Journal of Chromatography, 643 (1993) 169–172
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2720

Determination of alkylbenzenesulphonates in environmental water by anion-exchange chromatography

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ABSTRACT

A simple and selective method for the determination of μg/l levels of alkylbenzenesulphonates (ABSs) in environmental waters is presented. Selectivity for ABSs was obtained by using anion-exchange pre-column concentration followed by anion-exchange high-performance liquid chromatography separation and ultraviolet detection. The method is quantitative and easily applicable to the analysis of real samples. The concentrations of ABSs in tap water and river water were determined to be *ca.* 0.1 and 100 μg/l, respectively.

INTRODUCTION

Since various kinds of surfactants are synthesized and consumed in large quantities for various purposes, their qualitative and quantitative analyses are performed for different reasons. In many cases, the analyses of industrially produced surfactants such as detergents are relatively easy, because the analytes are the main constituents of the sample (in high concentration) and their compositions are usually less complicated [1,2]. On the other hand, identification and determination of surfactants in environmental samples are often difficult, because the concentration of the analytes in the sample is usually low and the matrix is very complex.

Since anionic surfactants are most widely used and discharged into the environment, their quantification methods have been studied by many workers. Anionic surfactants in waste water or in river water are often analysed by using several colorimetric methods based on ion-pair extraction with cationic colouring agents [3,4]. However, these methods are not specific for anionic surfactants such as alkylbenzenesulphonate (ABS), alkylsulphonate (ASO) and alkylsulphate (AS), and there are many interfering substances in environmental samples such as river water.

Recently, reversed-phase (RP) high-performance liquid chromatography (HPLC) methods have been developed for the specific determination of anionic surfactants [5–11]. Each class of ABS, ASO and AS is generally a mixture of homologues of various alkyl chain lengths and their positional isomers [1]. Therefore, a high-resolution RP column is required to separate and identify the individual homologues and isomers [7,9]. For the reliable RP-HPLC determination of ABSs it is necessary first to isolate the analytes from the sample matrices [7–11], because there are various compounds that show chromatographic behaviour similar to that of ABSs. From the standpoint of environmental analysis, it is more important to know the total amounts and the classes of anionic surfactants than the concentrations of the individual surfactants.

Ion-exchange HPLC methods have also been proposed for the determination of anionic surfactants [12,13]. The method is useful in identifying surfactant classes but inefficient in separating individual homologues and isomers. Since the anion-

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0021-9673/93/$06.00

exchange behaviour of anionic surfactants is very different from that of inorganic and hydrophilic organic anions, an anion-exchange precolumn has been skilfully used for both concentration and prepurification of linear alkylbenzenesulphonates (LASs) in river water as described in a previous paper [11]. When a sensitive and selective detector for anionic surfactants, *e.g.*, electrochemical detection [14], is developed, the ion-exchange HPLC method will facilitate their group analysis in environmental samples.

On the other hand, field desorption [15,16] and fast atom bombardment [16–18] mass spectrometry techniques have been proposed for the analysis of anionic surfactants. Although the mass spectra have demonstrated selectivities for the detection of the analytes, the methods seem to be unsuitable for routine analyses because of their expense and the high degree of skill required for their measurement.

This paper describes a simple and selective method for the determination of ABSs at μg/l levels in environmental water, using pre-column concentration followed by anion-exchange chromatography with a low-capacity column and ultraviolet detection.

EXPERIMENTAL

Reagents and samples

Three types of alkylbenzenesulphonates (ABSs) were used. Sodium linear dodecylbenzenesulphonate (C_{12} LAS, containing phenyl-position isomers) and sodium *n*-dodecylbenzenesulphonates (LASs, laundry-analysis grade, containing homologues of C_{10}–C_{14} alkyl chain length and their phenyl-position isomers) were purchased from Wako (Osaka, Japan). Sodium alkylbenzenesulphonates (branched ABSs), and sodium 4-toluene- and 4-ethylbenzenesulphonates (short-chain ABSs) were from Tokyo Kasei (Tokyo, Japan). Sodium alkylsulphates (ASs, C_{12}–C_{15}) and sodium alkylsulphonates (ASOs, C_{13}–C_{16}) were provided by Asahi Denka (Tokyo, Japan). Sodium perchlorate and acetonitrile of guaranteed grade were purchased from Wako. Water and acetonitrile were distilled before use. The above surfactants and other reagents were used without further purification.

