Synthesis of Cross-Linked Chitosan Resin Possessing Leucine Moiety for the Column Collection/Concentration of Molybdenum and Determination of Molybdenum by ICP-MS, ICP-AES and GFAAS

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A chitosan resin possessing the leucine moiety (leucine-type chitosan) was newly synthesized by using the chitosan cross-linked with ethylene glycol diglycidyl ether (EGDE) as a basic material. The adsorption behavior of trace amounts of metal ions on the leucine-type chitosan was systematically examined by packing it in a mini-column by ICP-MS (inductively coupled plasma mass spectrometry). Molybdenum was adsorbed on the resin quantitatively and was easily eluted with 1 M nitric acid. The optimized pH range was from 1 to 5, and Mo was collected by the chelation mechanism and/or the anion-exchange mechanism. The method was applied to the determination of Mo in sea and river water samples. A pretreatment with the resin could remove the matrix components in seawater. Preconcentration by 100-fold was accomplished by a column treatment, which had a sufficient concentration to measure trace Mo in river water samples by ICP-AES (inductively coupled plasma atomic emission spectrometry) and GFAAS (graphite furnace atomic absorption spectrometry): LODs with a 100-fold preconcentration by ICP-AES and GFAAS were 0.007 ng $\mathrm{mL^{-1}}$ and 0.009 ng $\mathrm{mL^{-1}}$, respectively, and the RSDs were both within 4.0%.

Molybdenum is a bio-essential nutrient element, but is toxic to humans when present in high concentrations.[1] In a WHO guideline, Mo in drinking water has been restricted to be under 70 ng $\mathrm{mL^{-1}}$.[2] Because the amounts of Mo in environmental water in Japan, such as drinking, river, and sea waters, are 0.11–6.2, 1, and 10 ng $\mathrm{mL^{-1}}$, respectively, sub-ppb levels of Mo must be accurately determined.[3,4] Some researchers determined Mo at the ppb level in pharmaceuticals, blood and human urine without preconcentration by flame AAS, GFAAS and ICP-MS.[5–7] The LODs of Mo by flame AAS, GFAAS, and ICP-MS were 129 ng $\mathrm{mL^{-1}}$, 0.6 ng $\mathrm{mL^{-1}}$, and 0.2 ng $\mathrm{mL^{-1}}$, respectively. Therefore, a preconcentration procedure was necessary for the determination of Mo at sub-ppb levels. To solve such a problem, other researchers proposed preconcentration techniques of Mo.[8–10] Yabutani et al. proposed a tandem preconcentration method for the simultaneous multielement determination of trace elements in seawater by ICP-MS.[10] In their method, Mo was recovered with other trace elements from seawater by a La coprecipitation method, followed by an adsorption process of elements using the Chelex 100 resin. The recovery and the RSDs of Mo of their method were 70.2% and 2.7%, respectively: Mo could not be recovered quantitatively. Rivas et al. synthesized a cross-linked polymer containing an acrylic acid moiety.[11] Molybdenum was selectively adsorbed on the resin at pH 1. However, the recoveries of Mo(Ⅵ) at around pH 1 were as low as 68–80%, and their resin was not suitable for effective preconcentration. Huang et al. synthesized a chelating resin, which contained a bis(2-aminoethylthio)methyl group, for the collection of Mo.[12] The recoveries of Mo from deionized water, tap water, and each spiked sample were 113.0, 106.3, and 113.9 and 82.1%, respectively. In this case, the matrices affected the recovery of Mo. Therefore, the resin could not be applied to the determination of Mo in seawater and river water samples.

Our previous work showed comparisons of the adsorption kinetics of synthesized chtiosan resin possessing an IDA (iminodiacetic acid) group with that of Chelex 100.[13] The rate of adsorption of metal ions on chitosan resins was faster in aqueous media than that on Chelex 100, which is due to the hydrophilicity of the chitosan resin. In general, chitosan resins are more hydrophilic than resins synthesized with such base materials as polyetheneimine, polystylene, poly(stylene-co-divinylbenzene), polyethylene, and polyurethane. However, the disadvantages of a commercially available cross-linked chitosan were shrinking in an acidic solution and swelling in neutral and alkaline solutions.[14] To overcome these drawbacks, we developed a novel cross-linked chitosan resin with ethylene glycol diglycidyl ether (EGDE, glycidyl = 2,3-epoxypropyl); the synthesized resin did not shrink even in a concentrated acidic solution.[15] The adsorption behavior of metal ions on the resin was examined by a column treatment method, and the resin was excellent for the collection/concentration of heavy metal ions.[15,16]

Eguchi et al. reported the chemical behavior of a Mo(Ⅵ)-leucine complex in an aqueous solution: the complex was found to be relatively stable.[17] In this work, we synthesized a novel chelating resin possessing a leucine moiety for the collection/concentration of Mo. A leucine moiety was combined to the amino group of cross-linked chitosan, and the resin was examined for the collection and concentration of Mo in water samples by ICP-MS, ICP-AES and GFAAS.

