



ELSEVIER

Journal of Chromatography A, 830 (1999) 211–217

JOURNAL OF
CHROMATOGRAPHY A

Short communication

Semi-micro ion chromatography of iodide in seawater

Kazuaki Ito

Department of Environmental Science, Faculty of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima 739-8527, Japan

Received 3 August 1998; received in revised form 20 October 1998; accepted 26 October 1998

Abstract

Large sample volume injections including both on-column analyte focusing and on-column matrix elimination techniques were examined for semi-micro ion chromatography of trace iodide (I^-) in seawater. A semi-microcolumn (35×1 mm I.D.) packed with styrene–divinylbenzene copolymer with high anion-exchange capacity and a mobile phase of 0.03 M $NaClO_4$ +0.5 M $NaCl$ +5 mM sodium phosphate buffer, pH 6.0, was used. Iodide in seawater was effectively concentrated on the column by both electrostatic and hydrophobic interactions and was eluted without peak broadening. ClO_4^- ($NaClO_4$) in the mobile phase was effective for the elution of iodide and Cl^- ($NaCl$) for both the concentration of iodide (I^-) with hydrophobicity and the removal of interference by the major anions. An excess of major anions in seawater did not disturb the detection of iodide at UV 226 nm. The relative standard deviations for successive injections of 5 and 1 $\mu g/l I^-$ (2 ml of 35‰ artificial seawater) were 1.5 and 5.8% ($n=5$, each), respectively. The slope of calibration curve (by peak area) using the semi-microcolumn was ~2.8-times higher than that for a conventional column with the same resin (150×4.6 mm I.D.) The present method had a detection limit of 0.2 $\mu g/l I^-$ for 2 ml of 35‰ artificial seawater and was successfully applied to seawater samples. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Sea water; Analyte focusing, on-column; Matrix elimination, on-column; Iodide

1. Introduction

The scale down of ion chromatographic (IC) systems has several advantages over IC using conventional columns. These include increased efficiency in a shorter time due to the reduction of sample dilution processes, lower mobile phase consumption, and the use of smaller amounts of packing materials. Thus, since the use of miniaturized IC by Rokushika and co-workers [1,2], scaled-down ICs have been examined using various packing materials (anion- and cation-exchange resins [1–4] and ODS coated with cetyltrimethylammonium [5], micellar taurine-conjugated bile salt [6], zwitterionic bile salt micelles [7,8] etc.) and detection systems (conduc-

tometric detection [1,4], and indirect and direct UV detection [2,3,5–8]). Sjögren et al. [4] recently demonstrated higher separation and detection efficiencies for inorganic and organic anions using a capillary-scale column and suppressed conductometric detection system. The efficiencies were comparable with those by capillary electrophoresis.

The use of miniaturized columns naturally requires the reduction of injection and detection volumes to maintain higher separation and detection efficiencies, which generally leads to a decrease in sensitivity. To overcome the reduced sensitivity, the use of flow cells with extended longitudinal path lengths for UV detection, for example, serves as a useful technique [9]. Larger sample volume injection might be a more

efficient method for the increase in sensitivity if the concentration of the analyte ions can be quantitatively accomplished. However, larger sample volume injection for scale-downed IC has been hardly examined. If samples contain an excess of ions, the elimination of interference from this source is also necessary.

In this study, large sample volume injection was examined for trace iodide analysis in seawater using semi-micro IC with UV detection. Iodine is a micro-nutrient for microorganisms and it exists mainly as iodide and iodate in seawater [10–14]. The iodide concentration in seawater is sensitive to surrounding conditions such as biological activities and redox conditions. The iodide level varies from 30 $\mu\text{g/l}$ in seashore and ocean surface waters to below $<1 \mu\text{g/l}$ in deep ocean seawater. Neutron activation analysis [11], the use of automated electrochemical procedures [12], and cathodic stripping square wave voltammetry [13] have been used for the determination of trace iodide in seawater. However, these methods require special apparatus and/or time-consuming procedures. Ion chromatography is a simple method for determination of iodide in seawater, but larger sample volume injection with analyte focusing is necessary for highly sensitive detection [14]. Furthermore, as seawaters contain an excess of anions, Cl^- , SO_4^{2-} , Br^- and HCO_3^- , it is also necessary to remove interference from coexisting anions. For columns with low anion-exchange capacity, higher NaCl was used for the elution of the analyte ions, I^- and SCN^- [15–19], NO_2^- and NO_3^- [20,21] in various saline samples containing Cl^- , SO_4^{2-} , Br^- etc. as matrix anions and was also used for on-column matrix elimination. However, resins with low anion-exchange capacities were not effective for on-column focusing of iodide in seawater. In this study, both on-column iodide focusing and on-column matrix elimination for large seawater sample injection (2 ml) were examined using a semi-micro-column (35 \times 1 mm I.D.) packed with the high-capacity anion-exchange resin of styrene–divinylbenzene copolymer. Two inorganic salts, NaClO_4 and NaCl, were selected as components of the mobile phases for on-column iodide focusing, its elution, and on-column matrix elimination. Thus, the feasibility of semi-micro ion chromatography is demonstrated for trace iodide in seawater.

