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Determination of bromide ions in seawater by capillary zone electrophoresis using diluted artificial seawater as the buffer solution

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Abstract

A novel capillary zone electrophoresis method was developed for the determination of bromide ion in seawater. A tenfold-diluted artificial seawater was adopted as the buffer solution, to prevent interference from high concentrations of chloride ion in seawater. No electroosmotic flow reverser was used to shorten the analysis time. It was found that the peak area and migration time for bromide ion were almost constant, despite differences in the salinity of sample solutions; the peak height decreased linearly with an increase in the salinity. The limit of detection for bromide ion was 0.46 mg/l ($S/N=3$). The values of the relative standard deviation for peak area and migration time for bromide ion were 1.4 and 1.5%, respectively. The proposed method was applied to the determination of bromide ion in seawater samples taken from the surface and the sea-bed. The analytical results obtained by the working curve method agreed with those obtained by the standard addition method. The method may be applicable to the determination of other ions, such as nitrite and nitrate ions, in seawater © 1998 Elsevier Science B.V.

Keywords: Water analysis; Buffer composition; Bromide; Inorganic anions

1. Introduction

It is well-known that chlorine-induced combined oxidants and halogenated organic compounds, such as trihalomethanes (THMs), which have a potential cancer risk, are formed through the chlorination of cooling water for anti-fouling in power plants. Power plants are usually located in coastal areas and, hence, seawater, which contains higher concentrations of bromide ion than that found in river waters [1], is used as the coolant. The presence of bromide ion

influences the formation and disappearance of the oxidants and the formation of THMs [2–4]. It is, therefore, important to determine bromide ion in coastal seawater, where the salinity varies, with the effect of river waters.

Bromide ion in seawater has been determined by ion chromatography using direct injection of diluted samples [2,5], solvent extraction [6], water as the mobile phase [7], reversed-phase ion-interaction high-performance liquid chromatography (HPLC) [8], HPLC with pre-column derivatization linked to solid-phase extraction [9] and by flow injection potentiometry with a bromide ion-selective electrode

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[10]. In our previous paper [11], capillary isotachopheresis (cITP) was used for the determination of bromide ion in seawater. In general, the concentrations of chloride and sulfate ions in seawater are about 290- and 14-times as high as that of bromide ion, respectively [1]. It was, therefore, necessary to separate bromide ion from large amounts of chloride and sulfate ions prior to the isotachopheretic measurement. A pretreatment procedure using a redox reaction in a gas–liquid separator was adopted and, hence, it was a little time-consuming.

Recently, capillary zone electrophoresis (CZE) was used for the separation of bromide ion with direct and indirect UV detection. However, there is no report concerning the determination of bromide ion in seawater by CZE. Sakai et al. [12] used 750 mM chloride containing 0.5 mM CIA-Pak OFM anion-BT (Waters, Milford, MA, USA) as the buffer solution to eliminate the interference caused by chloride ions for the determination of nitrite and nitrate ions in seawater; the peak areas for these ions (with constant concentrations) varied with the concentration of chloride ions in seawater. Several anions, including bromide ion, in subterranean waters that contain high concentrations of salts have been determined by Song et al. [13]; the buffer solution used was 100 mM sodium chloride with 2.0 mM cetyltrimethylammonium chloride. They found that the peak area for a constant concentration of an anion remained constant regardless of the concentration of salt in the sample. However, the relative standard deviations (R.S.D.) of the peak area and the limit of detection (LOD) for bromide ion were relatively high.

In this paper, diluted artificial seawater is proposed as the buffer solution for the determination of bromide ion in seawater, in order to solve the above problems. Optimum analytical conditions, such as wavelength, applied voltage and injection volume, were established for the determination of bromide ion in seawater. The effects of the concentration of artificial seawater in sample solutions on the peak area, peak height and migration time were also investigated. Finally, the proposed method was applied to the determination of bromide ion in seawater samples taken from the surface and the sea-bed, collected around the coastal area of Osaka Bay in June, 1997.

