

## Trace Metal Analysis by Air-Flow Injection/ICP-MS Combined with Chelating Resin Preconcentration

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Simultaneous multielement determination of trace elements in aqueous samples by air-flow injection/ICP-mass spectrometry (AFI/ICP-MS) coupled with a novel solid-phase collection/concentration system has been developed. A mini-scale filtration apparatus coupled with a chelating resin (iminodiacetate type: IDA) was used for enrichment of trace elements in natural water samples, and the enriched metal solution was measured by inductively coupled plasma-mass spectrometry (ICP-MS). Under the pretreatment condition of sample pH 5.5, fifteen rare earth elements (REEs) and Al, Ni, Co, Cu, Zn, Cd, and Pb, were quantitatively collected on the small chelating resin disk (5 mm i.d.). Alkali and alkaline earth metals in sample solutions were effectively separated from the target elements during the preconcentration step and washed out over 99.9%. The collected trace elements on the chelating resin disk were completely recovered with 0.1 mol dm<sup>-3</sup> nitric acid by using ultrasonication. A small amount (25 µl) of the concentrated metal solution was automatically injected and measured by ICP-MS assisted with an air flow injection (AFI) system. As a result, 22 elements in river water, lake water, and drinking water could be determined by the proposed method.

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In many fields, such as earth science, biology, environment, and electronics, the knowledge about elemental distributions, multielement pattern, multielement correlation, and yet their chemical speciation becomes to be more and more important.<sup>1</sup>

In spite of the highly sensitive detectability in ICP-MS, there are two big troubles on trace metal analysis in natural water samples. One is that the abundance ratios between major elements and trace elements are too large to control sample pretreatment and furthermore to measure ICP-MS by direct sample introduction. The other one is that there exist several elements having extremely low concentration such as below ppt (10<sup>-12</sup> g ml<sup>-1</sup>) or sub-ppt level.

Various preconcentration procedures for trace elements in aqueous samples have been employed, including solvent extraction of metal chelates,<sup>2,3</sup> coprecipitation,<sup>4-7</sup> and ion-exchange with cation-exchangers<sup>8</sup> and chelating resins.<sup>9-15</sup> Recently, the methods with chelating resins have been most widely used for enrichment of analyte metals and matrix elimination in highly saline water analysis prior to final sample introduction to an ICP-MS instrument. Most prevalent methods with chelating resins are batch-wised methods such as using a magnetic stirrer or a mini-packed column. However, these methods suffer from several disadvantages such as large sample volume, insufficient recovery for analyte elements, long pretreatment time, relatively high acid concentration for metal recovery and large volume of acid, contamination effect from ambient air or vessels, and so on.

In this study, the authors used a small-scale filtration/concentration devices<sup>16</sup> and micro-sampling system in ICP-MS measurement for trace elements in natural water samples. The main purposes of this system are: (1) to downsize

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.

The present study shows the application of natural water samples, such as river water, lake water and drinking water, prior to AFI/ICP-MS. In order to confirm the applicability and the reliability of the proposed method, an artificial river water sample and the river certified reference materials (JAC 0031 & JAC 0032) were investigated. As a result, fifteen REEs and Al, Co, Ni, Cu, Zn, Cd, and Pb in natural water samples were found to be quantitatively retained on the chelating resin disk. The analytical results obtained from the proposed method showed good agreement with the data obtained by AFI/ICP-MS combined with a chitosan-based chelating resin column preconcentration.<sup>11-13</sup>

### Experimental

#### Apparatus

A model SPQ 8000H ICP-MS instrument (Seiko Instruments Co., Tokyo, Japan) was used. A microsampling system using air-flow<sup>12</sup> as a carrier was AT-600 autosampler (Seiko Instruments Co.). One end of a nozzle (PTFE tubing, 1 mm i.d. x 3 mm o.d.) of AT-600 autosampler was connected to a suction tubing of ICP-MS main body. A small volume of air was sucked through the nozzle while only the robotic arm was moving from one tank to another. Less than 100 µl of sample solutions was discretely injected into the air stream, nebulized and introduced into a plasma source.

