



Determination of uranium in seawater by flow-injection preconcentration on dodecylamidoxime-impregnated resin and spectrophotometric detection

Koichi Oguma*, Toshihiro Suzuki, Kyoichi Saito

Department of Applied Chemistry and Bio-technology, Graduate School of Engineering, Chiba-University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

ARTICLE INFO

Article history:

Available online 15 December 2010

Keywords:

Uranium
Seawater
Dodecylamidoxime-impregnated resin
Flow injection analysis
Spectrophotometric detection

ABSTRACT

A flow injection method has been developed for the determination of uranium in seawater combining the on-line preconcentration with spectrophotometric detection. An aliquot (10 mL) of the seawater sample adjusted to pH 5.5 was injected into the analytical system and uranium was adsorbed on the column packed with styrene-divinylbenzene copolymer resin (Bio-Beads SM-2) modified with dodecylamidoxime which showed high selectivity to uranium. Uranium was then eluted with 0.01 M hydrochloric acid and detected spectrophotometrically after the reaction with Chlorophosphonazo III. Interference from calcium and strontium was masked with cyclohexanediaminetetraacetic acid added to the chromogenic reagent solution. The sample throughput, the detection limit (3σ), and the preconcentration factor were 23 per hour, 0.13 $\mu\text{g/L}$, and 20, respectively, when the sample injection volume was kept at 10 mL. The precision at the 2 $\mu\text{g/L}$ level was less than 4% (RSD). The proposed method was applied to the determination of uranium in the seawater samples collected off the Boso peninsula, Japan and the uranium concentration was found to be ca. 3 $\mu\text{g/L}$, which is close to the literature data. The yield of the recovery test ranged from 95% to 99%.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Atomic power has received much attention in recent years because reduction of carbon dioxide emissions is now an important issue for prevention of global warming. Uranium is the only nuclear fuel which is widely used. However, minerals for uranium are limited. On the other hand, seawater contains uranium at the level of about 3 $\mu\text{g/L}$ and the total amount of uranium in seawater is estimated around four and half billion tones [1]. Therefore, various researches have been carried out to develop the techniques to collect uranium in seawater economically. Uranium is also known to cause acute toxicological effects for human and its compounds are potential occupational carcinogens [2]. For driving such projects to recover uranium in seawater and also for the environmental monitoring, the rapid determination of uranium in seawater is important.

Seawater contains very high concentrations of salts and its uranium content is very low. Accordingly, the separation and preconcentration of uranium is usually involved in the analytical procedures used for the determination of uranium in seawater.

Solid-phase extraction (SPE) for the analysis of traces concentration of metals in various samples has recently attracted a great

deal of interest. SPE reduces solvent usage and waste, disposal costs and extraction time. Various non-modified sorbents for adsorption of metal chelates, and Amberlite XAD resins and other sorbents physically or chemically loaded with the various ligands are proposed as reviewed by Rao et al. [3], and described by Ghasemi et al. [4] and references therein. The impregnation of polymer matrices with common chelating ligands is an easy way to prepare chelating collectors.

Literature survey has revealed that a little information is available on flow injection methods of analysis for the determination of uranium in seawater using SPE for its preconcentration. Inductively coupled plasma mass spectrometry has been consistently used for detection and coupled with the on-line preconcentration by the column packed with adsorbents such as activated alumina [5], controlled-pore glass modified with iminodiacetate [6], and metal alkoxid glass modified with 8-quinolinol [7] or commercially available resins for extraction chromatography, TRU-Spec™ [8–11] or U/TEVA™ [12].

Functionalized polymeric materials in the forms of resins, beads, gels, or membranes have been prepared and applied to the recovery of uranium from seawater. Poly(acrylamidoxime) [13], 2,2'-dihydroxyazobenzene attached to polymer matrices [14], calixarenes [15,16], and macrocyclic hexacarboxylic acid [17] have been found to be hopeful for the recovery of uranium from seawater. Calixarenes and macrocyclic derivatives show high selectivity towards uranyl ions, but the main disadvantage of these ligands is their slow complexation with uranyl ions under seawater

* Corresponding author. Tel.: +81 43 250 7167; fax: +81 43 250 7167.
E-mail address: koguma@faculty.chiba-u.jp (K. Oguma).

