

Adsorption Behavior of Metal Ions on Cross-linked Chitosan and the Determination of Oxoanions after Pretreatment with a Chitosan Column

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The adsorption behavior of 60 elements at the 10 ng ml⁻¹ level on high-porous cross-linked chitosan in a packed mini-column was systematically examined. The chitosan used could adsorb anionic species quantitatively as oxoanions or chloro complex anions of metals, such as Ti, V, Mo, W, Ga, Bi, Au(III), Pt(IV) and Pd(II), in sample solutions by an ion-exchange mechanism, and could adsorb some metal ions by a chelating mechanism. Most of the metal ions adsorbed on the chitosan were eluted with 1 M nitric acid, and other noble metals, such as Au, Pt and Pd, were eluted by a solution containing 1 M hydrochloric acid and 0.05 M thiourea. The adsorption fraction of metal ions was investigated by measuring metal ions in eluates by ICP-MS. By using the proposed column pretreatment method, metal ions present as their oxoanions in river-water samples, such as Ti, V, Mo, W, Ga and Bi, were collected on the cross-linked chitosan, eluted and determined. The method was applied to an analysis of reference materials distributed by the Japan Society for Analytical Chemistry: JAC 0031 and JAC 0032. The analytical results agreed closely with other reference values.

(Received August 8, 2000; Accepted September 21, 2000)

Chitosan, an *N*-deacetylation product of chitin, is one of the useful chelating polymers, and is capable of adsorbing a number of metal ions. Muzzarelli *et al.* have reported that chitosan without cross-linking can adsorb transition-metal ions from aqueous solutions at neutral pH,^{1,2} and other researchers have reported that chitosan can adsorb Hg(II), Cu(II), Cr(III), Pb(II), UO₂⁺ and Cd(II).³⁻⁸ However, the adsorption behavior of metal ions has not yet been investigated in detail, though chitosan seems to possess a promising ability of metal collection.

Non-cross-linked chitosan can be easily soluble in some acidic media. Such a characteristic is one of the serious disadvantages from a practical viewpoint of metal collection and concentration. Therefore, several types of chemically cross-linked chitosan have been prepared and their metal adsorption properties have been examined. Cross-linking can make chitosan hardly soluble in acidic media. Ohga *et al.* reported that cross-linked chitosan, which was prepared by cross-linking with (chloromethyl)oxyrane after complexation of chitosan with metal ions, can act as effective adsorbents for Cu(II) and Hg(II),⁹ and Inoue *et al.* reported the adsorption behavior of 15 elements on cross-linked chitosan by a batchwise method.^{10,11} Koyama *et al.* and Kurita *et al.* also synthesized a cross-linked chitosan with glutaraldehyde, and examined the adsorption behavior of Cu.^{12,13} Further, Rorrer *et al.* examined adsorption isotherms of Cd(II) on porous chitosan beads cross-linked with glutaraldehyde at 25°C and pH 6.5 over the concentration range 1 – 1690 mg l⁻¹.¹⁴

Such studies mainly examined the adsorption behavior of several metal ions at ppm levels on a cross-linked chitosan by batchwise equilibration techniques, and did not aim to collect and concentrate trace amounts of metal ions at ppb and sub-

ppbs (1 ppb = 1 ng ml⁻¹). Further, few papers have reported so far about the desorption and recovery of metal ions adsorbed on cross-linked and non-cross-linked chitosan.

In this work, the authors examined in detail, for the first time, the adsorption behavior of a number of elements (60 elements) at the 10 ng ml⁻¹ level by a column pretreatment method using commercially available high-porous cross-linked chitosan beads (CHITOPPEARL AL-01) (Fuji Spinning Co., Ltd. Tokyo, Japan), and found the useful ability of the cross-linked chitosan as a packing material for collecting and concentrating trace amounts of metal ions in river-water samples. Furthermore, the determination of six oxoanions in river-water samples (reference materials distributed by the Japan Society for Analytical Chemistry: JAC 0031 and JAC 0032) was carried out using air-segmented flow injection/ICP-MS (AFI/ICP-MS) after preconcentration with a chitosan column. The analytical results obtained for the determination of oxoanions agreed well with other literature values.¹⁵⁻¹⁷