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Table 1. Operating Conditions for ICP-MS, ICP-AES and GFAAS Instrument

ICP-MS (inductively coupled plasma mass spectrometry)	
Instrument	Seiko SPQ 8000H: Quadrupole type
Frequency	27 MHz
Incident power	1.1 kW
Reflected power	<5 W
Plasma gas	Ar 15 L min^{-1}
Carrier gas	Ar 0.45 L min^{-1}
Auxiliary gas	Ar 1.0 L 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 (inductively coupled plasma atomic emission spectrometry)	
Instrument	Seiko Vista-PRO: Axial type
Wavelength	202.030 nm
Frequency	27 MHz
Incident power	1.1 kW
Reflected power	<5 W
Plasma gas	Ar 15 L min^{-1}
Carrier gas	Ar 0.9 L min^{-1}
Auxiliary gas	Ar 1.5 L min^{-1}
GFAAS (graphite furnace atomic absorption spectrometry)	
Instrument	Perkin Elmer 3300
Wavelength	313.5 nm
Slit width	0.70 nm
Lamp current	10.0 mA
Measurement type	Peak Area
Background correction	D_2 lamp
Sample volume	20 µL
Flow rate of Ar	300 mL min^{-1}

Experimental

Instruments. The ICP-MS system used to measure metal ions was of a Model SPQ 8000H (Seiko Instruments, Chiba, Japan). An ICP-AES (Vista-PRO, Seiko Instruments) and a GFAAS (Model 3300, Perkin-Elmer Japan Co., Kanagawa, Japan) were used to measure Mo. The optimized operating conditions of ICP-MS, ICP-AES, and GFAAS are summarized in Table 1. Infrared (IR) spectra (4300–500 cm^{-1}) were recorded on an FT/IR-5000 spectrometer (JASCO Co., Tokyo, Japan). An automatical titration system used for the acid-base titration of synthesized resin was a Model AT-310J (Kyoto Electronics Manufacturing Co., Kyoto, Japan).

Reagents and Materials. The chitosan (Tokyo Kasei Co. Ltd., Tokyo, Japan) used was a flake type, and its deacetylated degree was about 80%. All other reagents used for the synthesis were of analytical reagent grade.

A stock solution of an analytical standard for each metal ion was prepared by diluting a single element standard solution for atomic absorption spectrometry (1000 µg mL^{-1}, Wako Pure Chemicals, Osaka, Japan) with 0.1 M nitric acid. This stock solution was diluted just before a column pretreatment with 0.1 M nitric acid to give 10 ng mL^{-1} of each metal in 0.1 M nitric acid, followed by ICP-MS, ICP-AES, and GFAAS measurements. Accurate dilution of the standard solutions was carried out by weight.

Ultrapure grade nitric acid (60%, density 1.38 g mL^{-1}, Kanto Chemicals, Tokyo, Japan) was used throughout the experiment, and was diluted with ultrapure water. Acetic acid (minimum 96%) and aqueous ammonia (29%) used for preparing an ammonium acetate buffer solution were of an electronic industrial reagent grade (Kanto Chemicals).

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

Procedures for the Pretreatment of Sample Solutions with Small Columns. Before a column pretreatment, leucine-type chitosan was cleaned by removing residual metal impurities in the resin as follows: 20 mL of the wet resin was transferred into a 100 mL plastic beaker, 80 mL of 2 M nitric acid was added to it, it was then stirred carefully at a low speed for 6 h, and finally the resin was rinsed with ultrapure water. One milliliter of the thus-cleaned resin was packed in small-sized polypropylene columns (1 mL of volume, 5.0 mm i.d. × 50 mm, Muromachi Chemical, Kyoto, Japan), which were used to examine the collection/concentration of metals on the resin.