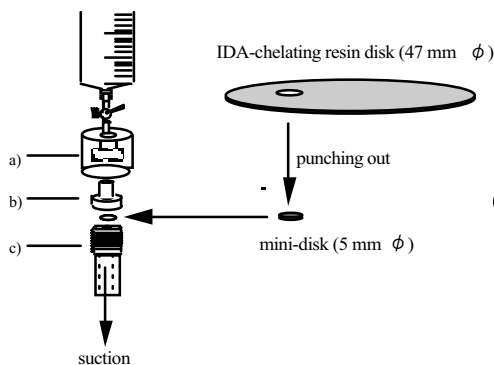


Fig. 1 Mini-scale filtration/concentration apparatus  
a) filter housing; b) upper filtering supporter;  
c) lower filtering supporter.

Dispersion was limited while the sample was flowing through the tube because the sample was not diluted with any other aqueous solution in a flowing path.

Mini-scale filtration/ concentration apparatus used in this study is shown in fig. 1. As is shown in Fig. 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<sup>3</sup> and eluent volumes from 0.5 to 1 ml of 0.1 M (1 M = 1 mol dm<sup>-3</sup>) nitric acid.

#### Reagents and materials

Analytical multielement standard solutions were prepared from single element standard solutions (1000 µg ml<sup>-1</sup>) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). Working standard solutions were diluted with 0.1 M HNO<sub>3</sub> just before AFI/ICP-MS measurement. Ultrapure water (18.2 MΩ cm resistivity) was prepared with a Milli-Q Element (Nihon Millipore, Tokyo, Japan). Ultrapure grade nitric acid (60%, Cica-MERCK) from Kanto Chemicals (Tokyo, Japan) was diluted with the ultrapure water to give adequate acid concentrations. Acetic acid (minimum 96%) and ammonia water (29%) used for preparing an ammonium acetate buffer solution were of electronic industrial reagent grade (Kanto Chemicals). A 4 M ammonium acetate solution for adjusting the pH of samples was prepared by mixing an ammonia and an acetic acid solution, which were an equimolar concentration.

An IDA-type chelating resin disk (5 mm φ) used in this study was prepared by cutting 3 M Empore<sup>TM</sup> Chelating Resin Disk (47 mm φ). The disk was somewhat hydrophobic since it consists of polystyrene-divinylbenzene (PS-DVB) copolymer and polytetrafluoroethylene (PTFE) fiber. The small disk was converted to be hydrophilic by soaking 1 M ammonia-acetic acid buffer solution for two days after rinsing with 3 M hydrochloric acid solution. The color change of the disk from white to pale yellowish was a finish sign of filter conditioning.

#### Samples

The river certified reference materials were issued from the committee of reference materials of the Japan Society for Analytical Chemistry. A couple of samples, unspiked (JAC0031) and spiked (JAC0032), were provided with adding nitric acid (about pH 1). Small amounts of elements were spiked into JAC0032.

Natural water samples examined in this study were as follows: a river water sample collected at Rhein River in Germany, a lake water sample collected at Towada Lake in Aomori Prefecture in Japan, and a drinking water was of a commercially available one

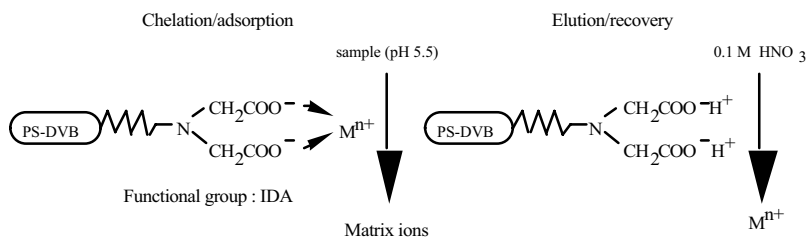


Fig. 2 Principle of metal chelation/ adsorption and elution/ recovery with IDA-type chelating resin disk

(Evian, France). These samples were acidified to about pH 1 by adding conc. nitric acid (4 ml per one liter) before filtration with a 0.45 µm membrane filter.

#### Procedures of the present method

A filtration/ concentration apparatus<sup>16</sup> used in this study has 1 mm of effective filtering diameter, and glassware was entirely avoided. The high-rate concentration (10 - 100-fold) can be easily attained by varying sample volumes from 10 to 50 ml and eluent volumes from 0.5 to 1 ml of 0.1 M nitric acid.

