# High-capacity chitosan-based chelating resin for on-line collection of transition and rare-earth metals prior to inductively coupled plasma-atomic emission spectrometry measurement

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## ARTICLE INFO

## ABSTRACT

High-capacity chitosan-based chelating resin, N-(2-hydroxyethyl)glycine-type chitosan, was synthesized using chloromethyloxirane (CMO) as a cross-linker and a coupling arms and hydroxylethylamine and bromoacetic acid as a synthesizer for the N-(2-hydroxyethyl)glycine chelating moiety. The CMO could bind with both of hydroxyl and amino group of the chitosan resin, and then couple with the chelating moiety. Increasing the amounts of chelating moiety could increase the capacity of the resin toward metal ions. Most transition and rare-earth metals could adsorb quantitatively on the resin at wide pH ranges and could be separated from alkaline and alkaline-earth metals. The resin was packed in a mini-column (40 mm length × 2 mm i.d.) which was installed in a Multi-Auto-Pret system. The Multi-Auto-Pret system coupled with ICP-AES was successfully applied to the determination of transition and rare-earth metals in river water samples.

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## 1. Introduction

The preconcentration of metal analytes prior to their measurement is of great interest in and of great importance for inductively coupled plasma-atomic emission spectrometry (ICP-AES). It facilitates not only the separation of target metal ions from large amounts of salts or other sample matrices, but also the improvement of detection limits for analytes by two or more orders of magnitude in certain samples [1–3].

On-line preconcentration using chelating resins have been widely used in the determination of trace metals by ICP-AES. In our previous paper, on-line preconcentration using a Multi-Auto-Pret system was proposed for the rapid determination of trace metals [4]. As a sorbent, a commercially available iminodiacetate resin, Muromac A-1, was employed in the system. Although the resin was used successfully for the preconcentration of trace metals in water samples [4–7], the characteristics of the resin used were less ideal. The less-selective properties of the iminodiacetate resin can lead to the high interferences from the alkaline-earth matrix due to their incomplete separation [8,9]. Further, at pH 6 or higher, the chelate complexes seem to be stronger [5]; it means that a high concentra-

tion of an acid solution must be used to break up the complex and thereby it may desorb the metal ions from the resin.

Ideally, the chelating resin should fulfill several criteria [10]:

1. The resin is selective for target metal ions. Since ICP-AES enables to perform multi-element detection simultaneously, it is desirable to make chelate with metal ions as many as possible. It is preferred that common metal ions such as $Na^+$, $Mg^{2+}$, and $Ca^{2+}$ cannot be taken up.
2. The metal chelates should be stable; that is, the chelates should be strongly adsorbed even when the concentrations of metal ions in the sample are very low. However the more stable the chelates, the more amount of acid was necessary to break up the chelates.
3. The formation rate of metal chelates must be rapid, especially when an on-line method is used.

The choice of chelating group into resins plays an important role in achieving selectivity [11,12]. Usually resins with oxygen and nitrogen as coordinating atoms can adsorb transition and rare-earth metals [13,14]. If the selectivity of resins is determined by the chelating group, other analytical properties of the resins, such as kinetic features, mechanical, chemical strength and regeneration, may depend on a polymer base [11,12]. In this study, chitosan was selected as a polymer base because of its unique combination properties like biodegradability, biocompatibility, and bioactivity,

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**Table 1**
ICP-AES operating conditions.

| System | ICP-AES VISTA - PRO |
|---|---|
| RF generator | Frequency 40 MHz, power 1.1 kW |
| Plasma gas flow | Ar 15.0 L min$^{-1}$ |
| Auxiliary gas flow | Ar 1.50 L min$^{-1}$ |
| Nebulizer gas flow | Ar 0.75 L min$^{-1}$ |
| Spray chamber | Glass cyclonic spray chamber |
| Nebulizer | K-style concentric glass nebulizer |
| Torch | One-piece low flow extended torch in the axial view mode |
| Measurement mode | Time scan mode |

in addition to attractive physical and chemical properties. Partial cross-linking of chitosan by di/polyfunctional reagents should be carried out to enable it to be used for metal complexation in acidic media [15].

Our research focuses on the development of chelating resin using cross-linked chitosan as a base material. As a cross-linker, ethyleneglycoldiglycidylether (EDGE) has been used [13,14,16,17]. When an amino group of the chitosan is protected as the formation of Shiff base with benzaldehyde, EGDE can bind with a hydroxyl group at the 6-position of chitosan. After removing the protection group, the amino group of the cross-linked chitosan can be used for the formation of chelating group, where only one side of chitosan, the amino group, can bind with the chelating group. To increase chelating sites of the resin, EGDE as a cross-linker can be replaced with chloromethyloxirane (CMO) [15,18,19]. The CMO can react with both of amino and hydroxyl group of the chitosan, and thereafter chelating groups can be introduced. Increasing the number of chelating moiety can lead to an increase in the capacity of the resin toward metal ions. In this study, N-(2-hydroxyethyl)glycine-type chitosan that possesses amino, hydroxyl and carboxylate groups was developed using CMO as a cross-linker and a coupling arms. Replacing EGDE for CMO not only increases the chelating moiety, but also can decrease the synthesis process, which may lead to the decrease in the synthesis time and cost.

The resin synthesized was packed in three mini-columns (40 mm length × 2 mm i.d.) and they were installed in a Multi-Auto-Pret system and used for the on-line preconcentration of transition and rare-earth metals coupled with ICP-AES.

