Determination of Sodium Linear Alkylbenzene Sulfonate in River Waters by High-Performance Liquid Chromatography and Concentration by Octadecylsilica Minicolumn

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Most residential wastewaters containing synthetic detergents are discharged into the environment without receiving any treatment. The main component of these synthetic detergents is an anionic surfactant typified by linear alkylbenzene sulfonate (LAS). Accordingly, a highly sensitive and simple method of determination of LAS by high performance liquid chromatography in conjunction with concentration by an octadecylsilica (ODS) minicolumn was developed. This method showed high values of 93.6%—95.5% in the recovery/addition rate and a coefficient of variation below 5%. By application of the present method to the analysis of river waters, the suspended component was shown to be responsible for the disappearance of LAS at low temperature.

Keywords anionic surfactant; sodium linear alkylbenzene sulfonate; HPLC; determination; concentration; octadecylsilica; river water; suspended solid; stability

Introduction

Most residential wastewaters containing synthetic detergents, except those treated in sewage facilities and community plants, are still being discharged into the environment without undergoing any treatment. Surfactants, the principal constituents of synthetic detergents, differ greatly by type, in their influence on aquatic organisms such as fish, their biodegradability as observed in the laboratory, and their degradation characteristics in sewage facilities.[1-4]

The total pollution load in river water around populated cities is reportedly derived primarily from residential wastewaters.[5] It is thus important to determine the conditions surrounding discharge of these residential wastewaters into a particular river in order to develop a counterplan for improving the river's water quality.

Synthetic detergent concentration in river water is one of the most significant indicators of the environment because such detergents seldom arise in nature but are the result of modern man's daily living.

The surfactants most widely used in synthetic detergents are sodium linear alkylbenzene sulfonates (LAS's). Several studies have been made on analytical methods for LAS's: calorimetries as methylene blue activating substance (MBAS) represented by the Longwell-Manice[6] method and the Abbott[7] method; gas chromatography (GC) through a derivative formation[8,9]; methyl isobutyl ketone (MIBK) extraction[10]; and high performance liquid chromatography (HPLC) using Amberite XAD-2.[11]

In recent years, HPLC[12] has been introduced for the trace analysis of the surfactants, and we have developed a series of steps to determinate LAS in sediment using this means.[13] An easy and rapid way of concentration and cleanup utilizes an octadecylsilica (ODS) cartridge, when HPLC reveals trace LAS in river water.

Experimental

Reagents Neopellex F-60®, with similar dispersion properties (C_{10} to C_{13}) as LAS in river water and available from Kaou Atlas Co., Ltd., was purified and dissolved in ethanol to prepare a LAS standard solution.[5] City water was distilled by a two-stage glass distillator, and the distilled water was purified by passing through a SEP-PAK C_{18} cartridge to remove impurities. A Waters' SEP-PAK C_{18} cartridge was used as the ODS minicolumn.

Instruments and Chromatographic Condition The liquid chromatograph was a Shimadzu LC-4A equipped with a Rheodyne syringe loading sample injector, and a Shimadzu SPD-2AS ultraviolet (UV) detector. Analyses of LAS's were carried out on a 250 × 4 mm i.d. column packed with 5 μm LiChrospher RP-8 (Merck) using acetonitrile–water (55:45) + 0.15 M sodium perchlorate as the mobile phase. The column effluent was monitored at an absorption wavelength of 225 nm. The flow-rate was maintained at 0.69 ml/min and injection volume was 50 μl. The column temperature was 52 °C. Determination of LAS (C_{10} to C_{13}) in river water specimens was carried out using a calibration curve obtained from the sum of peak-heights of LAS.

Treatment of a River Water Sample A 200 ml (maximum) specimen of river water, was filtered by suction through a GF/C glass filter, which was washed in 1 ml of methanol and 50 ml of distilled water. The filtrate together with the washings flowed down the SEP-PAK C_{18} at a rate of 30 ml/min to effect the sorption. After washing with 5 ml of water and then with 4 ml of CH_3CN–H_2O (25:75), elution was done with CH_3CN–H_2O (55:45). Exactly 1 ml of the eluate was, subjected to determination by a calibration curve obtained with 200 ml or less water containing 0—3200 ng of LAS, using a procedure similar to that for river waters.

