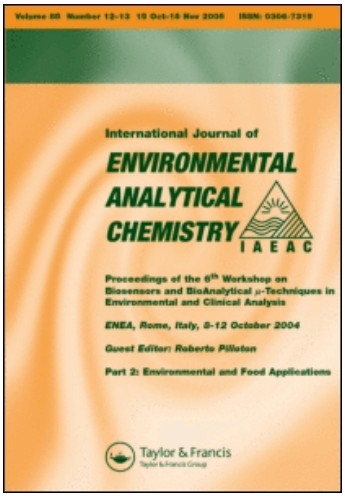

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HPLC Determination of Linear Alkylbenzenesulfonate (LAS) in Aquatic Environment. Seasonal Changes in LAS Concentration in Polluted Lake Water and Sediment

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An analytical method for linear alkylbenzenesulfonate (LAS) using HPLC was studied. It was found that the peaks of different LAS isomers with alkyl chain lengths between 11 and 14 could be separated by gradient elution with aqueous $NaClO_4$ solution and acetonitrile. The pretreatment of the LAS in the environmental samples was studied and an easy-to-use method involving solvent extraction with 4-methyl-2-pentanone was developed. By using these techniques the concentrations of the different LAS analogues in environmental samples could be measured respectively. The method was used to determine LAS in the aquatic environment; and the seasonal changes of these chemicals were clearly observed.

KEY WORDS: HPLC determination, specification of LAS, pretreatment, seasonal change of LAS in lake water and sediment.

INTRODUCTION

Linear alkylbenzenesulfonate (LAS) is a widely used anionic surfactant. In Japan, for example, about 200000 t/y of the chemical is produced for industrial and domestic detergents,[1] consequently

water pollution by the waste is a problem. Commercially used LAS is a mixture of homologues with alkyl chain lengths between 11 and 14; and moreover there are many isomers in which the site of benzenesulfonate substitution on the alkyl chain is varied. Therefore the properties of the chemicals should be different and their behavior in the aquatic environment should also vary.[2] From these, a study of the fate of each of these LAS analogues in environmental water systems is urgently needed.

A number of analytical methods for monitoring LAS have been reported. The methylene blue active substances method[3] is one of the most famous techniques, however, it is not specific for LAS. The gas chromatographic method[4,5] is both specific and sensitive but the handling of the analysis is rather complicated. High performance liquid chromatography[6–9] is one of the most useful techniques for specification of LAS.

In the present study, the analytical conditions for HPLC and the pretreatment of the samples before LAS determination were considered. The adopted method was then applied to the analysis of LAS behavior in the lake water and sediment.

MATERIALS AND APPARATUS

In the present paper the analogues of LAS are expressed as "$m\phi C_n$LAS" where "m" and "n" denote the site of benzenesulfonate substitution on the alkyl chain and the length of the alkyl chain, respectively.

All reagents used were of analytical grade. Standard surfactants were supplied by Kao Sorp Co., Japan or Wako Pure Chemical Industries Co., Japan. Percentage distribution of the different isomers for each LAS homologue are listed in Table 1.

Table 1 Percentage distribution of each LAS isomers used for standard samples

	2ϕ	3ϕ	4ϕ	5ϕ	6ϕ	7ϕ
C_{11}	35.5	22.4	17.4	24.7	nil	—[a]
C_{12}	30.3	19.9	16.4	(33.4)		—[a]
C_{13}	33.9	20.5	13.9	13.8	18.1	nil
C_{14}	31.81	18.03	12.91	14.26	22.99	nil

[a]Nonexistent.

Analysis of LAS was performed on a Shimadzu LC-4A liquid chromatograph with a Shimadzu SPD-2A spectrophotometric detector and a Shimadzu C-R3A data processor. Measurements were carried out at 222 nm. The separation of LAS was achieved with a reversed-phase ODS column, Shim-pack CLC-ODS (6.0 mmϕ × 15 cm, the guaranteed minimum number of theoretical plates is 9000.) The experiments were carried out at 298 K in a thermostated room.

