

Spectrophotometric Determination of Anionic Surfactants in River Water with Cationic Azo Dye by Solvent Extraction-Flow Injection Analysis

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Anionic surfactants in water were determined by a spectrophotometric flow injection technique coupled with solvent extraction. The ion associate which formed between an anionic surfactant and a cationic azo dye was extracted into an organic solvent and the absorbance was measured. The carrier was distilled water, and the reagent solution contained a cationic azo dye and sodium sulfate, the pH of which being adjusted to 5 with acetate buffer. A phase separator with a poly(tetrafluoroethylene) porous membrane (0.8 μm pore size) was used to separate the organic phase. Six derivatives of cationic azo dyes and several extracting solvents were examined; a pair of 1-methyl-4-(4-diethylaminophenylazo)-pyridinium cation and chloroform turned out best. The sampling rate was 30 samples per hour. Calibration graphs were linear up to 2×10^{-6} M or 3×10^{-5} M of anionic surfactant when injection volume was 300 or 100 μl , respectively. The relative standard deviation ($n=10$) was 1.5% for 300 μl of 1×10^{-6} M sodium dodecylsulfate. The detection limit was as little as 1×10^{-8} M of anionic surfactant. Anionic surfactants in river water were determined satisfactorily.

Keywords Anionic surfactant determination, cationic azo dye, ion associate extraction, spectrophotometry, flow injection analysis

Almost all spectrophotometric determinations of anionic surfactants depend on solvent extraction of an ion associate formed between a dye cation and an anionic surfactant.

Methylene Blue is one of the most frequently used cationic dyes.^{1,2} The Methylene Blue method, however, is very troublesome and its sensitivity is very low because of the small extractability of the ion associates between Methylene Blue cation and anionic surfactants. Recently, Higuchi *et al.*³ have developed a cationic dye more extractable than Methylene Blue. Motomizu *et al.*⁴ have also developed a solvent extraction-spectrophotometric method for anionic surfactants with Ethyl Violet: the method needs only a single extraction, and the its molar absorptivity of ion associate is about $1 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$.

Flow injection techniques coupled with solvent extraction have been widely used for analyte extraction, preconcentration and matrix isolation. Several types of phase separator with a poly(tetrafluoroethylene) (PTFE) porous membrane have been reported.⁵⁻⁸ In this work, the authors used a new phase separator with a PTFE membrane (pore size: 0.8 μm), which was designed by Motomizu *et al.*⁹, and examined the utility of the solvent extraction-flow injection analysis (FIA) for determination of micro amounts of anionic

surfactants in water with cationic azo dyes.

Experimental

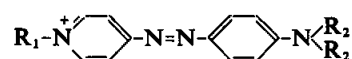
Reagents

All chemicals used were of analytical-reagent grade. **Standard anionic surfactant solutions.** Anionic surfactants used were sodium dodecylsulfate (Wako Pure Chemicals Ind., purity is more than 99.2%) and sodium dodecylsulfonate (Tokyo Kasei Kogyo Co. Ltd., GR grade). They were dried at 50°C under reduced pressure (about 3 mmHg) before use.

Cationic azo dyes. Cationic azo dyes were synthesized according to the literature.³ The purified

Table 1 Cationic azo dyes examined

	Abbreviated names					
	MMP	EMP	PMP	MEP	EEP	PEP
R ₁	CH ₃ ⁻	C ₂ H ₅ ⁻	C ₃ H ₇ ⁻	CH ₃ ⁻	C ₂ H ₅ ⁻	C ₃ H ₇ ⁻
R ₂	CH ₃ ⁻	CH ₃ ⁻	CH ₃ ⁻	C ₂ H ₅ ⁻	C ₂ H ₅ ⁻	C ₂ H ₅ ⁻