## 2. Experimental

### 2.1. Instruments

A Vista-Pro ICP-AES system of Seiko Instruments Co. (Chiba, Japan) was used and the operating conditions were listed in Table 1. The ICP-AES was coupled with a Multi-Auto-Pret system, as shown in Fig. 1. An automatic potentiometric titration system, Model AT-510 of Kyoto Electronics Manufacturing, Co. Ltd. (Kyoto, Japan), was used for the acid base titration of the resin. Infrared spectra (4000–400 cm$^{-1}$) were recorded on a Jasco FT/IR-4100 of Jasco International Co. Ltd. (Tokyo, Japan).

### 2.2. Reagents and solutions

Chitosan used in this work was a flake-type with deacetylated degree 80%, purchased from Tokyo Kasei Co. Ltd. (Tokyo, Japan). All other reagents used for the synthesis of the chelating resin were of analytical reagent grade.

A multi-element stock standard solution (57 elements, 1 μg mL$^{-1}$) was prepared by diluting analytical multi-element standard solutions, XSTC-13 (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), XSTC-1 (Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Sc, Tb, Tm, Yb, and Y), purchased from Spex CertiPrep Inc. (Metuchen, NJ, USA), and standard solutions for a single element for AAS (W, Ge, Zr, Pd, Sn, Sb, Te, Hf, Pt, and Au) from Wako Pure Chemicals Industries Ltd. (Osaka, Japan) in 0.01 M of a nitric acid solution. Working standard solutions were prepared daily by diluting the stock standard solution with nitric acid. All dilution procedures were performed by a weight method.

Nitric acid for the analysis of poisonous metals with 60–62%, density 1.38 g mL$^{-1}$ from Wako Pure Chemicals Industries Ltd. was used and diluted with an ultra-pure water to give a 0.01, or a 1.5 M solution.

A stock solution of 4 M ammonium acetate buffer solution was prepared by mixing appropriate amounts of concentrated acetic acid and a concentrated ammonia solution, and diluted with ultra-pure water. Both solutions were of electronic industrial reagent grade from Kanto Chemical Co. Inc. (Tokyo, Japan). Buffer solutions of 0.2 and 0.5 M ammonium acetate were prepared by diluting the stock buffer solution and adjusting to pH 3–9 with small amounts of concentrated ammonia or acetic acid.
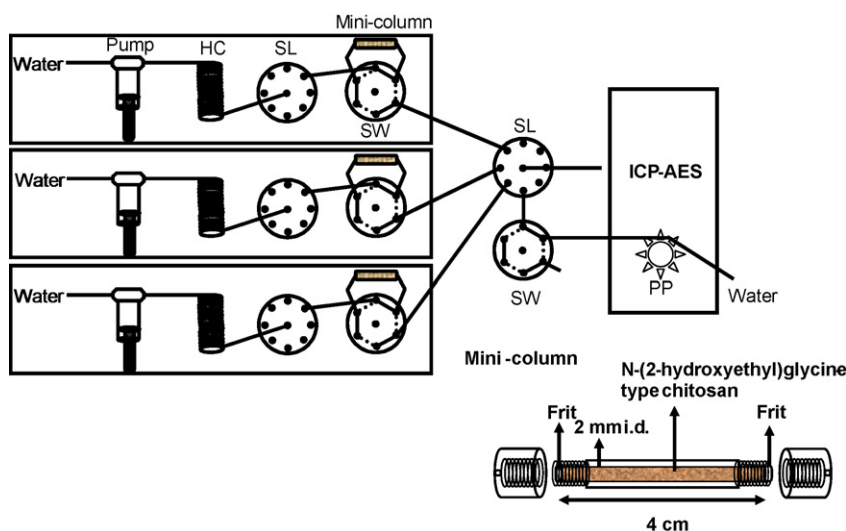


**Fig. 1.** Multi-Auto-Pret AES system. Pump, 10 mL syringe pump; HC, holding coil; SV, 8-port selection valve; SW, 6-port switching valve; PP, peristaltic pump equipped to ICP-AES system.
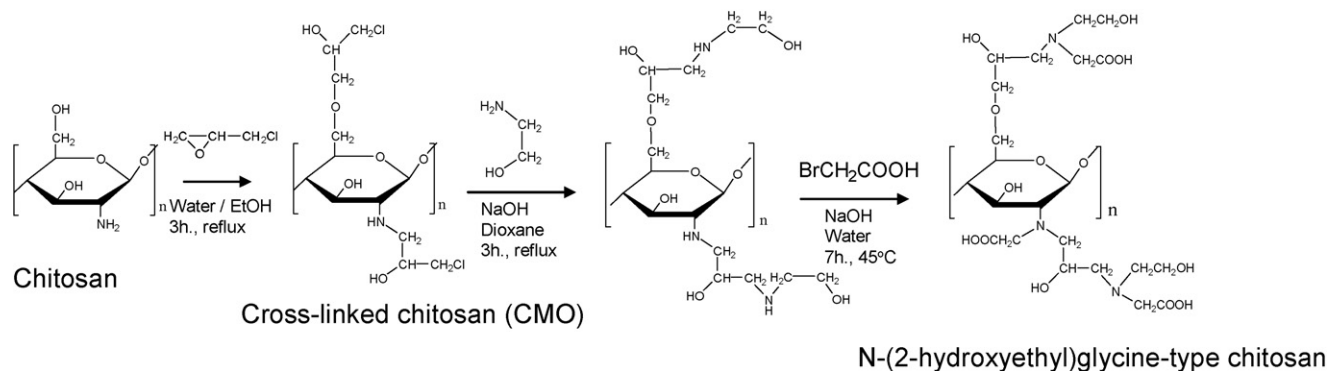
**Fig. 2.** Synthesis scheme of N-(2-hydroxyethyl)glycine-type chitosan resin.

The ultra-pure water (18.3 MΩ cm$^{-1}$ resistivity) was prepared by an Elix-3/Milli-Q element system, Nihon Millipore (Tokyo, Japan).

