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Ion chromatography with ultraviolet and amperometric detection for iodide and thiocyanate in concentrated salt solutions

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SUMMARY

An ion chromatographic system with ultraviolet (UV) and amperometric (AMP) detectors is described for the highly sensitive detection of iodide and thiocyanate. Solutions of four inorganic salts as mobile phases and three stationary phases were examined. The optimum separation was achieved by using a polymethacrylate-based anion-exchange column and 0.1 *M* sodium chloride–5 m*M* sodium phosphate buffer (pH 6.7) as the mobile phase. Conditions were established for UV and AMP detection on a electrochemically pretreated glassy carbon electrode. The method, which has the ability to eliminate most interferences from other anions, could be applied to the direct determination of ppb levels of iodide in sea water.

INTRODUCTION

Ion chromatography, introduced by Small *et al.*[1], has become one of the most important methods for the determination of inorganic anions[2]. This method makes possible the rapid separation and highly sensitive measurement of analyte ions. However, for a conventional ion chromatographic system using a polystyrene-based anion-exchange resin and a conductivity detector, both iodide and thiocyanate, with low hydration energies, are generally associated with long retention times and severe tailing of the anion peaks, owing to the strong affinity of the anions to the resin[1–3].

In order to solve this problem, many methods have been considered with combinations of various mobile phases, columns and detectors. The methods can be mainly classified into two groups, as follows. (1) One aims to increase the ionic strength in the mobile phase[4–9]. For single-column ion chromatography with conductivity detection, however, the ionic concentration in a mobile phase is limited to very dilute solutions as the detector shows responses to all ions[2]. For dual-column systems, the ionic strength is limited to the capacity of the suppressor[1–3]. Hence it is necessary to use other detectors with high sensitivity for iodide and thiocyanate and to select a mobile phase with high concentrations that do not show a response on the

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detectors. (2) The other approach is to use different kinds of columns. (a) For ion-exchange chromatography, the use of a silica-based resin does not result in tailing of the anion peaks[10,11]. The use of a polymer-based resin is accompanied by longer retention times, thus requiring an increase in ionic strength in the mobile phase. (b) For ion-interaction chromatography (or ion-pair chromatography)[12–17], sharp peaks with good resolution can be obtained by using reversed-phase alkyl-chain bonded silica or polystyrene where ion-interaction reagents and counter ion additives are added to mobile phases consisting of aqueous or aqueous–organic solutions.

This work concentrates on the first category of method. Ion chromatographic systems combining mobile phases with high ionic strength and ultraviolet (UV) and amperometric (AMP) detectors were studied for the separation and detection of iodide and thiocyanate. The use of such mobile phases has the advantage of almost eliminating the interference of faster eluting species from the analyte ions. The separations were examined for mobile phases of four inorganic salts and three ion-exchange columns. Solutions of nitrate salts were generally used as mobile phases[3,4,8,9]. However, as the solutions, which are very effective for amperometric detection systems, show strong UV absorption, it is desirable to use other mobile phases that do not respond to both ultraviolet and amperometric detectors. We previously reported on ion chromatography with amperometric detection of iodide using 0.1 *M* sodium chloride solution as the mobile phase[7]. The detection of iodide and thiocyanate has been achieved by the use of ultraviolet spectrophotometry[10–13,15–17], conductimetry[14], amperometry [platinum[4], glassy carbon (GC)[7,17] and silver[3,8,9] working electrodes] and potentiometry[5,6]. This paper describes a detection system for iodide and thiocyanate with ultraviolet spectrophotometry and amperometry (GC working electrode), which have high sensitivities for these ions, thus providing the optimum ion chromatographic system.

EXPERIMENTAL

Apparatus

The ion chromatographic system consisted of a computer-controlled pump (CCPM; Tosoh), a Rheodyne 7125 injection valve equipped with a 100-μl sample loop, a UV spectrophotometric detector (L-4200; Hitachi), an amperometric detector (VMD-101A and P-1000; Yanagimoto) and a dual-pen strip-chart recorder. The amperometric detection system uses a three-electrode potentiostat: a thin-layer flow system with a glassy carbon (GC) working electrode, a stainless-steel counter electrode and an Ag/AgCl reference electrode were used.