Fifty milliliters of seawater sample solution was adjusted to pH 5.5 by adding 1 ml of 1 M ammonia water and 1 ml of 4 M ammonia- acetic acid 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 rinsed by filtering 5 ml of ultrapure water. Then, the chelating resin disk was transferred into a small plastic capped vial, and to it 0.5 or 1 ml of 0.1 M nitric acid was added. The vial was kept in water under ultrasonication for 20 min.

The concentrated metal solution was subsequently measured by AFI/ICP-MS. A small amount (25 µl) of the concentrated sample solution was automatically injected and fifteen isotopes were simultaneously measured by AFI/ICP-MS. One milliliter was sufficient to obtain more than 20 replicates of the AFI/ICP-MS measurement; therefore 60 or more of elements in 1 ml samples can be measured by the AFI/ICP-MS method. Total measuring time for one sample was about 90 s.

## Results and discussion

#### Limits of detection (LODs) and limit of quantification(LOQs)

Instrumental LODs for AFI/ICP-MS, which were defined as the concentrations corresponding to three times of the standard deviations ( $\sigma$ ) of blank intensity for trace metals contained in 0.1 M HNO<sub>3</sub>, were obtained.

Table 1 Instrumental LODs by AFI/ICP-MS and LOQs for total process

Element	m/z	LOD <sup>a)</sup>	LOQ <sup>b)</sup>	Element	m/z	LOD <sup>a)</sup>	LOQ <sup>b)</sup>
		(pg ml <sup>-1</sup> )	(pg ml <sup>-1</sup> )			(pg ml <sup>-1</sup> )	(pg ml <sup>-1</sup> )
Al	27	90	12	Nd	146	1.1	0.03
Co	59	8	0.2	Sm	147	0.74	0.02
Ni	60	50	1	Eu	151	0.23	0.007
Cu	65	54	2	Gd	157	0.61	0.02
Zn	66	110	5	Tb	159	0.18	0.006
Cd	114	5	0.1	Dy	163	0.34	0.009
Pb	208	30	2	Ho	165	0.12	0.004
Y	89	0.36	0.01	Er	167	0.29	0.01
La	139	0.38	0.01	Tm	169	0.15	0.005
Ce	140	0.43	0.01	Yb	172	0.27	0.01
Pr	141	0.12	0.008	Lu	175	0.17	0.006

a) Instrumental limit of detection, 3  $\sigma$  (n=10, 0.1 M HNO<sub>3</sub>)

b) Limit of quantification, 10  $\sigma$  (n=10, 50 ml of 0.1 M HNO<sub>3</sub>, 100- fold preconcentration)

Furthermore, the LOQs for total process, which were defined as the concentrations corresponding to ten times of the standard deviations ( $\sigma$ ) of total blank intensity pretreated with 50 ml of 0.1 M  $\text{HNO}_3$ , were obtained. These values are summarized in Table 1.

The LODs for heavy metals were ranged from 10 to 100  $\mu\text{g ml}^{-1}$  levels and lanthanoids from 0.1 to 1  $\mu\text{g ml}^{-1}$  levels, respectively. As the LOQs for REEs were ppq ( $10^{-15}$   $\text{g ml}^{-1}$ ) level, there is no problem to determine the ppt ( $10^{-12}$   $\text{g ml}^{-1}$ ) or sub-ppt levels of REEs in natural water samples by the present method.

#### pH effect on adsorption

The artificial standard solutions<sup>12</sup> of river water were used to investigate the adsorption behavior of trace metals in the pretreatment with the chelating resin disk. The artificial standard solutions contained major elements, such as Na (20  $\mu\text{g ml}^{-1}$ ), K (10  $\mu\text{g ml}^{-1}$ ), Ca (50  $\mu\text{g ml}^{-1}$ ) and Mg (15  $\mu\text{g ml}^{-1}$ ), and also contained 60 elements at the same concentrations of 1  $\text{ng ml}^{-1}$ . By using this solution, the effect of pH on the adsorption of trace metals (1  $\text{ng ml}^{-1}$ ) in the preset pretreatment were investigated by varying the pHs from 1 to 9.