2. Experimental

2.1. Apparatus

A Perkin-Elmer (Foster City, CA, USA) Model 270A capillary electrophoretic analyzer was used with a UV–Vis absorbance detector. The rise-time for the detector was set at 0.50 s. A polyimide-coated fused-silica capillary (GL Sciences, Tokyo, Japan), 50 μm I.D. \times 375 μm O.D., served as the capillary electrophoresis column. The total length of the column was 54 cm and the effective length was 25 cm. Peak area and peak height were measured using a Hitachi (Tokyo, Japan) Model D-2500 Chromato-Integrator. A Unicam Analytical Systems (Cambridge, UK) PW9421 pH meter was used. A Denki Kagaku Keiki (Tokyo, Japan) Model HPH-110 pH meter and a Yellow Springs Instrument (Yellow Springs, OH, USA) Model 33 S-C-T meter were used for measuring the pH and salinity of seawater samples in situ, respectively. A reagent bottle with a thin rope and a Rigosha (Tokyo, Japan) Vandorn water sampler (2 l) were used for sampling seawater samples taken from the surface and the sea-bed. Seawater samples were filtered through a 0.45- μm pore size membrane filter (Toyo Roshi, Tokyo, Japan) and stored in 500 ml polypropylene bottles (Sanplatec, Osaka, Japan) inside a refrigerator on the day of collection.

2.2. Reagents

All reagents were of analytical-reagent grade and were used as received. Standard solutions of bromide ion (2–12 mg/l) were prepared from a 1000-mg/l potassium bromide (Wako, Osaka, Japan) solution. Distilled, demineralized water, obtained from a Yamato Kagaku (Tokyo, Japan) Model WG220 automatic still and a Nihon Millipore (Tokyo, Japan) Milli-Q II system, was used throughout. The preparation of artificial seawater was based on a Japanese Standard [14] minus the bromide ion. First, three groups of mixed solutions containing various salts were prepared. The first group was a mixed solution of sodium chloride and sodium sulfate. The second group was a mixed solution of magnesium chloride, calcium chloride and strontium chloride. The third group was a mixed solution of potassium chloride,

Table 1
Composition of artificial seawater

| Component | Concentration (g/l) |
|--------------------------------------|---------------------|
| NaCl | 24.54 |
| MgCl ₂ ·6H ₂ O | 11.10 |
| Na ₂ SO ₄ | 4.09 |
| CaCl ₂ | 1.16 |
| KCl | 0.69 |
| NaHCO ₃ | 0.20 |
| H ₃ BO ₃ | 0.03 |
| SrCl ₂ ·6H ₂ O | 0.04 |
| NaF | 0.003 |

sodium hydrogencarbonate, boric acid and sodium fluoride. Then the three groups were mixed to give the composition shown in Table 1. All solutions used in this study were filtered through a 0.45- μ m membrane filter before use.

2.3. Procedure

A seawater sample (10 ml) was diluted to 100 ml with water. The detection wavelength was set at 200 nm. The thermostat was maintained at 30°C. The capillary was washed with 0.1 M sodium hydroxide and water (3 min each). Then the capillary was filled with a buffer solution (tenfold-diluted artificial seawater, pH 7.0) by vacuum for 3 min. A small amount of the diluted sample (11 nl) was vacuum injected into the capillary electrophoresis apparatus for 2 s. A voltage of 11 kV was applied, with the sample inlet side as the cathode. Each step was run automatically. A calibration graph was prepared using synthetic standards.

