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Simultaneous determination of iodide and iodate in seawater by transient isotachophoresis–capillary zone electrophoresis with artificial seawater as the background electrolyte

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Abstract

We developed capillary zone electrophoresis with transient isotachophoresis (ITP) as an on-line concentration procedure for simultaneous determination of iodide and iodate in seawater. The effective mobility of iodide was decreased by addition of 20 mM cetyltrimethylammonium chloride to an artificial seawater background electrolyte so that transient ITP functioned for both iodide and iodate. Limits of detection for iodide and iodate were 4.0 and 5.0 μg/l (as iodine) at a signal-to-noise ratio of 3. Values of the relative standard deviation of peak area, peak height, and migration times for iodide and iodate were 2.9, 1.3, 1.0 and 2.3, 2.1, 1.0%, respectively. The proposed method was applied to simultaneous determination of iodide and iodate in seawater collected at a pond at our university.

Keywords: Water analysis; Isotachophoresis–capillary zone electrophoresis; Background electrolyte composition; Environmental analysis; Iodide; Iodate; Inorganic anions

1. Introduction

It is important to determine iodide and iodate to understand the geochemical behavior of iodine in seawater because the dominant species of iodine are generally iodide and iodate [1]. Iodate in seawater is generally determined by titration and colorimetry; iodide is oxidized to iodate and determined as the difference between the total iodate and iodate concentrations. Ito [2] developed a high-sensitive ion chromatography (IC) method for determination of iodide in seawater using high-capacity anion-exchange resin for both preconcentration and separation of iodide. The total inorganic iodine (iodide plus iodate) was also determined after reduction of iodate to iodide using ascorbic acid and acetic acid. Hu et al. [3] determined bromide, nitrate, and iodide concentrations in a real seawater sample by electrostatic IC using a zwitterionic-surfactant-coated ODS column.

Capillary zone electrophoresis (CZE) has been studied recently as a new approach to seawater analysis. Carou et al. [4] observed iodide in seawater samples by CZE using a mixture of 50 mM borate and 1.5 M sodium chloride (pH 9.3) as the background electrolyte (BGE). Mori et al. [5] successfully detected iodide spiked to an actual seawater sample using a BGE containing 0.3 M sodium chloride, 10 mM Zwittergent-3-14, 50 mM of a non-ionic surfactant Tween 20, and 5 mM phosphate (pH 7). We proposed a novel CZE method in which artificial seawater (pH 7.9) was used as the BGE and transient isotachophoresis (ITP) as the on-line concentration procedure for determination of iodide in seawater [6]. The effective mobility of iodide was decreased by addition of cetyltrimethylammonium chloride (CTAC, 10 mM) to the BGE to utilize transient ITP and to separate iodide from other coexisting anions such as bromide, nitrite, and nitrate in seawater samples. Quite recently, Ichihara et al. [7] presented sensitive CZE results for iodide in seawater using a similar procedure to that proposed by us [6]. We also proposed a CZE procedure for determination of iodate in seawater using a similar procedure to that in our previous paper [8]; the capillary was rinsed with 0.1 mM

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dilauryldimethylammonium bromide (DDAB) to reverse the electroosmotic flow (EOF) before the capillary was filled with BGE; the BGE was artificial seawater adjusted to pH 3.0 with phosphate buffer and the terminating ion solution was acetate adjusted to pH 2.6 with phosphate buffer [9].

As mentioned above, few studies have addressed determination of iodide or iodate in seawater by CZE, but there is no paper on simultaneous determination of iodide and iodate in seawater. In the present study, we developed a CZE procedure for simultaneous determination of iodide and iodate in seawater, improving the procedure described in our previous paper [6]. The following analytical conditions were examined: effects of kind of terminating ion, concentration of terminating ion solution, concentration of CTAC, injection periods of a sample solution, and a terminating ion solution, and wavelength on concentration of iodide and iodate. The proposed method was applied to determination of iodide and iodate in seawater taken from the surface of a pond at our university.