Experimental

Instrumentation

The ICP-MS system used for the determination of metal ions was a Model SPQ 8000H (Seiko Instruments Co., Tokyo, Japan). A micro-sampling system used for air-segmented flow injection (AFI) consisted mainly of an AT-600 autosampler (Seiko Instruments Co.) and MS software (trade name, MicroSuction ver. 1.8M) for data acquisition and to control the ICP-MS instrument. The experimental conditions were those suggested by our previous work.¹⁵

Materials and reagents

Cross-linked chitosan beads (trade name: CHITOPPEARL AL-

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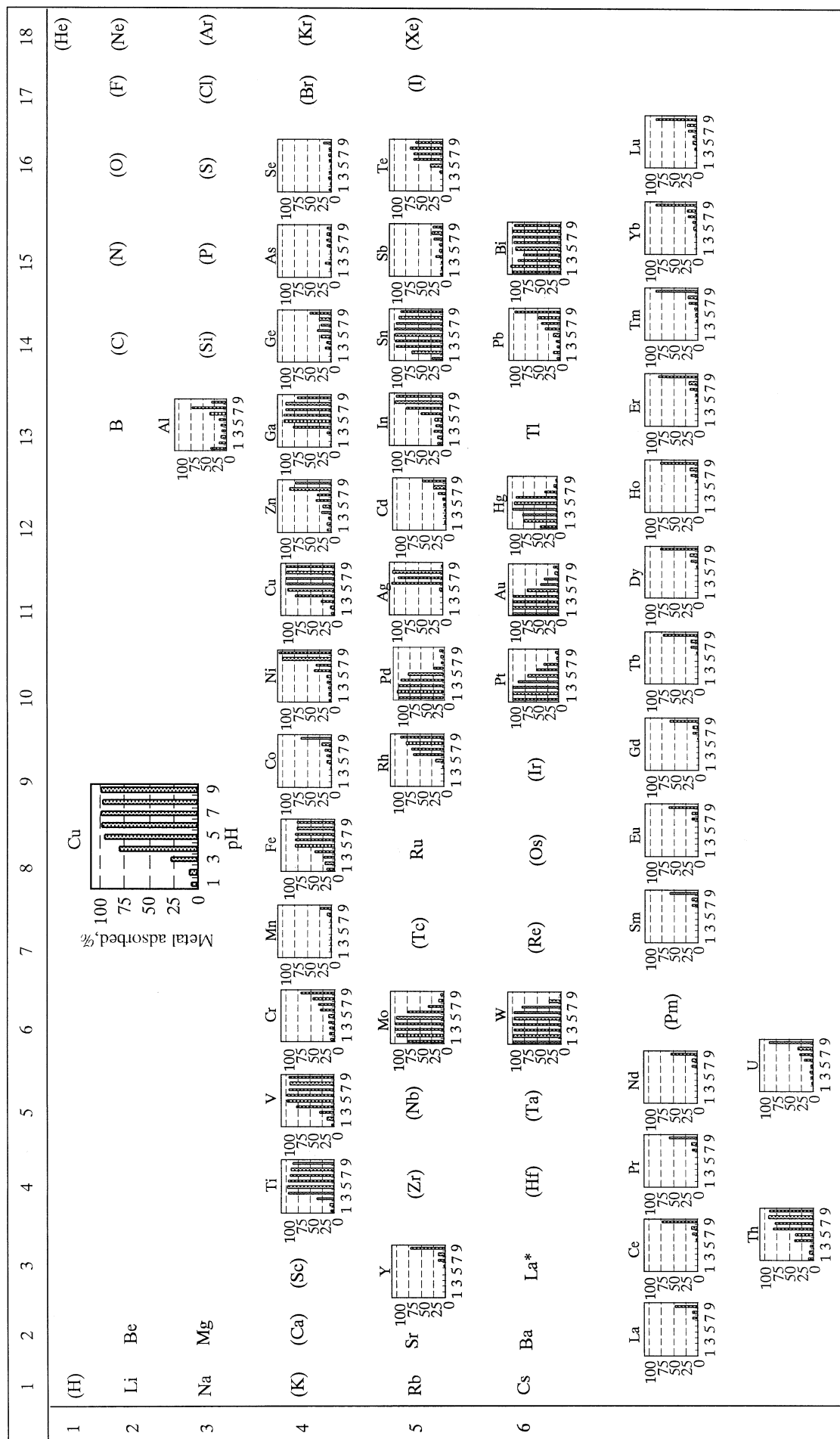