Change of LAS Content in Specimens After original river water specimens containing 20 mg/l of suspended solid (SS) was stored in various ways, LAS in these specimens was determined using the present method to evaluate its stability in the water. Collected specimens were kept under a freezing condition at −20 °C and on given days were thawed slowly at 4 °C over 24 h to determine the remaining LAS concentration. Some specimens were stored at 4 °C with or without filtration through GF/B glass-filter paper to periodically similarly determine the concentration.

Thawed river water specimens kept at 4 °C after their storage period were examined for the effect of filtration through GF/B glass-filter paper on the residual concentration.

Results and Discussion

Pretreatment of Samples with SEP-PAK C_{18} Cartridge LAS (1 μg) was brought into a sorption on the SEP-PAK C_{18} cartridge and then was successively eluted with 1 ml of several mobile phases. Use of ethanol or chloroform made the eluate unsuitable for direct introduction into HPLC because of its marked tendency for tailing. The tailing was diminished, however, by heating the eluate in nitrogen gas to dryness and dissolving the residue in a HPLC eluant to make an HPLC specimen.

When aqueous acetonitrile was used, the eluate could directly be introduced into HPLC. When the volume ratio of acetonitrile: water was varied, eluants were examined for the elution of LAS sorbed on the cartridge. Each eluate, in an exact volume of 1 ml, was subjected to determination of LAS. Figure 1(A) shows that eluation of total LAS was not observed up to the ratio of 25:75. At ratios of 35:65 and 45:55 (Fig. 1(B, C)) the elution patterns changed depending on the number of carbons of the alkyl chain of LAS. At

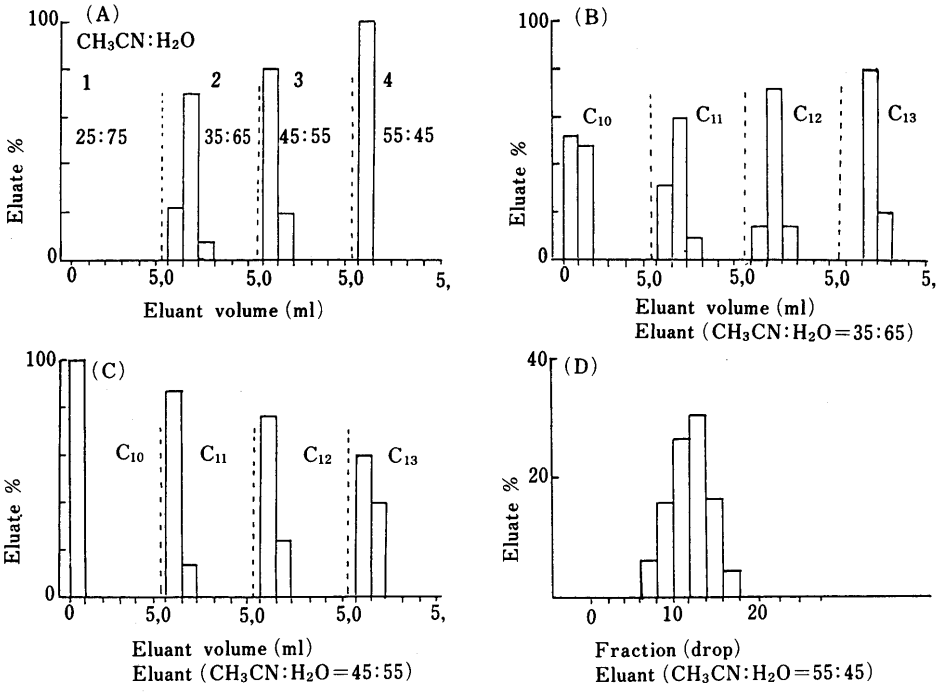

Fig. 1. Elution Pattern of LAS by ODS Minicolumn (SEP-PAK C_{18})

TABLE I. LAS Sorption and Elution Capacity of ODS Minicolumn (SEP-PAK C_{18})

	Concentration of sorption (μg/ml)					
	1.000	10.000	50.000	100.000	500.000	1000.000
Elution	0.997	9.525	47.490	96.880	482.531	820.139
	0.996	9.606	47.897	95.524	490.649	831.297
	0.995	9.660	47.962	96.880	485.835	841.766
Av.	0.996	9.597	47.783	96.428	486.353	831.085
Eluate (%)	99.6	95.9	95.5	96.4	97.2	83.1

the ratio of 55 : 45, all the LAS compounds with C_{10} to C_{13} were eluted into 1 ml of the eluate.

