Mini-Scale Solid-Phase Collection and Concentration of Ultra-Trace Elements in Natural Waters for the Simultaneous Multielement Determination by Air-Flow Injection/ ICP–Mass Spectrometry

Mitsuko Oshima, Kyue-Hyung Lee, Yunhua Gao, and Shoji Motomizu
Department of Chemistry, Faculty of Science, Okayama University, 3-1-1 Tsushimanaka, Okayama 700-8530

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A mini-scale solid-phase collection and concentration method for the multielement determination of ultra-trace rare earth elements (REEs) in natural water samples was developed by using a newly designed small-scale filtration apparatus. A small-size chelating resin disk (iminodiacetate type: IDA; 10 µm pore size; 5 mm diameter; 0.5 mm thickness) was used for high-enrichment preconcentration of REEs and for elimination of alkali and alkaline earth metals in sample solutions. At pH 5.5, REEs in artificial river waters were quantitatively collected on the chelating resin disk, and most of alkali and alkaline earth metals were removed. The REEs on the chelating resin disk were completely recovered by ultrasonication of the disk with 1 cm^3 or less of 0.1 mol dm^{-3} nitric acid. A small amount (25 µL) of the concentrated sample solution was automatically injected and measured by inductively coupled plasma – mass spectrometry (ICP–MS) coupled with an air flow injection (AFI) system.

The determination of ultra-trace REEs at ppt (10^{-12} g mL^{-1}) or sub-ppt levels has become increasingly important in the field of earth science, biology, environment, and so on.[1,2] The abundance of the REEs in natural waters is often lower than LOD (limit of detection) of ICP–MS, which is said to be the most sensitive among the analytical instruments now available. In ICP–MS, non-spectral interference from coexisting major components is also not negligible. Therefore, the development of a rapid and reliable method for selective separation and concentration of target elements from matrices is urgently needed.

In general, a preconcentration step prior to ICP–MS measurement is indispensable, and various preconcentration methods, such as coprecipitation,[3] solvent extraction,[4] and ion-exchange with cation-exchangers[5] and chelating resins,[6–10] have been used for enrichment of REEs. Among these techniques, the methods with chelating resins have been most widely employed for preconcentration and matrix elimination in highly saline water analysis. However, a batch-wise method[6] with chelating resins such as Chelex-100 has some disadvantages as follows: (1) long time (2 h) to reach the adsorption equilibria between IDA and target metals, (2) large sample volume (at least 500 cm^3) for 50-fold preconcentration, and (3) relatively high concentration of nitric acid (2 mol dm^{-3}) for metal recovery. Column treatment method with chelating resin[8–10] also has some disadvantages as follows: (1) the process is relatively time-consuming (more than 3 h) and very troublesome, (2) after the elution of target elements, an additional re-concentration step is necessary for the enrichment. In practice, several elements such as Al, Fe, Zn and Pb are prone to be contaminated from ambient air and vessels during evaporation step.

In this work, the authors report a mini-scale solid-phase collection and concentration system for ultra-trace elements in aqueous samples. The main purposes of this system are: (1) to downsize all experimental conditions, such as samples, reagents, materials, vessels and wastes, (2) to attain high enrichment effect, (3) to realize a rapid and simple operation (less than 1 h), and (4) to protect samples from contamination.

A filtration/concentration apparatus used in the present work is shown in Figure 1. The proposed system was newly designed by improving the prototype filtration/concentration apparatus developed by Motomizu et al.[11] for ultra-trace determination of phosphate ion in pure water samples. In the newly designed system, glassware was entirely avoided, and an effective filtering diameter was decreased from 2 mm to 1 mm. Furthermore, a lower filtering supporter (Figure 1) was changed from a simple pinhole type to a pinhole with a several radial grooves, which accelerates the flowing of filtrate through a filtering material to enhance the efficiency of filtration. As is shown in Figure 1, the filtering system consists of three main parts; a filter housing (poly(chlorotrifluoroethylene): PCTFE), an upper filtering supporter (poly(tetrafluoroethylene): PTFE), and a lower filtering supporter (PCTFE). The lower filtering supporter, which holds filter materials together with the upper filtering supporter, is tightened with the screw-capped filter housing. The high-rate concentration (10–100 fold) can be easily attained by varying sample volumes from 10 to 50 cm^3 and eluent volumes from 0.5 to 1 cm^3 of 0.1 mol dm^{-3} nitric acid.

