On – Line Flow Injection / Inductively Coupled Plasma – Mass Spectrometric Determination of Uranium in Sea Water

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Abstract

An on – line flow injection (FI) pretreatment system using a newly synthesized chitosan resin (particle size: 100 – 300 μm) was developed for the determination of uranium in sea water samples by inductively coupled plasma mass spectrometry (ICP – MS). The newly synthesized chitosan resin possessing serine moiety was used for the collection of trace uranium and the elimination of matrix cations (alkali and alkaline earth metals) in samples. The sea water samples (0.5 ml) adjusted to pH 3 were pretreated with the chitosan resin. Considering the elimination of high – concentration matrices, such as Na, Mg, K and Ca, a 0.5 M ammonium acetate solution (pH 3) was chosen as a sample carrier. Uranium adsorbed on the resin was eluted with 1 M nitric acid, and the eluate was flowed into the ICP – MS system. The running time for one sample was within 9 min. The calibration graph of uranium showed a good linearity in the range from 0.005 to 10 ppb. The proposed method was applied to the analysis of sea water. The result obtained by the proposed method using the on – line FI method agreed well with the value obtained by a batchwise column treatment method.

Keywords Flow injection, ICP – MS, uranium, sea water, on – line pretreatment

1. Introduction

Sea water contains 2.8 – 3.3 ppb of uranium [1]. From such values, the detection ability of inductively coupled plasma mass spectrometry (ICP – MS) may be considered to be sufficient to determine uranium in sea water, because the limit of detection (LOD) of uranium by ICP – MS is 1 ppt [2], whereas the direct determination of uranium in sea water by GF – AAS and ICP – AES is impossible, since the LODs of uranium by GF – AAS and ICP – AES are 10 ppm and 10 ppb, respectively [3]. In general, matrices in samples, such as Na, Mg, K and Ca, must be removed by any pretreatment methods prior to ICP – MS measurement. Therefore chelating resins have often been used for the removal of matrices in sea water [4]. Commercially available resins possessing chelating functional groups, such as an iminodiacetate (IDA) group and a dipentylpentylphosphonate (DPPP) group, were examined for the adsorption of uranium and the elimination of matrices [5][6][7][8]. Miura et al. studied the determination of uranium in mineral water by ICP – AES using a disk of chelating resin possessing an IDA group [5]. In the method, cyclohexanediamine – N, N, N', N' – tetraacetic acid (CyDTA) was added to samples as a masking reagent in order to recover uranium quantitatively from the mineral water. The resin possessing the DPPP group could adsorb uranium only in concentrated acidic solutions without a masking reagent [6][7][8]. However, there was a serious problem on a large amount of acidic waste water.

In our previous work [9], a new type cross – linked chitosan resin with ethyleneglycoldiglycidylether (EGDE cross – linked chitosan) was synthesized and examined for the removal of mercury existing as an impurity in commercially available concentrated hydrochloric acid [10]. For the collection / concentration of uranium, the EGDE cross –

linked chitosan possessing serine moiety (serine – type chitosan) was synthesized and the adsorption behavior of 56 kinds of elements on the resin was examined [11]. As a result, it was found that the serine – type chitosan could adsorb uranium at pHs from acidic to alkaline region by a chelation mechanism, and that uranium was recovered quantitatively from sea water, river water and tap water samples even at pH 3. Therefore, this resin was used for the pretreatment of practical sea and river water samples by a batchwise method. From the results obtained, it was concluded that the serine – type chitosan resin was possibly useful for the preconcentration of trace uranium in water samples.

For ICP – MS measurement of trace elements in sea water, a batchwise column pretreatment method has often been used for the determination of trace elements. However, the method was often time – consuming and often troublesome. The present work describes an on – line FI / ICP – MS system for the matrix elimination and the determination of trace uranium in sea water using a small column packed with the serine – type chitosan.