All of the sample solutions were acidified to pH 2 by adding nitric acid and filtered through 0.45 μm membrane filter made of mixed cellulose ester, Toyo Roshi Kaisha Ltd. (Tokyo, Japan) before storing. The pH of the sample solutions was adjusted to 5 just before the column pretreatment by adding small amounts of ammonia solution.

An SLRS-4 water reference material for trace metals was purchased from Institute for National Measurement Standards, National Research Council of Canada (Ontario, Canada).

### 2.3. Procedure

#### 2.3.1. Procedure for synthesis of N-(2-hydroxyethyl)glycine-type chitosan resin

The N-(2-hydroxyethyl)glycine-type chitosan resin was synthesized in two steps, as shown in Fig. 2.

Step 1:　synthesis of 2-aminoethanol-type chitosan.

Three grams of chitosan was suspended in 60 mL of a mixture of water–ethanol (1:1), and then 10 g of CMO was added to the suspension. The mixture was refluxed for 3 h, and then cooled. The solid product (cross-linked chitosan) was filtered with a filter paper and washed each three times with ethanol and water to remove the remained CMO. The solid product was suspended in 100 mL 2-aminoethanol, and to this 40 mL of 1 M sodium hydroxide was added. The suspension was refluxed for 3 h, and then cooled. The product was filtered with a filter paper, and washed each three times with ethanol and water.

Step 2:　synthesis of N-(2-hydroxyethyl)glycine-type chitosan.

The N-(2-hydroxyethyl)glycine-type chitosan resin was synthesized by modifying 2-aminoethanol-type chitosan with bromoacetic acid as follows. Bromoacetic acid, 3.9 g was dissolved in 16 mL of ice-cold water. To this solution, under cooling in an ice-water bath, was added 2.5 M NaOH until the pH reached 12. The 2-aminoethanol-type chitosan resin was suspended in 20 mL of water and mixed with a solution of bromoacetic acid, and then warmed to 40–45 °C in a water bath. The pH was kept at 12 for 6–7 h by adding a small amount of 2.5 M NaOH. The solid product (N-(2-hydroxyethyl)glycine-type chitosan resin) was filtered with a filter paper and washed each three times with ethanol and water. Through this reaction, carboxymethyl groups from bromoacetic acid could bind with the amino groups [20] of the 2-aminoethanol-type chitosan.

**Table 2**
Procedure for the preconcentration with Multi-Auto-Pret system.

| Step | Operation description | Pump | SV[a] | SW[b] | Flow rate (μL s$^{-1}$) | Volume (μL) | Action of flow | Time required (s) |
|---|---|---|---|---|---|---|---|---|
| 1 | Resin shaking ultra-pure water | IN | | 1 | 300 | 100 | Aspirate | 0.3 |
| | | OUT | 5 | 1 | 40 | 100 | Dispense | 2.5 |
| | | OUT | 5 | 1 | 40 | 100 | Aspirate | 2.5 |
| | | OUT | 5 | 1 | 40 | 100 | Dispense | 2.5 |
| | | OUT | 5 | 1 | 40 | 100 | Aspirate | 2.5 |
| | | OUT | 5 | 1 | 40 | 100 | Dispense | 2.5 |
| 2 | Conditioning 0.5 M buffer | OUT | 1 | 1 | 100 | 500 | Aspirate | 5 |
| | | OUT | 5 | 1 | 40 | 500 | Dispense | 12.5 |
| 3 | Sample loading sample | OUT | 6 | 1 | 100 | 5000 | Aspirate | 50 |
| | | OUT | 5 | 1 | 40 | 5000 | Dispense | 125 |
| 4 | Matrix removing ultra-pure water 0.2 M buffer | IN | | 1 | 300 | 500 | Aspirate | 1.7 |
| | | OUT | 2 | 1 | 100 | 500 | Aspirate | 5 |
| | | OUT | 5 | 1 | 40 | 1000 | Dispense | 25 |
| 5 | Eluting and cleaning ultra-pure water 1.5 M HNO$_3$ | IN | | 1 | 300 | 2000 | Aspirate | 6.7 |
| | | OUT | 3 | 1 | 100 | 1000 | Aspirate | 10 |
| | | OUT | 5 | 2 | 40 | 3000 | Dispense | 75 |
| | Pump/SV/SW moving | | | | | | | 51 |
| | TOTAL TIME | | | | | | | 379.7 s = 6.3 min |

[a] SV: port of selection valve.
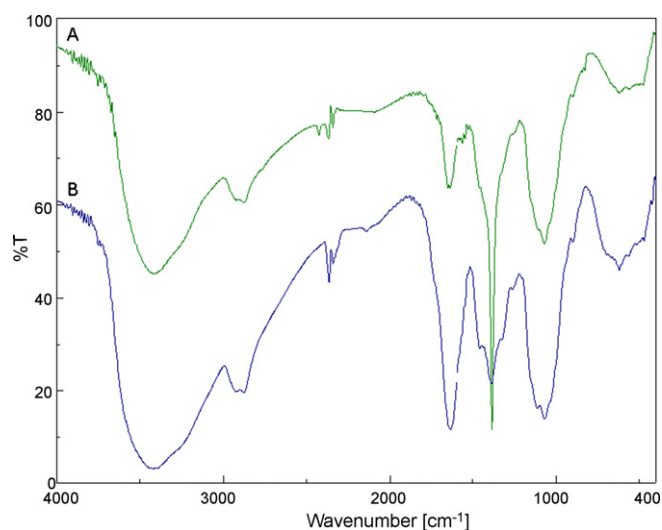[b] SW: port of switching valve.

**Fig. 3.** FTIR spectra of N-(2-hydroxyethyl)glycine-type chitosan resin: (A) aminoethanol-type chitosan; (B) N-(2-hydroxyethyl)glycine-type chitosan.