Three anion-exchange columns (with quaternary ammonium groups) were used: TSKgel IC-Anion-PW (50 × 4.6 mm I.D.) (Tosoh) and, for comparison, TSKgel IC-Anion-SW (50 × 4.6 mm I.D.) (Tosoh) and Yokogawa AX-1 [(50 + 250) × 4.6 mm I.D.] (Yokogawa). The flow-rate was maintained at 1.2 ml/min for TSKgel IC-Anion-PW and TSKgel IC-Anion-SW and at 2.0 ml/min for Yokogawa AX-1. Separations and measurements were carried out at *ca.* 23–25°C.

Reagents and mobile phase

All reagents were of analytical-reagent grade. Standard anion solutions were prepared from stock solutions (10–50 g/l), obtained by dissolution of the correspond-

ing sodium salts. Mobile phases of inorganic salt solutions containing 5 m*M* sodium phosphate buffer (pH 6.7) were prepared from stock solutions of 2 *M* NaCl, 0.6 *M* $NaNO_3$, 1.0 *M* Na_2SO_4, 0.25 *M* Na_2HPO_4, and 0.25 *M* NaH_2PO_4. Mobile phases of sodium phosphates were prepared from equimolar (0.25 *M*) Na_2HPO_4 and NaH_2PO_4. All solutions were prepared in distilled, deionized water and filtered through a 0.45-μm membrane filter (made of cellulose nitrate) before use.

Pretreatment of a GC working electrode

It has generally been recognized that somehow the electrochemical treatment of a GC electrode tends to enhance and stabilize the electrode response of electroactive compounds[18,19]. The following procedures were adopted in this study. The electrode was resurfaced to a mirror-like condition by polishing with a diamond compound (particle size, 1 μm) and rinsed with distilled, deionized water after the removal of residual polishing compound by ultrasonic treatment in a water-bath for at least 5 min. The electrode was then electrochemically treated by repeated anodization at + 1.6 V (*vs.* Ag/AgCl) for 5 min followed by cathodization at − 1.0 V for 2 min under a flow (0.5 ml/min) of 0.5 *M* sodium phosphate buffer (pH 6.7).

RESULTS AND DISCUSSION

Mobile phase

Fig. 1 shows the variation of the retention volumes of iodide and thiocyanate with the concentration of inorganic salts in the mobile phase. Separation was performed on a TSKgel IC-Anion-PW. The solutions of NaCl, $NaNO_3$ and Na_2SO_4

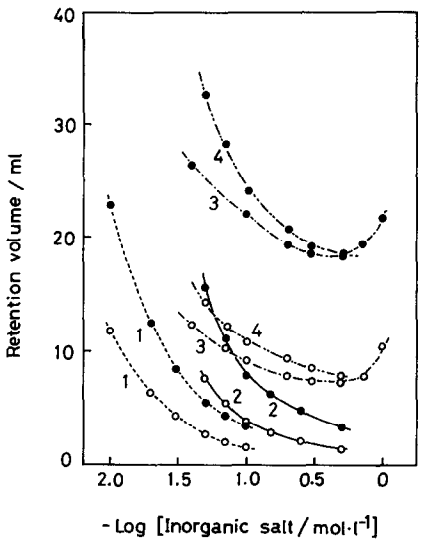


Fig. 1. Retention volumes of (○) I^- and (●) SCN^- as a function of the concentration of inorganic salts in the mobile phase. Mobile phase: 1 = $NaNO_3$; 2 = NaCl; 3 = Na_2SO_4; 4 = NaH_2PO_4–Na_2HPO_4; mobile phases 1–3 contain 5 m*M* sodium phosphate buffer (pH 6.7). Column: TSKgel IC-Anion-PW. Flow-rate: 1.2 ml/min.

contained 5 m*M* sodium phosphate buffer in order to stabilize the response of the amperometric detector. Although the eluting powers are relatively weak for the inorganic salt solutions in this study, it is possible to elute iodide at reasonable retention times using all the mobile phase systems with higher concentrations. The peaks of iodide for NaCl and $NaNO_3$ mobile phases are sharp compared with those for Na_2SO_4 and NaH_2PO_4–Na_2HPO_4. For Na_2SO_4 and NaH_2PO_4–Na_2HPO_4, in spite of an increase in concentration, the chromatograms of thiocyanate have longer retention times and show tailing of peaks, thus making it difficult to determine trace levels of thiocyanate. The effect of added salts in reducing the analyte retention follows the order $NO_3^- > Cl^- > SO_4^{2-} > H_2PO_4^-$–$HPO_4^{2-}$. Further, the effect remains constant over the ionic concentration range studied, except for SO_4^{2-} at high concentration. For SO_4^{2-}, the retention volumes of iodide and thiocyanate show a minimum value in the vicinity of 0.4 *M*. This suggests that the increase in the affinity of iodide and thiocyanate to the resin, due to an increase in the ionic strength of the mobile phase, is larger than the mass-action (ion-exchange) effect of SO_4^{2-} in reducing retention. Thus, reasonable retention times and sharp peaks of the analyte ions were obtained at 0.03 *M* $NaNO_3$ and 0.1 *M* NaCl.