2. Experimental

2.1. Apparatus

The capillary electrophoresis (CE) apparatus used throughout this study was a Perkin-Elmer 270A-HT with a UV-Vis absorbance detector (Foster City, CA, USA). A polyimide-coated fused-silica (GL Sciences, Tokyo, Japan), 75 μm i.d. × 375 μm o.d., served as the capillary electrophoresis column. Total length of the column ($L_{tot.}$) was 72 cm; effective length ($L_{det.}$) was 50 cm. Peak area, peak height, and migration time were measured using a Chromato-Integrator D-2500 (Hitachi, Tokyo, Japan). A seawater sample was taken from the surface of a pond at our university on 17 June 2003 using a glass reagent bottle (1 l) with a thin rope. An SCT meter (Model 30; Yellow Springs Instrument Co., Yellow Springs, OH, USA) was used for measuring the salinity of the seawater sample.

2.2. Reagents

The cationic surfactant CTAC, used for reversing EOF and adjusting the effective mobility for iodide, was obtained from Tokyo Kasei Kogyo (Tokyo, Japan). All reagents were of analytical-reagent grade and were used as received. Standard solutions containing nitrite (0.05 mg/l), nitrate (0.5 mg/l), iodide (0.02–0.1 mg/l), and iodate (0.02–0.1 mg/l) in artificial seawater for calibration graphs were prepared from 1000 mg/l sodium nitrite (Nacalai Tesque, Kyoto, Japan), sodium nitrate (Nacalai Tesque), potassium iodide (Nacalai Tesque), and potassium iodate (Nacalai Tesque) solutions. Nitrite and nitrate concentrations were expressed as nitrogen concentration and those of iodide and iodate were as iodine concentration. Sodium acetate trihydrate (Wako, Osaka, Japan) and sodium dihydrogen phosphate dihydrate (Nacalai Tesque) were used for preparation of terminating ion solutions. Distilled, demineralized water, obtained from an automatic still (WG220; Yamato Kagaku, Tokyo, Japan) and a Milli-QII system (Nihon Millipore, Tokyo, Japan), were used for all experiments. Preparation of artificial seawater (pH 7.9) was based on a Japanese Standard [10]. A previous paper describes the preparation procedure and artificial seawater composition [11]. All solutions used in this study were filtered through a 0.45-μm membrane filter before use.

2.3. Procedure

Iodide and iodate in the seawater sample were determined by the following procedure. A seawater sample was filtered through a 0.45-μm membrane before analysis. No pretreatment procedures were required except for filtration. The detection wavelength was set at 221 nm for CZE determination of iodide and iodate. The thermostat was maintained at 30 °C. A new capillary was washed with 1 M sodium hydroxide for 40 min and then with water for 10 min. The capillary was filled with BGE (artificial seawater containing 20 mM CTAC, pH 7.9) by vacuum for 3 min. After a sample was vacuum injected into the CE apparatus for 20 s (420 nl), the 2 M phosphate terminating ion solution was injected for 4 s (84 nl). The injection period of 1 s corresponds to the sample volume of 21 nl. A voltage of 8 kV was applied with the sample inlet side as the cathode. Each step was run automatically. Calibration graphs were prepared using synthetic standards.

3. Results and discussion

3.1. Kind and concentration of terminating ion

In general, it is difficult to analyze seawater samples by CZE with an ordinary BGE because of electrodispersion [12,13] in sample zone caused by high amounts of chloride (0.56 M) or its UV absorption which is not negligible owing to its high concentration [14]. In order to eliminate the interference of high concentrations of salt, Ding et al. [15] used a BGE containing 1.5 M sodium chloride. Woodland and Lucy [13] added a zwitterionic surfactant to the BGE to separate analyte peaks from the chloride matrix and diluted seawater samples five times. However, they had to use standard addition method for the determination of analytes. On the other hand, we showed that the concentrations of bromide, nitrite, and nitrate in seawater could be determined by the working curve method using artificial seawater as the BGE in spite of differences in the salinity of sample solutions [16]. Therefore, artificial seawater was also used as the BGE in the following experiments.