In a similar manner to our previous study,[15] the collection/concentration behavior of metal ions was examined by the column method. The resin, 1 mL, packed in the mini-column was washed with each 10 mL of 1 M nitric acid and ultrapure water. Then, 5 mL of a buffer solution (pH 1–2: nitric acid; $7 > \text{pH} > 3$: 0.5 M ammonium acetate buffer) was passed through the column for column conditioning. Sample solutions (10 mL), whose pHs were adjusted to be the same as those of the column conditioning, were passed through the columns. Then, 5 mL of 0.2 M buffer solutions (pH 1–7) was passed through the column for removing matrix ions adsorbed on the resin, such as alkali and alkaline earth metal ions. Then, 5 mL of ultrapure water was passed through the column to rinse the remaining buffer components. Finally, 10 mL of 1 M nitric acid was passed through the column to recover metal ions adsorbed on the resin. The metals in the four kinds of effluents, the sample, the buffer, the ultrapure water, and the nitric acid, were measured by ICP-MS, ICP-AES, and GFAAS. In the case of determining Mo with a 10-fold preconcentration, 100 mL of the sample solution was used, and was adjusted to pH 4. In the case of a 100-fold preconcentration, 10 mL of the final effluent was evaporated to dryness and dissolved in 1 mL of 1 M nitric acid.

Results and Discussion

Synthesis of Leucine-Type Chitosan. The leucine-type chitosan was synthesized as follows. First, cross-linked chitosan was synthesized in a similar manner to previous work, as shown in Fig. 1 (1).[15] After chitosan flake was broken into pieces, chitosan particles with diameters at 100–300 µm were collected with a sieve. The chitosan particles (20 g) were suspended in 200 mL of ethanol. To it, benzaldehyde (80 g) was added, and the mixture was stirred at room temperature for 12 h to protect amino groups of the chitosan as Schiff bases. The product was filtered with filter paper and washed 3 times with ethanol and 3 times with distilled water. The product was then refluxed with ethylene glycol diglycidyl ether (EGDE, 30 g) in 300 mL of dioxane and 40 mL of 1 M NaOH for 3 h. The product was filtered and washed 3 times each with ethanol and water. The Schiff base was deprotected by stirring in 1000 mL of 0.5 M hydrochloric acid solution at room temperature for 12 h, filtered, and washed 3 times with ethanol and 3 times with water. Second, leucine was combined to the cross-linked chitosan in two steps; the scheme for the synthesis is shown in Fig. 1 (2). The cross-linked chitosan (5 g) was suspended in a mixture of water (50 mL) and ethanol (50 mL),

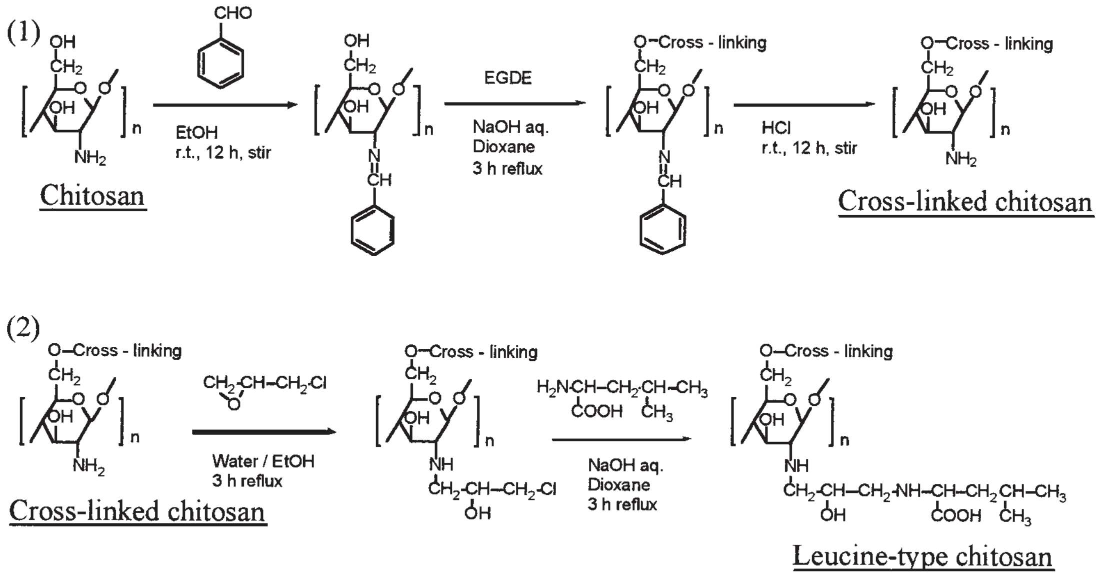
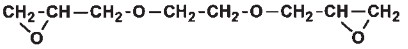


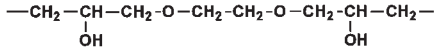
Fig. 1. Scheme for the synthesis of leucine-type chitosan.

