Development of Preconcentration Tools and Techniques for Highly Sensitive Multielement Analysis of Natural Water by Analytical Atomic Spectrometry

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Chapter 1   Introduction

1.1   Significance of studies on trace elements in natural water

The total natural water system surrounding the Earth is called the hydrosphere. It includes freshwater masses (river, pond, lake, etc.), oceans, atmosphere vapor, and biological waters.   The Arctic, Atlantic, Indian, and Pacific oceans cover approximately 70% of the Earth surface, and contain 97% of all natural water resource on the Earth.   The rest 3% is fresh water, including ice caps and glaciers.   These natural waters not only dominate the weather and climate on the Earth but also affect our daily lives directly and indirectly.

The natural water are constantly moving among reservoirs, for example, from a river to a lake or to an ocean through surface runoff, from an ocean to the atmosphere through evaporation, to the atmosphere through precipitation, etc..   Because the natural water contacts with the environment during its movement among reservoirs, it gets a variety of elements from the environmental media, such as soil, rock, and so on.[1]   The elements in the natural water might exist as various chemical species, such as cation, anion, complex, colloidal, and suspended particles.[2-5]   At the same time, human activities discharge waste water, solid waste, and aerosol into the environment, which influences the elemental component of the natural water.

Concentrations of the elements in the North Pacific Ocean water[6] and Lake Biwa water[7, 8] are plotted in **Fig. 1-1**.   It can be seen in **Fig. 1-1** that the concentrations of the elements in the natural water cover a wide range from 10^{-5} to 10^5 µg L^{-1}.   It is noted that the concentrations of Na, Mg, K, and Ca in both kinds of natural water were significantly higher than the concentrations of other elements.   Cations of the above-mentioned four elements are dominant ones in natural water.   Consequently, they are called "major elements" or "matrix elements" in the natural water. [9]   It is noted that the concentrations of matrix elements in seawater are significantly higher than those in lake water.   In fact, the total concentration of Na, Mg, K, and Ca in seawater exceeds 1%, which causes significant interferences with the measurement of trace elements.   Therefore, removal of matrix elements from seawater is commonly necessary prior to the measurement of trace elements in seawater.   On the one hand,

the concentrations of Na, Mg, K, and Ca in seawater of every area on the earth are almost constant, which is one of the characteristics of seawater. The reason could be attributed to the fact that their concentrations in seawater are too high to be affected either by chemical properties of the local crust or by anthropogenic inputs. On the other hand, their concentrations in fresh waters depend on the geochemical properties of drainage basin.

In **Fig. 1-1**, the concentrations of other elements except for Na, Mg, K, and Ca were generally below 10^3 µg L^{-1}; they are trace elements in the natural water. Because of their extremely low concentrations, the variations of their concentrations are sensitive to the anthropogenic inputs and the change of physico-chemical conditions in natural water. As a result, research on trace elements in natural waters attracted much attention from the researchers. They are investigated as the sensitive indicator of the natural water qualities and as probe of monitoring the water cycles.
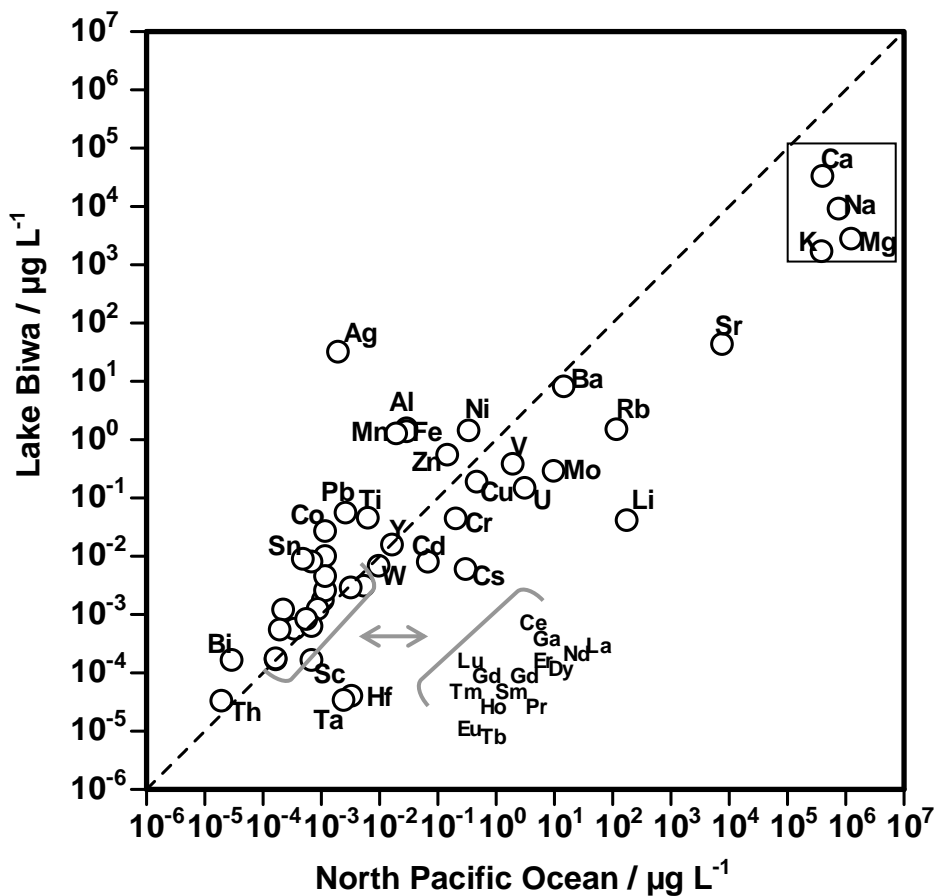
Fig. 1-1 The distribution of the elements in Lake Biwa water [7,8] and North Pacific Ocean [6]

Thanks to the rapid development of analytical atomic spectrometry, there are many analytical atomic spectrometry methods available for element determination, such as flame atomic absorption spectrometry (FAAS), glow discharge atomic absorption spectrometry (GD-AAS), graphite furnace atomic absorption spectrometry (GF-AAS), flame atomic emission spectrometry (FAES), glow discharge atomic emission spectrometry (GD-AES), inductively coupled plasma atomic emission spectrometry (ICP-AES), glow discharge atomic fluorescence spectrometry (GD-AFS), inductively coupled plasma atomic fluorescence spectrometry (ICP-AFS), glow discharge mass spectrometry (GD-MS), and inductively coupled plasma mass spectrometry (ICP-MS).

In the above mentioned methods, ICP-MS is the most popular one [7-10] because of its high sensitivity (exceed 100,000 counts per second when 1 μg L^{-1} of a mono-isotope solution was used for measurement), wide linear dynamic range (up to nine orders of magnitude), and ability to determine multiple elements (approximately 60 elements) simultaneously.

However, direct determination of most trace elements in natural water is still difficult even by ICP-MS, especially for seawater. One of the reason is the extremely low concentration of some trace elements, which are too low to be determined directly by ICP-MS. Another reason is the high-concentration of matrix elements in the samples, which not only cause spectral and non-spectral interferences with trace element measurement but also cause clogging of the introduction system of ICP-MS. In order to overcome these difficulties, preconcentration of trace elements and separation of them from the matrix elements are commonly necessary prior to the determination by ICP-MS.

1.2 Techniques for preconcentration of trace elements in natural water

Preconcentration techniques are required for measuring trace elements in natural water. Enrichment of trace element and removal of matrix elements are the major purposes of preconcentration. [11-13] For highly-precise quantification, trace elements

need to be enriched with a higher recovery (R) and a higher preconcentration factor (P).   The R and P can be defined with the Eqs. (1) and (2), respectively.

$$R \; = \; ([M]_{spiked} - [M]_{nonspiked}) / [M]_{added} \; \times \; 100\% \quad\quad (1)$$

$$P \; = \; V_i / V_a \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (2)$$

where $[M]_{spiked}$ and $[M]_{nonspiked}$ are the concentrations of element M observed in spiked sample and in nonspiked sample, respectively; $[M]_{added}$ is the known concentration of element M added to the spiked sample; V_i and V_a are the volume of the initial sample used for preconcentration and that of the analysis solution after preconcentration, respectively.

Based on the chemical mechanism, preconcentration techniques used for determining trace elements in natural water can be classified into three major types: coprecipitation [14-26], solvent extraction [27-32], and solid phase extraction [33-51].

1.2.1   Coprecipitation

Coprecipitation is one of the classical techniques for preconcentration of trace elements, in which trace elements are collected with precipitates formed in the sample solution after adding a small amount of coprecipitant reagent.   The major mechanisms of coprecipitation are surface adsorption, occlusion, inclusion, mixed crystal formation, and post precipitation.   Coprecipitation has been widely applied to preconcentration of trace element in natural water after the work by Bonner and Kahn[14].   Coprecipitation techniques can be classified into inorganic coprecipitation and organic coprecipitation according to the chemical properties of precipitate collector.   Some examples of coprecipitation for preconcentration of trace elements in natural water are summarized in **Table 1-1**.

In inorganic coprecipitation, trace elements are collected by hydroxides [15-20,21], oxide [19], or phosphates [20], etc..   It is noted that coprecipitation using hydroxides as the carrier of trace elements is the most often used one in inorganic coprecipitation, for example $Fe(OH)_3$, $Mn(OH)_3$, $Al(OH)_3$, $La(OH)_3$, $Zr(OH)_3$, $Th(OH)_3$, $Mg(OH)_2$, and $Ni(OH)_2$.   The reason can be attributed to two major facts.   One is that the hydroxides of most metals are insoluble in neutral pH solutions, which indicate that

the hydroxide carriers can preconcentrate most metals.   The other is that anion matrix is not generated from the carrier after dissolution of hydroxides with an acid solution, which benefit the measurement of trace elements.

In organic precipitation, trace elements are collected as metal complex with organic reagents, which usually have better selectivity for metals ion than inorganic reagents.[11-13]   The organic reagents, which often cause interferences with the measurements of trace elements, in the preconcentrated sample can be removed by combustion.

Table 1-1   Example of preconcentration of trace element by co-precipitation

Precipitated elements	Precipitant	pH condition and operation	Method of determination	Sample	Ref. / year
Inorganic					
Se (IV)	Fe (III) hydroxide	pH 5-6	Spectrometry	Seawater	15 / 1965
V, Mo, U					16 / 1966
As, Sb, Bi, Se, Te	La - hydroxide	pH 9	Hydride generation	River water	17 / 1981
V, Cr(III), Mn, As(III/V), Se(IV), Y, Sn, Sb(III), Sb(V), W, Bi, U		pH 9.5	ICP-MS	Seawater	18 / 2000
As III, As V-	Hf (IV) hydroxide	pH 9	Hydride generation AAS	Spiked water	20 / 1992
Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Y, Zr, Sn, La, Pb, Th, U	Gallium	pH 10	ICP-MS & ICP-AES	Seawater	21 / 1995
Mo	Mn (IV) oxide	pH 5-6	Electrothermal-AAS	River water	19 / 1999
Fe(III), Pb	La-phosphate	pH 3	ICP-AES	Spiked water	22 / 2001
Organic					
Cu, Ni, Cd	Co-PDTC		Flameless - AAS	Seawater	24/ 1977
Cu, Fe, Pb, Mn, Zn, Cd, Ni	Co-DDTC	pH 6	AAS	Seawater	23/ 1997
Se, Cu, Pb, Zn, Fe, Co, Ni, Mn, Cr, Cd	Na-DDTC	pH > 4.5	ICP-AES	River water	25 / 1998
As (III), As (V)	Ni-PDTC	pH 2-3	Electrothermal - AAS	Seawater	26 / 2004.

1.2.2 Solvent extraction

Solvent extraction, also known as liquid-liquid extraction, is another technique used for preconcentration of trace elements in natural water. Preconcentration of trace elements using solvent extraction is based on the relative solubilities of trace elements in water and in an organic solvent that is immiscible with water. [11-13] The organic solvent by itself cannot extract trace elements from the water since trace elements exist as ionic species, which are highly electrostatic. Therefore, chelating reagents, such as dithizone[27], 8-hydroquinoline[28], APDTC[29-31], and DDTC[31], are commonly added into the organic solvent for extraction of trace elements. **Table 1.2** summarized some examples of researches on solvent extraction for preconcentration of trace elements in natural water. In most cases, trace elements extracted into the organic solvent are re-extracted into an acid solution so that the measurements can be easily performed with an atomic spectrometer. [30, 31]

Table 1-2 Example of preconcentration of trace elements by solvent extraction

Elements to concentrate	Complexes agent and solvent	Experiment condition and operation	Method of determination	Sample	Ref. / year
Co, Cu, Pb, Ni, Zn	APDC MIBK	pH 4 - 5	Flame AAS	Seawater	29 / 1967
Cu, Ni, Fe, Mn, U, Co	8-hydroquinoline $CH_3OH–CHCl_3$	A kinetic clamp pump and a ring over were used in deposition step.	X ray fluororesence spectrometry	Seawater	28 / 1971
Cd, Cu, Fe, Ni, Pb, Zn	APDC-DDTC $CHCl_3$/Freon/MIBK	pH 4.5 Bach extraction by using HNO_3	Flame AAS	Seawater	31 / 1981
Cd, Co, Cu, Fe, Ni, Pb, Zn	APDC DIBK	pH 4.5 Bach extraction by using Hg solution	Graphite Furnace AAS	Seawater	30 / 1996
Zn, Cd, Cu	Dithizone- MIBK	pH 4.3	Graphite Furnace AAS	Artificial water sample	27 / 2005

MIBK = methyl-isobutyl ketone.   DIBK = di-isobutyl ketone.

1.2.3 Solid phase extraction

The principles of solid phase extraction (SPE) are similar to those of solvent extraction, except for that the organic solvent phase was replaced by a solid phase. The solid phase could be cation-exchange resin, anion-exchange resin, chelating resin,[33-42] or silica and activated carbon,[43-50] or organic porous polymers such as styrene-divinylbenzene, polyurethane, cellulose, chitin and chitosan.[51,52] The most common base of the resins used in SPE is the synthetic copolymers of polystyrene and divinylbenzene (PV-DVB), to which ion exchange or chelating functional groups were introduced.[11] Generally, nitrogen (as amines, amides, nitriles), oxygen (as carboxylic, hydroxyl, phenolic, ether, carbonyl) and sulfur (as thiols, thiocarbamates, thioethers) are the key atoms of functional groups in SPE.[53,54]

By avoiding the use of harmful organic solvent, SPE techniques are environmentally unfriendly alternative approaches compared with solvent extraction.[54,55] Nowadays, SPE techniques are often applied for determinations of trace elements in natural water, [33-52] which can be attributed to the advantages of simpler operation, higher concentration factor, less sample volume requirement, and more convenient to automation. In SPE techniques, chelating resins are the most preferred solid phase because of their high selectivity to trace elements, [33-35] most of which are transition metals. Chelating resins also have the merits of high exchange velocity and capacity, high physical and chemical stability, and reusability. [11] Another merit of chelating resins is that they form extremely weak complexes with Ca and Mg and do not form complexes with Na and K, which benefit to the effective removal of matrix elements during preconcentration of trace elements in seawater. Some researches on development of SPE methods for preconcentration of trace elements in natural water are summarized in **Table 1-3.**

In SPE operations for preconcentration of trace elements in natural water, the samples were adjusted to an optimum pH condition and passed through the solid phase so that trace elements can be retained. These trace elements were then eluted from the solid phase by an appropriate solvent and subjected to measurement.[54,55] **Fig. 1-2** illustrates a representative procedure of SPE method for preconcentration of trace elements in natural water. It is noted that the first step in **Fig. 1-2** is washing and conditioning of the solid phase. The reason is that commercial available resins often have impurities of trace elements, which are not negligible compared with the concentrations of trace elements in natural water sample.

Table 1-3 Example of preconcentration of trace element in natural water by solid
phase extraction

Sorbent	Adsorbent elements	Operation / exp. condition	Method of determination	Sample	Ref. / year
Silica	Cu, Co, Ni, Fe	Glass column	X ray fluorescence	Lake water	43 / 1976
Silica – 8-HQ	Cd, Pb, Zn, Cu, Fe, Mn., Ni, Co	Glass column / pH 8	GF-AAS	Seawater	44 / 1981
Silica – APDTC	Cd	C_{18} column / pH 2	On-line GF-AAS	Seawater	45 / 1998
Silica - PT [a]	Cu, Cd, Co	C_{18} column- / pH 5-6	FI-on-line FAAS	Seawater	46 / 1999
Chelex 100	Mn, Fe, Zn, Al, Ti, Cd, Co, Ni, Cu, Ag, Ta, Bi, Ba, Sc, Mg	Glass column / pH 7.6	AAS	Seawater	33 / 1968
Chelex 100	REEs	Polyethylene bag / pH 6	Neutron - activation	River water	34 / 1978
Chelex 100	MN, Fe, Co, Zn, Ni, Cu, Cr	Bath / pH 5.5 – 6.6	ICP-AES	Seawater	35 / 1984
Amberlite XE-305 - 8-HQ	Cd, Zn, Pb, Cu, Fe, Mn, Ni, Cr, Co	Glass column / pH 8	ET-AAS	Seawater	36 / 1983
TSK - 8-HQ	Al, Mn, Fe, Co, Cu, Zn, Cd	Glass column / pH 7	AAS	Seawater	37 / 1986
MAF - 8-HQ	V, Co, Ni, Ga, Y, Mo, Cd, REEs, W, U	PFA[b] Column / pH 5	HR-ICP-MS	Seawater	38 / 1998
PAN [c] – 8-HQ	REEs	Glass column / pH 6	ICP-MS	Seawater	52 / 1999
Muromac A-1	Al, V, Mn, Co, Ni, Cu, Zn, Mo, Cd, Pb, U	PFA[b] column / pH 5	On-line ICP-MS	Seawater	39 / 2001
Activated alumina	Cr (III), Cr (VI)	PTFE column / pH 7 for Cr (III), pH 2 for Cr (VI)	FI- FAAS	Lake water and tap water	47 / 1992
Activated carbon - PV [c]	Cu, Mn, Co, Cd, Ni, Cr	Column / pH 4 - 8	AAS	Drinking water	48 / 2000
NTA [d]	Mn, Co, Ni, Cu, Zn, Cd, Sb, Pb, U, REEs,	PEEK[e] -chromatographic column / pH 5.28	On-line IC-ICP-MS	Seawater	40 /1998
AAPTC [f]	REEs	Column / pH 3-6	ICP-MS	Seawater	50 / 1998
AF Chelate 650M	REEs	Column / pH 5.5	FI-on-line-ICP -TOF-MS	Seawater	41 / 2001
Chromosorb-103 - 8-HQ	Fe, Pb	SCM[g] / pH > 6	FAAS	River water	42 / 2005
APAR [h]	REEs	Column (4.6 mm x 50 mm) / pH 6	FI-ICP-MS	Seawater	49 / 2007

[a] 1,10 phenanthroline.   [b] Polyethylene low dencity.   [c] Polyacrylonitrile   [d] Nitriloacetate
[e] Polyether ether ketone   [f] Poly(acrylaminophosphoric dithiocarbamate)
[g] Syringe connected minicolumn.   [h] Alkyl phosphinic acid resin
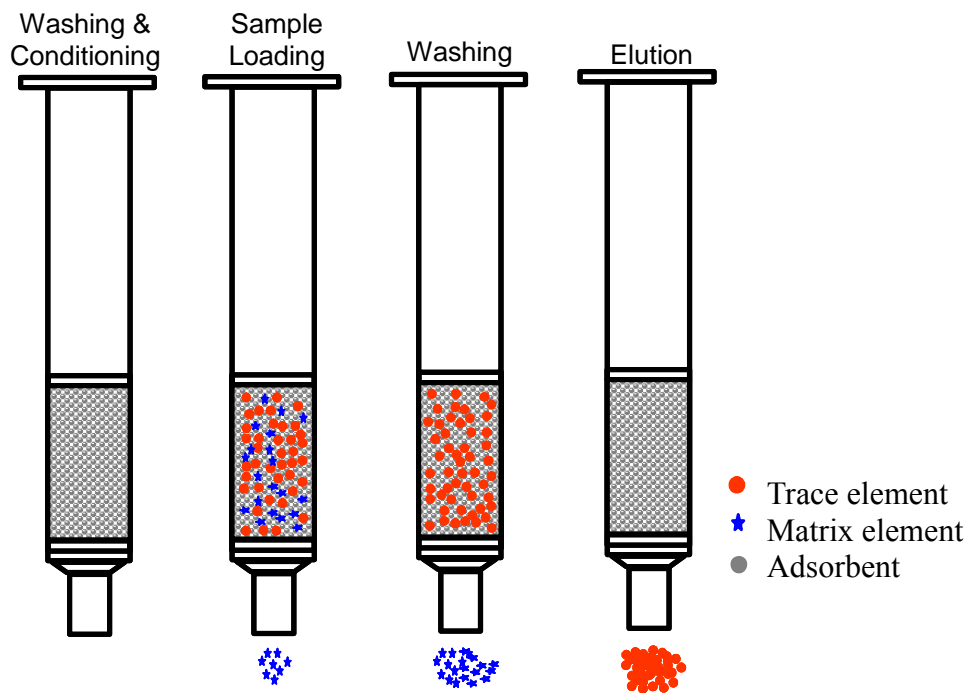
Fig. 1-2   Step process of solid phase extraction

It is also noted that, in **Fig. 1-2**, the chelating resins were packed in a syringe body.   This kind of devices is convenient for multi-sample processing and on-site pretreatment.   Another kind of devices is chelating resins packed in a column mountable to and removable from a syringe, which permits both the on-site treatment and the on-line connection and on-line measurement of trace elements.