2. Experimental

2.1. Instruments and procedures for measurement

An ICP – MS system used for trace uranium analysis was a Model SPQ 8000H (Seiko Instrument Co., Tokyo, Japan). An ICP – AES system used for the determination of alkali and alkaline earth elements was a Model Vista – PRO (Seiko Instrument Co., Tokyo, Japan). Operating conditions are summarized in Table 1. 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. 1. A peristaltic pump (Model ALITEA – XV, Sweden) was used for propelling solutions. The synthesized chitosan resin was packed in a column (5.0 x 50 mm), which was installed in a loop of a six – way valve in the FI

Table 1 Operating parameters for ICP – MS and ICP – AES systems

ICP - MS	
Instrument	Seiko SPQ 8000H Quadrupole type
Frequency	27 MHz
Incident power	1.1 kW
Reflected power	< 5 W
Plasma gas	Ar 15 dm^3 min^{-1}
Carrier gas	Ar 0.45 dm^3 min^{-1}
Auxiliary gas	Ar 1.0 dm^3 min^{-1}
Sampling depth	10 mm from load coil
Sampling cone	Copper 1.1 mm orifice diameter
Skimmer cone	Copper 0.35 mm orifice diameter
ICP - AES	
Instrument	Seiko Vista - PRO Axial type
Frequency	27 MHz
Incident power	1.1 kW
Reflected power	< 5 W
Plasma gas	Ar 15 dm^3 min^{-1}
Carrier gas	Ar 0.9 dm^3 min^{-1}
Auxiliary gas	Ar 1.5 dm^3 min^{-1}
Wavelength	589.592 nm (Na)
	279.553 nm (Mg)
	766.490 nm (K)
	396.847 nm (Ca)

Fig. 1 Schematic diagram of flow injection (FI) system coupled with ICP – MS.

Fig. 2 Chemical structure of serine – type chitosan.
Cross – linking: —CH$_2$—CH—(CH$_2$-O—CH$_2$)$_2$-CH—CH$_2$—
with OH groups

manifold. All connections in the manifold were made using 0.5 mm i.d. PTFE tubing.

In the FI manifold in Fig. 1, at the load state, 1 M nitric acid was flowed through the valve into the ICP – MS nebluizer 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 matrix components in sample solutions, such as alkali and alkaline earth metals, were not retained on the resin because such metal ions were eliminated by the ammonium acetate solution. At the measuring stage, uranium adsorbed on the resin was eluted with 1 M nitric acid, and the eluent stream flowed into the ICP – MS neblizer. 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 at a flow rate of 1.0 ml min^{-1}.

Using the proposed system, uranium in the effluent was measured by ICP – MS, and the integrated peak area was used for the determination. For measuring the peak area of uranium, the optimum integration range of flow signals was examined by using a 10 ng ml^{-1} uranium standard solution. The ICP – MS measurement was carried out by injecting several kinds of solutions as a following order: (1) a blank solution, (2) a series of working standard solutions 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 resin with the pH 3 solution (2 min), sampling and loading the sample on the resin (2 min), eluting the analyte with 1 M nitric acid (1 min), integrating the time for sample zone (1.5 min) and washing the resin (2 min).
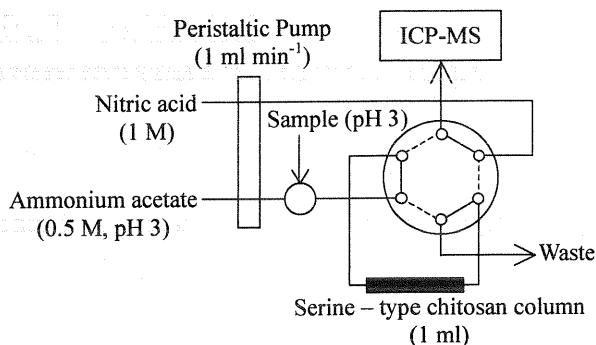
2.2. Materials and reagents
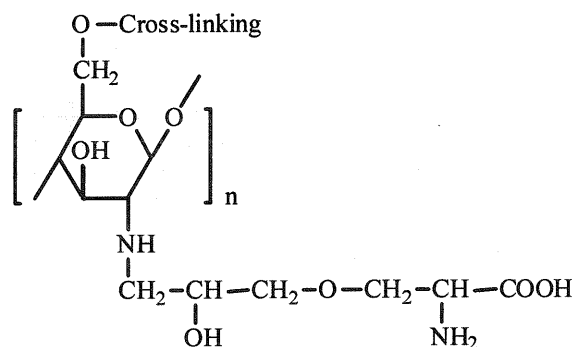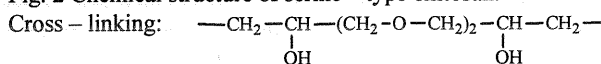
Serine – type chitosan was synthesized in the similar manner as in the previous works [9][11]. The chemical structure of the resin is shown in Fig. 2.