Fig. 1 Adsorption behavior of trace elements on cross-linked chitosan resin as a function of pH. Sample volume, 10 ml; concentration of each metal, 10 ng ml⁻¹. (): the elements were not measured.

01) were purchased from Fuji Spinning Co. (Tokyo, Japan). Before use, cleaning of AL-01 was accomplished by removing residual metal impurities: a 20-ml volume of wet beads was transferred to a 100-ml plastic beaker, mixed with 80 ml of 2 M nitric acid, cautiously stirred at low speed for 6 h, and rinsed with ultrapure water. The beads were then mixed with 80 ml of 1 M hydrochloric acid containing 0.1 M thiourea, and slowly stirred for 4 h, then rinsed with ultrapure water. Small-size polypropylene columns (1 ml of volume) were purchased from Muromachi Chemical (Kyoto, Japan), and were used for a pretreatment with chitosan columns.

Analytical multi-element standard solutions were prepared by diluting a mixed standard solution containing $10 \mu\text{g ml}^{-1}$ metal ions for ICP-MS (XSTC-13, Spex CertiPrep Inc., New Jersey, USA). This solution contained 31 elements: Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, Th and U. Other stock standard solutions were as follows: $10 \mu\text{g ml}^{-1}$ of mixed solutions: (1) Au, Pt and Pd and Hg in 0.1 M hydrochloric acid; (2) rare earth elements (REEs), Sc and Y in 0.1 M nitric acid; (3) Ti, Sn, Sb, Te, Rh and Ru in 0.1 M nitric acid; (4) B, Mo, W and Ge in ultrapure water. These solutions (1)–(4) were prepared by diluting single-element standard solutions ($1000 \mu\text{g ml}^{-1}$) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). These stock solutions were mixed to give adequate concentrations in 0.1 M nitric acid just before column pretreatment, followed by an ICP-MS measurement.

Ultrapure grade nitric acid (60%, density 1.38 g ml^{-1} , Kanto Chemicals, Tokyo) and hydrochloric acid for trace analysis (35.0%, Kanto Chemicals, Tokyo) were diluted with ultrapure water to give a 0.1 M or 1 M solution. Accurate dilution of the standard solutions was carried out by weight. The acetic acid (minimum 96%) and ammonia water (29%) used for preparing an ammonium acetate buffer solution were of electronic industrial reagent grade (Kanto Chemicals).

Ultrapure water ($18.3 \text{ M}\Omega \text{ cm}$ resistivity) was prepared by a Milli-Q Element (Nihon Millipore, Tokyo, Japan).

Pretreatment procedures for sample solutions

The adsorption/concentration of metal ions by a column pretreatment was carried out using mini-columns packed with the cross-linked chitosan cleaned in the same manner as described above. One milliliter of resins packed in the mini-column ($5.0 - 5.5 \text{ mm i.d.} \times 50 \text{ mm}$) were first washed with 5 ml of 2 M nitric acid and then 10 ml of water. After 5 ml of buffer solution (pH 1–2, nitric acid; pH>3, 0.2 M acetate buffer, whose pHs were adjusted with glacial acetic acid or ammonia water) was passed through the column for column conditioning, 10 ml of the sample solution (pH 1–9: pH is adjusted to the pH for column conditioning with the buffer solution) was passed through the column. Then, 5 ml of a 0.2 M buffer solution (pH 1–9) was passed through the column to eliminate matrix ions, such as alkali and alkaline earth metals. After that, 5 ml of purified water was passed through the column for rinsing the residual buffer components in the column. Finally, 10 ml of 1 M nitric acid was passed through the column to recover metal ions adsorbed on the resin. The eluate (1 M nitric acid) was transferred to a 50-ml PTFE beaker and evaporated to dryness on a hot plate (120°C) in the evaporation chamber where clean-air was flowing from an air supply pump. The evaporation chamber was covered with a clear polyvinyl sheet to prevent samples from contamination. The residue in the beaker was redissolved with 10 ml of 0.1 M nitric acid.