3. Results and discussion

3.1. Effect of chloride ion

In seawater, the high concentration of chloride ion migrates in front of nitrite and nitrate ions and interferes with the CZE determination of these ions [12]. The limiting molar conductivity of bromide ions (78.1 S cm² mol⁻¹ at 25°C) is closer than those for nitrite (71.8 S cm² mol⁻¹) and nitrate (71.5 S cm² mol⁻¹) ions to that of chloride ions (76.3 S cm²

mol⁻¹) [15]. It can be presumed that chloride ions also interfere with the determination of bromide ion in seawater by CZE. In order to confirm this, tenfold-diluted artificial seawater, containing 6.8 mg/l bromide ion, was analyzed using a mixed solution of 20 mM phosphoric acid and 20 mM sodium dihydrogenphosphate as the buffer solution. The pH of the buffer solution was adjusted to 3.0 to suppress the electroosmotic flow (EOF). Bromide ion was not separated from high concentrations of chloride ion, as shown in Fig. 1A. On the other hand, a sharp peak of bromide ion was observed within 4 min using artificial seawater that had been diluted tenfold as the buffer solution, as shown in Fig. 1B. When non-diluted artificial seawater was used, the current was too high and it was impossible to lower the baseline. Therefore, all subsequent experiments were carried out using tenfold-diluted artificial seawater as the buffer solution.

In general, an EOF reverser is used for the detection of anions whose electrophoretic mobilities are larger than that the electroosmotic mobility. No EOF reverser was used to shorten the analysis time, as bromide ion was detected within 4 min.

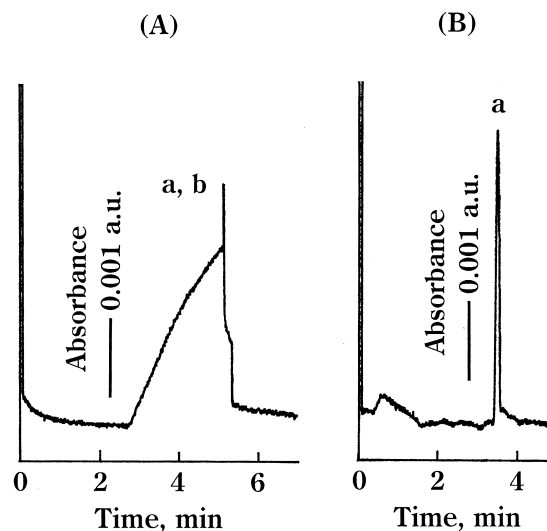


Fig. 1. Electropherograms for the separation of bromide ion. (A) Buffer, 20 mM H₃PO₄ + 20 mM NaH₂PO₄ (pH 3.0); (B) buffer, tenfold-diluted artificial seawater. (a) Br⁻; (b) Cl⁻. Sample, tenfold-diluted artificial seawater containing 6.8 mg/l Br⁻.

3.2. Wavelength

It has been shown that bromide ions absorb UV light below 210 nm [16]. Over the wavelength range of 190–215 nm, tenfold-diluted artificial seawater, containing 6.8 mg/l bromide ion, was analyzed to select the optimum wavelength for determination of bromide ion. Both maximum peak area and maximum peak height were observed at 195–200 nm, as illustrated in Fig. 2. However, baselines were unstable at 190–195 nm. Therefore, 200 nm was adopted as the optimum wavelength for the determination of bromide ion.

3.3. Applied voltage

The effects of applied voltage on the reproducibilities of the peak area, peak height and migration time (CZE parameters) for bromide ion were studied over the range 6–16 kV. The R.S.D. values for peak area, peak height and migration time were minimized at 11 kV, as evident in Table 2. The migration time increased with a decrease in the applied voltage. At 16 kV, baseline instability and noise were increased compared to values found at 11 kV. Therefore, 11 kV was adopted as the optimum voltage for the de-