CONSIDERATION OF HPLC CONDITION

HPLC determination as already reported[6–9] is usually carried out using isocratic elution media. However, under these conditions it is usually observed that the shape of the peaks in the chromatogram are not sharp and hence separation of the LAS analogues would not be clear. In the present study, in order to obtain a distinct chromatogram for each LAS isomer a gradient elution method was considered.

By trial and error, the most favorable conditions were obtained. The experimental conditions are summarized in Table 2. Figure 1 shows a typical chromatogram for standard C_{11} to C_{14} LAS isomers obtained by using the conditions listed in Table 2. As seen from Figure 1, the peak separation is not perfect, however, the area ratio for each peak was obtained by computer analysis. By comparing the area ratio for each peak in the chromatogram with the percentage distribution of each analogue listed in Table 1, the peaks could be

Table 2 HPLC condition obtained

Time/min	*% AN*[a]	*% AQ*[b]	*Mode*
0	50	50	inject
			isocratic
10	50	50	
			gradient (2% min^{-1})
25	80	20	
			isocratic
30	80	20	end

Flow rate = 1 ml min^{-1}.
[a]Acetonitrile.
[b]Aqueous 0.02 M $NaClO_4$ solution.

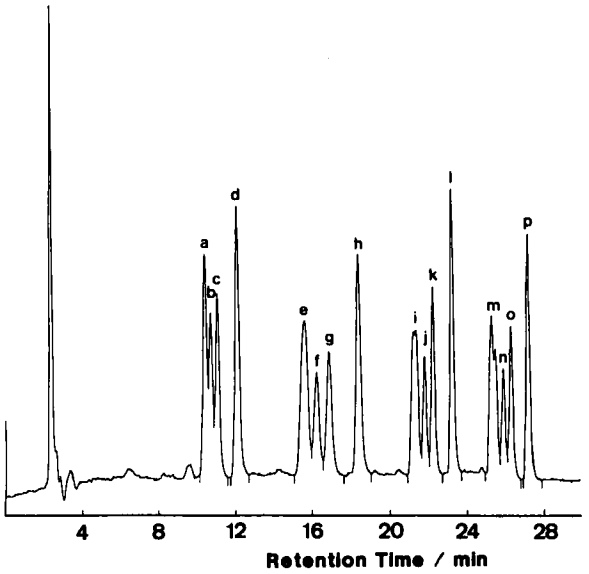

Figure 1 Typical chromatogram of LAS using the present method. Content of each LAS homologue is 0.1 μg. The peaks obtained are defined as follows: (a) 5~6ϕC_{11}, (b) 4ϕC_{11}, (c) 3ϕC_{11}, (d) 2ϕC_{11}, (e) 5~6ϕC_{12}, (f) 4ϕC_{12}, (g) 3ϕC_{12}, (h) 2ϕC_{12}, (i) 5~7ϕC_{13}, (j) 4ϕC_{13}, (k) 3ϕC_{13}, (l) 2ϕC_{13}, (m) 5~7ϕC_{14}, (n) 4ϕC_{14}, (o) 3ϕC_{14}, and (p) 2ϕC_{14}.

clearly identified as denoted in Figure 1. By using these conditions about a few ng order of each LAS analogue can be measured with a high degree of reproducibility.

PRETREATMENT OF LAS IN ENVIRONMENTAL SAMPLES

In most cases, especially in sediment samples, many substances coexisted with LAS and they often interfered with the UV determination of LAS. To avoid such problems, many methods of pretreatment have been studied. The sublation method[3] or ion-exchange method[10] is the most popular technique but the procedure is rather complicated. The method by using an ODS mini column[9] is easy-to-use and the preconcentration of the sample is high. However, this method is not suitable for UV determination because separation of LAS from

coexistence substances is not achieved completely. Moreover, for monitoring polluted aquatic systems a high degree of preconcentration is unnecessary. The solvent extraction method[11] is one of the most suitable techniques for this type of study and the possibility of using this method was considered.

At first, the extraction of LAS into the organic solvent was measured. A portion of aqueous solution containing 1 ppm of each standard homologue and an equal volume of 4-methyl-2-pentanone (MIBK) were placed in a stoppered glass tube and the two phases were agitated mechanically for 10 min. After the phase separation by centrifugation (2000 rpm for 10 min) the amount of LAS remained in the aqueous phase was determined. The extractability of LAS increased with the addition of KCl to the aqueous phase. Figure 2 shows the results obtained. More than 95% of the LAS was extracted when the concentration of added KCl was higher than 0.2 M.

