

Synthesis of Chitosan-Based Resins Functionalized with Serine Moiety and Its Application to Determination of Trace Amounts of Uranium by FI/ICP-MS System

Koji Oshita^{1,*}, Toshio Takayanagi², Mitsuko Oshima² and Shoji Motomizu²

¹ Department of International Conservation Studies for Cultural Properties, Faculty of Cultural Properties, Kibi International University, 8 Iga-machi, Takahashi, Okayama 716-8508, Japan

² Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530, Japan

Abstract

Cross-linked chitosan resins possessing serine moiety (serine-type chitosan resins) were synthesized for the collection of trace uranium and the separation of matrices in seawater prior to ICP-MS measurement. The serine moiety has a carboxyl group and an amino group at the β -carbon position of ethanol. The adsorption behavior of trace elements on two types of chitosan resin, coupled with the hydroxyl group of serine (type 1) and with the amino group of serine (type 2), was investigated by using a proposed column procedure. The serine-type chitosan resin (type 1) adsorbed U(VI) over wide pH regions from 2 – 9, and especially could collect U(VI) at acidic pH regions selectively by forming stable chelate with the amino group and the carboxyl group of the serine moiety introduced to chitosan. Further, the flow injection/ICP-MS system was developed for the determination of trace uranium in seawater using a small column packed with the resin. The proposed system could be applied to the uranium analysis.

Keywords Chitosan resin, Uranium, Serine, On-line pretreatment, ICP-MS

1. Introduction

Seawater contains about 3 ng mL⁻¹ of uranium. It should be accurately determined for evaluating the uranium behavior in seawater. Some methods have been developed for the determination of trace uranium, whereas they can not be applied to the accurate analysis; LODs (LOD: limit of detection) are above ppm level (1 ppm = 1 μ g mL⁻¹) [1,2]. An ICP-MS measurement is one of the powerful analytical methods for the trace analysis: LOD is about 0.001 ng mL⁻¹. However, high concentrations of matrices, such as Na, K, Mg and Ca, in seawater can give serious damage to mass spectrometer of ICP-MS and the deposition of such matrix constituents on the torch and nebulizer can seriously affect the accuracy of analytical results. In order to overcome these problems, solid-phase extraction methods have been used as preconcentration techniques prior to trace analysis [3–12]. Commercially available resins, such as UTEVA and Dowex 1-X8, have been used for the uranium collection [4–7]. They adsorb U(VI) only in high concentrations of acidic solution. Some researchers have reported on solid materials modified with succinic acid, maleic acid, *o*-vaniline semicarbazone and 8-hydroxyquinoline moieties, which adsorb uranium only over narrow pH regions [8–12].

In our previous work, chitosan resins were synthesized for concentration of trace elements in aquatic samples and elimination of matrices, because the adsorption rate of ionic species on chitosan resins is faster in aquatic media than that on synthetic base materials like polystyrene-divinylbenzene, polyethylene, and polyurethane, which is due to the hydrophilicity of chitosan itself [13]. Chitosan resins possessing various chelating moieties were synthesized for the trace analysis by the ICP-MS measurement [13–15].

In this study, two types of chitosan resin modified with serine moiety (type 1 and type 2) were synthesized for elucidating the adsorption behavior of cationic and anionic species on the resins in

detail. Also, the synthesized chitosan resin was applied to the uranium determination by FI/ICP-MS system.

2. Experimental

2.1. Reagents

The chitosan used was in a flake form, whose deacetylated degree was about 80%. It was purchased from Tokyo Kasei Co. Ltd. (Tokyo, Japan). All other reagents used for the synthesis of chitosan resins were of analytical reagent grade.

The stock solutions of analytical standard for elements were prepared by diluting several kinds of single-element standard solution for atomic-absorption spectrometry (1000 μ g mL⁻¹; Wako Pure Chemicals, Osaka, Japan) and multi-element standard solution for ICP-MS, provided by Spex CertiPrep Inc. (Metuchen, New Jersey, USA). These stock solutions were diluted by weight just before a column procedure with 0.1 M nitric acid to give 10 ng mL⁻¹ of each element. Ultrapure-grade nitric acid (60%; density, 1.38 g mL⁻¹; Kanto Chemicals, Tokyo, Japan) was diluted with ultrapure water. Acetic acid (minimum 96%) and ammonia water (29%) used for the preparation of an ammonium acetate solution were of an electronic industrial reagent grade, purchased from Kanto Chemicals (Tokyo, Japan). Ultrapure water (18.3 M Ω cm⁻¹ resistivity), prepared by an Elix 3/Milli-Q Element system (Nihon Millipore, Tokyo, Japan), was used throughout.