1.3 Proposal of monolithic chelating adsorbent for preconcentration of trace elements in natural water

Over the last decade, monolithic columns have emerged as an alternative to traditional particle packed-columns, and have steadily gained acceptance due to the novel characteristics such as high permeability and efficient mass transfer, allowing high-speed separation with minimum loss of column efficiency. [56-62]

Monolith is a continuous unitary porous material with a bimodal pore structure.

The concept and prototype development of monolithic separation media had already been reported at the end of the 1960s [63-66], but nearly two decades were required before Hjerten *et al.* developed compressed soft polyacrylamide gels called "continuous beds" and successfully applied them to the chromatographic separation of proteins in 1989. [67]   Subsequently, Svec and Frechet in 1992 introduced rigid macroporous organic polymer monoliths and afforded distinct procedure and vision for the preparation. [68]   By virtue of their systematic studies on the control of porous properties, various novel organic polymer monoliths have been produced and extensively applied to chromatographic and electrophoretic separations mainly for large biomolecules such as proteins and DNA. [69-73]   Shortly afterward, in 1996, practically useful silica-based monoliths were also produced by Minakuchi *et al.* [74], and became commercially available in 2000. [56-59, 75-80]

These silica-based and organic polymer-based monoliths have their own advantages and disadvantages.   Silica monoliths produced by a sol–gel process have quite regularly controlled pore structures and enable highly efficient separations especially for small molecules.   However, silica-based monoliths suffer from its weak resistance to high pH.   Side effects from silanol, which often cause irreversible adsorption, may also be a serious problem, especially in the analysis of biological samples.   In contrast, organic polymer monoliths may be a little bit inferior to silica monoliths in terms of mechanical strength and fine control of the skeletal and through-pore sizes.   But substantially, organic polymer monoliths have several potential advantages and promising future.   In addition to wide pH stability and absence of deleterious silanol effect, the flexibility and versatility of organic polymer in modification including molecular imprinting may be particularly beneficial for further advancement.   Then, the applications are now extended from the original separation media to solid-phase extractors and microreactors. [81-83]

1.4 Objectives of the present research

The main objective of the present research is to develop simple and practically useful preconcentration tools and techniques for trace elements in natural water samples.   In particular, the attention was focused on the development of practical

procedures with minimal complications and minimum sample consumption. Throughout the present work, sample handling for preconcentration was manually carried out with a syringe and a syringe-mountable filter tip. Therefore, it can be used for on-site pretreatment of natural waters. The use of a monolithic adsorbent in SPME of trace metals in another main subject and is reported in the latter part.

In Chapter 2, the downsizing of a chelating resin-packed minicolumn is described, where two commercially available syringe filters and a small amount (0.088 g in wet weight) of chelating resin (Chelex 100, 200-400 mesh, Bio Rad Laboratories) are used. The preconcentration conditions, such as sample solution pH for metal adsorption, sample loading flow rate, rinsing solution for eliminating matrix elements, and eluent HNO_3 concentration and volumes for elution of target trace metals, were optimized, in order to obtain higher recoveries. The optimized method was applied to the preconcentration of trace elements in seawater certified reference materials (CRMs ; CASS-3, NASS-4, and NASS-5).

In Chapter 3, a tandem preconcentration method using a chelating resin-packed minicolumn and La-coprecipitation is attempted for the determination of as many elements as possible by ICP-MS. After the optimization, 56 elements in Lake Baikal water could be determined.

In Chapter 4, an *in-syringe* La-coprecipitation method with a low sample consumption was exploited for preconcentration of oxo-anion forming elements prior to measurement by ICP-MS. The importance of La removal from the analysis solution using a cation-exchange column is discussed in this chapter.

In Chapter 5, a syringe-based sample preconcentration tool, named "tip-in chelating monolith" is proposed for simple and facile solid phase microextraction (SPME) of trace elements in natural waters. The tip-in monolith was directly prepared inside a commercially available syringe filter tip by a two-step process: 1) in situ polymerization of glycidyl methacrylate (GMA) with ethylene glycol dimethacrylate (EDMA) and 2) subsequent modification with iminodiacetate (IDA) via ring opening reaction of epoxide. The composition of porogenic solvent was first optimized to make a rigid-porous material that has high permeability and ample surface area as much as possible. Then, the pH and concentration of the IDA modification solution were examined to obtain higher chelating capacity. The metal adsorption properties of the obtained chelating monolith were evaluated through an adsorption/desorption experiment. After optimization of some parameters such as

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sample solution pH, eluent concentration and the volume, good recoveries of more than 80% were obtained for 28 elements including REEs, Fe, Co, Ni, Cu, Zn, Ga, Pb and Th in a single extraction step. The proposed SPME method was validated through the analysis of two river water certified reference materials (CRMs: JSAC 0301-1 and NMIJ 7201-a).

Finally, summary of the present research and future prospects are described in Chapter 6.

References

1. Brit Salbu, and Eiliv Stennes, *"Trace Elements in Natural Water"*, CRC Press LLC, (1995).

2. Y. Tanizaki, T. Shimokawa, and M. Yamazaki, *Wat. Res.*, **26**, 55 (1992).

3. G.R. Choppin, *Journal of the Less-Common Metals*, **126**, 307 (1986).

4. T.I. Moiseenko, and N.A. Gashkina, *Water Resources*, **34**, 423 (2007).

5. H.A. Roditi, N.S. Fisher, and S.A. Sanudo-Wilhelmy, *Environ. Sci. Technol.*, **34**, 2817 (2000).

6. H. Haraguchi, *J. Anal. At. Spectrom.*, **19**, 5 (2004).

7. 藤永　太一郎、"海と湖の化学"、京都大学、(2005).

8. H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 1163 (1999).

9. 原口　紘き、生命と金属の世界、名古屋大学、(2005).

10. Y. Zhu, R. Hattori, D. Rahmi, S. Okuda, A. Itoh, E. Fujimori, T. Umemura, and H. Haraguchi, *Bull. Chem. Soc. Jpn,* **78**, 1970 (2005).

11. Zeev B. Alfassi, "*Determination of Trace Elements*", Balaban Publishers, (1994).

12. Z.B. Alfassi, and C.M. Wai, "*Preconcentration Technique for Trace Elements*", CRC Press Inc., Florida, (1992).

13. Y.A. Zolotov, and N.M. Kuzmin, *"Preconcentration of Trace Elements"*, Elsevier, Tokyo, (1990).

14. Bonner NA, and Kahn M., *Nucleonics*, **8**, 40 (1951).

15. Y.K. Chau, and J.P. Riley, *Anal. Chim. Acta,* **33**, 36 (1965).

16. K.M. Chan and J.P. Riley, *Anal. Chimi. Acta*, **34**, 337 (1966).

17. M. Thomson, B. Pahlavanpour, and L.T. Thorne, *Water Research*, **15**, 407 (1981).

18. T. Yabutani, S. Ji, F. Mouri, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **73**, 895 (2000).

19. T. Shimizu, H. Ito, H. Kawaguchi, and Y. Shijo, *Bull. Chem. Soc. Jpn.*, **72**, 43 (1999).

20. J. Ueda, and S. Kagaya, *Bull. Chem. Soc. Jpn.*, **65**, 1496 (1992).

21. H. Sawatari, E. Fujimori, and H. Haraguchi, *Anal. Sci.*, **11**, 369 (1995).

22. S. Kagaya, M.Saiki, Z.A. Malek, Y. Araki, and K. Hasegawa, *Fresenius J. Anal. Chem.,* **371**, 391 (2001).

23. L. Elci, U. Sahin, and S. Oztas, *Talanta*, **44**, 1017 (1997).

24. E.A. Boyle, and J.M. Edmond, *Anal. Chimi. Acta*, **91**, 189 (1977).

25. D. Atanassova, V. Stefanova, and R. Russeva, *Talanta*, **47**, 1237 (1998).

26. Q. Zhang, H. Minami, S. Inoue, and I. Atsuya, *Anal. Sci., Acta*, **508**, 99 (2004).

27. Q. Cheng, and H. Doung, *Anal. Sci.*, **150**, 59 (2005).

28. B. Armitage, and H. Zeitlin, *Anal. Chimi. Acta,* **53**, 47 (1971).

29. R.R. Brooks, B.J. Presley, and I.R. Kaplan, *Talanta,* **14**, 809 (1967).

30. G.J. Batterham, and D.L. Parry, *Mar. Chem.*, **55**, 381 (1996).

31. B. Magnusson and S. Westerlund, *Anal. Chim. Acta.*, **131**, 63 (1981).

32. Frank J. Welcher, Ph.D, "*Standard Methods of Chemical Analysis*", sixth edition, D.Van Nostrand co.Inc, (1962).

33. J.P. Riley, and D. Taylor, *Anal. Chimi. Acta*, **40**, 479 (1968).

34. A. Hirose, and K. Ishii, *Anal. Chimi. Acta*, **97**, 303 (1978).

35. R. Boniforti, R. Ferraroli, P. Frigieri, D. Heltai, and G. Queirazza, *Anal. Chim. Acta*, **162**, 33 (1984).

36. S.N. Willie, R.E. Sturgeon, and S.S. Berman, *Anal. Chem. Acta*, **149**, 59 (1983).

37. W.M. Landling, C. Haraldsson, and N. Paxeus, *Anal. Chem.*, **58**, 3031 (1986).

38. Y. Sohrin, S. Iwamoto, S. Akiyama, T. Fujita, T. Kugii, H. Obata, E. Nakayama, S. Goda, Y.Y. Fujushima, H. Hasegawa, K. Ueda, and M. Matsui., *Anal. Chim. Acta*, **363**, 11 (1998).

39. S. Hirata, Y. Ishida, M. Aihara, K. Honda, and O. Shikino, *Anal. Chem. Acta*, **438**, 205 (2001).

40. H. Kumagai, M. Yamanaka, T. Sakai, T. Yokoyama, T.M. Suzuki, and T. Suzuki, *J. Anal. At. Spectrom.*, **13**, 579 (1998).

41. S.N. Willie, and R.E. Sturgeon, *Spectrochim. Acta Part B*, **56**, 1707 (2001).

42. Y. Bakircioglu, D. Bakircioglu, and N. Tokman, *Anal. Chimica Acta*, **547**, 26 (2005).

43. D.E. Leyden, G.H.Luttrell, A.E.Sloan, and N.J. DeAngells, *Anal. Chim Acta*, **84**, 97 (1976).

44. R.E. Sturgeon, S.S. Berman, S.N. Willie, and J.A. Desauliers, *Anal. Chem.*, **53**, 2337 (1981).

45. D. Colbert, K.S. Johson, and K.H. Coale, *Anal. Chimi. Acta*, **377**, 255 (1998).

46. A. Ali, X. Yin, H. Shen, Y. Ye, and X. Gu, *Anal. Chim. Acta*, **392**, 283 (1999).

47. M. Sperling, S. Xu, and B. Welz, *Anal. Chem.*, **64**, 3101 (1992).

48. I. Narin, M. Soylak, L. Elci, and M. Dogan, *Talanta,* **52**, 1041 (2000).

49. Q. Fu, L. Yang, and Q. Wang, *Talanta*, **72**, 1248 (2007).

50. T. Zang, X. Shan, R. Liu, H. Tang, S. Zhang, *Anal. Chem.*, **70**, 3964 (1998).

51. Riccardo A.A., Muzzarelli, and Ottavio T., *Talanta*, **16**, 1571 (1969).

52. B.Wen, X-G. Shan, and S-G. Xu, *Analyst*, **124**, 621 (1999).

53. E.M. Thurman, M.S. Mills, *Solid-Phase Extraction; Principles and Practice*, Wiley, New York, (1998).

54. Valerie Camel, *Spectrochimica Acta Part B*, **58**, 1177 (2003).

55. F.C. Nachod, and W. Wood, *J. Am. Chem. Soc.*, **67**, 629 (1945).

56. K. Cabrera, D. Lubda, H.-M. Eggenweiler, H. Minakuchi, K.Nakanishi, *J. High Resol. Chromatogr.*, **23**, 93 (2000).

57. P. Hatsis, C.A. Lucy, *Analyst*, **127**, 45 (2002).

58. E. Sugrue, P.N. Nesterenko, B. Paull, *J. Chromatogr. A*, **1075**, 167 (2005).

59. D.A. Volmer, S. Brombacher, B. Whitehead, *Rapid Com. MS*, **16**, 2298 (2002).

60. A. Podgornik, M. Barut, J. Jančar, A. Štrancar, T.B. Tennikova, *Anal. Chem.*, **71**, 2986 (1999).

61. S. Xie, R.W. Allington, F. Svec, J.M.J. Fréchet, *J. Chromatogr. A*, **865**, 169 (1999).

62. D. Lee, F. Svec, J.M.J. Fréchet, *J. Chromatogr. A*, **1051**, 53 (2004).

63. M. Kubín, P. Špaček, R. Chromeček, Coll. Czechosl. *Chem. Commun.,* **32**, 3881 (1967).

64. W.D. Ross, R.T. Jefferson, *J. Chromatogr. Sci.,* **8**, 86 (1970).

65. L.C. Hansen, R.E. Sievers, *J. Chromatogr.,* **99**, 123 (1974).

66. T.R. Lynn, D.R. Rushneck, A.R. Cooper, *J. Chromatogr. Sci.*, **12**, 76 (1974).

67. S. Hjérten, J.L. Liao, R. Zhang, *J. Chromatogr.,* **473**, 273 (1989).

68. F. Svec, J.M.J. Fréchet, *Anal. Chem.*, **54**, 820 (1992).

69. C. Ericson, S. Hjertén, *Anal. Chem.*, **71**, 1621 (1999).

70. A.K. Palm, M.V. Novotny, *Rapid Commun. Mass Spectrom.*, **18**, 1374 (2004).

71. E.F. Hilder, F. Svec, J.M.J. Fréchet, *Anal. Chem.,* **76**, 3887 (2004).

72. G. Hlözl, H. Oberacher, S. Pitsch, A. Stutz, C.G. Huber, *Anal. Chem.,* **77**, 673 (2005).

73. S. Zhang, X. Huang, J. Zhang, C. Horváth, *J. Chromatogr. A*, **887**, 465 (2000).

74. H. Minakuchi, K. Nakanishi, N. Soga, N. Ishizuka, N. Tanaka, *Anal. Chem.*, **68**, 3498 (1996).

75. N. Ishizuka, H. Minakuchi, K. Nakanishi, N. Soga, H. Nagayama, K. Hosoya, N. Tanaka, *Anal. Chem.*, **72**, 1275 (2000).

76. A. Asperger, J. Efer, T. Koal, W. Engewald, *J. Chromatogr. A*, **937**, 65 (2001).

77. M. Kele, G. Guiochon, *J. Chromatogr. A*, **960**, 19 (2002).

78. D.V. McCalley, *Anal. Chem.*, **75**, 3404 (2003).

79. B. Chankvetadze, T. Ikai, C. Yamamoto, Y. Okamoto, *J. Chromatogr. A,* **1042**, 55 (2004).

80. K. Kato, M.J. Silva, L.L. Needham, A.M. Calafat, *Anal. Chem.*, **77**, 2985 (2005).

81. D. Moravcová, P. Jandera, J. Urban, J. Planeta, *J. Sep. Sci.,* **26**, 1005 (2003).

82. P. Coufal, M. Čihák, J. Suchánková, E. Tesařová, Z. Bosáková, K. Štulík, *J. Chromatogr. A,* **946**, 99 (2002).

83. Y. Ueki, T. Umemura, J. Li, T. Odake, K. Tsunoda, *Anal. Chem.*, **76**, 7007 (2004).

Chapter 2   Multielement Determination of Trace metals in Seawater by ICP-MS with Aid of Down-sized Chelating Resin-packed Minicolumn for Preconcentration

2.1 Introduction

Nowadays, 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 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, our research group have reported a chelating resin-packed 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 Micro Mist nebulizer is now commercially available as a micro-sampling device, which can be operated efficiently at very low solution uptake rates (down to 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 Micro Mist nebulizer. Thus, the combined system of ICP-MS with a Micro Mist 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).

2.2 Experimental

2.2.1 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 2-1**, 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 2-1**. 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.

2.2.2 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 μg 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 2-2**, in which Ge, In, Re, and Tl were added as the internal standard elements to be 10 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 μm) and acidified to pH 1 with conc. nitric acid.

2.2.3 Design of a down-sized chelating resin-packed minicolumn

The structure of the down-sized chelating resin-packed minicolumn is shown in **Fig. 2-1**, 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. 2-1**, the size of the minicolumn was 34 mm×17 mm, while that of the old one was 39 mm×29 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.   The pore sizes of built-in membrane filters (d) in both syringe filters were 0.45 μm.   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 ± 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).

