

Flow Injection Analysis of Anionic Surfactants in River Water Using Teflon Filter Tube Preconcentration

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Abstract

A method was developed to determine anionic surfactants in river water using Teflon (PTFE) filter tube preconcentration. PTFE adsorbs hydrophobic and electrically neutral chemical species on its surface. This allows the surface of PTFE filter tube to adsorb and concentrate an ion pair formed between a cationic detecting agent and an anionic surfactant in aqueous solution. The detecting agent and the model anionic surfactant used were Co-5-Cl-PADAP, a highly sensitive detecting agent, and sodium dodecyl sulfate, respectively. After the ion pair was concentrated at a flow rate of 1.5 mL/min for 5 min on a 7 cm long filter tube (inner diameter: 1.5 mm), the ion pair was eluted with ethanol at a flow rate of 2.0 mL/min. The detection limit was 2 ng mL⁻¹ (3 × standard deviation of blank). The sensitivity of this method was equal to or higher than that of the conventional solvent extraction method. This method and the Ethyl Violet method (EV method, JIS) gave somewhat different analytical results for a standard solution containing various anionic surfactants because the sensitivities of the methods are different for each surfactant, while they yielded the same analytical results for river water samples.

Keywords FIA, Anionic surfactants, Teflon filter tube, River water

1. Introduction

Surfactants are roughly classified into four types, among which anionic type ones are used most frequently. Since surfactants of any type are easily released into the environment, they cause river water to foam and arouse concern about their possible harmful effects on the ecosystem due to their toxicity. Then, the analysis of samples taken from the environment often becomes necessary. Anionic surfactants are determined frequently by the batch methods and rarely by flow injection analysis (FIA). One of the well-known batch methods is the Methylene Blue (MB) method (JIS [1]) in which the ion pair formed between the dye and an anionic surfactant is extracted into chloroform and the amount of the ion pair in the solvent is determined spectroscopically. This method is troublesome in its operations, however, and unsuitable for rapid analysis. Moreover, it involves some other problems such as the need of a large amount of chloroform, instability of coloration, and extraction of Methylene Blue-active substances (MBAS) other than anionic surfactants. Motomizu et al. [2] developed a solvent extraction-spectrophotometric method for determining anionic surfactants in water using Ethyl Violet-anionic surfactant ion pair to solve the above-mentioned problems. This method is less inhibited by MBAS than the MB method and adopted in JIS¹⁾ enacted in 1993. Meanwhile, regulations to control the discharge of organic solvents including chloroform, toluene, benzene have recently become severer from a viewpoint of environmental pollution and the use of separation methods using solvent extraction has been avoided as much as possible. Various separation methods using no solvent extraction process have therefore been proposed. A typical method proposed is based on the partition of dye-surfactant ion pair between a solid (membrane filter) and a liquid (water) [3,4]. This extraction-concentration method is highly sensitive [5], the detection limit of which is 0.0043 mg L⁻¹, but it is complicated in its operations. Another method proposed is flow injection analysis (FIA), which has attracted attention because of its

rapidness and simplicity. We have made efforts to develop a highly sensitive analytical method using FIA coupled with concentration and reported several techniques with special interest in using Teflon (PTFE) capillary tube that allows easy elution. However, while the capillary tube is effective in concentrating metal cations, it adsorbs hydrophobic chemical species only weakly and hardly yields high concentration efficiency. Fortunately, PTFE filter has an adsorbability higher than that of PTFE capillary tube. PTFE filter has been used mainly in gas separation and applied as an adsorption-concentration material for phenol [6]. The present work aims to establish a simple and rapid analytical method using FIA coupled with concentration by means of PTFE filter tube instead of PTFE tube as a solid extraction field.

