

## DOWN SIZED CHELATING RESIN-PACKED MINICOLUMN PRECONCENTRATION FOR MULTIELEMENT DETERMINATION OF TRACE METALS BY ICP-MS

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### Abstract

Chelating resin-packed minicolumn preconcentration was used for multielement determination of trace metals in seawater by inductively coupled plasma mass spectrometry (ICP-MS). The chelating resin-packed minicolumn was constructed with two syringe filters (DISMIC 13HP and Millex-LH) and an iminodiacetate chelating resin (Chelex 100, 200-400 mesh), with which trace metals in 50 mL of original seawater sample were concentrated into 0.50 mL of 2 M nitric acid, and then 100-fold preconcentration of trace metals was achieved. Then, 0.50 mL analysis solution was subjected to the multielement determination by ICP-MS equipped with a MicroMist nebulizer for micro-sampling introduction. The preconcentration and elution parameters such as the sample-loading flow rate, the amount of 1 M ammonium acetate for elimination of matrix elements and the amount of 2 M nitric acid for eluting trace metals was optimized to obtain good recoveries and analytical detection limits for trace metals. The analytical results for V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U in three kinds of seawater certified reference materials (CRMs; CASS-3, NASS-4, and NASS-5) agreed well with their certified values. The observed values of rare earth elements (REEs) in the above seawater CRMs were also consistent with the reference values. Therefore, the compiled reference values for the concentrations of REEs in CASS-3, NASS-4, and NASS-5 were proposed based on the observed values and reference data for REEs in these CRMs.

*Keywords: chelating resin-packed minicolumn, ICP-MS, micro-sampling introduction, seawater certified reference material, trace metals*

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### 1. Introduction

At the present, inductively coupled plasma mass spectrometry (ICP-MS) has become one of the most powerful analytical techniques for trace element analysis with high sensitivity as well as with wide linear dynamic range and simultaneous multielement detection capability [1,2]. However, weak tolerance to dissolved salts and polyatomic interferences is the principal disadvantage of ICP-MS, and makes it difficult to perform direct injection analysis of seawater containing *ca.* 3% of dissolved salts. Furthermore, the concentrations of most trace metals in seawater are extremely low at  $\text{pg mL}^{-1}$  levels [1]. In order to overcome these difficulties, various methods such as solvent extraction [3,4], coprecipitation [5-8], and chelating resin adsorption [9-21] have been developed for preconcentration of trace metals in seawater. Among them, the chelating resin adsorption technique is the most promising approach because of no use of harmful organic solvent and low risk of contamination.

Recently, the present authors have reported a chelating resin minicolumn for preconcentration of trace metals in seawater [22], where trace metals in 50 mL of original seawater sample were concentrated into 2.5 mL of 2 M nitric acid (final solution). It has been proved that the minicolumn is a convenient preconcentration device for trace metals in seawater as well as in mineral waters prior to the determination by the ICP-MS instrument equipped with a conventional concentric nebulizer [22,23].

A MicroMist nebulizer is now commercially available as a micro-sampling device, which can be operated efficiently at very low solution uptake rates (down to  $\text{sub-mL min}^{-1}$ ) [24]. Then, the simultaneous multielement determination may be performed using only 0.1-0.2 mL of sample solution with the MicroMist nebulizer. Thus, the combined system of ICP-MS with a MicroMist nebulizer is expected to be a next generation analytical method for the multielement determination of trace metals in seawater, if a proper preconcentration technique is established.

In the present paper, hence, a downsized syringe-driven chelating resin-packed minicolumn was developed to obtain the large preconcentration factors for trace metals in seawater, *i.e.* from 50 mL of original seawater to 0.5 mL of analysis solution. Then, the experimental parameters were optimized for the multielement determination by micro-sampling ICP-MS. The present analytical method was validated by analyzing seawater certified reference materials (CRMs; CASS-3, NASS-4, and NASS-5) issued by the National Research Council of Canada (NRCC).

## 2. Experiment

**Instrumentation.** An ICP-MS instrument (Agilent HP 4500, Yokogawa, Tokyo, Japan) was used for the multielement determination of trace metals in seawater, which was equipped with a MicroMist nebulizer (AR35-1-FM01E, Glass Expansion Pty Ltd, West Melbourne, Australia). This micro-sampling ICP-MS system allowed us to determine 40 trace metals with less than 0.5 mL of analysis solution. The operating conditions for micro-sampling ICP-MS are summarized in Table 1, all of which were optimized for each instrumental parameter. For comparison, the operating conditions for conventional ICP-MS with a concentric nebulizer (Conikal, AR35-1-FC1E, Glass Expansion Pty Ltd) are also given in Table 1. A syringe pump (KDS200, KD Scientific, MA, USA), which could flow the solution at the adjustable flow rate automatically, was used for *on-line* monitoring of the signal profiles for trace metals and matrix elements with ICP-MS as well as for passing the rinsing solutions through the column.