Column

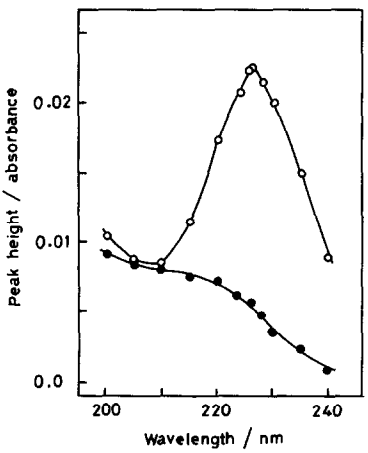
The effect of the stationary phase on analyte retention was studied using a mobile phase of 0.1 *M* NaCl–5 m*M* sodium phosphate buffer (pH 6.7). Table I shows the retention volumes for the three columns. Both TSKgel IC-Anion-PW and TSKgel IC-Anion-SW gave shorter retention volumes and sharper peaks. They also gave the same elution order ($IO_3^- < NO_2^- < NO_3^- < I^- < SCN^-$) with similar retention volumes, although the anion-exchange capacity of the PW- is about one-tenth that of the SW-type column. This can be ascribed to the difference in packing materials: polymethacrylate has a slightly stronger affinity to iodide and thiocyanate than silica, which is very weak in hydrophobicity. Polystyrene with high hydrophobicity (Yokogawa AX-1) has a strong affinity to iodide and thiocyanate, resulting in larger retention volumes. Hence it is preferable to use columns with weak hydrophobicity. In practice, however, TSKgel IC-Anion-PW is effective as the silica-based column in-

TABLE I

RETENTION VOLUMES OF IODIDE AND THIOCYANATE

Mobile phase, 0.1 *M* NaCl–5 m*M* sodium phosphate buffer (pH 6.7). Anion-exchange columns with quaternary ammonium groups; TSKgel IC-Anion-PW [50 × 4.6 mm I.D.; packing material, polymethacrylate; particle size, 10 μm; exchange capacity, 0.03 mequiv./ml (dry)]; TSKgel IC-Anion-SW [50 × 4.6 mm I.D.; packing material, silica; particle size, 5 μm; exchange capacity, 0.4 mequiv./ml (dry)]; and Yokogawa AX-1 [(50 + 250) × 4.6 mm I.D.; packing material, polystyrene; particle size, 10 μm; exchange capacity, 0.02 mequiv./g].

Column	*Retention volume (ml)*	
	I^-	SCN^-
TSKgel IC-Anion-PW	3.7	7.7
TSKgel IC-Anion-SW	4.0	6.2
Yokogawa AX-1	7.8	22.6



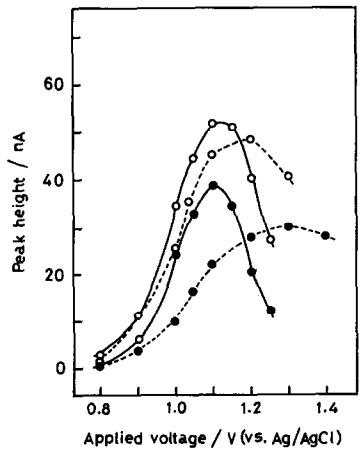


Fig. 2. Effect of wavelength on peak height of (○) I^- and (●) SCN^- (1 mg/l each). Mobile phase: 0.1 *M* NaCl–5 m*M* sodium phosphate buffer (pH 6.7).

Fig. 3. Effect of applied voltage on peak height of (○) I^- and (●) SCN^- (0.1 mg/l each). Mobile phase: solid lines, 0.1 *M* NaCl–5 m*M* sodium phosphate buffer (pH 6.7); dashed lines, 0.03 *M* $NaNO_3$–5 m*M* sodium phosphate buffer (pH 6.7).

dicates a slow decrease in the retention volumes, probably owing to dissolution of silica[11] under the conditions of the mobile phase.

