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Determination of iodide in seawater and edible salt by microcolumn liquid chromatography with poly(ethylene glycol) stationary phase

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Abstract

An ion chromatography method for rapid and direct determination of iodide in seawater and edible salt is reported. Separation was achieved using a laboratory-made C30 packed column (100 mm × 0.32 mm i.d.) modified with poly(ethylene glycol) (PEG). Effects of eluent composition on retention behavior of inorganic anions have been investigated. Both cation and anion of the eluent affected the retention of analyte anions. The retention time of anions increased with increasing eluent concentration when lithium chloride, sodium chloride, potassium chloride, sodium sulfate, magnesium sulfate were used as the eluent, while it decreased with increasing eluent concentration when ammonium sulfate was used as the eluent. The detection limit for iodide obtained by injecting 0.2 μl of sample was 9 μg/l (S/N = 3). The present method was successfully applied to the rapid and direct determination of iodide in seawater and edible salt samples. Partition may be involved in the present separation mode.

Keywords: Water analysis; Stationary phases, LC; Edible salt; Iodide; Poly(ethylene glycol)

1. Introduction

The determination of iodine in seawater has long been an essential task in marine chemistry. Iodine species in seawater, an essential micronutrient for many organisms, exist as iodide and iodate. Iodide is usually a minor species in seawater compared to iodate, and its distribution gives clues to understanding the marine environment. In addition, determination of iodide and iodate in environmental samples attracts more attention because iodine may play a role in taste and odor problems [1]. On the other hand, iodide is an essential component of the thyroid hormones that plays a decisive role in human growth and metabolism, especially of the brain. Iodide deficiency in humans could cause several diseases or problems, such as goiter, stillbirth and miscarriage, neonatal and juvenile thyroid deficiency, dwarfism, mental defects, deaf mutism, spastic weakness and paralysis [2]. One of the methods for maintaining the iodide status is to supplement iodide with edible salt for people who live in areas where iodine levels are deficient.

Inductively coupled plasma mass spectrometry (ICPMS) [3], radiochemical neutron activation analysis [4] and capillary electrophoresis [5] have been developed for the determination of trace iodide. ICPMS and radiochemical neutron activation analysis for the determination of iodide can achieve the required sensitivity and accuracy. However, none of the two techniques are easily accessible due to the high level of specialization needed and high cost involved [6]. Capillary electrophoresis is a powerful tool for the determination of iodide, but its concentration sensitivity is not enough to apply to less concentrated samples [5].

For the last two decades, a simple method, ion chromatography has been attracting attention in the determination of iodide in seawater. Low-capacity anion-exchange columns, as well as C18 reversed-phase columns coated with cetyltrimethylammonium ion in water–methanol mixtures, have been applied to the determination of iodine species in seawater [7]. A high-capacity anion-exchange resin with polystyrene-divinylbenzene matrix was also used for preconcentration and separation of iodide [8]. Ito [9] has used a semi-microcolumn packed with styrene-divinylbenzene

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copolymer and a mobile phase including 0.03 M sodium perchlorate, 0.5 M sodium chloride and 5 mM sodium phosphate buffer, for the determination of trace iodide in seawater. An electrostatic ion chromatographic method for rapid and direct determination of iodide in seawater has also been reported where a reversed-phase C18 packed column modified with Zwittergent-3–14 micelles, and an eluent comprising an aqueous solution containing 0.2mM sodium perchlorate and 0.3 mM Zwittergent-3–14 are used [10]. Cook et al. [11] conducted a comprehensive investigation into the effects of the mobile phase anion and cation on the retention of analytes in zwitterion ion chromatography and proposed a new retention mechanism based on chaotropic selectivity [11]. They reported that the retention followed the Hofmeister (chaotropic) series: $IO_3^- < SO_4^{2-} < Cl^- < NO_2^- < CNO^- < ClO_3^- < ClO_4^-$. It was also demonstrated that longer retention times for sample anions as the mobile-phase cation is changed from Na^+ to Mg^{2+} to Ce^{3+}. The selectivity was explained by ion exclusion and chaotropic interactions [11].

