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Concentration of chlorophenols in water with sodium dodecylsulfate–γ-alumina admicelles for high-performance liquid chromatographic analysis

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Abstract

Chlorophenols in water were sorbed onto sodium dodecylsulfate (SDS)–alumina (γ-form) admicelles. The extent of sorption increased with increasing amount of SDS and decreasing solution pH. Conditions for good recovery were obtained when 100 mg SDS and 1.5 g alumina was used at pH 2. However, the yield decreased with a further increase in the SDS concentration due to the formation of normal SDS micelles. The extent of sorption also increased with increasing hydrophobicity of the chlorophenol, indicating that hydrophobic interactions predominate for the collection of analytes. When a cartridge column filled with admicelles was used, >90% of tetrachlorophenol and pentachlorophenol in 200 ml of water samples were rapidly recovered. The sorbed analytes were eluted with 1 ml acetonitrile. The accuracy and precision of the present method were demonstrated for the HPLC analysis with ultraviolet (290 nm) detection of μg l^{-1} levels of tetrachlorophenol and pentachlorophenol in river water samples.

Keywords: Micelles; Water analysis; Environmental analysis; Admicelles; Chlorophenols; Phenols; Alumina; Sodium dodecylsulfate

1. Introduction

Surfactant molecules tend to aggregate and thus form micelles that can incorporate hydrophobic compounds. Such properties of surfactant micelles have been used extensively for the basis of several efficient separation methodologies, including cloud-point extraction [1–4] and micelle-enhanced ultrafiltration [5,6]. However, micelles are extremely small and hence are difficult to separate from the bulk aqueous solution. Additionally, the viscous properties of concentrated micellar solutions significantly reduce the efficiency of concentration and the manipulation of micelle-mediated separation techniques.

Recently, we established a novel concentration method based on the sorption of hydrophobic metal chelates onto surfactant-coated solid surfaces, in which negatively charged sodium dodecylsulfate (SDS) molecules cooperatively adsorb onto positively charged γ-alumina surfaces in acidic media and

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form aggregates termed admicelles [7–13]. Traces of heavy metal ions in water were efficiently collected into the admicelles after the formation of hydrophobic metal chelates with appropriate chelating agents. The sorption of metal chelates can be explained by the incorporation of the chelates into the hydrophobic medium provided by the admicelles. Although basic studies on the incorporation of hydrophobic organic compounds in water have been performed [14–16], there have been few applications of admicelles in the area of trace analysis of organic substances.

Among organic compounds, chlorophenols are important analytes because they are used extensively as preservative agents, fungicides, pesticides, antiseptics, disinfectants, and intermediates in many industries [17–19]. Recently, it was also pointed out that chlorophenols are generated by the chlorine treatment of drinking water [20]. These compounds are carcinogenic and remarkably persistent [21,22]. Thus, a rapid and efficient method is required for concentrating these analytes in different water samples prior to instrumental analysis.

In this study, an admicelle-mediated separation methodology was applied to concentrate traces of chlorophenols in water. The analytes, with different numbers of chloro substituents, were collected into SDS–γ-alumina admicelles in order to clarify the predominant factor for their incorporation. The prerequisites for performing a rapid and efficient concentration were investigated. The compatibility of the present method with HPLC analysis with photometric detection was examined.

2. Experimental

2.1. Chemicals and materials

Alumina (γ-form, 10–50 μm, for column chromatography, Katayama Chemicals, Osaka, Japan) was washed ultrasonically with 1 *M* nitric acid for 3 min and thoroughly rinsed with water. A Bond Elut Jr. cartridge column (Varian, Victoria, Australia), filled with 500 mg alumina, was employed after rinsing with 50 ml 0.01 *M* nitric acid. SDS (for biochemistry) was purchased from Wako (Tokyo, Japan). Chlorophenols (2-chlorophenol, 2,4-dichlorophenol, 2,3,4-trichlorophenol, 2,3,4,6-tetrachlorophenol, and pentachlorophenol) were obtained from Tokyo Kasei (Tokyo, Japan). Other reagents used were of analytical grade. Water was prepared using a Milli-Q SP reagent water system from Millipore (Milford, MA, USA).