2.2. Synthesis of chitosan resins

The examined chitosan resins were shown in Fig. 1. Cross-linked chitosan resin (particle size; 100 – 300 μ m) with EGDE (ethyleneglycoldiglycidylether) and serine-type chitosan resin (type 1) were synthesized in a similar manner to our previous work [15,16]. Serine-type chitosan resin (type 2) was newly synthesized as follows. A serine moiety was introduced to the cross-linked chitosan resin in three steps. First, the cross-linked chitosan resin (5 g) was suspended in ethanol (200 mL), then

* Corresponding author.
E-mail: oshita@kiui.ac.jp

glutaraldehyde (40 g) was added to the suspension, and the mixture was stirred at room temperature for 3 h. After the reaction, the product was filtered and washed each 3 times with ethanol and ultrapure water to remove any residual reagents. Secondly, the product and serine (10 g) were suspended in diluted sodium hydroxide aqueous solution (500 mL), and the suspension was stirred at room temperature for 24 h. And then, the product was filtered and washed each 3 times with ethanol and ultrapure water. The product and sodium tetrahydroborate (10 g) were suspended in ethanol (100 mL) and stirred at room temperature for 3 h. After that, the final product was filtered and washed each 3 times with ethanol and with ultrapure water. The chitosan resins were characterized by measuring their IR spectra.

2.3. Apparatus

An ICP-MS system used to measure elements was a Model SPQ 8000H (Seiko Instruments, Chiba, Japan), and an ICP-AES was a Model Vista-PRO (Seiko Instruments, Chiba, Japan). The IR spectra were taken by the KBr pellet method using an FT/IR-4100 spectrometer (JASCO Co. Tokyo, Japan).

2.4. Procedures

2.4.1. Batchwise column method

The column procedure was similar to our previous work [15,16]. Each chitosan resin was cleaned up to remove any residual metallic impurities as follows: the wet resin (20 mL) was transferred to a plastic beaker (100 mL), containing 2 M nitric acid (80 mL), which was carefully stirred at a low speed for 6 h. The resin was then filtered and rinsed with ultrapure water. The resin (wet volume, 1 mL) was packed in polypropylene mini-column (1 mL of volume, 5.0 i.d. x 50 mm, Muromachi Chemical, Kyoto, Japan), which was used for examining the adsorption behavior of trace elements. For washing, each 10 mL of 1 M nitric acid and ultrapure water was passed through the column. Then, 5 mL of a conditioning solution (pH 1 – 2, 0.1 M and 0.01 M nitric acid; pH 3 – 7, 0.5 M ammonia-acetate solution) was passed through the column for pH adjustment. A sample solution (10 mL), whose pH was adjusted with the conditioning solution, was passed through the column. Then, a 5 mL aliquot of a rinsing solution (pH 1 – 2, 0.1 M and 0.01 M nitric acid; pH 3 – 7, 0.2 M ammonia-acetate solution) was passed through each column to remove any matrices remaining in the column. Then, a 5 mL portion of ultrapure water was passed through the column to rinse the remaining components of the rinsing solution. Finally, each 10 mL portion of 1 or 3 M nitric acid was passed through the column to recover the elements adsorbed on the resin. The elements in each effluent were determined by ICP-MS. Throughout all of the column procedure, the flow rate was maintained at about 1 mL min⁻¹.

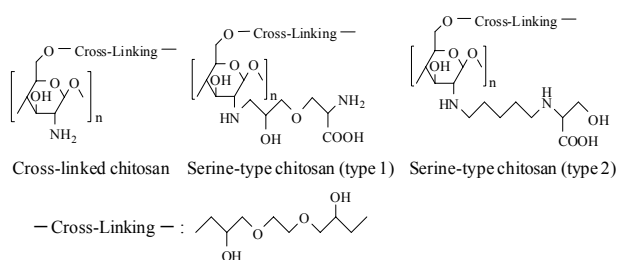


Fig. 1 Chemical structures of chitosan resin.