It is possible to show that an aqueous solution of 5% poly(ethylene glycol) (PEG) with nominal average molecular weight of 20,000 is homogeneous. However, sodium sulfate is added in the solution, the solution becomes inhomogeneous and finally separates into two phases with increasing sodium sulfate concentration. For example, when 5% PEG 20,000 dissolved in 500 mM sodium sulfate aqueous solution, two phases are clearly separated. It is expected that these two separated phases can be employed for partition chromatographic separation. PEG can be fixed on appropriate hydrophobic adsorbents such as C18 and C30. Since C30 is more hydrophobic than C18, it is expected that PEG adsorbed on the C30 stationary phase is more stable than that on the C18 stationary phases. C30 stationary phases possess another advantage over C18 stationary phases that the retention time of analytes is stable even when aqueous solution such as pure water is used as the eluent. This is because aqueous eluent is not excluded from mesopores of C30 packing materials during the operation [12]. It is presumed that ions or ion pairs distribute between aqueous solution and PEG..

The present study proposes a new separation method for the determination of iodide in seawater and edible salt by microcolumn liquid chromatography (μLC). PEG is examined as the stationary phase for the separation of iodide. The modification conditions of PEG onto hydrophobic C30 stationary phases as well as the eluent conditions are examined in this paper.

2. Experimental

2.1. Apparatus

A μLC system was comprised from an MF-2 Micro Feeder (Azumadenkikogyo, Tokyo, Japan) equipped with an MS-GAN 050 gas-tight syringe (0.5 ml; Ito, Fuji, Japan) as a pump, a model 7520 injector with an injection volume of 0.2 μl (Rheodyne, Cotati, CA, USA), a 100 mm × 0.32 mm i.d. microcolumn, and a UV-2070 plus UV detector (Jasco, Tokyo, Japan). The flow-rate of the pump was kept at 2.1 μl/min and the UV detector was operated at 220 nm. The data were acquired by a Chromatopac C-R7Ae plus data processor (Shimadzu, Kyoto, Japan). A conventional-size PEG-bonded column with 150 mm × 4.6 mm i.d., Discovery HS PEG HPLC column (Sigma-Aldrich, Tokyo, Japan), was also used for comparison.

2.2. Regents

The reagents employed were of guaranteed reagent grade and were obtained from Nacalai Tesque (Kyoto, Japan), unless otherwise noted. PEGs with nominal average molecular weight of 1,000, 10,000, and 20,000 were also obtained from Nacalai Tesque. Sodium sulfate and magnesium sulfate were of extra pure reagent grade (Nacalai Tesque). Purified water was produced in the laboratory by using a GS-590 water distillation system (Advantec, Tokyo, Japan). The eluent was prepared using the purified water.

2.3. Column preparation

Fused-silica capillary was packed with 5 μm C30 (Nomura Chemical, Seto, Japan) by using a slurry packing method previously reported [13], and then conditioned with purified water. An aqueous solution containing PEG was then passed into the fused-silica capillary at a flow-rate of 2.1 μl/min for ca. 3 h, followed by washing with purified water for ca. 20 min until the baseline was stabilized. The concentration and molecular weight of PEG dissolved in water as the modification solution were examined. The column was operated at room temperature (ca. 25 °C).

3. Results and discussion

3.1. Effect of modification conditions

UV-absorbing anions such as iodate, nitrate, iodide and thiocyanate were chosen as the test analytes for this study, and 100 mM sodium sulfate was chosen as the mobile phase. To begin with, PEG with nominal average molecular weight of 1,000–20,000 were used for modification of C30 column, where 1% (w/w) each PEG aqueous solution was used as the modification agent. The retention factor of the analytes was not strongly dependent on the molecular weight of PEG, as shown in Table 1. The elution order was iodate, nitrate, iodide and thiocyanate in this order, which was the same as that observed in common ion chromatography. Among the PEG examined, PEG 20,000 provided the best resolution of the above test anions.

