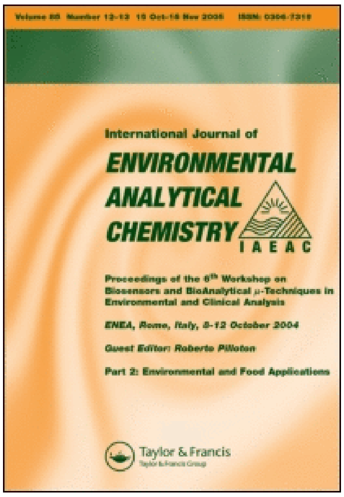

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DETERMINATION OF NONIONIC SURFACTANTS IN RIVER WATER USING A CHEMICALLY MODIFIED STYRENE-DIVINYLBENZENE RESIN

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A highly sensitive and simple method for the determination of heptaoxyethylene dodecylether (HOE) by fluorescent derivatized high performance liquid chromatography in conjunction with preconcentration by an α-hydroxyethylated styrene-divinylbenzene resin column was developed. This method showed a recovery rate as high as 92% with a standard deviation below 10%. The lower limit of determination in river water was 1 μg/l.

KEY WORDS: Chemically modified resin, nonionic surfactant, preconcentration, fluorescent derivatization, HPLC, river water

INTRODUCTION

Synthetic surfactants, which are chemical substances not existing in nature but discharged as a result of human activity, can serve as an indicator for assessing the river water pollution caused by household wastewaters[1,2]. Several methods have been developed for their determination[3–6], among which high performance liquid chromatography (HPLC) using UV absorption or fluorescence emission detection has been found very useful[7–10]. However, environmental waters have a low concentration of surfactants with frequent coexistence of complex foreign substances. Therefore, their determination require pretreatment and preconcentration, which can probably be done simply and conveniently by the use of an adsorbent[11,12].

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In the present paper we describe a new adsorbent derived by the introduction of a functional group with a hydrophilic part (α-oxoalkyl or α-hydroxyalkyl groups) into the hydrophobic styrene-divinylbenzene resin. The resin should interact with the hydrophilic and the hydrophobic moieties of nonionic surfactants[13,14]. The α-hydroxyethylated resin, which exhibited the highest adsorbing capacity among the resins prepared, was then subjected to fundamental investigations for its application as a preconcentrating agent for nonionic surfactants, and further applied to the determination of nonionic surfactants in river water samples.

EXPERIMENTAL

Materials and instruments

The styrene-divinylbenzene (St-DVB) resin (10.0% DVB, MR type, 100–200 mesh), synthesized by suspension polymerization[15] was used as the starting material to be chemically modified (Figure 1)[13,14]. Triethylamine and 9-anthroylnitrile were products of Wako Pure-Chemical Industries LTD (Osaka, Japan). Heptaoxyethylene-dodecylether (HOE), the standard surfactant, was purchased from Wako Pure-Chemical Industries LTD (Osaka, Japan).

A column (150 × 10 mm I.D.) packed with α-hydroxyethylated resin, which was found to provide good results in batch and column processes was used[13,14]. HOE, the standard substance in the JIS method[16], was used as the nonionic surfactant, with consideration for application with the samples.

The HPLC instrument used was a Hitachi Liquid Chromatograph 665A-12 (Hitachi Co., Ltd, Tokyo, Japan). The fluorimetric detector was a Hitachi Fluorescence Detector F-1050 (Hitachi Co., Ltd, Tokyo, Japan).

Preconcentration and determination of nonionic surfactants

The HOE surfactant solution was prepared to flow down at a rate of 0.3 ml/min by use of a microtube pump (Tokyo Rika, MP-3) through a glass column (150 × 10 mm I.D.), packed