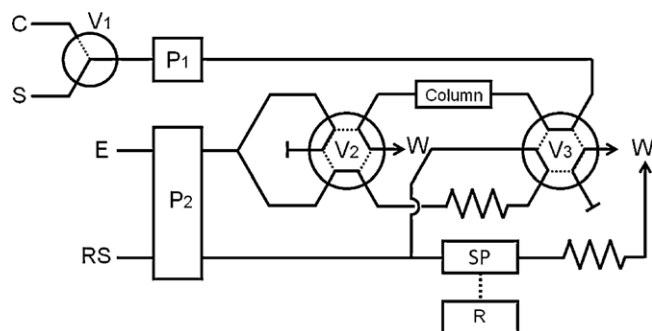


Fig. 1. Block diagram of flow injection analysis system used for the determination of uranium in seawater. C: carrier (1 mM acetate buffer); S: sample solution (10 mL); E: eluent (0.01 M HCl); CR: chromogenic reagent solution (2 μ M Chlorophosphonazo-III–0.5 mM CyDTA in 1 M HCl); V1: three-way valve; P1: peristaltic pump (10 mL/min); P2: double plunger type pump (1.6 mL/min); V2, V3: six-way valve; Column: packed with dodecylamidoxime-impregnated resin (2 mm i.d. \times 8 mm); Sp: spectrophotometric detector; R: data-processor; W: waste.

conditions. The poly(acrylamidoxime) was found to be more promising for uranium recovery from seawater especially due to its selectivity towards uranium and ease with which amidoxime groups can be anchored to diverse polymer matrices of various types and sizes as mentioned by Das et al. [18] and references therein.

This work was undertaken to prepare simply chelating resin by impregnating styrene-divinylbenzene copolymer with dodecylamidoxime and apply it to the on-line selective preconcentration of uranium in seawater prior to spectrophotometric detection with Chlorophosphonazo III.

2. Experimental

2.1. Instruments and apparatus

In preliminary experiments, uranium was measured spectrophotometrically by an Arsenazo III method with a Hitachi U-3210 spectrophotometer (Hitachi, Tokyo) or by an ICP-atomic emission spectrometric method with a Seiko SPS1200AR ICP-AES (Seiko Electronics Industries, Tokyo) equipped with a supersonic nebulizer U-5000AT⁺ to improve the sensitivity. A Shimadzu AA-630-12 atomic absorption/flame spectrophotometer (Shimadzu, Tokyo) was used for flame atomic absorption spectrometry (FAAS) of sodium, potassium, lithium, magnesium and strontium. Thorium and zirconium were measured spectrophotometrically by an Arsenazo III method. Other metals were measured by a Shimadzu ICPV-1000 (Shimadzu, Tokyo). The ICP-AES and FAAS were operated under the experimental conditions recommended by the manufacturers.

A Toa-Denpa Industry HM-7E pH meter (Toa-Denpa Industries, Tokyo) was used to measure pH of solutions. An FT-IR A-202 spectrophotometer (JASCO, Tokyo) was used for qualitative analysis of synthesized amidoximes.

Fig. 1 shows the schematic diagram of the FIA system finally used for the determination of uranium in seawater. The flow system was assembled from 1 mm bore PTFE tubing. The eluent and chromogenic reagent solutions, and the carrier and sample solutions were delivered by a double plunger type pump RX-704T (Sanuki Kogyo, Tokyo) and a peristaltic pump MP-3N (Tokyo Rika Kikai, Tokyo), respectively. The absorbance of the colored uranium complex was monitored by a Soma S-3250 spectrophotometric detector (Soma Optics, Tokyo) and recorded by a Hitachi Data-processing unit, D-250 (Hitachi, Tokyo).

2.2. Reagents

All reagents used were of analytical reagent grade. Uranium, calcium, and vanadium stock solutions (1 mg/mL) were prepared by dissolving uranyl nitrate hexahydrate, calcium carbonate, and ammonium vanadate, respectively, in 0.1 M hydrochloric acid and standardizing by chelatometric titration. The other metal stock solutions were standard solutions for atomic absorption spectrometry (Wako Pure Chemical Industries, Tokyo).

Distilled, deionized water was further purified by a Milli Q system (Nippon Millipore, Tokyo).

Styrene-divinylbenzene copolymer resin, Bio-Beads SM-2 (Bio-Rad Japan, Tokyo), was used to prepare amidoxime-impregnated resin.