2. Experimental

2.1 Reagents

Anionic surfactant solution: Sodium dodecyl sulfate (SDS, reagent grade, Wako Pure Chemicals) was dissolved in water to give an aqueous solution. Similarly, an aqueous solution of sodium *n*-dodecyl sulfonate (ABS, reagent grade, Wako Pure Chemicals) was prepared by dissolving the salt in water. Coloring agent solution: [2-(5-chloro-2-pyridylazo)-5-diethylaminophenol] cobalt complex (0.007 g) (Dojin Kagaku) was dissolved in water (100 mL) to yield a 1 × 10⁻⁴ M solution. This solution was appropriately diluted at the time of use. Other reagents: The other reagent grade chemicals (Wako Pure Chemicals) were dissolved in water to give aqueous solutions.

2.2 Apparatus

A UV-970 spectrophotometer (Nihon Bunko), SP-D-3201U double plunger-type pump (Nihon Seimitsu Kagaku), desk autobalance recorder (Nihon Denshi Kagaku), and U-228 pH meter (Toa Denpa HM-30E type) were used. The Teflon filter

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tube used (Asahi Glass) was 7cm long and had outer and inner diameters of 2.0 and 1.5mm, respectively, and a pore size of 1.0 μ m. The flow system was made of a Teflon tube (Chuko Kasei Kogyo) with outer and inner diameters of 1.5 and 0.5mm.

3. Procedure

Flow system and its operation

Figure 1 shows the flow system used in the present work, where C, D, B, A, P, E, In, UV, R, and W denote respectively sample solution, detecting agent solution, washing solution, eluent, pump, PTFE filter tube, injector, absorbance detector, recorder, and waste solution. Spectrophotometric determination of anionic surfactant was conducted in the following way. Two solutions from two passages, C and D, were combined to allow the formation of an ion pair between the detecting agent and an anionic surfactant and the ion pair formed was permitted to adsorb on the PTFE filter tube for a given time. After completion of the adsorption, the filter tube was washed with 10% methanol and the ion pair was eluted out of the tube with 90% ethanol (0.1M HNO₃). Finally, the absorbance of Co-5-Cl-PADAP, the detecting agent in the ion pair, was measured at 560nm.

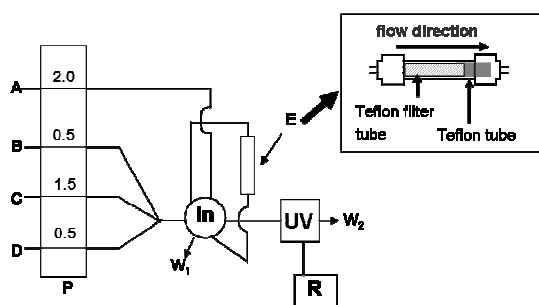


Fig. 1 Schematic illustration of flow system.

A: eluent{90% ethanol(0.1M HNO₃)}; B: washing solution; C: sample solution; D: reagent solution; E: Teflon filter tube in the Teflon tube; In: injector; UV: detector; P: pump; R: recorder; W: waste.

4. Results and Discussion

4.1 Selection of detecting agent

The method described in JIS is based on the extraction into toluene of an ion pair formed between an anionic surfactant and Methylene Blue (MB). Since anionic surfactants are detected through the absorbance of MB cation bound to the surfactant anion, some other colored cations would be usable as detecting agent. The principle of determination on surfactants is similar to the present method. Then, the concentration efficiency and sensitivity of MB, Rhodamine B, and Co-5-Cl-PADAP (cationic azo-dye) were examined. When compared with Co-5-Cl-PADAP, MB and Rhodamine B adsorbed strongly on PTFE filter tube and were hardly washable, thus giving a high blank test value. These two dyes were less sensitive than the cobalt complex because the ion pairs formed between the two dyes and anionic surfactants were released from the tube by excessive washing. The cobalt complex is a reagent synthesized by Taguchi et al. and used as a highly sensitive detecting agent for anionic surfactants [7-9]. The complex was selected as detecting agent in this work because it gave a clear difference between net and blank test values in our PTFE filter tube concentration in

preliminary experiments. The model anionic surfactant used was SDS.