Table 2-1   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^{-1}	Ar 15.0 L min^{-1}
auxiliary gas flow rate	Ar 1.0 L min^{-1}	Ar 1.0 L min^{-1}
carrier gas flow rate	Ar 1.0 L min^{-1}	Ar 1.0 L min^{-1}
sampling depth	5.5 mm from load coil	9 mm from load coil
Nebulizer:	MicroMist	Conikal
sample uptake rate	0.1 mL min^{-1}	1 mL min^{-1}
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

Table 2-2   Multielement standard solutions for calibration [a]

Group	Element	Concentration / ng mL^{-1}
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

[a] Each of the multielement standard solutions contains Ge, In, Re, and Tl (10 ng mL^{-1} each) as internal standard elements.
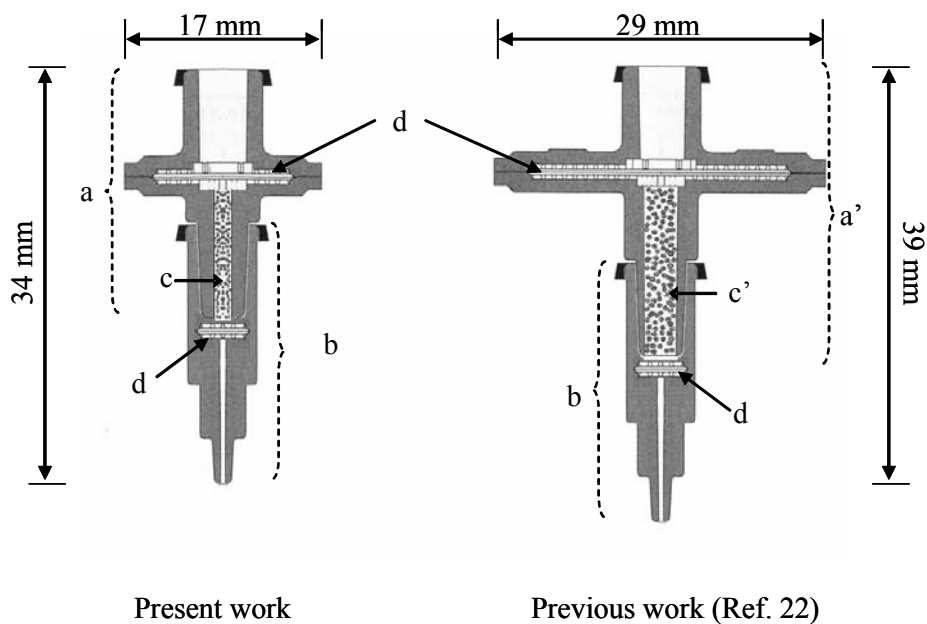
Fig. 2-1 A schematic structure of the chelating resin-packed minicolumn. (a) prefilter tube (DISMIC-13HP, ADVANTEC); (a') prefilter tube (DISMIC-25HP, ADVANTEC); (b) prefilter tube (Millex-LH, Nihon Millipore Kogyo); (c) Chelex 100 resin, 200-400 mesh, 0.088 g; (c') Chelex 100 resin, 100-200 mesh, 0.40 g; (d) built-in membrane filter (pore size 0.45 μm)

2.2.4 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^{-1} 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^{-1} 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 HNO3 into a test tube, in which 0.05 mL of internal standard solution (Ge, In, Re, and Tl; 100 ng mL^{-1} 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.

2.3 Results and Discussion

2.3.1 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^{-1} at the interval of 0.2 mL min^{-1}, 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^{-1}, 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^{-1} was chosen as the optimum condition to obtain the better recovery.

2.3.2 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 mL min^{-1} with the KDS200 syringe pump. The elution signal profile of Ca is shown in **Fig. 2-2**, as a typical example.   It is seen from **Fig. 2-2** 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 μg mL^{-1}, respectively.   As a result, the total concentration of Na, K, Mg, and Ca in the analysis solution was less than 100 μg 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.
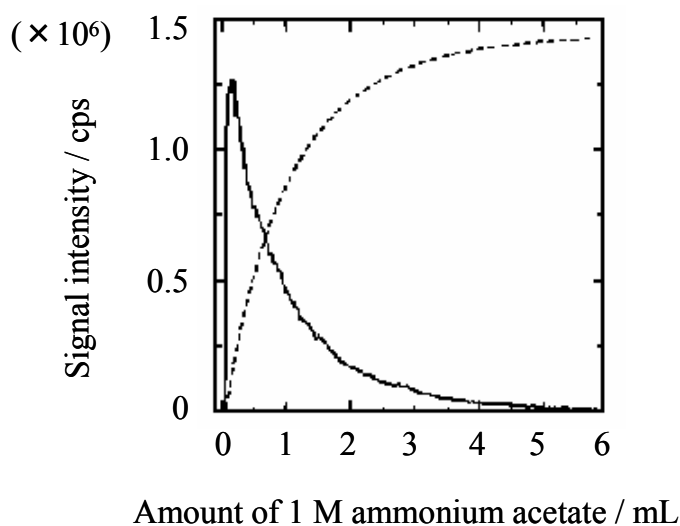
Fig. 2-2   Elution signal profile of Ca^{2+} from the minicolumn with 1 M ammonium acetate (pH 6.0)

2.3.3 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 mL min-1 with the KDS200 syringe pump.   The signal profiles for Zn, Cu, and Y are shown in **Fig. 2-3**, 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.
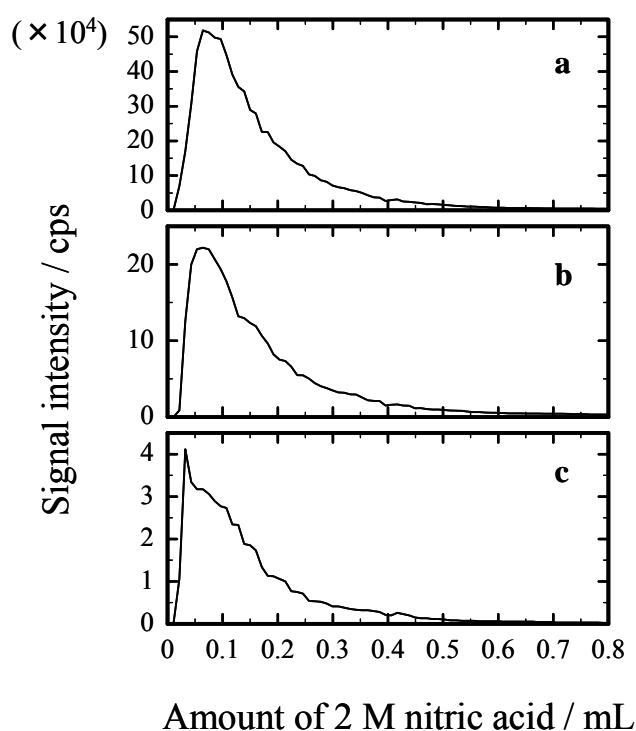
Fig. 2-3   Elution signal profiles of trace metals from
the minicolumn   with 2 M nitric acid
a, Zn;   b, Cu;   c, Y

2.3.4 Analytical figures of merit

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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 2-3**, 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 2-3**, 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.   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^{-1} each).   The analytical detection limits for 24 elements were in the range from 0.001 ng mL^{-1} of Ni to 0.000006 ng mL^{-1} 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^{-1}, 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 $^{44}Ca^1H+$, $^{43}Ca^{16}O$, $^{43}Ca^{16}O^1H^+$, $^{48}Ca^{16}O^1H^+$, and $^{141}Pr^{16}O$ with ^{45}Sc, ^{59}Co, ^{60}Ni, ^{65}Cu, and ^{157}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.

Table 2-3 Recoveries and analytical detection limits for trace metals

Element	m/z	Spike / ng mL^{-1}	Recovery, [a] %			ADL / ng mL^{-1}	
						Present work [b]	Previous work [c]
Co	59	1.00	96.3	±	0.4	0.00003	0.0004
Ni	60	1.00	95.2	±	0.2	0.001	0.002
Cu	65	1.00	95.4	±	0.9	0.0003	0.001
Zn	68	1.00	89.9	±	0.8	0.0007	0.009
Y	89	0.100	85	±	1	0.000008	0.0001
Cd	111	1.00	89	±	1	0.0006	0.003
La	139	0.100	85.9	±	0.5	0.00001	0.0001
Ce	140	0.100	86.8	±	0.7	0.00001	0.0001
Pr	141	0.100	86.7	±	0.6	0.000006	0.00007
Nd	143	0.100	92	±	2	0.00006	0.0003
Sm	147	0.100	85.3	±	0.9	0.00003	0.0005
Eu	153	0.100	85.3	±	0.2	0.00001	0.0001
Gd	157	0.100	86.4	±	0.4	0.00005	0.0004
Tb	159	0.100	85.9	±	0.7	0.000006	0.00008
Dy	163	0.100	87.2	±	0.3	0.00002	0.0003
Ho	165	0.100	85.6	±	0.1	0.00001	0.00007
Er	166	0.100	87	±	1	0.00003	0.0002
Tm	169	0.100	87.1	±	0.5	0.000008	0.00008
Yb	172	0.100	86	±	1	0.00003	0.0003
Lu	175	0.100	87.5	±	0.4	0.000006	0.00006
Pb	207	1.00	89.3	±	0.4	0.0001	0.001
U	238	10.0	97.6	±	0.5	0.00002	0.00008
V	51	10.0	39.5	±	0.4	0.0001	0.0007
Mn	55	10.0	40.3	±	0.5	0.0006	0.02
Mo	98	10.0	28	±	1	0.0005	0.001

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

Table 2-4　Analytical results for trace metals in seawater CRMs

Element	m/z	Observed value [a] / µg L^{-1}			Certified value / µg L^{-1}		
CASS-3							
(V) [b]	51	(1.4	±	0.2)	1.43	±	0.04 c
(Mn) [b]	55	(2.8	±	0.3)	2.51	±	0.36
Co	59	0.038	±	0.002	0.041	±	0.009
Ni	60	0.38	±	0.03	0.39	±	0.06
Cu	65	0.48	±	0.03	0.52	±	0.06
Zn	68	1.4	±	0.2	1.24	±	0.25
(Mo) [b]	98	(9.0	±	0.5)	8.95	±	0.26
Cd	111	0.031	±	0.003	0.030	±	0.005
Pb	207	0.010	±	0.005	0.012	±	0.004
U	238	3.0	±	0.2	2.84 [d]		
NASS-4							
(V) [b]	51	(1.3	±	0.3)	1.18	±	0.16
(Mn) [b]	55	(3.0	±	0.3)	2.78	±	0.19
Co	59	0.010	±	0.002	0.009	±	0.001
Ni	60	0.22	±	0.02	0.228	±	0.009
Cu	65	0.21	±	0.01	0.228	±	0.011
Zn	68	0.12	±	0.03	0.12	±	0.02
(Mo) [b]	98	(8.5	±	0.6)	8.78	±	0.86
Cd	111	0.018	±	0.001	0.016	±	0.003
Pb	207	0.012	±	0.004	0.013	±	0.005
U	238	3.0	±	0.2	2.68	±	0.12
NASS-5							
(V) [b]	51	(1.0	±	0.3)	1.2 [d]		
(Mn) [b]	55	(0.88	±	0.6)	0.919	±	0.057
Co	59	0.011	±	0.001	0.011	±	0.003
Ni	60	0.24	±	0.00	0.25	±	0.03
Cu	65	0.27	±	0.01	0.30	±	0.05
Zn	68	0.07	±	0.04	0.10	±	0.04
(Mo) [b]	98	(9.3	±	0.7)	9.6	±	1.0
Cd	111	0.024	±	0.001	0.023	±	0.003
Pb	207	0.006	±	0.003	0.008	±	0.005
U	238	2.8	±	0.1	2.60 [d]		

[a] Mean ± standard deviation, $n = 5$.　[b] Recovery values were less than 85%.
[c] Reference value, cited from Ref. 11.　[d] Information value issued by NRCC.

Table 2-5   Analytical results for REEs in seawater CRMs

Element	m/z	Concentration [a]/ ng L⁻¹					
		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	± 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	0.20	± 0.02

[a] Mean ± standard deviation, n = 5.

Table 2-6   Compiled data for the concentrations of REEs in seawater CRMs

Element	m/z	Concentration [a]/ ng L⁻¹					
		CASS-3 [a]		NASS-4 [b]		NASS-5 [c]	
Y	89	23.6 [d]		18.7 [e]		20.7 [f]	
La	139	13	± 2	9	± 1	12.2	± 0.5
Ce	140	5.4	± 0.9	3.9	± 0.4	4.6	± 0.6
Pr	141	1.9	± 0.2	1.54	± 0.07	1.8	± 0.3
Nd	143	8.3	± 0.5	7.4	± 0.2	9	± 1
Sm	147	6.7	± 0.1	3.2	± 0.3	4.3	± 0.3
Eu	153	0.36	± 0.03	0.26	± 0.03	0.27	± 0.02
Gd	157	2.3	± 0.7	1.7	± 0.7	1.57	± 0.04
Tb	159	0.32	± 0.06	0.24	± 0.05	0.25	± 0.04
Dy	163	2.0	± 0.1	1.63	± 0.06	1.71	± 0.09
Ho	165	0.50	± 0.02	0.40	± 0.03	0.39	± 0.04
Er	166	1.6	± 0.2	1.4	± 0.1	1.35	± 0.03
Tm	169	0.23	± 0.02	0.18	± 0.01	0.16	± 0.02
Yb	172	1.5	± 0.2	1.2	± 0.1	1.14	± 0.05
Lu	175	0.25	± 0.02	0.18	± 0.02	0.19	± 0.01

[a] Mean ± standard deviation, n = 3, calculated from the data in the present work, Refs. 11 and 21.
[b] Mean ± standard deviation, n = 4, calculated from the data in the present work, Refs. 21, 31, and 32.
[c] Mean ± standard deviation, n = 3, calculated from the data in the present work, Refs. 16, and 32.
[d] Mean, n = 2, calculated from the data in the present work and Ref. 11.
[e] Mean, n = 2, calculated from the data in the present work and Ref. 31.
[f] Single data, cited from the present work.

2.3.5 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 2-4**.   It is seen in **Table 2-3** 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.   The analytical results for REEs are summarized in **Table 2-5**.   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 complied 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 2-6**.   As is seen in **Table 2-6**, 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. 2-4**, 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. 2-4** 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.
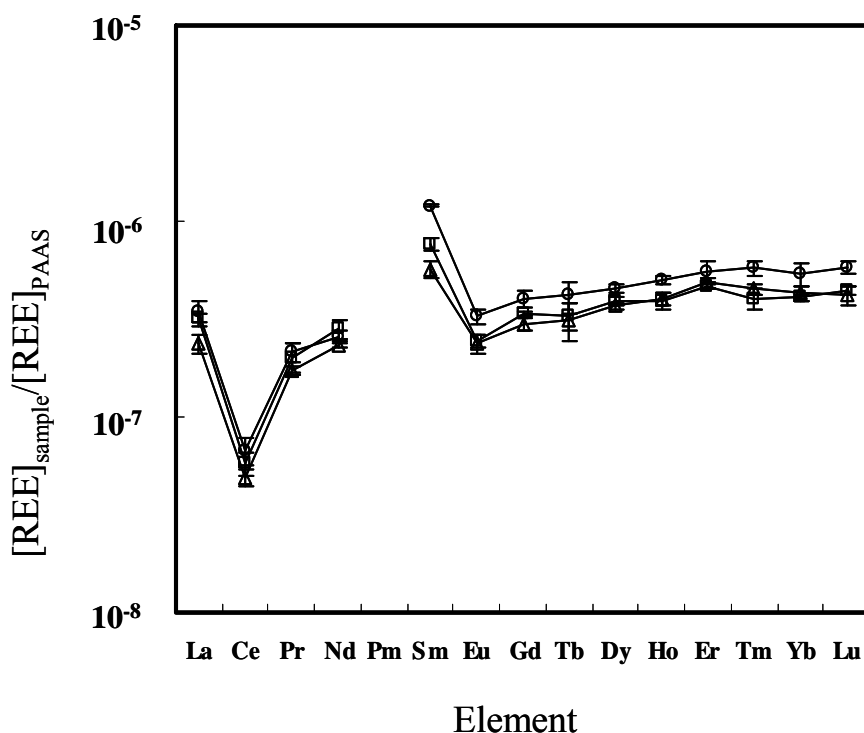

Fig. 2-4   Shale-normalized REE distribution patterns for seawater CRMs, based on their complied data. ○, CASS-3; △, NASS-4; □, NASS-5

2.4 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 $\leq$ 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.

References

1.   H. Haraguchi, *J. Anal. At. Spectrom.*, **19**, 5 (2004).

2.   H. Haraguchi. *Bull. Chem. Soc. Jpn.*, **72**, 1163 (1999).

3.   M.B. Shabani, T. Akagi, H. Shimizu, A. Masuda, *Anal. Chem.*, **62**, 2709 (1990).

4.   G.J. Batterham, N.C. Munksgaard, D.L. Parry, *J. Anal. At. Spectrom.*, **12**, 1277 (1997).

5.   H. Sawatari, T. Hayashi, E. Fujimori, A. Hirose, H. Haraguchi, *Bull. Chem. Soc. Jpn.*, 69, 1925 (1996).

6.   T. Yabutani, S. Ji, F. Mouri, A. Itoh, K. Chiba, H. Haraguchi, *Bull. Chem. Soc. Jpn.,* **73**, 895 (2000).

7.   C.L. Chou, J.D. Moffatt, Fresen. *J Anal. Chem.*, **368**, 59 (2000).

8.   D. Weiss, E.A. Boyle, V. Chavagnac, M. Herwegh, J.-F. Wu, *Spectrochim. Acta*, **55B**, 363 (2000).

9.   C.J. Cheng, T. Akagi, H. Haraguchi, *Anal. Chim. Acta,* **198**, 173 (1987).

10.   H. Sawatari, T. Toda, T. Saizuka, C. Kimata, A. Itoh, H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **68**, 3065 (1995).

11.   T. Yabutani, S. Ji, F. Mouri, H. Sawatari, A. Itoh, K. Chiba, H. Haraguchi, *Bull. Chem. Soc. Jpn.* **72**, 2253 (1999).

12.   Y. Sohrin, S. Iwamoto, S. Akiyama, T. Fujita, T. Kugii, H. Obata, E. Nakayama, S. Goda, Y. Fujishima, H. Hasegawa, K. Ueda, M. Matsui, *Anal. Chim. Acta*, **363**, 11 (1998).

13.   S. Mito, M. Ohata, N. Furuta, *Bunseki Kagaku*, **52**, 575 (2003).

14. T. Sumida, T. Nakazato, H. Tao, *Bunseki Kagaku*, **52**, 619 (2003).

15. M.S. Jimenez, R. Velarte, J.R. Castillo, *Spectrochim. Acta*, **57B**, 391 (2002).

16. S.N. Willie, R.E. Sturgeon, *Spectrochim. Acta*, **56B**, 1707 (2001).

17. K.W. Warnken, G.A. Gill, L.-S. Wen, L.L. Griffin, P.H. Santschi, *J. Anal. At. Spectrom.*, **14**, 247 (1999).

18. S. Hirata, Y. Ishida, M. Aihara, K. Honda, O. Shikino, *Anal. Chim. Acta*, **438**, 205 (2001).

19. K.-H. Lee, M. Oshima, S. Motomizu, *Analyst*, **127**, 769 (2002).

20. T. Miura, T. Morimoto, K. Hayano, T. Kishimoto, *Bunseki Kagaku*, **49**, 245 (2000).

21. Y. Takaku, Y. Kudo, J. Kimura, T. Hayashi, I. Ota, H. Hasegawa, S. Ueda, *Bunseki Kagaku*, **51**, 539 (2002).

22. Y. Zhu, A. Itoh, H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **78**, 107 (2005).

23. H. Haraguchi, Y. Zhu, R. Hattori, A. Itoh, T. Umemura, *Biomed. Res. Trace Elements*, **15**, 355 (2004).

24. A. Montaser, *"Inductively Coupled Plasma Mass Spectrometry"*, Wiley-VCH Inc, p. 543-548 (1998).

25. G.J. Piepgras, G.*J. Wasserburg, Science*, **217**, 207 (1982).

26. C.R. German, T. Masuzawa, M.J. Greaves, H. Elderfield, J.M. Edmond, *Geochim. Cosmochim. Acta*, **59**, 1551 (1995).

27. J. Zhang, Y. Nozaki, *Geochim. Cosmochim. Acta*, **60**, 4631 (1996).

28. H. Elderfield, M.J. Greaves, *Nature*, **296**, 214 (1982).

29. E.R. Sholkovitz, D.L. Schneider, *Geochim. Cosmochim. Acta,* **55**, 2737 (1991).

30. R.H. Byrne, K.-H. Kim, *Geochim. Cosmochim. Acta,* **54**, 2645 (1990).

31. T. Yabutani, K. Chiba, H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **74**, 31 (2001).

32. T.J. Shaw, T. Duncan, B. Schnetger, *Anal. Chem.*, **75**, 3396 (2003).

33. S.R. Taylor, S.M. McLennan, *"The Continental Crust: Its Composition and Evolution. An examination of the Geochemical Record Preserved in Sedimentary Rocks"*, Blackwell, p. 30 (1985).