2. Experimental

2.1. Apparatus

The ion chromatographic system was composed of a computer-controlled pump (CCPM: Tosoh, Tokyo, Japan), a Rheodyne 7125 injector equipped with sample loop of 0.5 or 2 ml (Cotati, CA, USA), a UV–Vis detector (L-4200: Hitachi, Tokyo, Japan), and a chromato-processor (SC-8010: Tosoh). TSKgel SAX (Tosoh; styrene–divinylbenzene copolymer with ~ 3.7 mequiv./g of anion-exchange capacity; functional group, benzyltrimethylammonium type; particle size 5 μm) was used as packing material for the semi-micro column (35 \times 1 mm I.D.) and a conventional column (150 \times 4.6 mm I.D.). The resin which was dispersed in 0.5% sodium acetate solution was packed by the slurry packing technique at flow-rates of 0.6 and 2.0 ml/min, respectively. A mini-column packed with ODS (10 \times 4 mm I.D., Capcellpak C₁₈, Shiseido, Tokyo, Japan) was set up before a semi-micro column and was used as a prefilter.

2.2. Reagent, mobile phase, sample

All inorganic sodium salts of reagent grade were used for preparation of standard anionic solutions and mobile phases. Standard anion solutions were prepared by mixing and diluting stock solutions of each anion (10 g/l). Stock solutions of 0.3 M NaClO_4 , 2 M NaCl, and 0.5 M sodium phosphate buffer (0.15 M Na_2HPO_4 +0.35 M NaH_2PO_4) were used for mobile phase preparation. The mobile phases prepared were passed through a membrane filter (pore size, 0.1 μm) before use. Artificial seawaters were prepared according to the Lyman-Fleming formula [22]. For example, 35‰ artificial seawater contains four major anions, 19 300 mg/kg Cl^- , 2700 mg/kg SO_4^{2-} , 65 mg/kg Br^- , and 142 mg/kg HCO_3^- . Two seawater samples (200 m deep) were collected near Japan.