**Chemicals and samples.** Nitric acid, acetic acid and aqueous ammonia solutions of electronics industry grade were purchased from Kanto Chemicals (Tokyo, Japan). The multielement standard solutions for making the working calibration curves were prepared by diluting the single-element standard stock solutions ( $1000 \mu\text{g mL}^{-1}$ ) for atomic absorption spectrometry

(Wako Pure Chemicals, Osaka, Japan). The multielement standard solutions were prepared in three groups, as is shown in Table 2, in which Ge, In, Re, and Tl were added as the internal standard elements to be  $10 \text{ ng mL}^{-1}$  each. The Chelex 100 resin in 200-400 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA). Before packing the chelating resin into the minicolumn, the resin was cleaned by soaking in fresh 5 M HCl, which was changed daily for five days. The resin was collected on a G4 glass filter, and after rinsing with 2 M nitric acid and pure water, it was kept in a 0.1 M of ammonium acetate at pH 6.0. Pure water used throughout the present experiment was prepared by a Milli-Q purification system (Element A-10, Nihon Millipore Kogyo, Tokyo, Japan).

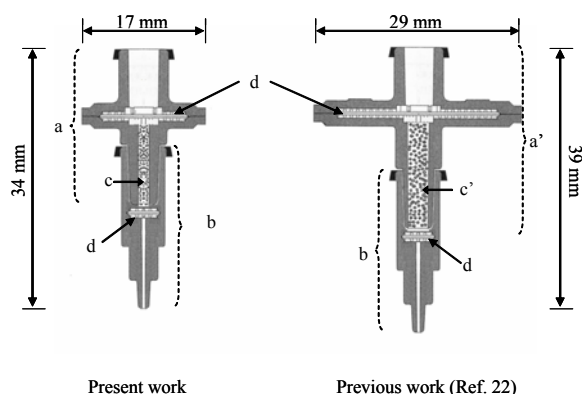
Three kinds of seawater CRMs (CASS-3, NASS-4, and NASS-5) were purchased from NRCC. Coastal seawater sample collected from the shore near the Take Island (Gamagori, Aichi Prefecture, Japan) was used for optimizing the experimental conditions of the present preconcentration method. It was filtered with a membrane filter (pore size  $0.45 \mu\text{m}$ ) and acidified to pH 1 with *conc.* nitric acid.

**Design of a down-sized chelating resin-packed minicolumn.** The structure of the down-sized chelating resin-packed minicolumn is shown in Fig. 1, where the previous minicolumn [22] is also shown for comparison of size. The minicolumn was constructed with three components, *i.e.* two syringe filters (a: DISMIC-13HP, Advantec, Tokyo, Japan; and b: Millex-LH; Nihon Millipore Kogyo, Tokyo, Japan) and a Chelex 100 resin (c: 200-400 mesh, Bio-Rad Laboratories, Richmond, CA, USA).

As is shown in Fig. 1, the size of the minicolumn was  $34 \text{ mm} \times 17 \text{ mm}$ , while that of the old one was  $39 \text{ mm} \times 29 \text{ mm}$ , as a result, the bed volume (c) for packing the chelating resin could be reduced from 0.08 mL in the previous minicolumn to 0.01 mL in the present one.

**Table 1. Operating Conditions with Micro-sampling and Concentric Nebulization for ICP-MS Instrument**

| Operating parameters    | Operating conditions        |                                      |
|-------------------------|-----------------------------|--------------------------------------|
|                         | Micro-sample nebulization   | Conventional concentric nebulization |
| Plasma conditions:      |                             |                                      |
| incident power          | 1.3 kW                      | 1.3 kW                               |
| coolant gas flow rate   | Ar 15.0 L min <sup>-1</sup> | Ar 15.0 L min <sup>-1</sup>          |
| auxiliary gas flow rate | Ar 1.0 L min <sup>-1</sup>  | Ar 1.0 L min <sup>-1</sup>           |
| carrier gas flow rate   | Ar 1.0 L min <sup>-1</sup>  | Ar 1.0 L min <sup>-1</sup>           |
| sampling depth          | 5.5 mm from load coil       | 9 mm from load coil                  |
| Nebulizer:              | MicroMist                   | Conikal                              |
| sample uptake rate      | 0.1 mL min <sup>-1</sup>    | 1 mL min <sup>-1</sup>               |
| Data acquisition:       |                             |                                      |
| measurement mode        | Peak hopping                | Peak hopping                         |
| dwell time              | 50 ms/point                 | 50 ms/point                          |
| data point              | 3 points/peak               | 3 points/peak                        |
| number of scans         | 100                         | 100                                  |



**Figure 1. A Schematic Structure of the Chelating Resin-packed Minicolumn**

- a) prefilter tube (DISMIC-13HP, ADVANTEC)
- a') prefilter tube (DISMIC-25HP, ADVANTEC)
- b) prefilter tube (Millex-LH, Nihon Millipore Kogyo)
- c) Chelex 100 resin, 200-400 mesh, 0.088 g
- c') Chelex 100 resin, 100-200 mesh, 0.40 g
- d) built-in membrane filter (pore size 0.45  $\mu\text{m}$ )

