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Rapid and direct determination of iodide in seawater by electrostatic ion chromatography

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Abstract

An electrostatic ion chromatographic (IC) method for rapid and direct determination of iodide in seawater is reported. Separation was achieved using a reversed-phase ODS packed column (250×4.6 mm I.D.) modified by coating with Zwittergent-3-14 micelles, with an eluent comprising an aqueous solution containing 0.2 mM NaClO₄ and 0.3 mM Zwittergent-3-14 and using UV detection at 210 nm. Samples prepared by dissolving NaIO₃, NaNO₂, NaBr, NaBrO₃, NaNO₃, NaI, and NaSCN in artificial or real seawaters were analyzed using this IC system. Nitrite, iodate, bromide, bromate, and nitrate showed very little or no retention, while iodide and thiocyanate were well separated, being eluted within 6 and 16 min, respectively. The detection limit for iodide obtained by injecting 400 μL of sample was 0.011 μM (*S/N* = 3), and the precision values obtained by analyzing samples containing 0.1 or 0.3 μM iodide in real seawater samples were 2.3% RSD and 1.2% RSD, respectively. Direct determination of iodide in real seawater samples was possible using this proposed IC system. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of iodine in seawater has long been an essential task in marine chemistry. As stated in the review of Wong [1], “iodine is the most abundant biophilic minor element in the oceans”, playing critical roles in biologically and inorganically mediated oxidation/reduction reactions in the marine environment. Iodine in seawater appears mainly as inorganic iodide and iodate [2,3], although a very small portion of iodine might also be present as organic iodine [4].

A number of analytical methods have been developed for the determination of iodide or iodate in seawater. Polarography [5], colorimetry [6], and tritrimetry [7] are particularly useful for the determination of iodate, while approaches based on the separation and preconcentration of iodide from seawater (e.g. precipitation [8] and ion exchange [9]) have been used widely for the determination of iodide. Ion exchange has the advantage of being suitable for on-line application and this approach has evolved into modern ion chromatography (IC) for the determination of iodide in seawater.

The use of IC for the determination of iodide in seawater was initially reported by Ito and Sunahara [10], who used aqueous solutions containing high

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concentrations of NaCl or artificial seawater as eluents. This technique, later termed “on-column matrix elimination” by Brandao et al. [11] requires the anion-exchange stationary phase to be conditioned with the major matrix ion of the sample (in this case, chloride ion). Since the ion-exchange sites are already saturated with chloride, injection of a sample containing a high level of chloride does not result in additional band broadening and trace components of the sample can therefore be eluted as sharp peaks. Provided the analytes can be detected in the high ionic strength eluent, which in the present case can be achieved using direct UV absorbance detection, an effective analytical system for seawater can be established.

Hu et al. [12] have reported an alternative IC system which is also applicable for the direct determination of iodide in seawater, but avoids the requirement for adding matrix ions at very high concentrations to the eluent. This system is established using an adsorbed layer of sulfobetaine-type zwitterionic surfactants as the stationary phase and shows no affinity for sulfate and very low affinity for chloride. This method has been termed electrostatic ion chromatography (EIC), and it has been shown to have practical utility for the determination of nitrate, nitrite, and iodide in seawater [13,14]. Iodide determination by EIC can be accomplished using either dilute NaCl solution or dilute artificial seawater as eluent, and under these conditions iodide was eluted at approximately 30 min [13]. The retention time for iodide can be reduced to 15 min by using ammonium-sulfobetaine-1 [14] as the surfactant for preparation of the stationary phase, but this reagent is very expensive (about 100 times more than Zwittergent-3-14).

It was found in our recent studies on the separation mechanism of EIC [15,16] that when perchlorate was used as the eluent anion, iodide was eluted rapidly from the column. This behaviour was attributed to the very strong chaotropic (“structure disrupting”) interaction of perchlorate with the quaternary ammonium functionality of the zwitterion. When the eluent cation showed weak interaction with the sulfonate group of the zwitterion (e.g. for sodium ions), significant electrostatic repulsion effects occurred for analyte anions, leading to further decreases in retention. Accordingly, aqueous solu-

tions of sodium perchlorate should be optimal as eluents for the rapid elution of iodide in seawater using an EIC system and this approach has been investigated in this study.