1-alkyl-4-(4-dialkylaminophenylazo)-pyridinium

products were ascertained by using NMR spectroscopy on a Hitachi Model R600. The data of the ^1H NMR (δ , CDCl_3) of the cationic azo dyes in Table 1 are as follows. MMP: 3.26 (s, 6H), 4.62 (s, 3H), 6.80 (d, 2H), 7.92 (d, 2H), 8.10 (d, 2H), 9.12 (d, 2H), 1.05 (t, 3H); EMP: 1.72 (t, 6H), 3.26 (s, 6H), 4.90 (q, 4H), 6.80 (d, 2H), 7.92 (d, 2H), 8.10 (d, 2H), 9.25 (d, 2H); PMP: 1.05 (t, 3H), 2.20 (m, 2H), 3.26 (s, 6H), 4.82 (t, 2H), 6.79 (d, 2H), 7.93 (d, 2H), 8.06 (d, 2H), 9.23 (d, 2H); MEP: 1.31 (t, 6H), 3.59 (q, 4H), 4.59 (s, 3H), 6.80 (d, 2H), 7.96 (d, 2H), 8.08 (d, 2H), 9.11 (d, 2H); EEP: 1.31 (t, 6H), 1.72 (t, 3H), 3.60 (q, 4H), 4.95 (d, 2H), 6.80 (d, 2H), 7.95 (d, 2H), 8.10 (d, 2H), 9.24 (d, 2H); PEP: 1.21 (t, 3H), 1.32 (t, 6H), 2.20 (m, 2H), 3.61 (q, 4H), 4.86 (t, 2H), 6.80 (d, 2H), 7.93 (d, 2H), 8.11 (d, 2H), 9.25 (d, 2H). Iodides of cationic azo dyes were converted to their chlorides by passing the aqueous solution of iodides through an anion-exchanger column.¹⁰

Chromogenic reagent solution. This solution contained cationic azo dye (chloride), acetate buffer (0.1 M, pH 5) and sodium sulfate (0.1 M).

Carrier solution. Distilled water was used.

Extracting solvent. Several organic solvents and their mixtures were used without further purification.

Apparatus

A diagram of the extraction-flow injection system is shown in Fig. 1. A carrier solution, a reagent solution and an extracting solvent were propelled with two double-plunger micro pumps (Sanuki Kogyo, DM-2M-1024) at a flow rate of 0.8 ml min^{-1} . A sample solution was introduced into the carrier stream by using a six-port sample injection valve. At the mixing point of the aqueous and organic phases, a T-shaped segmentor was used to obtain a regular pattern of the alternate aqueous and organic-solvent segment. A porous PTFE membrane sheet (Sumitomo Electric Industries, $0.8 \mu\text{m}$ pore size) was used for the phase separator. The absorbance of the organic phase

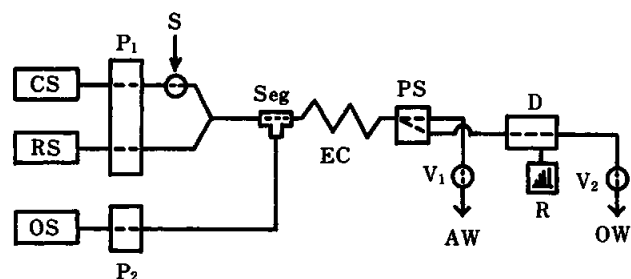


Fig. 1 Schematic diagram of the extraction-flow injection system. CS, H_2O ; RS, cationic azo dye ($5 \times 10^{-5} \text{ M}$) + Na_2SO_4 (0.1 M) + EDTA (0.001 M) + acetate buffer (0.1 M, pH 5); OS, extracting solvent; P₁, P₂, pumps (0.8 ml min^{-1}); S, sample injection ($300 \mu\text{l}$); Seg, segmentor; EC, extraction coil (0.5 mm i.d., 4 m); PS, phase separator; D, detector (564 nm); R, recorder; V₁, V₂, needle valves; AW, aqueous phase waste; OW, organic phase waste.

separated was measured at 564 nm with a spectrophotometer (Shimadzu UV-140-02) equipped with a micro flow cell (10-mm light path, $18 \mu\text{l}$ volume) and recorded with a Toa Dempa FBR-251A recorder. Flow lines were made of PTFE tubing (0.5 mm i.d.).

Results and Discussion

Selection of cationic dye and extracting solvent

The spectrophotometric method with Ethyl Violet⁴ is very sensitive, but Ethyl Violet is easy to adsorb on PTFE tubing and flow cell walls. In FIA using PTFE flow lines, cationic azo dye is preferable to Ethyl Violet. Cationic azo dyes shown in Table 1 were synthesized and examined. The results obtained by using some extracting solvents are summarized in Table 2. The maximum absorbances were obtained near 564 nm in all the cationic azo dyes. It was found that, of the pairs of dye and extracting solvent showing good baselines, the largest response was obtained by using 1-methyl-4-(4-diethylaminophenylazo)-pyridinium ion (MEP) as a counter cation and chloroform as an extracting solvent, while peak heights for dodecylsulfonate and dodecylsulfate were almost equal. Further experiments were carried out by using

