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Determination of iodide in seawater and urine by size exclusion chromatography with iodine–starch complex

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Abstract

A novel method for the determination of iodide by size exclusion chromatography was established. The method was simple and highly sensitive with good precision. Iodide was converted to iodine, then sequestered with starch, and separated from the matrix using a Shim-pack DIOL-150 (250×7.9 mm) size exclusion column with methanol–0.01 mol l^{-1} aqueous phosphoric acid (10:90, v/v) as mobile phase at 1.2 ml min^{-1} and UV detection at 224 nm. The calibration graph was linear from 1.0 ng ml^{-1} to 100.0 ng ml^{-1} for iodide with a correlation coefficient of 0.9992 (n=6). The detection limit was 0.2 ng ml^{-1}. The method was successfully applied to the determination of iodide in seawater and urine. The recovery was from 92% to 103% and the relative standard deviation was in the range of 1.5% to 3.7%.

Keywords: Seawater; Iodide

1. Introduction

Iodide is an essential component of the thyroid hormones that play an important role in human development, growth and metabolism. Iodide deficiency in humans can produce several diseases or problems, which include spontaneous abortion, increased infant mortality, and cretinism. One of the recommended methods for assessing the iodide status within a group of individuals is to measure the iodine excretion in urine [1,2]. Iodine is also an essential micronutrient for many organisms. Determination of iodide in seawater is helpful for understanding the marine environment [3].

In the literature, several methods including spectrophotometry [2,4], neutron activation analysis [5], inductively coupled plasma–mass spectrometry [1], ion chromatography [3,6–9], have been proposed for the determination of iodide in seawater and urine. The spectrophotometry for the determination of iodide in urine is based on the ceric–arsenious acid reaction, and thiocyanate and ascorbic acid in urine interfere directly the determination of iodide [2,4]. The neutron activation analysis and inductively coupled plasma–mass spectrometry for the determination of iodide in seawater and urine have the required sensitivity and accuracy. However, none of the two techniques are easily accessible due to the

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high level of specialization needed and the high cost involved.

In recent years, ion chromatography has been used to separate and determine iodide in seawater. However, the large amount of matrix ions (chloride, sulfate) saturate the active sites of ion-exchange column and thereby impede the separation of the target analytes; and the high ionic strength of the sample causes self-elution of the sample band during injection, leading to peak broadening and loss of separation efficiency. To overcome these difficulties, ''matrix elimination ion chromatography'' was adopted. But, some practical problems persist, including the requirement to use nonmetallic hardware to avoid corrosion [6]. Ion chromatography has been also used to determine iodide in urine [8,9]. However, the iodine anion is strongly retained on the anion resins and therefore an eluent with high strength is necessary to elute this anion, and usually seriously asymmetrical peaks are observed; and ion chromatography instrumentation is not used as widely as high-performance liquid chromatography (HPLC) instrumentation, especially in developing countries [10]. On the other hand, HPLC with complex has become more significant in the separation of inorganic ions [11–14], but only a few papers deal with the determination of anions [15,16]. In this paper, we report a novel method for the determination of iodide by size exclusion chromatography with I_2–starch complex. The proposed method was simple and highly sensitive. The method was applied to determine iodide in seawater and urine.

2. Experimental

2.1. Apparatus

The HPLC system used throughout this study consisted of a Waters 510 pump (Waters, Milford, MA, USA), a sample injector (Rheodyne, Cotati, CA, USA) with a 20 μl loop, and a Waters 996 photodiode array detector. Evaluation and quantification were made on a millennium chromatography data system (Waters, Milford, MA, USA). The column used was a Shim-pack DIOL-150 size exclusion column (250×7.9 mm I.D., Shimadzu, Kyoto, Japan), and its exclusion limit was 4×10^5.

2.2. Reagents

All solutions were prepared with analytical reagent grade compounds. Reverse osmosis–Milli Q water (18 MΩ) (Millipore Corp., USA) was used for all solutions and dilutions. The iodide stock solution was 1.0 mg ml^{-1} which was prepared by dissolving 0.1308 g of potassium iodide (Sigma, USA) in 100 ml of water and stored in the dark. The working standard solution was prepared by suitable dilution of the stock solution with water. The potassium dichromate (Sigma, USA) solution was 0.03 mol l^{-1}, the starch (from rice, product number S 7260, mean molecular mass 3.6×10^4, Sigma, USA) solution was 1.0 mg ml^{-1}, and sulfuric acid (BDH, UK) was 0.5 mol l^{-1}. All other solutions were prepared by dissolving appropriate amounts of commercially available chemicals in water.

2.3. Procedures

All chromatographic separations were carried out at ambient temperature. The mobile phase was methanol–0.01 mol l^{-1} aqueous phosphoric acid (10:90, v/v) and the flow-rate was 1.2 ml min^{-1}. The injection volume was 20 μl. The column eluate was monitored at 224 nm. The mobile phase was filtered through a 0.45 μm membrane and degassed by sonication prior to use.