The adsorption rate of trace elements changed with changing the pH of the solutions. The adsorption trend for REEs and several trace elements which are quantitatively adsorbed to the chelating resin disk are shown in Fig. 3 and Fig. 4.

Nearly 100% of adsorption rate was obtained for Al, Ni, Co, Cu, Zn, Cd and Pb over pH 5. Most of Li, Rb, Sr, Cs and Ba were lost during the preconcentration procedure. At pH 8, the adsorption rate of Co abruptly decreased. This phenomenon may result from the formation of cobalt-ammine complex to pass through the resin disk. As a result, pH of the sample solution was adjusted to 5.5, taking into consideration the efficient and the reproducible adsorption and recovery of as many elements as possible.

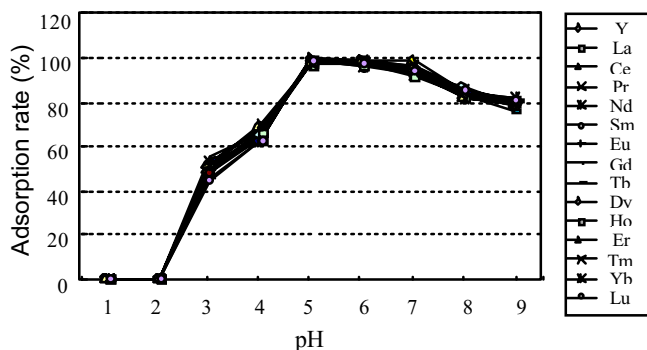


Fig. 3 Effect of pH on metal adsorption (REEs)

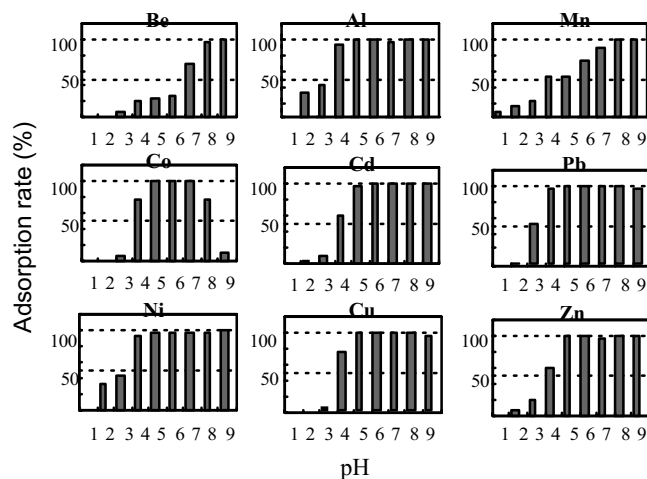


Fig. 4 Effect of pH on metal adsorption (Be, Al and several heavy metals)

#### Analysis of river certified reference materials

In order to evaluate the accuracy and the precision of the proposed method, a couple of river certified reference materials (JAC 0031 and JAC 0032) were investigated. The 10-fold preconcentration for JAC 0031 and 25-fold preconcentration for JAC 0032, respectively, were carried out at the same time as follows; five 10-ml aliquots of the JAC 0031 samples and five 25-ml aliquots of the JAC 0032 samples were treated with the ten independent filtration/concentration apparatuses and the analytical results were obtained by the AFI/ICP-MS method.

Analytical results of seven trace elements in river reference materials were listed in Table 2. As a whole, the analytical results in JAC 0031 and JAC 0032 obtained by the present method were in good agreement with the certified values within 10% error.

Table 2 Analytical results of several trace elements in JAC 0031 and JAC 0032 by the proposed method