4.2 Co-5-Cl-PADAP concentration

Figure 2 shows the effect of Co-5-Cl-PADAP concentration on the absorbance of surfactant-cobalt complex ion pair. The absorbance was measured in a cobalt complex concentration range between 6.0×10^{-7} and 3.0×10^{-5} M keeping SDS concentration at 7.0×10^{-7} M. A constant absorbance was attained at cobalt complex concentrations above 5.0×10^{-6} M. A concentration of 1.0×10^{-5} M was then chosen for the complex considering the range of analysis though 5.0×10^{-6} M, a minimum necessary concentration, would be suitable to reduce the effect of coexisting ions and raise the selectivity. The adsorption behavior of the complex was similar to that of the surfactant-complex ion pair and remained unchanged at concentrations above 5.0×10^{-6} M.

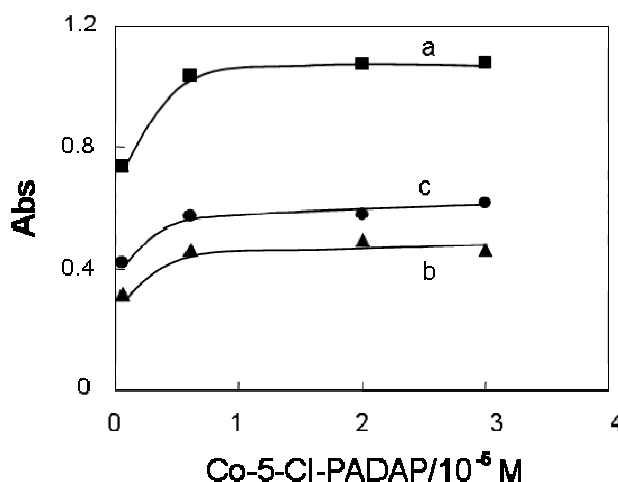


Fig.2 Effect of Co-5-Cl-PADAP concentration on absorbance. SDS: 7×10^{-7} M ; concentration time: 10min; pH: 3.5; washing solution: 10% methanol; cleaning time: 1min; eluent: 90% ethanol (0.1M nitric acid); wavelength: 560nm; a: sample; b: net; c: reagent blank.

4.3 Effect of pH on concentration

The effect of pH value was investigated on PTFE filter tube concentration of the ion pair. Adjustment of pH value was made by addition of nitric acid and potassium hydroxide to the medium. The concentration was found to give a constant absorbance for [Co-5-Cl-PADAP⁺-DS⁻] ion pair at pH values between about 2 and 6, above which the absorbance decreased (Fig. 3). In contrast to our flow method, the batch method gave a constant absorbance for the ion pair over a wide range of pH values [7]. The reduction in the absorbance observed at pH values above 7 in the flow method would be due to a reduction in the adsorption efficiency of the ion pair on PTFE filter tube in alkaline solutions since it is highly unlikely that this method causes the dissociation or decomposition of the ion pair in alkaline solutions to happen at high pH values. Hydroxide ions are reported to replace fluoride ions on the surface of PTFE in alkaline solutions to make adsorption sites for cations [10]. Then, the adsorption of nonpolar [Co-5-Cl-PADA⁺-DS⁻] ion pair would be prevented on the polar PTFE surface in alkaline solutions. A pH value of 3.5 was chosen as the optimum one in the present method because coexisting acidic substances would dissociate to form anions at pH values higher than 7 in river

water samples, thereby disturbing the determination of anionic surfactants.

4.4 Effect of concentration time

Figure 4 shows the effect of concentration time on the adsorption of the ion pair. Although the absorption became constant when adsorption-concentration time was longer than 20min at sample and detecting agent flow rates of 1.5 and 0.5mL/min, respectively, concentration time was set at 5min to increase the number of sample measurements. The finding that a constant absorbance at concentration time longer than 20min indicates that the adsorption of the ion pair on PTFE filter tube attains an equilibrium.