For the comparison, N-(2-hydroxyethyl)glycine-type chitosan resin in which EGDE was used as a cross-linker was also synthesized. The cross-linking procedures with EGDE used in this synthesis were described in our previous works [13,14,16,17].

### 2.3.2. Collection and concentration of trace metals using Multi-Auto-Pret AES system

The procedures for the collection/concentration of trace metals using the Multi-Auto-Pret AES system was done in four steps, and an additional step for resin shaking was inserted before the preconcentration procedure, as shown in Table 2. The resin-shaking step (Step 1) was applied to restore the resin packed in the column before next cycle, in order to avoid a high pressure that might be happened in the resin packed in the columns.

The preconcentration procedure was carried out as follows. The mini columns (2.0 mm i.d. × 40 mm) were filled with the synthesized chitosan resin. At the loading stage (switching valve, SW, at the position 1), 0.5 mL of 0.5 M ammonium acetate buffer solutions (pH 5) was passed through the column for conditioning (Step 2). After the pretreatment of the column, 5 mL of sample solutions at pH 5 was passed through the column (Step 3), followed by passing 0.5 mL of 0.2 M ammonium acetate buffer solutions (pH 5) and 0.5 mL ultra-pure water for eliminating sample matrix (Step 4). The switching valve was moved to the position 2 for the eluting stage, then 1 mL of 1.5 M nitric acid was passed through the column for eluting metals adsorbed on the resin, followed by passing 2 mL ultra-pure water for cleaning the resin for the next cycle (Step 5). At this stage (Step 5), all of the solutions were flowed to the ICP-AES.

The time required for the whole procedures was 6.3 min for 5 mL samples and 15 min for 20 mL samples. As the Multi-Auto-Pret AES system consisted of three sets of the single Auto-Pret system, the sample throughput was 27 and 11 h$^{-1}$ for 5 and 20 mL samples, respectively.

## 3. Results and discussion

### 3.1. Characteristics of N-(2-hydroxyethyl)glycine-type chitosan resin

Infrared spectra (4000–400 cm$^{-1}$) were recorded (Fig. 3). Some new bands at 1300 and 1400 cm$^{-1}$ were appeared when car-
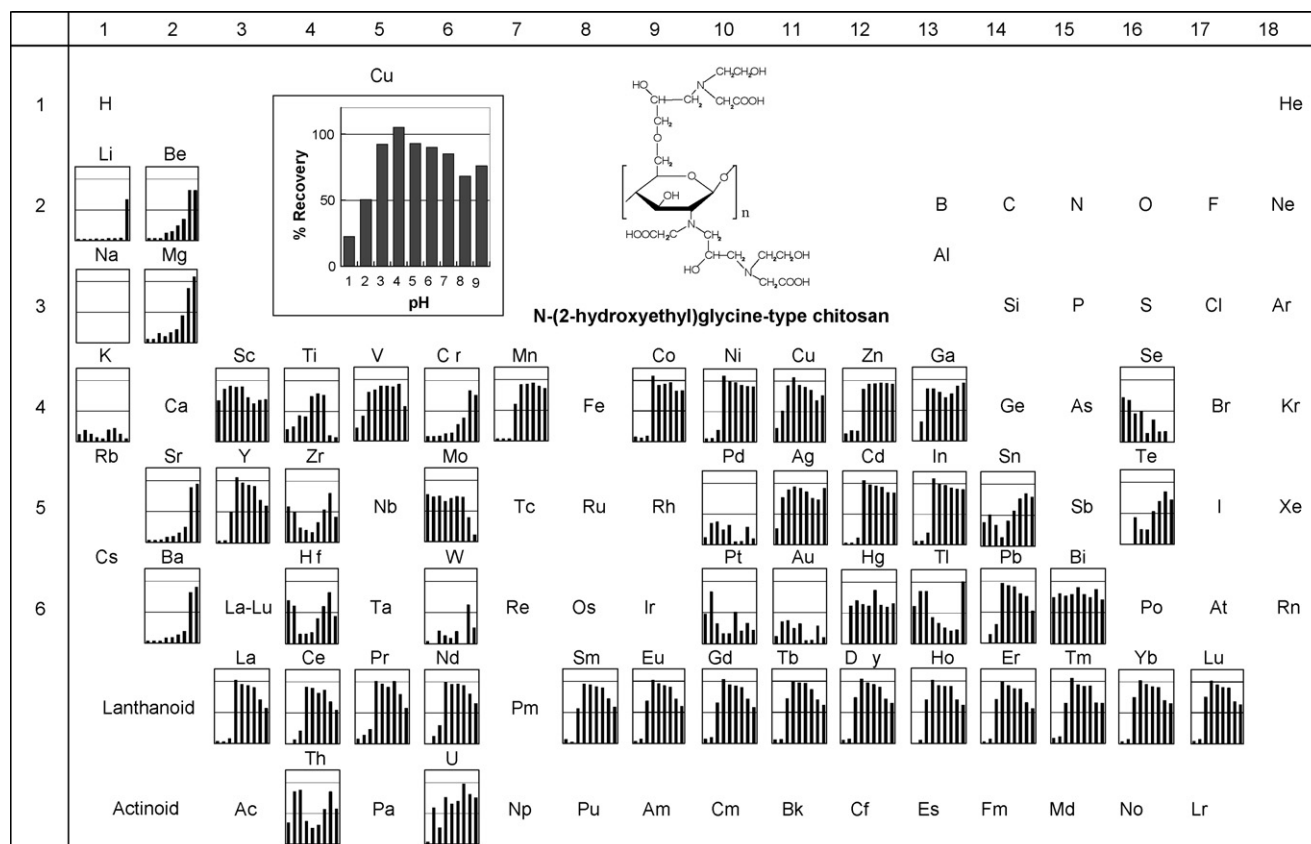