3. Results and discussion

3.1. Semi-microcolumn system for iodide

Fig. 1 shows anion separations on a semi-micro-

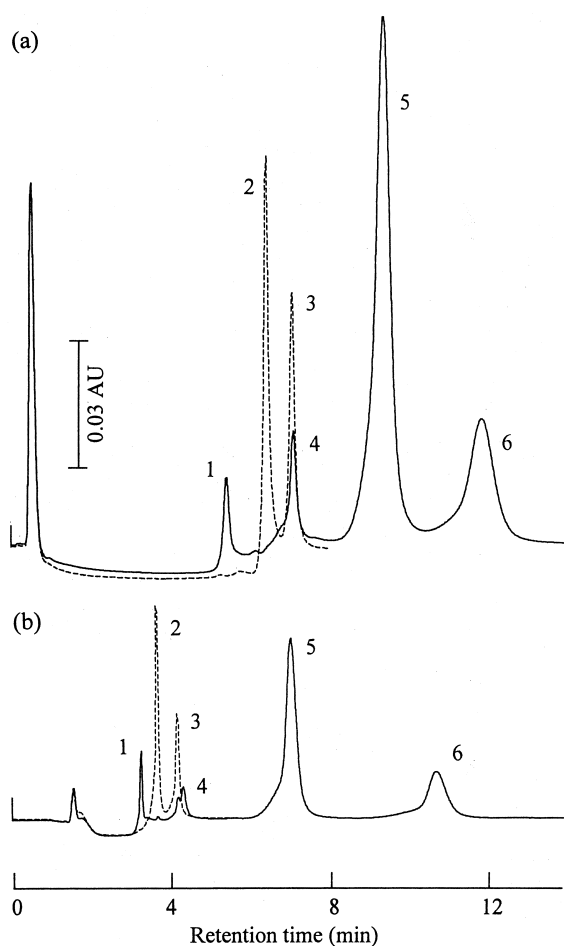


Fig. 1. Ion chromatograms of inorganic anions. Conditions: (a) semi-microcolumn (TSKgel SAX resin, 35×1 mm I.D.); mobile phase, 0.03 M NaClO₄+0.5 M NaCl+5 mM sodium phosphate buffer, pH 6.0; flow-rate, 0.3 ml/min. (b) Conventional column (TSKgel SAX resin, 150×4.6 mm I.D.); mobile phase, 0.35 M NaClO₄+10 mM sodium phosphate buffer, pH 6.1; flow-rate, 1 ml/min. Sample volume, 2 ml; 1, IO₃⁻-I (0.1 mg/l); 2, NO₂⁻ (0.05 mg/l); 3, NO₃⁻ (0.05 mg/l); 4, Br⁻ (1 mg/l); 5, I⁻ (0.1 mg/l); 6, SCN⁻ (0.1 mg/l). Detection, UV absorbance at 226 nm.

column (35×1.0 mm I.D.) and a conventional column (150×4.6 mm I.D.). The solid and dotted chromatograms represent separate runs. Anion peaks were sharp for both column systems in spite of large sample loop injection (2 ml). This shows that on-column focusing of anions was effectively accomplished due to the use of the high-capacity anion-exchange styrene–divinylbenzene copolymer resin. The reasons for the mobile phase selection are given

in Section 3.2. The peak heights of I⁻ and SCN⁻ with hydrophobicity on a semi-microcolumn were ≈2.9 and 2.7 times higher, respectively, than those on conventional columns with sample loop (Fig. 1b) and a concentrator column (10×4 mm I.D., same resin) [14]. This suggests the strong affinity of I⁻ and SCN⁻ to the resin and also the reduction of the sample dilution on a semi-microcolumn. Similar results were obtained for NO₃⁻ and Br⁻, but the effect was small for IO₃⁻ and NO₂⁻ due to weak retention.

A mini-column packed with ODS (10×4 mm I.D.) was examined as a prefilter before a semi-microcolumn. It did not affect the peak shapes of I⁻ and SCN⁻, although the peaks of IO₃⁻ and NO₂⁻ became broad due to sample dilution. The mini-column was thereafter used for iodide in seawater.

3.2. Effects of NaClO₄ and NaCl in mobile phases

Fig. 2 shows anion separation on a semi-micro-

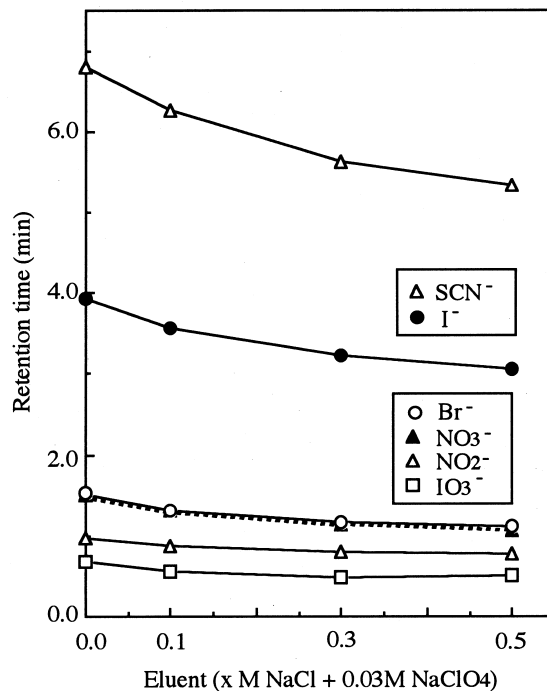


Fig. 2. Dependence of anion separation on NaCl concentration in mobile phases, 0.03 M NaClO₄+x M NaCl+5 mM sodium phosphate buffer. Sample, 5–10 mg/l of each anion (sample volume, 30 μl). Other conditions as in Fig. 1a.