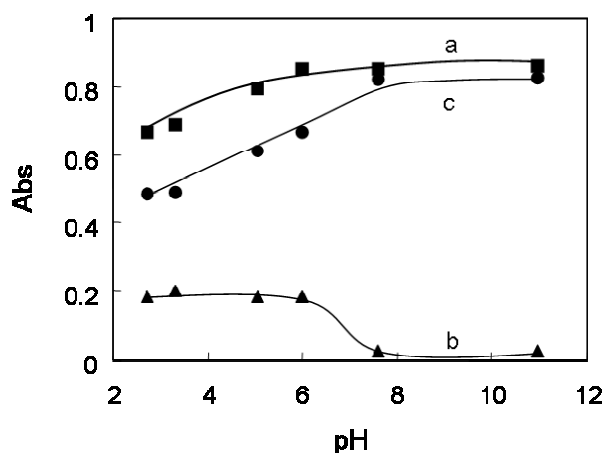


Fig. 3 Effect of pH on absorbance. SDS: $2 \times 10^{-7} \text{M}$; Co-5-Cl-PADAP: $1 \times 10^{-5} \text{M}$; concentration time: 10min; cleaning time: 1min; pH: 3.5; washing solution: 10% methanol; eluent: 90% ethanol (0.1M nitric acid); wavelength: 560nm; a: sample; b: net; c: reagent blank.

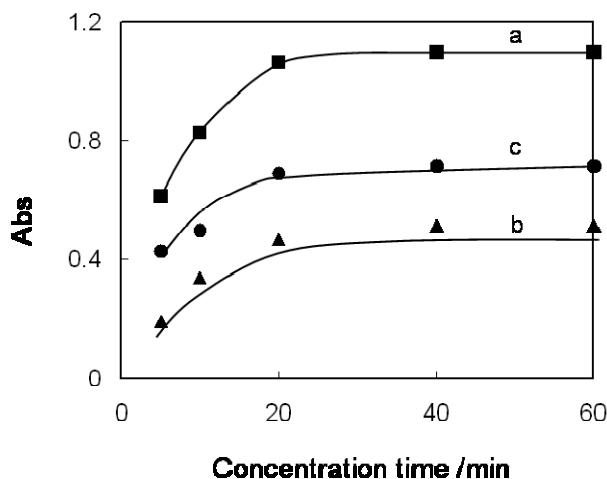


Fig. 4 Effect of concentration time on absorbance. SDS: $2 \times 10^{-7} \text{M}$; Co-5-Cl-PADAP: $1 \times 10^{-5} \text{M}$; cleaning time: 1min; pH: 3.5; washing solution: 10% methanol; eluent: 90% ethanol (0.1M nitric acid); wavelength: 560nm; a: sample; b: net; c: reagent blank.

4.5 Effects of methanol concentration for washing and washing time

When the ion pair is adsorbed and concentrated on PTFE filter

tube, excess unreacted Co-5-Cl-PADAP molecules are also adsorbed. This causes the absorbance in reagent blank test to rise, thereby making the detection limit higher and the detection of minute amounts of anionic surfactants harder. Washing of PTFE filter tube was then attempted to remove Co-5-Cl-PADAP molecules adsorbed on the tube. Since the ion pair is soluble in organic solvents including alcohols, the use of 100% methanol in washing allows both the ion pair and the cobalt complex to detach from the tube. Then, methanol, acetone, 1-propanol, and ethylenediamine were tested after all of them were diluted with distilled water to 10%. While 10% acetone and 10% ethylenediamine were found to hardly reduce the blank test value, 10% 1-propanol was less effective than methanol. Consequently, methanol was chosen as washing liquid. Figure 5 shows changes in the absorbance of the ion pair when the concentration of methanol in distilled water was varied from 0 to 30%. The absorbance remained constant at methanol concentrations up to 20%, beyond which it decreased probably because both the ion pair and cobalt complex were released from the tube. The absorbance of the ion pair was also measured changing the time of washing (0.5mL/min) from 0 to 3min. Washing for longer than 2min gave an almost constant absorbance of excess cobalt complex. The time of washing was then set at 2min.