**Fig. 4.** Adsorption behavior of N-(2-hydroxyethyl)glycine-type chitosan for metals at various pH values. Sample volume, 3 mL; concentration of each metal, 20 ng mL$^{-1}$; eluent, 3 mL of 1.5 M nitric acid.
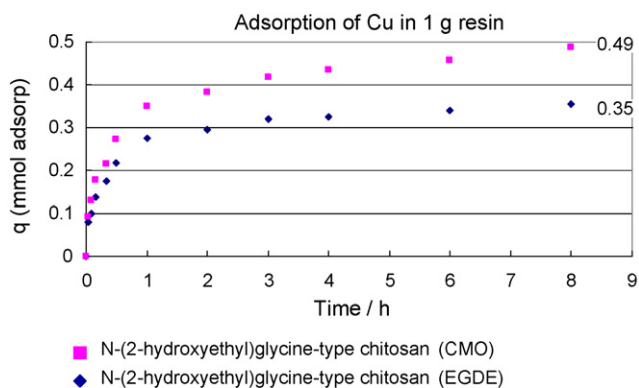
**Fig. 5.** Adsorption capacity of N-(2-hydroxyethyl)glycine-type resin for Cu(II). Resin volume, 1 mL; concentration of Cu, 0.002 M; $Cu^{2+}$ solution, 100 mL.

boxymethyl group connected to the 2-aminoethanol-type chitosan resin. The band at $1300\,cm^{-1}$ confirms the C–O stretch of carboxylic acid, while the band at $1400\,cm^{-1}$ confirms the zwitter ions of carboxylic acid [21]. Some bands between 1500 and $1600\,cm^{-1}$, which confirm a scissoring primary amine of the 2-aminoethanol-type chitosan (Fig. 3A), were disappeared in the spectrum of the N-(2-hydroxyethyl)glycine-type chitosan (Fig. 3B), which means that almost all of the free amino groups were converted to N,N-dicarboxymethyl amino groups.

### 3.2. Potentiometric titration of N-(2-hydroxyethyl)glycine-type chitosan resin

For the potentiometric titration, one milliliter of N-(2-hydroxyethyl)glycine-type chitosan resin was soaked in 2 M nitric acid and stirred with a low speed for 2 h to protonate the resin, filtered and washed with ultra-pure water until pH of the efflu-

ent was almost the same as pH of ultra-pure water. Then the resin in 20 mL ultra-pure water was titrated with 0.065 M NaOH. There are two end points in the titration graph. The $pK_a$ of the resin was determined to be 3.7 ($pK_1$) and 9.7 ($pK_2$), respectively. The $pK_1$ corresponds to carboxyl groups of the N-(2-hydroxyethyl)glycine-type chitosan, while the $pK_2$ corresponds to the amino groups of the resin. The $pK_a$ of ethanol is about 16; therefore, it could not be neutralized with NaOH in this titration. For comparison, glycine has $pK_1 = 2.3$, $pK_2 = 9.6$ and tricine has $pK_1 = 2.3$, $pK_2 = 8.2$ [22]

#### 3.2.1. Adsorption behavior of metal ions on the N-(2-hydroxyethyl)glycine-type chitosan resin

The adsorption behavior of 57 elements on the N-(2-hydroxyethyl)glycine-type chitosan at various pH values was investigated by an off-line method using the Multi-Auto-Pret system, and measured by ICP-AES. As shown in Fig. 4, most of the transition and rare-earth metals could be collected on the resin quantitatively from pH 4 to 7, and recovered by more than 95% with 3 mL of 1.5 M nitric acid. The resin did not adsorb both alkali and alkaline-earth metals in acidic media (pH <7). Therefore, the resin could be used favorably for the collection/concentration of transition and rare-earth metals.

#### 3.2.2. Adsorption capacity of N-(2-hydroxyethyl)glycine-type chitosan resin

Though a number of metals can adsorb on the proposed resin, Cu(II) was selected for examining the adsorption capacity of the N-(2-hydroxyethyl)glycine-type chitosan resin. The adsorption capacity of the resin was examined by a batch-wise method. One milliliter of the resin (equal to 0.27 g) was equilibrated in 100 mL of 0.002 M Cu(II) ion at pH 5. The adsorption capacity of Cu(II) on the resin was 0.13 mmol $mL^{-1}$ of the resin or 0.49 mmol $g^{-1}$ of the resin, and the $t_{1/2}$, of Cu(II) adsorbed is less than 15 min, as shown in Fig. 5, where as the capacity of cross-linked with EGDE was

