AN *IN-SYRINGE* La CO-PRECIPITATION METHOD FOR PRE-CONCENTRATION OF OXO-ANIONS FORMING ELEMENTS IN SEAWATER FOLLOWED BY ICP-MS MEASUREMENT

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ABSTRACT

A lanthanum (La) co-precipitation method was explored for pre-concentration of oxo-anion forming elements followed by measurement with Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The co-precipitation and subsequent washing and elution steps were performed in a 25 mL-volume syringe in order to save the sample consumption and to avoid the contamination from the experimental environment. In the present work, various parameters such as the concentration of La added into the sample solution, the pH, aging time, and so on were optimized to obtain good recoveries and analytical detection limits for V, As, Se, Sb, and W. Generally, in the co-precipitation method, high concentration of precipitant (in this case, La) causes a serious problem of signal memory effect in ICP-MS measurement. To reduce such memory effect, in the present experiment, high level of La was removed by passing the analyte solution (i.e., lanthanum hydroxide dissolved in 1 M HNO_3) through a mini column packed with cation-exchange resins. The method thus obtained was evaluated through the measurement of V, As, Se, Sb and W in seawater reference materials (CASS-4 and NASS-5). The recoveries exceeded 80%, and the observed values were in good agreement with the certified values. Thus, the present method was applied to the determination of trace elements in real seawater sample.

Keywords: *Lanthanum, pre-concentration*

INTRODUCTION

Inductively coupled plasma mass spectrometry (ICP-MS) has excellent analytical features such as simultaneous multi element detection capability, extremely high sensitivity, and wide linear dynamic range[1-5]. However, direct analysis of seawater by ICP-MS is still a difficult task, not only because the concentration levels of trace elements are quite low, but also because high salt matrix interfere with the determination. Thus, a variety of pre-treatment techniques such as pre-concentration and matrix elimination have been exploited, which include chelating-resin adsorption, solvent extraction, and co-precipitation. Among them, chelating resin methods are most widely employed because iminodiacetate-based chelating resin can adsorb almost all the trace metals from high levels of salt.

Recently, the present authors have reported a Chelex 100 resin-packed mini column method for pre-concentration and determination of 25 elements in seawater[4] using a small sample volume, where trace metals in 50 mL of original seawater sample were concentrated into 0.5 mL of 2 M nitric acid (final solution). From the results, it has been proved that the mini column is a convenient pre-concentration device for trace metals in seawater as well as in mineral waters prior to the determination by ICP-MS.

As mentioned above, the chelating-resin adsorption method is not suitable for the pre-concentration of oxo-anion forming elements such as As, Se, Sb, V, W and so on. For highly sensitive measurement of As, Se, and Sb, hydride generation method is one of the most popular approaches, while co-

precipitation method may be another major approach for pre-concentration of such oxo-anion forming elements. In order to enlarge our in-syringe pre-concentration technique, in the present paper, co-precipitation was attempted in a 25-mL syringe, where lanthanum hydroxide was employed as a collector of oxo-anion forming elements. In the co-precipitation method, high concentration of La causes a serious problem of signal memory effect in ICP-MS measurement. In order to remove high level of lanthanum (200 mg dm^{-3}) and to avoid the spectral interference from them, a cation-exchange minicolumn packed with AG® 50W-X8 was employed[6,7].

EXPERIMENTAL

Apparatus

An ICP-MS instrument (model Agilent HP4500, Yokogawa Analytical Systems, Tokyo, Japan) equipped with a quadrupole mass filter was used. The operating conditions for the ICP-MS instrument are shown in Table 1. A pH meter of model TWIN pH meter from Horiba (Kyoto, Japan) was used for pH adjustment. A HSW plastic syringe was used as a vessel and reactor. DISMIC-25HP membrane filter (ADVANTEC, Tokyo, Japan) with pore sizes of 0.20 μm was used for collecting lanthanum hydroxide precipitate. A laboratory-made minicolumn[3] was constructed as a combination of two commercially available syringe filters (DISMIC-25HP and Millex-LH). A syringe pump (model KDS200, KD Scientific, MA, US) was used for pumping the sample solution into the minicolumn.