2. Experimental

2.1. Apparatus

The high-performance liquid chromatographic (HPLC) system was a Shimadzu (Kyoto, Japan) LC-10AT system comprising a Shimadzu LC-10AT pump, a Shimadzu SIL-10A auto-injector, a Shimadzu CTO-10A column oven (the temperature was maintained at 30 °C during the analysis), and a Shimadzu CR-6A Chromatopac data system. A Shimadzu SPD-6A UV-visible detector operated at 210 nm and a Shimadzu CDD-6A conductivity detector were used in tandem for the detection and identification of the analytes.

2.2. Reagents

The sulfobetaine-type zwitterionic surfactant used to create the stationary phase was 3-(*N,N*-dimethylmyristylammonio)propanesulfonate (Zwittergent-3-14) and was obtained from Fluka (Buchs, Switzerland). Analytical-reagent-grade chemicals used to prepare solutions of the model analytes and the eluents were obtained from Wako (Osaka, Japan).

2.3. Column preparation

The separation column was obtained by initially loading Zwittergent-3-14 onto a reversed-phase ODS column (L-column, 250×4.6 mm I.D.; 5 μm particle size, 120 Å pore size, 17% C/Si, 340 m² g⁻¹, obtained from Chemicals Evaluation and Research Institute, Tokyo, Japan) by passing 40 mL of aqueous 30 mM Zwittergent-3-14 solution through the column at a flow-rate of 1.0 mL/min. The column was then conditioned with eluent at a constant flow-rate of 1.0 mL/min until a steady baseline was obtained and these conditions were then used for sample separations. To maintain a constant amount of Zwittergent-3-14 on the stationary phase the

eluents used always contained 0.3 mM Zwittergent-3-14.

3. Results and discussion

3.1. Use of NaClO_4 solutions as eluents

Samples were prepared using model analyte anions (nitrite, nitrate, bromide, bromate, iodide, iodate, and thiocyanate) dissolved in deionized water, artificial seawater, or real seawater. The artificial seawater was prepared using the method of Lyman and Fleming [17] and contained chloride (0.5657 M), sulfate (0.02906 M), bromide (0.00006 M), sodium (0.51868 M), potassium (0.01063 M), magnesium (0.05489 M), and calcium (0.01062 M). These samples were separated using 10 mM NaClO_4 as the eluent. Nitrite, nitrate, bromide, bromate, and iodate showed very little retention, but iodide and thiocyanate were well retained and well separated from each other. Iodide was eluted within 4 min, and thiocyanate within 8 min. The NaClO_4 eluent was therefore applicable only for the separation of highly polarizable analyte anions. When seawater was analyzed under the same conditions, a sharp peak ($t_R = 4.5$ min) corresponding to the elution of iodide was observed, but this peak appeared on the shoulder of a very large peak attributed to the unretained components of the sample.

Retention data obtained for iodide and thiocyanate when the concentration of NaClO_4 in the eluent was varied over the range 0.05–20 mM were used to construct plots of $\log k'$ versus $\log[\text{NaClO}_4]$. Straight lines with slopes of -0.30 and -0.29 were obtained for iodide and thiocyanate, respectively, and these plots were used to find optimal conditions for the separation of iodide. Fig. 1 shows the separation of iodide in spiked and unspiked seawater samples using 0.2 mM NaClO_4 solution as the eluent. The retention time for iodide was relatively short ($t_R = 6.4$ min) and the iodide peak was very well separated from matrix components present in the sample.