Seawater samples were collected off the Boso peninsula and acidified by adding 10 mL of hydrochloric acid per liter of the seawater at the sampling locations and filtered with a membrane filter (pore size 0.45 μ m) after coming back to the laboratory.

A chromogenic reagent solution was prepared as follows: a mixture of 2 mL of 0.5 mM Chlorophosphonazo III (Wako Pure Chemical Industries, Tokyo), 0.0911 g of *trans*-1,2-diaminocyclohexane-*N,N,N',N'*-tetraacetic acid monohydrate (CyDTA, Wako Pure Chemical Industries, Tokyo) and 43.1 mL of hydrochloric acid was diluted to 500 mL with water.

2.3. Preparation of amidoxime-impregnated resin

Three kinds of nitrile compounds, i.e. nonanenitrile, tridecanenitrile and heptadecanenitrile (Tokyo Chemical Industry, Tokyo), were tested to synthesize amidoxime compounds mostly according to the procedure for the preparation of chelating resins containing amidoxime groups by Egawa et al. [19].

Five grams (0.072 mol) of hydroxyammonium hydrochloride was dissolved in 50 mL of methanol, 2.8 g of sodium hydroxide was added and the pH of the solution was adjusted to 7 with dilute sodium hydroxide solution. The hydroxyammonium solution was then added dropwise to the nonanenitrile solution which had been prepared by dissolving five grams (0.036 mol) of nonanenitrile in 20 mL of methanol. A reflux condenser was attached, and the mixture was heated at about 70 °C with stirring for 5 h. A residual nonanenitrile was removed by shaking the reaction mixture with 30 mL of cyclohexane. About 100 mL of water was added to the lower layer to deposit a white crystalline precipitate. The product was purified by recrystallization from methanol and confirmed qualitatively by the presence of absorption peaks for N–H (around 3300 cm^{-1}) and C=N (around 1660 cm^{-1}) stretching bands in infrared spectra.

Hydroxyammonium hydrochloride was reacted with tridecanenitrile or heptadecanenitrile in a similar manner as above by keeping the molar ratio of hydroxyammonium hydrochloride to nitrile at about 2.

Among the three kinds of nitrile compounds, which were used as raw materials for the synthesis of amidoxime compounds, tridecanenitrile gave the most suitable amidoxime (dodecylamidoxime) for our purposes as described in Section 3.1. Therefore, dodecylamidoxime was used to modify Bio-Beads SB-2.

About 0.05 g (0.2 mmol) of dodecylamidoxime was dissolved in 3 mL of methanol and 1 g of Bio-Beads SM-2 was added, followed by stirring for 2 h. Methanol was then evaporated slowly under an IR lamp. The prepared resin was soaked in water before use. The dodecylamidoxime-impregnated resin will hereinafter be abbreviated as DAIR.

2.4. Investigation of adsorption characteristics of DAIR for metal ions

A 200 mL solution of the fixed pH containing 100 µg of the metal ion of interest was passed through the column (9 mm i.d. and 35 mm bed height) packed with 1 g of DAIR at the fixed flow rate controlled by a peristaltic pump. The metal ions adsorbed on the column was eluted with 1 M hydrochloric acid and determined by spectrophotometry, FAAS or ICP-AES.

2.5. General procedure for flow-injection determination of uranium in seawater

Eighty milliliters of acidified seawater was taken and neutralized with solid sodium hydroxide and sodium hydroxide solution, followed by adjusting the pH of the sample solution to 5.5 with 0.1 M acetic acid or 0.1 M sodium acetate solution and diluting to 100 mL with water. First, the DAIR column (2 mm i.d. × 8 mm) was conditioned by passing an acetate buffer solution (pH 5.5) at a flow rate of 10 mL/min for 10 s. A 10 mL aliquot of the sample solution prepared as above was introduced into the flow injection analysis system (10 mL/min). The DAIR column was then washed with the acetate buffer solution (pH 5.5) for 10 s and uranium adsorbed on the column was eluted with 0.01 M hydrochloric acid (1.6 mL/min) for about 2 min. The effluent was merged with the chromogenic reagent solution and the absorbance of uranium–Chlorophosphonazo III complex was monitored at 670 nm. The calibration curve was constructed by using uranium(VI) standard solutions containing major cations and anions in seawater for matrix matching as follows: Na(I), 10.6 mg/L; Mg(II), 1.27 mg/L; Ca, 0.40 mg/L; K(I), 0.38 mg/L; Sr(II), 13 mg/L; Cl[−], 0.535 M; SO₄^{2−}, 28 mM; Br[−], 0.8 mM; H₃BO₃, 0.4 mM.