Chapter 3   Determination of 56 Elements in Lake Baikal Water by High-Resolution ICP-MS with the Aid of a Tandem Preconcentration Method

3.1 Introduction

Efforts to preserve the ecological environment of Lake Baikal, which is the deepest and most voluminous freshwater lake on the Earth,[1-3] were stimulated by increasing industrial activities around the surrounding area since the last few decades of the 20th century. [2,3]   Determining the elements in Lake Baikal is a primary requirement for drawing a baseline for an examination of future anthropogenic perturbations.[3,4]   In the past few years, the distributions of approximately 30 elements in Lake Baikal were reported by some researchers.[3-7]   Falkner *et al.* investigated the distribution of Ca, Mg, Na, K, Cl, S, Sr, Li, Ba, Rb, Al, Si, Be, Zn, Cu, Ni, Cd, Ge, Cs V, Cr, Hg, and U in Lake Baikal water.[3-4]   Sugiyama *et al.* carried out studies on Al, Ba, Ca, Fe, K, Mg, Mo, Na, P, Si, Sr, V, and W in Lake Baikal water and suspended particles.[7]   These studies provided a great deal of valuable information about the above-mentioned elements in Lake Baikal.   Taking into consideration the fact that increasing numbers of trace elements are being used in modern industry, anthropogenic inputs of various trace elements to Lake Baikal are expected to be observed in the near future.   To date, nevertheless, trace elements other than the above-mentioned ones in Lake Baikal water have rarely been reported.   One of the reasons for a lack of trace-element data in Lake Baikal water is the extremely low concentrations of trace elements, which could not be measured directly by analytical instruments.

On the other hand, the developments of analytical instruments and preconcentration techniques have made it possible to determine at least 60 elements in natural water samples.[8]   In our research group, inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) were successfully applied to a multielement determination of environmental samples and bio-samples.[9,10]   Furthermore, coprecipitation and chelating resin

adsorption techniques were successfully developed to concentrate trace elements in natural water samples.[11,12]

Our research group are trying to investigate the distributions of as many elements as possible in Lake Baikal.   In the present experiment, Lake Baikal water samples were first subjected to a direct multielement determination by high resolution ICP-MS (HR-ICP-MS), where analytical results for 24 elements were obtained. Furthermore, a tandem preconcentration method integrating chelating resin adsorption and La-coprecipitation was applied to the pretreatment of lake water samples.   In the tandem preconcentration, trace elements in the sample were first concentrated with a chelating-resin packed minicolumn, where trace elements were adsorbed on the iminodiacetate-based resin.   Thereafter, some elements (in the effluent sample) those had passed through the minicolumn without being retained were subjected to La-coprecipitation, where trace elements were captured by a $La(OH)_3$ precipitate, and subsequently dissolved with nitric acid.   In addition to the above-mentioned 24 elements directly determined, another 32 elements were determined by HR-ICP-MS with the aid of this tandem preconcentration.

A discussion on the analytical results was carried out by a comparison with reference data of elemental concentrations in Lake Baikal.

3.2 Experimental

3.2.1 Instrumentation

A double-focusing single-collector HR-ICP-MS instrument of model Finnigan Element2 (Thermo Fisher Scientific, Germany), which was equipped with a concentric-type nebulizer (Conikal, AR35-1-FC1E, Glass Expansion Pty. Ltd., West Melbourne, Australia), was used to measure trace elements in Lake Baikal water directly and after tandem preconcentration.   The operating conditions of the HR-ICP-MS instruments were generally similar to those reported elsewhere.[13]   These operating conditions were chosen after optimization of each instrumental parameter.

A non-contact type pH meter (Twin pH meter B212; Horiba, Kyoto, Japan) was used for pH adjustment in the chelating resin preconcentration, where the sample

solution was being stirred with a magnetic stirrer of model SR100 (ADVANTEC, Tokyo, Japan).   A laboratory-made 8-port syringe pump was used to load multi-samples simultaneously.

Two kinds of syringe filters (DISMIC-25HP from ADVANTEC, Tokyo, Japan, and Millex-LH from Nihon Millipore Kogyo, Tokyo, Japan) were used to construct minicolumns (*i.d.*, 2.5 mm; *l*, 13.6 mm); the pore sizes of built-in membrane filters in both syringe filters were 0.45 μm.   The DISMIC-25HP syringe filter was also used to collect $La(OH)_3$ precipitate.   Single-use syringes of Terumo series (Terumo Corporation, Tokyo, Japan) were used throughout the present experiment.

3.2.2 Chemicals and samples

Nitric acid, acetic acid and an aqueous ammonia solution of electronic industry-grade were purchased from Kanto Chemicals (Tokyo, Japan).   Multielement standard solutions for making working calibration curves were prepared from single-element standard stock solutions (1000 μg mL^{-1}) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan).   Chelex 100 resin in 200 - 400 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA).   The resin was purified according to a previously reported method.[11]   Lanthanum nitrate $[La(NO_3)_3]$ of extra-pure-grade was purchased from Wako Pure Chemicals.   It was dissolved in 0.1 M HNO_3, and used as a coprecipitant for trace elements.   The pure water used throughout the present experiment was prepared by a Milli-Q purification system of model Element A-10 (Nihon Millipore Kogyo).

The present water samples were collected in August, 2003, at two sampling sites (A, N51°42'02", E104°35'43"; B, N52°08'46", E105°54'52") located in the southern basin of Lake Baikal.   The samples were collected with a go-flow sampler at the surface of site A, and at the surface, 20 m depth, 600 m depth, and 1200 m depth of site B, respectively.   The above-mentioned samples will be referred to as Surface-A, Surface-B, 20-B, 600-B, and 1200-B, respectively, in the following text.   The samples were acidified to pH 1 with conc. nitric acid, and were then preserved in polypropylene bottles, which were pre-cleaned by soaking in 6.0 M HNO_3 for more than one week, and rinsed with pure water before use.   In order to avoid contamination, filtration was not carried out for the present samples.

3.2.3 Procedure for the tandem preconcentration of trace elements

In order to determine as many elements as possible, Lake Baikal water samples were subjected to a pretreatment by a tandem preconcentration method, which integrated a chelating resin-packed minicolumn method by Zhu *et al.*[11] and a La coprecipitation method by Yabutani *et al.*.[12]

At the first preconcentration stage, the sample was subjected to preconcentration using a chelating resin-packed minicolumn, which was constructed with two syringe filters (DISMIC-25HP and Millex-LH) in the same manner as that reported by Zhu *et al.*.[11] Chelex 100 resin of 200 - 400 mesh was employed as the adsorbent, which permitted high-recovery preconcentration for trace elements at a sample loading flow-rate of approximately 10 mL min^{-1}. The operation procedure was as follows. First, the sample was adjusted to pH 5.0, and taken into a 50 mL syringe. Second, the sample was loaded into a minicolumn at 7.0 mL min^{-1}, where trace elements were adsorbed on the resins packed in the minicolumn. Meanwhile, the sample effluent solution that passed through the minicolumn was collected in a glass beaker, and subjected to the second step of preconcentration. Third, 5 mL of pure water was passed through the minicolumn for rinsing. Fourth, 1.8 mL of 2 M nitric acid was passed through the minicolumn to elute trace elements, which were collected and subjected to measurements by HR-ICP-MS. Before each measurement, 0.2 mL of an internal standard solution (Ge, In, Re, and Tl, 10 ng mL^{-1} each in 2 M nitric acid) was added to the analysis solution for the purpose of an instrumental signal drift correction and a matrix effect correction. The concentration factor for trace elements was 25-fold.

Some trace elements, such as As, Zr, and Hf, were obtained with quite low recovery values in the preconcentration using a chelating resin-packed minicolumn, because of their abilities to form oxyanions or hydroxide complexes in natural water. In order to overcome this difficulty, La coprecipitation was carried out on a sample solution collected at the sample loading step of the first preconcentration stage.

The procedure for the second preconcentration stage was as follows. First, 1 mL of a La(NO$_3$)$_3$ solution (10 mg mL^{-1} of La, 0.1 M HNO$_3$) was added into the sample solution as a coprecipitant. Second, the sample solution was adjusted to pH 9.5 with NH$_4$OH, and then aged for 30 min to form a La(OH)$_3$ precipitate, in which trace elements were enriched. Third, the sample was passed through a syringe filter

to collect the precipitate.　Fourth, the precipitate was dissolved using 1.8 mL of 2 M nitric acid, which was collected in a 5 mL test tube and subjected to a measurement of trace elements by HR-ICP-MS.　Here, 0.2 mL of an internal standard solution (Y and Re, 10 ng mL^{-1} each in 2 M nitric acid) was added to the analysis solution.　The concentration factor for trace metals in the second pretreatment stage was also 25-fold.

A trace-element spiked lake-water sample and a 0.1 M nitric acid solution were used for a recovery test and a blank test, respectively, which were subjected to tandem preconcentration in the same manner as the Lake Baikal water sample.

3.3 Results and Discussion

3.3.1 Analytical figures of merit

The detection limits, the recovery values and the blank values for the elements are summarized in **Tables 3-1** and **3-2**, respectively, as analytical figures of merit of the present method.　In the present work, the numbers in parentheses are lower digits of the standard deviations.　For example, 17900(900) and 7.91(5) mean 17900 ± 900 and 7.91 ± 0.05, respectively.

The detection limits of 24 elements determined directly by the HR-ICP-MS are summarized in **Table 3-1**.　The analytical detection limits for these elements were equal to the instrumental detection limits (IDL), which were defined as the concentrations corresponding to 3-times the standard deviations (n = 10-times measurements) of signal intensities in a 2 M nitric acid solution.　**Table 3-1** gives the analytical detection limits for these elements, from 8 ng mL^{-1} of Ca to 0.0001 ng mL^{-1} of Cs.

At the same time, the analytical detection limits, the recovery values and the blank values for 32 elements determined after tandem preconcentration are summarized in **Table 3-2**.　The recovery values and the blank values for the elements listed in **Table 3-2** are the mean values estimated from 3-times repeated experiments. Lake-water samples spiked with a certain amount of trace elements were used as the recovery test solution, while 50 ml of 0.1 M nitric acid was used as the blank test

solution.   The same preconcentration and measurement procedures as those for lake-water samples were performed for the test solutions.   It can be seen in **Table 3-2**, the recovery values for the elements were near to, or higher than, 70%, except for Cr (VI) (50 ± 8%).   It is noted that the standard deviations of the recovery values were generally less than 5%.   All of the following analytical results for these elements were corrected with the recovery values.   The blank values for most of these elements shown in **Table 3-2** were not detected, or were almost negligible, because they were much lower than the concentrations of analyte elements in lake-water samples.   The analytical detection limits for the elements listed in **Table 3-2** are shown as method detection limits (MDL), which were calculated from the instrumental detection limits, while taking into account the concentration factor (25) and the recovery values.   The analytical detection limits for these elements were in the range from 7 pg mL^{-1} of Se to 0.005 pg mL^{-1} of Lu.

3.3.2 Analytical results for elements in Lake Baikal water

The analytical results for elements in Lake Baikal water samples are also summarized in **Table 3-1** (determined directly) and **Table 3-2** (determined after preconcentration), respectively.   It is seen that the analytical results of the elements in Lake Baikal covered a range of nine orders of magnitude, from approximately 17 μg mL^{-1} of Ca to less than 50 fg mL^{-1} of Tm.   Variations of the concentrations of Fe, Zn, Cu, Pb, and Cd among different samples can be observed in **Tables 3-1** and **3-2**. However, the variations are still in the range of those reported by Falkner *et al.*,[3,4] Suturin *et al.*,[5] Grosheva *et al.*[6] and Sugiyama *et al.*.[7]

A comparison of the present results with reference data is summarized in **Table 3-3**.   It can be seen in **Table 3-3** that the present results for most of the elements were coincident with reference data.   However, the present results concerning the concentrations of Al, Pb, and Se were much higher than all of the reference data, while those of Cs, Zr, and Th were much lower than the results report by Grosheva *et al.*.[6]

It is noted that the results concerning Al by Suturin *et al.*[5] were higher than those by Falkner *et al.*[4] and Sugiyama *et al.*[7]; however all of the reported data were lower than those observed in the present work.   The differences could be attributed to the different pretreatments of water samples.   Falkner *et al.*[4] measured Al after filtration with a filter of 0.2 μm pore size (no filtration for determination of other elements),

while Suturin *et al.*[5] used a filter of 0.45 μm pore size for filtration; filtration was not performed on the present samples.   At the same time, the data of Sugiyama *et al.*[7] showed that the concentration of Al in suspended particles was quite high.   On the other hand, according to Itoh *et al.*,[14] the distribution of Al in a pond water was as follows: < 0.05 μm fraction (*ca.* 2.0%), 0.05 - 0.2 μm fraction (*ca.* 1.6%), 0.2 - 0.4 μm (*ca.* 5.2%), 0.4 - 1.2 μm (*ca.* 30.8%), 1.2 - 3.0 μm (*ca.* 31.8%), > 3.0 μm (*ca.* 28.6%). Therefore, it indicates that the pretreatment of filtration with different pore-sized filters influenced the analytical results of Al in natural water.   Similar influence may also be observed for Fe, Ag, rare earth elements (REEs, 15 lanthanides), Pb, and Bi.

The reasons for the differences of Cs, Se, Zr, and Th between the present results and the references are not clear, because there are not sufficient references for such a discussion.   However, the present results concerning Th were lower than that reported by Grosheva *et al.*[6] by a factor of almost two orders of magnitude, which indicates that the result of Grosheva *et al.*[6] might be affected by some contamination of Th.   On the other hand, the maximum concentration of Cd observed by Falkner *et al.*[4] was much higher than the minimum and those observed by other researchers. This could be attributed to the Cd contamination of some samples in the experiment by Falkner *et al.*,[4] as mentioned in their paper.

It is noted that only 32 elements are given in **Table 3-3**, because the remaining 24 elements determined in the present experiment had rarely been reported. Therefore, further studies on such elements in Lake Baikal are necessary to provide basic data concerning elemental chemistry in Lake Baikal, and for assessing the future environmental status of pollutants in Lake Baikal.

3.4   Conclusion

Lake Baikal water samples were analyzed by HR-ICP-MS directly and after a tandem preconcentration integrating chelating resin adsorption and La coprecipitation. Analytical results of 56 elements were acquired with a single instrument.   A comparison of the present results and reference data indicate that the present results were generally in the ranges of those reported by other researchers.   Some differences between the present results and the reference data were also observed and

discussed.　　However, data concerning the multi-elemental distribution in Lake Baikal are still scarce, which has limited further discussion.　　Therefore, further studies on Lake Baikal are needed in order to assess the lake environment, and to provide more information for future assessments of the environment of Lake Baikal.

Table 3-1　　Detection limits and analytical results obtained by direct measurements[a]

Element	Ca	Na	Mg	K	Si	Sr	B	Li
m/z	44	23	24	39	28	88	11	7
Resolution[b]	medium	medium	medium	high	medium	low	low	medium
IDL[c]	4	2	0.5	0.5	8	0.02	2	0.4
Surface-A	17900(900)	4800(600)	4000(400)	1050(10)	490(10)	107(1)	10.1(1)	7.91(5)
Surface-B	17200(600)	4600(200)	3800(200)	910(10)	400(10)	94.8(3)	8.82(4)	6.9(2)
20-B	15100(700)	4000(300)	3300(100)	910(40)	390(10)	93.0(2)	8.85(3)	6.23(3)
600-B	17000(900)	4600(300)	3800(200)	990(60)	480(20)	97.7(3)	9.29(7)	6.33(3)
1200-B	15100(800)	4000(300)	3303(200)	900(10)	430(10)	92.9(4)	8.83(3)	6.02(2)
Element	Ba	P	Fe	Al	Mo	Zn	Mn	Rb
m/z	135	31	56	27	95	66	55	85
Resolution[b]	low	medium	medium	medium	low	medium	medium	low
IDL[c]	0.03	0.6	0.07	0.06	0.02	0.01	0.005	0.0002
Surface-A	8.4(2)	4.8(1)	4.8(3)	2.5(4)	1.4(2)	1.35(1)	0.89(4)	0.590(3)
Surface-B	8.6(3)	2.47(3)	2.7(3)	2.1(1)	1.1(1)	1.15(1)	0.37(2)	0.484(2)
20-B	12.0(4)	3.8(4)	11.7(3)	1.8(4)	16.5(3)	1.13(1)	0.47(1)	0.474(2)
600-B	12.3(7)	2.1(1)	4.4(2)	2.2(1)	2.3(2)	1.19(1)	0.30(1)	0.499(3)
1200-B	11.9(3)	2.30(5)	2.3(1)	2.1(4)	1.2(1)	1.11(1)	0.25(1)	0.503(1)
Element	U	As	V	Cu	Pb	W	Y	Cs
m/z	238	75	51	63	206	182	89	133
Resolution[b]	low	medium	medium	medium	low	low	low	low
IDL[c]	0.0002	0.002	0.0006	0.008	0.004	0.001	0.0003	0.0001
Surface-A	0.52(1)	0.501(2)	0.41(1)	0.311(2)	0.33(1)	0.062(2)	0.0064(2)	0.0039(1)
Surface-B	0.50(1)	0.437(2)	0.27(2)	0.163(1)	0.283(7)	0.050(1)	0.0051(1)	0.0035(2)
20-B	0.46(1)	0.435(3)	1.95(7)	3.02(1)	0.272(4)	0.073(1)	0.0063(1)	0.0032(2)
600-B	0.49(1)	0.456(1)	0.415(7)	0.335(3)	0.287(8)	0.052(2)	0.0052(2)	0.003(2)
1200-B	0.45(4)	0.431(2)	0.32(3)	0.143(2)	0.269(4)	0.048(3)	0.0051(1)	0.0028(1)

a. The analytical results were given as mean (standard deviation).　　Concentration unit: ng mL^{-1}.
b. Resolution: high, $m/\Delta m$= 10000; medium, $m/\Delta m$= 4000; low, $m/\Delta m$ = 300.
c. Instrumental detection limits.