2.4.2. FI method

A Micro Suction version 1.8 MA software was used for the data acquisition from flow signals and the control of the ICP-MS system. A schematic diagram of an FI/ICP-MS manifold is shown in Fig. 5. A peristaltic pump (Model ALITEA-XV, Sweden) was used for propelling solutions. The serine-type chitosan resin (type 1) was packed in a column (5.0 x 50 mm), which was installed in a loop of a six-way valve in the FI manifold. All connections in the manifold were made using 0.5 mm i.d. PTFE tubing. The FI manifold at the load state in Fig. 5 shows 1 M nitric acid was flowed through the valve into the ICP-MS nebulizer at flow rate of 1.0 mL min⁻¹, while a carrier solution (0.5 M ammonium acetate, pH 3) was flowed into the loop with the column at flow rate of 1.0 mL min⁻¹, and finally it was wasted. The sample solution (0.5 mL, pH 3) was injected into the stream of the carrier solution, and then passed through the column. Most of the matrices in sample solutions were not retained in the column, because the matrices were eliminated with the ammonium acetate solution. At measuring stage, uranium adsorbed on the resin was eluted with 1 M nitric acid, and the eluent stream flowed into the ICP-MS nebulizer. The carrier and the eluent stream flowed into the column in the opposite direction. Memory effect and carryover was not observed, since ICP-MS system and the resin were repeatedly rinsed with 1 M nitric acid. The ICP-MS measurement was carried out by injecting several kinds of solutions as a following order: (1) blank solution, (2) series of working standard solution and (3) sample solutions. The total processing time for the measurement of one sample was within 9 min, which included the time required for adjusting pH of the column with the pH 3 solution (2 min), sampling and loading the sample on the column (2 min), eluting the analyte with 1 M nitric acid (1 min), integrating the time for sample zone (1.5 min) and washing the column (2 min).

3. Results and discussion

3.1 Adsorption behavior of cationic and anionic species on synthesized chitosan resins

The adsorption capacity of Cu(II), which forms stable chelates with various chelating reagents, on serine-type chitosans (type 1 and type 2) was 0.08 and 0.06 mmol ml⁻¹ at pH 3, respectively. These resins had sufficient capacity for the collection of trace metal ions, and could use at pH 1–7 repeatedly. The adsorption behavior of trace elements in aquatic media on chitosan resins as shown in Fig. 1 was examined by the column procedure.

Figure 2 shows the adsorption behavior of each 10 ng mL⁻¹ of metal ions, such as Be(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Y(III), Ag(I), Cd(II), In(III), Pb(II), Bi(III), in the pH range from 1 to 7, which are existing as cationic species in aqueous solution. These cationic species adsorbed on the resins were quantitatively recovered with 10 mL of 1 M nitric acid as an eluent. Especially, only Bi(III) adsorbed on the serine-type chitosan resin (type 1) could be eluted by using 10 mL of 3 M nitric acid thoroughly. Serine-type chitosan resin (type 1) could adsorb Bi(III) over a wide pH region from 1 to 5 quantitatively, whereas the other chitosan resins adsorb it weakly. Probably, Bi(III) might be adsorbed strongly by forming stable chelate with a primary amino group (-NH₂) and a carboxyl group (-COOH) of serine moiety in the serine-type chitosan resin (type 1). Serine-type chitosan resins (type 1 and type 2) could adsorb Co(II), Cu(II), Zn(II), Y(III), Cd(II), In(III) and Pb(II) at lower pH than cross-linked chitosan resin as a base material. Especially, Cu(II)

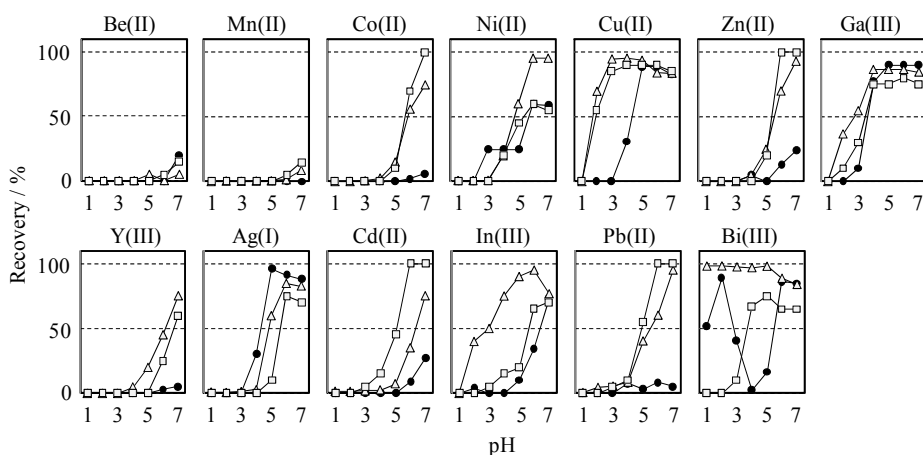


Fig. 2 Adsorption behavior of metals at pH 1 – 7 on chitosan resins. Sample, 10 mL; concentration of each element, 10 ng mL⁻¹; column, 1 mL; eluent, 10 mL of 3 M nitric acid for Bi(III), 1 M nitric acid for other elements. ●, Cross-linked chitosan resin; △, serine-type chitosan resin (type 1); □, serine-type chitosan resin (type 2).