3. Results and discussion

3.1. Choice of amidoxime compounds

Three kinds of nitrile compounds, i.e. nonanenitrile, tridecanenitrile and heptadecanenitrile, were used to synthesize amidoxime compounds as described in Section 2.3. The FT-IR spectra revealed that nonanenitrile and tridecanenitrile reacted with hydroxyammonium hydrochloride to form the corresponding amidoximes, but in the case of heptadecanenitrile, most raw materials were recovered. Octylamidoxime and dodecylamidoxime were obtained in 35% and 40% yields. The amidoxime with a longer alkyl chain is suitable to prepare amidoxime-impregnated resin by the hydrophobic interaction between the amidoxime and adsorbent resin so that dodecylamidoxime was chosen as the chelating agent.

The preparation of dodecylamidoxime-impregnated resin is much more simple as described in Experimental than the modification of glass with chelating reagents [6,7] and far inexpensive than commercially available resins, TRU-SpecTM [8–11] and U/TEVATM [12].

3.2. Characterization of dodecylamidoxime-impregnated resin (DAIR)

3.2.1. Adsorption of metal ions on DAIR

Fig. 2 shows the effect of pH on the adsorption of uranium(VI). Uranium(VI) in simple buffered solutions is quantitatively adsorbed on the DAIR column at pH of more than 5. However, uranium(VI) in 3% sodium chloride solutions (mock seawater) is quantitatively collected on the DAIR at the pH of more than 5.5. Therefore, pH of sample solutions to be passed through the DAIR column was adjusted at pH 5.5.

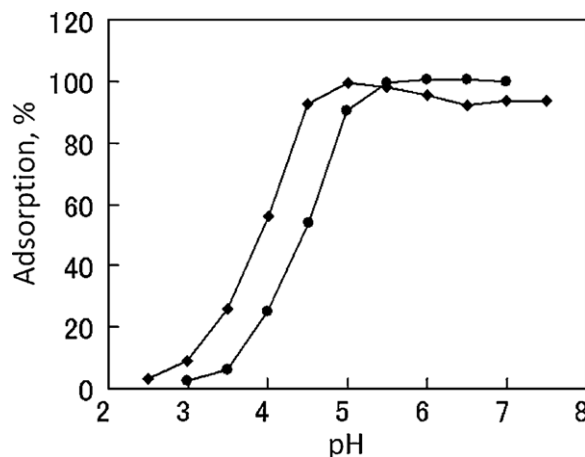


Fig. 2. Adsorption of uranium(VI) on dodecylamidoxime impregnated resin as a function of pH.

Column: 1 g dodecylamidoxime impregnated resin (9 mm i.d. and 35 mm bed height), Sample solution: 200 mL of 0.5 µg U/mL (3 mL/min), Eluent: 10 mL of 1 M hydrochloric acid (3 mL/min).

◆: uranium(VI) alone, ●: uranium(VI) in the presence of 3% sodium chloride.

Fig. 3 illustrates the adsorption dependence of other metal ions on pH. Alkali and alkaline earth metal ions are practically not adsorbed on DAIR. Adsorption of manganese(II), cobalt(II), and nickel(II) increases with increasing pH, reaching at 20% or less at pH 6. Aluminum(III) and copper(II) are strongly adsorbed on DAIR at pH higher than 5.5. Titanium(IV), vanadium(V), and iron(III) are almost quantitatively adsorbed on DAIR at pH higher than 4. Adsorption of zirconium(IV) shows the maximum at pH 6 and that of thorium(IV) increases monotonously with increasing pH. Titanium(IV), iron(III) and zirconium(IV) hydrolyze at pH 2–3 [20] and they seem to be retained on DAIR as their hydroxides. It is presumed that the metal ions, which showed appreciable adsorption on DAIR, do not interfere with the determination of uranium in seawater because their contents in seawater are very low compared with that of uranium [21].