**Table 2. Multielement Standard Solutions for Calibration<sup>a</sup>**

| Group     | Element              | Concentration (ng mL <sup>-1</sup> ) |
|-----------|----------------------|--------------------------------------|
| Group I   | V, Co, Pb            | 50                                   |
|           | Dy, Ho, Er, Tm, Lu   | 5                                    |
| Group II  | Cu, Zn, Cd           | 50                                   |
|           | La, Ce, Pr, Nd, Yb   | 5                                    |
| Group III | Mn, Ni, Mo           | 50                                   |
|           | Y, Sm, Eu, Gd, Tb, U | 5                                    |

<sup>a</sup> The multielement standard solutions contains 10 ng mL<sup>-1</sup> of internal standard Ge, In, Re and Tl

The pore sizes of built-in membrane filters (d) in both syringe filters were 0.45  $\mu\text{m}$ . After the Chelex 100 resin was soaked in 0.1 M of ammonium acetate buffer (pH 6.0) overnight, the slurry of Chelex 100 resin was packed into the space from the outlet of the syringe filter (a), and then a smaller syringe filter (b) was capped to construct the minicolumn. The amount of Chelex 100 resin in the column was (0.088 $\pm$ 0.004) g ( $n = 10$ ) in wet weight. All the sample, rinsing, and eluent solutions were loaded automatically using the KDS200 syringe pump, into the minicolumn with different single-use plastic syringes of Terumo series (Terumo Corporation, Tokyo, Japan).

**Preconcentration procedure for trace metals in seawater.** The procedure for preconcentration of trace metals in seawater was almost similar to that in previous work [22]. First, the seawater sample was adjusted to pH 6.0 with ammonia solution and acetic acid, and 50 mL of pH-adjusted seawater sample was loaded into the minicolumn at the flow rate of 1.0 mL min<sup>-1</sup> with a 50 mL volume syringe. Second, 3 mL of 1 M ammonium acetate buffer (pH 6.0) was passed into the minicolumn at the flow rate of 1 mL min<sup>-1</sup> to rinse matrix elements, such as Mg and Ca, which were partly

adsorbed on the resin. Then, trace metals adsorbed on the chelating resin were eluted with 0.45 mL of 2 M HNO<sub>3</sub> into a test tube, in which 0.05 mL of internal standard solution (Ge, In, Re, and Tl; 100 ng mL<sup>-1</sup> each) was added for correction of matrix effects. The final analysis solution was subjected to the determination of trace metals by ICP-MS equipped with the MicroMist nebulizer.

In the recovery test, trace metals were spiked in the coastal seawater sample, taking into consideration their concentrations in seawater. The same preconcentration procedure as described above was carried out to estimate the concentration recoveries for trace metals by the calibration method.

### 3. Results and Discussion

**Optimization of sample-loading flow rate.** Since the present down-sized chelating resin-packed minicolumn was packed with less amount of chelating resins, compared to the previous one [22], the operating parameters such as sample-loading flow rate, matrix element elimination, and trace metal elution were carefully optimized for the present minicolumn. The pH dependence of the recoveries for trace metals in seawater obtained with the Chelex 100 resin was almost the same as that reported in detail in the previous paper [22], in which pH 6.0 was recommended as the compromised pH condition to obtain the better recoveries for most elements. In the present experiment, thus, the preconcentration was carried out at pH 6.0.

Using the coastal seawater sample adjusted to pH 6.0, the sample-loading flow rate was optimized in the range from 0.2 to 1.4 mL min<sup>-1</sup> at the interval of 0.2 mL min<sup>-1</sup>, where the syringe pump (KDS200) was used for loading the seawater samples into the column. When the flow rate was larger than 1.0 mL min<sup>-1</sup>, the recoveries for analyte elements decreased significantly, where the recoveries were estimated in a similar manner to the procedure described in Experimental Section. Then, the sample-loading flow rate of 1.0 mL min<sup>-1</sup> was chosen as the optimum condition to obtain the better recovery.

**Elution profile of matrix elements from the minicolumn.** Matrix elements such as Na, K, Mg, and Ca in seawater often cause instrumental drift, isobaric polyatomic interferences, and signal suppression in the determination of trace metals by ICP-MS. In order to reduce such interferences, matrix elements adsorbed on the resin are usually eliminated by rinsing the chelating resin with ammonium acetate buffer solution [9-11,15,22]. However, the use of excessive amount of rinsing solution often results in losses of analyte metals. Therefore, the optimization for the amount of ammonium acetate buffer solution (1 M, pH 6.0) should be carefully performed in the sample pretreatment. In the present experiment, thus,