3.2. Separation mechanism

Despite the fact that the seawater samples contained molar concentrations of chloride and sulfate

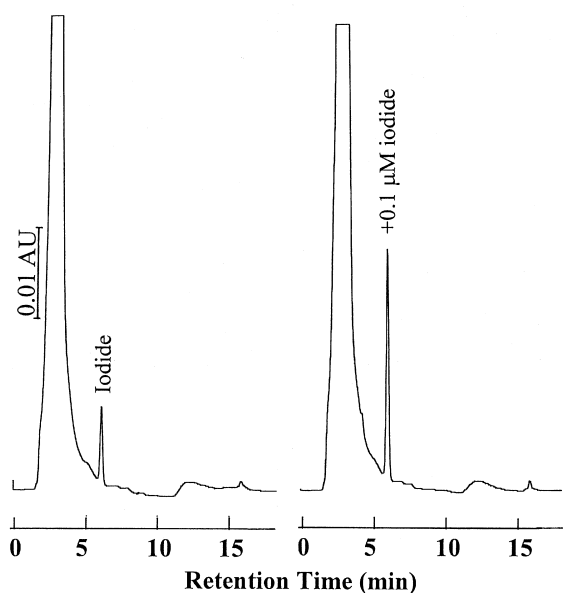


Fig. 1. Direct determination of iodide in unspiked seawater (left trace) and seawater spiked with 0.1 μM iodide (right trace) using EIC. Eluent: 0.2 mM NaClO_4 and 0.3 mM Zwittergent-3-14. Column: ODS-packed column (250 \times 4.6 mm I.D.) coated with Zwittergent-3-14. Flow rate: 1.0 mL/min. Detection: UV at 210 nm. Sample injection volume: 400 μL .

which were greatly in excess of the eluent concentration of perchlorate (2828 times and 145 times for chloride and sulfate, respectively), the retention of these analyte ions was very small. In this respect, EIC differs markedly from matrix-elimination IC, which requires very concentrated eluents for effective performance. The reasons for this difference lie in the nature of the stationary phase and the manner in which interaction with the functional groups occurs. In matrix-elimination IC, the stationary phase contains only a single type of functional group, namely a quaternary ammonium group. This functionality shows strong affinity for sulfate and iodide, and to reduce this affinity in order to achieve rapid elution of iodide, a very concentrated NaCl eluent is needed. Alternatively, a mixed eluent comprising a small amount (50 mM) of NaClO_4 and 300 mM NaCl can be used, as demonstrated by Ito and Hirokawa [18,19].

On the other hand, EIC requires the presence of two oppositely charged functional groups in close proximity. The outermost sulfonate group establishes

a Donnan membrane effect which causes electrostatic repulsion of analyte anions, in much the same manner as applies in ion-exclusion chromatography [16]. The degree of repulsion depends on the magnitude of the negative surface potential of the sulfonate group, which varies according to the degree of interaction between this group and the eluent cation. Strongly interacting cations reduce the negative surface potential, thereby decreasing the electrostatic repulsion effects and increasing the retention of analyte anions. Hence, sodium ion is a good choice as the eluent cation if rapid elution is required. The eluent anion interacts with the quaternary ammonium group on the zwitterion, with chaotropic anions showing the greatest interaction and therefore leading to decreased retention of analyte anions. Perchlorate is therefore a good choice as the eluent anion if rapid elution is desired.

Fine-tuning of the separation can be achieved by varying the concentration of either the eluent anion or cation. For example, adding NaCl to the NaClO₄ eluent will increase the eluent concentration of sodium ions, which should reduce the negative surface potential and the electrostatic repulsion effects for analyte anions, thereby leading to increased retention. This behaviour is illustrated in Fig. 2, which shows the retention times of iodide and thiocyanate in eluents containing a fixed concentration of NaClO₄ (10 mM) and varying amounts of NaCl (0–100 mM). Retention times for both iodide and thiocyanate increased as the concentration of