A leading and terminating ion must be present in the capillary to produce transient ITP at the initial stage of CZE separation. A terminating ion must be loaded in the

capillary because chloride acts as the leading ion, but there is no terminating ion in the artificial seawater BGE. We already found that acetate and 600 mM were the optimum terminating ions and its concentration for transient ITP–CZE determination of nitrite and nitrate in seawater [17]. In addition, phosphate was presumed to be the alternative terminating ion for determination of iodate in seawater by a similar procedure [9]. Therefore, the following experiment was performed to determine which was more effective as the terminating ion for both iodide and iodate. An artificial seawater sample containing 1.0 mg/l nitrite, nitrate, iodide, and iodate was injected into the CE apparatus for 2 s and analyzed using artificial seawater BGE containing 10 mM CTAC. After the sample injection, 600 mM acetate or phosphate was injected into the analyzer for 1 or 5 s, respectively, as the terminating ion. The detection wavelength was set at 220 nm, because we already found that above anions could be detected at 220 nm in the previous paper [6]. Fig. 1A–C show those results. When acetate was used as the terminating ion, the iodide peak height was 1.6 times higher than that obtained without transient ITP (Fig. 1B); the iodate peak

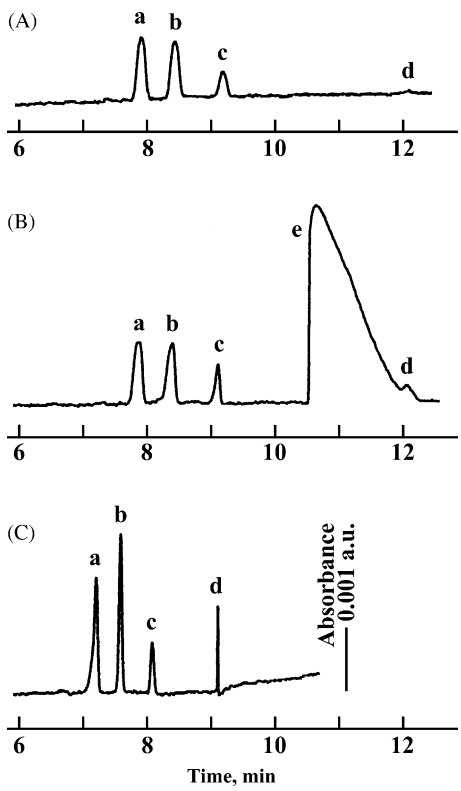

Fig. 1. Effects of terminating ion type on concentration of iodide and iodate. Electrophoretic conditions: capillary, $L_{tot.} = 72$ cm, $L_{det.} = 50$ cm, 75 μm i.d. × 375 μm o.d.; BGE, artificial seawater containing 10 mM CTAC (pH 7.9); voltage, −8 kV; wavelength for detection, 220 nm. Sample, artificial seawater containing 1.0 mg/l NO_2^-, 1.0 mg/l NO_3^-, 1.0 mg/l I^-, and 1.0 mg/l IO_3^-; vacuum injection period, 2 s (42 nl). (A) Without transient ITP. (B) With transient ITP; terminating ion, 600 mM acetate; injection period, 1 s. (C) With transient ITP; terminating ion, 600 mM phosphate; injection period, 5 s. Peaks: a = NO_2^-; b = NO_3^-; c = I^-; d = IO_3^-; e = CH_3COO^-.