**Table 3**
Wavelengths, slope ratio, enrichment factors and detection limits.

| Elements | Wavelength (nm)[a] | Slope ratio, artificial river water/$HNO_3$[b] | Enrichment factor[c] | LOD (ng $mL^{-1}$) | |
|---|---|---|---|---|---|
| | | | | This work[d] | Direct ICP-AES[e] |
| Cd | 226.502 | 1.0537 | 106[f] | 0.004[f] | 0.3 |
| Co | 228.615 | 1.0157 | 87[f] | 0.023[f] | 0.8 |
| Cu | 324.754 | 1.0420 | 32 | 0.068 | 0.3 |
| Mn | 257.610 | 0.9088 | 14 | 0.018 | 0.7 |
| Ni | 231.604 | 0.9996 | 16 | 0.13 | 0.9 |
| Pb | 220.353 | 1.0914 | 102[f] | 0.085[f] | 3.7 |
| Sc | 361.383 | 1.0095 | 25 | 0.008 | 0.3 |
| V | 292.401 | 0.9446 | 18 | 0.17 | 0.8 |
| Zn | 213.856 | 1.0902 | 21 | 0.05 | 1.2 |
| Y | 371.029 | 0.9953 | 21 | 0.020 | 0.2 |
| Ce | 418.659 | 1.0452 | 102 | 0.12[f] | 1.8 |
| Dy | 353.171 | 0.9473 | 85 | 0.020[f] | 0.3 |
| Er | 337.275 | 0.9789 | 89 | 0.010[f] | 0.5 |
| Eu | 381.967 | 0.9573 | 83 | 0.010[f] | 0.3 |
| Gd | 342.246 | 1.1080 | 86 | 0.028[f] | 0.4 |
| Ho | 345.600 | 0.9229 | 85 | 0.01[f] | 0.5 |
| La | 408.671 | 0.9836 | 83 | 0.019[f] | 0.3 |
| Lu | 261.541 | 0.9727 | 92 | 0.002[f] | 0.08 |
| Nd | 401.224 | 0.9130 | 94 | 0.25[f] | 2.4 |
| Pr | 390.843 | 0.9804 | 100 | 0.025[f] | 1.2 |
| Sm | 359.259 | 0.9328 | 88 | 0.029[f] | 1.6 |
| Tb | 350.914 | 1.0167 | 87 | 0.054[f] | 0.6 |
| Tm | 346.220 | 0.9498 | 88 | 0.047[f] | 0.6 |
| Yb | 328.937 | 0.9762 | 90 | 0.002[f] | 0.07 |

[a] Emission wavelengths were selected to give the best intensity without any interferences [19,21].
[b] Comparison of slopes of the calibration graph of trace metals in artificial river water and that in standard samples.
[c] Enrichment factor, the ratio of peak height obtained by proposed system and that by conventional nebulization of ICP-AES.
[d] Limit of detection, corresponding to 3 (S/N).
[e] Limit of detection of instrument, corresponding to 3 S.D. (standard deviation) of blank solution ($n = 10$) which was measured by the conventional nebulization of ICP-AES.
[f] Sample volume was 20 mL for Cd, Co and Pb, while for other elements was 5 mL.

0.35 mmol g$^{-1}$; that is the adsorption capacity of the resin cross-linked with CMO was increased to about 40% per g resin compared with that of with EGDE.

### 3.2.3. Optimization of the experimental parameters of Auto-Pret AES procedures

The experimental parameters of Auto-Pret system, such as a sample pH, a sample loading flow rate, an eluent flow rate, and an eluent concentration, should be optimized in order to obtain the suitable result. The Auto-Pret parameters were optimized using a 5 mL standard solution containing 1 ng mL$^{-1}$ of metal ions.

As was described earlier, the resin can adsorb most of the transition and rare-earth metals quantitatively from pH 4 to 7. When the Multi-Auto-Pret system was used for on-line measurement, pH 5 of the sample solutions gave the highest peak intensity for all of the metal ions examined. Therefore, pH 5 was selected for the next investigations.

The sample loading flow rate was studied by varying from 10 to 50 µL s$^{-1}$, when the eluent flow rate of 35 µL s$^{-1}$ was used to optimize the sample loading flow rate. There was no significant difference in the signal intensity, therefore a faster flow rate was preferred to decrease the measuring time and to increase sample throughput. However, to avoid probable high pressure in the mini-column, a sample loading flow rate of 40 µL s$^{-1}$ was adopted.

The eluent flow rate was examined by varying from 10 to 50 µL s$^{-1}$ when the sample loading flow rate was kept constant at 40 µL s$^{-1}$. The increase in the eluent flow rate up to 25 µL s$^{-1}$ increased the signal peak intensity for all of the metal ions examined. The signal intensity of the peak became constant between 25 and 40 µL s$^{-1}$ of the eluent flow rate and at the then decreased after 40 µL s$^{-1}$. Therefore, a 35 µL s$^{-1}$ of the eluent flow rate was selected.

As an eluent, nitric acid used; its concentrations were examined by varying from 0.5 to 3.0 M. The sample loading flow rate of 40 µL s$^{-1}$ and the eluent flow rate of 35 µL s$^{-1}$ were used to investigate the eluent concentration. The increase in the nitric acid concentration from 0.5 to 1.5 M can lead to an increase in the peak height intensity. The intensity became identical at the concentrations higher than 1.5 M. Lower concentrations of nitric acid was preferable to decrease the amount used and wasted, and therefore, 1.5 M of nitric acid was adopted as an eluent.From the analytical signal of metal ions, it could be calculated that 0.72 mL of 1.5 M HNO$_3$ was enough to elute metal ions from the resin. Therefore, for completing the recovery of the elements and cleaning the resin for the next cycle, 1 mL of 1.5 M HNO$_3$ was used.

### 3.2.4. Effect of river water matrix on the determination of trace metals

The effect of river water matrix was studied using artificial river water containing alkali and alkaline-earth metal salts that usually present in the river water. The slopes of calibration graphs of trace metal ions in artificial river water were compared with those in standard samples. As shown in Table 3, both calibration graphs for metal ions were in good agreement with one another (slope ratio was about 1). It means that the river water matrix did not interfere with the collection of trace metals on the column containing the N-(2-hydroxyethyl)glycine-type chitosan resin.

### 3.2.5. Enrichment factors and detection limits

The enrichment factors (EFs) and the limits of detection (LoD) of metal ions at their wavelengths obtained by the Multi-Auto-Pret AES system are shown in Table 3. The emission wavelengths were selected to give the highest intensity without any interferences [21,23].