A certain volume of potassium iodide standard solution was transferred to a 10 ml volumetric flask. Then, 0.5 ml of 0.5 mol l^{-1} sulfuric acid, 1 ml of 0.03 mol l^{-1} potassium dichromate solution, and 4 ml of 1 mg ml^{-1} starch solution were added. Finally, the solution was diluted to the mark with water [17].

Seawater was obtained from Victoria Harbour in Hong Kong. The seawater and urine samples were carried through a Water Sep-Pak C_{18} cartridge [18]. A certain volume of the filtrate (4 ml for seawater and 2 ml for urine) was placed in a 10 ml volumetric flask, and the other procedures were the same as for potassium iodide standard solution as described above. The sample solution was also filtered through a 0.45 μm membrane filter before injection.

3. Results and discussion

The present method for the determination of iodide was based on the precolumn oxidation of iodide to iodine, and then complexation with starch to give I_2–starch complex [17,19,20], which was then determined by size exclusion chromatography. That is, $6I^- + Cr_2O_7^{2-} + 14H^+ = 3I_2 + 2Cr^{3+} + 7H_2O$, and I_2+starch=I_2–starch.

Preliminary HPLC studies were carried out on a C_{18} reversed-phase column with mobile phases of methanol–water, and methanol–acetonitrile–water in different ratios. I_2–starch complex dissociated I_2 and starch in column. Starch was strongly retained on the C_{18} column so it was difficult to elute starch with the eluent. In subsequent studies, a size exclusion column Shim-pack DIOL-150 (250×7.9 mm) was tested because I_2–starch complex was an enormous molecule. A sharp peak of the I_2–starch complex was obtained with the gel filtration column. The methanol–0.01 mol l^{-1} aqueous phosphoric acid (10:90, v/v) was chosen as mobile phase and the flow-rate was set at 1.2 ml min^{-1}.

The spectrum of the I_2–starch complex was measured in range of 200 nm to 700 nm. The absorption peaks of the I_2–starch complex in ultra spectrum range and visible spectrum range were at 224 nm and 582 nm, respectively. The absorbance of the I_2–starch complex at 224 nm was much stronger than that at 582 nm (data not shown). Thus, the wavelength, 224 nm was chosen as detection wavelength. Under these conditions, the representative chromatograms of iodide in standard solution, seawater and urine are shown in Fig. 1, 2A and B, respectively.

A calibration graph obtained was linear from 1 ng ml^{-1} to 100 ng ml^{-1} for iodide with a correlation coefficient of 0.9992 (n=6). A detection limit (S/N= 3 [21]) was 0.2 ng ml^{-1} (for concentration injected). The relative standard deviation was 1.8% for determination of 20 ng ml^{-1} iodide standard solution (n=8).

The interference of a number of different ions was studied by spiking 10 ng ml^{-1} of iodide with known quantities of foreign materials and analyzing it by the present method. Under the present conditions of determination, no interference (relative error less than ±5%) were observed at ratios (m/m) of 1000/1

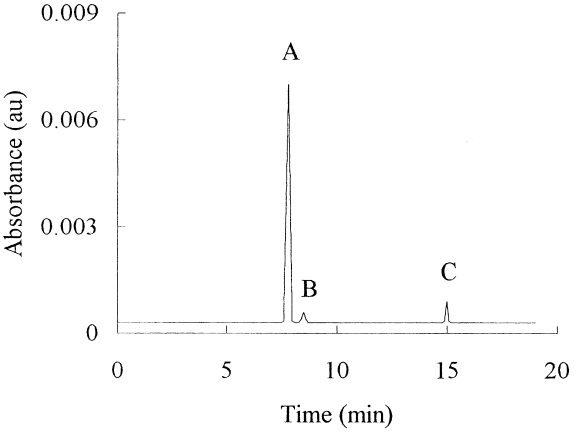

Fig. 1. Chromatogram of iodide standard at 50 ng ml^{-1}. Conditions: column, Shim-pack DIOL-150; eluent, methanol–0.01 mol l^{-1} aqueous phosphoric acid (10:90); flow-rate, 1.2 ml min^{-1}; detection, 224 nm; injection volume, 20 μl; peak, A=iodine–starch complex; B=starch; C=$K_2Cr_2O_4$.

for K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, NO_3^-, NO_2^-, SCN^-, Cl^-, F^-, Br^-, and SO_4^{2-}. The organic matter, especially macromolecule, could be removed by passing the seawater or urine sample through a Waters Sep-Pak C_{18} cartridge before precolumn derivatization (complexation).

The present method was applied to determine iodide in seawater and urine. Results are given in Table 1. As shown in Table 1, the recovery was from 92% to 103% and the relative standard deviation (RSD) was in the range of 1.5% to 3.7%.