For the determination of oxoanion species, such as Ti, V, Ga, Mo, W and Bi, a 10-fold preconcentration was carried out using

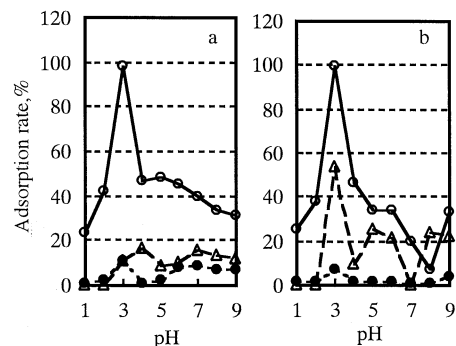


Fig. 2 Adsorption efficiency of As and Se on cross-linked chitosan as a function of pH. a, As; b, Se. Sample volume, 10 ml; concentration of each metal, 10 ng ml^{-1} . \circ , data obtained by using the eluents without rinsing the column with a buffer and water; \triangle , data obtained by using the eluents after rinsing the column with 10 ml of water; \bullet , data obtained by using the eluents after rinsing the column with 5 ml of the buffer and 5 ml of water according to the standard procedure.

10 ml of a sample solution (pH 5). The residue in the beaker was redissolved with 1 ml of 0.1 M nitric acid. The thus-prepared solutions were used as samples for ICP-MS measurements.

Such metal ions as Au, Pd and Pt, which were adsorbed on the cross-linked chitosan, were eluted with 10 ml of a solution containing 1 M hydrochloric acid and 0.05 M thiourea. The obtained eluates were used as samples for ICP-MS measurements without the procedure for evaporating the eluates to dryness.

The thus-prepared samples were transferred into a sample vial of AT-600, and each $80 \mu\text{l}$ of the samples was used for an AFI/ICP-MS measurement. Throughout all of these column procedures, the flow rate of the samples, the rinsing solutions and the eluent was maintained at about 0.5 ml min^{-1} . The time required for a column pretreatment was about 2 h. The water purified with a Milli-Q Element system was used throughout the experiment.

Results and Discussion

Adsorption behavior of metal ions on cross-linked chitosan resin

Figure 1 shows the efficiency of the adsorption of a number of metal ions on the cross-linked chitosan at pH from 1 to 9. Most of the metal ions adsorbed on the chitosan, except for Au, Pd and Pt, were completely recovered with 10 ml of 1 M nitric acid as the eluent.

The cross-linked chitosan showed strong adsorption efficiency for Mo and W at pH from 1 to 6, for Sn at pH >2, for Bi at pH 1 to 9, and for Ti, V and Ga at pH >4. The adsorption behavior of As(V) and Se(VI) is shown in Fig. 2. The recovery of these metals was more efficient when rinsing with the buffer solution and water was omitted, and 100% recovery was achieved at pH 3. When the column treatment was carried out by the standard procedure, As and Se were recovered at levels below 10%. This is probably because the $\text{p}K_{\text{a}1}$ values of As(V) and Se(VI) are 2.25 ($\text{p}K_{\text{a}2} = 6.77$, $\text{p}K_{\text{a}3} = 11.53$ of As(V)) and 2.05, respectively,¹⁸ and As(V) and Se(VI) are present as an anionic species in the solution at pH >2. Such results show that the adsorption efficiency of As(V) and Se(VI) is so weak that they can be easily eluted by the buffer solution and water.

