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Reversed-phase high-performance liquid chromatographic determination of linear alkylbenzenesulphonates in river water at ppb[a] levels by precolumn concentration

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ABSTRACT

A high-performance liquid chromatography method for the determination of linear alkylbenzenesulphonates (LASs) in river waters has been developed. The ppb levels of LASs can be determined by reversed-phase high-performance liquid chromatography with ultraviolet detection after on-line anion-exchange concentration and successive injection. LASs were quantitatively concentrated on the anion-exchange precolumn and easily cleaned up from river water matrix, because of its specific affinity, for the anion-exchange resin. A weak non-polar reversed-phase column was useful for the determination of LASs. The relationships between concentration and summation of peak areas were linear from 10 to 200 ppb for total LAS concentrated from 5 ml of standard solutions. Overall recovery for total LAS was found to be 99%. Total LAS in the Tama River waters was determined to be around 100 ppb by the proposed method.

INTRODUCTION

Synthetic anionic surfactants are extensively used as detergents, and their subsequent direct disposal into waste water causes environmental pollution. In particular, linear alkylbenzenesulphonates (LASs), a major constituent of laundry detergents, are consumed in great quantity and discharged into environmental waters. Thus various kinds of techniques for the determination of trace levels of LASs in environmental samples such as river waters have been proposed by many workers.

Colorimetric methods [1], which provide information on total anionic surfactants in aqueous samples, are not specific for LAS.

Gas chromatography techniques have been used for the specific determination of LASs in environmental samples; however, complicated desulphonation [2,3] or derivatization [4,5] is required to convert LASs into volatile compounds.

Recently a ^{13}C NMR technique [6] has been proposed. This is, however, a qualitative method for the confirmation of LAS-type compounds.

High-performance liquid chromatography (HPLC) is widely accepted as a spe-

[a] Throughout this article, the American billion (10^9) is meant.

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cific method for the determination of LASs in various environmental samples. Nakae *et al.* have proposed a reversed-phase HPLC technique, using an ODS silica gel column, for the separation of LASs consisting of a mixture of homologues of various alkyl chain length and their phenyl position isomers [7], and for the determination of trace amounts of LASs in river waters [8]. The method seems to be useful for relatively clean samples because no clean-up procedures have been described. Ion-exchange HPLC has also been applied to the separation and determination of mixtures of ionic surfactants [9,10]. However, the methods are not suitable for the determination of LASs in environmental samples.

In order to extend the column life, the injection of environmental samples such as river waters directly into the analytical column should be avoided. In addition, it is necessary to concentrate trace levels of analytes in water for their microdetermination. Thus, several concentration and clean-up procedures prior to HPLC determination of trace levels of LASs have been proposed recently. Solvent extraction procedures [11,12] are somewhat cumbersome. Because of its simplicity, solid-phase extraction is frequently used for the prepurification of LASs from various environmental matrices [5,13–15].

This paper presents a newly developed on-line precolumn concentration and clean-up procedure prior to reversed-phase HPLC determination of LASs in river waters. Ion-exchange precolumns were successfully employed for the pretreatment of such anionic surfactants. Adequate conditioning of the precolumn was necessary for the on-line introduction of LASs into the reversed-phase analytical column. The application of this procedure to other types of anionic and cationic surfactants is also described.

EXPERIMENTAL

Chemicals

Sodium linear 4-alkylbenzenesulphonates (laundry analysis grade, C_{10}–C_{14}) as LAS standards were obtained from Wako (Osaka, Japan), hard sodium alkylbenzenesulphonates (branched ABSs) from Tokyo Kasei Kogyo (Tokyo, Japan), sodium alkylsulphates (ASs, C_{12}–C_{15}) from Asahi Denka Kogyo (Tokyo, Japan), alkyltrimethylammonium salts (ATMAs) —*n*-dodecyl-, *n*-tetradecyl- and *n*-hexadecyltrimethylammonium bromide— from Tokyo Kasei Kogyo, and sodium perchlorate and acetonitrile of guaranteed grade from Wako. Water and acetonitrile were distilled before use.