2.2. Batch extraction

To prepare admicelles, an aqueous solution containing 0–250 mg SDS was added to an aqueous suspension of 1.5 g γ-alumina with vigorous mixing. The solution pH was adjusted to 2.0 with nitric acid. The total volume of the solution system was 50 ml. To the admicelle system was added 50 μl ethanol solution containing 1 m*M* chlorophenols. After shaking the solution for 5 min, a 20-μl aliquot of the supernatant was injected into the HPLC system, which consisted of a Jasco (Tokyo, Japan) PU-980 intelligent pump, a UV-970 intelligent ultraviolet detector, and an 807-IT integrator. A 60% (v/v) aqueous acetonitrile solution was used as mobile phase. The wavelength employed for monitoring chlorophenols was 290 nm.

2.3. Column method

To prepare the admicelle column, 50 ml 0.01 *M* nitric acid containing 33 mg SDS was passed through a Bond Elut Jr. cartridge column. River water sampled from the Nagara River (Gifu, Japan) was centrifuged at 10 000 rpm for 30 min in order to remove suspended solids. The sample solution (200 ml) was adjusted to pH 2 by the addition of concentrated nitric acid. Sample loading was performed by injecting the sample solution into the column with a glass syringe. After washing the column with 50 ml Milli-Q water, chlorophenols were eluted with 1.0 ml acetonitrile. A 20-μl aliquot of the eluate was injected into the HPLC system, where the operating conditions were the same as those described above.

3. Results and discussion

3.1. Effect of the amount of SDS

In the absence of SDS, chlorophenols hardly sorb onto γ-alumina. In contrast, the extent of sorption

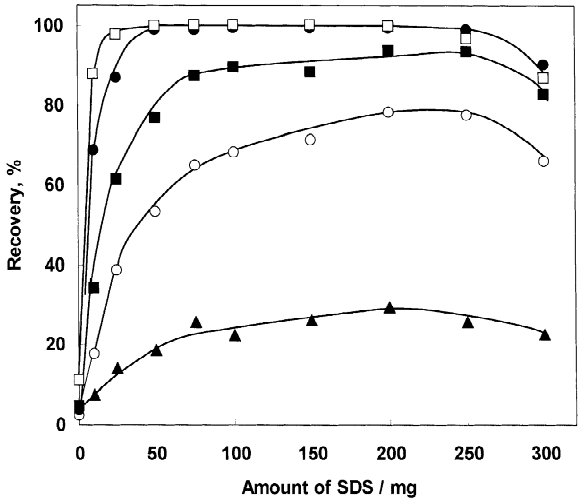

Fig. 1. Effect of the amount of SDS on the sorption of 1 μ*M* chlorophenols onto 1.5 g γ-alumina at pH 2. (▲) 2-Chlorophenol, (○) 2,4-dichlorophenol, (■) 2,3,4-trichlorophenol, (●) 2,3,4,6-tetrachlorophenol, (□) pentachlorophenol.

increased remarkably with increasing amount of SDS (Fig. 1). Admicelles are dynamic micelle-like aggregates and, therefore, form hydrophobic media that can incorporate hydrophobic solutes. The increase in sorption can be explained by the gradual formation of hydrophobic admicelles on the γ-alumina surface. Maximum sorption was obtained in the range 100–200 mg SDS.

However, the extent of sorption decreased with a further increase in the amount of SDS. According to our previous experiment, the adsorption capacity of SDS onto γ-alumina (1.5 g) is approximately 250 mg [9]. When more SDS was added, the SDS molecules are present in the bulk aqueous solution and can form normal micelles. The decrease in sorption can be explained by the distribution of chlorophenols into the normal SDS micelles. In the present study, the optimum amount of SDS was 100 mg versus 1.5 g γ-alumina.