Following this, back-extraction of LAS from the resulting MIBK solution was attempted. It was found that the distribution of LAS between MIBK and water was in favor of the former solvent. However, when fresh hexane was added to the organic phase LAS was stripped into the water. Figure 3 gives the percentage of back-extracted LAS as a function of the added hexane. As seen from Figure 3, it was found that recovery by back-extraction was not complete in the case of LAS homologues whose alkyl chain was longer than C_{12}. For example, when the volume ratio of MIBK, hexane, and water was 1 to 5 to 1, C_{14}LAS was stripped only about

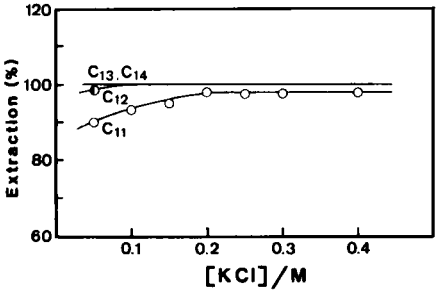

Figure 2 Effect of KCl concentration on the extraction of C_{11} to C_{14}LAS into MIBK.

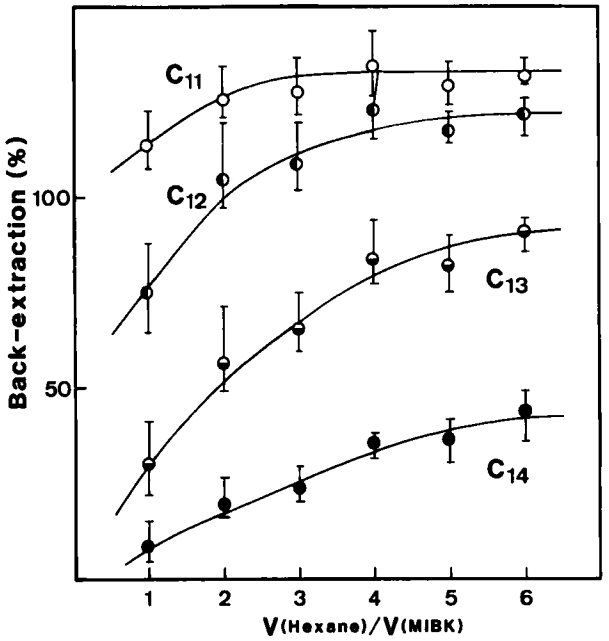

Figure 3 Recovery of C_{11} to C_{14}LAS from the MIBK phase as a function of the added volume of hexane to MIBK.

40%. However, by keeping the ratio between MIBK and water constant for both samples and standard, it was possible to accurately determine the concentration of LAS in the samples. It was also observed that recovery of C_{11} and C_{12} LAS was more than 100%, the reason for this is unknown. One possible reason could be the change in volume of the aqueous phase due to dissolution into the organic phase during extraction, however, this is not clear.

Figure 4 shows the scheme of the analytical method developed. By the first extraction LAS was separated from coexisting substances with "hydrophilic" tendency and by the next back-extraction it was separated from those with "organophilic" tendency. For example, a yellow-colored material coexisted with LAS in a sediment sample was extracted into MIBK however after back-extraction it remained in the MIBK-hexane phase and separated from the LAS.

It is possible to concentrate the LAS by the change of the volume ratio in the first extraction. However, the volume of water after the

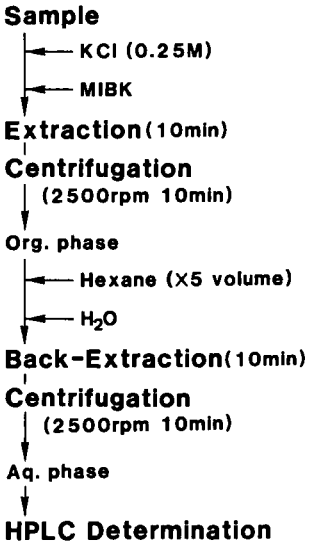

Figure 4 Scheme of the pretreatment method for LAS.

extraction decreased due to dissolution into MIBK and the magnitude of the volume change is affected by the volume ratio between water and MIBK. Consequently a more than 10 fold increase in concentration would not be necessary.

