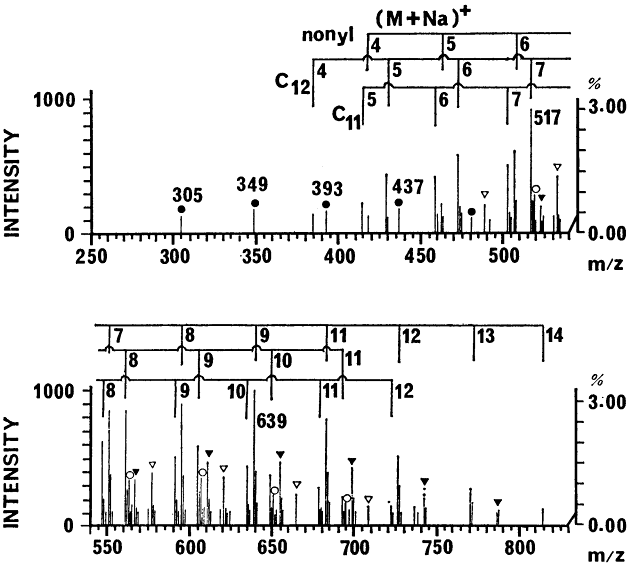

Fig. 6. FD mass spectrum of the fraction 1. ○, ▽, ▼, and ● indicate $(M+K)^+$ ions of POE undecyl, dodecyl, nonylphenyl ethers, and $(M+Na)^+$ ions of polyethylene glycol, respectively.

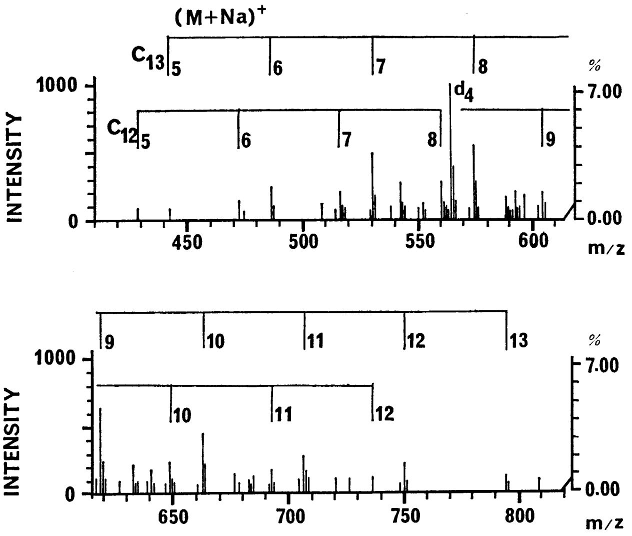

Fig. 7. FD mass spectrum of the fraction 3.

decyl ethers, and that fractions 2 and 3 contained POE dodecyl, tridecyl ethers, and the spiked internal standard. The result means that POE dodecyl ethers were contained in every fraction. In the reversed phase separation, the compounds having alkyl groups are generally eluted according to the number of carbon atoms in each alkyl group, that is, retention time increases with increase in the number of carbon atoms in each alkyl group, but compounds having branched alkyl groups have shorter retention time than those having normal alkyl groups of the same carbon number. This suggests the presence of POE compounds having branched alkyl groups in the extract. Indeed, the spiked internal standard was not found in fraction 1. Since the internal standard has a dodecyl group, the isomers of POE dodecyl ethers found in the fraction 1 may be POE methyl-substituted undecyl ethers, which are usually used as detergents. From the comparison between the relative intensity of *m/z* 545 to *m/z* 549 in fraction 3 and that in the extract (Fig. 4), the mole ratio of POE methyl-substituted undecyl ethers to POE dodecyl ethers was estimated to be 0.2.

The concentration of POE alkyl and alkylphenyl ethers were calculated on the assumption that sensitivities do not depend upon the number of carbon atom in alkyl group, and the total concentration of POE derivatives was determined to be 202 μg/L (Table 3).

The present study has demonstrated that POE alkyl ethers in water at trace levels can be easily determined by FDMS. Cation attachment ionization in FDMS makes selective and sensitive determination of POE derivatives possible. Distinction between normal and branched alkyl group in POE alkyl ethers may become possible by HPLC-FDMS.

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