was involved in the large acetate peak even with 1 s injection of acetate. On the other hand, the peak height for iodide and iodate were 2.0 and 21 times higher than those obtained without transient ITP, respectively, when phosphate was used (Fig. 1C). It is noteworthy that nitrite and nitrate were also concentrated (1.9 times for nitrite and 2.9 times for nitrate) using phosphate terminating ion whereas only nitrate was slightly concentrated (1.1-fold) using the acetate terminating ion. We have shown that the lower the mobility for a terminating ion, the larger the concentration ratio for nitrite and nitrate in transient ITP [17]. According to this tendency, a higher concentration ratio should be obtained for acetate than that for phosphate. If the BGE is well-buffered around pH 7.9, the effective mobilities for acetate and phosphate are 38×10^5 and 45×10^5 cm^2/(V s), respectively [18]. The effective mobility of phosphate might be decreased owing to the kinetically labile complex of phosphate with calcium in the artificial seawater BGE. A similar phenomenon was observed when sulfate was used as the terminating ion for artificial seawater BGE [19]. The dissociation constant for the complex of hydrogenphosphate with calcium is 2.7 and that of sulfate with calcium is 2.3 [20].

The effect of phosphate concentration on enrichment effects for iodide and iodate was investigated. Artificial seawater containing 0.05 mg/l nitrite, 0.5 mg/l nitrate, 0.1 mg/l iodide, and 0.1 mg/l iodate was analyzed according to a similar procedure to that described above. As the terminating ion, 600 mM and 2 M phosphate were injected into the apparatus for 8 and 10 s, respectively. Maximum concentration of 2 M was employed in view of the solubility of sodium dihydrogen phosphate in water [48.5% (w/w) at 25 °C] [21]. Maximum concentration ratios for iodide and iodate were obtained when injection periods for 600 mM and 2 M phosphate were 8 and 10 s, respectively. The injection period for the sample was varied over the range of 10–20 and 10–35 s for 600 mM and 2 M phosphate, respectively. When 600 mM phosphate was used, the peak height for iodide was almost constant; the peak height for iodate increased with increasing injection period up to 15 s, but then it almost leveled off. When 2 M phosphate was used, the peak height for iodide increased with an increase in the sample injection period up to 15 s, but then decreased; the peak height for iodate increased with increasing injection period up to 30 s, but then almost leveled off. When the sample and 2 M phosphate were injected for 15 and 10 s, respectively, the peak height for iodide was 8.2 times higher than that obtained with 600 mM phosphate (injection periods for the sample and 600 mM phosphate were 15 and 8 s, respectively). When 2 M phosphate was used, the peak height for iodate was the same as that when 600 mM phosphate was used. Therefore, 2 M phosphate was adopted as the terminating ion and its concentration.

3.2. Concentration of CTAC

Concentration of CTAC in the BGE was varied in the range of 10–25 mM. Injection periods for the sample

(artificial seawater containing 0.05 mg/l nitrite, 0.5 mg/l nitrate, 0.1 mg/l iodide, and 0.1 mg/l iodate) and terminating ion (2 M phosphate) solutions were as follows: the sample solution, 15 s and the terminating ion solution, 10 s for 10 mM CTAC; 15 and 6 s for 15 mM CTAC; 20 and 4 s for 20 mM CTAC; 20 and 2 s for 25 mM CTAC. The maximum amount of the terminating ion was injected into the capillary so that baseline separation of iodide and iodate could be accomplished thereby yielding a higher concentration ratio. The migration time for iodide increased linearly with increased concentration of CTAC up to 25 mM, whereas the migration time for iodate was almost constant. When the CTAC concentration was 25 mM, the iodide and iodate peaks overlapped. The peak height for both iodide and iodate increased with increasing concentration of CTAC up to 20 mM, but then decreased. Therefore, 20 mM was adopted as the CTAC concentration.

3.3. Injection period of a sample solution

The injection period for the sample solution used in the previous sections was varied in the range of 10–25 s using the BGE containing 20 mM CTAC. The injection period for 2 M phosphate was fixed at 4 s. The peak height for both iodide and iodate increased with increased injection period up to 20 s, but then decreased. Consequently, 20 and 4 s were adopted as injection periods for the sample solution and 2 M phosphate, respectively.