Table 2 Results of the examination of cationic azo dyes and extracting solvents

	Peak height/mm			
	DCE	DCE+ MIBK(1+1)	DCE+ MIBK(1+2)	MIBK
MMP				
$\text{C}_{12}\text{-SO}_3\text{Na}$	26	44	50	36
$\text{C}_{12}\text{-OSO}_3\text{Na}$	39	46	47	38
Base line	G	G	G	G
EMP	CF	DCE+CF(1+2)	DCM+CF(1+1)	
$\text{C}_{12}\text{-SO}_3\text{Na}$	65	70	63	
$\text{C}_{12}\text{-OSO}_3\text{Na}$	62	66	62	
Base line	G	G	G	
PMP		DCB+CF(1+1)	CF	DCM+CF(1+2)
$\text{C}_{12}\text{-SO}_3\text{Na}$		56	67	68
$\text{C}_{12}\text{-OSO}_3\text{Na}$		60	67	67
Base line		G	G	S
MEP	DCB+ CF(1+1)	CF	DCM+ CF(1+2)	DCM+ CF(1+1)
$\text{C}_{12}\text{-SO}_3\text{Na}$	62	79	74	67
$\text{C}_{12}\text{-OSO}_3\text{Na}$	64	81	72	64
Base line	G	G	S	S
EEP	DCB+CF(1+1)		DCB+CF(1+2)	CF
$\text{C}_{12}\text{-SO}_3\text{Na}$	64		74	84
$\text{C}_{12}\text{-OSO}_3\text{Na}$	62		71	83
Base line	G		G	B
PEP	DCB	DCB+CF(2+1)	DCB+CF(1+1)	
$\text{C}_{12}\text{-SO}_3\text{Na}$	55	60	65	
$\text{C}_{12}\text{-OSO}_3\text{Na}$	55	55	61	
Base line	G	S	S	

Concentration of anionic surfactant, $1 \times 10^{-6} \text{ M}$. Wavelength, 564 nm. MIBK, methylisobutylketone; DCE, 1,2-dichloroethane; DCM: dichloromethane; CF, chloroform; DCB: 1,2-dichlorobenzene; $\text{C}_{12}\text{-SO}_3\text{Na}$, sodium dodecylsulfonate; $\text{C}_{12}\text{-OSO}_3\text{Na}$, sodium dodecylsulfate; G, good; S, sufficient; B, bad.

MEP and chloroform.

Composition of the reagent solution

Concentration of MEP was examined. The equal peak heights were obtained above 5×10^{-5} M of MEP: 5×10^{-5} M solution was adopted.

Acidity of the reagent solution was examined by varying the pH from 3.5 to 8 with acetate and phosphate buffer solutions. The equal peak heights were obtained above pH 5: pH 5 (acetate buffer, 0.1 M) was adopted.

Sodium sulfate was added to the reagent solution to improve phase separation and salting out effect: 0.1 M was enough for the purpose.

Phase separator and segmentors

Six kinds of phase separators with porous PTFE membrane previously reported by the authors⁹ were examined for this purpose. The phase separator, which has a sloped groove (2-mm width and 2-mm maximum depth) was found to be the best for smooth, long-term, efficient phase separation.

Several kinds of PTFE membranes (Sumitomo Electric Industries) were examined. Of nine pore sizes tested (pore size: 0.10–1.5 μm), 0.8 μm is the best for smooth, long-term phase separation.

Segmentors were also examined by using T-shaped and Y-shaped connectors. The peak heights obtained in these segmentors are equal in the difference of $\pm 10\%$. In further experiments, a T-shaped segmentor, in which the aqueous solution goes straight and the extracting solvent flows into the aqueous solution at a right angle, was used.

Effect of extraction coil

In order to examine the efficiency of extraction, the length of the extraction tubing was studied. Figure 2 shows that the maximum peak heights were obtained

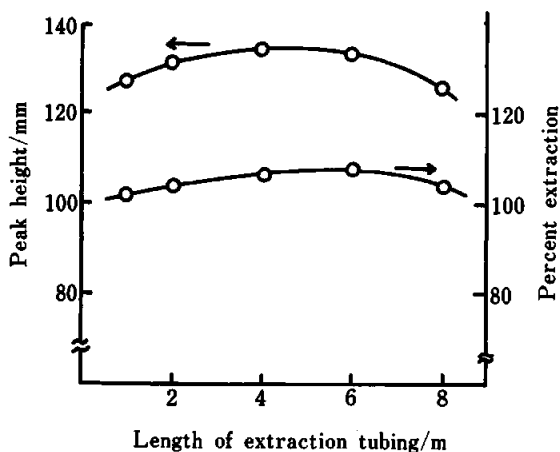


Fig. 2 Effect of extraction coil length. Sample, 300 μl of sodium dodecylsulfate (1×10^{-6} M); extraction coil, 0.5 mm i.d. PTFE.

when the tubing was about 4 m long.