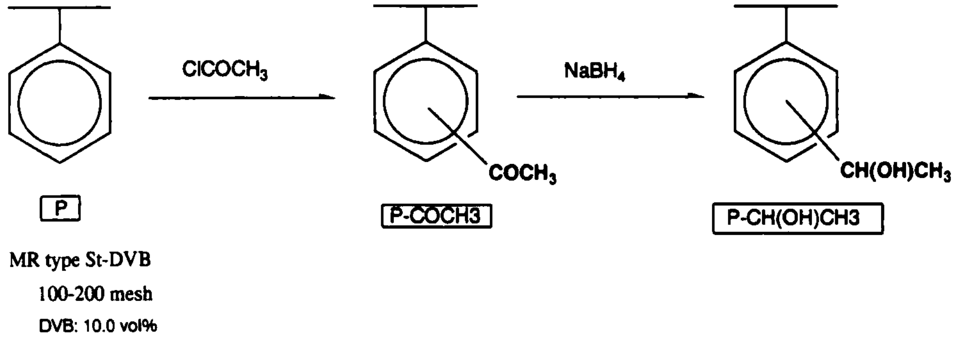

Figure 1 Synthetic route of the α-hydroxyethylated resin

Figure 2 Chromatogram of heptaoxyethylene dodecylether (HOE) in Kengun river water
Column: LiChrosorb RP-18, 5 µm, 4 mm I.D. × 250 mm
Eluant: H_2O: CH_3CN=20:80, 1.5 ml min^{-1}
Temperature: 52°C
Detection fluorescence wavelength: Ex395 nm, E_M 450 nm

with 1.0 g of α-hydroxyethylated resin. After washing the column with water, the surfactant adsorbed was eluted with 10 ml of ethanol. The ethanol was evaporated under reduced pressure, the residue was redissolved in 1 ml of acetonitrile containing triethylamine (0.2%), and the surfactant was derivatized via reaction with 9-anthroylnitrile (1 mg) for two hours at 45°C[17]

Determinations were carried by HPLC, using a LiChrosorb RP-18 column (5 µm, 250 × 4 mm I.D., Merk Co., Ltd, Darmstadt Germany). The mobile phase, 80% aqueous solution of acetonitrile, was passed at a flow rate of 1.5 ml/min, and the detection was made by UV-fluorescence with an excitation wavelength of 395 nm and a fluorescence wavelength of 450 nm.

Preparation of real water samples

Environmental samples consisted in river water (of several places in Kumamoto Prefecture), filtered through a glass fiber filter (GF/C, Whatman International Ltd, Maidstone England).

RESULTS AND DISCUSSION

Preconcentration of nonionic surfactants

Table 1 shows the results of the determination for the test solution prepared by addition of 0.10, 0.50, 1.00, 2.50, 5.00 and 10.00 µg of HOE to 100 ml of distilled water. The recovery rates all exceeded 92%.

The effect of flow rate, for test solutions passed through the column, is illustrated in Table 2. The recovery rates for the flow rates of 0.20, 0.33, 0.53, 0.66, 3.33, 6.66 and 13.33 bed volume/ml (0.3, 0.5, 0.8, 1.0, 5.0, 10.0 and 20.0 ml/min) indicated that they tend to drop

Table 1 Precision and recovery of HOE added to distilled water.

Added µg	*Found* µg					*Average Recovery* %
0.10	0.09	0.08	0.09	0.11	0.09	92.0±9.7
0.50	0.48	0.52	0.49	0.48	0.49	98.4±2.9
1.00	0.94	1.05	0.97	1.11	0.98	101.0±6.1
2.50	2.34	2.30	2.49	2.51	2.43	96.5±3.2
5.00	4.88	4.71	5.50	4.81	4.82	98.8±5.6
10.00	9.89	9.82	9.25	10.07	9.88	98.0±2.8

Sample volume: 100 ml

Table 2 Effect of flow rate on recovery of HOE using α-hydroxyethylated resin column.

Flow rate ml/min (bed vol./min)	*Average recovery % (n=3)*
0.3(0.20)	96.5±3.2
0.5(0.33)	97.6±8.4
0.8(0.53)	94.5±5.3
1.0(0.66)	90.2±6.7
5.0(3.33)	89.2±3.4
10.0(6.66)	86.5±5.6
20.0(13.33)	73.8±10.7

HOE concentration: 25 µg/l

slightly when the flow rate raises over 10 ml/min, but even at this rate satisfactory adsorption can be obtained for practical determination. Rapid operation is very important in practice, to ensure the determination of a large number of samples in a short time.