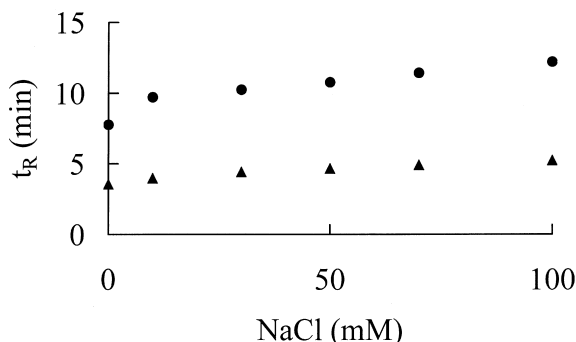


Fig. 2. Retention times for iodide and thiocyanate obtained using eluents containing 10 mM NaClO₄ and varying amounts of NaCl. Sample: NaI and NaSCN (1.0 μ M each) dissolved in seawater. Sample injection volume: 100 μ L. Other conditions as for Fig. 1.

NaCl in the eluent was increased. Similar changes in retention times in the EIC system were also found when NaF, NaH₂PO₄, and Na₂SO₄ were added to the NaClO₄ eluent. By contrast, use of mixed NaCl–NaClO₄ eluents in matrix-elimination IC [19] showed a reduction in retention times for iodide and thiocyanate compared to NaClO₄ alone.

Finally, it should be noted that chromatograms obtained using conductivity detection showed a large negative peak at a retention time of 15 min, even when a sample of pure water only was injected. This peak was attributed either to elution of water itself or to a system peak caused by disturbance of the electrostatic double layers existing at the stationary phase surface. This peak made it problematic to use conductivity detection in the present system.

3.3. Analytical performance characteristics

Samples prepared by dissolving NaI in seawater were analyzed to study detection limits and other operational aspects of the EIC system for iodide. Plots of peak areas versus concentration of the added iodide gave a linear calibration curve ($r^2 = 0.9994$) up to 4.5 μ M of iodide, using a sample injection volume of 400 μ L. The detection limit for iodide was 0.011 μ M ($S/N = 3$; sample injection volume 400 μ L; eluent 0.2 mM NaClO₄, UV detection at 210 nm). Under the same HPLC conditions, the detection limit for thiocyanate was 0.021 μ M ($S/N = 3$; sample injection volume 400 μ L). Identical standard samples (0.1, 0.15, and 0.2 μ M NaI added to seawater) were analyzed 20 times using the conditions shown in Fig. 1. Relative standard deviations (RSDs) for retention time, peak areas and peak heights were all less than 2.2%. Recoveries of added iodide were in the range 99.1–100.9% for these spiked samples. UV-absorbing sulfur oxyanions (such as sulfite and thiosulfate), which occur naturally in seawater, showed no affinity toward the Zwittergent-3-14 stationary phase and therefore did not interfere in the detection of iodide.

Three seawater samples were analyzed with the EIC system and the results were compared to those obtained using the on-line matrix-elimination IC system. The analytical data obtained are summarized in Table 1 and show that the proposed EIC method gave equivalent results to the matrix-elimination IC

Table 1

Determination of iodide in seawater samples by EIC and on-column matrix-elimination IC. Each sample was analyzed five times and the result shown is the average value. EIC conditions were as for Fig. 1, whilst matrix-elimination IC was performed using a C₁₈ column modified with cetyltrimethylammonium chloride and an eluent containing 500 mM NaCl and 50 mM NaClO₄. Sample injection volume was 400 μL. The standard errors for a set of five measurements for both EIC and IC were better than $\pm 0.12 \cdot 10^{-2} \mu\text{M}$

	Iodide (μM)		
	Seawater No. 1	Seawater No. 2	Seawater No. 3
EIC	$4.76 \cdot 10^{-2}$	$4.25 \cdot 10^{-2}$	$3.86 \cdot 10^{-2}$
IC	$4.62 \cdot 10^{-2}$	$4.30 \cdot 10^{-2}$	$3.85 \cdot 10^{-2}$

approach, but had the advantage of shorter analysis times. EIC performed with a dilute NaClO₄ eluent is the simplest system yet reported for the practical, direct determination of iodide in seawater. This system should also be applicable for the direct determination of both iodide and thiocyanate in other samples of high ionic strength, such as urine and serum.

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