For examining the adsorption behavior of Hg(II), the eluate of

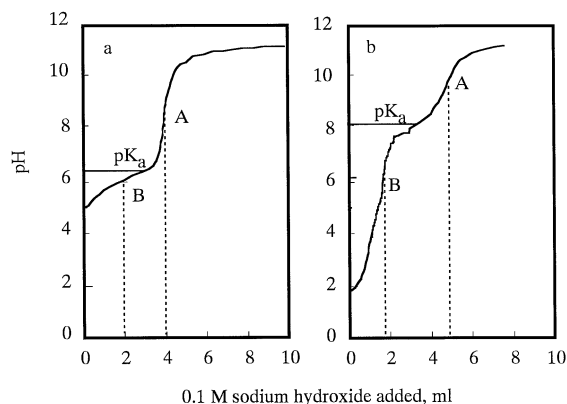


Fig. 3 Titration curves for non-cross-linked chitosan and cross-linked chitosan. a: 25 ml of solution containing 1 ml (wet volume) chitosan, 2 ml of 0.1 M HCl and 15 ml of 0.1 M NaCl (chitosan was available from Wako Pure Chemicals, Japan). b: 25 ml of solution containing 2 ml (wet volume) cross-linked chitosan (CHITOPPEARL AL-01), 2 ml of 0.1 M HCl and 15 ml of 0.1 M NaCl. A: the point of inflection of chitosan. B: the point of inflection of hydrochloric acid.

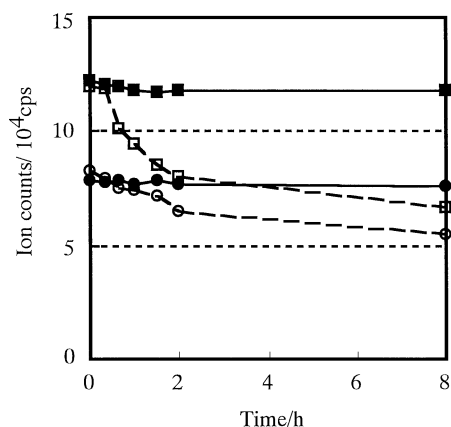


Fig. 4 Stability of Pd(II) and Au(III) in 0.1 M nitric acid and 0.1 M HCl. Pd(II) and Au(III): 10 ng ml⁻¹. ■, Au in 0.1 M HCl; □, Au in 0.1 M nitric acid; ●, Pd in 0.1 M HCl; ○, Pd in 0.1 M nitric acid.

10 ml of 1 M nitric acid was directly measured by ICP-MS, because evaporating to dryness resulted in the evaporation of Hg(II), and we could not detect Hg. Mercury(II) adsorbed on the cross-linked chitosan at pH from 3 to 6, whereas other noble metals, such as Au, Pd and Pt, strongly adsorbed at pH <5. The recovery of the noble metal ions is described later, since the adsorbed Au, Pd and Pt can not be completely eluted by 1 M nitric acid. Probably, these metals are strongly adsorbed on the cross-linked chitosan as their chloro complex anions.

Copper(II) strongly adsorbed at pH from 4 to 9. Probably, copper(II) can be adsorbed on cross-linked chitosan by a coordination mechanism with the amino group of the chitosan.

The recovery of other transition metal ions and rare earth metal ions was very scarce at pH <7.

Almost all of the alkali and alkaline-earth metal ions, as well as Be and Tl, were lost during the pretreatment procedures.