3.2. Extractability of chlorophenols

As shown in Fig. 1, sorption also increased with increasing number of chlorine groups. In particular, 2,3,4,6-tetrachlorophenol and pentachlorophenol were collected quantitatively. On the other hand, chlorophenols with fewer chloro substituents were insufficiently collected. The hydrophobic properties of chlorophenols increase as the number of chloro substituents increases. The extent of hydrophobicity is often represented by water–octanol distribution constants {log $K_{o/w}$ = 2.15 (for 2-chlorophenol), 3.17 (for 2,4-dichlorophenol), 3.61 (for 2,3,4-trichlorophenol), 4.45 (for 2,3,4,6-tetrachlorophenol), and 5.18 (for pentachlorophenol) [23]}. The results of the present study clearly indicate that the hydrophobic interaction is predominant for incorporation into admicelles. Furthermore, the extent of collection may be estimated from the equilibrium constants, because the solvent properties of SDS–γ-alumina admicelles estimated using a spectrometric method [24] correspond to those of 1-octanol.

3.3. Effect of pH

Fig. 2 shows the pH dependence of the sorption yield of 2,3,4,6-tetrachlorophenol by SDS–γ-alumina admicelles. Almost quantitative recoveries (>98%) were obtained in the pH range from 2 to 5. However, the yields decreased dramatically in the higher pH region. The sorption of SDS onto γ-alumina surfaces decreased significantly with increasing solution pH, because of the decrease in the positive charge of γ-alumina [16]. The decrease in the sorption of 2,3,4,6-tetrachlorophenol can be ascribed to the decrease in the volume fraction of the admicellar medium. In addition, the pK_a value (5.22 [25]) indicates that some proportion of the 2,3,4,6-tetra-

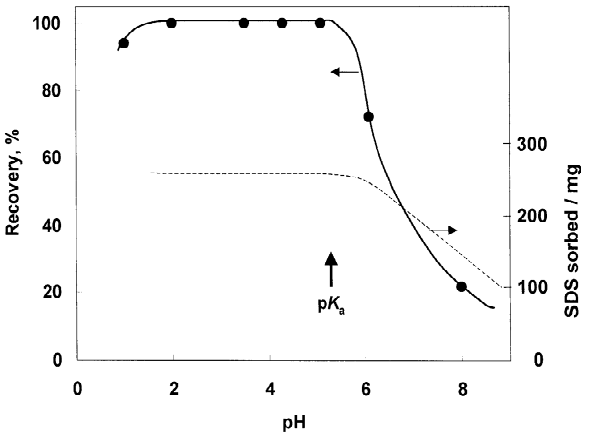

Fig. 2. Effect of pH on the sorption of 1 μ*M* 2,3,4,6-tetrachlorophenol onto admicelles consisting of 100 mg SDS and 1.5 g γ-alumina. The dotted line represents the amount of SDS sorbed on 1.5 g of γ-alumina estimated based on the data in Ref. [9].

chlorophenol was present as anionic species. Acid dissociation of the compound may be another reason for the decrease in recovery. On the other hand, the slight decrease in sorption below pH 1 may be explained by the reduced sorption of SDS molecules, probably due to protonation of their sulfate groups. Therefore, the solution pH was adjusted to 2.

3.4. Sample loading to the admicelle cartridge

Admicelles filled in a cartridge column were then prepared in order to apply the present method to the determination of chlorophenols in environmental water samples. To prepare the admicelle column, a commercially available pre-packed cartridge column (Bond Elut Jr., alumina, 500 mg) was used, because of its good water permeability. The amount of SDS loaded was 33 mg, because of the equivalent SDS/γ-alumina ratio (100 mg/1.5 g) compared with batch experiments. Further loading of SDS resulted in a lowering of the water permeability.

Table 1 lists the yields of chlorophenols on the admicelle column. Similarly to batch extraction, 2-chlorophenol and 2,4-dichlorophenol were hardly extracted. In contrast, 2,3,4,6-tetrachlorophenol and pentachlorophenol, having highly hydrophobic properties, were collected. This indicates the potential of the admicelle-mediated extraction method for collecting these particularly hydrophobic compounds.

The analytes collected on the admicelles were eluted with water-miscible organic solvents such as methanol, ethanol, 1-propanol, and acetonitrile. Among the solvents, acetonitrile was the best choice, because the analytes could be eluted quantitatively with the least amount (1 ml) of solvent. The recoveries of chlorophenols for the whole procedure are also listed in Table 1.