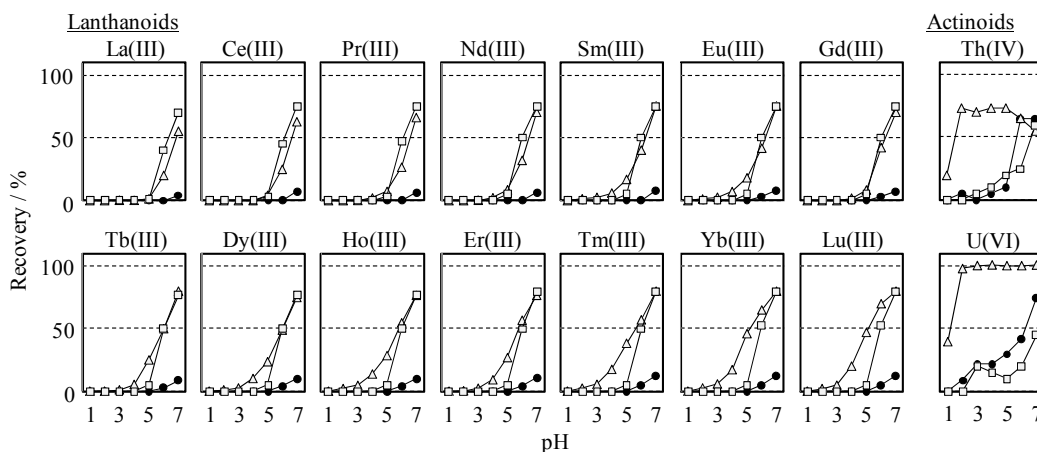


Fig. 3 Adsorption behavior of lanthanoids and actinoids at pH 1 – 7 on chitosan resins. The experimental conditions and symbols were the same as Fig.2.

could be adsorbed at a lower pH region. It was caused by the modification with serine. The cationic species might be adsorbed on the resins by a chelating mechanism with a carboxyl group and an amino group of serine.

Figure 3 shows the adsorption behavior of lanthanoids and actinoids on chitosan resins at pH from 1 to 7. Lanthanoids exist as cationic species, Ln(III), in aqueous solution. Chitosan resins possessing serine moieties (type 1 and type 2) could adsorb such species more effectively than cross-linked chitosan resin as the base material. On the other hand, the adsorption behavior of actinoids, such as Th(IV) and U(VI), on serine-type chitosan resin (type 1), was quite different from that of lanthanoids on it. Uranium(VI) and Th(IV) could be adsorbed on it over wider pH

regions. Especially, U(VI) could be adsorbed on the serine-type chitosan resin (type 1) at pH 2 – 7 quantitatively, and could be eluted with 1M nitric acid (10 mL) thoroughly. Therefore, U(VI) could form stable chelate with a primary amino group (–NH₂) and a carboxyl group (–COOH) of serine moiety in the serine-type chitosan resin (type 1), whereas it might be difficult to form its chelate with a secondary amino group (–NH–) and a carboxyl group (–COOH) in serine-type chitosan resins (type 2).

Figure 4 shows the adsorption behavior of oxo-acids, such as V(V), Ge(IV), Mo(VI) and W(VI), on chitosan resins. In the acidic pH region, such oxo-acids can exist predominantly as neutral or protonated species. On the other hand, oxo-acid species can exist as anionic species, around the neutral pH region. Such anionic species might be adsorbed on the resins by a combination between chelating mechanism, anion-exchange mechanism and hydrogen bonding with the amino group and the carboxyl group of serine moiety in chitosan resins.

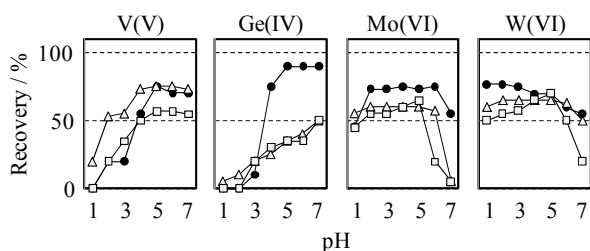


Fig. 4 Adsorption behavior of oxo-acids at pH 1 – 7 on the chitosan resins. The experimental conditions and symbols were the same as in Fig. 2.