column by the mobile phases, 0.03 M NaClO₄+x(0~0.5) M NaCl+5 mM sodium phosphate buffer. The sample volume was 30 μl. As iodide is retained strongly on the column by electrostatic and hydrophobic interactions, ClO₄⁻ with hydrophobicity is effective in displacing iodide with hydrophobicity [14]. The addition of NaCl to mobile phases resulted in a decrease in anion retention. However, as the eluting power of NaCl is not generally strong, the rate of decrease was small and the order of the anion retention did not change. For example, the addition of 0.5 M NaCl decreased the retention times from 1.54, 3.92 and 6.80 min to 1.11, 3.07 and 5.33 min for Br⁻, I⁻, and SCN⁻, respectively.

The effect of NaCl in the samples was different to that of NaCl in the mobile phase. Fig. 3 shows the dependence of retention times of I⁻ (20 μg/l) and Br⁻ (67 mg/l) on Cl⁻ concentration in 0.5 ml of

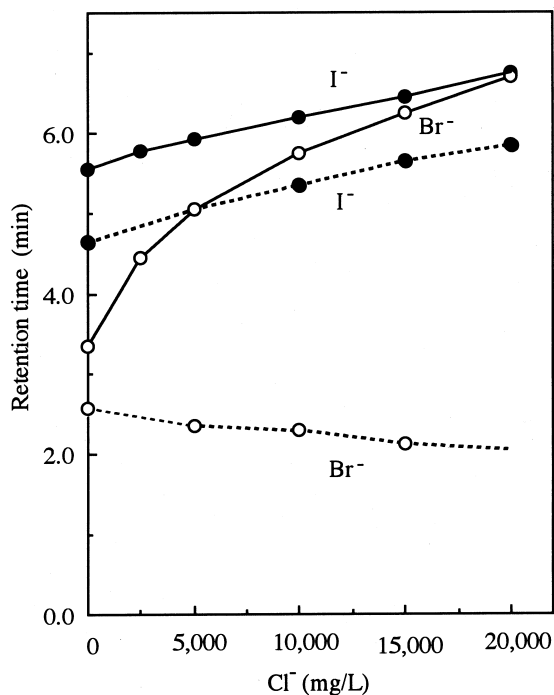


Fig. 3. Dependence of iodide and bromide separation on Cl⁻ concentration in samples. —, for mobile phase, 0.03 M NaClO₄+5 mM sodium phosphate buffer and ---, for 0.03 M NaClO₄+0.5 M NaCl+5 mM sodium phosphate buffer. Sample, 20 μg/l I⁻ and 67 mg/l Br⁻ containing various Cl⁻ concentrations (sample volume, 0.5 ml). Other conditions as in Fig. 1a.

sample. Retention times of I⁻ increased with Cl⁻ concentration for both eluent systems, 0.03 M NaClO₄ and 0.03 M NaClO₄+0.5 M NaCl. On the other hand, retention volumes of Br⁻ increased with Cl⁻ for 0.03 M NaClO₄ but decreased with increase in Cl⁻ for 0.03 M NaClO₄+0.5 M NaCl. Br⁻ at Cl⁻=20 000 mg/l was not detected because the peak was hidden in the big peak of the matrix anions. SO₄²⁻ in samples had a similar effect to Cl⁻ for both mobile phases.

These results can be explained as follows: excess Cl⁻ in samples converted the ClO₄⁻-form of a semi-microcolumn to partly the Cl⁻-form for both eluent systems. For example, 17.7% of Cl⁻ in 35‰ artificial seawater (sample volume, 2 ml) were trapped in the column in the ClO₄⁻-form (10×4 mm I.D.) [14]. The conversion resulted in the stronger affinity of iodide to the column, owing to the large difference in selectivity between I⁻ and Cl⁻ compared with that between I⁻ and ClO₄⁻. Whereas, Cl⁻ which was generated in the recovery process to the ClO₄⁻-form was weak in eluting power for iodide. For example, retention time of I⁻ for mobile phase of 1.4 M NaCl was 24.2 min. This leads to the delay of iodide elution. The difference in retention times of I⁻ between both mobile phases is attributed to the eluting power of 0.5 M NaCl.