Reagents and chemicals

Nitric acid, acetic acid, and aqueous ammonia solution of electronic industry grade were purchased from Kanto Chemicals (Tokyo). The multielement standard solution for making the working calibration curves were prepared from the single-element standard stock solutions (1000 μg L^{-1}) for atomic absorption spectrometry (Kanto Chemicals, Tokyo). The La solution as a co-precipitation carrier was prepared by dissolving 3 g of La (NO$_3$)$_3$ 6 H$_2$O (Wako Chemicals, Osaka, Japan) in 100 ml of 0.1 M HNO$_3$ to provide 10 g L^{-1} La and diluted to be 5 g L^{-1}.

AG® 50W-X8 resin was purchased from Nippon Bio-Rad Laboratories. This resin was purified by soaking in 5 M HCl for 5 days and then in pure water. After that, the purified resin (0.42 ± 0.01 g wet weight) was filled into a minicolumn consisting of two syringe filters. Pure water was prepared by a Milli Q purification system (model Element A-10, Nihon Millipore Kogyo).

Table 1. Operation condition for ICP-Q-MS instrument

ICP-Q-MS Agilent HP4500	
Plasma conditions:	
incident power	1.3 kW
coolant gas flow rate	Ar 15.0 l min^{-1}
auxiliary gas flow rate	Ar 1.0 l min^{-1}
carries gas flow rate	Ar 1.1 min^{-1}
sampling depth	9 mm from load coil
Nebulizer:	Concentric-type
sampling uptake rate	0.7 ml min^{-1}
Data acquisition:	
measurement mode	Peak hopping
dwell time	50 ms/point
data point	3 points/peak
number of scans	100

Samples

Seawater reference materials of CASS-4 and NASS-5, which were issued from National Research Council of Canada, were used to evaluate the analytical procedure. A coastal seawater sample collected from the shore near the Take Island (Gamagori, Aichi Prefecture, Japan) was also used. The real sample was filtered with a membrane filter (pore size 0.45 μm) and acidified to pH 1 with *conc.* nitric acid.

Procedure

The procedure was composed of two steps: La-co-precipitation (Step 1) and La-removal from the pre-concentration solution (Step 2).

Step1. Twenty ml sample adjusted to pH 9.5 was filled into a syringe. Then, 0.2 mL of 5 g L^{-1} of La solution was added into the syringe with shaking for 3 min. The solution was allowed to stand for 1 h at room temperature for complete precipitation. Afterward, the precipitation was collected on a 0.2 μm membrane filter by filtration.

Step 2. The precipitate in Step 1 was dissolved with 2 ml of 2 M HNO_3 and diluted 2-fold with pure water to a final concentration of 1 M HNO_3. Then, this solution was passed through the cation exchange minicolumn at a flow rate of 0.2 mL min^{-1}.

RESULT AND DISCUSSION

Effect of the amount of lanthanum added into seawater sample on the recoveries for oxo-anion forming elements

Co-precipitation efficiencies are influenced by various parameters such as pH[1,6], temperature, aging time, and the amount of precipitant (i.e., La) added into the sample. Among them, the concentration and volume of La as a collector may be the principal parameters, because an excess of La causes significant interference in ICP-MS measurement. Thus, first of all, the effect of the amount of lanthanum on the co-precipitation of As, Se, Sb, V, and W with lanthanum hydroxide was examined. In general, large number of researchers[1,2,6-7] was used more than 200 mg L^{-1} lanthanum to obtained lanthanum hydroxide. In this study, therefore, the recoveries of oxo-anion forming elements were determined after the concentrations lanthanum series (25, 50, 75, 100, 125, and 150 mg L^{-1}) excesses in the samples.