Analytical columns

A Wakosil 5C4 (150 × 4.6 mm I.D., butyl silica gels, particle size 5 μm, weak non-polar reversed-phase column) obtained from Wako was used for all analytical separations.

Precolumns

A TSK precolumn IC-Conc-A (Tosoh, anion-exchange precolumn, 10 × 3 mm I.D., capacity 2.1 μequiv. per column) was used for the concentration of LASs (or ASs), and a TSK precolumn IC-Conc-C1 (Tosoh, cation-exchange precolumn, 10 × 3 mm I.D., 0.85 μequiv. per column) was used for the concentrations of ATMAs.

Instruments

The chromatography system consisted of an Erma (Tokyo, Japan) Model ERC-3510 degasser, a Tosoh (Tokyo, Japan) Model CCPE pump, a Rheodyne (Cotati, CA, USA) 7125 sample loop injector, a Gasukuro Kogyo (Tokyo, Japan) Model 502T variable-wavelength UV detector and a Hitachi (Tokyo, Japan) Model D-2000 integrator. A Shimadzu (Kyoto, Japan) Model RID-6A refractive index (RI) detector was used for detecting UV-transparent ASs and ATMAs. The two detectors were set in series. A line filter (Gasukuro Kogyo, with a 2-μm stainless-steel frit) was located between pump and injector to remove insoluble substances resulting from abrasion of plunger seals in the pump heads and/or insoluble substances from the eluent reservoir. A column inlet filter (Rheodyne 7335) was also placed between injector and analytical column.

Chromatography conditions

Acetonitrile–water (50:50, v/v) containing 0.1 *M* sodium perchlorate was used as the mobile phase, which was sonicated for 5 min after preparation. All separations were carried out by isocratic elution at ambient temperature. The flow-rate of the mobile phase was kept at 1.0 ml/min throughout the experiments. The wavelength of the UV detector was adjusted to 220 nm for the detection of LASs.

Concentration and clean-up procedure

(1) The anion-exchange precolumn was connected to the proper valve ports of the Rheodyne 7125 injector in place of a sample loop.

(2) At the LOAD position of the valve, 1 ml of 0.1 *M* sodium perchlorate was passed through the precolumn from the needle port with a 2.5-ml gas-tight syringe (Hamilton, Reno, NV, USA) to convert the anion exchanger into ClO_4^- form.

(3) The precolumn was rinsed with 1 ml of distilled water.

(4) A 5.0-ml aliquot of sample water, previously filtered through a 0.2-μm disposable cellulose acetate filter (Advantec, Tokyo, Japan), was repeatedly introduced into the precolumn with the 2.5-ml gas-tight syringe from the needle port of the Rheodyne valve at the rate of about 5-ml/min.

(5) The needle port and the precolumn were rinsed with 1 ml of distilled water.

(6) A 1-ml sample of 0.1 *M* sodium perchlorate was passed through the precolumn. In the case of a standard or a clean solution of LASs, this step can be omitted.

(7) The precolumn was rinsed with 1 ml of distilled water.

(8) A 1-ml volume of acetonitrile–water (50:50, v/v) was passed through the precolumn.

(9)The valve was turned to the INJECTION position, and the concentrated LAS on the precolumn was introduced into the analytical column.

RESULTS AND DISCUSSION

Precolumn concentration and clean-up

Reversed-phase silica gel cartridges have been used to concentrate LASs in environmental samples [5,13]. However, it is thought, that several kinds of neutral compounds act together with LASs on the reversed-phase cartridge and therefore probably interfere with the determination of LASs. The specific concentration and clean-up of LASs seem to be difficult.

In the method presently described, the anion-exchange precolumn was efficiently used for the concentration and clean-up of LASs in river waters.