3.4. Wavelength

Iodide and iodate could be detected at the wavelength of 220 nm. However, the effect of wavelength on peak heights for iodide and iodate was studied in detail over the range of 218–225 nm to obtain absorbances as large as possible. The artificial seawater sample containing the same concentrations of iodide and iodate, etc. as used before was analyzed using the optimum conditions that were so far established. The peak height for iodide increased linearly with increasing wavelength. The peak height for iodate, on the contrary, decreased linearly with an increase in wavelength. The two straight lines intersect each other at 221 nm. Therefore, 221 nm was adopted the wavelength for iodide and iodate determination. Fig. 1A and B show electropherograms of the artificial seawater sample containing 0.05 mg/l nitrite, 0.5 mg/l nitrate, 0.1 mg/l iodide, and 0.1 mg/l iodate with and without transient ITP. Iodide and iodate peaks were not observed clearly without transient ITP (Fig. 2A). On the contrary, sharper peaks were observed with baseline separation using transient ITP (Fig. 2B).

As described above, we could find the analytical conditions of the ITP–CZE method for simultaneous determination of iodide and iodate although the use of chemometrics can be beneficial in this kind of experiments containing subtle interactions [22].

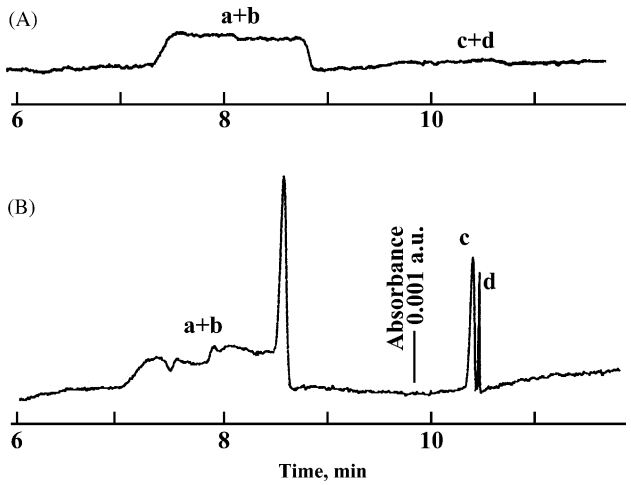

Fig. 2. Concentration effects for iodide and iodate using transient ITP. Sample, artificial seawater containing 0.05 mg/l NO_2^-, 0.5 mg/l NO_3^-, 0.1 mg/l I^-, and 0.1 mg/l IO_3^-; vacuum injection period, 20 s. Concentration of CTAC in the BGE, 20 mM; wavelength for detection, 221 nm. (A) Without transient ITP. (B) With transient ITP; terminating ion, 2 M phosphate; injection period, 4 s. Other electrophoretic conditions and identification of peaks are as in Fig. 1.

3.5. Calibration graphs

Standard solutions for iodide and iodate were prepared using artificial seawater containing 0.05 mg/l nitrite and 0.5 mg/l nitrate. Calibration graphs for iodide and iodate were linear using both peak area and peak height. Regression equations relating area response to concentration for iodide (x, 0–0.1 mg/l) and iodate (x, 0–0.1 mg/l) were $y = 7.27 \times 10^4 x + 4$ (correlation coefficient, 0.9997) and $y = 1.18 \times 10^4 x + 344$ (0.9885), respectively; those relating peak height were $y = 2.53 \times 10^4 x - 6$ (0.9997) and $y = 2.02 \times 10^4 x + 247$ (0.9979). Table 1 summarizes values of relative standard deviation (R.S.D.) and limit of detection (LOD) for iodide and iodate. The R.S.D.s of peak areas, peak heights, and migration times for iodide and iodate were not larger than 2.9, 2.1, and 1.0%, respectively. Table 2 summarizes LODs of determination of iodide and iodate in previous reports. The LOD for iodide in our method was superior to the LOD in the CE method reported by Carou et al. [4], but inferior to the LODs in the ion chromatography methods reported by Ito

Table 1
Precision and detection limits of determination of iodide and iodate[a]

	R.S.D. (%)[b]			LOD ($S/N = 3$) (μg/l)
	Area	Height	Time	
I^-	2.9	1.3	1.0	4.0
IO_3^-	2.3	2.1	1.0	5.0

[a] Electrophoretic conditions are as in Fig. 2.
[b] Sample, artificial seawater containing 0.05 mg/l NO_2^-, 0.5 mg/l NO_3^-, 0.1 mg/l I^-, and 0.1 mg/l IO_3^-, seven determinations.