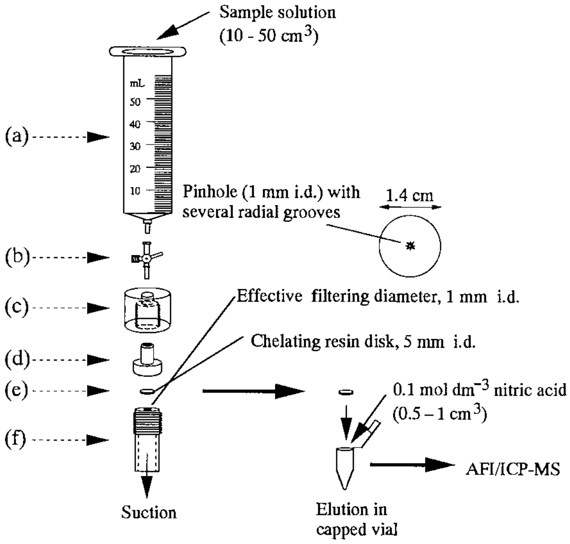

Figure 1. Mini-scale filtration/ concentration apparatus. (a) plastic syringe; (b) three-way cock valve; (c) filter housing; (d) upper filtering supporter; (e) filter material; (f) lower filtering supporter.

An IDA-type chelating resin disk (5 mm ϕ) used in this study was prepared by cutting 3M Empore™ Chelating Resin Disk (47 mm ϕ). This chelating resin consists of 90 wt% of IDA- polystyrenedivinylbenzene (PS-DVB) copolymer and 10 wt% of PTFE fiber. Recently, some papers[12–14] were published, and reported the determination of several heavy metals in water samples by ICP–AES coupled with the preconcentration using 3M Empore™ Chelating Resin Disk. Their experimental conditions, however, were a large-scale system: sample volumes were 2 dm^3 for 200-fold concentration: that is, a critical disadvantage of these methods is that the required sample volumes (1–2 dm^3) are too large to analyze when a sample volume is limited. In this study, an AFI/ ICP–MS system[8–10] for microsampling was employed in order to reduce sample volumes used for ICP–MS measurement. Measurements were carried out using Seiko 8000H ICP–MS equipped with a TR-30-C2 concentric nebulizer (J. E. Meinhard Co.). A microsampling system used consisted of an autosampler (Seiko, AT-600) and a software (MS ver 1.8) for data acquisition and controlling ICP–MS measurement. Analytical multielemental REEs standard solutions were prepared from single element standard solutions (1000 $\mu g\ mL^{-1}$) for atomic absorption spectrometry (Wako Pure Chemicals). All the other reagents used were of guaranteed reagent grade.

To evaluate the usefulness of the proposed filtration/concentration apparatus, we applied the proposed system with the mini-scale filtering apparatus to the determination of REEs in river water samples by AFI/ ICP–MS. In the pre-experiments using an artificial river water sample,[9,10] the recovery of REEs from the solution containing large amounts of alkai and alkaline earth metals (Na; 20 $\mu g\ mL^{-1}$, K; 10 $\mu g\ mL^{-1}$, Mg; 15 $\mu g\ mL^{-1}$ and Ca; 50 $\mu g\ mL^{-1}$) as matrix ions was examined. Ten milliliters of an artificial river water sample (each REE content was 1 ng mL^{-1}, and 0.1 mol dm^{-3} HNO_3 was contained) was adjusted to pH 5.5 by adding 1 cm^3 of 1 mol dm^{-3} ammonia water and 1 cm^3 of 4 mol dm^{-3} ammonium acetate buffer solution (pH 6.25). After the sample solution was passed through the chelating resin disk equipped to the mini-scale filtering apparatus, the disk was washed by filtering 5 cm^3 of ultrapure water. Then, the chelating resin disk was transferred into a small plastic capped vial, and to it 1 cm^3 of 0.1 mol dm^{-3} nitric acid was added. The vial was kept in water under ultrasonication for 20 min. Eight sets of filtering apparatus were simultaneously used to investigate reproducibility of the procedure. The results are shown in Table 1. Recovery for fifteen elements was almost 100% and their RSDs (relative standard deviations) ranged from 2.1% (Dy) to 4.4% (Er). On the contrary, the recovered amounts of four matrix ions were less than 1%; that is, most of alkali and alkaline earth metal ions could be removed from the final sample solution. In the case of 100-fold preconcentration, 50 ml of an artificial river water sample (each REE content was 1 pg mL^{-1}) was passed through the chelating resin disk like the same manner as above procedure, and the REEs were recovered with 0.5 cm^3 of 0.1 mol dm^{-3} nitric acid. As is shown in Table 1, the recovery for all REEs was almost 100%, and their RSD s obtained from seven apparatuses were within 10%.