the elution signal profiles for matrix elements after the sample loading were *on-line* monitored by ICP-MS with passing ammonium acetate buffer solution through the minicolumn at the flow rate of  $0.9 \text{ mL min}^{-1}$  with the KDS200 syringe pump. The elution signal profile of Ca is shown in Fig. 2, as a typical example. It is seen from Fig. 2 that more than 95% of Ca was eluted from the minicolumn when 3 mL of ammonium acetate was passed. After this rinsing process, the concentrations of Na, K, Mg, and Ca in the residual solution were 20, 3, 39, and  $37 \mu\text{g mL}^{-1}$ , respectively. As a result, the total concentration of Na, K, Mg, and Ca in the analysis solution was less than  $100 \mu\text{g mL}^{-1}$ , which was low enough to correct matrix effects by the internal standard correction method [11]. Consequently, 3 mL of ammonium acetate buffer solution was chosen as the optimum volume for rinsing the chelating resin-packed minicolumn.

#### Elution profiles of trace metals from the minicolumn.

In the present experiment, trace metals adsorbed on the chelating resin were eluted with 2 M nitric acid. It is apparent that the larger concentration factor can be obtained when the eluent of 2 M nitric acid is used as less as possible. Then, after loading the sample, the elution signal profiles of trace metals were *on-line* monitored by ICP-MS, with flowing 2 M nitric acid solution into the minicolumn at the flow rate of  $0.9 \text{ mL min}^{-1}$  with the KDS200 syringe pump. The signal profiles for Zn, Cu, and Y are shown in Fig. 3, as the representatives. When 0.45 mL of 2 M nitric acid was passed through the minicolumn, all of these trace metals were eluted almost completely. Therefore, 0.45 mL of nitric acid was found to be enough to elute trace metals from the minicolumn. It was also enough for the determination of more than 40 trace metals by the ICP-MS equipped with a MicroMist nebulizer.

**Analytical figures of merit.** First, the recoveries for trace metals in the present preconcentration procedure were evaluated by spiking certain amounts of trace metals in the seawater samples. The results for the recoveries of 24 trace metals are summarized in Table 3, although 35 elements were examined in total. They were selected as the elements whose certified, information or reference values were available. The recoveries for Co, Ni, Cu, Zn, Y, Cd, rare earth elements (REEs), Pb, and U were better than 85% with good reproducibility less than 2% (RSD). The recoveries for V, Mn, and Mo were smaller than 50% with their RSDs less than 2%, which indicate that the analytical results for these elements should be treated carefully because of their poor recoveries.

The analytical detection limits obtained by the present method were summarized in Table 3, along with those obtained using the old-type chelating resin-packed minicolumn. They were calculated from the instrumental detection limits, taking into account the concentration factor (100) and the recovery values for trace metals.

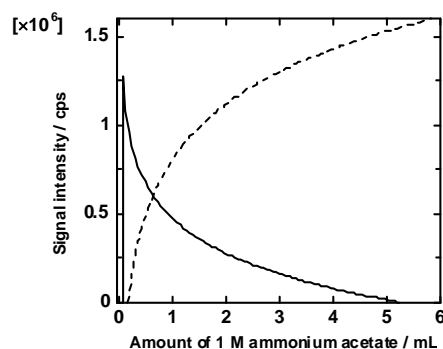


Figure 2. Elution Signal Profile of  $\text{Ca}^{2+}$  from the Minicolumn with 1 M Ammonium Acetate (pH 6.0)

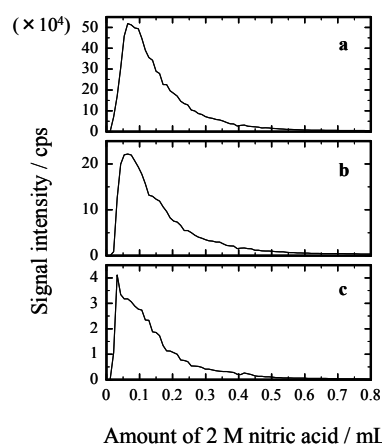


Figure 3. Elution Signal Profiles of Trace Metals (a. Zn, b. Cu, c. Y) from the Minicolumn with 2 M Nitric Acid

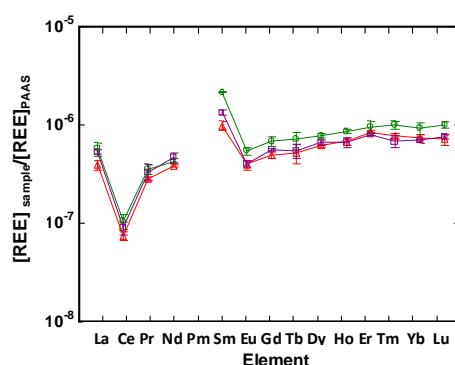


Figure 4. Shale-normalized REE Distribution Patterns for Seawater CRMs, based on Their Complied Data; CASS-3 (○), NASS-4 (Δ), NASS-5 (□)

The instrumental detection limits were defined as the concentrations corresponding to 3-fold the standard deviation of the background signal intensities, which were estimated from the 10-times duplicated measurements of the blank solution (2 M nitric acid

solution) containing internal standard elements (Ge, In, Re, and Tl; 10 ng mL<sup>-1</sup> each). The analytical detection limits for 24 elements were in the range from 0.001 ng mL<sup>-1</sup> of Ni to 0.000006 ng mL<sup>-1</sup> of Pr, Tb, and Lu. The present analytical detection limits were significantly better than the previous ones, because the concentration factors for trace metals in the present method was 5-fold larger than those obtained in the previous work [22].