Table 1
Effect of the modifier molecular weight on the retention factor of analytes

	PEG 1000	PEG 10,000	PEG 20,000
Retention factor			
IO_3^-	0.33	0.30	0.25
NO_3^-	0.49	0.52	0.47
I^-	0.83	0.85	0.83
SCN^-	2.09	2.26	2.23

Modifier: 1% (w/w) PEG 1000, PEG 10,000 or PEG 20,000. Eluent: 100 mM sodium sulfate. Flow-rate: 2.1 μl/min.

Secondly, the concentration of PEG for the modification was examined by using PEG 20,000. The retention time slightly increased with increasing PEG 20,000 concentration in the region from 1 to 5% (w/w). The retention time of iodide on the 1%-modified column was 4.75 min, whereas that on the 5%-modified column was 4.84 min. For the latter case, the resolution between iodide and nitrate was 3.5, whereas that between iodide and thiocyanate was 10. Higher concentration of PEG was not tried because of its higher viscosity.

Since the C30 column modified with 5% PEG 20,000 provided the best separation result, C30 columns were modified with 5% PEG 20,000 in the following experiments.

In addition, the modified column could be used for two weeks. Spent columns can easily be regenerated by passing 50% aqueous acetonitrile solution, followed by passing PEG solution.

3.2. Optimization of eluent for anion separation

Fig. 1 shows the retention behavior of iodide on the C30 column modified with 5% PEG 20,000 using different eluents. It can be seen that both cation and anion of the eluent affect the retention of iodide. When lithium chloride, sodium chloride, potassium chloride, sodium sulfate, and magnesium sulfate were used, the retention time of iodide increased with increasing eluent concentration. On the contrary, when ammonium sulfate was used as the eluent, the retention time of iodide decreased with increasing eluent concentration. Since there is no ion-exchange site in the present separation system, the retention of analytes may not be caused by electrostatic interaction, but by partition. It is presumed that the retention of an analyte anion on the PEG stationary phase increases with increasing its hydrophobic property. A kind of salting effect may cause the increase in the retention time due to the increase in the eluent salt concentration. This means that the retention of an analyte anion is also affected by its counter cation, viz., the eluent cation. Considering the phase separation observed in the PEG/water/sodium sulfate system, it is also suggested that water is transferred from the PEG phase to the bulk phase as the eluent salt concentration increases. This in turn means that the PEG stationary phase becomes more hydrophobic with increasing eluent salt concentration.

Fig. 1 shows that the retention time of iodide also depended on the combination of the eluent anion and the eluent cation. For example, when the eluent concentration was 100–200 mM, ammonium sulfate, sodium sulfate and magnesium sulfate achieved longer retention time for iodide in this order. The observed retention strength order was different from that observed in zwitterion ion chromatography [11]. In the latter case, the larger the eluent cation's charge, the larger the retention of iodide was observed. On the other hand, when chloride was chosen as the eluent anion, slightly larger retention time of iodide was observed for lithium chloride than sodium chloride and potassium chloride.

Among the eluents examined, it is expected From Fig. 1 that ammonium sulfate can achieve good separation, but it could not separate iodide and thiocyanate. Considering the above results, sodium sulfate with higher concentration was selected as the eluent, as demonstrated in Fig. 2. It can be seen that iodide is eluted in ca. 5 min and well separated from nitrate and thiocyanate. In addition, a negative peak appeared in ca. 11.2 min is due to a component contained in sodium sulfate used as the eluent. When purified water is injected, the negative peak appeared at the same time.