As can be seen in Fig. 1, with concentration 50 mg L^{-1} or up lanthanum in the sample, the recoveries of V, As, Se, Sb and W were more than 80 %. In order to a great efficiency the amount of lanthanum in the sample, henceforth, in the present work 50 mg L^{-1} lanthanum in the sample was used to collected the oxo-anion forming elements.
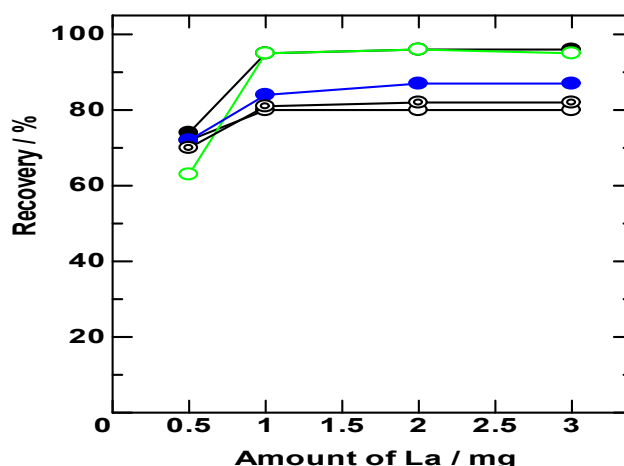

Fig 1. The recoveries of the elements after added various amount La in 20 mL samples ◯: V ●: As
◯ :Se ● : Sb ◎: W
A cation exchange capacity

In ICP-MS measurement, matrix elements often cause isobaric and polyatomic interferences as well as signal suppression[1-5, 8]. Unfortunately for co-precipitation pre-concentration methods, high concentration of precipitant in the sample constitute a matrix element source. In lanthanum co-precipitation pre-concentration, high concentration lanthanum in the analysis sample may be the source of possible interferences from polyatomic, isobaric and divalent ions such as $^{139}La^{14}N$, $^{139}La^{16}O$, $^{139}La^{17}O$, $^{139}La^{18}O$, $^{139}La^{16}O^1H$, $^{139}La^{16}O_2{}^+$, $^{139}La^{40}Ar$, $^{139}La^{+2}$ [1]. Thus, ^{69}Ga and rare earth elements by ICP-MS could not be determined simultaneously by ICP-MS. In addition, the signal memory effect from La itself is a serious problem in the ICP-MS measurement. From these reasons, in the present work, La was removed using cation exchange resins.

Furthermore, the sample conditions such as the effect of molarities HNO_3 the sample and a capacity of a cation exchange resin-packed minicolumn on La removal rate were observed. Firstly, high concentration La in various molarities HNO_3 solutions (0.1, 0.5, 1, 1.5 and 2 M) were passed to a minicolumn filled 0.42 $\pm$ 0.01 wet weight the resins. The result as is shown in Fig.2, the removal rate of La in 1 M

HNO_3 solution or less was more than 99 %. In the present work, oxo-anion forming elements were dissolved with 2 M HNO_3, subsequently, this analysis solution was diluted 2-fold to make it be 1 M HNO_3 before passing trough the cation exchange resin. Secondly, various amounts of La in 10 mL of 1 M HNO_3 solutions (the concentration are 100, 200, 250, 300, 400, 500, 600, 700 and 800 mg L^{-1}) were passed through a cation exchange resins-packed minicolumn. As can be seen in Fig. 3, the concentration of lanthanum remains in the solution after passed 500 mg L^{-1} La to a cation exchange resins was less then 3 mg L^{-1}. In the present work, therefore, about 250 mg L^{-1} La in 4 ml analysis sample was removed using this resin.

Analytical figure of merit

The recoveries, blank values and analytical detection limits are show in Table 2. The recoveries of V, As, Se, Sb and W were more than 80 %, with good reproducibility of less than 6 %. In previous research, by using chelating resin pre-concentration method, V[3,4,10] and W[3,10] could be determined. However, the recoveries of these elements used the chelating resin pre-concentration were less than 50 %.
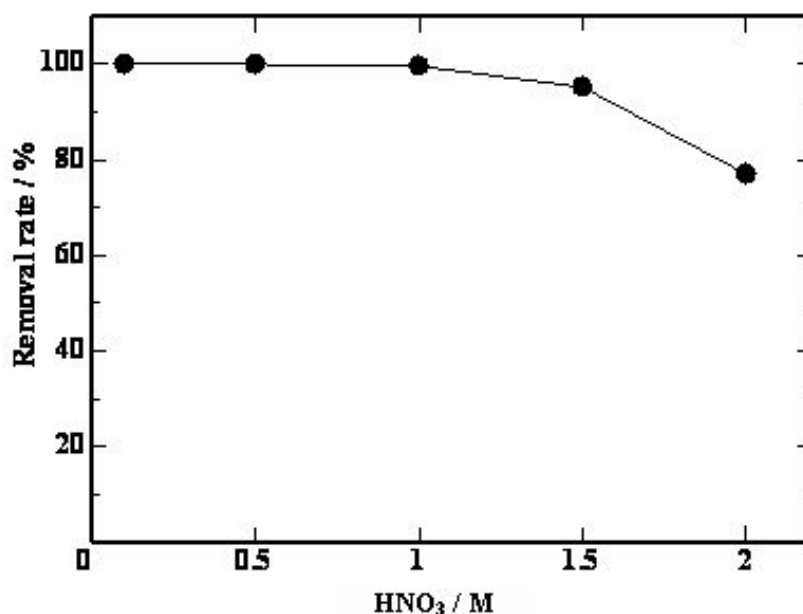