The experimental results indicate that the adsorption of several metals existing as oxo acids on the protonated chitosan can take place as their anionic species. Thus, cross-linked chitosan can act effectively as an anion-exchange resin at pH <7 for heavy metal ions existing as oxo acids; it can also act as a chelating

Table 1 Recovery of noble metals from cross-linked chitosan resin with various eluents

Eluent	Recovery, % ^a		
	Pd	Pt	Au
1 M HNO ₃ (10 ml)	7.0	46.0	7.0
1 M HCl (10 ml)	4.0	22.5	5.2
1 M HCl (20 ml)	4.9	24.0	7.0
2 M HCl (10 ml)	1.9	20.0	10.0
1 M HCl + 0.05 M thiourea (10 ml)	94.2	98.9	98.4
1 M HCl + 0.05 M thiourea (20 ml)	99.3	102.1	99.4

a. Sample volume, 10 ml; concentration of each metal, 10 ng ml⁻¹.

resin for stable chelate-forming metal ions, and as a chelating resin at pH >8, which can be explained by the pK_a value of the cross-linked chitosan. Figure 3 shows the titration curves of chitosan without being cross-linked and the cross-linked chitosan. The pK_a was about 6.3 for chitosan without being cross-linked and about 8 for the cross-linked chitosan. The shift of the pK_a values toward higher pH is due to the cross-linking.

Adsorption and recovery of Au, Pt and Pd

Noble metals, Au and Pd, were unstable in diluted nitric acid. Figure 4 shows the stability of each 10 ng ml⁻¹ of Au and Pd in 0.1 M nitric acid. The ion counts decreased with increasing standing time after the preparation. Therefore, the standard sample solutions of noble metals were prepared with 0.1 M hydrochloric acid, because the noble metals can form stable chloro complexes with chloride ion. Table 1 shows the effect of different eluents on metal recovery from the column at pH 2. Ten milliliters of 1 M nitric acid and 1 M hydrochloric acid could partly elute Au, Pd and Pt. However, a solution containing 1 M hydrochloric acid and 0.05 M thiourea could elute these metals, and their recovery was about 100% when 20 ml of the eluent was used. This is because the noble metal ions can form stable complexes with thiourea.

Adsorption/concentration and determination of oxoanions in river water samples

Oxoanions, such as Ti, V, Mo, W, Ga and Bi, can strongly be adsorbed on cross-linked chitosan at a wide pH region, as is shown in Fig. 1. Further, adsorption experiments for these oxoanions were carried out at pH 5, taking into consideration the adsorption efficiency and the reproducible recovery of these oxoanions.

The elution behavior of trace oxoanions was examined by varying the concentrations of nitric acid in the eluent from 0.1 to 4 M, where the pH of the 10 ml of sample solution containing each metal (1 ng ml⁻¹) as its oxoanion was adjusted to 5. The results are shown in Fig. 5, where the volume of the eluent (nitric acid solution) was 10 ml. The metals were quantitatively adsorbed on the chitosan, and were almost completely recovered at above 1 M nitric acid in the eluent. The higher were the nitric acid concentrations, the more easily the metals could be recovered. However, the higher was the nitric acid concentration, the greater was the contamination from the nitric acid. In this work, for safety, a 15-ml volume of 1 M nitric acid was selected as the eluent. The results of the total blank values, analytical limits of detection and the recovery percentages of the metals obtained under the optimized column

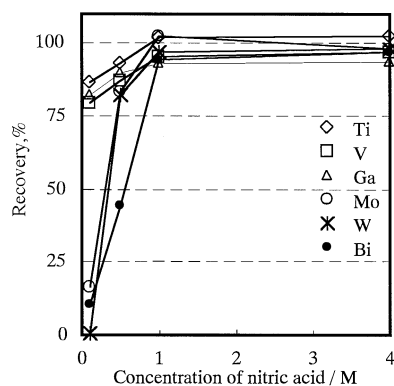


Fig. 5 Effect of the concentration of nitric acid in eluents on the recovery of metals adsorbed on a cross-linked chitosan resin. Sample volume, 10 ml; concentration of each metal, 1 ng ml⁻¹. Volume of nitric acid, 10 ml.