Compared with the spectrophotometric method [2,4] for the determination of iodide in urine, the present method had no interference from SCN^- and ascorbic acid. The proposed method was about 100 times more sensitive than the spectrophotometric method of I_2–starch complex [17]. Compared with previous HPLC methods [22,23], the present method was more sensitive, and their detection limits were 5 ng ml^{-1} [22], 5 ng ml^{-1} [23] and 0.2 ng ml^{-1} (present method), respectively. Compared with the ion chromatographic methods [3,6–8], the detection limits achieved in the present method was comparable, and their detection limits were 0.2 ng ml^{-1} [3], 0.8 ng ml^{-1} [6], 0.2 ng ml^{-1} [7], 3 ng ml^{-1} [8] and 0.2 ng ml^{-1} (present method), respectively. In Miyashita and Yamashita's method [24], β-cyclodextrin was added to the mobile phase to decrease

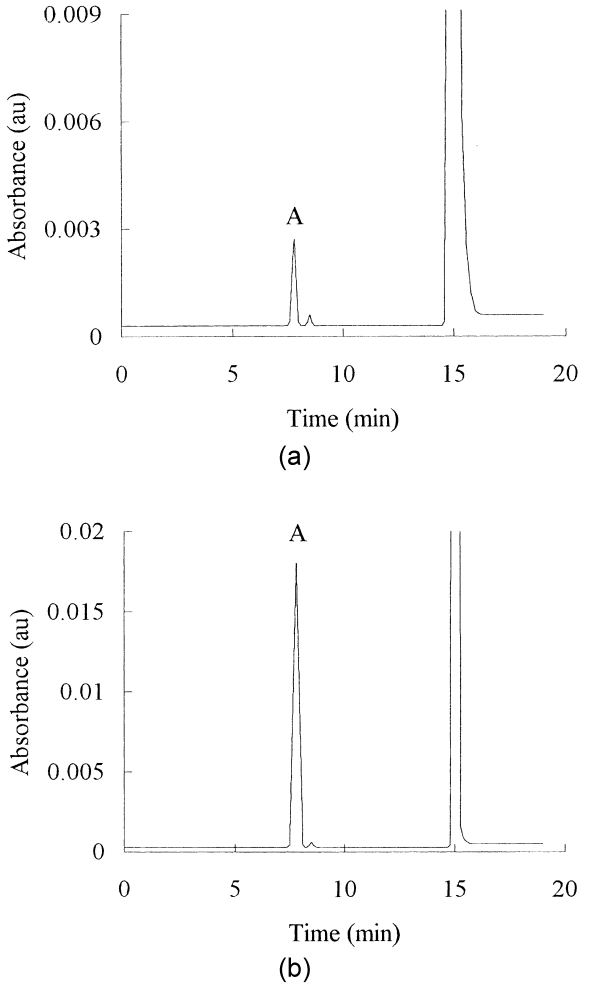

Fig. 2. Chromatograms of iodide in seawater (A) and urine (B). Conditions: column, Shim-pack DIOL-150; eluent, methanol–0.01 mol l^{-1} aqueous phosphoric acid (10:90); flow-rate, 1.2 ml min^{-1}; detection, 224 nm; injection volume, 20 μl; peak, A=iodine–starch complex. The concentrations of iodide in seawater and urine were 9.2 ng ml^{-1} and 132 ng ml^{-1}, respectively.

the retention of I^- in ion-pair reversed-phase (RP)–HPLC to obtain a reasonable analysis time. Compared with Miyashita and Yamashita's method [24], the present method was more sensitive. The detection limits were 6 ng ml^{-1} using Miyashita and Yamashita's method [24] and 0.2 ng ml^{-1} using the present method, respectively, and their molar absorptivities were 1.38×10^4 l mol^{-1} cm^{-1} at 226 nm [24] and 5.01×10^5 l mol^{-1} cm^{-1} at 224 nm [17], respectively.

Table 1
Determination of iodide in seawater and urine[a]

Samples	Found iodide (ng ml^{-1})	RSD[b] (%)	Added iodide (ng ml^{-1})	Recovery (%)
Seawater 1	8.1	3.1	10	97
Seawater 2	7.8	3.7	10	94
Seawater 3	9.2	2.6	10	103
Urine 1	125.0	2.1	100	95
Urine 2	178.0	1.9	100	98
Urine 3	96.0	3.1	100	92
Urine 4	274.0	1.5	200	96
Urine 5	56.0	3.5	200	102
Urine 6	132.0	2.4	200	99

[a] Average of five determinations.
[b] $n=8$.

In conclusion, a new method for the determination of iodide by size exclusion chromatography was described. The proposed method was simple and highly sensitive with good precision. The present method was successfully applied to the determination of iodide in seawater and urine. The proposed method can be adopted as a routine analytical method for the determination of trace iodide.

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