The enrichment factors were estimated by comparing a peak height obtained when 2 ng mL$^{-1}$ standards was pretreated using Multi-Auto-Pret system with that of 20 ng mL$^{-1}$ standard measured by a conventional nebulization method by ICP-AES. The enrichment factors of the trace metals were in the range of 14 (Mn) to 32 (Cu), when 5 mL of the sample solution was used, and the enrichment factors until 106-fold could be obtained for Cd when 20 mL of sample solution was used.

**Table 4**
Analytical results of trace metals in SLRS-4[a] (ng mL$^{-1}$).

| Elements | This study | Certified | Ref. [1][b] | Ref. [2][c] |
|---|---|---|---|---|
| Cd | 0.014 ± 0.003[d] | 0.012 ± 0.002 | | |
| Co | 0.039 ± 0.008[d] | 0.033 ± 0.006 | | |
| Cu | 1.85 ± 0.01 | 1.81 ± 0.08 | | |
| Mn | 3.25 ± 0.25 | 3.37 ± 0.18 | | |
| Ni | 0.66 ± 0.10 | 0.67 ± 0.08 | | |
| Pb | 0.082 ± 0.002[d] | 0.086 ± 0.007 | | |
| Sc | (0.025 ± 0.001)[e] | – | | |
| V | 0.30 ± 0.05 | 0.32 ± 0.03 | | |
| Zn | 0.88 ± 0.06 | 0.93 ± 0.10 | | |
| Y | (0.13 ± 0.02)[d,e] | | 0.15 ± 0.01 | 0.14 ± 0.01 |
| Ce | (0.33 ± 0.04)[d,e] | | 0.36 ± 0.01 | 0.38 ± 0.01 |
| Dy | (0.023 ± 0.003)[d,e] | | 0.024 ± 0.002 | 0.024 ± 0.001 |
| Er | (0.015 ± 0.004)[d,e] | | 0.013 ± 0.001 | 0.014 ± 0.001 |
| Eu | < 0.010[d] | | 0.0080 ± 0.0006 | 0.0081 ± 0.0006 |
| Gd | (0.030 ± 0.003)[d,e] | | 0.034 ± 0.002 | 0.035 ± 0.001 |
| Ho | < 0.010[d] | | 0.0047 ± 0.0003 | 0.0049 ± 0.0001 |
| La | (0.29 ± 0.03)[d,e] | | 0.29 ± 0.01 | 0.30 ± 0.01 |
| Lu | (0.003 ± 0.001)[d,e] | | 0.0019 ± 0.0001 | 0.0019 ± 0.0001 |
| Nd | (0.30 ± 0.04)[d,e] | | 0.27 ± 0.01 | 0.28 ± 0.01 |
| Pr | (0.070 ± 0.008)[d,e] | | 0.069 ± 0.002 | 0.074 ± 0.001 |
| Sm | (0.054 ± 0.003)[d,e] | | 0.057 ± 0.003 | 0.059 ± 0.001 |
| Tb | <0.054 | | 0.0043 ± 0.0004 | 0.0045 ± 0.0002 |
| Tm | <0.047 | | 0.0017 ± 0.0002 | 0.0019 ± 0.0001 |
| Yb | (0.010 ± 0.001)[d,e] | | 0.012 ± 0.000 | 0.012 ± 0.001 |

[a] River water reference material for trace metals issued by National Research Council Canada.
[b] Cited from Yeghicheyan et al. [24].
[c] Cited from Lawrence et al. [25].
[d] Sample volume was 20 mL.
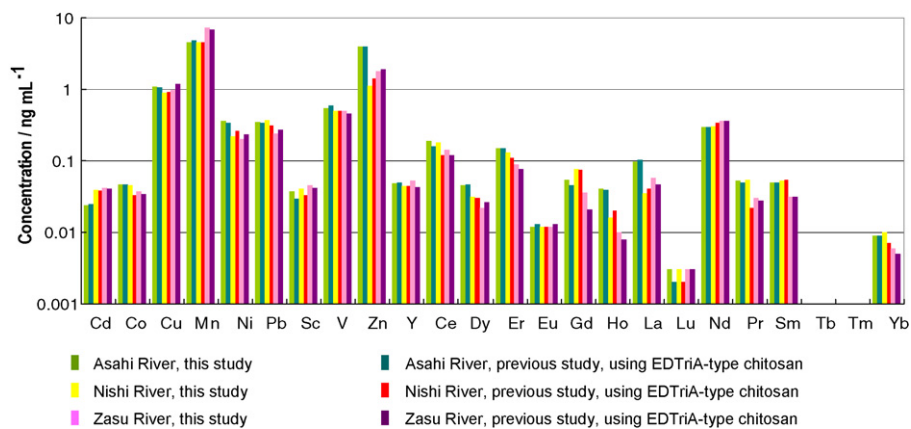[e] Figures in parentheses were information values.

**Fig. 6.** Application to river water samples.

The LoDs obtained in this work were determined as the concentrations corresponding to three-times the signal-to-noise ratio of the background. The LoDs of ICP-AES instrument were determined as the concentrations corresponding to three times the standard deviation of the blank solution (for 10 measurement replicates) which were measured by the conventional nebulization of ICP-AES. From the obtained results, the proposed method with only 5 mL of sample solution was found to be sensitive enough for determining most of the transition metals in river water samples, while 20 mL of a sample solution was found to be necessary for determining the rare-earth metals. Such LoDs were almost comparable to those obtained by an inductively coupled plasma-mass spectrometry (ICP-MS) [14].

Without any preconcentration step, only Cu and Mn in river water samples could be determined directly, while other metal ions could not be determined because their concentrations were much lower than their detection limits.

### 3.2.6. Accuracy of the proposed method

The river water standard reference material for trace metals, SLRS-4, issued by the National Research Council of Canada (Ottawa, Ontario, Canada) was used to evaluate the accuracy of the proposed method using the synthesized resin. The sample pH was adjusted to 5, and was used in the similar manner as in the standard solution.