In stage 4 of the concentration procedure, described in the Experimental section, LASs were quantitatively adsorbed and concentrated on the anion-exchange resin of ClO_4^- form by means of both ion-exchange interaction and hydrophobic interaction. A 5.0-ml portion of the sample solution was injected into the precolumn correctly with using a 2.5-ml syringe with less than 0.1% deviation in the sum of the volumes. Inorganic cations and very polar compounds were removed from the precolumn by water in stage 5. In stage 6, hydrophilic anions were completely eluted from the precolumn by 0.1 *M* sodium perchlorate. LASs remain in the precolumn because of their hydrophobicity. In stage 8, non-polar compounds, non-ionic surfactants and cationic surfactants were eluted from the precolumn by the aqueous, salt-free, acetonitrile solution. LASs are never eluted from the precolumn because of ion-exchange interaction between LASs and anion-exchange resin.

The last conditioning step (stage 8) just before the injection of concentrated LASs should never be omitted. The acetonitrile concentration of the conditioning solution must be the same as that of the mobile phase used for the analytical HPLC. If this step is omitted, a large volume (the dead volume of the precolumn) of aqueous solution of different composition from that of the mobile phase containing acetonitrile is injected into the analytical column. Consequently, the equilibrium between the mobile phase and the stationary phase is destroyed, and a large number of pseudo peaks appear on the chromatogram. It then becomes difficult to differentiate the analyte peaks from the pseudo peaks. This is because of the difference in UV absorptivity between water and acetonitrile at low wavelengths such as 220 nm. In contrast, there is no baseline problem at detection wavelengths higher than 260 nm, which are unavailable for the detection of LASs. In such a case, analytes are often dissolved in the mobile phase. However, the present method does not, of course, allow rinsing of the precolumn with the mobile phase. Since 0.1 *M* sodium perchlorate is transparent to UV radiation at 220 nm, the salt-free mobile phase was adequate for the conditioning solvent of the precolumn.

Aliphatic anionic surfactants such as ASs, also concentrated in the precolumn, could be cleaned up and determined as well as LASs.

The present procedure can be applied to the prepurification of cationic surfactants such as ATMAs by using a cation-exchange precolumn in the same way.

Although non-ionic surfactants such as polyoxyethylenenonylphenylether could be concentrated into an ODS precolumn, the determination was not successful because of the loss of the analytes at the final conditioning step.

Analytical column for LAS determination

Reversed-phase HPLC with an ODS silica gel column is widely used for the qualitative analysis of LAS homologues and phenyl position isomers [7,15]. It is thought, however, that such a non-polar column is not suitable for the determination of LASs because the detection sensitivity of LASs is decreased due to the peak distribution. Recently, a weak non-polar reversed-phase column, providing a single peak for the individual homologues, has been used for the determination of LASs [15].

As a result of examining several commercially available columns for the present method, a 15-cm Wakosil 5C4 column was found to be adequate for the purpose,

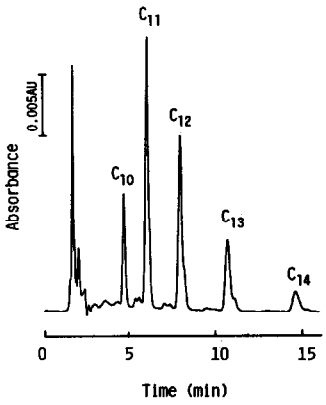

Fig. 1. Chromatogram of an LAS standard. Column: Wakosil 5C4, 150 × 4.6 mm I.D. Mobile phase: 0.1 *M* sodium perchlorate in acetonitrile–water (50:50, v/v). Flow-rate: 1 ml/min. Detection: UV 220 nm. Sample size: 100 ppb × 5.0 ml.

giving a simple chromatogram for LASs, as shown in Fig. 1. Each peak corresponds to an LAS homologue of alkyl chain length between C_{10} and C_{14}. No separation of their phenyl isomers is observed. The mobile phase system used was based on the procedure previously reported by Nakae *et al.* [7,8].

On the other hand, it seems difficult to determine branched ABSs because it gives irregularly complicated peaks at retention times between 3 and 8 min.