To discuss the efficiency of extraction more clearly, the amount of substance (mole) of the analyte (in this study, anionic surfactants) extracted into the organic phase was calculated by means of the following equation (1):

$$m = \int_{t_i}^{t_f} C_{\text{org}} \frac{F_{\text{org}}}{1000} dt = \frac{F_{\text{org}}}{1000\epsilon} \int_{t_i}^{t_f} (\text{Abs}) dt = \frac{F_{\text{org}} P_A}{1000\epsilon} \quad (1)$$

where m is the amount of substance of the analyte in the organic phase in mol, C_{org} the molar concentration of the analyte in the organic phase, F_{org} the flow rate of the organic phase (ml min^{-1}), which goes through the membrane and flow cell, t_i and t_f the times when the peak is initiated and finished, ϵ the molar absorptivity of the analyte, (Abs) the absorbance of the analyte of the organic phase and P_A the peak area (absorbance \times min), respectively.

In this work, peak area (P_A) was obtained by cutting out the peaks from the recorder chart paper and weighing them. In Fig. 2, the percent extraction of dodecylsulfate is also shown. In the calculation of m , $6.7 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ was used as the molar absorptivity, ϵ^3 . The calculated values were more than 100%: 102% to 108%. That is because a few parts of ion associate in the organic phase will adsorb on the flow cell walls. As a result of such adsorption of ion associate, the peak tailing was longer with increase in the concentration of anionic surfactant. In further experiments, 4-m long tubing was used.

Effect of volume of sample injection

The effect of sample injection volume on peak shape was examined. The volume of sample injected was varied by changing the length of the sample loop in the

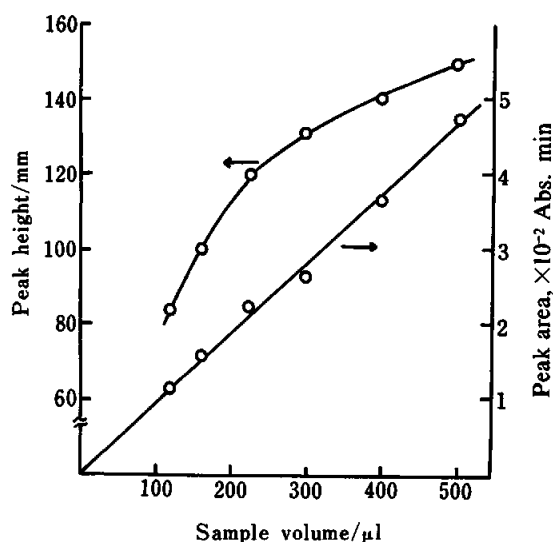


Fig. 3 Effect of sample volume. Sample, sodium dodecylsulfate (1×10^{-6} M).

injection valve. The results obtained are shown in Fig. 3. Although the peak height increased with increase in sample size, the peak width also became broader. There is no linear relation between sample size and peak height. However, there is a good linearity between sample size and peak area. This means that the method involving the use of peak areas to make a calibration graph is more sensitive than that using peak heights when large sample sizes are injected to improve the sensitivity. By considering the sensitivity and sampling rate, 300 μl of sample was injected.

Effect of flow rate on the peak shape

The flow rate of the three streams (carrier, reagent and extracting solvent) was varied from 0.4 to 1.0 ml min^{-1} . The results obtained are shown in Table 3. When the flow rates of each stream were identical (A in Table 3), that is, the ratio of the organic phase to the aqueous phase was 1:2, the peak height and percentage extraction were almost equal. When the flow rate of the extracting solvent was 0.8 ml min^{-1} , but the flow rates of the carrier and the reagent solutions were varied (B in Table 3), the peak height increased with

Table 3 Effect of flow rate

(A) Flow rates of each stream are identical.