When the eluants CH_3CN–H_2O (55 : 45) were examined for LAS elution (10 μg) sorbed on cartridge, two drops of each eluate were subjected to determination of total LAS's. The total LAS (compounds with C_{10} to C_{13}) were eluted into 24 (1 ml) drops of the eluate (Fig. 1(D)).

Water adjusted to contain 1—1000 μg of LAS was passed through the SEP-PAK C_{18}. Elution was done with CH_3CN–H_2O (55 : 45), and the eluate was subjected to determination.

As can be seen in Table I, the cartridge had a sorption capacity of 500 μg of LAS, indicating the capability for a quantitative eluation through sorption by SEP-PAK C_{18} of a LAS from 200 ml of a 2 μg/ml LAS solution.

Determination of LAS in River Water Specimens As shown in Fig. 2(B), when the LAS of a river water specimen on SEP-PAK C_{18} was directly eluted with CH_3CN : H_2O = 55 : 45, the determination became difficult because of the abundance of impurities in the eluate. As CH_3CN : H_2O = 25 : 75 could not elute LAS, the concentration of LAS on SEP-PAK C_{18} was cleaned up, then eluted with CH_3CN : H_2O = 55 : 45, and introduced into HPLC; the chromatogram obtained is shown in Fig. 2(A).

The above procedure makes possible the removal of highly polar substances contained in river water and hence

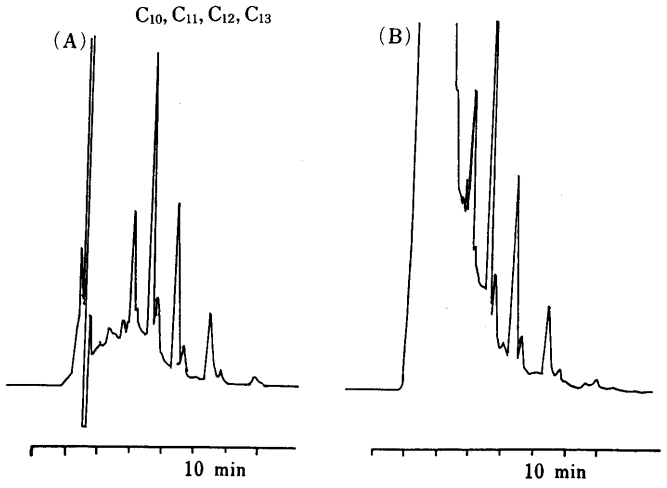

Fig. 2. HPLC Chromatograms for LAS

Packed column: LiChrospher RP-8, 5 μm, 250 × 4 mm i.d. Eluant: H_2O + 0.15 M $NaClO_4$ (pH 2.3): CH_3CN = 45 : 55, 0.69 ml/min. Temperature: 52 °C. Wavelength for detection: UV-225 nm, range = 0.005.

stabilization of the chromatogram base line. However, in some river waters the t_R values of LAS's having up to C_{10}—C_{13} overlapped each other. To avoid such overlapping, the sorption of LAS on SEP-PAK C_{18} was subjected to cleanup by letting 1 ml of 40% methanol and 4 ml of CH_3CN : H_2O = 25 : 75 successively flow down the column, and the HPLC determination was carried out by the same procedure. The final solution consisting of CH_3CN : H_2O = 55 : 45 gave results with linearity in the range of 0—160 ng, indicating that the solution can be used as a final eluant for the sorption of LAS on a SEP-PAK C_{18} (ODS) cartridge and as a solvent for introduction into HPLC.