Table 3-2   Detection limits and analytical results obtained after tandem preconcentration[a]

Element	Se	Cr	Ni	Ti	Sb	Zr	Sn	Co
m/z	82	52	60	47	121	90	119	59
Resolution[b]	low	medium	Medium	medium	low	low	low	medium
Recovery[c], %	97(4)	50(8)	87(6)	86(3)	95(2)	107(7)	73.2(4)	108(1)
Blank value[d]	38(2)	27(2)	31(3)	n.d.[f]	3.6(1)	9.1(4)	n.d.[f]	3.1(4)
MDL[e]	7	4	1	5	0.04	0.2	1	0.1
Surface-A	340(21)	178(21)	143(3)	28(1)	27(3)	22.0(8)	9(1)	8.9(9)
Surface-B	220(20)	110(10)	450(90)	40(10)	37.4(2)	48(8)	12(2)	7(2)
20-B	240(20)	130(10)	780(10)	90(10)	79.4(2)	4.9(4)	32(3)	14(3)
600-B	250(20)	90(10)	500(90)	20(1)	41.2(1)	30(1)	11(2)	7(1)
1200-B	200(20)	70(1)	460(70)	20(1)	40.4(7)	37(1)	13(1)	6(1)
Element	Cd	Rh	Ce	Te	La	Nd	Hf	Nb
m/z	111	103	140	125	139	143	177	93
Resolution[b]	low	low	Low	low	low	low	low	low
Recovery[c], %	100(5)	81(8)	86(6)	83(6)	94(5)	104(1)	91(8)	87(7)
Blank value[d]	n.d.[f]	0.4(2)	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	2.5(1)	n.d.[f]
MDL[e]	0.2	0.02	0.1	0.4	0.09	0.07	0.1	0.5
Surface-A	8.8(5)	7.4(9)	7.33(4)	6.2(1)	5.16(4)	3.4(2)	3.1(5)	2.3(2)
Surface-B	19(4)	4.9(9)	4.00(8)	91(2)	3.1(6)	2.2(7)	6(1)	1.3(2)
20-B	99(10)	3(1)	12(3)	90(10)	9(2)	5.9(1)	4.6(6)	1.4(1)
600-B	23(4)	2.3(2)	5.0(2)	110(2)	3.8(2)	3.1(3)	0.7(3)	1.2(2)
1200-B	120(20)	17(9)	3.0(1)	140(10)	2.8(2)	1.9(3)	0.8(4)	0.9(1)

Table 3-2 (*Continued*)

Element	Ru	Ga	Pr	Sm	Sc	Dy	Gd	Yb
m/z	101	69	141	149	45	163	157	172
Resolution [b]	low	medium	Low	low	medium	low	low	low
Recovery [c], %	72(2)	76(4)	95(1)	82.0(7)	76.7(5)	81(2)	103(8)	109(2)
Blank value [d]	0.44(2)	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]
MDL[e]	0.03	0.2	0.02	0.009	0.08	0.009	0.003	0.05
Surface-A	1.22(2)	1.1(1)	0.91(3)	0.80(5)	0.7(3)	0.50(4)	0.47(4)	0.38(1)
Surface-B	18(1)	1.5(1)	0.56(9)	0.42(2)	1.4(4)	0.37(8)	0.3(1)	0.16(5)
20-B	6.0(1)	1.2(3)	1.6(2)	0.84(7)	1.1(2)	0.67(6)	0.5(1)	0.27(6)
600-B	6.2(1)	1.4(4)	0.75(7)	0.5(1)	0.95(8)	0.49(7)	0.43(6)	0.23(8)
1200-B	42(3)	1.4(2)	0.47(4)	0.33(9)	0.85(9)	0.42(5)	0.36(9)	0.22(5)
Element	Er	Th	Bi	Ho	Eu	Tb	Lu	Tm
m/z	167	232	209	165	151	159	175	169
Resolution [b]	low	low	Low	low	low	low	low	low
Recovery [c], %	81(3)	68(3)	78.0(5)	75(1)	93(4)	86(1)	107(2)	92.0(4)
Blank value [d]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]	n.d.[f]
MDL[e]	0.06	0.04	0.03	0.01	0.02	0.007	0.005	0.009
Surface-A	0.30(1)	0.29(4)	0.19(4)	0.16(1)	0.12(1)	0.084(7)	0.058(8)	0.05(1)
Surface-B	0.18(4)	0.28(4)	0.68(9)	0.10(5)	0.08(2)	0.06(2)	0.03(1)	0.020(9)
20-B	0.35(8)	0.40(1)	1.2(2)	0.06(3)	0.18(2)	0.10(3)	0.07(1)	0.05(1)
600-B	0.27(5)	0.30(1)	1.0(1)	0.06(2)	0.14(4)	0.055(7)	0.048(7)	0.039(3)
1200-B	0.21(5)	0.22(1)	0.9(1)	0.11(2)	0.06(1)	0.051(9)	0.04(1)	0.033(4)

[a] The analytical results were given as mean (standard deviation).   Concentration unit: pg mL^{-1}.   [b] Resolution: high, $m/\Delta m$ = 10000; medium, $m/\Delta m$ = 4000; low, $m/\Delta m$ = 300.   [c] Mean (standard deviation), n = 3.   [d] Mean (standard deviation), n = 3.
[e] Method detection limits were calculated from instrumental detection limits taking into consideration the concentration factor (25) and recovery values.   [f] Not detected.

Table 3-3 Concentration of the elements in Lake Baikal water reported by different researchers (units: ng mL^{-1})

Element		Ca	Na	Mg	K	Si	Sr	P	Ba	B	Fe	Al
Falkner et al.	Min[a]	15600	3490	3010	907		113		9.23			
(1991)	Max[b]	18500	4540	3100	1110		137		12.3			
Falkner et al.	Min[a]					750			9.1			0.04
(1997)	Max[b]					2014			10.5			0.18
Suturin et al.	Min[a]	14800	2800	2600	770	300	87	6.52	8.0	3.4		0.20
(2003)	Max[b]	16600	3800	3600	1120	1040	112	9.78	13.3	20		0.67
Grosheva et al. (2000)							42.6				6.3	
Sugiyama <0.2 µm	Min[a]	14500	3290	2840	899	146	99.9	0.09	9.2		0.0017	n.d.[d]
et al.	Max[b]	16400	3950	3180	958	1350	117	14.4	10.9		0.0039	0.0003
(2001) >0.2 µm	Min[a]	0.81	0.36	0.25	2.92	0.02	0.004	0.11	0.006		0.79	0.67
	Max[b]	8.66	0.97	1.91	4.97	0.14	0.050	7.50	0.126		3.22	4.42
Present work	Avg[c]	16500	4400	3641	952	438	97.1	10.6	9.19	6.67	3.55	3.11

Element		Li	Zn	Mo	U	As	Ni	Mn	Rb	Cu	V	Se
Falkner et al.	Min[a]	1.99			0.34				0.53			
(1991)	Max[b]	2.13			0.47				0.65			
Falkner et al.	Min[a]						0.05			0.10	0.32	
(1997)	Max[b]						0.16			0.36	0.48	
Suturin et al.	Min[a]	1.49	0.64	1.0	0.28	0.30	0.31	0.05	0.40	0.54	0.30	
(2003)	Max[b]	2.35	6.48	1.5	0.89	0.63	0.96	0.33	0.58	1.11	0.72	
Grosheva et al. (2000)			2.9	0.14	0.16	0.08		1.3	0.24	0.31	0.1	0.04
Sugiyama <0.2 µm	Min[a]			1.19							0.33	
et al.	Max[b]			1.26							0.35	
(2001) >0.2 µm	Min[a]		n.d.[d]				n.d.[d]	0.14		n.d.[d]	n.d.[d]	
	Max[b]		0.22				0.065	0.29		0.076	0.061	
Present work	Avg[c]	2.15	1.5	1.19	0.51	0.48	0.47	0.46	0.45	0.35	0.29	0.25

Table 3-3 (*Continued*)

Element		Pb	Cr	Sb	Cd	Ti	Zr	Co	W	Cs	Th
Falkner *et al.* (1991)	Min[a]										
	Max[b]										
Falkner *et al.* (1997)	Min[a]		0.06		0.03						
	Max[b]		0.09		2.52						
Suturin *et al.* (2003)	Min[a]	0.028	0.034	0.08	0.003			0.02			
	Max[b]	0.064	0.062	0.22	0.01			0.07			
Grosheva *et al.* (2000)		0.12	0.06	0.11	0.03		0.39	0.02		0.02	0.02
Sugiyama *et al.* (2001) <0.2 µm	Min[a]								0.040		
	Max[b]								0.048		
>0.2 µm	Min[a]		n.d.[d]			n.d.[d]					
	Max[b]		0.099			0.247					
Present work	Avg[c]	0.24	0.12	0.045	0.043	0.033	0.028	0.009	0.0047	0.003	0.0003

[a] Minimum.   [b] Maximumu.   [c] Average.   [d] Not detected.

References

1. T. Kira, " *Compact-size Edition of Data Book of World Lake Environments: Asia and Oceania*", Miyagawa Printing Co., Ltd. (1995).

2. R. F. Weiss, E. C. Carmack, and V. M. Koropalov, *Nature*, **349**, 665 (1991).

3. K. K. Falkner, C. I. Measures, S. E. Herbelin, J. M. Edmond, and R. F. Weiss, *Limnol. Oceanogr.*, **36**, 413 (1991).

4. K. K. Falkner, M. Church, C. I. Mesures, G. LeBaron, D. Thouron, C. Jeandel, M. C. Stordal, G. A. Gill, R. Mortlock, P. Froelich, and L.-H. Chan, *Limnol. Oceanogr.*, **42**, 329 (1997).

5. A. N. Suturin, L. F. Paradina, V. N. Epov, A. R. Semenov, V. I. Lozhkin, and L. L. Petrov, *Spectrochim. Acta*, **58(B)**, 277 (2003).

6. E. I. Grosheva, G. N. Voronskaya, and M. V. Pastukhove, *Aquatic Ecosystem Health & Management*, **3**, 229 (2001).

7. M. Sugiyama, N. Kimura, and Y. Harita, *Transactions of The Research Institute of Oceanochemistry* (in Japanese), **14**, 77 (2001).

8. T. Fujinaga, Y. Sohrin, and K. Isshiki, "*Chemistry of Marine and Lake-Investigated by Trace Element* (in Japanese)", Kyoto University Press, (2005).

9. H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **72**, 1163 (1999).

10. H. Haraguchi, *J. Anal. At. Spectrom.*, **19**, 5 (2004).

11. Y. Zhu, A. Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **78**, 107 (2005).

12. T. Yabutani, S. Ji, F. Mouri, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **73**, 895 (2000).

13. Y. Zhu, K. Kashiwagi, M. Sakaguchi, M. Aoki, E. Fujimori, and H. Haraguchi, *J. Nucl. Sci. Tech.*, **43**, 474 (2006).

14. A. Itoh, T. Nagasawa, Y. Zhu, K.-H. Lee, E. Fujimori, and H. Haraguchi, *Anal. Sci.*, **20**, 29 (2004).

Chapter 4   An in-syringe La-coprecipitation Method for the Preconcentration of Oxo-anion Forming Elements in Seawater Prior to an ICP-MS Measurement

4.1   Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has excellent analytical features, such as simultaneous multielement detection capability, extremely high sensitivity, and a wide linear dynamic range.[1-5]   However, the 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 a high salt matrix interferes with the determination.   Thus, a variety of pretreatment techniques, such as preconcentration and matrix elimination have been exploited, which include solid phase extraction (SPE), solvent extraction, and coprecipitation.   Among them, SPEs using chelating resins are most widely employed due to their simplicity, high concentration factor, small sample requirement, and no need for a harmful organic solvent.   Recently, the present authors have reported on a simple and practical syringe-based column method for the SPE of trace metals in seawater [4] using a laboratory-made minicolumn packed with a Chelex 100 resin, where trace metals in 50 mL of the original seawater sample were concentrated into 0.5 mL of 2 M nitric acid (final solution).   From the results, it was proved that the minicolumn is a convenient preconcentration device for trace metals in seawater as well as in mineral water samples prior to determination by ICP-MS.

The chelating-resin adsorption method is not suitable for the preconcentration of oxo-anion forming elements, such as V, As, Sb, W and so on.   For highly sensitive measurements of As and Sb, the hydride generation method is one of the most popular approaches, but a special experimental set-up is a requisite.   The coprecipitation method is another promising approach.   This coprecipitation method has a potential to overcome the limitation of SPEs due to the different mechanism of extraction, although it is tedious, and time-consuming, and involves several steps.

A syringe-based sample manipulation system has recently attracted much attention in the field of sample pretreatment because of its simplicity and practicality. Therefore, in the present work, coprecipitation was attempted in a 25-mL syringe to simplify the manipulation, where lanthanum hydroxide was employed as a collector of oxo-anion forming elements.   In the case of multielement analysis by ICP-MS, a high concentration of the precipitant (in this case, La) raises new problems of serious memory effects and interferences in the measurements of other samples for different analytical purposes.[6,7]   Then, in the present experiment, a high level of La was removed by passing the analyte solution (*i.e.*, "target elements-enriched" lanthanum hydroxide precipitate dissolved in HNO3) through a cation-exchange resin-packed minicolumn prior to an ICP-MS measurement.   Under the optimized conditions, the recoveries for V, As, Sb, and W exceeded 80%, and the observed values were in good agreement with the certified or information ones.   Also, as a result of the present study, the concentration value of Sb in NASS-5 was provided for the first time.

4.2 Experimental

4.2.1 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 given in **Table 4-1**.   A pH meter of a model TWIN pH meter from Horiba (Kyoto, Japan) was used for pH adjustment.   A HSW plastic syringe was used as a vessel and reactor.   A DISMIC-25HP membrane filter (ADVANTEC, Tokyo, Japan) with a pore sizes of 0.20 μm was used for collecting the lanthanum hydroxide precipitate.   A minicolumn for lanthanum removal was laboratory-made, consisting of two commercially available syringe filters (DISMIC-25HP and Millex-LH) and cation-exchange resin, according to our previous paper. [3]   A syringe pump (model KDS200, KD Scientific, MA) was used for pumping the sample solution into the minicolumn.

Table 4-1 Operation conditions the 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 L 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

4.2.2 Reagents and chemicals

Nitric acid, acetic acid, and an aqueous ammonia solution of electronic industry grade were purchased from Kanto Chemicals (Tokyo). Standard stock solutions for V(V) and W(VI), Mo(VI), U(VI) were prepared from single-element standard stock solutions (1000 μg L^{-1}) for atomic absorption spectrometry (Kanto Chemicals, Tokyo). The standard stock solutions for As(III), As (V), Sb(III) and Sb(V) were prepared as follows: The As(III) and As(V) solutions were prepared by dissolving potassium arsenite and potassium arsenate of chemical grade (Wako Chemicals, Osaka, Japan) in pure water, while Sb(III) and Sb(V) solutions were prepared by dissolving dipotassium bis(tartrato)diantimonate(III) and potassium hexahydroxoantimonate(V) of guaranteed reagent grade (Nacalai Tesque, Kyoto, Japan) in a 3 M HCl solution, respectively. A lanthanum solution as a coprecipitation carrier was prepared by dissolving La (NO$_3$)$_3$ 6 H$_2$O (Wako Chemicals) in 0.1 M HNO$_3$.

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 used throughout the experiments was prepared by a Milli Q purification system (model Element A-10, Nihon Millipore Kogyo).

4.2.3 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.

4.2.4 Pretreatment procedure

The procedure is mainly composed of two steps: La-coprecipitation (Step 1) and La-removal from the preconcentrated sample (Step 2).

Step 1. Twenty-mL of a sample adjusted to pH 9.5 was filled into a 25-mL volume syringe. Then, 0.2 mL of a 5 g L^{-1} La solution was added into the syringe. The solution was shaken vigorously for 3 min, and allowed to stand for 1 h at room temperature for complete precipitation. Afterward, the precipitate was collected on a 0.2 μm membrane filter by filtration. The precipitate was dissolved with 2 mL of 2 M HNO_3.

Step 2. The solution in Step 1 was diluted 2-fold with pure water to a final concentration of 1 M HNO_3. Then, this solution was passed through a La-removal minicolumn packed with an AG$^®$ 50W-X8 cation-exchange resin at a flow rate of 0.2 mL min^{-1}.

4.3 Results and Discussion

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

Coprecipitation 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 amount of La added as a precipitant precursor may be the most important parameter: for example, because an excess of high concentration La causes a memory effect in an ICP-MS measurement, and is hence prone to analytical errors. Thus, first of all, the effect of the amount of La on the coprecipitation of V(V), As(III+V), Sb(III+V), and W(VI) into La(OH)$_3$ was

examined.   So far, more than 200 mg L^{-1} of La(NO$_3$)$_3$ was employed to definitely obtain lanthanum hydroxide, [1,2,6,7]   but in the present work La(NO$_3$)$_3$ solutions with lower concentrations of 25, 50, 100, and 150 mg L^{-1} were used to reduce the risk of instrument damage and signal interference as much as possible.

Figure 4-1 shows the dependence of the recoveries of V(V), As(III+V), Sb(III+V), and W(VI) (10 μg L^{-1} each of target analytes) on the amount of La added to a 20 mL seawater sample, into which a known amount (10 μg L^{-1} each) of the target elements were also preliminarily added, and the sample solution was subjected to La coprecipitation in the same manner as that of a non-spiked sample.   As can be seen from **Fig. 4-1**, all of the target elements were quantitatively recovered by adding more than 1 mg of La (corresponding to 50 mg L^{-1}) to the 20 mL seawater sample.   It was found that 1.0 mg of La was sufficient for the coprecipitation and preconcentration of the target 5 oxo-anion forming elements from seawater samples, and thus 1.0 mg of La was selected for the following experiments.
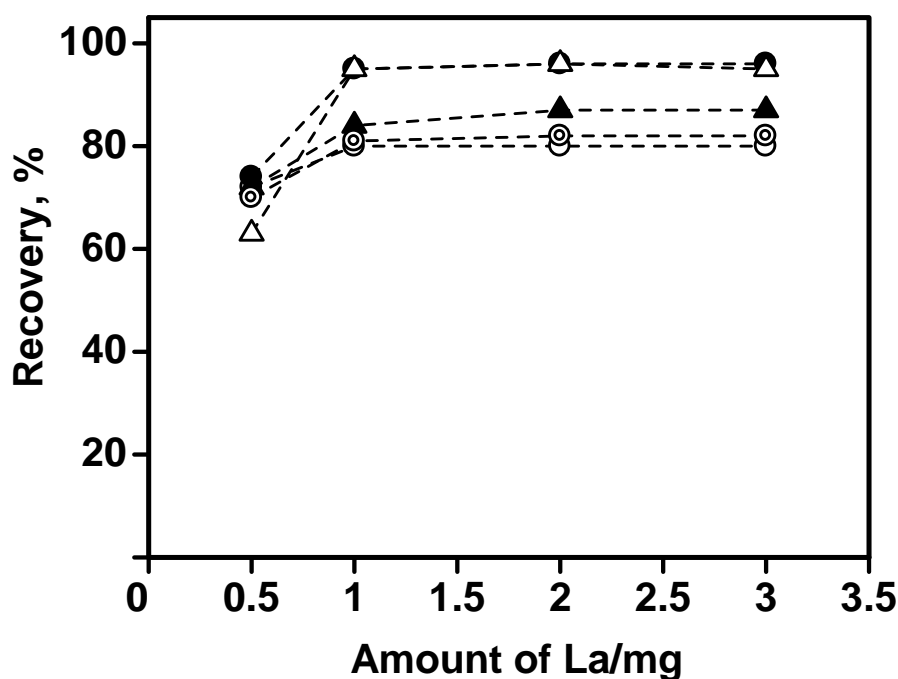
Fig. 4-1   Recoveries of a elements after the addition of various amount of La to 20 mL of samples.   ○, V(V) ;   ●, As(III+V) ;   △, Sb(III+V) ;   ▲: W(VI).