Repetition of the enrichment procedure may give rise to repeated swellings and contractions of the resin, which might affect its durability. However, actually less than one-hundred repetitions did not change the resin at all, suggesting sufficient durability.

The effect of foreign substances on the recovery rate was next investigated. Particularly, anionic surfactants, coexisting as surfactants in the water samples, can competitively interfere the determination of HOE in the cobalt thiocyanate method (JIS method)[17]. However, as shown in Table 3 dodecylbenzene sulphonate (DBS) had no significant effect in the present procedure.

The effect of humic acids, an ubiquitously organic substance found in surface water and having a hydrophilic part like a surfactant, and decaethylene glycol nonylphenyl monoether (NP-EO(10)) were also investigated, but they were found not to interfere in the recovery of HOE.

Determination for environmental samples

As described above, the preconcentration method using α-hydroxyethylated resin was considered to be applicable to the determination of nonionic surfactants in environmental

Table 3 Effect of foreign substances on recovery of HOE.

Compound	*Added*	*HOE % recovery (n=3)*
DBS	10μg	102.1±9.2
	100μg	96.4±6.5
Humic acid	5mg	94.8±4.3
	10mg	94.4±8.2
NP-EO(10)	2.5μg	96.5±2.4
	10μg	96.4±4.3

Sample volume: 100 ml; HOE concentration: 25 μg/l
DBS: Dodecylbenzenesulphonate
NP-EO(10); Decaethyleneglycol nonylphenyl monoether

Table 4 Analysis of HOE in river water samples.

Specimen (Location)	*Added μg*	*Found μg/100ml (n=3)*	*Recovery %*
Shirakawa (meigo-bridge)	0	<0.10	
	2.50	2.30	92.0±4.4
Midorikawa (jounan-bridge)	0	<0.10	
	2.50	2.51	100.4±3.7
Tsuboikawa (rokkou-bridge)	0	<0.10	
	2.50	2.43	97.2±3.5
Kengunkawa (shinhoka)	0	1.10	
	2.50	3.52	96.8±3.9

Sample volume: 100 ml

water samples. Using a column packed with this resin, several river water specimens were further analysed. The results are indicated in Table 4. The present preconcentration method was found to give high recovery rates even with river water. As an example, for a specimen taken in Kengun River (an illustrative chromatogram is shown in Figure 2), the existence of a nonionic surfactant in such a trace amount, that was below the sensitivity of the JIS method (<10 μg/100ml), was confirmed. However, nonionic surfactants were not found in the water of other rivers even by the present method.

Household detergents are usually a well known source of surfactants in rivers. They contain anionic species as their main component, and also polyoxyethylene (POE)-type nonionic components although in small quantities. Kengun River,[18] where nonionic surfactants were detected in the present investigation, is situated relatively upstream the densely populated districts of Kumamoto City still having inadequate sewage treatment facilities, and moreover, is a river having a low rate of headstream water and a higher rate of household wastewater. Nonionic surfactants were expected to exist in Kengun River. However, they were difficult to determine by the JIS method, because of presence of anionic surfactants, the main components of home detergents, and the low sensitivity of the method (Table 5).

Table 5 Water quality of river water.

Specimen (Location)	*pH*	*BOD*[(a)] *mg/L*	*Nonionic*[(b)] *surfactant* *µg/100 ml*
Shirakawa (meigo-bridge)	7.2	1.2	<10
Midorikawa (jounan-bridge)	7.6	<0.5	<10
Tsuboikawa (rokkou-bridge)	7.5	2.4	<10
Kengunkawa (shinhoka)	8.9	12.6	<10

a; biochemical oxygen demand
b; cobalt thiocyanate method

CONCLUSION

The present fluorescent derivatized HPLC method using α-hydroxyethylated resin as the preconcentrating agent was found to be capable of determining trace quantities of nonionic surfactants in river water, probably originated from household detergents.

High recovery rates were obtained in addition experiments with a wide variety of conditions. In river water specimens, the determination limit of the cobalt thiocyanate method (JIS method) was 10 µg/100ml for HOE, but that of the present method was 0.10 µg/100ml for HOE.

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