The blank values were also estimated using 50 mL of 0.1 M nitric acid as a test solution, for which the same preconcentration and measurement procedures as those for seawater samples were performed. The blank values for Pb and Zn were observed to be 0.0080 and 0.06 ng mL<sup>-1</sup>, respectively, which might be originated from the impurities in the reagents. They were not negligible compared to the concentrations in seawater samples, and then the analytical results for Pb and Zn were obtained by subtracting the blank values. The blank values for V, Co, Ni, Cu, La, and Ce were observed, but they were negligibly small compared to the concentrations of these elements in seawater.

In the ICP-MS measurements, major and trace elements in the sample solution often cause polyatomic interferences [24]. In the present experiment, the polyatomic interferences due to <sup>44</sup>Ca<sup>1</sup>H<sup>+</sup>, <sup>43</sup>Ca<sup>16</sup>O,

<sup>43</sup>Ca<sup>16</sup>O<sup>1</sup>H<sup>+</sup>, <sup>48</sup>Ca<sup>16</sup>O<sup>1</sup>H<sup>+</sup>, and <sup>141</sup>Pr<sup>16</sup>O with <sup>45</sup>Sc, <sup>59</sup>Co, <sup>60</sup>Ni, <sup>65</sup>Cu, and <sup>157</sup>Gd, respectively, were observed and corrected by the interference correction coefficient method reported by Yabutani *et al.* [11].

In the present experiment, however, the polyatomic interferences were less than 5% of the observed values.

**Analytical results for trace metals in seawater CRMs (CASS-3, NASS-4, and NASS-5).** Trace metals in one coastal seawater CRM (CASS-3) and two open seawater CRMs (NASS-4 and NASS-5) were determined by the analytical method proposed in the present experiment. The analytical results for V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U, whose certified or information values have been issued by NRCC, are summarized in Table 4. It is seen in Table 3 that all the observed values for trace metals examined agreed quite well with the certified values. This agreement indicates that the present method was accurate enough for the determination of trace metals in seawater. It should be noted here that large relative standard deviations (RSD > 25%) were found for the observed values of Pb in all the three seawater CRMs and those of Zn in NASS-4 and NASS-5. Such large RSDs for Pb and Zn may be attributed to their low concentrations close to the blank values.