APPLICATION TO ENVIRONMENTAL SAMPLES

Monitoring of LAS in the lake water and sediment was made by using the above mentioned analytical method. Figure 5 shows a map of the sampling sites where monitoring took place. Marsh Tega is between Abiko and Kashiwa cities and due to domestic water from these cities it is regarded as the worst polluted lake in Japan, for example, average value of COD for the lake in 1985 was about $24\,mg\,l^{-1}$.[12] Sampling of the water and the sediment was made at two points in the lake as shown in Figure 5; St. 1, located at the estuary of the Oohori river, was seriously polluted by the domestic water from the basin residential area and St. 2 located at the outlet of the lake. The hydrological retention time of the lake is about 20

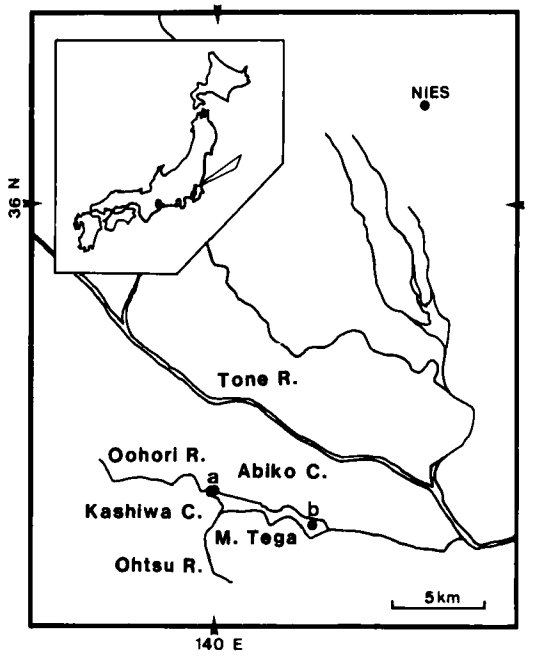

Figure 5 Illustration of the sampling sites. (a): St. 1 (Estuary of Oohori R.), (b): St. 2 (Outflow of M. Tega.), NIES: Authors' Institute.

days in winter and 15 days in summer,[13] therefore the movement of LAS from St. 1 to St. 2 can be regarded as taking about 2 to 3 weeks.

The water sample was collected directly into a polyethylene bottle from the lake surface and filtered by a glass fiber paper, GF/C (Whatman Co.) The sediment sample was collected by core-sampler and the layer from surface to 2 cm depth was used. Pretreatment of the sediment samples were made by a supersonic extraction[14] as follows. Freeze-dried sample (0.5 g) was taken into a glass tube and 10 ml of methanol was added. They were agitated in a supersonic bath for 30 min and then centrifuged. The methanol solution was collected in a volumetric flask. This extraction procedure was repeated three times and the collected methanol was filtered. The methanol solution was diluted with water (1:9 for MeOH:H_2O) and then the extraction of LAS with MIBK was done by using the

method presently developed. The coexistence of 10% of methanol did not affect the MIBK extraction procedure. Recovery of LAS was checked by the change of amount of LAS extracted as a function of the number of extractions. When the extraction was repeated more than three times the amount of LAS extracted did not increase.

Figures 6 and 7 show the seasonal changes in total LAS concentration in the water and sediment; and also the percentage distribution of each LAS analogue. As seen from Figure 6, the content of LAS both in the water and sediment varied with the change in atmospheric temperature; being increased in winter and decreased in summer. From Figure 7, it was observed that the percentage distribution of each LAS analogue varied for the different of monitoring sites and between water and sediment samples. For example, the longer alkyl chain groups and 2ϕ isomers were more evident at St. 1 than at St. 2 and they were also more evident in sediment than water.