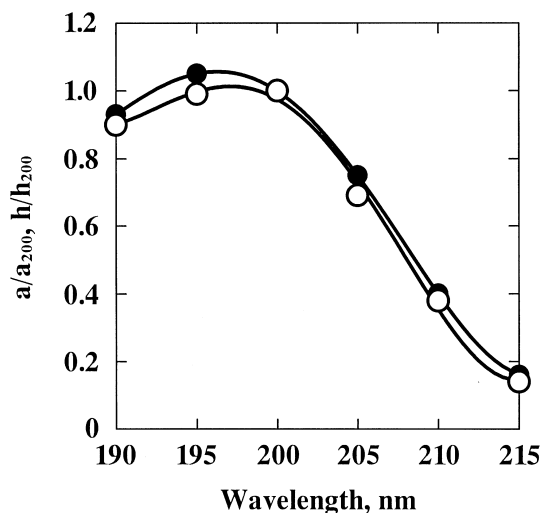


Fig. 2. Effects of wavelength on the peak area and peak height for bromide ion. a , \circ = Peak area; a_{200} = peak area at 200 nm; h , \bullet = peak height; h_{200} = peak height at 200 nm. Buffer, tenfold-diluted artificial seawater; sample, tenfold-diluted artificial seawater containing 6.8 mg/l Br^- .

Table 2

Effect of applied voltage on the reproducibility of the peak area, peak height and migration time for bromide ion

| Voltage (kV) | R.S.D. (%) | | | Migration time (min) |
|--------------|------------|--------|------|----------------------|
| | Area | Height | Time | |
| 6 | 2.2 | 1.0 | 2.0 | 6.6 |
| 11 | 1.4 | 0.3 | 1.5 | 3.5 |
| 16 | 12 | 1.1 | 8.0 | 2.1 |

Sample: Tenfold-diluted artificial seawater containing 6.8 mg/l Br^- .

Number of determinations, four.

termination of bromide ion. It is well-known that the reproducibility in CE analysis can be improved if the capillary is washed with an alkaline solution. We also found that washing the capillary with 0.1 M sodium hydroxide between each run gave the most reproducible values.

3.4. Injection volume

The effects of injection volume on the reproducibilities of CZE parameters for bromide ion were studied over the range 5–16 nl. The injection volume was varied by changing the period for vacuum injection. The injection periods, 1, 2 and 3 s, correspond to the injection volumes, 5, 11 and 16 nl, respectively. The volume of material injected per unit time (V_i , nl/s) is determined by the following equation [17]

$$V_i = \frac{\Delta P D^4 \pi}{128 \eta L} \quad (1)$$

where ΔP equals the pressure drop, D is the internal diameter of the capillary, η is the viscosity and L is the length of the capillary. The lowest R.S.D. values of CZE parameters were obtained when the injection volume was 11 nl, except for that of peak area, which was sufficiently low, as evident in Table 3. It can also be observed that the sample plug length should be no more than 1% of the capillary length to generate a maximum of 10% of peak-broadening [17]. One-percent of the 54 cm long capillary corresponds to 11 nl. Therefore, 11 nl sample solutions were injected in all subsequent experiments. The number of theoretical plates (N) in Table

Table 3

Effect of injection volume on the reproducibility of the peak area, peak height and migration time, and the plate number for bromide ion

| Volume (nl) | R.S.D. (%) | | | Plate number |
|-------------|------------|--------|------|--------------|
| | Area | Height | Time | |
| 5 | 1.0 | 1.6 | 4.0 | 26 000 |
| 11 | 1.4 | 0.3 | 1.5 | 10 000 |
| 16 | 2.6 | 1.1 | 4.8 | 5100 |

Vacuum injection: 1, 2, 3 s.

Sample: Tenfold-diluted artificial seawater containing 6.8 mg/l Br⁻.

Number of determinations, four.

3 was calculated by the following equation, which was proposed by Tsuda [18]

$$N = 2\pi \left(\frac{ht_R}{A} \right)^2 \quad (2)$$

where A is the peak area, h is the peak height and t_R is the retention time. The magnitude of N decreased with increasing injection volumes.