3.2.2. Effect of flow rate of sample loading on recovery of uranium

Two hundred milliliters of the solution (pH 5.5) of 0.5 µg U/mL was passed through the column packed with 1 g of DAIR (9 mm i.d. and 35 mm bed height) at the flow rate ranging from 12 to 24 mL/min and uranium retained on the column was eluted with 10 mL of 1 M hydrochloric acid for its determination by ICP-AES. Uranium was quantitatively adsorbed at the flow rate of up to 20 mL/min. This suggests that the relatively higher flow rate can be used for the sample introduction to the FIA system, yielding the corresponding higher sample throughput.

3.2.3. Durability of DAIR

The durability of DAIR was examined by repeating the adsorption of uranium(VI) from 200 mL of sample solution (0.5 µg U/mL, pH 5.5) on a single column packed with 1 g of DAIR, and the subsequent elution of uranium(VI) with 10 mL of 1 M hydrochloric acid. The quantitative adsorption and subsequent elution of uranium(VI) were then feasible at least 50 times on the single column of DAIR.

3.2.4. Adsorption capacity for uranium of DAIR

A sample solution of 5 µg U/mL adjusted at pH 5.5 was passed continuously through a column packed with 1 g of DAIR at 3 mL/min and the uranium content in the effluent was monitored. The overall adsorption capacity [22] was estimated to be 4.9 mg U/g of DAIR from the constructed breakthrough curve.

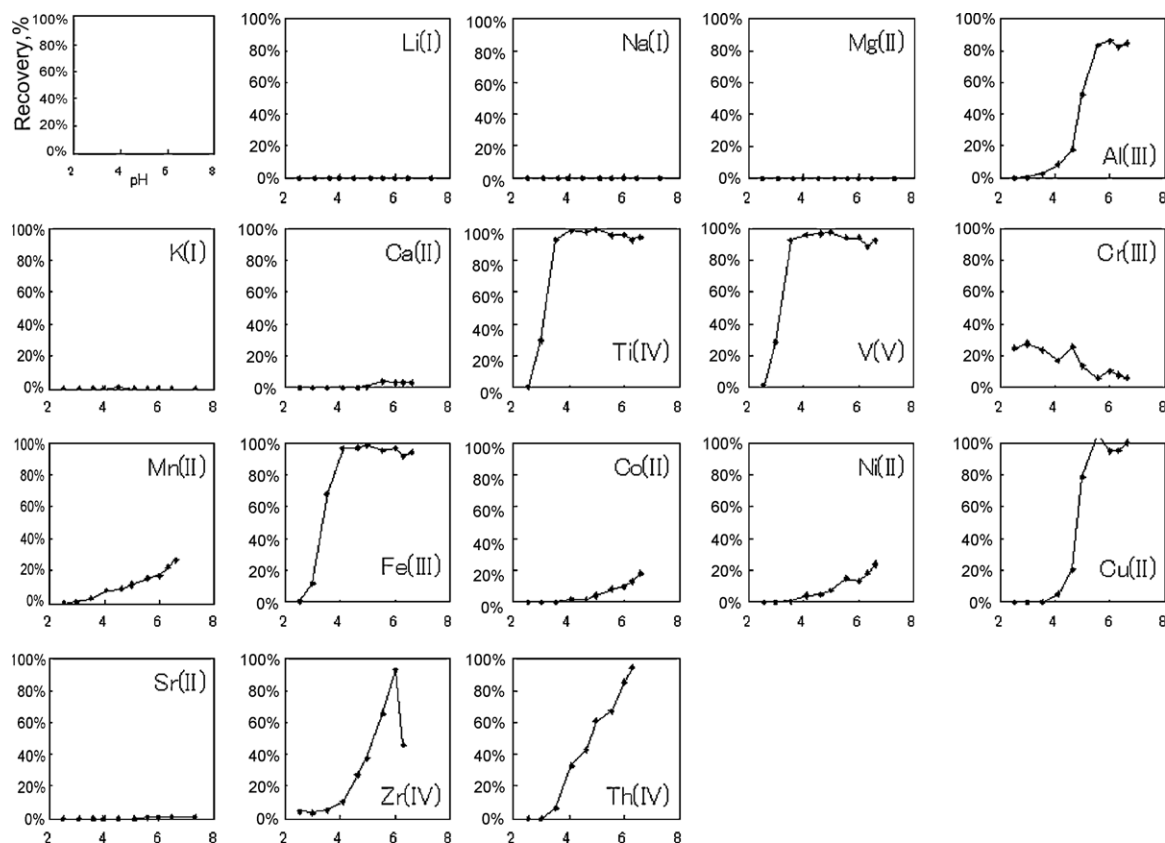


Fig. 3. Adsorption of metal ions on dodecylamidoxime impregnated resin as a function of pH.