EGDE:



$$\underset{\diagdown O \diagup}{CH_2-CH}-CH_2-O-CH_2-CH_2-O-CH_2-\underset{\diagdown O \diagup}{CH-CH_2}$$

Cross-linking:



$$-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-O-CH_2-CH_2-O-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-$$

then (chloromethyl)oxirane (10 g) was added to the suspension, and the mixture was refluxed for 3 h. After the reaction was completed, the product was filtered, and washed 3 times with ethanol and 3 times with water to remove unreacted (chloromethyl)oxirane. Leucine (15 g) and the cross-linked chitosan possessing 3-chloro-2-hydroxypropane arms at the amino groups, were suspended in dioxane (100 mL). After 1 M NaOH (40 mL) was added to the suspension, the mixture was refluxed for 3 h for coupling the amino group of leucine with the terminal chloro group of the arm of the cross-linked chitosan. The product was filtered and washed 3 times with ethanol and 3 times with water. The IR spectrum of leucine-type chitosan showed an additional band at 1748 cm^{-1} compared with the cross-linked chitosan. This seemed to originate from the ligand moiety, and is characteristic of carboxylate group vibration.

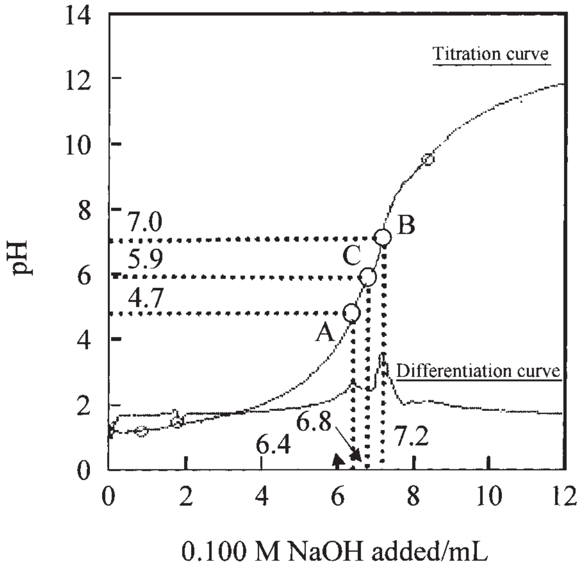


Fig. 2. Acid-base titration curve for the leucine-type chitosan. Titrant: 0.100 M NaOH solution; a sample solution: 1 mL of the leucine-type chitosan (wet volume), 2 mL of 0.1 M hydrochloric acid, and 28 mL of the ultrapure water. A: The inflection point of hydrochloric acid; B: The inflection point of leucine-type chitosan; C: A half point of the equivalent point.

Fundamental Characteristics of Leucine-Type Chitosan. Figure 2 shows the results of acid-base titration for the synthesized leucine-type chitosan (wet volume, 1 mL; dry weight, 0.23 g) in 30 mL of an acidic solution with a 0.100 M NaOH solution. The pK_a value obtained was about 5.9. The pK_a values of a carboxyl group of commercially available cation exchange resins of a weak acid type, such as Amberite IRC50 and Amberite IRC76, are 5.6 and 6.1, respectively. Therefore, the pK_a value, 5.9, is attributed to that of the carboxyl group of the leucine moiety introduced to the cross-linked chitosan. To neutralize the carboxyl group, 0.8 mL of 0.100 M NaOH was used, as shown in Fig. 2, which means that 0.08 mmol of the carboxyl group existed in 1 mL of the leucine-type chitosan. One milliliter of the resin corresponds to 0.23 g by weight. If each leucine moiety is attached to each unit of the cross-linked chitosan, 0.51 mol of carboxyl group may exist in 1 mL of the resin. As a conclusion, the molar ratio of leucine moiety and the unit of the chitosan may be 0.08:0.51. Figure 3 shows the adsorption behavior of Mo(VI) and Cu(II) on leucine-type chitosan. The resin, 1 mL, was equilibrated with each metal ion for 10 h at pH 4 in the presence of an excess amount of each metal ion. The adsorption capacities for Mo(VI) and Cu(II) were 0.23 and 0.09 mmol mL^{-1}, respectively. From Fig. 3, it is found that Cu(II) can be adsorbed more quickly on the resin than Mo(VI). However, the leu-