River water, collected in polyethylene bottles, was filtered through a 0.2-μm cellulose acetate filter and stored at −20°C before analysis.

Instrument and materials

The chromatography system consisted of a Tosoh (Tokyo, Japan) CCPM metal-free pump, a Rheodyne (Cotati, CA, USA) 7125 injector with a 100-μl sample loop, a Tosoh UV-8000 UV–VIS spectrophotometric detector and a System Instrument (Tokyo, Japan) Chromatocorder 11 integrator.

A TSKgel IC-Anion-PW (Tosoh, polymer-based anion-exchange column, 50 × 4.6 mm I.D., 30 μequiv./ml) was used for the analytical separation. A TSK precolumn IC-Conc-A (Tosoh, anion-exchange precolumn, 10 × 3 mm I.D., 2.1 μequiv. per column) was used for the preliminary concentration of diluted standard or of river water.

Chromatographic conditions

Acetonitrile–water (40/60, v/v) containing 10 m*M* sodium perchlorate was used as the mobile phase. The flow-rate was 1.0 ml/min. The detection wavelength was 220 nm. All separations were performed by isocratic elution at ambient temperature. The sample size was 100 μl for direct injections.

Concentration of ABS in water sample

The concentration and clean-up procedure was the same as described in a previous paper [11]. An aliquot of 10–100 ml of water sample was passed through the precolumn (ClO_4^- form) by using a conventional LC pump at a flow-rate of 2 ml/min. Water, 0.1 *M* sodium perchlorate, water and acetonitrile–water (50:50, v/v) were then passed through the precolumn in order.

RESULTS AND DISCUSSION

Separation column

A silica-based anion-exchange column such as Tosoh TSKgel IC-Anion-SW was not suitable for the separation, because its column life was shortened as a result of irreversible adsorption of environmental matrices. Although IC-Anion-PW is not guaranteed for the use of organic solvent, the column performance was unchanged in more than 6 months.

Chromatographic conditions

Acetonitrile–aqueous sodium perchlorate solution was used as the mobile phase for the anion-

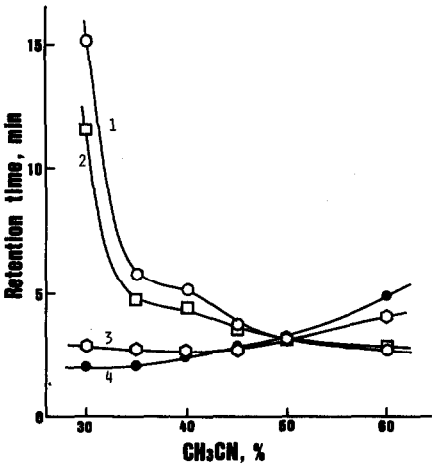

Fig. 1. Effect of acetonitrile concentration of the mobile phase (10 m*M* sodium perchlorate) on the retention times of LASs (1), branched ABSs (2), short-chain ABSs (3) and nitrate (4) ions.

exchange separations because of the hydrophobicity of anionic surfactants [11]. A methanol–water system was not suitable because of its high viscosity. ClO_4^- was used as the eluting ion because of its UV transparency and eluting power.

Fig. 1 shows the effect of the acetonitrile concentration of the mobile phase (10 m*M* sodium perchlorate) on retention of LASs, branched ABSs, short-chain ABSs and nitrate ions. The retention times of such small ions were independent of acetonitrile concentration, but those of the long-chain ABSs were greatly changed. The peak sharpness was improved by an increase in the acetonitrile concentration. At a concentration of 50% (v/v) acetonitrile, the retention times of the small and the large ions were nearly the same. Therefore, 35–40% (v/v) acetonitrile was adequate for the separation.

Fig. 2 shows the relationship between the concentration of sodium perchlorate and the capacity factor (k') of C_{12} LAS, LASs and ABSs. Both logarithmic plots were linear, and the slope for each analyte was 0.95. This indicates the ion-exchange elution of monovalent analyte ions by monovalent eluting ions [19]. Using as a criterion the separation of ABS ions and NO_3^-, 10 m*M* of sodium perchlorate was chosen.