A stock standard solution of uranium (1 μg ml^{-1}) was prepared from the analytical multi – element standard solution (XSTC – 13, Spex CertiPrep Inc.). Working standard solutions were prepared by diluting the stock standard solution with 0.1 M nitric acid before on – line FI / ICP – MS measurement.

Ultrapure grade nitric acid (60 %, density 1.38 g ml^{-1}, Kanto Chemicals, Tokyo) was diluted with ultrapure water to give a 0.1 M or 1 M nitric acid solution. Accurate dilution of the standard solutions was carried out by weight. The acetic acid (minimum 96 %) and ammonia water (29 %) used for preparing the ammonium acetate solution were of electronic industrial reagent grade (Kanto Chemicals).

Ultrapure water (18.3 MΩ cm^{-1} resistivity) was prepared by an Elix 3 / Milli – Q Element system (Nihon Millipore, Tokyo, Japan).

3. Results and discussion

3.1. Optimization of on – line FI / ICP – MS

In our previous work [11], the adsorption behavior of trace amounts of 56 elements on the synthesized serine – type chitosan was systematically investigated by packing it in the mini – column (volume, 1 ml), passing metal solutions through it and measuring metal ions by ICP – MS. It was found from such experiments that uranium adsorbed on the resin characteristically at pHs from acidic to alkaline region. As shown in Fig. 3, uranium can adsorb on the resin
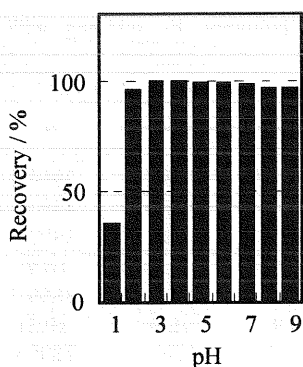
Fig. 3 Adsorption behavior of uranium at various pHs with serine − type chitosan. Sample, 10 ml; concentration of uranium, 10 ng ml^{-1}; eluent, 10 ml of 1 M nitric acid; column, 1 ml of the resin.
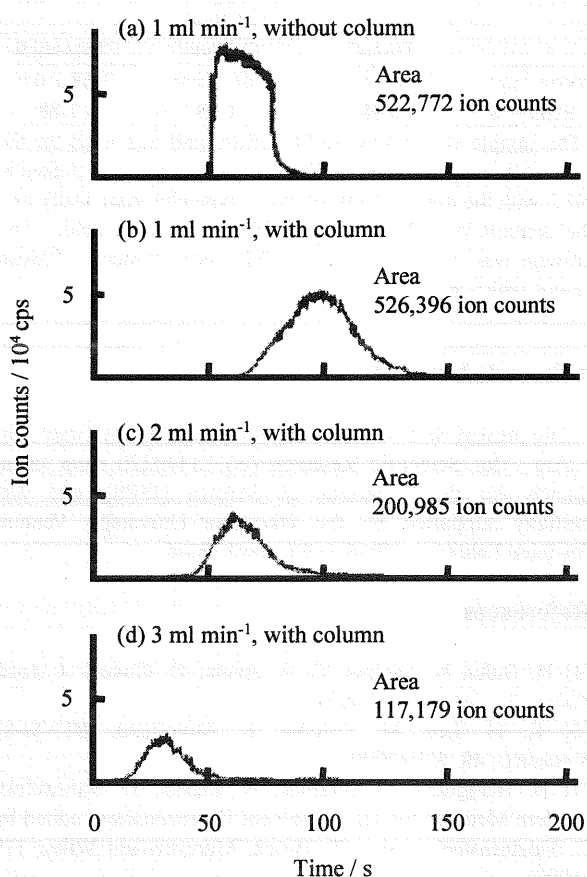