Since there are no certified values for rare-earth metals, the results obtained in this work were compared with the reference values reported by Yeghicheyan et al. [24] and Lawrence et al. [25]. As shown in Table 4, the results obtained in this work were in good agreement with the certified and the reference values, except for Tb and Tm, which could not be measured because results were lower than their LoDs. This result indicates that the present method has a good accuracy and is applicable to the multi-element preconcentration and determination of transition and rare-earth metals in river water samples.

### 3.2.7. Application to real samples

The proposed method was successfully applied to the determination of trace metals in river water samples of Asahi River, Nishi River, and Zasu River, sampled in Okayama City. The result was also compared to that obtained in the previous study that using EDTriA-type chitosan resin [26]. As shown in Fig. 6, the transition and rare-earth metals can be determined simultaneously and the result was comparable to that obtained in the previous study [26], except for Tb and Tm, which could not be measured because the results were lower than their LoDs.

## 4. Conclusion

The N-(2-hydroxyethyl)glycine-type chitosan resin was synthesized for the first time and was used for the multi-element collection/concentration of trace metal ions. The resin can fulfill the chelating resin criteria: (1) at pH 5 the transition and rare-earth metal ions can be collected quantitatively and separated from alkali and alkaline-earth metals, (2) the resin can be used for the collection of low concentrations of metal ions in the sample, and the metals adsorbed on the resin can be easily eluted with 1.5 M nitric acid solution, (3) the formation rate of metal chelates is rapid, with $t_{1/2}$ is less than 15 min.

The Multi-Auto-Pret AES system with the synthesized resin was successfully applied to the on-line determination of the transition and rare-earth metals in river water samples: sample throughput was 27 and 11 h$^{-1}$ for 5 and 20 mL samples, respectively.

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## References

[1] Y.A. Zolotov, N.M. Kuzmin, Preconcentration of Trace Elements, Elsevier Science Publisher B.V., The Netherlands, 1990, pp. 211–222.
[2] J.M. Mermet, J. Anal. Atom. Spectrom. 20 (2005) 11.
[3] S.J. Hill, Inductively Coupled Plasma Spectrometry and Its Applications, Sheffield Academic Press Ltd., England, 1999, pp. 23–25.
[4] R.K. Katarina, L. Hakim, M. Oshima, S. Motomizu, J. Flow Injection Anal. 25 (2008) 166.
[5] R.K. Katarina, N. Lenghor, S. Motomizu, Anal. Sci. 23 (2007) 343.
[6] T. Sumida, T. Nakazato, H. Tao, M. Oshima, S. Motomizu, Anal. Sci. 22 (2006) 1163.
[7] E. Vassileva, N. Furuta, Spectrochim. Acta B 58 (2003) 1541.
[8] S.N. Willie, R.E. Sturgeon, Spectrochim. Acta B 56 (2003) 1707.
[9] S.N. Willie, J.W.H. Lam, L. Yang, G. Tao, Anal. Chim. Acta 447 (2001) 143.
[10] J.S. Fritz, Analytical Solid-Phase Extraction, Wiley-VCH, USA, 1999, pp. 140–160.
[11] D. Bilba, D. Bejan, L. Tofan, Croat. Chem. Acta 71 (1998) 155.
[12] V. Camel, Spectrochim. Acta B 58 (2003) 1177.
[13] Y. Gao, K. Oshita, K.H. Lee, M. Oshima, S. Motomizu, Analyst 127 (2002) 1713.
[14] R.K. Katarina, T. Takayanagi, K. Oshita, M. Oshima, S. Motomizu, Anal. Sci. 24 (2008) 1537.
[15] A.J. Varma, S.V. Despande, J.F. Kennedy, Carbohydr. Polym. 55 (2004) 77.
[16] K. Oshita, Y. Gao, M. Oshima, S. Motomizu, Anal. Sci. 17 (Supplement) (2001) a317.
[17] R.K. Katarina, T. Takayanagi, M. Oshima, S. Motomizu, Anal. Chim. Acta 558 (2006) 246.
[18] K. Ohga, Y. Kurauchi, H. Yanase, Bull. Chem. Soc. Jpn. 60 (1987) 444.
[19] Y. Baba, H. Hirakawa, Y. Kawano, Chem. Lett. 23 (1994) 117.
[20] G.A. Zachariadis, D.C. Kapsimali, J. Pharmaceut. Biomed. 41 (2006) 1212.

[21] T.J. Bruno, P.D.P. Svoronos, CRC Handbook of Basic Tables for Chemical Analysis, CRC Press Inc., United States, 1989, pp. 284–295, 374–377.

[22] R.M. Smith, A.E. Martell, Critical Stability Constant, Vol. 6: Second Supplement, Plenum Press, New York, NY, USA, 1989, p. 1, 502.

[23] EPA Method 200.7 - Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma-Atomic Emission Spectrometry, U.S. Environmental Protection Agency Office of Science and Technology, Washington, 2001.

[24] D. Yeghicheyan, J. Carignan, M. Valladon, M.B.L. Coz, F.L. Cornec, M.C. Rouelle, M. Robert, L. Aquilina, E. Aubry, C. Churlaud, A. Dia, S. Deberdt, B. Dupre, R. Freydier, G. Gruau, O. Henin, A.M.D. Kersabiec, J. Mace, L. Marin, N. Morin, P. Petitjean, E. Serrat, Geostandard Newslett. 25 (2001) 465.

[25] M.G. Lawrence, A. Greig, K.D. Collerson, B.S. Kamber, Appl. Geochem. 21 (2006) 839.

[26] R.K. Katarina, M. Oshima, S. Motomizu, Talanta 78 (2009) 1043–1050.