Column: 1 g dodecylamidoxime impregnated resin (9 mm i.d. and 35 mm bed height), Sample solution: 200 mL of 0.5 $\mu\text{g/mL}$ (15 mL/min), Eluent: 10 mL of 1 M hydrochloric acid (3 mL/min).

3.3. Optimization of experimental conditions of FIA

3.3.1. Eluent and its flow rate

At the start of elution of uranium adsorbed on the DAIR column, the inside space of the column is filled with acetate solution (pH 5.5). Therefore, elution of uranium with 0.1–1 M hydrochloric acid gave noisy signals for uranium due to the irregularities of refractive index around the interface of acetate and hydrochloric acid solutions. Dilution of hydrochloric acid solution as the eluent to the range of 0.05–0.005 resulted in the calm baseline and appro-

priate signals for uranium. However, when 0.005 M hydrochloric acid was used as the eluent, uranium showed slight tailing. On the other hand, 0.02 M hydrochloric acid gave small blank peaks. Consequently, 0.01 M hydrochloric acid was ultimately chosen as the eluent for uranium.

The flow rate of the eluent (0.01 M hydrochloric acid) was varied from 0.4 to 2.8 mL/min. The peak height increased with the increase in the eluent flow rate, and showed the plateau at 1.2 mL/min or above. Accordingly, the eluent flow rate was fixed at 1.6 mL/min.

3.3.2. Concentration of Chlorophosphonazo III

The three calibration curves for uranium were constructed using 0.5, 2.0 or 3.0 μM Chlorophosphonazo III solutions, respectively. As shown in Fig. 4, 2.0 μM Chlorophosphonazo III solution gave reasonably linear plots. The concentration of Chlorophosphonazo III in the chromogenic reagent solution was, therefore, adjusted to 2.0 μM .

3.3.3. Sample-injection volume

In the preliminary experiments, a sample injection valve was used to inject sample solutions into the FIA system. Unfortunately,

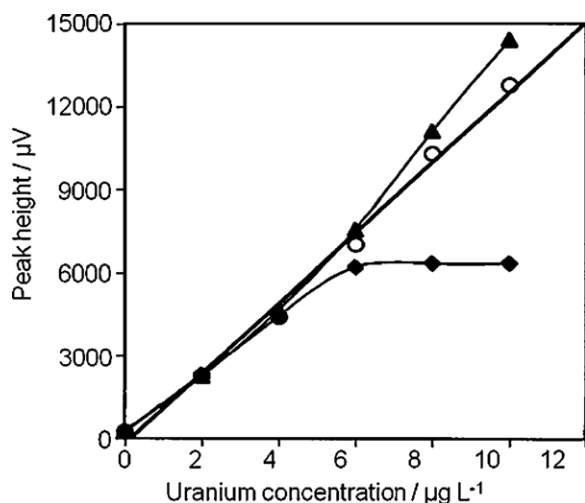


Fig. 4. Effect of Chlorophosphonazo-III concentration.

◆, 0.5 μM ; ○, 2.0 μM ; ▲, 3.0 μM .

Table 1

Effect of major metal ions in seawater on determination of uranium.*

Metal ion	Added (mg/L)	U found ($\mu\text{g/L}$)
Na ⁺	10,770	2.6
K ⁺	380	2.7
Mg ²⁺	1290	2.9
Ca ²⁺	412	5.1
Sr ²⁺	60	5.4

* 3.0 $\mu\text{g/L}$ added. Sample solution: 55 mL loaded at 16.6 mL/min.