The delay in the Br⁻ elution with 0.03 M NaClO₄ was attributed to the longer time needed for recovery to the ClO₄⁻-form, irrespective of stronger eluting power of Cl⁻ for Br⁻ (retention volume of Br⁻ was for example 8.02, 5.28, 2.83 min for mobile phases of 0.2, 0.3 and 0.6 M NaCl only, respectively). On the other hand, with 0.03 M NaClO₄+0.5 M NaCl, the retention time of Br⁻ decreased with salinity in sample, because of faster recovery to original anion-forms and also of stronger eluting power by Cl⁻. A faster recovery is possibly due to the lower conversion rate from ClO₄⁻ to Cl⁻ in the process of sample injection. Thus, Cl⁻ in sample exerted effectively for Br⁻ elution but not for I⁻ elution.

3.3. Iodide in seawater

Fig. 4 shows the separation of 20 μg/l iodide in artificial seawater (salinity 35‰; sample volume, 0.5 ml). Using the mobile phase 0.03 M NaClO₄, iodide coeluted with 65 mg/kg bromide (Fig. 4a), as

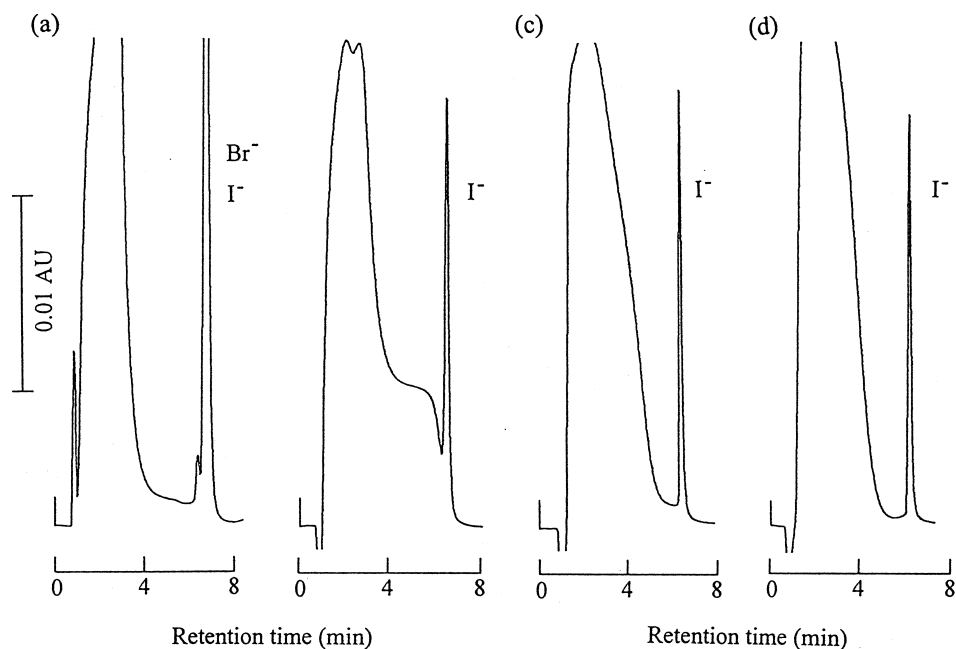


Fig. 4. Dependence of iodide separation on NaCl concentration in mobile phases, 0.03 M NaClO₄+*x* M NaCl+5 mM sodium phosphate buffer. (a) 0 M NaCl, (b) 0.1 M NaCl, (c) 0.3 M NaCl and (d) 0.5 M NaCl. Sample, 20 µg/l iodide in 35‰ artificial seawater (sample volume, 0.5 ml). Other conditions as in Fig. 1a.

expected from Fig. 3. On the other hand, the addition of NaCl to the mobile phase was effective for faster elution of bromide and also for elimination of interference by salinity. A sharp iodide peak with a flat baseline was obtained using the mobile phase containing 0.5 M NaCl (Fig. 4d). These results indicate that both on-column iodide focusing and on-column matrix elimination were effectively achieved, indicating the effectiveness of high-capacity anion-exchange resin of styrene–divinylbenzene copolymer and the mobile phase containing NaCl. The effect of more NaCl in the mobile phases on I⁻ elution was, however, small and the retention times of I⁻ decreased a little (from 6.67 to 6.05 min) with addition of 0.5 M NaCl, indicating that the elution of I⁻ was mainly accomplished by ClO₄⁻. These results are different from those of the columns with low anion-exchange capacities: NaCl brought about both elution of the analyte ions, I⁻ and SCN⁻ [15–19], NO₂⁻ and NO₃⁻ [20,21] and also the elimination of interference by matrix anions such as Cl⁻ and SO₄²⁻. For the column with increasing anion-exchange capacity, it was possible to increase the separation

efficiency of NO₂⁻ and NO₃⁻ in samples containing an excess of anions [20,21].