3.2. Application to uranium determination by FI/ICP-MS system

Serine-type chitosan resin (type 1) could adsorb trace uranium quantitatively and selectively even at pH 3, which easily eluted with 1 M nitric acid. In this study, the FI/ICP-MS system was developed for the determination of trace uranium in seawater using a small column packed with the serine-type chitosan resin (type 1)

as shown in Fig. 5, which use the integrated peak area for the uranium measurement. The optimum integration range of flow signals was examined by using a 10 ng mL⁻¹ of uranium standard solution. Optimum conditions were examined as following. The effect of the flow rate of the carrier on flow signals was investigated by varying it from 1.0 to 3.0 mL min⁻¹. When the flow rate was 1.0 mL min⁻¹, the recovery of uranium was almost 100%, which value was calculated by using the product of the peak area and the flow rate, and then uranium adsorbed on the resin was eluted within 1.5 min. When the flow rate was more than 1 mL min⁻¹, the adsorption efficiency of uranium was found to be lower. Consequently, the flow rate was adjusted to 1.0 mL min⁻¹. In order to examine the effect of sample volume on the linearity of the calibration graph, 0.5 – 2.0 mL of sample volumes were tested at the constant flow rate (1.0 mL min⁻¹). The peak areas of signal were increased in proportion to sample volumes. In the further experiments, a 0.5 mL of sample volume was chosen to reduce the sampling time and the pretreatment time, because the sensitivity was enough for the uranium determination in seawater. Then, the linearity of the calibration graph for uranium determination obtained by the proposed system was examined. The calibration graphs were obtained by injecting 0.5 mL of the standard solutions containing uranium of 0–0.1, 0–1 and 0–10 ppb. The correlation coefficients of calibration graphs were good over wide concentration ranges, which indicate quantitative adsorption and complete elution of uranium by the system. In order to eliminate high concentrations of matrices, such as Na (11500 ppm), Mg (1200 ppm), K (3900 ppm) and Ca (400 ppm), in sea water, the matrix elimination was examined with rinsing solution (carrier: 0.5 M ammonium acetate solution, pH 3). An artificial sea water (0.5 mL, pH 3) was used as a sample. The sample was injected and the carrier was flowed for 1 – 4 min, and then the eluent (1 M HNO₃) was flowed. Uranium in the effluent was measured by ICP-MS and matrices in the effluent were measured by ICP-AES. The matrices were removed efficiently with increasing the washing time. The washing time of 2 min was sufficient to remove the matrix components, while uranium was recovered quantitatively under such conditions.

In order to evaluate the accuracy and the precision of the FI/ICP-MS measurement, a practical seawater sample was analyzed by the system. Five replicate analyses were performed for the real seawater. The analytical data obtained by direct measurement (direct ICP-MS after 20-fold dilution of the sample), batchwise column procedure (ICP-MS measurement with the column pretreatment), and FI/ICP-MS measurement were 2.62 ± 0.03 (RSD, relative standard deviation: 1.0%), 2.66 ± 0.03 (RSD: 1.1%), 2.68 ± 0.05 (RSD: 1.9%), respectively. These results were good agreement with each other. In the direct measurement, high concentrations of matrices, such as Na, Mg, K and Ca, in seawater can damage seriously the mass spectrophotometer. On the other hand, the pretreatment time of batchwise column procedure was

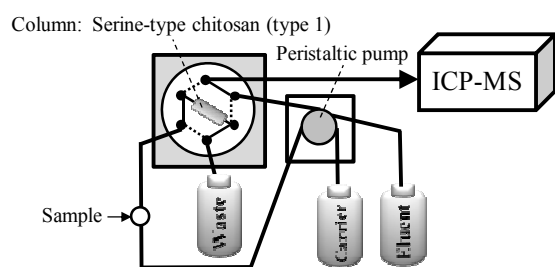


Fig. 5 Schematic diagram of flow injection (FI) system coupled with ICP-MS.

about 1 h, which is time-consuming. The precision (RSD) for the uranium determination by the proposed FI/ICP-MS system was within 2 %, which was good performance for uranium analysis.

4. Conclusion

The adsorption properties of cationic and anionic species on synthesized chitosan resins were systematically examined by column procedure. Such species could be adsorbed on the resins by a chelating mechanism, an anion-exchange mechanism and a hydrogen bonding. Serine-type chitosan resin (type 1) could adsorb U(VI) at pH 2 – 7 more effectively, and U(VI) adsorbed on the resin could be readily eluted with 1 M nitric acid. In this study, FI/ICP-MS system with the serine-type chitosan resin (type 1) column was developed for the determination of uranium. The main advantages of the proposed system are: (1) simple and fast procedure, (2) effective elimination of matrix substances, and (3) high reproducibility (RSD: within 2%). The system could be applied to the trace analysis.

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