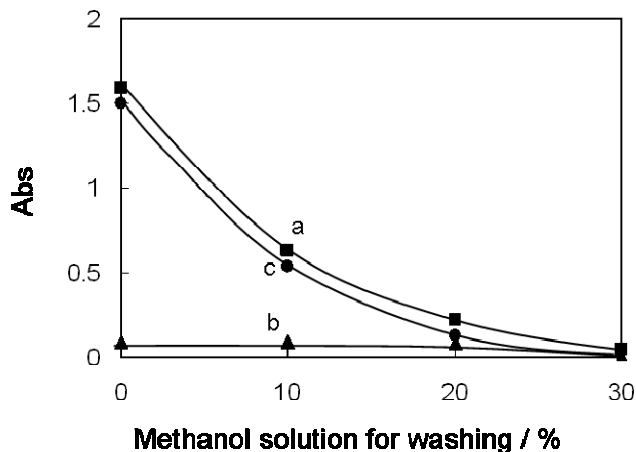


Fig. 5 Effect of methanol concentration for washing on absorbance.

SDS: $2 \times 10^{-7} \text{M}$; Co-5-Cl-PADAP: $1 \times 10^{-5} \text{M}$; concentration time: 5min; cleaning time: 1min; pH: 3.5; eluent: 90% ethanol (0.1 M nitric acid); wavelength: 560nm; a: sample; b: net; c: reagent blank.

4.6 Effect of methanol addition to cobalt complex solution

An attempt was made to lower the blank test value to improve the detection limit. While reduction in Co-5-Cl-PADAP concentration caused a decrease in the blank test value, it also produced a reduction in the sensitivity. Methanol was added to the cobalt complex solution ($1 \times 10^{-5} \text{M}$) to see if it could reduce the absorbance in the blank test through amplifying the difference in adsorption between the ion pair and the cobalt complex. As shown in Table 1, methanol addition caused the absorbance of the ion pair to remain constant while it produced a reduction in the absorbance in the blank test. This would indicate that the presence of methanol reduces the permittivity of the medium, thereby causing a decrease in the adsorption of the cobalt complex on PTFE filter tube through a reduction in the partition of the complex. The change in the permittivity would hardly produce changes in the adsorption of the ion pair that

adsorbs on the tube more strongly than the complex.

Table.1 Effect of methanol added into Co-5-Cl-PADAP solution on absorbance

	Co-5-Cl-PADAP, 1×10^{-5} M	
	0% methanol	10% methanol
Sample	0.592	0.527
Blank	0.327	0.259
Net	0.265	0.273

SDS: 3×10^{-7} M; concentration time: 5min; cleaning time: 2min; pH: 3.5; wash solution: 10% methanol; eluent: 90% ethanol (0.1M nitric acid); wavelength: 560nm.

4.7 Elution curve

Figure 6 shows the elution curves of [Co-5-Cl-PADAP] complex and [Co-5-Cl-PADAP⁺-DS⁻] ion pair. The eluent used was 90% ethanol containing 0.1M HNO₃. Elution started upon injection of the eluent. The curves a) and b) are for the cobalt complex (blank test) and a sample containing the complex and SDS at 0.084ppm (3×10^{-7} M). Those were double-peaked. The three-dimensional spectrum of the ion pair constructed by wavelength, time, and absorbance was then measured using a diode array to examine the peaks in detail. The first peak was suggested to be due to the water/eluent boundary because it appeared independently of wavelength (Fig. 7). The ion pair collected in PTFE filter tube is concentrated in about 0.5mL of the eluent as seen from Fig. 6. In other words, when the sample volume was 7.5mL (concentration time: 5min, sample flow rate: 1.5mL/min), the ion pair was 15 times concentrated if its collection rate was assumed to be 100%. The true collection rate was calculated to be about 60% using the concentration of DS⁻ in the eluent obtained from the area under peak.