These results may be explained by the adsorption of LAS to the sediment and/or by the biodegradation of the chemicals. In general, it is known that the order of both adsorption and biodegradation of LAS analogues is; $C_{14}>C_{13}>C_{12}>C_{11}$ and $2\phi>3\phi>4\phi>5\phi$.[7,15]

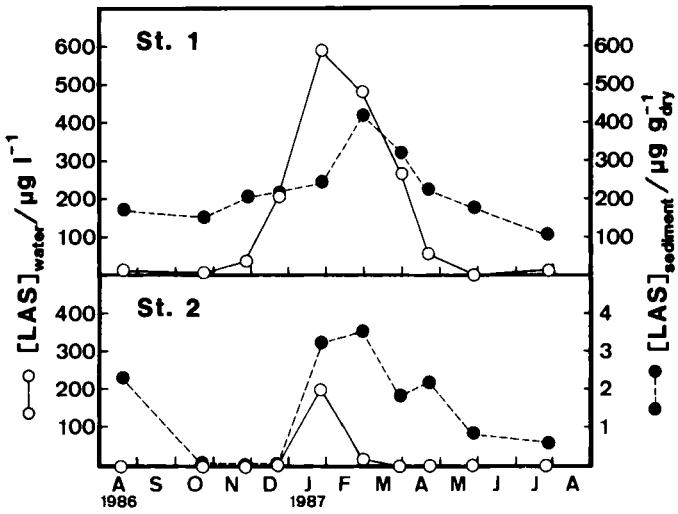

Figure 6 Seasonal changes in the total LAS concentration in water and sediment from M. Tega.

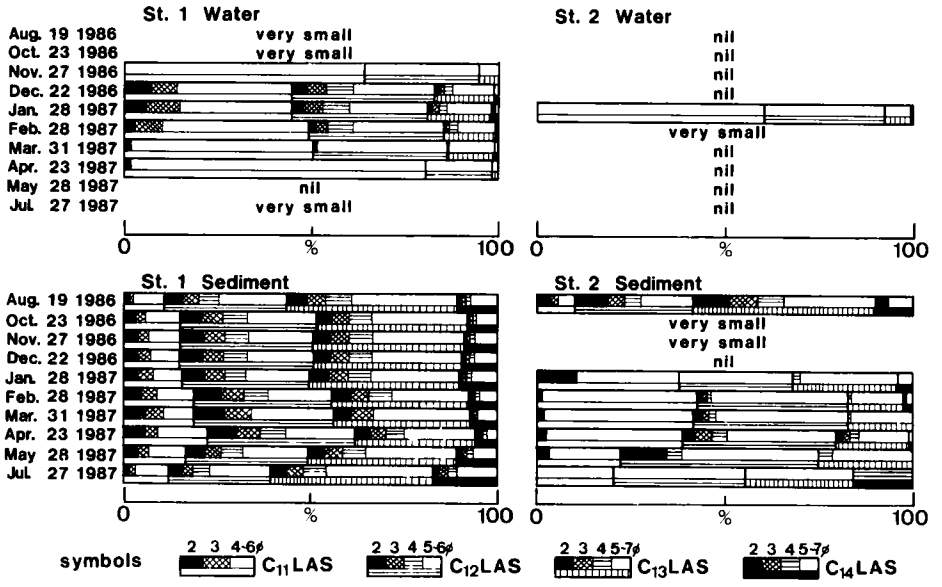

Figure 7 Seasonal changes in the percentage distribution of each LAS analogue in water and sediment from M. Tega.

It is also well known that microbial activity is affected by change in temperature, and thus, the degree of the biodegradation should also change with the temperature.[2] From this viewpoint, the decrease in LAS content during the summer may be caused by biodegradation while the difference in the distribution of LAS isomers between water and sediment may be due to the disparity in the adsorptivity of these chemicals. The differences in both content and isomer distribution between the different sampling sites appears to be caused by both effects.[7,16]

CONCLUSION

From the present study, it is concluded that the concentration of each LAS analogue which was distributed in environmental water or sediment can be determined by using HPLC with the gradient elution technique. Sensitivity of the present method is not much

higher than with the previous methods. However, easier pretreatment and clearer isomer separation makes this technique useful to analyze the fate of each LAS analogue in aquatic environment.

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