Table 2
Detection limits of determination of iodide and iodate in previous reports

LOD (μg/l)		Methods	Reference
I^-	IO_3^-		
4.0 ($S/N = 3$)	5.0 ($S/N = 3$)	CZE	Proposed method
0.2 ($S/N = 2$)	–	IC	[2]
0.8	–	IC	[3]
13 ($S/N = 3$)[a]	–	CZE	[4]
3.0 ($S/N = 3$)	–	CZE	[6]
0.9 ($S/N = 3$)	–	CZE	[7]
–	12 ($S/N = 3$)	CZE	[9]

[a] Recalculated by the authors.

[2] and Hu et al. [3]. The LOD for iodate was superior to the LOD in the CE method reported by Yokota et al. [9].

3.6. Seawater analysis

The proposed method was applied to determination of iodide and iodate in a seawater sample (salinity, 24.8‰) taken from the surface of a pond at our university on 17 June 2003. Concentrations of iodide and iodate in the sample solution were 0.038 and 0.037 mg/l, respectively; average concentrations were calculated by duplicate analyses using peak area. Figure 3 represents an electropherogram of the surface seawater. The iodide concentration was in the range of iodide concentrations (0.024–0.036 mg/l) which were obtained at the same sampling site in our previous study [6], but slightly larger than those (0.021 and 0.025 mg/l) obtained by Ito et al. [23]. The iodate concentration was also similar to those (0.030 and 0.027 mg/l) obtained for seawater samples collected from the Seto Island Sea, Japan by Ito et al. [23] using ion chromatography with a low-capacity anion-exchange column; iodate concentration was obtained as the difference between total inorganic iodine and iodide after iodate was reduced to iodide. Truesdale [24] reported that the concentrations of iodide and iodate in the surface seawater of coastal area were 0.019 and 0.033 mg/l, respectively. He also pointed out that iodate is reduced to iodide by organic matter originated in land in the surface seawater of coastal area.

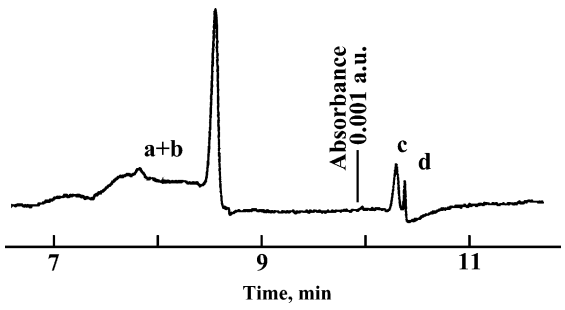

Fig. 3. Electropherogram of surface seawater from the pond at Kobe University of Mercantile Marine. Electrophoretic conditions and identification of peaks are as in Fig. 2 and Fig. 1, respectively.

4. Conclusions

We developed a transient ITP–CZE method for simultaneous determination of iodide and iodate in seawater. This is the first method by which simultaneous determination of iodide and iodate in seawater with direct detection is successfully carried out. However, it is necessary to analyze seawater samples collected at both surface and seabed in several sampling sites to further confirm its applicability to analysis of coastal seawater that contains relatively high concentrations of iodide and iodate. The standard addition experiments should be also performed to validate the method. In addition, further improvement of the LODs was desirable for lower concentrations of iodide and iodate in seawater such as open seawater or deep seawater. Iodide concentration decreases steeply with an increase in depth although the total inorganic iodine concentration is conservative with salinity [2].

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