Table 1
Recovery of chlorophenols onto SDS–γ-alumina admicelles at pH 2

Compound	Recovery (%)	
	Sorption	Sorption and desorption
2-Chlorophenol	16±6	10±4
2,4-Dichlorophenol	50±3	49±3
2,3,4-Trichlorophenol	91±2	91±3
2,3,4,6-Tetrachlorophenol	100±1	95±3
Pentachlorophenol	100±1	90±4

Concentration of each chlorophenol: 1 μ*M*, $n=5$.

In order to clarify the limitation of the sample loading volume, increasing volumes of an acidic solution (pH 2) containing 0.1 μ*M* 2,3,4,6-tetrachlorophenol were passed through the admicelle column. The curve of the peak area in the chromatogram obtained by the injection of the eluate from the admicelles as a function of sample loading volume was straight up to 250 ml sample volume, indicating quantitative recovery of the analyte. At larger sample volumes, the slope of the curve gradually decreased, probably due to insufficient recovery of 2,3,4,6-tetrachlorophenol. The inflection point of the curve was independent of concentration from 0.1 μ*M* to 1 m*M*. Thus, the insufficient recovery can be attributed to the release of SDS molecules from the alumina support. In the present study, the sample volume loaded was 200 ml.

3.5. Application to river water

The application of the present method to HPLC analysis is shown in Fig. 3. When a river water sample spiked with 10 n*M* 2,3,4,6-tetrachlorophenol and pentachlorophenol was injected directly into the HPLC system, no peak appeared in the chromatogram (Fig. 3A). In contrast, two peaks were observed (Fig. 3B) after concentration by admicelle-mediated extraction. When these chlorophenols were not

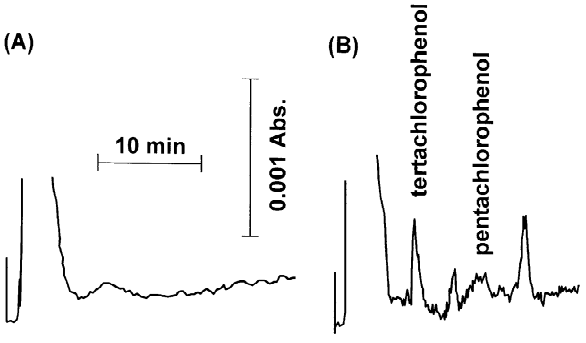

Fig. 3. Chromatograms of river water to which 10 n*M* 2,3,4,6-tetrachlorophenol and pentachlorophenol were spiked. (A) Without concentration, (B) with admicelle-mediated extraction. Column, Mightysil RP-18-GP (5 μm) 150 mm×4.6 mm; mobile phase, 60% (v/v) water–acetonitrile; flow-rate, 1.0 ml min^{-1}; detection wavelength, 290 nm.

spiked, no peaks were observed at the respective retention times. Linear relationships between peak areas and concentrations were obtained for these chlorophenols in the concentration range 10–100 n*M*. At 50 n*M*, the relative standard deviations ($n=5$) were 8% (for 2,3,4,6-tetrachlorophenol) and 10% (for pentachlorophenol). Thus, the present method is useful for the determination of these compounds at trace ($\mu g\ l^{-1}$) levels.

Finally, the present method is comparable to solid-phase extraction (SPE) with polymer-based solid materials or hydrophobically modified silica gels [26–28]. These solid materials are chemically stable and, hence, have an advantage for the repeatable collection of analytes. However, the low water permeability of these hydrophobic solid materials results in slow mass transfer between the bulk aqueous solution and the solid. Therefore, a limited flow-rate of water through the SPE cartridge (typically 10–20 ml min^{-1}) lengthens the sample loading time [29,30]. In contrast, because of the excellent water permeability of admicelles, a higher flow-rate (>100 ml min^{-1}) can be applied for sample loading. This is particularly advantageous if large quantities of sample have to be loaded onto the cartridge column.

4. Conclusion

The use of admicelles is effective for concentrating traces of chlorophenols in water prior to chromatographic analysis with photometric detection. Good recovery of chlorophenols, particularly those with a large number of chloro substituents, is favorable for the selective concentration of derivatives having high toxicity and persistence. The ability to concentrate hydrophobic compounds greatly extends the feasibility of applying the present method to several hydrophobic pollutants in a variety of water samples. Study of the combination of surfactants and solid materials will also be fruitful for designing highly efficient systems for concentrating traces of analytes.

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