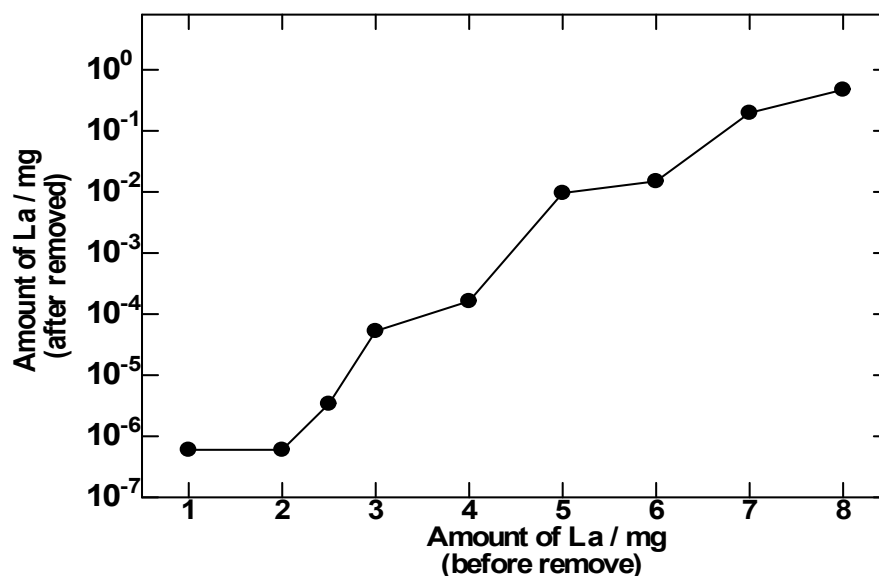**Fig 2.** Effect of molarities HNO3 the sample on La removal rate

Fig 3. The concentrations of La before and after passed trough the cation exchange resin packed minicolumn of various amount La in 10 mL 1 M HNO_3

The analytical detection limits (ADLs) were calculated from instrumental detection limits of each element, concentration factor (5), and the recovery values. The instrumental detection limits were estimated as the analyte concentration correspondence the standard deviation of the signal intensities 10-times measurement of blank solution. The ADLs of V, As, Se, Sb and W were 0.001, 0.001, 0.05, 0.001 and 0.003 $\mu g\ L^{-1}$, respectively.

The blank values of As, Se and Sb have been presented in the present work. As can be seen in Table 2, the blank values of As, Se and Sb were 0.031 $\mu g\ L^{-1}$, 0.035 $\mu g\ L^{-1}$ and 0.0035 $\mu g\ L^{-1}$, respectively.

The analytical results of oxo-anion forming elements in seawater sample

In order to evaluate this method, oxo-anion forming elements in seawater certified reference materials (CRMs) of NASS-5 and CASS-4 were determined by ICP-MS. A syringe was used as a reactor of co-precipitation pre-concentration where it could be decreased volume of the sample until 20 mL for 10-fold pre-concentration. The analytical result was shown in Table 3.

The observed values of V and As were good agreement with those in both of certified values. Total Se could not be compared in the present work, because certified and/or reference values are not available for comparing right now. The observed value of total Se in NASS-5 was higher 100-fold than Se(IV) in certified value. The observed value of Sb in CASS-4 was in good agreement with that used a microflow nebulization ICP-SFMS which it was reported by Clara.T *et.all*[9].