The performance of semi-micro ion chromatography for iodide in seawater was thus examined using 0.03 M NaClO₄+0.5 M NaCl+5 mM sodium phosphate buffer. Peak areas of iodide decreased with increased salinities of samples although the rate was relatively small: $y=157.0-0.489x$, R^2 (correlation coefficient)=0.849; y , peak area (5 µg/l I⁻, 2 ml); x , salinity ($x=0\sim 40\%$). On the other hand, retention volumes increased gradually from 9.90 min (0‰) to 12.50 min (40‰). Theoretical plates per column for I⁻ increased with salinities in samples at first from 4700 (0‰) to 20 600 (5‰) and 38 000 (15‰) but then decreased with an increase in salinity, 34 400 (25‰), 23 700 (35‰) and 21 000 (40‰). These results indicate that salinity in 2 ml of sample exerted both iodide focusing on a semi-microcolumn and partly its elution. The calibration curve of I⁻ by the peak area method was $y=36.5+28.2x$ ($x=0\sim 10$ µg/l, 2 ml of 35‰ sample) $R^2=0.999$. The slope was ~2.8 times higher than those with conventional columns (150×4.6 mm I.D.) with

both sample loop and concentrator column systems [14]. The ghost peak of I^- for 35‰ artificial seawater ($I^- = 0 \mu\text{g/l}$) was obtained due to the strong affinity of I^- to the column and the peak area increased with salinity. However, as the I^- peak areas at $0 \mu\text{g/l}$ I^- were almost constant for the samples with same salinity, it did not affect the iodide determination. The relative standard deviations (R.S.D.s) for successive injections of 5 and $1 \mu\text{g/l}$ I^- (2 ml of 35‰ sample) were 1.5 and 5.8% ($n=5$ each), respectively. The detection limit by a semi-microcolumn system ($3 \times$ standard deviation of peak area at $0 \mu\text{g/l}$ I^-) was $0.2 \mu\text{g/l}$ I^- for 2 ml of 35‰ artificial seawater.

Fig. 5 shows the separation of iodide in seawater samples. A sharp iodide peak was obtained without any interferences: the concentrations were 1.3 and $6.5 \mu\text{g/l}$ (Fig. 5a and b), respectively, and recoveries were 98.4 and 97.0% for addition of 2 and $5 \mu\text{g/l}$ I^- , respectively.

In conclusion, larger sample volume injection method will be a useful technique for increasing sensitivity if scale-downed IC conditions can be optimized.

Acknowledgements

I am grateful to Dr. S. Ohtsuka of Fisheries Laboratory, Faculty of Applied Biological Science, Hiroshima University for offering the seawater samples.

References

- [1] S. Rokushika, Z.Y. Qie, H. Hatano, *J. Chromatogr.* 260 (1983) 81–87.
- [2] S. Rokushika, Z.Y. Qie, Z.L. Sun, H. Hatano, *J. Chromatogr.* 280 (1983) 69–76.