Under these conditions, the analytes provided a single peak, which was somewhat broadened by the presence of many homologous compounds.

Quantitative analysis

Fig. 3 shows chromatograms of LAS standard in three different concentrations of 2 mg/l (sample size: 100 μl), 20 μg/l (10 ml) and 2 μg/l (100 ml). The relationship between the concentration and the peak area was linear from 0.1 to 10 mg/l for direct injections. The pre-column concentration followed by the analytical anion-exchange chromatography was nearly quantitative, and recoveries were nearly 100%.

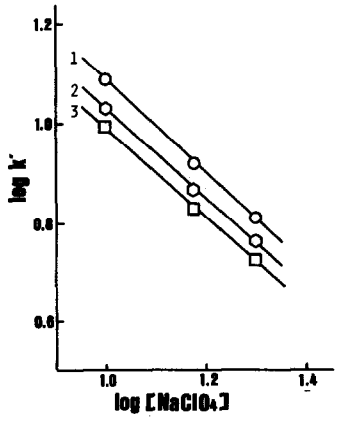

Fig. 2. Relationship between the concentration of sodium perchlorate and the capacity factor (k') of C_{12} LAS (1), LASs (2) and branched ABSs (3), in 35% (v/v) acetonitrile.

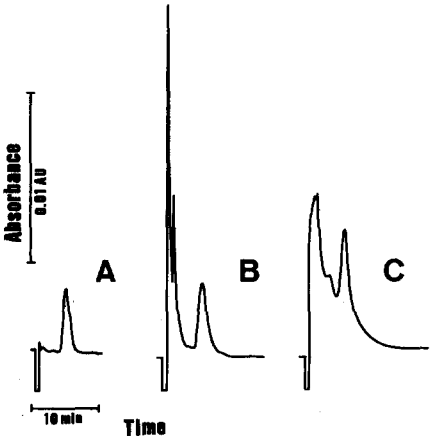

Fig. 3. Chromatograms of LAS standard in concentration of (A) 2 mg/l (× 100 μl), (B) 20 μg/l (× 10 ml) and (C) 2 μg/l (× 100 ml). For conditions, see text.

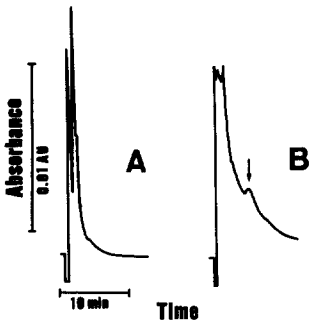

Fig. 4. Chromatograms of 100 ml of (A) Milli-Q water and (B) tap water. For conditions, see text.

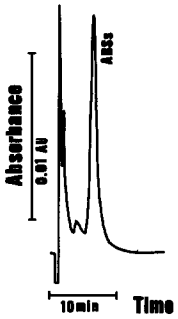

Fig. 5. Chromatogram of 2 ml of Tama River water. For conditions, see text.

Selectivity

The preliminary concentration and clean-up procedure was fairly selective for anionic surfactants. Hydrophilic neutral species and common anions and cations are removed from the analytes by passing 0.1 *M* sodium perchlorate through the precolumn. Most hydrophobic neutral and cationic species are also removed by passing acetonitrile–water (50:50). Moreover, the presence of cationic and non-ionic surfactants did not affect the determination of ABSs, because they were eluted near the solvent front. Although aliphatic anionic surfactants such as ASs and ASOs act like ABSs in the present method, they were eluted before ABSs under the proposed chromatographic conditions. Likewise their UV transparency did not affect the determination of ABSs.

Application to the analisis of river water

Fig. 4 shows the chromatograms of 100 ml of Milli-Q (Nihon Millipore) water and tap water. ABSs were not detected in the Milli-Q water but were detected in the tap water (*ca.* 0.1 μg/l).

Fig. 5 shows the chromatogram of 2 ml of river water from the Tama River in Tokyo. When the sample (50 μl) was directly injected into the analytical column, the UV-absorbing nitrate was detected as an extremely large peak. The concentration of total ABSs in the river water was about 100 μg/l.

Since the previously reported method using a reversed-phase HPLC [11] was not applicable to the determination of branched ABSs, the present anion-exchange method is useful for the quantitative evaluation of total amounts of ABSs.

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