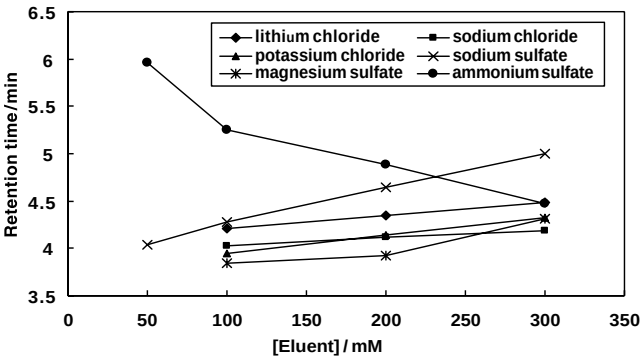

Fig. 1. Retention time of iodide as a function of the eluent concentration. Column: laboratory-made C30 packed column (100 mm × 0.32 mm i.d.) modified with 5% PEG 20,000. Eluent: lithium chloride, sodium chloride, potassium chloride, sodium sulfate, magnesium sulfate, and ammonium sulfate, as indicated. Flow-rate: 2.1 μl/min. Injection volume: 0.2 μl. Analyte: 1 mM iodide. Wavelength of UV detection: 220 nm.

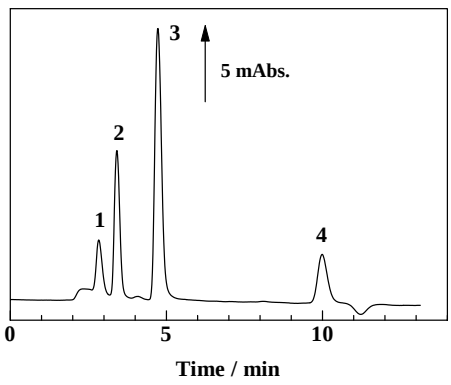

Fig. 2. Separation of authentic mixture of UV-absorbing anions on the modified C30 column. Eluent: 300 mM sodium sulfate. Peaks: 1, iodate; 2, nitrate; 3, iodide; and 4, thiocyanate. Analyte concentration: 0.2 mM each. Other operating conditions as in Fig. 1.

The reproducibility of the retention time, peak area and peak height was examined under the conditions in Fig. 2. The relative standard deviations (R.S.D.s, for $n = 6$) of the retention times and peak height/areas were 0.2–1.0% for all anions. These values show good reproducibility of the present method.

3.3. Separation on chemically bonded PEG stationary phase

Generally speaking, chemically-bonded PEG columns are superior to physically-modified PEG stationary phases in terms of the stability. Silica-based chemically-bonded-type PEG columns are commercially available. Actually, the retention factors obtained on a Discovery HS PEG HPLC column (Sigma-Aldrich) under the same eluent condition as in Fig. 2 were 0.77 and 1.31 for iodide and thiocyanate, respectively. These values are smaller than those obtained on the physically-modified PEG column under the conditions in Fig. 2, e.g., the retention factors achieved for iodide and thiocyanate are 1.03 and 3.28, respectively. The detail of the Discovery HS PEG HPLC column is not available from the manufacturer. In the case of the determination of iodide in sea water samples, iodide should be retained to some degree so that it can be separated from matrix components. Therefore, C30 columns modified with PEG 20,000 were used for the determination of iodide in real samples.

The chemically-bonded-type Discovery HS PEG HPLC column was convenient to examine the effect of organic modifier in the eluent because the PEG stationary phase does not bleed from the column independent of the mobile phase condition. Table 2 shows the retention time of iodate, iodide and thiocyanate for the eluents containing different concentrations of acetonitrile. It can be seen that the retention of hydrophobic anions such as iodide and thiocyanate decrease with increasing acetonitrile concentration. The results in Table 2 support that partition mode is involved in the present separation system.