The observed value of W obtained using the present method was slightly lower than that used a chelating resin co-precipitation pre-concentration[3,10]. A low observed value of W may be because the recovery of W obtained in the present method was higher than the recovery of it in chelating resin pre-concentration.

Furthermore, this method was applied to the determination of oxo-anion forming elements in real seawater sample. In natural water environmental, V, As, Se and Sb is essential elements for biological systems[11-14]. The observed values of those elements in real seawater sample were shown in Table 4. The observed value of V was in good agreement with the reference value[3].

In Take Shima seawater sample, the observed value of As was almost the same as that in North Pacific seawater (1.11 µg L^{-1})[15] and was slightly higher than that in Pasific coastal seawater (1.06 µg L^{-1})[12]. Total Se in Take Shima was compared with that in other seawater and lake water. It was found that the observed value of Se in Take Shima seawater sample which obtained in the present method was twice higher than that in San Francisco Bay (0.44 µg L^{-1})[16]. On the other hand, the total Se in Take Shima seawater was lower than that in East lake water[17].

The observed value of Sb in the present work was slightly lower than that in the North Pacific Ocean reference value[18]. The observed value of W in Take Shima seawater sample was slightly lower with reference value [3].

Table 2. Analytical figures of merit for oxo-anion forming elements

Element	m/z	Recovery [a] / %			Blank [a] /µg L^{-1}			ADL [c] /µg L^{-1}
V	51	80	±	5	0.040	±	0.007	0.001
As	75	96	±	5	0.031	±	0.008	0.001
Se	82	95	±	5	0.035	±	0.008	0.05
Sb	121	85	±	3	0.0035	±	0.0008	0.001
W	184	81	±	4	n.d. [b]			0.003

a) Mean ± standard deviation, *n* = 3 b) Not detected
c) The analytical detection limit (ADL) was calculated from instrument detection limit, taking into account of the concentration
  factor (5) and recovery values

Table 3. Analytical results for trace elements in seawater CRMs (NASS-5 and CASS-4)

Element	m/z	Concentration / µg L^{-1}											
		Observed value NASS-5			Certified Value			Observed value CASS-4			Certified Value		
V	51	1.20	±	0.05	1.20[a]			1.15	±	0.08	1.18	±	0.16
As	75	1.30	±	0.12	1.27	±	0.12	1.13	±	0.09	1.11	±	0.16
Se	82	1.86	±	0.25	0.018 [b]			1.03	±	0.17			
Sb	121	0.076	±	0.008				0.22	±	0.01	0.24[c]	±	0.02
W	182	0.0095	±	0.0001	0.010 [d]	±	0.001	0.016	±	0.001	0.042 [e]	±	0.004

a)   Information value, issued by National Research Council Canada
b)   Information value of Se(IV), issued by National Research Council Canada
c)   Literature value, cited from Ref.9
d)   Literature value, cited from Ref. 3
e)   Literature value, cited from Ref.10

Table 4. The observed values of trace elements in Take Shima water sample

Element	m/z	Take Shima [a] /µg L^{-1}			Reference		
V	51	1.37	±	0.07	1.40 [b]	±	0.06
As	75	1.10	±	0.03	1.115 [c]		
Se	82	0.95	±	0.03			
Sb	121	0.264	±	0.004	0.277 [d]	±	0.028
W	184	0.041	±	0.005	0.045 [e]	±	0.003

a) Mean ± standard deviation, *n* = 3   b) Literature value, cited from Ref.14

c) Literature value, cited from Ref.18 d) Literature value, cited from Ref. 3

CONCLUSION

An *in-syringe* La co-precipitation pre-concentration method was performed for determination of V, As, Se, Sb, and W in seawater samples. High concentration of lanthanum in analysis sample was removed by using a cation exchange resins before determination of oxo-anion forming elements by ICP-MS. The removal rate of lanthanum dissolved in 1 M HNO_3 analysis sample was more than 99 %. The recoveries of oxo-anion forming elements were more than 80 %. The observed values of these elements in seawater reference material samples were agreed well with certified values or references.

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