Reproducibility of the Determination and Addition/Recovery Experiment The addition/recovery experiment was performed by addition of a definite amount of LAS to the specimen. As can be seen in Table II, reproducibility

Table II. Precision of LAS Determination and Addition/Recovery

(a)		1 μg added		2 μg added		3 μg added	
	Conc. μg/10 ml	Conc. μg/10 ml	Recovery %	Conc. μg/10 ml	Recovery %	Conc. μg/10 ml	Recovery %
	0.219	1.126	90.7	2.209	99.5	2.971	91.7
	0.207	1.133	92.6	2.069	93.1	3.142	97.8
	0.213	1.174	96.1	2.206	99.6	3.154	98.0
	0.213	1.130	91.7	2.208	99.7	3.117	96.8
	0.209	1.140	93.1	2.005	89.8	3.159	98.3
	0.215	1.163	94.8	2.017	94.6	3.004	92.6
Av.	0.212		93.1		96.0		95.8
C.V.	1.8		1.9		3.9		2.7

(b)		1 μg added		2 μg added		3 μg added	
	Conc. μg/100 ml	Conc. μg/100 ml	Recovery %	Conc. μg/100 ml	Recovery %	Conc. μg/100 ml	Recovery %
	0.203	1.133	93.1	2.056	92.7	3.044	94.7
	0.204	1.187	98.3	2.198	99.7	3.113	96.9
	0.198	1.157	95.9	2.037	91.5	3.190	99.7
	0.203	1.040	83.7	2.167	98.2	3.114	97.0
	0.197	1.160	96.3	2.085	94.4	3.098	96.7
	0.214	1.153	93.9	2.157	97.1	3.042	94.2
Av.	0.203		93.5		95.6		96.5
C.V.	2.7		5.0		3.0		1.8

Table III. LAS Analysis in River Waters

Specimen location	Concentration μg/ml	Specimen location	Concentration μg/ml
Nakiri R.	0.023	Kuma R. (upper)	0.001
Urakawa R.	0.205	Kuma R. (lower)	0.002
Koushi R.	0.013	Hikawa R.	0.003
Kikuchi R.	0.001	Sunagawa R.	0.014
Ikusue R.	<0.001	Oono R.	0.164
Sakai R.	0.024	Tenmeishinkawa R.	0.001
Tsuboi R.	0.014	Kawabe R.	<0.001
Horikawa R.	0.839	Shirakawa R.	0.018

of the determination was very satisfactory with a coefficient of variation below 5%. Concentration and cleanup have generally been practiced using an ODS cartridge[14]; the present procedure offers the aspects of precision and sensitivity, and is especially excellent in the greater ease and rapidity with which it can be accomplished compared to other methods.

Table III shows the results of determining LAS concentration of river waters by the present method.

Stability of LAS in Cryopreserved Specimens LAS disappears through biodegradation by autobiotic bacteria.[15] It has also been known that LAS can change through a sorption on suspended solid (SS) or be influenced by a complex formation with cations.[16]

As shown in Fig. 3(A), LAS in sediment specimens retains stability during the frozen storage period and 94, 93 and 90% of the initial concentration is kept respectively 14, 28 and 140 d after the freezing treatment.[17] It is thus considered that the sediment obtained in LAS analysis can be effectively stored and used as an analytical specimen.

In cryopreserved river water specimens, no LAS was lost during the frozen storage period (see Fig. 3(B)). Accordingly, frozen storage is an effective process for LAS analysis in river water similarly as in sediment. When cryopreserved river water is used as an analytical specimen, however, it must be carefully thawed over a period of time to prevent LAS decomposition and the conversion of other components. The stability of thawed specimens and conditions under which they can be kept for a shorter period of time were examined. As shown in Fig. 3(B), when an original river water specimen was stored at 4 °C without freezing or removing ordinary suspended solid, LAS concentration in the specimen decreased 50% within about 5 d; when the suspended solid had been removed earlier, 50% decrease was observed within about 10 d. In a cryopreserved specimen which had been stored and then thawed, it took about 15 d for LAS concentration to fall to 50%, and this was extended to 30 d when the suspended solid was removed.