UV and AMP detection

Fig. 2 shows the dependence of peak height (UV absorbance) on the wavelength for the injection of 1 mg/l iodide and thiocyanate solutions. Iodide has maximum UV absorbance at *ca.* 226 nm, where the background absorbance of 0.1 *M* NaCl is low. Thiocyanate has a strong absorbance at lower wavelength. However, as the UV absorbance of 0.1 *M* NaCl increases at that wavelength, it is necessary to measure at a wavelength longer than 210 nm.

Fig. 3 shows the dependence of peak height (AMP response) on applied potential for the injection of 0.1 mg/l iodide and thiocyanate solution. As the potential is increased, the peak height initially increases to a maximum. The reason for this is that the gain in background current at higher potential is larger than that in response to the analyte ions. The potential of the peak current response is *ca.* +1.1 V for iodide and thiocyanate in 0.1 *M* NaCl mobile phase and +1.2 and +1.3 V for iodide and thiocyanate, respectively, in 0.03 *M* $NaNO_3$ mobile phase. The higher peak potential in $NaNO_3$ than in NaCl is ascribed to the lower background current of the $NaNO_3$, probably owing to its lower concentration and stability towards oxidation. The optimum voltage to keep a constant background signal from the mobile phase was *ca.* +1.0 V in 0.1 *M* NaCl. Although a higher voltage can be acceptable in 0.03 *M* $NaNO_3$, the applied potential was similarly selected as +1.0 V in order to suppress the response of other ions.

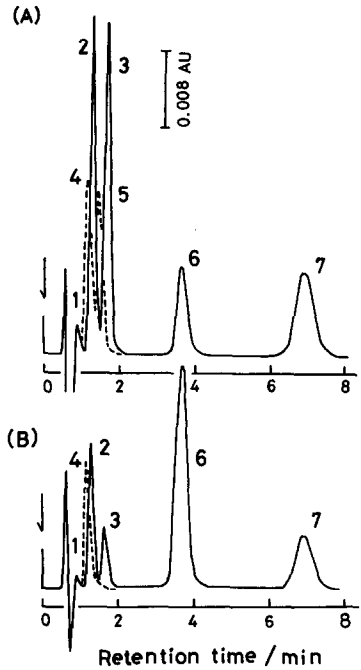


Fig. 4. Ion chromatograms of inorganic anions. 1 = IO_3^- (1 mg/l); 2 = NO_2^- (0.5 mg/l); 3 = NO_3^- (0.5 mg/l); 4 = $S_2O_3^{2-}$ (1 mg/l); 5 = Br^- (1 mg/l); 6 = I^- (1 mg/l); 7 = SCN^- (1 mg/l). Column, TSKgel IC-Anion-PW; mobile phase, 0.1 *M* NaCl–5 m*M* sodium phosphate buffer (pH 6.7); detection, UV absorbance at (A) 210 nm and (B) 226 nm; flow-rate, 1.2 ml/min; sample volume, 100 μl.

Ion chromatogram

Fig. 4 shows chromatograms of a mixture of UV-absorbing ions at 210 and 226 nm. They have two characteristics. (1) Iodide and thiocyanate are completely separated from the other anions; the hydrophilic ions (iodate, thiosulphate, nitrite, nitrate and bromide) are eluted within 2 min. On the other hand, the elution of iodide and thiocyanate with smaller hydration energy is relatively retarded. Hence matrix effects apart from the ion-exchange effect are exerted on the column used, as described under *Column*. (2) The wavelengths of maximum UV-absorbance for the other anions are shifted downwards compared with iodide (*ca.* 226 nm). These results indicate that the use of UV detection and 0.1 *M* NaCl as the mobile phase makes it possible to determine trace levels of iodide and thiocyanate in solutions containing large amounts of other anions.

Fig. 5 shows chromatograms of a mixture of electroactive anions using 0.1 *M* NaCl and 0.03 *M* $NaNO_3$ mobile phases. Although a good separation and highly sensitive detection of iodide and thiocyanate are obtained with both mobile phases, the elution of the faster eluting species with 0.1 *M* NaCl is faster than that with 0.03 *M* $NaNO_3$. Hence it is considered that NaCl is to be preferred to $NaNO_3$ in ion chromatography with amperometric detection. In addition, NaCl can be applied with a UV detection system.