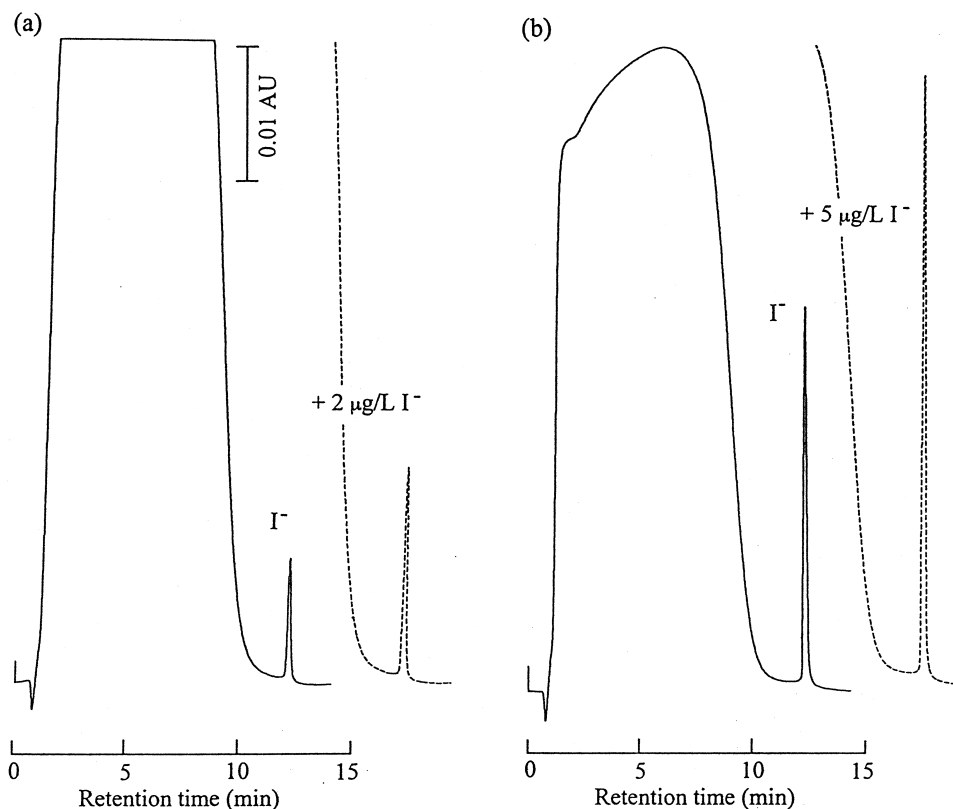


Fig. 5. Ion chromatograms of seawater samples (sample volume, 2 ml). Conditions as in Fig. 1a.

- [3] T. Takeuchi, E. Suzuki, D. Ishii, *Chromatographia* 25 (1988) 582–584.
- [4] A. Sjögren, C.B. Boring, P.K. Dasgupta, J.N. Alexander, IV, *Anal. Chem.* 69 (1997) 1385–1391.
- [5] T. Takeuchi, E. Suzuki, D. Ishii, *J. Chromatogr.* 447 (1988) 221–224.
- [6] H. Wu, T. Takeuchi, H. Haraguchi, *Anal. Chim. Acta* 267 (1992) 141–146.
- [7] H. Wu, T. Takeuchi, H. Haraguchi, *Anal. Chem.* 65 (1993) 2204–2208.
- [8] H. Wu, H. Haraguchi, *Anal. Chem.* 66 (1994) 765–767.
- [9] J.P. Chervet, R.E.J. Van Soest, M. Ursem, *J. Chromatogr.* 543 (1991) 439–449.
- [10] P.G. Brewer, *Chemical Oceanography*, 2nd ed. Vol.1. in: J.P. Riley, G. Skirrow (Editors), Academic Press, London, 1975, Ch. 7.
- [11] G.T.F. Wong, P.G. Brewer, *Anal. Chim. Acta* 81 (1976) 81–90.
- [12] E. Nakayama, T. Kimoto, S. Okazaki, *Anal. Chem.* 57 (1985) 1157–1160.
- [13] G.W. Luther III, C.B. Swartz, W.J. Ullman, *Anal. Chem.* 60 (1988) 1721–1724.
- [14] K. Ito, *Anal. Chem.* 69 (1997) 3628–3632.
- [15] K. Ito, H. Sunahara, *Bunseki Kagaku* 37 (1988) 292–295.
- [16] K. Ito, H. Sunahara, *J. Chromatogr.* 502 (1990) 121–129.
- [17] K. Ito, E. Shoto, H. Sunahara, *J. Chromatogr.* 549 (1991) 265–272.
- [18] Marheni, P.R. Haddad, A.R. McTaggart, *J. Chromatogr.*, 546 (1991) 221–228.
- [19] A.C.M. Brandão, W.W. Buchberger, E.C.V. Butler, P.A. Fagan, P.R. Haddad, *J. Chromatogr. A* 706 (1995) 271–275.
- [20] K. Ito, Y. Ariyoshi, F. Tanabiki, H. Sunahara, *Anal. Chem.* 63 (1991) 273–276.
- [21] K. Ito, Y. Ariyoshi, H. Sunahara, *J. Chromatogr.* 598 (1992) 237–241.
- [22] J. Lyman, R.H. Fleming, *J. Mar. Res.* 3 (1940) 134–146.