4.3.2 Redissolution of the lanthanum hydroxide precipitate and La removal from the analysis solution

The collection of a target elements enriched in the precipitate is another important step in the coprecipitation method. According to a previous paper, nitric acid was chosen for redissolution of the coprecipitate, and the concentration and volume of HNO3 were optimized for quantitative collection. As a result of some preliminary experiments, it was found that the coprecipitate could be fully dissolved by using HNO_3 of more than 1 M, and that more than 2 mL of HNO_3 was needed. Thus, 2 mL of 1 M HNO_3 was concluded to be optimum, and was used in following experiments.

Under these conditions, the target elements and La in a 20 mL sample were collected into a one-tenth volume of nitric acid (2 mL of HNO_3), leading to 10-fold concentration. This means that the concentration of La in the final analysis solution is ca. 500 mg L^{-1} (1 mg in 2 mL). The direct introduction of such a La-rich solution imposes a heavy burden on the ICP-MS instrument. Besides, the residual La-memory effect in the ICP-MS instrument adversely affects the following experiments of other colleagues, where a trace amount of La might be one of the target analytes. Thus, prior to a measurement by ICP-MS, a cation-exchange minicolumn was employed in the present work to remove La from the analysis solution, where the target analytes forming stable oxo-anions were passed through the minicolumn without any interaction. Therefore, the La concentration in the analysis solution passed through the minicolumn was expected to be less than 1 μg L^{-1}, which is low enough for introduction into the ICP-MS.

The results for the recoveries of oxo-anion forming elements in the present *in-syringe* coprecipitation method are summarized in **Table 4.2**, together with the data obtained by a chelating resin preconcentration method. [3] The recoveries of the target elements (V(V), As (III+V), Sb (III+V), and W (VI)) was apparently higher than those by a chelating resin-column method, which exceeded 80% with good reproducibility (RSD ≤ 5%). As previously reported,[1] the recoveries of As and Sb were about 100%, regardless of their oxidation states. The recoveries of the present method were high enough for quantitative preconcentration and determination. The recoveries of Mo and U were *ca*. 9.7 and 40%, respectively. At pH 9.5, Mo and U may be in the chemical forms of MoO_4^{2-} and UO_2^{2+} in the sample solution, while V, As, Se, Sb, and

W may be in the chemical forms such as $H_2VO_4^-$, $As(OH)_4^-$, $HSeO_3^-$, $Sb(OH)_3$, and HWO_4^-, respectively. Oxoacids possessing hydroxyl groups in them may be efficiently adsorbed on hydroxide colloids.[8-10] As a result, V, As, Se, Sb, and W were completely coprecipitated with lanthanum hydroxide colloids. In contrast, Mo and U were hardly coprecipitated with lanthanum hydroxide colloids.

Table 4-2 Recoveries (%) of trace elements obtained after *in-syringe* La-coprecipitation preconcentration

Element	m/z	Present work			Chelating resin-column preconcentration [a)]		
		Recovery, % [a]					
V(V)	51	80	±	5	43	±	5
As(III+V)	75	96	±	5	1.8	±	0.6
Mo(VI)	95	9.7	±	0.1	63	±	4
Sb(III+V)	121	85	±	3	0.3	±	0.1
W(VI)	184	81	±	4	23	±	3
U(VI)	238	40	±	6	95.2	±	0.3

Mean ± standard deviation, $n = 3$.
[a)] The recoveries from SPE on Chelex 100 resin at pH 6.

4.3.3 Analytical results of oxo-anion forming elements in seawater samples

Two seawater CRMs (NASS-5 and CASS-4) were analyzed to verify the effectiveness of the present method. NASS-5 is open seawater, while CASS-4 is coastal seawater. The analytical results are summarized in **Table 4-3**. The observed values and blank values listed in **Table 4-3** were the mean values and standard deviations (SDs) of three independent experiments. It can be seen in **Table 4-3** that the analytical results of V(V) and As(III+V) in both CRMs were in good agreement with the certified values or information values, which indicate that the present method was effective for the analysis of V(V) and As(III+V) in open seawater and coastal seawater. It's difficult to assess the accuracy of the analytical results of Sb(III+V) and W(VI) in the present CRMs because of there were neither information values nor certified values issued for these elements. Although a certified values are not available, the analytical results of Sb(III+V) in CASS-4 and W(VI) in NASS-5

were coincident with the reference data.[3,11]   The observed value of W(VI) in CASS-4 was apparently lower than the reference data, which might be attributed to the different recovery value of W(VI) obtained in the present work and the chelating resin adsorption technique. [12]

On the other hand, the blanks used in the present method are also summarized in **Table 4-3**.   As can be seen, the blank values were much lower than the abundances of the analyte elements in seawater, and thus they were almost negligible.

In order to evaluate the lower limit of determination by the present method, the analytical detection limits (ADLs) were estimated from the instrumental detection limits, while taking into consideration the concentration factor and the recovery values, where the instrumental detection limits were calculated as the analyte concentration corresponding to three-times the standard deviation of the blank signals.   The ADLs of V(V), As(III+V), Sb(III+V) and W(VI) were 0.001, 0.001, 0.04, and 0.0003 μg L^{-1}, respectively.

4.4 Conclusions

La coprecipitation preconcentration method was exploited for the determinations of V(V), As(III+V), Sb(III+V), and W(VI) in seawater samples. The La in the analysis solution was removed by passing through a cation-exchange resin-packed minicolumn, which effectively lowered the La matrix burden on the ICP-MS.   The recoveries of the oxo-anion forming elements were better than 80%.   The effectiveness of the present method was verified by the analysis of two seawater CRMs and a real seawater sample.

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

Element	m/z	NASS-5/μg L⁻¹ Observed value[b]	Certified value	CASS-4/μg L⁻¹ Observed value[b]	Certified value	Blank value/μg L⁻¹	ADL[a] /μg L⁻¹
V(V)	51	1.20 ± 0.05	1.2[c]	1.15 ± 0.08	1.18 ± 0.16	0.040 ± 0.007	0.001
As(III+V)	75	1.30 ± 0.12	1.27 ± 0.12	1.13 ± 0.09	1.11 ± 0.16	0.031 ± 0.008	0.001
Sb(III+V)	121	0.076 ± 0.008		0.215 ± 0.004	0.240[d] ± 0.018	0.0035 ± 0.0008	0.0006
W(VI)	184	0.0095 ± 0.0001	0.010[e] ± 0.001	0.016 ± 0.001	0.042[f] ± 0.004	n.d.[g]	0.0003

[a] The analytical detection limit (ADL) was calculated from instrument detection limit, with taking into account the concentration factor (5) and recovery values.

[b] Mean ± standard deviation, $n = 3$.

[c] Information value, issued by National Research Council Canada.

[d] Literature value, cited from Ref. 11.

[e] Literature value, cited from Ref. 3.

[f] Literature value, cited from Ref. 12.

[g] Not detected.

References

1. T. Yabutani, S.Ji, F. Mouri, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn*, **73**, 895 (2000).

2. T. Yabutani, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **174**, 31 (2000).

3. Y. Zhu, A.Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn.,* **78**, 107 (2005).

4. D. Rahmi, Y. Zhu, E. Fujimori, T. Umemura, and H. Haraguchi, *Talanta,* **72**, 2, 600 (2007).

5. T. Yabutani, S. Ji, F. Mouri, H. Sawatari, A. Itoh, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn.,* **72**, 2253 (1999).

6. H. Saisho and Y. Fujimura, *Anal.　Sci.*, **6**, 619 (1990).

7. E. P. Vazquez, A. B. Barrera, and P. B. Barrera, *J. Anal. At. Spectrom.*, **20**, 1344 (2005).

8. H. Yamazaki, S. Gouda, and Y. Nishikawa, *Bunseki kagaku*, **29**, 58 (1980).

9. H. Yamazaki, K. Tsujimoto, S. Gouda, K. Hiraki, and Y. Nishikawa, *Bunseki kagaku*, **28**, 424 (1979).

10. D. R. Turner, M. Whitfield, and A. G. Dickson, *Geochim. Cosmochim. Acta*, **45**, 855 (1981).

11. C. Turetta, G. Cozzi, C. Barbante, G. Capodaglio, and P. Cescon, *Anal. Bioanal. Chem.*, **380**, 258 (2004).

12. Y. Zhu, A. Itoh, E. Fujimori, T. Umemura, and H. Haraguchi, *Bull. Chem. Soc. Jpn.,* **78**, 659(2005).

Chapter 5   Preparation of Monolithic Chelating Adsorbent inside a Syringe Filter Tip for Solid Phase Microextraction of Trace Elements in Natural Water prior to their Determination by ICP-MS

5.1 Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) has been accepted as the most powerful and sophisticated atomic spectrometric technique, because of its excellent features such as high sensitivity, wide dynamic range, and simultaneous multielement detection capability, and so on. [1-3]   However, direct analysis of natural water samples 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 often interferes with their determination. [4-10]   Thus, an enrichment/separation has become an essential part of spectrometric analysis, including solvent extraction [11,12], coprecipitation [13-15], and solid phase extraction (SPE) [16-24].   Among them, SPE on chelating resin has attracted the most attention due to its simplicity, high concentration factor, small sample requirement, and no need for harmful organic solvent, and has widely been used in both batch and column modes.   This SPE technique has continued to undergo improvement, and recently syringe connected-minicolumn (SCM) method has emerged as a hybrid technique combining the characteristics of batch and column methods. [25-27]

In chromatographic separation and purification, over the past several years, a single piece of porous material so-called "monolith" has gained popularity as an alternative to particle-packing configuration. [28-31]   Due to the novel characteristics such as low flow resistance, efficient mass transfer, and high reaction efficiency, their applications are now extended from the original separation media to extraction media and catalyst supports.   Monoliths can be classified into two categories; silica-based and organic polymer-based monoliths, each with their own advantages and disadvantages.   The major advantages of polymer-based monoliths include wide pH stability and less irreversible adsorption of biomolecules, and we have so far tried to

prepare well-ordered porous polymer monoliths for high-throughput and high-efficiency separations. [32-35]

Organic polymer monoliths have also the advantage of facile synthesis and modification, and they have great potential in solid phase microextraction (SPME) of trace elements (metals and metalloids) in natural water samples. [36-39] However, little work has been reported on the use of monolithic materials in such a chelating resin adsorption.   In the present work, thus, the preparation of a monolithic adsorbent has been attempted for SCM-mode SPME.   Glycidyl methacrylate (GMA), which has a reactive epoxy group for further derivatization, was copolymerized with ethylene glycol dimethacrylate (EDMA) inside a commercially available syringe filter tip. Subsequently, the epoxides at the monolith surface were reacted with one of the most popular chelating ligands, iminodiacetate (IDA) [40].   The metal adsorption properties of the obtained chelating adsorbent, named herein "tip-in monolith", were evaluated through an adsorption-desorption experiment, where the effect of sample solution pH on the adsorption of a total of 53 elements was systematically examined to obtain higher recoveries for as many elements as possible in a single extraction step. In addition, the accuracy of the proposed SCM-mode SPME tool and technique was tested by analyzing two river water certified reference materials.

5.2 Experimental

5.2.1 Apparatus

A syringe filter tip for HPLC (model DISMIC-3JP from Advantec, Tokyo, Japan) was used as a vessel and chamber for SPME.   A conventional Termo-syringe (Terumo Corporation, Tokyo, Japan) was used for loading the samples solution, rinsing the tip-in monolith with Milli-Q water, and eluting the analytes with nitric acid. A model LC-10Ai pump (Shizuoka, Kyoto, Japan) was used for the measurement of pressure drop across the tip-in monolith.   For parallel multi-sample pretreatment, a gravity-driven 8-port syringe pump was laboratory-made and used. [42]

A high resolution ICP-SFMS instrument of model Finnigan Element 2 (Thermo Fisher Scientific, Bremen, Germany) equipped with a single collector and a

concentric-type nebulizer (Conikal, AR35-1-FC1E, Glass Expansion Pty. Ltd., West Melbourne, Australia) was used for the measurement of trace elements. The operating conditions for ICP-SFMS are summarized in **Table 5-1**. An ICP-AES instrument of model IRIS intrepid II XPS DUO (Thermo Fisher Scientific) was also used for the measurement of high concentrations of elements. The morphology of GMA-based monoliths formed inside the filter tip was examined using a scanning electron microscope (model S-3000N, Hitachi High-Technologies Corporation, Tokyo, Japan).

Table 5-1 Operating conditions for the HR-ICP-MS instrument

HR-ICP-MS Element2	
Plasma conditions:	
incident power	1.0 kW
coolant gas flow rate	Ar 16.0 L min^{-1}
auxiliary gas flow rate	Ar 0.8 L min^{-1}
carrier gas flow rate	Ar 0.9 L min^{-1}
Nebulizer:	Concentric-type
sample uptake rate	0.2 mL min^{-1}
Data acquisition:	
mass window	150%
integration window	80%
sampling points per peak	15 points
integration times (runs × passes)	3 × 3 times

5.2.2 Chemicals

Glycidyl methacrylate (GMA), ethylene glycol dimethacrylate (EDMA), and 2,2`-azoisobutyronitrile (AIBN) were purchased from Wako Pure Chemicals (Osaka Japan). Solvents (1-propanol, 1,4-butandiol, cyclohexanol, toluene) and inorganic salts (NaCl, Na$_2$CO$_3$, Cu(NO$_3$)$_2$) were also obtained from Wako Pure Chemicals. Iminodiacetic acid (IDA) was obtained from Sigma-Aldrich (Steinheim Germany). Nitric acid, acetic acid and aqueous ammonia solution were of electronic industry grade from Kanto Chemicals (Tokyo, Japan). Multielement standard solutions for calibration were prepared from single-element standard stock solutions (1000 μg

mL^{-1}) for atomic absorption spectrometry (Wako Pure Chemicals).   Pure water used throughout the present experiment was prepared by a Milli-Q purification system of model Element A-10 (Nihon Millipore Kogyo).   Two river water CRM samples, JSAC 0301-1 issued by the Japan Society for Analytical Chemistry and NMIJ 7201-a issued by the National Metrology Institute of Japan, were purchased from Tama Chemicals (Kawasaki, Japan) and Seishin Trading Co., Ltd, respectively.

5.2.3 Preparation of tip-in chelating monolith for SPME

The procedure for preparation of tip-in chelating monolith was almost the same as that for monolithic capillary column. [33]   Briefly, GMA, EDMA and a porogenic solvent were mixed at an appropriate ratio in a bottle, into which AIBN (1 wt.% with respect to the amount of total monomers) was added.   After stirring and degassing, an aliquot of the mixture was drawn into a syringe and was immediately poured into the gap space confined between the DISMIC-3JP filter tip and the syringe.   The filter tip filled with the monomer solution was sealed with tape, and then was put into a water bath for thermal polymerization.   After the polymerization was completed, the tip-in monolith was washed with ethanol and then pure water to remove any unreacted reagents.   Subsequently, the coupling of IDA to the monolith surface was carried out by reacting with an aqueous sodium iminodiacetate solution.   Schematic illustration of the tip-in monolith is shown in **Fig. 5-1**.   As can be seen in **Fig. 5-1**, diameter and length of the cylindrical monolithic adsorbent were 4 mm and 3-4 mm, and its volume was 40-50 μl (ca. 20 μg).

5.2.4 Measurement of chelating capacity

A chelating capacity of the tip-in monolith was estimated from the amount of Cu^{2+} adsorbed on the monolith in the following manner.   First, a plenty amount (10 mL) of 0.5 M Cu(NO$_3$)$_2$ aqueous solution (pH around 4.3) was passed through the tip-in monolith at a flow rate of 0.3 mL min^{-1}.   Secondly, the tip-in monolith was rinsed with 10 mL pure water to eliminate Cu^{2+} ions remaining in the through-pores of the monolith.   Thirdly, the Cu^{2+} ions adsorbed on the monolith were eluted with a plenty amount (5 mL) of 2 M HNO$_3$.   Finally, the concentration of Cu^{2+} in the eluate solution was measured by ICP-AES.

The chelating capacity was calculated from the following expression:

$$Q = (C \times V) / W$$

Where Q (mmol g-1) is the adsorption capacity of the chelating polymer, C (mmol L^{-1}) is the concentration of Cu^{2+} in the eluate. V (L) and W (g) are the volume of the eluate and the dry weight of chelating polymer monoliths, respectively.
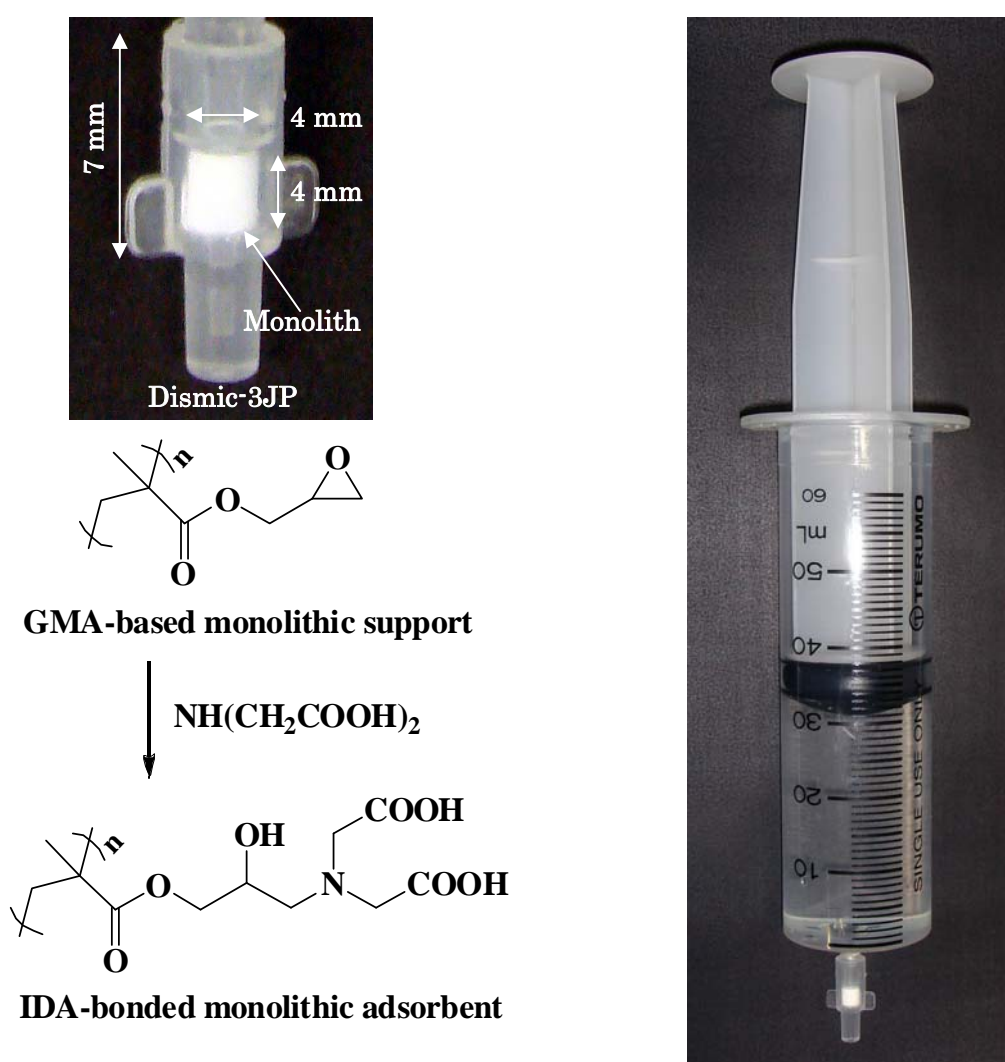