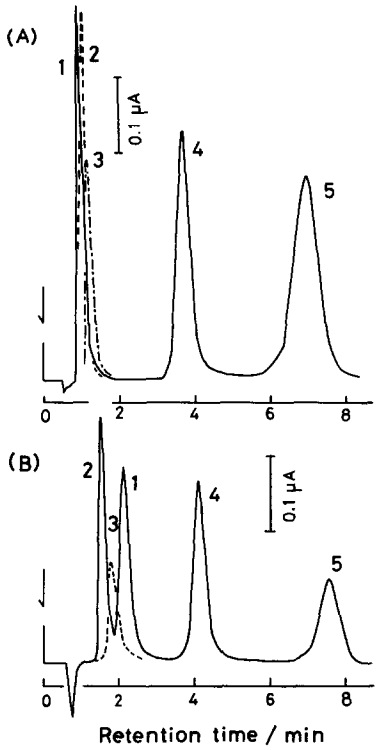


Fig. 5. Ion chromatograms of inorganic anions. 1 = $S_2O_3^{2-}$ (1 mg/l); 2 = NO_2^- (0.5 mg/l); 3 = Br^- (100 mg/l); 4 = I^- (1 mg/l); 5 = SCN^- (1 mg/l). Mobile phase, (A) 0.1 *M* NaCl–5 m*M* sodium phosphate buffer (pH 6.7) and (B) 0.03 *M* $NaNO_3$–5 m*M* sodium phosphate buffer (pH 6.7); detection, amperometry using a GC working electrode (+1.0 V *vs.* Ag/AgCl); other conditions as in Fig. 4.

Calibration graph, detection limit and repeatability

The calibration graphs of iodide and thiocyanate based on peak-height measurements were linear up to a concentration of 20 mg/ml with UV detection. With AMP detection using both mobile phases the upper limit of linearity was about one tenth (2 mg/l) of that for UV detection. Further, at concentrations below 0.1 mg/l the calibration graphs showed downward curvatures. With a 100-μl injection, the detection limits (at a signal-to-noise ratio of 2) were 5 μg/l for I^- (226 nm) and 10 μg/l for SCN^- (210 nm) by the UV method and 5 and 5 μg/l for I^- and SCN^- respectively, by the AMP method using 0.1 *M* NaCl. The reproducibility of five replicate injections of 0.1 mg/l I^- and SCN^- was good; the relative standard deviation (R.S.D.) for UV detection at 210 and 226 nm was 2.8 and 3.0%, respectively, for I^- and 2.0 and 2.2%, respectively, for SCN^-. For AMP detection with 0.1 *M* NaCl and 0.03 *M* $NaNO_3$, the R.S.D. values were 3.1 and 2.1%, respectively, for I^- and 3.6 and 2.7%, respectively, for SCN^-.

Interferences

The effects of eleven inorganic anions (Cl^-, SO_4^{2-}, F^-, HCO_3^-, $H_2PO_4^-$, IO_3^-,

SeO_4^{2-}, Br^-, NO_2^-, $S_2O_3^{2-}$, NO_3^-, 1–10 g/l) on the detection of iodide and thiocyanate (1 mg/l each) were examined using a TSKgel IC-Anion-PW column and 0.1 *M* NaCl as the mobile phase. The peaks of the anions (retention volumes are within 2 ml) are separated completely from iodide (3.7 ml) and thiocyanate (7.7 ml). For UV detection at 210 and 226 nm, the chromatograms (1 mg/l) of the analyte ions were baseline resolved with those of 10 g/l solutions of both UV-transparent ions (Cl^-, SO_4^{2-}, F^-, HCO_3^- and $H_2PO_4^-$) and UV-absorbing ions (IO_3^-, $SeSO_4^-$ and Br^-). For AMP detection, baseline resolution of I^- and SCN^- (1 mg/l) was obtained for 10 g/l solutions of electroinactive Cl^-, SO_4^{2-}, F^-, HCO_3^-, $H_2PO_4^-$, IO_3^- SeO_4^{2-}, NO_3^- and Br^-. However, the peak heights of iodide in each solution (10 g/l) were reduced by *ca.* 5% (Cl^-), 10% (SO_4^{2-}) and 20% (Br^-) for UV detection at 226 nm and by *ca.* 5% (Cl^-), 20% (Br^-) and 25% (NO_3^-) for AMP detection. On the other hand, the effects on the peak height of thiocyanate were small. The retention times were reduced by *ca.* 0.1 min for iodide and 0.2 min for thiocyanate.