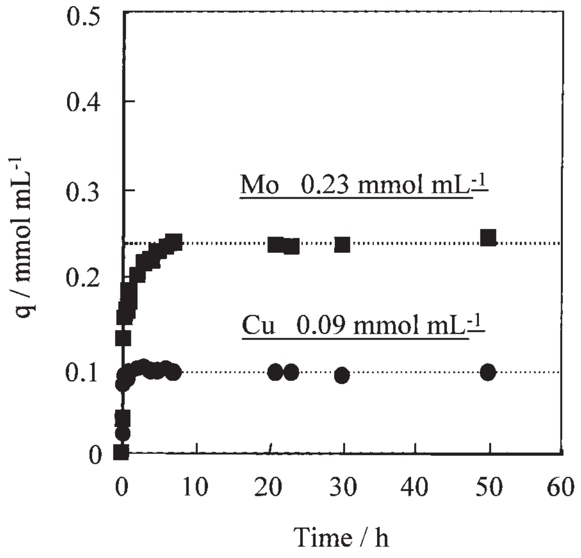


Fig. 3. Relationship between the time for the adsorption and the amount (q/mmol mL^{-1}) of Mo(Ⅵ) and Cu(Ⅱ) adsorbed on leucine-type chitosan at pH 4. Leucine-type chitosan: 1 mL (0.23 g); concentration of metal ions: 0.1 M of molybdenum or copper; volume of metal ions solution: 100 mL.

cine-type chitosan can adsorb a larger amount of Mo(Ⅵ).

Adsorption Behavior of Metal Ions on Leucine-Type Chitosan. Figure 4 shows the recovery of trace elements (each 10 ppb) at pH from 1 to 7 with the leucine-type chitosan. The recovery was examined with the standard column procedure. Copper(Ⅱ) and Mo(Ⅵ) was quantitatively adsorbed on the resin over a wide pH region and effectively recovered with 10 mL of 1 M nitric acid, and this resin was especially selective for Mo and 100% recovery was accomplished at pH 4.

Figure 4 shows that the leucine-type chitosan could adsorb Cu(Ⅱ) ion at pH values from 3 to 7. In our previous work, the cross-linked chitosan resin could adsorb Cu at pH 5–7 by the chelation mechanism.[15] In the case of the leucine-type chitosan resin, Cu could be adsorbed at a lower pH of 3. This is because Cu can form a chelate with carboxyl and amino groups in the leucine moiety and the cross-linked chitosan. On the other hand, the adsorbed and recovered amounts of Mo with the leucine-type chitosan resin at pH 1–6 were more than 90%, whereas in the cross-linked chitosan, the adsorbed amounts of Mo at pH 1–7 were less than 75%. This is because Mo(Ⅵ) existing as some oxoacid species in aqueous solutions could be adsorbed at the acidic region by an anionic exchange mechanism. By introducing of the leucine moiety to the cross-linked chitosan, the adsorption of Mo(Ⅵ) is considered to be improved by combining both effects of anionic exchange and the chelation mechanism.

Determination of Trace Amounts of Mo in Seawater and River Water Samples. The proposed method was applied to the determination of trace amounts of Mo in seawater and river samples. Molybdenum in such samples is contained above LOD (0.006 ng mL^{-1}) and LOQ (0.02 ng mL^{-1}) of ICP-MS, whereas major elements, such as Na^{+}, K^{+}, Mg^{2+}, and Ca^{2+}, can affect the ICP-MS measurement of trace elements due to the matrix effect, and seriously damage the detector of the ICP-MS. Removal of the matrix ions was carried out by using artificial seawater containing reasonable concentra-