Fig. 5-1 Schematic illustration of tip-in chelating monolith

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Table 5-2 Composition of the test solution used for the addition-recovery experiment

Element[a]		m/z	Amount spiked [b] / μg L^{-1}	Element		m/z	Amount spiked [b] / μg L^{-1}
Al	[Al(NO$_3$)$_3$]	27	10	Te	[TeCl$_4$]	125	0.1
Sc	[Sc(NO$_3$)$_3$]	45	1	Cs	[CsNO$_3$]	133	0.1
Ti	[Ti(SO$_4$)$_2$]	47	1	Ba	[Ba(NO$_3$)$_2$]	138	10
V	[NH$_4$VO$_3$]	51	1	La	[La(NO$_3$)$_3$]	139	0.1
Cr	[K$_2$Cr$_2$O$_7$]	52	10	Ce	[Ce(NO$_3$)$_3$]	140	0.1
Mn	[Mn(NO$_3$)$_3$]	55	1	Pr	[Pr(NO$_3$)$_3$]	141	0.1
Fe	[Fe(NO$_3$)$_3$]	56	10	Nd	[Nd(NO$_3$)$_3$]	143	0.1
Co	[Co(NO$_3$)$_2$]	59	1	Sm	[Sm(NO$_3$)$_3$]	147	0.1
Ni	[Ni(NO$_3$)$_2$]	60	10	Eu	[Eu(NO$_3$)$_3$]	151	0.1
Cu	[Cu(NO$_3$)$_2$]	63	10	Gd	[Gd(NO$_3$)$_3$]	157	0.1
Zn	[Zn(NO$_3$)$_2$]	64	10	Tb	[Tb(NO$_3$)$_3$]	159	0.1
Ga	[Ga(NO$_3$)$_3$]	69	1	Dy	[Dy(NO$_3$)$_3$]	163	0.1
As	[As$_2$O$_3$]	75	1	Ho	[Ho(NO$_3$)$_3$]	165	0.1
Rb	[RbCl]	85	0.1	Er	[Er(NO$_3$)$_3$]	167	0.1
Sr	[SrSO$_4$]	88	10	Tm	[Tm(NO$_3$)$_3$]	169	0.1
Se	[SeO$_2$]	82	10	Yb	[Yb(NO$_3$)$_3$]	172	0.1
Y	[Y(NO$_3$)$_3$]	89	0.1	Lu	[Lu(NO$_3$)$_3$]	175	0.1
Zr	[ZrO(NO$_3$)$_2$]	91	1	Hf	[HfCl$_4$]	178	1
Nb	[NbF$_5$]	93	1	Ta	[TaF$_4$]	181	1
Mo	[(NH$_4$)$_6$Mo$_7$O$_{24}$]	95	10	W	[Na$_2$WO$_4$]	182	10
Ru	[RuCl$_3$]	99	0.1	Pt	[H$_2$PtCl$_6$]	195	0.1
Rh	[RhCl$_3$]	103	0.1	Au	[AuCl]	197	0.1
Pd	[Pd(NO$_3$)$_2$]	105	0.1	Pb	[Pb(NO$_3$)$_2$]	208	1
Ag	[AgNO$_3$]	109	1	Bi	[Bi(NO$_3$)$_3$]	209	1
Cd	[Cd(NO$_3$)$_2$]	111	1	Th	[Th(NO$_3$)$_4$]	232	1
Sn	[SnCl$_2$]	118	1	U	[UO$_2$(NO$_3$)$_2$]	238	1
Sb	[SbCl$_3$]	121	0.1				

a) Chemical form of metal/metalloid in parenthesis denotes the reagent used for the element standard solution.

b) The concentration in the final solution.   Each element standard solution was added to 0.1 M HNO$_3$.

5.2.5 Procedure for SCM-mode SPME

The effect of sample pH on the extraction of trace elements from water samples was examined through the following experiment.   First, 50 mL of a pH-adjusted test solution containing 0.1, 1 or 10 μg L-1 each of metals and metalloids (as shown in **Table 5-2**) was loaded into the tip-in monolith at a flow rate of 0.3 mL min-1 by using a 50 mL-volume syringe.   Then, 1 mL of Milli-Q water was passed through the

monolithic adsorbent at a flow rate of 1 mL min^{-1} to eliminate matrix elements remaining on the monolith to as low as possible level.   After that, trace elements adsorbed on the monolith were eluted with 0.9 mL of 2 M HNO$_3$ and collected   in a test tube, into which 0.1 mL of internal standard solution (Ge, In, Re, and Tl; 10 μg L^{-1} each) was added for interference correction.   Finally, the eluate solution was subjected to the determination of trace elements by ICP-SFMS.

5.3 Results and discussion

5.3.1 Effect of porogenic solvent on porous property of monolith

Support material bearing reactive epoxide groups in its matrix permits further modification with functional molecules and/or ligands.   To form such a reactive epoxide-containing polymer matrix, GMA was chosen and polymerized with EDMA as a cross-linker for forming a 3-dimensional network structure.   In general, there are several parameters that influence the porous properties and the resulting extraction performance, including the type and concentration of porogenic solvent, polymerization temperature and time, and the percentage of cross-linker and initiator.[34]   Among them, porogenic solvent in the polymerization mixture play the most important role in monolithic morphology.   Thus, the composition and ratio of porogenic solvent were first adjusted, taking into account the following points: low flow resistance and high surface area.   Low flow-resistance monoliths are preferable to reduce working pressure as low as possible, resulting in making manual operation easy, but such highly-permeable monoliths usually have low surface area and low adsorption capacity, leading to poor extraction performance.   According to previous papers and our preliminary results, in the present paper, two kinds of porogenic solvents, (1) a ternary mixture of 1-propanol, 1,4-butanediol, and water (P/B/W) and a binary mixture of cyclohexanol and toluene (C/T) were examined, where total monomer concentration (%T) and the proportion of cross-linker (%C) were fixed at 30 (w/v) and 25% (w/w), respectively.[33,34]

The recipes of the polymerization mixtures used in this experiment are summarized in **Table 5-3**.   As in the case of monoliths in the capillary format, both

the ternary and the binary porogenic solvent systems gave rigid and macroporous monolithic materials.   The permeabilities of the monoliths were evaluated through the relationship between the flow volume (flow rate) and the pressure drop.   For the purpose, the flow volume in Milli-Q water was examined at a constant pressure of 5 atm across the monolith.   As can be seen in **Table 5-3**, the flow volumes ranged from 2 to 4 mL min-1 at 5 atm.   It was also found that the monoliths obtained from P/B/W ternary porogenic solvent were a little bit better than those from C/T binary porogenic solvent in terms of preparation reproducibility.

Table 5-3   Compositions of polymerization reaction mixtures and characteristics of the monoliths

In-tip Monolith	Composition of monomers				Composition of porogenic solvent		Permeability [c] (n=3)
	GMA	EDMA	%T	%C	C/T[a]	P/B/W[b]	
I	22.5	7.5	30	25	40:60, v/v	-	3.4±0.4
II	22.5	7.5	30	25	50:50, v/v	-	3.2±0.5
III	22.5	7.5	30	25	60:40, v/v	-	2.1±0.4
IV	22.5	7.5	30	25	-	30:60:10, v/v	3.4±0.3
V	22.5	7.5	30	25	-	40:50:10, v/v	3.0±0.3
VI	22.5	7.5	30	25	-	50:40:10, v/v	2.7±0.3
VII	22.5	7.5	30	25	-	60:30:10, v/v	2.2±0.2

a) Cyclohexanol/Toluene   b) 1-Propanol/1,4-Butanediol/Water
c) Flow volume at 5 atm in Milli-Q water (mL min^{-1})

Figure 5-2 shows the mechanical strength of the produced monoliths.   Linear relationship was observed between the flow rate and the pressure drop in the range of up to at least 10 atm.   The SEM photos are also shown in **Fig. 5-2**.   Heterogeneous polymer globules with diameters of 3-8 μm were observed, and the globules were interconnected to form a monolithic structure.   There are no significant differences in morphology.

As a result of the best balance of low-flow resistance, high surface area, and good preparation reproducibility, in the present paper, the ternary porogenic solvent of 1-propanol, 1,4-butandiol, and water at the volume ratio of 5:4:1 was selected and used for further experiments .
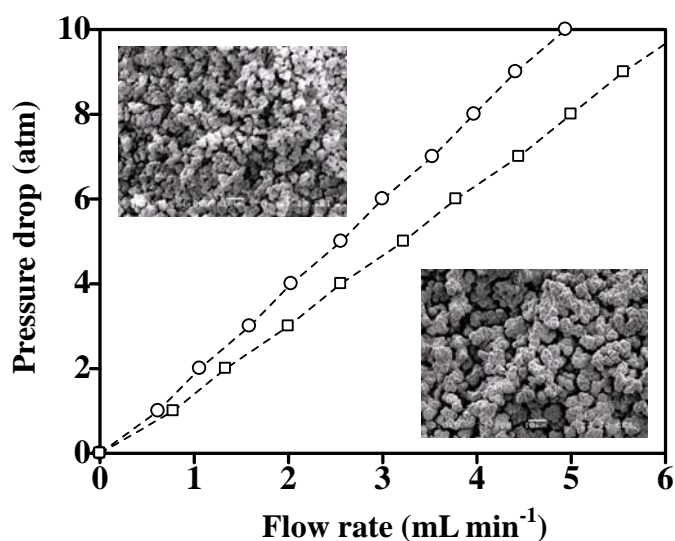
Fig. 5-2   Relationship between flow rate and pressure drop
□   monolith IV ○   monolith VI

5.3.2 Coupling of IDA to monolith surface

Iminodiacetate (IDA) is one of the most popular ligands with the ability to bind a variety of metal/metalloid ions. [40]   Therefore, as the next step, the optimization of the coupling of IDA to GMA-based monolith was carried out.   The scheme for covalent attaching of IDA to epoxy group is shown in **Fig. 5-1**.

The preparation of chelating monoliths with higher capacities is the most important subject.   The chelating capacity is dependent on many parameters such as the IDA concentration, reaction pH, reaction temperature, and reaction time.   In the present experiment, IDA concentration and reaction pH were optimized to obtain higher chelating capacity.   The prepared IDA solution was filled into the flowthrough pores of the tip-in monolith.   According to our preliminary experiments, reaction temperature and reaction time were set at 80°C and 20 h, respectively.   IDA modification solution was prepared by dissolving IDA and NaCl at a weight ratio of 5:1 into 50 mL of 2 mol L-1 Na_2CO_3, and the solution pH was adjusted to the intended value with NaOH or HNO_3.

The effect of IDA concentration on the chelating capacity was first examined in

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the concentration range of 0.1 to 2 M. **Figure 5-3** shows the chelating capacity of the adsorbent as a function of the IDA concentration, where the reaction was carried out at pH 10. It was found that maximum chelating capacity could be obtained at IDA concentrations higher than 1 M. **Figure 5-4** shows the variation in the chelating capacity with the pH of the 1 M IDA solution. As the solution pH increased from 6 to more alkaline pH values, the capacity increased and reached maximum value of 1.6 μmol/tip for Cu(II). According to these results, the optimum conditions of IDA concentration and reaction pH were found to be 1 M and pH 10, respectively.
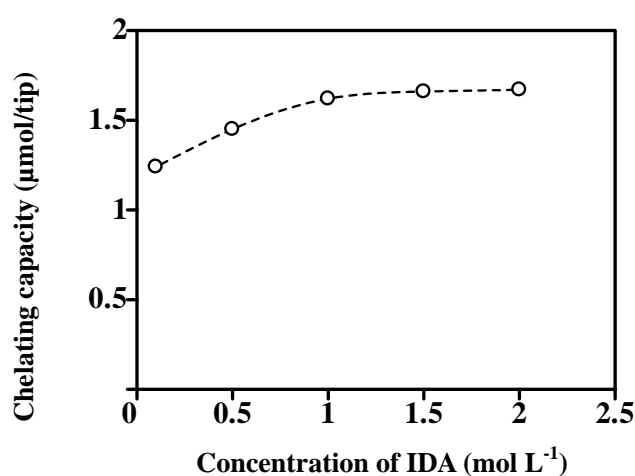

Fig. 5-3 Chelating capacity as a function of IDA concentration
Reaction time, temperature, and pH were fixed at
20 h, 80°C, and 10, respectively

5.3.3 Effect of sample solution pH on the recoveries of trace elements

For quantitative recoveries of as many elements as possible from the IDA-bonded chelating monolith, the procedure for SPME was optimized with respect to sample pH, eluent type and its volume, as described in experimental section. In order to obtain higher concentration factors, minimum requirement of the eluent was first examined. Referring to previously reported data [41-43], nitric acid was used as an eluent, and the recovery of Cu^{2+} from the tip-in monolith was measured at different eluent conditions. It was found from the experiment that over 85% of Cu^{2+} adsorbed

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on the monolith was eluted only with 0.5 mL of 2 M HNO_3, and that the adsorbed Cu^{2+} was almost completely (more than 95%) recovered under the elution condition of 0.9 mL of 2 M HNO_3.   Thus, 0.9 mL of 2 M HNO3 was used for subsequent studies.
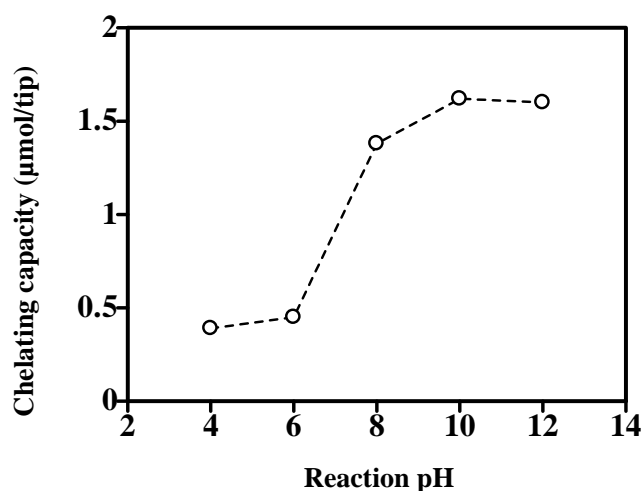

Fig. 5-4   Variation in chelating capacity with the ring-opening reaction pH of epoxide with IDA.
IDA concentration, reaction time, and temperature were fixed at 1 M, 20 h, and 80°C, respectively.

Sample solution pH has significantly influenced both the chemical forms of ligand (IDA) and analytes (metals/metalloids) and the resulting adsorption of trace elements on the chelating monolith.   Then, the effect of sample pH on the recoveries for different elements was systematically examined in the range of pH 3 to pH 9. For the addition-recovery (adsorption-elution) experiment, a test solution shown in Table 2 was prepared and employed.   The solution pH was adjusted to the intended value just before passing through the tip-in monolith for SPME.

The pH-dependent recoveries for 53 elements are summarized in **Fig. 5-5**.   As can be seen in **Fig. 5-5**, the produced IDA-bonded GMA-EDMA monolith provided different recovery characteristics for each element.   The recovery characteristics were essentially similar to those obtained with commercially available Chelex-100 resin, which has IDA groups in a styrene-divinylbenzene matrix.
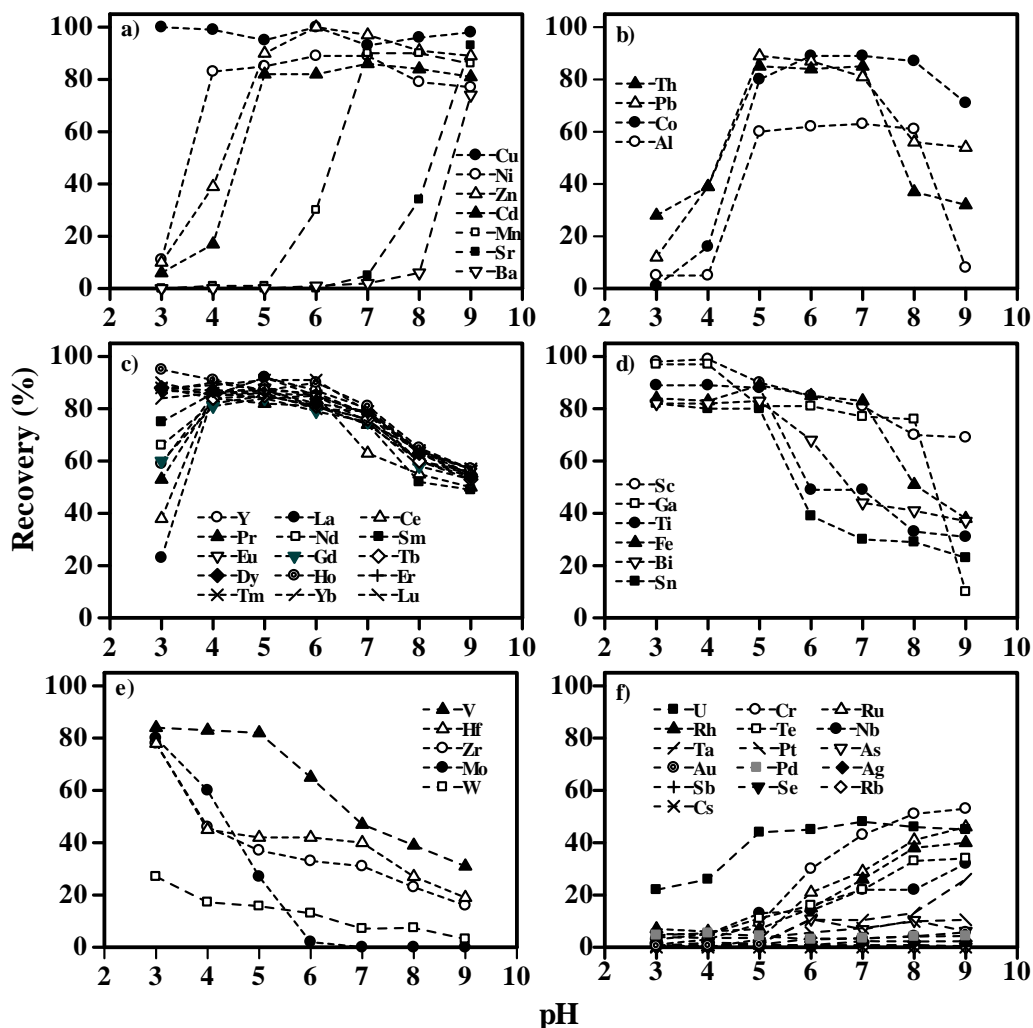
Fig. 5.5 pH-dependent recoveries for different metals and metalloids

a. ●:Cu ○:Ni △:Zn ▲:Cd □:Mn ■: Sr ▽:Ba
b. ▲:Th △:Pb ●:Co ○:Al
c. ○:Y ●:La △:Ce ▲:Pr □:Nd ■: Sm ▽:Eu ▼:Gd
   ◇:Tb ◆:Dy ◎:Ho +:Er ×:Tm /:Yb /:Lu
d. ○:Sc □:Ga ●:Ti ▲:Fe ▽:Bi ■:Sn
e. ▲:V △:Hf ○:Zr ●:Mo □:W
f. ■:U ○:Cr △:Ru ▲:Rh □:Te ●:Nb /:Ta \:Pt
   ▽:As ◎:Au ■:Pd ◆:Ag +:Sb ▼:Se ◇:Rb ×:Cs

In general, IDA-metal complex has higher stability constant at higher pH values, and then it is expected that the recovery (adsorption) would be enhanced by increasing the sample pH.   But, at pH values higher than 5, the hydrolysis of metals may have

an adverse effect on the recovery.   In the pH range of 4-6, therefore, maximum recoveries were obtained for a large majority of transition metals.   In the case of some elements such as V, Mo, W, Hf, and Zr, higher recoveries were obtained at the lower pH, and their recoveries exceeded 80% at pH 3.   The recoveries for several elements such as Au, Pd, As, Ag, Sb, Se, Rb and Cs were poor and did not exceed 30% in the pH range examined.   The recoveries are strongly dependent on the chemical form of the element in the sample, and now a more detailed examination is in progress.   In any case, it was found that good recoveries exceeding 80% could be obtained for 28 elements at the pH value of 5.   Thus, further experiments were carried out at pH 5.