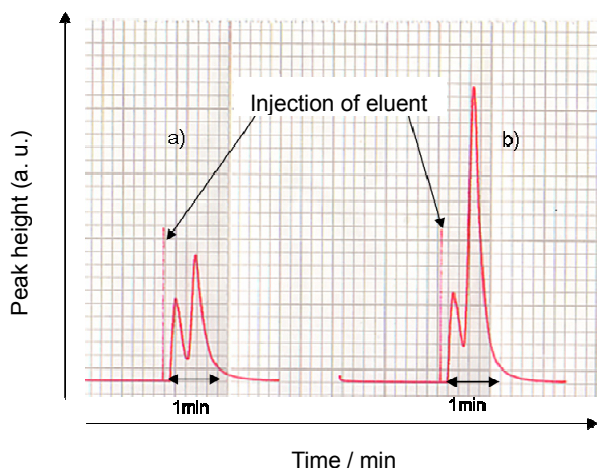


Fig.6 Elution curves.

a) reagent blank, b) DS⁻: 0.084ppm (3×10^{-7} M).

4.8 Calibration curve

The calibration curve constructed in the experimental conditions used in the present work (concentration time: 5min, washing time: 2min, sample flow rate: 1.5mL/min, cobalt complex solution flow rate: 0.5mL/min, and eluent flow rate: 2.0mL/min, without methanol addition to Co-5-Cl-PADAP) gave a correlation coefficient of 0.995 and the detection limit ($3 \times$ standard deviation of blank, $n=7$) was 2ng mL⁻¹ DS⁻. This

sensitivity is equal to or even higher than that for the EV method adopted in JIS (detection limit: 5ng mL⁻¹) [1] and the analytical method using a soluble membrane filter (detection limit: 4.3ng mL⁻¹) [5]. The number of samples treated was 10/hr and the variation coefficient was 1.4% ($n = 8$), thus showing a good reproducibility.

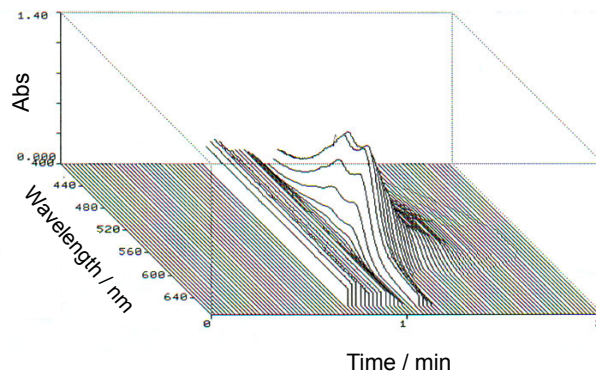


Fig.7 Three-dimensional adsorption spectrum of ion association (Co-5-Cl-PADAP⁺-DS⁻). DS⁻: 0.084ppm (3×10^{-7} M).

4.9 Effect of coexisting chemical species

The effect of coexisting chemical species was investigated on the adsorption-concentration of [Co-5-Cl-PADAP⁺-DS⁻] in the flow system using the calibration curve described in 4.8. Chloride ion, Cl⁻, showed a positive inhibition of 9% even at 53ppb. Monovalent anions with a relatively large ionic radius including halide and perchlorate ions are reported to inhibit the ion pair extraction-concentration at their relatively low concentrations (Br⁻: +3% at 90ppb, I⁻: 11% at 140ppb, ClO₄⁻: +7% at 11ppm) [7]. Since river water usually contains chloride ion at about 10ppm, its inhibiting action is predicted. The effect of silver nitrate as masking agent was then examined but the salt failed to mask chloride ion because it reacted with SDS. As a consequence, methanol was added to the cobalt complex solution (1×10^{-5} M) as described in 4.6 to increase the selective adsorption of the ion pair by changing its partition to PTFE filter tube. The effect of halide and similar ions was thus studied on the amount determined of SDS in the presence of methanol. As a result, experimental errors were found to fall to about 8% even in the presence of chloride ion at 30ppm as shown in Table 2.