The strongly UV-absorbing ions, $S_2O_3^{2-}$ (5 g/l), NO_2^- (1 g/l) and NO_3^- (1 g/l), did not interfere with the baseline separation of iodide at 226 nm, but interfered at 210 nm. The tailing portions of chromatograms of 1 g/l $S_2O_3^{2-}$ and NO_2^-, which are electroactive, partly overlapped with iodide.

Determination of iodide in sea water

The determination of iodide in sea water was examined in order to clarify the highly sensitive detection of trace levels of ions in solutions containing an excess of salts. Fig. 6A shows chromatograms of iodide (0.1 mg/l) in artificial sea water (salinity 35‰) with UV detection. The artificial sea water, which was prepared according to the Lyman and Fleming Formula[20], contains 19 300 mg/kg of Cl^-, 2710 mg/kg of SO_4^{2-}, 142 mg/kg of HCO_3^- and 67 mg/kg of Br^-. A good iodide peak and high sensitivity were obtained at 226 nm compared with 210 nm, mainly because the

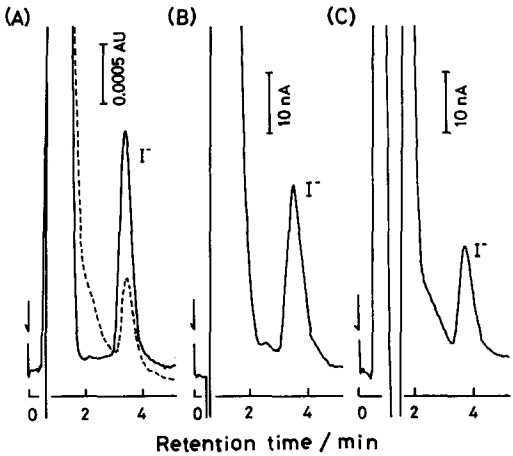


Fig. 6. Ion chromatograms of I^- (0.1 mg/l) in artificial sea water (salinity 35‰). Mobile phase, (A), (B) 0.1 *M* NaCl–5 m*M* sodium phosphate buffer (pH 6.7) and (C) 0.03 *M* $NaNO_3$–5 m*M* sodium phosphate buffer (pH 6.7); detection, (A) UV absorbance at 226 nm (solid line) and 210 nm (dashed line) and (B), (C) amperometry (+1.0 V *vs.* Ag/AgCl); other conditions as in Fig. 4.

TABLE II

ANALYTICAL RESULTS FOR IODIDE (μg/ml) IN SEA WATER

Average results for two determinations.

Sample	*UV detection*	*AMP detection*[7]
Standard sea water (England)	0.008	0.006
Standard sea water (Japan)	0.011	0.010
Sea water (Seto Inland Sea):		
No. 1	0.022	0.020
No. 2	0.030	0.032

absorbance of Br^- at 226 nm is small compared with that at 210 nm, as is shown in Fig. 4. Fig. 6B and C show chromatograms of iodide (0.1 mg/l) with AMP detection. The use of 0.1 *M* NaCl as the mobile phase gives a sufficient resolution of iodide compared with that obtained with 0.03 *M* $NaNO_3$, which elutes bromide slowly, as is shown in Fig. 5.

The NaCl system was applied to the determination of trace levels of iodide in standard sea water (England and Japan) and real sea water samples. The real samples were collected at Hiroshima bay in the Seto Inland Sea (Japan), filtered through a 0.45-μm membrane filter (made of cellulose nitrate) and pretreated by passage through a Sep-Pak C_{18} cartridge (Waters Assoc.). The calibration graphs for iodide (0–0.1 mg/l) in artificial sea water (salinity 35‰) were used for determination, as the peak heights in the artificial sea water were *ca.* 20% low compared with those in deionized water. The results are summarized in Table II. The agreement between the UV and AMP methods was good. Moreover, fairly quantitative recoveries (80–120%) were obtained for the addition of 0.01 and 0.03 mg/l of iodide, although the precision was poor owing to the low concentration of iodide.

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