3.4. Determination of iodide in seawater sample and edible salt

To illustrate an application of the developed method, seawater sample was collected from Nagoya port for the determination of iodide. The seawater sample was filtered by a 0.45 μm membrane filter before injection. However, iodide was not observed for the seawater sample when 300 mM sodium sulfate was used as the eluent under the conditions as in Fig. 2. The result may be because of high concentration of chloride contained in the seawater sample. In order to avoid the effect of chloride in the seawater sample, 50 mM sodium chloride was incorporated into the eluent. Fig. 3 demonstrates the separation of iodate, nitrate, iodide and thiocyanate using the eluent containing 300 mM sodium sulfate and 50 mM sodium chloride. The retention time of iodide observed under the conditions in Fig. 3 is about a half minute shorter than that observed in Fig. 2, but iodide is still resolved from nitrate and thiocyanate. The retention factor of iodide under the conditions in Fig. 3 was 0.92, which was slightly smaller than the result obtained by the zwitterionic stationary phase [10]. The retention factor of the latter was estimated to be 1.6 assuming that the porosity of the column employed in the literature [10].

Under the conditions in Fig. 3 a peak due to iodide was actually observed for the seawater sample, as demonstrated in Fig. 4. Iodide contained in the seawater sample was

Table 2
Effect of acetonitrile concentration on the retention time of analytes

Analyte	Acetonitrile concentration/%			
	0	1	5	10
Retention time/min				
IO_3^-	1.78	1.78	1.77	1.77
I^-	2.29	2.28	2.25	2.22
SCN^-	2.86	2.81	2.73	2.60

Column: Discovery HS PEG HPLC column. Eluent: 100 mM sodium sulfate including acetonitrile as indicated. Flow-rate: 1.0 ml/min.

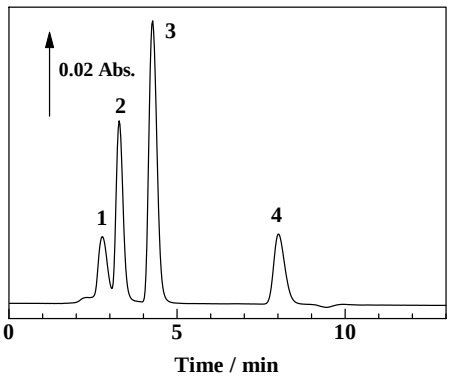

Fig. 3. Separation of authentic mixture of UV-absorbing anions using eluent containing 300 mM sodium sulfate and 50 mM sodium chloride as the eluent. Operating conditions as in Fig. 2 except for the eluent.

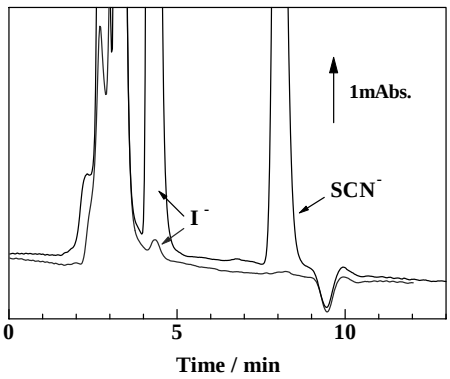

Fig. 4. Separation of iodide in seawater sample. Upper trace: 0.2 mM each of iodate, nitrate, iodide and thiocyanate. Lower trace: 0.2 μl seawater. Other operating conditions as in Fig. 3.

determined to be 90 μg/l by using a standard addition method. Under the operating conditions in Fig. 4, the limit of detection was 9 μg/l (S/N = 3), and the limit of quantitation was 30 μg/l (S/N = 10), whereas the R.S.D.s ($n = 6$) of retention time, peak area and peak height of iodide were 0.7, 1.6 and 1.2%, respectively. The linear range of quantification of iodide was 30 μg/l–2.5 mg/l.

The present system was also applied to the determination of iodide contained in edible salt. The edible salt was dissolved in purified water and 0.2 μl of the 5% aqueous solution was injected. Iodide in the edible salt was determined to be 0.21 mg/100 g salt.

4. Conclusion

A simple and rapid determination method for iodide by μLC has been proposed. The method utilizes a 10 cm laboratory-made C30 microcolumn modified with PEG. The present system allowed the determination of iodide in seawater when 300 mM sodium sulfate containing 50 mM sodium chloride was used as the eluent. More work will be required for the elucidation of the retention mechanism involved in the present separation system.

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