Table 2
Determination of uranium in seawater samples.*

Sampling location	U ($\mu\text{g/L}$)		Added	Found	Added	Found
	Added	Found				
Offshore of Inage (Tokyo Bay)	0	2.83	1.99	4.80	5.96	8.65
Estuary of Nabaki River (Pacific Ocean)	0	3.00	2.98	5.90	5.96	8.68
Offshore of Daitozaki (Pacific Ocean)	0	3.08	2.98	5.98	5.96	8.94

* Collected off the Boso peninsula (Chiba prefecture, Japan).

it took a long time to rinse thoroughly the inside of the sample loop, of which inner volume was 10 mL, with the sample solution. Therefore, the volume of sample solutions to be introduced to the FIA system was controlled by the time to propel the sample solutions at a fixed pumping rate. Five to 55 mL (at 5.5 mL intervals) of 3 $\mu\text{g U/L}$ sample solution (pH 5.5) were injected (17 mL/min) and the linear relationship was obtained between the observed peak height and the injected sample volume over the whole volume tested, showing that 165 ng of uranium could be quantitatively adsorbed on the column.

3.3.4. Interference by foreign metal ions

Sodium(I), potassium(I), calcium(I), magnesium(II) and strontium(II) are apparently not adsorbed on DAIR as shown in Fig. 3. However, the concentrations of alkaline earth metals in seawater are several orders of magnitude higher than that of uranium(VI). Furthermore, calcium(II), magnesium(II) and strontium(II) are known to react with Chlorophosphonazo III to form the colored complexes, which are used for their spectrophotometric determination [23,24]. Therefore, the effects of these alkali metal and alkaline earth metal ions were examined and the results obtained are summarized in Table 1. No complex formation with Chlorophosphonazo-III is known for sodium(I) and potassium(I), and magnesium(II) does not react with Chlorophosphonazo-III at pH less than 6 [25]. Accordingly, adsorption of uranium(VI) on the small DAIR column might be encumbered by large quantity of sodium(I), potassium(I), or magnesium(II) at a high sample injection speed (16.6 mL/min), so that the lower recoveries were obtained. The lower flow rate, 10 mL/min, was then used for sample injection as described in Section 2.5. This flow rate is still higher than those (≤ 3.2 mL/min) used for the columns packed with glass beads modified with chelating reagents [6,7], TRU-SpecTM [8–11], or U/TEVATM [12]. Therefore, DAIR is well suited for the rapid preconcentration of uranium compared with the conventional adsorbents.

In order to mask alkaline earth metals, CyDTA was added to the chromogenic reagent solution. About 15 mL of a sample solution containing 3 $\mu\text{g U(VI)/L}$ and 412 mg Ca(II)/L was injected into the FIA system at 15 mL/min and eluted uranium(VI) was detected with the 2 μM Chlorophosphonazo III- x mM CyDTA solution ($x=0-5$). The recovery of uranium(VI) is 100% using the chromogenic solutions containing CyDTA in 0.1–1 mM. When 5 mM CyDTA was included in the chromogenic solution, excessive CyDTA seemed to mask uranium(VI), too and remarkably reduced the absorbance for standard uranium(VI) solutions which were free from calcium(II), resulting in the apparent higher recovery for the sample solution containing calcium(II). Based on the above observations, the CyDTA concentration in the chromogenic reagent solution was hereinafter fixed at 0.5 mM.

The slight memory effect was recognized for uranium(VI) when injected as the simple uranium(VI) solutions. However, the effect was eliminated on injection of the uranium(VI) solutions prepared as artificial seawater. Accordingly, calibration curves for uranium(VI) were constructed using the standard uranium(VI) solutions containing major cations and anions in seawater as mentioned in Section 2.5.

3.4. Performance of the FIA system

A sample volume of 10 mL resulted in the preconcentration factor of 20, the sample throughput of 23 per hour, and the detection limit (3σ) of 0.13 $\mu\text{g/L}$. Uranium could also be quantitatively adsorbed on the column by passing 57 mL of the artificial seawater solution containing 3 $\mu\text{g/L}$ at a flow rate of 17 mL/min. In this case, the preconcentration factor was estimated to be 110.

3.5. Determination of uranium in artificial seawater

Based on the above observations, the calibration curve for uranium(VI) was constructed using the uranium standard solutions in the presence of the major constituents of seawater as described in Section 2.5. The calibration curve obtained as above was used to determine 3 $\mu\text{g U(VI)/L}$ in solutions containing the salts of the concentrations ranging from one fourth to two times as those shown in Section 2.5. Almost quantitative results (97.0–103.4%) were obtained regardless the total concentration of coexisting salts.