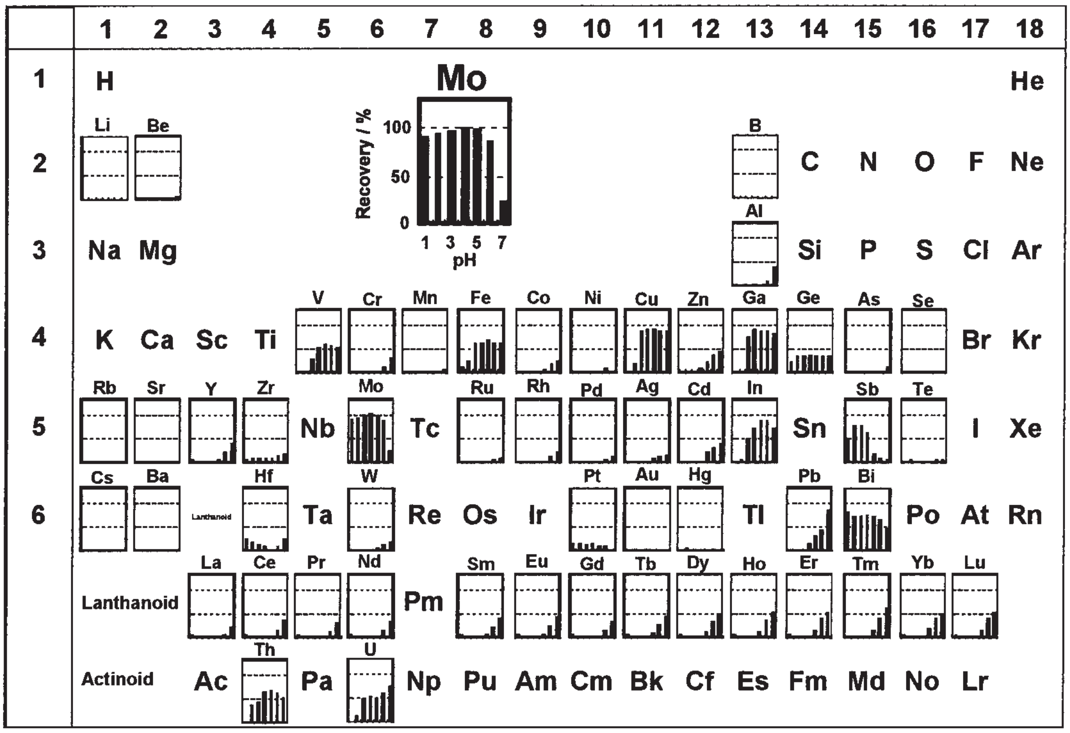


Fig. 4. Adsorption behavior of trace elements at various pHs with leucine-type chitosan. Sample, 10 mL; concentration of each element, 10 ng mL^{-1}; eluent, 10 mL of 1 M nitric acid; column, 1 mL of the resin. Typical presentation of all squares was shown at the top as an example for Mo.

Table 2. Analytical Results of Mo in Seawater by ICP-MS, ICP-AES, and GFAAS

	Mo found/ng mL^{-1} a)			
	Direct b)	With pretreatment c)		
Sample d)	ICP-MS	ICP-MS	ICP-AES	GFAAS
Artificial seawater	9.91 ± 0.47	9.97 ± 0.09	10.00 ± 0.37	10.11 ± 0.17
Natural seawater	10.10 ± 0.33	9.92 ± 0.30	9.90 ± 0.33	10.05 ± 0.15

a) Mean value of 5 measurements with $\pm\sigma$. b) The sample was diluted to 20-fold with 1 M nitric acid. c) The sample, 10 mL, was treated with the column (leucine-type chitosan: 1 mL) at pH 4. Eluent (1 M HNO_3): 10 mL. d) The artificial seawater contains 10 ng mL^{-1} of Mo, 10800 µg mL^{-1} of Na, 400 µg mL^{-1} of K, 1200 µg mL^{-1} of Mg and 400 µg mL^{-1} of Ca. The natural seawater was sampled at Shibukawa in Okayama, sampled on 3rd March, 2002.