Flow rate/ ml min^{-1}	P_H^a / mm	P_A^b , 10^{-2} Abs min	Anionic surfactant extracted ^c $m/10^{-10}$ mol	E , %
1.00	139	2.12	3.16	105
0.90	140	2.31	3.10	103
0.80	139	2.65	3.16	105
0.65	135	3.10	3.01	101
0.55	133	3.87	3.18	106
0.40	130	5.16	3.08	103

(B) Flow rates of carrier and reagent streams are variable (flow rate of extracting solvent stream is 0.80 ml min^{-1}).

V_{aq}/V_{org}^d	P_H /mm	P_A , 10^{-2} Abs min	Anionic surfactant extracted $m/10^{-10}$ mol	E , %
2.5	163	2.65	3.16	105
2.3	147	2.62	3.13	104
2.0	137	2.75	3.28	109
1.5	115	2.58	3.08	103
1.3	104	2.56	3.06	102
1.0	71	2.48	2.96	99
0.7	47	2.32	2.77	92

300 μl of 1×10^{-6} M sodium dodecylsulfate were injected.

a. Maximum peak height

b. Peak area (absorbance \times time)

c. Anionic surfactant extracted into the organic phase, which calculated by using P_A ; m is the amount of substance (mol) and E is the percentage.

d. V_{aq} : total flow rate of the aqueous phase, V_{org} : flow rate of extracting solvent.

increase in the flow rates of the aqueous phase. The percent extraction, however, exhibited a maximum at 0.8 ml min^{-1} of the carrier and the reagent solutions. This indicates that the greater or the smaller the ratio of the aqueous phase to the organic phase, the worse the mixing of the two phases and the less the percent extraction is.

Effect of phase-separation efficiency on the peak shape

The peak shape depended on the fraction of the organic phase that passes through the membrane filter, as shown in Fig. 4. The peak height decreased and the peak width increased with decrease in the recovery of the organic phase. In our system, 100% recovery of the organic phase was easily achieved by adjusting the needle valves. In all subsequent experiments, the recovery of the organic phase was 100%.

Calibration graph for anionic surfactant

Calibration graph was linear up to 2×10^{-6} M and up to 3×10^{-5} M of anionic surfactant, when 300 μl and 100 μl of sample were injected, respectively. Sampling rate was about 30 h^{-1} .

The relative standard deviation was 1.5%, when 300 μl samples of 1×10^{-6} M sodium dodecylsulfate were injected 10 times. The detection limit corresponded to $S/N=3$ is 1×10^{-8} M of anionic surfactant.

Determination of anionic surfactant in river water

Effect of coexisting ions. Interferences from coexisting ions were examined. The results are shown in Table 4. The amounts of ions that generally exist in river water samples analyzed here are smaller than those listed in Table 4. Iron(III) at concentrations above 10^{-5} M affected the peak shape because of the

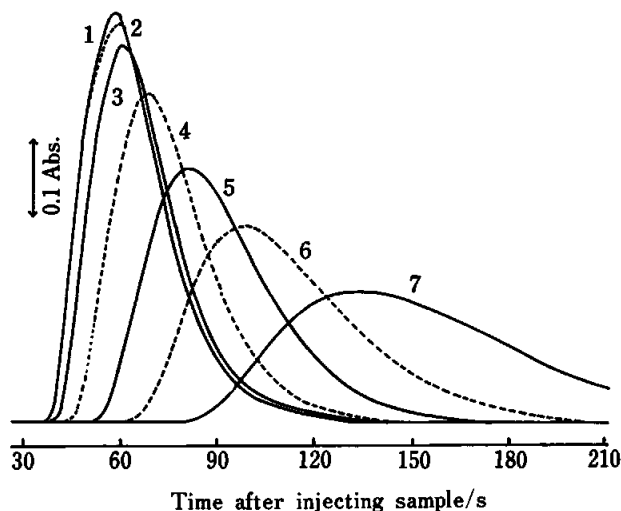


Fig. 4 Effect of phase-separation efficiency on the peak shape. Sample, 300 μl sodium dodecylsulfate (1×10^{-6} M); phase-separation efficiency (%): (1)100, (2)80, (3)63, (4)48, (5)30, (6)23, (7)15.