Quantification

It was necessary to concentrate 5 ml of a sample solution for the determination of ppb levels of LASs. Calibration plots were constructed from measurements of peak areas *versus* known concentrations of total LAS in the standard solutions. The distribution of LAS homologues was dependent on the standard LAS reagent used.

The calibration data are summarized in Table I. The total peak area calculated by the summation of areas of individual homologues was reproducible. Total

TABLE I

CALIBRATION DATA FOR LAS DETERMINATION

Alkyl chain length	C.V. (%) of peak area ($n=5$)	Regression line (10–200 ppb)[a]	Regression coefficient (r)
C_{10}	0.7	$y=0.352\cdot10^3x-0.04\cdot10^3$	0.9999
C_{11}	1.1	$y=1.004\cdot10^3x-0.01\cdot10^3$	0.9999
C_{12}	2.2	$y=0.798\cdot10^3x-0.12\cdot10^3$	0.9997
C_{13}	7.0	$y=0.463\cdot10^3x-0.64\cdot10^3$	0.9975
C_{14}	21.0	$y=0.184\cdot10^3x-1.16\cdot10^3$	0.9871
Total LAS	3.0	$y=2.800\cdot10^3x-1.94\cdot10^3$	0.9997

[a] y = Peak area (integration units); x = concentration (ppb).

TABLE II

RECOVERY DATA FOR LAS DETERMINATION ($n=3$)

	Alkyl chain length					Total LAS
	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	
Recovery (%)	96	97	98	105	104	99

amounts of LASs could be determined with a coefficient of variation (C.V.) of 3%, although the C.V. values of the peak areas of C_{13} and C_{14} homologues were relatively large. The relationship between the total LAS concentration and the total peak areas was linear from 10 to 200 ppb, although there were some differences in the linearity of the calibration plots for individual homologues. The recovery of total LAS, examined by 100 ppb standard LAS solution, was calculated to be 99%, as shown in Table II.

The method can be applied to other anionic and cationic surfactants. Typical chromatograms of ASs and ATMAs concentrated from 5 ml of sample volume are shown in Figs. 2 and 3, respectively. ATMAs concentrated on the cation-exchange precolumn were separated under the same eluting conditions as used in the LAS determination. The regression coefficients for calibration plots of ASs and ATMAs are listed in Table III. Since these surfactants have less UV detectability, their detection sensitivities are considerably lower than those of LASs. Sub-ppm to ppm levels could be determined by means of concentration of a 5 ml sample.

Interference for LAS determination

Aliphatic anionic surfactants such as ASs probably interfere in the determina-

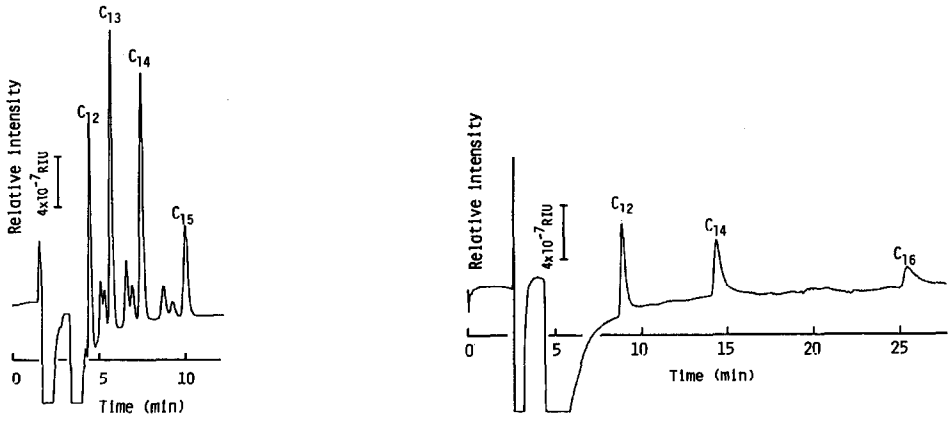

Fig. 2. Chromatogram of an AS standard. Column: Wakosil 5C4, 150 × 4.6 mm I.D. Mobile phase: 0.1 *M* sodium perchlorate in acetonitrile–water (50:50, v/v). Flow-rate: 1 ml/min. Detection: RI. Sample size: 5 ppm × 5.0 ml.