Table 3. Analytical Results of Mo in River Water Samples by ICP-MS, ICP-AES, and GFAAS

	Mo found/ng mL^{-1} a)					
	ICP-MS		ICP-AES		GFAAS	
	Direct	With pretreatment b)	With preconcentration		With preconcentration	
Sample			10-fold c)	100-fold d)	10-fold c)	100-fold d)
Artificial river water e) (0.5 ng mL^{-1})	0.49 ± 0.01	0.49 ± 0.01	0.47 ± 0.01	—	0.48 ± 0.01	—
Artificial river water e) (0.05 ng mL^{-1})	0.050 ± 0.001	—	—	0.052 ± 0.002	—	0.051 ± 0.002
Natural river water (A) f)	0.87 ± 0.01	0.88 ± 0.02	0.88 ± 0.03	—	0.90 ± 0.03	—
Natural river water (B) f)	0.94 ± 0.003	0.93 ± 0.01	0.95 ± 0.02	—	0.96 ± 0.03	—

a) Mean with $\pm\sigma$. b) The sample, 10 mL, was treated at pH 4 with the column (leucine-type chitosan: 1 mL). Eluent (1 M HNO_3): 10 mL. c) The sample, 100 mL. Eluent (1 M HNO_3), 10 mL. d) The sample, 100 mL. Eluent (1 M HNO_3), 10 mL, was evaporated and dissolved with 1 mL of 1 M HNO_3. e) The artificial river water contains metal ions as follows: Na, 20 µg mL^{-1}; K, 10 µg mL^{-1}; Mg, 15 µg mL^{-1}; Ca, 50 µg mL^{-1}; Mo, 0.5 ng mL^{-1} (upper); Mo, 0.05 ng mL^{-1} (under). f) The natural river water: (A), Asahi River in Okayama; (B), Zasu River in Okayama, sampled on 3rd March, 2002.

tions of Na, K, Mg and Ca, which are given in Table 2. The leucine-type chitosan could adsorb Mo quantitatively at pH 4, whereas almost all of the alkali and alkaline earth metal ions could be removed by the column pretreatment. In seawater samples, because Mo was contained above LOD of ICP-MS, ICP-AES and GFAAS, so that Mo was determined accurately by these instruments. The analytical results with a column pretreatment were in good agreement with those obtained by the direct measurement of 20-fold diluted samples by ICP-MS, as shown in Table 2.

Table 3 shows the analytical results of Mo in artificial and natural river water samples. In general, the average concentration of Mo in river water samples in Japan is about 0.5 ng mL^{-1}. Such a trace concentration of Mo can be determined directly by ICP-MS without any preconcentration, but it can not be determined directly by ICP-AES or GFAAS, because it is less than the LODs (0.50 ng mL^{-1} and 0.63 ng mL^{-1}). In this work, preconcentration (10 and 100-fold) using a small column packed with leucine-type chitosan was investigated. Artificial river water samples containing 0.5 ng mL^{-1} Mo and relatively high concentrations of Na, Mg, K, and Ca were examined. The results obtained by 4 kinds of measurements were reported: by a direct measurement using ICP-MS, with a pretreatment prior to ICP-MS measurement, and by a method with a 10-fold preconcentration prior to ICP-AES and GFAAS measurement, as shown in Table 3. The 10-fold preconcentration with 100 mL of the sample solution was sufficient for determining Mo in river-water samples, and the analytical values were in good agreement with each other. Next, a higher concentration method was examined for convenient apparatus and precise measurements. Preconcentration was applied to a solution containing 0.05 ng mL^{-1} Mo, which is one tenth of the average of Mo in river water and of the LOD of Mo by ICP-AES and GFAAS. Column preconcentration by 100-fold was carried out, as discussed in the procedure section. The obtained results are given in Table 3. The analytical results obtained by ICP-AES and GFAAS coupled with 100-fold preconcentration were in good agreement with those obtained by ICP-MS by direct measurements. The blank levels with 100-fold preconcentration by ICP-AES and GFAAS were 0.030 ng mL^{-1} and 0.032 ng mL^{-1} and the LODs were 0.007 ng mL^{-1} and 0.009 ng mL^{-1}, respectively. The recovery of Mo with 100-fold preconcentration was almost 100%. The proposed concentration methods were successfully applied to determine Mo in river water samples.

Conclusion

A novel chelating resin, leucine-type chitosan, was developed for the collection/concentration of Mo with a small column. The main advantages of the newly synthesized resin are as follows: (1) Mo can be selectively and quantitatively adsorbed on the resin even at acidic pH, (2) Mo at around the 50 ppt level concentrations can be easily concentrated by 100-fold with a small column (resin volume: 1 mL), (3) a large amount of alkali and alkaline earth elements in seawater can be eliminated only by passing through the resin column, and (4) trace amounts of Mo in seawater and river water can be accurately determined by ICP-MS, ICP-AES, and GFAAS coupled with the column methods.

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