Table 4 Effect of co-existing ions

Ion	Added as	Tolerable concentration/M ^a
Na ⁺ , Cl ⁻	NaCl	10 ⁻³
K ⁺	KCl	10 ⁻³
NH ₄ ⁺	NH ₄ Cl	10 ⁻³
Ca ²⁺	CaCl ₂	10 ⁻³
Mg ²⁺	MgSO ₄	5 × 10 ⁻⁴
Fe ³⁺ b	Fe ₂ (SO ₄) ₃	10 ⁻⁵
NO ₃ ⁻	KNO ₃	10 ⁻⁴
HCO ₃ ⁻	NaHCO ₃	5 × 10 ⁻⁴
H ₂ PO ₄ ⁻	NaH ₂ PO ₄	10 ⁻³
SO ₄ ²⁻	Na ₂ SO ₄	10 ⁻²
SiO ₃ ²⁻	Na ₂ SiO ₃	10 ⁻⁴

Sodium dodecylsulfate: 1 × 10⁻⁶ M

a. Maximum tested concentrations. These ions at such concentrations had an effect on the peak height of less than ±2%.

b. 0.01 M EDTA was contained.

Table 5 Determination of anionic surfactants in water

Water	Anionic surfactants, ppb ^a	
	This work	Methylene Blue method
Tap water ^b	24 ± 2	
Asahi River ^b	28 ± 1	
Zasu River ^b	79 ± 3	
Asahi River ^c	28 ± 1	
Yoshii River ^c	31 ± 1	
Suna River ^c	80 ± 2	
Zasu River ^d I	56 ± 3	55 ± 3
II	94 ± 2	95 ± 2
III	127 ± 3	146 ± 2
Nishi River ^e I	53 ± 4	57 ± 3
II	62 ± 2	60 ± 2
III	76 ± 3	74 ± 2
IV	89 ± 3	85 ± 2
Sasagase River ^f I	262 ± 6	262 ± 3
II	292 ± 6	274 ± 5
Kojima Lake		
Koori A ^g	146 ± 2	85 ± 5
B ^h	285 ± 3	93 ± 4
Urayasu A ^g	213 ± 1	138 ± 5
B ^h	252 ± 3	104 ± 7
Fujita A ^g	265 ± 2	233 ± 5
B ^h	282 ± 2	78 ± 4

Symbols I - IV denote the order of sampling downstream.

a. Average of three determinations.

Sampled on b=Oct. 1, 1985; c=Oct. 23, 1985; d=Dec. 18, 1985; e=Dec. 16, 1985; f=Dec. 12, 1985; g=Jan. 10, 1986; h=Jan. 13, 1986.

formation of colloidal hydroxide precipitation. This interference was removed by adding EDTA to the sample: the EDTA concentration was adjusted to 0.01 M.

River water samples were filtered with a glass filter to remove any solid substances. To 5 ml of the filtrates, 0.5 ml of 0.1 M EDTA solution were added. The sample size injected was 300 μl. The results obtained by the FIA method are shown in Table 5, where the results obtained by the Methylene Blue batch method¹ are shown. In river water samples, the results obtained by the FIA method are in good agreement with those obtained by the Methylene Blue batch method. In lake water samples, which were very polluted and turbid, the values obtained by the Methylene Blue batch method were lower than those obtained by the FIA method. This is because emulsion and/or precipitate formation occurred between the aqueous and the organic phases by shaking and ion associates of anionic surfactant and Methylene Blue was readily adsorbed on emulsion and/or precipitate in the Methylene Blue batch method. In the FIA method, emulsion and precipitate formation did not occur between the two phases, because there was no shaking.

References

1. APHA-AWWA-WPCF, "Standard Methods for Examination of Water and Waste Water", 14th ed., p. 600, American Public Health Association, Washington, DC (1975).
2. Japanese Industrial Standard Committee, "JIS K0102", Japanese Standards Association, Tokyo (1974).
3. K. Higuchi, S. Monya, Y. Shimoishi, H. Miyata and K. Tôei, *Bunseki Kagaku*, **29**, 180 (1980).
4. S. Motomizu, S. Fujiwara, A. Fujiwara and K. Tôei, *Anal. Chem.*, **54**, 392 (1982).
5. J. Kawase, A. Nakae and M. Yamanaka, *Anal. Chem.*, **51**, 1640 (1979).
6. J. Kawase, *Anal. Chem.*, **52**, 2124 (1980).
7. T. Imasaka, T. Harada and N. Ishibashi, *Anal. Chim. Acta*, **129**, 195 (1981).
8. K. Ogata, K. Taguchi and T. Imanari, *Anal. Chem.*, **54**, 2127 (1982).
9. S. Motomizu and M. Oshima, *Analyst* [London], **112**, 295 (1987).
10. S. Motomizu and K. Tôei, *Bunseki Kagaku*, **30**, 245 (1981).

(Received March 9, 1987)

(Accepted May 1, 1987)