Table 2 Total blank, limit of detection and recovery of 1 ng metals in 10 ml sample from the column preconcentration procedure

Element	<i>m/z</i>	Total blank ^a / ng ml ⁻¹	Analytical LOD ^b / ng ml ⁻¹	Recovery, % ^c
Ti	49	0.37±0.04	0.11	100.5±5.4
V	51	0.030±0.008	0.03	95.2±3.2
Ga	69	0.018±0.003	0.008	90.1±3.8
Mo	96	0.44±0.02	0.06	102.5±4.0
W	182	0.16±0.06	0.19	97.4±6.7
Bi	209	0.038±0.007	0.022	98.7±1.9

- a. Total blank includes the contamination from the column preconcentration procedure ($n = 4$).
 b. Limit of detection for the whole procedure, 3σ ($n = 4$).
 c. Sample volume, 10 ml; concentration of each metal, 0.1 ng ml⁻¹. The metals adsorbed on the resin were eluted with 15 ml of 1 M nitric acid. The eluents were evaporated to dryness, and the residues were dissolved in 1 ml of 0.1 M nitric acid ($n = 6$).

preconcentration conditions are summarized in Table 2. These data show the average values obtained by using four independent columns packed with 1 ml of the resin.

The determination of the oxoanions with the cross-linked chitosan resin was examined with two kinds of the river certified reference materials. Tables 3 and 4 show the results obtained by the proposed method for JAC 0031 and JAC 0032. The mean and standard deviations of four replicate determinations of samples are given in Tables 3 and 4. Since the certified values of Ti, V, Ga, Mo, W and Bi are still not available in the river certified reference materials, the values obtained by this work are compared with the literature values (see Tables 3 and 4).¹⁵⁻¹⁷ The analytical data obtained by the proposed method are in good agreement with the literature values.

The adsorption behavior of metal ions on cross-linked chitosan resin was systematically investigated in detail. The main advantages of this resin are as follows: (1) the efficiency and the selectivity of metal adsorption/collection are different in the kinds of metals and in the pH range, which is attributed to the chelation and ion-exchange mechanisms. In addition, the interfering potential of alkaline earth metals, such as Ca²⁺ and Mg²⁺, was very low. A strong interaction between anionic species of metals, such as Ti, V, Mo, W, Ga, Bi and noble

Table 3 Analytical results for the certified reference material of spiked river water (JAC0031) obtained by AFI/ICP-MS with sample treatment (ng ml⁻¹)

Element	This work	ICP-MS ^a	ICP-MS ^b	INAA ^c
Ti	0.13±0.01	(0.6) ^f	0.15	<8.4
V	7.56±0.09	7.4±0.5	7.8±0.5	7.4±0.4
Ga	0.025±0.004	0.036±0.002		<1.3
Mo	0.33±0.04	(0.4) ^f	0.50±0.008	0.41±0.05
W	[0.02] ^d	(0.02)		0.0143±0.0019
Bi	n.d. ^e			

- a. Cited from Ref. 15.
 b. Cited from Ref. 16.
 c. Cited from Ref. 17.
 d. The value is below the limit of detection.
 e. Not determined.
 f. Information value.

Table 4 Analytical results for the certified reference material of spiked river water (JAC0032) obtained by AFI/ICP-MS with sample treatment (ng ml⁻¹)

Element	This work	ICP-MS ^a	ICP-MS (ICP-AES) ^b	INAA ^c
Ti	0.24±0.01	(1.1) ^f	0.15	
V	7.27±0.08	7.3±0.5	7.9±1.0	7.5±0.2
Ga	0.026±0.002	0.041±0.002		<1.3
Mo	0.327±0.014	(0.4) ^f	0.49±0.01	0.40±0.03
W	[0.02] ^d	(0.02)		<0.03
Bi	n.d. ^e			

- a. Cited from Ref. 15.
 b. Cited from Ref. 16.
 c. Cited from Ref. 17.
 d. The value is below the limit of detection.
 e. Not determined.
 f. Information value.

metals, and the chitosan was found over a wide pH region. By combining AFI/ICP-MS with the efficient concentration/recovery method for oxoanions with the chitosan column, it was favorably possible to determine trace amounts of oxoanions in river-water samples.

Acknowledgements

The present work was partially supported by Okayama University Venture Business Laboratory, and also partially by the Grant-in-Aid for Scientific Research (B, No. 10558084) from the Ministry of Education, Science, Sports and Culture, Japan.

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