Table 1. Recovery of REEs from an artificial river water samples by preconcentration using chelating resin disk and mini-scale filtering apparatuses

m/z	Element	Recovery					
		Sample 1[a]			Sample 2[b]		
		Avr.	SD	RSD/%	Avr.	SD	RSD/%
89	Y	101.0	4.0	3.9	98.5	4.6	4.7
139	La	96.8	3.0	3.1	97.6	6.2	6.4
140	Ce	97.5	2.7	2.8	99.0	4.9	5.0
141	Pr	97.2	3.8	3.9	98.2	7.4	7.5
146	Nd	97.1	3.5	3.6	97.9	9.5	9.7
147	Sm	100.2	3.2	3.2	96.4	8.0	8.3
151	Eu	98.5	3.1	3.1	99.2	4.5	4.5
157	Gd	97.7	3.0	3.1	96.3	7.7	8.0
159	Tb	98.0	2.6	2.6	102.0	6.8	6.7
163	Dy	97.5	2.0	2.1	95.5	7.0	7.3
165	Ho	97.2	2.7	2.7	97.5	5.9	6.1
167	Er	98.6	4.4	4.4	94.9	8.1	8.5
169	Tm	97.5	2.4	2.4	99.7	4.8	4.8
172	Yb	97.9	2.8	2.8	98.1	6.6	6.7
175	Lu	99.4	2.7	2.8	97.3	5.8	6.0

[a] Each REE content is 1 ng mL^{-1}, and 10-fold preconcentration (n=8).
[b] Each REE content is 1 pg mL^{-1}, and 100-fold preconcentration (n=7).

Table 2. Analytical results of ultra-trace REEs in natural water sample by the present metod and column method

Element	This study[a]			Column/IDA[b]		
	pg ml^{-1}			pg ml^{-1}		
Y	0.20	±	0.02	0.15	±	0.01
La	1.0	±	0.15	1.0	±	0.1
Ce	4.5	±	0.2	4.8	±	0.2
Pr	0.55	±	0.04	0.70	±	0.05
Nd	2.0	±	0.15	2.4	±	0.2
Sm	0.23	±	0.02	0.26	±	0.02
Eu	0.05	±	0.01	0.06	±	0.01
Gd	0.48	±	0.06	0.43	±	0.05
Tb	0.07	±	0.01	0.06	±	0.01
Dy	0.23	±	0.02	0.23	±	0.03
Ho	0.07	±	0.01	0.05	±	0.01
Er	0.16	±	0.02	0.17	±	0.02
Tm	0.03	±	0.01	0.02	±	0.01
Yb	0.12	±	0.03	0.10	±	0.02
Lu	0.03	±	0.01	0.03	±	0.01

[a] 100-fold preconcentration (n=7).
[b] Cited from Ref. 10, 50-fold preconcentration (n=3).

Shiogama water, the source of Asahi River in Okayama Prefecture, was treated with the proposed chelating resin disk, and the REEs were concentrated by 100-fold according to the proposed procedures. The sample solution containing concentrated REEs was measured by the AFI/ICP–MS, and the data obtained by the chelating column method[10] were also summarized in Table 2. The analytical results obtained by both methods were agreed closely with each other.

From these results, it can be seen that the new filtration/concentration apparatus is a very useful tool for collecting ultra-trace elements because of its simplicity, rapidity, repeatability, and compactness. The proposed solid-phase collection/concentration system coupled with IDA-chelating resin disk can be applicable to the preconcentration of trace elements in natural waters such as river water, lake water, mineral water, and so on. Now our research for highly saline solution such as seawater is going on progress.

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