3.5. Concentration of artificial seawater in sample solutions

Sample solutions containing 6.8 mg/l bromide ion and 0–10% artificial seawater were prepared and analyzed by the method to examine the effects of the concentration of artificial seawater on the CZE parameters for bromide ion. The results are illustrated in Fig. 3. In Fig. 3, 10% on the abscissa represents tenfold-diluted artificial seawater. The values on the ordinate show the ratios of the peak area, peak height and migration time to those for the sample solution containing no artificial seawater. The peak area and migration time were approximately constant over the range of 0 to 10% artificial seawater. The R.S.D. of the peak area was 3.6%, which was calculated using the eleven values of the peak area given in Fig. 3. The R.S.D. obtained by our experiment was much lower than those obtained by Song et al. [13], 9.7–19.9%; the concentration of bromide ion in our experiment, 6.8 mg/l ($8.5 \cdot 10^{-2}$ mM), was lower than the concentrations (4–40 mM) used in their experiment. The peak height increased linearly with decreasing concentrations of artificial seawater. This is due to the stacking effect caused by

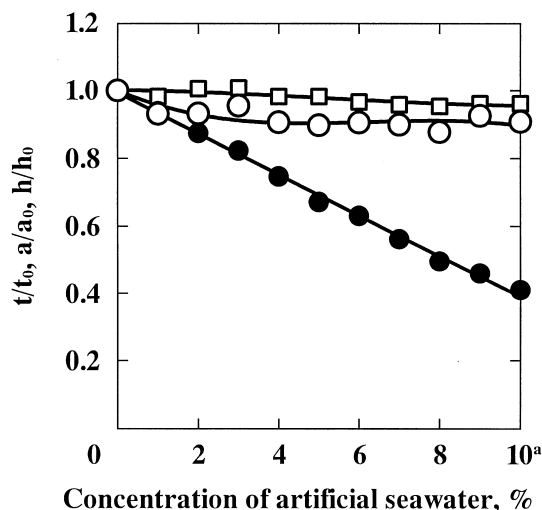


Fig. 3. Effects of the concentration of artificial seawater in sample solutions on the peak area, peak height and migration time for bromide ion. a , ○=Peak area; a_0 =peak area for the sample solution containing no artificial seawater; h , ●=peak height; h_0 =peak height for the sample solution containing no artificial seawater; t , □=migration time; t_0 =migration time for the sample solution containing no artificial seawater. 10^a , tenfold-diluted artificial seawater. Buffer and the concentration of Br⁻ are the same as in Fig. 2.

the difference between the field strength of the sample zone and that of the electrolyte zone. Therefore, the concentration of bromide ion in seawater can be determined using the peak area in spite of differences in the salinity of the sample solutions. The salinity of the non-diluted artificial seawater was ca. 35‰. In general, the salinity of seawater is above 14‰, except for those that are strongly affected by river waters.

3.6. Analysis of seawater samples

Calibration graphs for bromide ion were linear using both peak area and peak height, up to at least 12 mg/l. The regression equation relating area response (y , arbitrary units) to concentration (x , 0–12 mg/l) for bromide ion was $y = 2510x + 204$ (correlation coefficient, 0.9998). The regression equation relating height response to concentration was $y = 521x + 10$ (correlation coefficient, 0.9999). Since the magnitude of the slope of the regression line for the area response was five-times larger than that for the

height response, the peak area was used for calculation of the concentration of bromide ion in seawater. The LOD for bromide ion, 0.46 mg/l ($S/N=3$), was one seventh of the LOD obtained by Song et al. [13], 3.1 mg/l ($S/N=2$).

The proposed method was applied to the determination of bromide ion in seawater samples taken from the surface and the sea-bed and collected from around the coastal area of Osaka Bay, between Port of Amagasaki and Port of Kobe, on 13 June 1997. The seawater samples, diluted tenfold, with 1.0–4.0 mg/l of bromide ion added, were also analyzed by the method. The results obtained by the working curve method agreed with those obtained by the standard addition method, as shown in Table 4. The correlation coefficient between both results was 0.9100. Our results are within the range of bromide concentrations reported by Yamamoto et al. [2]. The relation between salinity and the concentration of bromide ion in seawater samples was also examined. The correlation coefficient was 0.9383. An electropherogram of surface seawater from Port of Amagasaki is shown in Fig. 4A. Nitrate ion was also detected. The concentration of nitrate ion was found to be 3.0 mg/l by analyzing a sample to which 1.0 mg/l nitrate ion had been added. The sea-bed seawater sample from Port of Amagasaki also contained 0.68 mg/l nitrate ion. This region is a closed area of the sea with two flood gates and two rivers