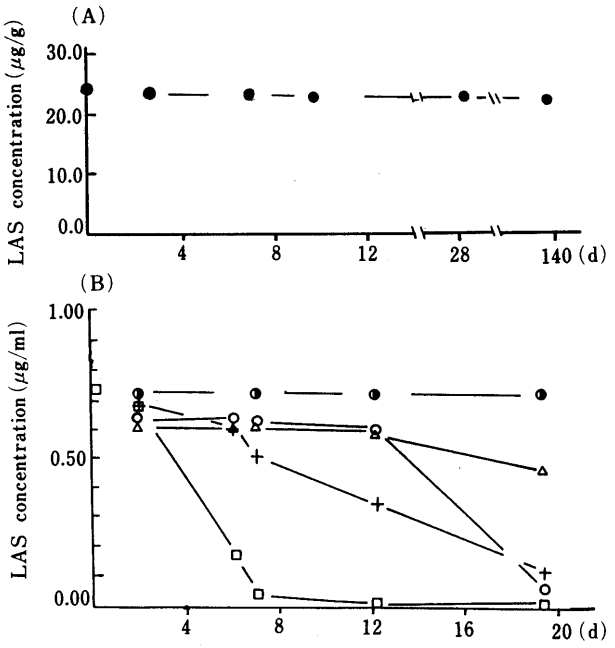

Fig. 3. Change of LAS Concentration

□: 4 °C-storage. +: 4 °C-storage (SS removed). ○: 4 °C-storage after −20 °C-freeze-thaw. △: 4 °C-storage after −20 °C-freeze-thaw (SS removed). ◑: −20 °C-storage. ●: −20 °C-storage. (A) Sediment. (B) River water.

For shorter term storage such as 2 or 3 d, it is thus sufficient to keep a specimen at 4 °C after removal of the suspended solid for later analysis. Frozen storage is the best way to keep a specimen for a long period, however, it should then be thawed carefully over a long period of time. Once thawed, it should not be frozen again for further analysis; thus, the suspended solid should be removed and the specimen kept at 4 °C.

Its suspended solid content is thought to be responsible for the disappearance of LAS in a specimen stored even at low temperature.

Conclusion

This is an easy method of measuring low-concentration LAS in water through maximum utilization of an HPLC determination system.[13] The method, was proved to be rapid and highly precise, and used an ODS minicolumn to extract, purify, and concentrate LAS in river water, the eluate then being introduced into HPLC.

Frozen storage is the best way to keep a specimen long term. Once thawed, it should not be refrozen for further analysis, and thus the suspended solid should be removed and the specimen kept at 4 °C. The suspended solid content of river water specimens is considered to be responsible for the disappearance of LAS.

References

1) Arthur D. Little, Inc., "Science of Surfactant" translated by Y. Kuroiwa, Flegulance Journal Inc., Tokyo, 1981.
2) "Investigation report of the influence of surfactant in water environment," Japan Society on Water Pollution Research, Tokyo, 1986.
3) M. Kikuchi and M. Wakabayashi, *Nippon Suisan Gakkaishi*, **50**, 1235 (1984).
4) M. Kikuchi, *Nippon Suisan Gakkaishi*, **51**, 1859 (1985).
5) Y. Yamanaka, *Yosui To Haisui*, **21**, 1005 (1979).
6) J. Longwell and W. D. Maniece, *Yosui To Haisui*, **80**, 167 (1955).
7) D. C. Abbott, *Analyst.* (London), **87**, 286 (1962).
8) T. Tsukioka, H. Seki, and K. Nagase, *Nagano-ken Eisei Kogai Kenkyujo Kenkyu Hokoku*, **2**, 28 (1980).
9) M. Imaida, T. Sumitomo, M. Yada, M. Yoshida, K. Koyama, and N. Kunita, *Shokuhin Eiseigaku Zasshi*, **16**, 218 (1975).
10) T. Matsue, Y. Osaki, and N. Shigee, *Bunseki Kagaku*, **31**, 59 (1982).
11) S. Kojima and M. Simizu, *Nagoya-shi Kogai Kenkyu Shoho*, **10**, 33 (1980).
12) Y. Suzuki and K. Tsuji, *Bunseki*, **1989**, 121.
13) Y. Ozasa and T. Tobino, *Kumamoto-ken Eisei Kogai Kenkyu Shoho*, **13**, 34 (1983).
14) A. Marcomini, S. Capri, and W. Giger, *J. Chromatogr.*, **403**, 243 (1987).
15) Y. Kobuke, *Jpn. J. Limnol*, **49**, 27 (1988).
16) A. Utsunomiya, S. Naito, and I. Tomita, *Eisei Kagaku*, **35**, 152 (1989).
17) Y. Ozasa and T. Tobino, *Kumamoto-ken Eisei Kogai Kenkyu Shoho*, **14**, 29 (1984).