Fig. 4 Effect of flow rate on profiles of flow signals by on − line FI / ICP − MS. (a) 1.0 ml min^{-1}, without column, (b) 1.0 ml min^{-1}, (c) 2.0 ml min^{-1}, (d) 3.0 ml min^{-1}. Sample, 10 ng ml^{-1} of uranium solution (pH 3); sample volume, 0.5 ml; carrier, 1.0 ml min^{-1} of 0.5 M ammonium acetate solution (pH 3); eluent, 1.0 ml min^{-1} of 1 M nitric acid.

quantitatively even at pH 3. Uranium adsorbing on the resin was easily eluted with 1 M nitric acid. Accordingly, the preconcentration of uranium and the elimination of matrices (Na$^+$, K$^+$, Mg^{2+} and Ca^{2+}) in samples were possible by using the column packed with the serine − type resin.

In this work, the serine − type chitosan was used for the on − line ICP − MS measurement. The optimum conditions for on − line treatment were examined. The effect of the flow rate of the carrier on the flow signals was investigated by
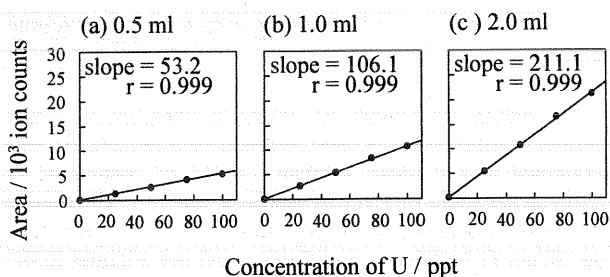

Fig. 5 Effect of sample volumes on linearity of calibration graphs. Sample volume: (a) 0.5 ml, (b) 1.0 ml, (c) 2.0 ml; sample, uranium solution (pH 3); carrier, 1.0 ml min^{-1} of 0.5 M ammonium acetate solution (pH 3); eluent, 1.0 ml min^{-1} of 1 M nitric acid.
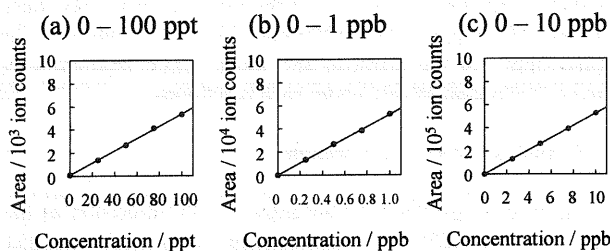

Fig. 6 Calibration graphs obtained by FI / ICP − MS. (a) 0 − 100 pg ml^{-1}, (b) 0 − 1 ng ml^{-1}, (c) 0 − 10 ng ml^{-1}. Sample, uranium solution (pH 3); sample volume, 0.5 ml; carrier, 1.0 ml min^{-1} of 0.5 M ammonium acetate solution (pH 3); eluent, 1.0 ml min^{-1} of 1 M nitric acid.

varying it from 1.0 to 3.0 ml min^{-1}. The signal profiles of the uranium standard solution are shown in Fig. 4. When the flow rate was 1.0 ml min^{-1}, the area of the sample zone (b) in Fig. 4 was almost the same as the one of the sample zone (a) in Fig. 4. It indicates that the recovery of uranium was almost 100 %. Uranium adsorbed on the resin was eluted within 1.5 min. However, the peak area of uranium decreased with increasing the flow rate, because the time for integrating the peak area became shorter. When the flow rate was 2 ml min^{-1} and 3 ml min^{-1}, the adsorption efficiency of uranium was found to be about 76 % and 67 %, respectively, which values were calculated by using the product of the peak area and the flow rate. Consequently, the flow rate was adjusted to 1.0 ml min^{-1}.

To examine the effect of sample volume on the linearity of the calibration graph, three kinds of sample volumes (0.5, 1.0 and 2.0 ml) were tested at the constant flow rate (1.0 ml min^{-1}). The peak areas of the signals were increased in proportion to the sample volumes, as shown in Fig. 5. 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 sea water.

The linearity of the calibration graph for uranium determination obtained by the proposed method was examined; the results obtained are shown in Fig. 6. 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 the calibration graphs were good over wide concentration ranges, which indicates that uranium can adsorb on the resin quantitatively, and can be eluted from it completely by the proposed procedures.