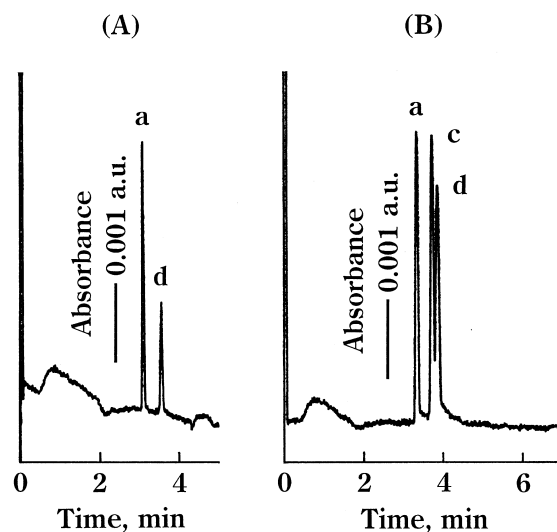


Fig. 4. Electropherograms for the separation of bromide, nitrite and nitrate ions. (A) Sample, surface seawater from the Port of Amagasaki; (B) sample, tenfold-diluted artificial seawater containing 6.8 mg/l Br^- , 3.0 mg/l NO_2^- and 1.0 mg/l NO_3^- . (a) Br^- ; (c) NO_2^- and (d) NO_3^- .

flowing into it. It can therefore be presumed that eutrophication is currently in progress in the area.

A sample solution containing 6.8 mg/l bromide ion, 3.0 mg/l nitrite ion and 1.0 mg/l nitrate ion in tenfold-diluted artificial seawater was analyzed. These ions were separated from each other, although

Table 4
Analytical results for bromide ion in seawater

| Sampling site | Depth (m) | Temperature (°C) | pH | S (‰) | Found, mg/l | |
|---------------------|-----------|------------------|------|-------|-------------|------|
| | | | | | W.C. | S.A. |
| Port of Amagasaki | 0 | 25.0 | 8.55 | 20.8 | 39.1±0.7 | 35.7 |
| Port of Amagasaki | 3.5 | 22.3 | 7.80 | 24.8 | 46.4±0.6 | 45.3 |
| Mouth of Muko river | 0 | 22.5 | 7.95 | 25.3 | 46.6±2.1 | 52.5 |
| Mouth of Muko river | 5.5 | 20.2 | 7.72 | 29.2 | 52.1±0.8 | 55.7 |
| Pond at KUMM | 0 | 22.2 | 8.39 | 29.8 | 50.1±1.0 | 55.8 |
| Pond at KUMM | 4.5 | 20.8 | 7.89 | 28.9 | 54.8±1.4 | 54.2 |
| Rokko Island | 0 | 22.8 | 8.22 | 27.8 | 47.3±0.3 | 51.7 |
| Rokko Island | 13.5 | 20.1 | 7.66 | 31.6 | 55.8±1.3 | 60.1 |
| Port of Kobe | 0 | 22.0 | 8.19 | 29.5 | 51.8±0.7 | 56.1 |
| Port of Kobe | 6.0 | 21.3 | 7.79 | 30.1 | 54.4±2.8 | 56.2 |

KUMM, Kobe University of Mercantile Marine; S, salinity; W.C., working curve method; S.A., standard addition method.

Number of determinations, two.

Sampling date, June 13 1997.

the separation between nitrite and nitrate ions was not sufficient, as evident in Fig. 4B.

4. Conclusions

The CZE method using tenfold-diluted artificial seawater as the buffer solution is simple, rapid and possesses sufficient precision and freedom from the interference of chloride ion and from differences in salinity to be useful for the determination of bromide ion in seawater. The method may be applicable to the determination of other ions, such as nitrite and nitrate ions in seawater, by improving the detection power and the resolution between nitrite and nitrate ions.

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