5.3.4 Application to analysis of river water samples

In order to validate the proposed SPME method, two river water CRMs, JSAC 0301-1 and NMIJ 7201-a, were analyzed.   The analytical results are given in **Table 5-4**, where 50 mL of river water sample was passed through the tip-in monolith.   The elements adsorbed on the monolith were eluted with 0.9 mL of 2 M HNO3, and into which 0.1 mL of internal standard solution was added, resulting in concentration factor of 50.   As can be seen in **Table 5-4**, the experimental values for JSAC 0301-1 were in good agreement with the certified or information values.   The experimental values for NMIJ 7201-a were also in good agreement with the certified values, and the concentration levels of a total of 27 elements were provided.

5.4 Conclusion

A syringe filter tip fitted with a monolithic chelating adsorbent, tip-in chelating monolith, was prepared by in-situ copolymerisation of GMA and EDMA in the presence of a ternary porogenic solvent (1 propanol, 1,4 butanediol, water) and subsequent modification with IDA via epoxide opening reaction.   Extraction conditions were optimized to measure as many trace elements as possible with a minimum effort required for sample preparation.   As a result, adequate recoveries exceeding 80% for 28 elements were obtained at pH 5.   The proposed SPME method

was applied to the analysis of two certified reference materials, and good agreement was obtained between experimental values and certified or information values.

Table 5-4 Analytical results for trace elements in CRMs
(JSAC 0301-1 and NMIJ 7201-a)

| Element | m/z | JSAC 0301-1 / μg L^{-1} | | | | | NMIJ 7201-a / μg L^{-1} | | | | |
		Observed value[a]			Certified or reference[c] value			Observed value[a]			Certified value		
Al	27	19.5	±	0.1	19.0	±	0.9	6.1	±	0.2	6.1	±	0.4
Sc	45	(0.0036	±	0.0002)[b]	0.0025[c]	±	0.0002	0.0042	±	0.0001			
Ti	47	0.152	±	0.011	0.148[c]	±	0.005	0.072	±	0.008			
Fe	56	4.2	±	1.4	4.7	±	0.3	2.04	±	0.12	2.02	±	0.14
Co	59	0.0078	±	0.0005	0.0080[c]	±	0.0003	0.004	±	0.001			
Ni	60	0.040	±	0.002	0.032[c]	±	0.002	0.047	±	0.004	0.048	±	0.002
Cu	63	0.49	±	0.01	0.57	±	0.07	0.130	±	0.002	0.137	±	0.015
Zn	64	0.22	±	0.04	0.19	±	0.03	0.278	±	0.065	0.294	±	0.013
Ga	69	0.015	±	0.001	0.013[c]	±	0.003	0.0018	±	0.0001			
Y	88	0.0042	±	0.0003	0.0041[c]	±	0.0001	0.0074	±	0.0002			
Cd	111	0.0023	±	0.0007	0.0023	±	0.0007	0.0020	±	0.0004	0.0018	±	0.0002
Sn	118	0.0057	±	0.0009	0.0060[c]	±	0.0030	0.0132	±	0.0006			
La	139	(0.00316	±	0.00020)[b]	0.00090[c]	±	0.00003	0.015	±	0.008			
Ce	140	0.00148	±	0.00008	0.00112[c]	±	0.00006	0.0058	±	0.0002			
Pr	141	0.00029	±	0.00001	0.00025[c]	±	0.00002	0.00167	±	0.00007			
Nd	143	0.00155	±	0.00010	0.00147[c]	±	0.00008	0.0065	±	0.0002			
Sm	147	0.00041	±	0.00003	0.00039[c]	±	0.00006	0.00124	±	0.00002			
Eu	151	0.00015	±	0.00002	0.00013[c]	±	0.00002	0.000338	±	0.000007			
Gd	157	0.00067	±	0.00004	0.00056[c]	±	0.00004	0.00186	±	0.00004			
Tb	159	0.000084	±	0.000006	0.000076[c]	±	0.000008	0.000204	±	0.000005			
Dy	163	0.00061	±	0.00002	0.00059[c]	±	0.00002	0.00104	±	0.00003			
Ho	165	0.00016	±	0.00001	0.00014[c]	±	0.00001	0.00024	±	0.00001			
Er	167	0.00063	±	0.00003	0.00053[c]	±	0.00001	0.00071	±	0.00007			
Tm	169	0.000115	±	0.000007	0.000080[c]	±	0.000006	0.000110	±	0.000004			
Yb	172	0.00086	±	0.00003	0.00068[c]	±	0.00006	0.00074	±	0.00005			
Lu	175	0.000226	±	0.000008	0.000186[c]	±	0.000003	0.000129	±	0.000002			
Bi	209	0.000455	±	0.000114	0.000053[c]	±	0.000009	0.00127	±	0.00007			

a) Mean ±standard deviation, n = 3.
b) The value in the parentheses was close to the blank value.
c) Reference 42

References

1. M.J. Bloxham, S.J. Hill, P.J. Worsfold, *J. Anal. Atom. Spectrom.*, **9**, 935 (1994).

2. H. Sawatari, T. Hayashi, E. Fujimori, A. Hirose, H. Haraguchi, *Bull. Chem. Soc.*

Jpn., **69**, 1925 (1996).

3. T. Yabutani, K. Chiba, H. Haraguchi, *Bull. Chem. Soc. Jpn.*, **74**, 31 (2001).

4. M. Wells, K.W. Bruland, Mar. Chem., **63**, 145 (1998).

5. R.E. Sturgeon, S.S. Berman, S.N. Willie. J.A.H. Desaulniers, *Anal. Chem.*, **53**, 2337 (1981).

6. S.N. Willie, R.E. Sturgeon, S.S. Berman, *Anal. Chim. Acta,* **149**, 59 (1983).

7. Komjarova, R. Blust, *Anal. Chim. Acta*, **576**, 221 (2006).

8. S. Hirata, Y. Ishida, M. Aihara, K. Honda, O. Shikino, *Anal. Chim. Acta*, **438**, 205 (2001).

9. Y.H. Gao, K. Oshita, K.H. Lee, M. Oshima, S. Motomizu, *Analyst* **127**, 1713 (2002).

10. K.-H. Lee, M. Oshima, T. Takayanagi, S. Motomizu, *Anal. Sci.,* **16**, 731 (2000).

11. J.L. Manzoori, F. Shemirani, *J. Anal. Atom. Spectrom.*, **10**, 881 (1995).

12. M. Camino, M.G. Bagur, M. Sanchez-Vinas, D. Gazquez, R. Romero, *J. Anal. Atom. Spectrom.*, **16**, 638 (2001).

13. S. Kagaya, Z.A. Malek, Y. Araki, K. Hasegawa, *Anal. Sci.*, **18**, 923 (2002).

14. N. Tokman, S. Akman, Y. Bakircioglu, *Microchim. Acta,* **146**, 31 (2004).

15. T. Minami, Y. Sohrin, J. Ueda, *Anal. Sci.*, **21**, 1519 (2005).

16. R.A. Nickson, S.J. Hill, P.J. Worsfold, *Anal. Chim. Acta* , **351**, 311 (1997).

17. Y. Guo, B. Din, Y.W. Liu, X.J. Chang, S.M. Meng, M.Z. Tian, *Anal. Chim. Acta*, **504**, 319 (2004).

18. S. Saracoglu, L. Elci, *Anal. Chim. Acta*, **452**, 77 (2002).

19. Y.Q. Cai, G.B. Jiang, J.F. Liu, *Talanta*, **57**, 1173 (2002).

20. K. Oshita, S. Motomizu, *Bunseki Kagaku*, **57**, 291 (2008).

21. W.M. Landing, C. Haraldsson, N. Paxeus, *Anal. Chem.*, **58**, 3031 (1986).

22. V.A. Lemos, P.X. Baliza, *Talanta*, **67**, 564 (2005).

23. S.D. Çekiç, H. Filik, R. Apak, *Anal. Chim. Acta*, **505**, 15 (2004).

24. M.L. Firdaus, K. Norisuye, T. Sato, S. Urushihara, Y. Nakagawa, S. Umetani, Y. Sohrin, *Anal. Chim. Acta*, **583**, 296 (2007).

25. S. Akman, M. Ozcan, E. Demirel, *J. Anal. Atom. Spectrom.*, **17**, 743 (2002).

26. N. Tokman, S. Akman, M. Ozcan, *Talanta*, **59**, 201 (2003).

27. Y. Bakircioglu, D. Bakircioglu, N. Tokman, *Anal. Chim. Acta*, **547**, 26 (2005).

28. F. Svec, C.G. Huber, *Anal. Chem.*, **78**, 2100 (2006).

29. F. Svec, *J. Sep. Sci.* **27**, (2004) 747.

30. E.G. Vlakh, T.B. Tennikova, *J. Sep. Sci.*, **30**, 2801 (2007).

31. L. Geiser, S. Eeltink, F. Svec, J.M.J. Fréchet, *J. Chromatogr. A*, **1140**, 140 (2007).

32. Y. Ueki, T. Umemura, J. Li, T. Odake, K. Tsunoda, *Anal. Chem.*, **76**, 7007 (2004).

33. Y. Ueki, T. Umemura, Y. Iwashita, T. Odake, H. Haraguchi, K. Tsunoda, *J. Chromatogr. A*, **1106**, 106 (2006).

34. T. Umemura, Y. Ueki, K. Tsunoda, A. Katakai, M. Tamada, H. Haraguchi, *Anal. Bioanal. Chem.,* **386**, 566 (2006).

35. T. Umemura, N. Kojima, Y Ueki, *Bunseki Kagaku*, **57**, 517 (2008).

36. M. Zhang, F. Wei, Y.F. Zhang, J. Nie, Y.Q. Feng, *J. Chromatogr. A*, **1102**, 294 (2006).

37. C. Yu, M.H. Davey, F. Svec, J.M.J. Frechet, *Anal. Chem.*, **73**, 5088 (2001).

38. A. Tan, S. Benetton, J.D. Henion, *Anal. Chem.*, **75**, 5504 (2003).

39. Y. Fan, M. Zhang, S.L. Da, Y.Q. Feng, *Analyst*, **130**, 1065 (2005).

40. Q. Luo, H. Zou, X. Xiao, Z. Guo, L. Kong, X. Mao, *J. Chromatogr. A*, **926**, 255 (2001).

41. Y. Zhu, A. Itoh, E. Fujimori, T. Umemura, H. Haraguchi, *Bull. Chem. Soc. Jpn.*,

78, 659 (2005).

42. Y. Zhu, R. Hattori, E. Fujimori, T. Umemura, H. Haraguchi, *Anal. Sci.*, **21**, 199 (2005).

43. D. Rahmi, Y. Zhu, E. Fujimori, T. Umemura, H. Haraguchi, *Talanta*, **72**, 600 (2007).

Chapter 6   Conclusion and Future Prospect

6.1   Summary of the Present Research

In the present research, the preconcentration techniques and tools for highly sensitive multielement analysis were developed.   In order to preconcentrate trace levels of elements as well as to eliminate a large amount of matrix elements, a down-sized chelating resin-packed minicolumn, tandem preconcentration, a syringe La-coprecipitation and tip-in chelating monolith were explored for determination of trace elements in natural water by ICP-MS.

The down-sized 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).   The trace metals in 50 mL of original seawater sample were concentrated into 0.50 mL of 2 M nitric acid (100-fold preconcentration) and followed by multielement determination with ICP-MS.   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 were optimized to obtain good recoveries and analytical detection limits for trace metals.   After optimization, 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 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.

A tandem preconcentration method integrating chelating resin adsorption and La coprecipitation was developed for the determination of as many elements as possible with a limited volume of sample, and applied to an analysis of Lake Baikal water by high-resolution ICP-MS.   As a result, a total of fifty-six elements were determined in Lake Baikal water: Ca, Na, Mg, K, Si, Sr, B, Li, Ba, P, Fe, Al, Mo, Zn, Mn, Rb, U,

As, V, Cu, Pb, W, Y, Cs, Se, Cr, Ni, Ti, Sb, Zr, Sn, Co, Cd, Rh, Te, Hf, Nb, Ru, Ga, Sc, Th, Bi, and all-rare earth elements (all-REEs), except for Pm.   The concentrations of these elements covered a range of nine orders of magnitude, from approximately 17 µg mL-1 of Ca to less than 50 fg mL-1 of Tm.

A lanthanum (La) coprecipitation method with low sample consumption was explored for the preconcentration of oxo-anion forming elements prior to a measurement by inductively coupled plasma mass spectrometry (ICP-MS).   The preconcentration procedure was composed of two main steps: (1) the formation of a coprecipitate with the lowest possible La and (2) the redissolution of target analytes with a minimal use of nitric acid, and the elimination of a high concentration La from the analysis sample.   Each step was performed in a 25 mL-volume syringe to reduce the sample consumption and to avoid contamination from the experimental environment.   The thus-obtained method was evaluated through the analysis of seawater reference materials (CASS-4 and NASS-5).   The recoveries exceeded 80%, and the observed values were in good agreement with the certified values.

A tip-in chelating monolith has been developed for simple and facile SPME of trace elements in natural waters.   The tip-in monolith was prepared by two-step processes: 1) in situ polymerization of glycidyl methacrylate (GMA) with ethylene glycol dimethacrylate (EDMA) and 2) subsequent modification with iminodiacetate (IDA) via ring opening reaction of epoxide within confines of a commercially available syringe filter tip.   In order to make a rigid-porous material that has high permeability and ample surface area as much as possible, the composition of porogenic solvent was first optimized.   After that, to obtain higher chelating capacity, the pH and concentration of the IDA modification solution were examined.   Good recoveries of more than 80% were obtained for 28 elements including REEs, Fe, Co, Ni, Cu, Zn, Ga, Pb and Th in a single extraction step.   The proposed SPME method was validated through the analysis of two river water certified reference materials (CRMs: JSAC 0301-1 and NMIJ 7201-a).

6.2 Future Prospects of Preconcentration Techniques for Trace Elements in Natural Water

The information on the concentration levels and the distributions of trace elements is required to understand their behavior in aquatic environment including geochemical background, bioavailability and toxicities. However, direct determination of trace elements in natural water is still difficult even, because the concentration of trace element in natural water are very low and the high concentration of matrix element. In the present research, quite simple and practically useful preconcentration tools and techniques were developed. In the down-sized chelating resin-packed minicolumn method, only 50 mL of sample was used for 100-fold preconcentration of trace elements. The advantages of this method include small sample requirement and no needs for special apparatus. Then, the methods developed might be applied to on-site pretreatment.

Iminodiacetate-type chelating resin has low affinities for elements in anionic forms in the sample solution. Then, it is difficult to preconcentrate oxo-anion forming elements such as As, Se, Mo, and W and chloride complex forming elements such as Pd, Pt, Ag, and Au. In the present paper, tandem preconcentration technique was exploited. Development of element-selective chelating resin or monolith will be another important research subject. In the present research, a GMA-EDMA polymer monolith was modified with iminodiacetate as a functional group for preconcentration of transition metals in natural water. Organic polymer monolith has more potential in further modification with a variety of functional groups for element selective-chelating. There are many functional groups such as iminodiacetonitrile-hydroxylamine (IDAN), α−amino pyridine (AP) and 8-hydroxyquinoline (8-HQ), etc.

Speciation of trace elements in natural water samples is another important and challenging subject, because the geochemical cycles of trace elements are strongly dependent on their chemical forms. At the next step, thus, I would like to develop a hyphenated system for the separation of chemical species and the inorganic trace analysis.

List of Publications

I. Original Papers

1. Multielement Determination of Trace Metals in Seawater by ICP-MS with Aid of Down-sized Chelating Resin-packed Minicolumn for Preconcentration.
   Dwinna Rahmi, Yanbei Zhu, Eiji Fujimori, Tomonari Umemura, and Hiroki Haraguchi, *Talanta,* **72**, 600-606 (2007).

2. Vertical Distribution of Lead in Lake Baikal Water Measured by ID-ICP-MS.
   Yanbei Zhu, Dwinna Rahmi, Tomonari Umemura, Hiroki Haraguchi, and Koichi Chiba, *J. Nuc. Sci. Tech.*, **5**, 65-68 (2008).

3. Preparation of Monolithic Chelating Adsorbent inside a Syringe Filter Tip for Solid Phase Microextraction of Trace Elements in Natural Water prior to their Determination by ICP-MS.
   Dwinna Rahmi, Yanbei Zhu, Hiroharu Kobayashi, Yuka Takasaki, Sigeji Konagaya Hiroki Haraguchi and Tomonari Umemura, *Anal. Chim. Acta*, submitted

4. Fractional Distributions of Trace Metals in Surface Water of Lake Biwa as Studied by Ultrafiltration and ICP-MS.
   Yanbei Zhu, Ryota Hattori, Dwinna Rahmi, Satoshi Okuda, Akihide Itoh, Eiji Fujimori, Tomonari Umemura, and Hiroki Haraguchi, *Bull. Chem. Soc. Jpn.*, **78**, 1970-1976 (2005).

II. Notes Papers

1. Determination of 56 Elements in Lake Baikal Water by High-Resolution ICP-MS with the Aid of a Tandem Preconcentration Method.
   Dwinna Rahmi, Yanbei Zhu, Tomonari Umemura, Hiroki Haraguchi, Akihide Itoh, and Koichi Chiba, *Anal. Sci.*, **24**,1513-1517 (2008).

2. An in-syringe La-coprecipitation Method for Preconcentration of Oxo-anion Forming Elements in Seawater prior to ICP-MS Measurement.

Dwinna Rahmi, Yanbei Zhu, Eiji Fujimori, Takuya Hasegawa, Tomonari Umemura, Shigeji Konagaya, and Hiroki Haraguchi, *Anal. Sci.,* **24**,1189-1192 (2008).

III. Proceedings

1. Multielement Determination of Trace Metals in Lake Baikal Water by HR-ICP-MS with the Aid of Chelating Resin-packed Minicolumn Preconcentration

Dwinna Rahmi, Yanbei Zhu, Eiji Fujimori, Tomonari Umemura, and Hiroki Haraguchi , 7th Symposium on Asian Academic Network for Environmental Safety and Waster Management, p. 271-274 (2005).

2. A Syringe Filter Tip Filled with a Chelating Polymer Monolith for Solid Phase Microextraction of Trace Metals in Natural Water prior to their Determination by ICP-MS

Dwinna Rahmi, Yanbei Zhu, Takuya Hasegawa, Shigeji Konagaya, Tomonari Umemura, and Hiroki Haraguchi, International Symposium on Metallomics 2007, p. 156 (2007).

3. Tip-in Monolith for Solid Phase Microextraction of Trace Elements in Natural Water ;

Dwinna Rahmi, Hiroharu Kobayashi, Takuya Hasegawa, Yanbei Zhu, Shigeji Konagaya, Hiroki Haraguchi, and Tomonari Umemura, Third Asia-Pacific Winter Conference on Plasma Spectrometry, p. 81 (2008).

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