3.2. Matrix elimination by washing with ammonium acetate solution

The matrix elimination was tested by using an off – line system. Ammonium acetate solution (0.5 M, pH 3) was examined as a washing solution. A 0.5 ml aliquot of an artificial sea water (pH 3) was used as a sample. The sample was injected and the carrier was flowed for 1 – 4 min, then the eluent (1 M HNO_3) was flowed, and the uranium in the effluent was measured by ICP – MS. Matrices, such as Na, Mg, K and Ca, in the effluent were measured by ICP – AES. As shown in Table 2, the matrices were removed efficiently with increasing the washing time. From the results, the washing time of 2 min was sufficient to remove the matrix components on the resin. The recovered (residued) concentrations of the matrix ions were negligible compared with the initial concentrations of the matrix components, such as Na (11500 ppm), Mg (1200 ppm), K (3900 ppm) and Ca (400 ppm), in the artificial sea water, while uranium was recovered quantitatively under such conditions.

3.3. Analysis of sea water sample

In order to evaluate the accuracy and the precision of the on – line FI / ICP – MS measurement, a practical sea water sample was analyzed by the proposed method. Five replicate analyses were performed for the sea water sample. The analytical data obtained by the on – line FI / ICP – MS with the column of the serine – type chitosan are summarized in Table 3. The result obtained by the proposed method are in good agreement with the values obtained by a direct determination method after 20 – fold dilution of the sample and by the ICP – MS measurement after the batchwise column pretreatment with the mini – column of the serine – type chitosan. The precision (relative standard deviation: RSD) for the uranium determination was within 2 %. In the direct method, high concentrations of matrices, such as Na, Mg, K and Ca, can damage seriously the mass spectrophotometer; therefore, the direct method is not favorable for sea water analysis. The pretreatment time with the batchwise column method was about 1 h, which is much longer than that in the proposed method. Further, the proposed method was much simpler, less time – consuming, and smaller sample size than the batchwise method.

4. Conclusion

The determination of uranium in sea water sample was successfully achieved by the proposed on – line FI / ICP – MS with the column packed with the synthesized serine – type chitosan resin. It was found that the serine – type chitosan was very useful for the pretreatment of sea water sample prior to ICP – MS measurement. The main advantages of the proposed method are: (1) uranium can adsorb selectively on the serine – type chitosan at pH 3, (2) the on – line system is very simple and fast, (3) the results are very reproducible (RSD: ± 2 %), and (4) the sample size required is very small (0.5 ml). The on – line collection of the analyte and the elimination of high – concentration matrix substances with the column of the serine – type chitosan were a useful technique for the determination of uranium by ICP – MS measurement. The proposed system is very promising for the application to the determination of trace uranium in various water samples.

Table 2 Matrix elimination by washing with ammonium acetate solution

Washing time (min)	Eliminated amount (Recovered amount) / ppm			
	Na	Mg	K	Ca
1	11401.9 (98.1)	1189.0 (11.0)	3860.8 (39.2)	394.2 (5.8)
2	11498.4 (1.6)	1198.6 (1.4)	3899.5 (0.5)	399.9 (0.1)
3	11499.1 (0.9)	1199.1 (0.9)	3899.7 (0.3)	399.8 (0.2)
4	11499.7 (0.3)	1199.6 (0.4)	3899.9 (0.1)	399.7 (0.3)

An artificial sea water sample contains metal ions as follows: Na, 11500 ppm; Mg, 1200 ppm; K, 3900 ppm; Ca, 400 ppm.

Table 3 Analytical results of uranium in sea water

	Method		
	Direct[a]	Column[b]	This study
Mean / ppb[c]	2.62 ± 0.03	2.66 ± 0.03	2.68 ± 0.05
RSD / %	0.98	1.08	1.88

[a] The sample was diluted to 20 – fold, and was used for the ICP – MS measurement. [b] The sample, 10 ml, was treated at pH 3 with the mini-column (serine – type chitosan: 1 ml), and the uranium was eluted with 10 ml of 1 M nitric acid. The effluent was used for the ICP – MS measurement. [c] Mean values with ± σ.

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