Table.2 Effect of diverse ions on the determination results

Ion	Added as	mg L ⁻¹	Error, %
Cl ⁻	NaCl	30	+8
F ⁻	NaF	10	+11
Br ⁻	NaBr	10	-2
I ⁻	NaI	0.5	+19
ClO ₄ ⁻	NaClO ₄	0.05	+2
NO ₂ ⁻	NaNO ₂	10	+17

SDS: 90ppb; Co-5-Cl-PADAP: 1×10^{-5} M (10 % methanol); concentration time: 5min; cleaning time: 2min; pH: 3.5; washing solution: 10% methanol; eluent: 90% ethanol (0.1M nitric acid); wavelength: 560nm.

4.10 Application to synthetic sample

River water contains various kinds of chemical species other

than halide ions and they may adversely affect the present analytical method. Then, the standard river water sample JAC0032 authorized by the Japan Society of Analytical Chemistry was used as synthetic sample after being added 0.1ppm SDS. Since the river water sample is stored with 0.1M HNO₃ and hence its analysis may be affected by NO₃⁻, a 10 times diluted water sample was analyzed. The analytical error for this sample was -0.04%, showing no inhibition of NO₃⁻.

4.11 Application to river water

River water samples from the Edo river (Chiba Prefecture) were analyzed by the present method and the EV method (JIS) and the results of SDS determination were compared with each other. The amount of SDS determined by the former was higher than that by the latter. This suggests the presence in the sample of certain chemical species (other than halide ions) which inhibit the analysis in the positive direction. Phenols, picric acid, sulfonates including saccharin, carboxylates, and phosphorus compounds in addition to halide ions are present in river water [11] and supposed to inhibit the analysis in the positive direction. Re-examination of washing solution was then made to remove ion associates of these chemical species with the cobalt complex in the washing step.

4.12 Re-examination of washing solution

Ethanol, 2-methoxyethanol, and 2-ethoxyethanol, highly water-soluble organic solvents, were examined to see if they are suitable as washing liquid. As a result, 2-methoxyethanol was chosen as washing liquid because ethanol failed to raise the desorption selectivity and 2-ethoxyethanol had a high washability and released both the cobalt complex and [Co-5-Cl-PADAP⁺-DS⁻]. When 10% 2-methoxyethanol was used as washing solution, a slight effect of the inhibitive chemical species was observed. In contrast, the use of 20% 2-methoxyethanol produced no inhibition.

4.13 Application to river water (washing solvent: 2-methoxyethanol)

Table 3 gives the analytical results for anionic surfactants in river water samples (from the Ohori river, Kashiwa city, Chiba Prefecture, the Tone canal, Noda city, Chiba Prefecture, the Tama river, Setagaya Ward, Tokyo, the Oba river, Misato city, Saitama Prefecture, and the Tega marsh, Abiko city, Ibaraki Prefecture) obtained with the present and EV methods.

Table 3 Determinations of anion surfactants in river and pond by the present and EV methods.

Sample	Present method / ppm	EV method / ppm
No. 1	0.100±0.010	0.096±0.014
No. 2	0.121±0.011	0.097±0.020
No. 3	0.072±0.006	0.055±0.007
No. 4	0.113±0.010	0.096±0.020
No. 5	0.084±0.013	0.082±0.013

No.1 Ohori river(kashiwa), No.2 Tone canal(noda), No.3 Tama river(setagayaku), No.4 Ohba river(misato), No.5 Teganuma pond(abiko); Co-5-Cl-PADAP: 1×10^{-5} M (10% methanol; concentration time: 5min; cleaning time: 2min; pH:3.5; eluent: 90 % ethanol (0.1M nitric acid); washing solution: 20% 2-methoxyethanol; wavelength: 560nm.

These two methods gave slightly different results for No. 2, 3, and 4 samples presumably because the river water samples contained several anionic surfactants as described before, while they yielded the same results for No. 1 and 5 samples probably due to a smaller number of anionic surfactants contained in the samples. In conclusion, the results obtained in this work demonstrates the usefulness of the present analytical method since it needs no organic solvents including toluene and chloroform and no solvent extraction.

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