**Table 3. Recoveries and Analytical Detection Limits for Trace Metals**

| Element | M(z) | Spike (ng mL <sup>-1</sup> ) | Recovery, <sup>a</sup> % | ADL (ng mL <sup>-1</sup> ) |                            |
|---------|------|------------------------------|--------------------------|----------------------------|----------------------------|
|         |      |                              |                          | Present work <sup>b</sup>  | Previous work <sup>c</sup> |
| Co      | 59   | 1                            | 96.3 ± 0.4               | 3 x 10 <sup>-5</sup>       | 4 x 10 <sup>-4</sup>       |
| Ni      | 60   | 1                            | 95.2 ± 0.2               | 10 x 10 <sup>-3</sup>      | 2 x 10 <sup>-3</sup>       |
| Cu      | 65   | 1                            | 95.4 ± 0.9               | 3 x 10 <sup>-4</sup>       | 10 x 10 <sup>-3</sup>      |
| Zn      | 68   | 1                            | 89.9 ± 0.8               | 7 x 10 <sup>-4</sup>       | 9 x 10 <sup>-3</sup>       |
| Y       | 89   | 0.1                          | 85 ± 1                   | 8 x 10 <sup>-6</sup>       | 10 x 10 <sup>-4</sup>      |
| Cd      | 111  | 1                            | 89 ± 1                   | 6 x 10 <sup>-4</sup>       | 3 x 10 <sup>-3</sup>       |
| La      | 139  | 0.1                          | 85.9 ± 0.5               | 10 x 10 <sup>-5</sup>      | 10 x 10 <sup>-4</sup>      |
| Ce      | 140  | 0.1                          | 86.8 ± 0.7               | 10 x 10 <sup>-5</sup>      | 10 x 10 <sup>-4</sup>      |
| Pr      | 141  | 0.1                          | 86.7 ± 0.6               | 6 x 10 <sup>-6</sup>       | 7 x 10 <sup>-5</sup>       |
| Nd      | 143  | 0.1                          | 92 ± 2                   | 6 x 10 <sup>-5</sup>       | 3 x 10 <sup>-4</sup>       |
| Sm      | 147  | 0.1                          | 85.3 ± 0.9               | 3 x 10 <sup>-5</sup>       | 5 x 10 <sup>-4</sup>       |
| Eu      | 153  | 0.1                          | 85.3 ± 0.2               | 10 x 10 <sup>-5</sup>      | 10 x 10 <sup>-4</sup>      |
| Gd      | 157  | 0.1                          | 86.4 ± 0.4               | 5 x 10 <sup>-5</sup>       | 4 x 10 <sup>-4</sup>       |
| Tb      | 159  | 0.1                          | 85.9 ± 0.7               | 6 x 10 <sup>-6</sup>       | 8 x 10 <sup>-5</sup>       |
| Dy      | 163  | 0.1                          | 87.2 ± 0.3               | 2 x 10 <sup>-5</sup>       | 3 x 10 <sup>-4</sup>       |
| Ho      | 165  | 0.1                          | 85.6 ± 0.1               | 10 x 10 <sup>-5</sup>      | 7 x 10 <sup>-5</sup>       |
| Er      | 166  | 0.1                          | 87 ± 1                   | 3 x 10 <sup>-5</sup>       | 2 x 10 <sup>-4</sup>       |
| Tm      | 169  | 0.1                          | 87.1 ± 0.5               | 8 x 10 <sup>-6</sup>       | 8 x 10 <sup>-5</sup>       |
| Yb      | 172  | 0.1                          | 86 ± 1                   | 3 x 10 <sup>-5</sup>       | 3 x 10 <sup>-4</sup>       |
| Lu      | 175  | 0.1                          | 87.5 ± 0.4               | 6 x 10 <sup>-6</sup>       | 6 x 10 <sup>-5</sup>       |
| Pb      | 207  | 1                            | 89.3 ± 0.4               | 10 x 10 <sup>-4</sup>      | 3 x 10 <sup>-3</sup>       |
| U       | 238  | 10                           | 97.6 ± 0.5               | 2 x 10 <sup>-5</sup>       | 8 x 10 <sup>-5</sup>       |
| V       | 51   | 10                           | 39.5 ± 0.4               | 10 x 10 <sup>-4</sup>      | 7 x 10 <sup>-4</sup>       |
| Mn      | 55   | 10                           | 40.3 ± 0.5               | 6 x 10 <sup>-4</sup>       | 2 x 10 <sup>-2</sup>       |
| Mo      | 98   | 10                           | 28 ± 1                   | 5 x 10 <sup>-5</sup>       | 3 x 10 <sup>-3</sup>       |

<sup>a</sup> Mean ± standard deviation, n = 3. <sup>b</sup> Analytical detection limit, calculated from instrumental detection limits, taking into account the concentration factor (100) and recovery values. <sup>c</sup> Cited from Ref. 22.

**Table 4. Analytical Results for Trace Metals in Seawater CRMs**

| Element           | m(z) | Observed value <sup>a</sup> ( $\mu\text{g L}^{-1}$ ) | Certified value( $\mu\text{g L}^{-1}$ ) |
|-------------------|------|--|---|
| <u>CASS-3</u>     |      |  |   |
| (V) <sup>b</sup>  | 51   | (1.4 $\pm$ 0.2)                                      | 1.43 $\pm$ 0.04 <sup>c</sup>            |
| (Mn) <sup>b</sup> | 55   | (2.8 $\pm$ 0.3)                                      | 2.51 $\pm$ 0.36                         |
| Co                | 59   | 0.038 $\pm$ 0.002                                    | 0.041 $\pm$ 0.009                       |
| Ni                | 60   | 0.38 $\pm$ 0.03                                      | 0.39 $\pm$ 0.06                         |
| Cu                | 65   | 0.48 $\pm$ 0.03                                      | 0.52 $\pm$ 0.06                         |
| Zn                | 68   | 1.4 $\pm$ 0.2  | 1.24 $\pm$ 0.25                         |
| (Mo) <sup>b</sup> | 98   | (9.0 $\pm$ 0.5)                                      | 8.95 $\pm$ 0.26                         |
| Cd                | 111  | 0.031 $\pm$ 0.003                                    | 0.03 $\pm$ 0.005                        |
| Pb                | 207  | 0.01 $\pm$ 0.005                                     | 0.012 $\pm$ 0.004                       |
| U                 | 238  | 3 $\pm$ 0.2  | 2.84 <sup>d</sup>                       |
| <u>NASS-4</u>     |      |  |   |
| (V) <sup>b</sup>  | 51   | (1.3 $\pm$ 0.3)                                      | 1.18 $\pm$ 0.16                         |
| (Mn) <sup>b</sup> | 55   | (3.0 $\pm$ 0.3)                                      | 2.78 $\pm$ 0.19                         |
| Co                | 59   | 0.01 $\pm$ 0.002                                     | 0.009 $\pm$ 0.001                       |
| Ni                | 60   | 0.22 $\pm$ 0.02                                      | 0.228 $\pm$ 0.009                       |
| Cu                | 65   | 0.21 $\pm$ 0.01                                      | 0.228 $\pm$ 0.011                       |
| Zn                | 68   | 0.12 $\pm$ 0.03                                      | 0.12 $\pm$ 0.02                         |
| (Mo) <sup>b</sup> | 98   | (8.5 $\pm$ 0.6)                                      | 8.78 $\pm$ 0.86                         |
| Cd                | 111  | 0.018 $\pm$ 0.001                                    | 0.016 $\pm$ 0.003                       |
| Pb                | 207  | 0.012 $\pm$ 0.004                                    | 0.013 $\pm$ 0.005                       |
| U                 | 238  | 3 $\pm$ 0.2  | 2.68 $\pm$ 0.12                         |
| <u>NASS-5</u>     |      |  |   |
| (V) <sup>b</sup>  | 51   | (1.0 $\pm$ 0.3)                                      | 1.2 <sup>d</sup>                        |
| (Mn) <sup>b</sup> | 55   | (0.88 $\pm$ 0.6)                                     | 0.919 $\pm$ 0.057                       |
| Co                | 59   | 0.011 $\pm$ 0.001                                    | 0.011 $\pm$ 0.003                       |
| Ni                | 60   | 0.24 $\pm$ 0.02                                      | 0.25 $\pm$ 0.03                         |
| Cu                | 65   | 0.27 $\pm$ 0.01                                      | 0.3 $\pm$ 0.05                          |
| Zn                | 68   | 0.07 $\pm$ 0.04                                      | 0.1 $\pm$ 0.04                          |