Fig. 3. Chromatogram of an ATMA standard. Column: Wakosil 5C4, 150 × 4.6 mm I.D. Mobile phase: 0.1 *M* sodium perchlorate in acetonitrile–water (50:50, v/v). Flow-rate: 1 ml/min. Detection: RI. Sample size: 500 ppb each × 5.0 ml.

TABLE III

REGRESSION COEFFICIENTS (r) OF CALIBRATION LINES FOR ASs AND ATMAs

	r					Total
	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	
AS (0.2–5 ppm)	0.999	0.999	0.999	0.996		0.999
ATMA (0.1–1 ppm)	0.997		0.996		0.973	

tion of LASs, because they act like LASs in the precolumn and are chromatographed as shown in Fig. 2. However, the amounts of intact aliphatic anionic surfactants in environmental waters are thought to be smaller than those of LASs, and their UV sensitivity is two orders of magnitude lower than that of LASs. Therefore, the influence of aliphatic anionic surfactants on the determination of LASs is negligible unless they coexist in large quantities with LASs.

Application to river waters

The total amount of LASs in the Tama River in Tokyo (sampling points: Gasu Bridge and Maruko Bridge) was determined by the proposed method. A typical chromatogram of the Tama River water (Gasu Bridge) is shown in Fig. 4. The composition of LAS homologues in Tama River was consistent with that previously reported by Nakae *et al.* [8], *i.e.* LASs in the river water consisted of shorter alkyl chain length homologues compared with the standard LASs shown in Fig. 1. The

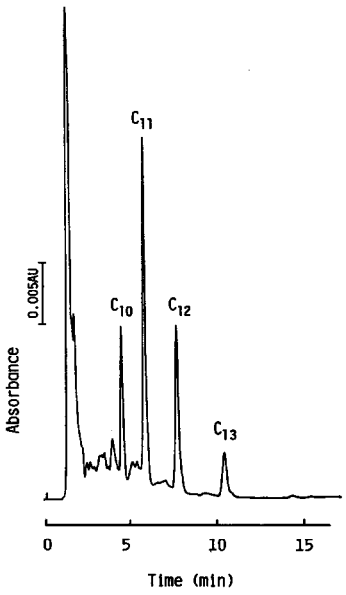

Fig. 4. Chromatogram of Tama River water (Gasu Bridge). Column: Wakosil 5C4, 150 × 4.6 mm I.D. Mobile phase: sodium perchlorate in acetonitrile–water (50:50, v/v). Flow-rate: 1 ml/min. Detection: UV 220 nm. Sample size: 5.0 ml.

alkyl chain distribution was not related to the location of the sampling point.

Total LAS was determined to be 86 ppb and 91 ppb for the river waters from Gasu Bridge and Maruko Bridge, respectively. The results were obtained 5 h after sampling.

The concentration of LASs in the Tama River waters gradually decreased after sampling, and the chromatographic peaks corresponding to LASs disappeared after 72 h at room temperature. In contrast, the 100 ppb standard LASs, which was dissolved in distilled water and stored in a polypropylene bottle at room temperature, was stable and its concentration was unchanged for a long time. Although the concentration of 100 ppb LASs dissolved in tap water did not change after 72 h, the concentration of LASs dissolved in water from the Shiraito Falls (a relatively clean environment in Japan) decreased to 70% of the initial concentration at 72 h after preparation. This may have been the result of biodegradation. The results clearly show that measurements must be made immediately after sampling if LASs in environmental waters are to be quantified accurately.

The above discussion shows that the precolumn concentration procedure presently described is useful for the immediate fixation of LASs, being easy to execute at the site of sampling. The proposed method is useful for the microdetermination of LASs in river waters.

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