3.6. Determination of uranium in seawater

Uranium in seawater samples collected at three locations, off the Boso peninsula (Chiba prefecture, Japan) was determined and the results obtained are summarized in Table 2. The uranium contents in the samples of the offshore of Inage and estuary of Nabaki River are lower than that in the sample of the offshore of Daitozaki. Part of the reason is that former two seawater samples are diluted by freshwater which is provided by neighboring rivers. The yield of the recovery test ranges from 95% to 99%.

4. Conclusion

A novel adsorbent, which showed high selectivity to uranium, was prepared by impregnating styrene-divinylbenzene copolymer with dodecylamidoxime. The dodecylamidoxime-impregnated resin was applied to the flow injection on-line preconcentration of uranium in seawater prior to its determination by spectrophotometric detection. The proposed flow injection method of analysis does not require any skilled matrix separation and analyte preconcentration steps, and has good precession.

References

- [1] Uranium from seawater report, issued by United Kingdom Atomic Energy Authority, October 1976.
- [2] Agency for Toxic Substances and Disease Registry, U.S. Public Health Service, Chapman and Hall, New York, 2000.
- [3] T.P. Rao, P. Metilda, J.M. Gladis, Talanta 68 (2006) 1047.
- [4] J.B. Ghasemi, E. Zolfonoun, Talanta 80 (2010) 1191.
- [5] S. Dadfarnia, C.W. McLeod, Appl. Spectrosc. 48 (1994) 1331.
- [6] S.M. Nelms, G.M. Greenway, D. Koller, J. Anal. At. Spectrom. 11 (1996) 907.
- [7] S. Hirata, T. Kajiya, N. Takano, M. Aihara, K. Honda, O. Shikino, E. Nakayama, Anal. Chim. Acta 499 (2003) 157.
- [8] J.H. Aldstadt, J.M. Kuo, L.L. Smith, M.D. Erickson, Anal. Chim. Acta 319 (1996) 135.
- [9] J.B. Truscott, L. Bromley, P. Jones, E.H. Evans, J. Turner, B. Fairman, J. Anal. At. Spectrom. 14 (1999) 627.
- [10] J.B. Truscott, P. Jones, B.E. Fairman, E.H. Evans, Anal. Chim. Acta 433 (2001) 245.

- [11] E.R. Unsworth, J.M. Cook, S.J. Hill, *Anal. Chim. Acta* 442 (2001) 141.
- [12] T. Seki, K. Oguma, *Bunseki Kagaku* 53 (2004) 353.
- [13] N. Kabay, H. Egawa, *Sep. Sci. Technol.* 29 (1994) 135.
- [14] B.-B. Jang, K. Lee, W.J. Kwon, J. Suh, *J. Polym. Sci. Part A: Polym. Chem.* 37 (1999) 3169.
- [15] S. Shinkai, H. Koreishi, K. Ueda, T. Arimura, O. Manabe, *J. Am. Chem. Soc.* 109 (1987) 6371.
- [16] S. Shinkai, Y. Shiramama, H. Satoh, O. Manabe, *J. Chem. Soc. Perkin Trans. II* (1989) 1167.
- [17] I. Tabushi, Y. Kobuke, K. Ando, M. Kishimoto, E. Ohara, *J. Am. Chem. Soc.* 102 (1980) 5948.
- [18] S. Das, A.K. Pandey, A. Athawale, V. Kumar, Y.K. Bhardwaj, S. Sabharwal, V.K. Manchanda, *Desalination* 232 (2008) 243.
- [19] H. Egawa, H. Harada, T. Nonaka, *Nippon Kagaku Kaishi* (1980) 1767.
- [20] I.M. Kolthoff, E.B. Sandell, E.J. Meehan, S. Bruckenstein, *Quantitative Chemical Analysis*, 4th ed., Macmillan, Toronto, 1969, p. 252.
- [21] Y. Nozaki, *Chikyu Kagaku* 19 (1985) 59.
- [22] F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962, p. 424.
- [23] H. Onishi, *Photometric Determination of Traces of Metals, Part IIA*, 4th ed., John Wiley & Sons, New York, 1986, p. 370.
- [24] H. Onishi, *Photometric Determination of Traces of Metals, Part IIB*, 4th ed., John Wiley & Sons, New York, 1989, p. 416.
- [25] J.W. Ferguson, J.J. Richard, J.W. O'Laughlin, C.V. Banks, *Anal. Chem.* 36 (1964) 796.