<sup>a</sup> Mean  $\pm$  standard deviation, n = 5. <sup>b</sup> Recovery values were less than 85%.

<sup>c</sup> Reference value, cited from Ref. 11. <sup>d</sup> Information value issued by NRCC.

The analytical results for REEs are summarized in Table 5. Although all of REEs in seawater CRMs examined were extremely low, they were determined with fairly good reproducibility in the present experiment. However, the certified or information values for REEs have not been issued by NRCC yet.

As stated above, the certified or information values for REEs in seawater CRMs are not available even now. However, REEs in seawater have been widely investigated as the tracers of water masses and ocean circulation as well as a valuable probe for investigating the scavenging processes of particulate matter in the ocean [25-30].

Therefore, the reliable reference values for REE concentrations in seawater CRMs are necessary to promote further development of marine chemistry. Then, the compiled data for REEs in seawater CRMs were proposed in the present paper. Such compiled data were estimated as the mean values of their reference values [11,16,21,31,32] including the data obtained in the present work. The results are shown in Table 6. As is seen in Table 6, the compiled data for all seawater CRMs were within fairly small standard

deviations. Thus, the compiled data summarized in Table 6 may be available as the tentatively certified reference values for REEs in seawater CRMs.

In addition, the shale-normalized REE distribution patterns plotted against atomic number, which are usually shown as the relative concentrations of REEs normalized to their concentrations in shale, were examined in order to evaluate the reliability of the compiled data for REEs in seawater CRMs.

The REE distribution patterns for seawater CRMs are shown in Fig. 4, in which the compiled data for the concentrations of REEs were normalized to those in post-Archean average Australian shale (PAAS) [33]. It is seen in Fig. 4 that the REE distribution patterns show the typical characteristic pattern for seawater [10], *i.e.*, smooth curves as well as slight enrichment of heavy REEs and clear negative anomalies of Ce in all seawater CRMs. However, it should be noted here that the significantly higher concentrations of Sm were observed for all seawater CRMs, which were seemingly due to the possible contamination caused during preparation process of these CRMs.

**Table 5. Analytical Results for REEs in Seawater CRMs**

| Element | m/z | Concentration a/ ng L <sup>-1</sup> |        |        |        |        |        |
|---------|-----|-------------------------------------|--------|--------|--------|--------|--------|
|         |     | CASS-3                              |        | NASS-4 |        | NASS-5 |        |
| Y       | 89  | 23.3                                | ± 0.9  | 18     | ± 1    | 20.7   | ± 0.7  |
| La      | 139 | 13.9                                | ± 0.6  | 9.9    | ± 0.6  | 11.8   | ± 0.4  |
| Ce      | 140 | 5.6                                 | ± 0.2  | 3.9    | ± 0.2  | 5.23   | ± 0.05 |
| Pr      | 141 | 1.9                                 | ± 0.1  | 1.5    | ± 0.1  | 1.84   | ± 0.06 |
| Nd      | 143 | 7.8                                 | ± 0.4  | 7.2    | ± 0.3  | 7.5    | ± 0.1  |
| Sm      | 147 | 6.6                                 | ± 0.4  | 3      | ± 0.1  | 4.5    | ± 0.3  |
| Eu      | 153 | 0.33                                | ± 0.03 | 0.24   | ± 0.02 | 0.29   | ± 0.02 |
| Gd      | 157 | 1.7                                 | ± 0.1  | 1.4    | ± 0.1  | 1.59   | ± 0.08 |
| Tb      | 159 | 0.27                                | ± 0.03 | 0.21   | ± 0.03 | 0.24   | ± 0.02 |
| Dy      | 163 | 1.8                                 | ± 0.1  | 1.6    | ± 0.1  | 1.8    | ± 0.2  |
| Ho      | 165 | 0.48                                | ± 0.04 | 0.39   | ± 0.02 | 0.43   | ± 0.02 |
| Er      | 166 | 1.4                                 | ± 0.1  | 1.2    | ± 0.2  | 1.36   | ± 0.08 |
| Tm      | 169 | 0.22                                | ± 0.02 | 0.18   | ± 0.02 | 0.18   | ± 0.01 |
| Yb      | 172 | 1.3                                 | ± 0.1  | 1.1    | ± 0.1  | 1.13   | ± 0.07 |
| Lu      | 175 | 0.23                                | ± 0.02 | 0.17   | ± 0.01 | 0.2    | ± 0.02 |

<sup>a</sup> Mean ± standard deviation, n = 5.

**Table 6. Compiled Data for the Concentrations of REEs in Seawater CRMs**

| Element | m/z | Concentration / ng L <sup>-1</sup> |        |                     |        |                     |        |
|---------|-----|------------------------------------|--------|---------------------|--------|---------------------|--------|
|         |     | CASS-3 <sup>a</sup>                |        | NASS-4 <sup>b</sup> |        | NASS-5 <sup>c</sup> |        |
| Y       | 89  | 23.6 <sup>d</sup>                  | ± 2    | 18.7 <sup>e</sup>   | ± 1    | 20.7 <sup>f</sup>   | ± 0.5  |
| La      | 139 | 13                                 | ± 0.9  | 9                   | ± 0.4  | 12.2                | ± 0.6  |
| Ce      | 140 | 5.4                                | ± 0.2  | 3.9                 | ± 0.07 | 4.6                 | ± 0.3  |
| Pr      | 141 | 1.9                                | ± 0.5  | 1.54                | ± 0.2  | 1.8                 | ± 1    |
| Nd      | 143 | 8.3                                | ± 0.1  | 7.4                 | ± 0.3  | 9                   | ± 0.3  |
| Sm      | 147 | 6.7                                | ± 0.03 | 3.2                 | ± 0.03 | 4.3                 | ± 0.02 |
| Eu      | 153 | 0.36                               | ± 0.7  | 0.26                | ± 0.7  | 0.27                | ± 0.04 |
| Gd      | 157 | 2.3                                | ± 0.06 | 1.7                 | ± 0.05 | 1.57                | ± 0.04 |
| Tb      | 159 | 0.32                               | ± 0.1  | 0.24                | ± 0.06 | 0.25                | ± 0.09 |
| Dy      | 163 | 2                                  | ± 0.02 | 1.63                | ± 0.03 | 1.71                | ± 0.04 |
| Ho      | 165 | 0.5                                | ± 0.2  | 0.4                 | ± 0.1  | 0.39                | ± 0.03 |
| Er      | 166 | 1.6                                | ± 0.02 | 1.4                 | ± 0.01 | 1.35                | ± 0.02 |
| Tm      | 169 | 0.23                               | ± 0.2  | 0.18                | ± 0.1  | 0.16                | ± 0.05 |
| Yb      | 172 | 1.5                                | ± 0.02 | 1.2                 | ± 0.02 | 1.14                | ± 0.01 |
| Lu      | 175 | 0.25                               |        | 0.18                |        | 0.19                |        |

<sup>a</sup> Mean ± standard deviation, n = 3, calculated from the data in the present work, Refs. 11 and 21.

<sup>b</sup> Mean ± standard deviation, n = 4, calculated from the data in the present work, Refs. 21, 31, and 32.

<sup>c</sup> Mean ± standard deviation, n = 3, calculated from the data in the present work, Refs. 16, and 32.

<sup>d</sup> Mean, n = 2, calculated from the data in the present work and Ref. 11.

<sup>e</sup> Mean, n = 2, calculated from the data in the present work and Ref. 31.

<sup>f</sup> Single data, cited from the present work.

## 4. Conclusion

A down-sized chelating resin-packed minicolumn was developed as the efficient preconcentration tool for trace metals in seawater. The optimized preconcentration procedure was proposed for 100-fold preconcentration of trace metals using only 50 mL of seawater. The recoveries for most trace metals were larger than 85% with good reproducibility (standard deviation ≤ 2%). The analytical results for V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, and U in seawater CRMs were consistent with their certified or information values from NRCC. In addition, based on the observed and reference values for REEs in these CRMs, the compiled data for the concentrations of REEs in CASS-3, NASS-4, and NASS-5 were estimated

which may be available as the information values of REEs in seawater CRMs.

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