Elem-ent	m/z	JAC 0031		JAC 0032	
		This study <sup>a)</sup> ( $\text{ng ml}^{-1}$ )	Certified ( $\text{ng ml}^{-1}$ )	This study <sup>b)</sup> ( $\text{ng ml}^{-1}$ )	Certified ( $\text{ng ml}^{-1}$ )
Al	27	14.0 $\pm$ 0.4	13.4 $\pm$ 0.7	59 $\pm$ 2	61 $\pm$ 2
Co	59	0.024 $\pm$ 0.003	-	0.02 $\pm$ 0.005	-
Ni	60	0.15 $\pm$ 0.02	-	9.6 $\pm$ 0.3	10.2 $\pm$ 0.3
Cu	65	0.91 $\pm$ 0.02	0.88 $\pm$ 0.03	9.2 $\pm$ 0.2	10.5 $\pm$ 0.2
Zn	66	0.77 $\pm$ 0.03	0.79 $\pm$ 0.05	10.6 $\pm$ 0.4	11.3 $\pm$ 0.4
Cd	114	0.003 $\pm$ 0.001	(0.003) <sup>c)</sup>	1.02 $\pm$ 0.03	1.00 $\pm$ 0.02
Pb	208	0.031 $\pm$ 0.005	0.026 $\pm$ 0.003	10.0 $\pm$ 0.1	9.9 $\pm$ 0.2

a) AFI/ICP-MS coupled with filtration/concentration method using IDA-type chelating resin disk (25-fold preconcentration, n=5).

b) AFI/ICP-MS coupled with filtration/concentration method using IDA-type chelating resin disk (10-fold preconcentration, n=5).

c) Information value.

#### Analysis of natural waters

Three kinds of natural water samples, a river water, a lake water and a drinking water, were treated with the proposed chelating resin disk, and the metal ions were concentrated by 50-fold for the determination of REEs and concentrated by 10-fold for the determination of Al, Ni, Co, Cu, Zn, Cd and Pb according to the proposed procedures. The sample solutions containing concentrated metal ions were measured by the AFI/ICP-MS method, and the data obtained by AFI/ICP-MS coupled with chitosan-based chelating resin column<sup>11</sup> were also summarized in Table 3.

Entirely, the metal abundance of Rhein River water was still higher than that of Towada Lake water or Evian drinking water.

As a whole, both analytical results obtained from the proposed method and AFI/ICP with chelating resin column method showed very good agreement with each other.

Among these, exceptionally large difference data for zinc in Towada Lake water and lead in Rhein River water sample were found, respectively. This may be ascribed to the contamination effect during column pretreatment procedure.

As was expected, the abundance of REEs in these natural water samples were too extremely low to detect in direct sample introduction. The concentrations of Y and 14 REEs in these natural samples ranged from 0.46  $\text{ng ml}^{-1}$  of La in Rhein River water to 0.0001  $\text{ng ml}^{-1}$  of Eu in Evian water

#### Conclusion

In this study, the determination of 22 trace elements in natural waters was successfully achieved by AFI/ICP-MS with the pretreatment procedure using IDA-type chelating resin disk. The performance of ICP-MS connected with the flow introduction of samples using an air flow carrier (AFI method) was done.

Table 3 Analytical results of trace elements in natural water samples by AFI/ICP-MS with filtration/concentration method using IDA-type chelating resin disk

Element	m/z	Rhein River		Towada Lake		Evian	
		This study <sup>a)</sup> (ng ml <sup>-1</sup> )	Column <sup>b)</sup> (ng ml <sup>-1</sup> )	This study <sup>a)</sup> (ng ml <sup>-1</sup> )	Column <sup>b)</sup> (ng ml <sup>-1</sup> )	This study <sup>a)</sup> (ng ml <sup>-1</sup> )	Column <sup>b)</sup> (ng ml <sup>-1</sup> )
Al	27	24.5 ± 0.2	25.8	12.2 ± 0.3	11.8	1.5 ± 0.2	1.96
Co	59	0.05 ± 0.01	0.09	0.015 ± 0.002	0.013	0.009 ± 0.001	0.010
Ni	60	1.8 ± 0.05	1.60	0.33 ± 0.03	0.52	0.50 ± 0.02	0.49
Cu	65	2.3 ± 0.02	2.43	1.5 ± 0.02	1.65	0.58 ± 0.03	0.66
Zn	66	1.0 ± 0.1	2.16	2.6 ± 0.2	11.3	1.1 ± 0.2	2.70
Cd	114	0.044 ± 0.002	0.05	0.025 ± 0.001	0.03	0.004 ± 0.001	0.01
Pb	208	0.13 ± 0.02	1.43	0.28 ± 0.02	0.45	0.30 ± 0.03	0.39
Y	89	0.21 ± 0.01	0.20	0.032 ± 0.002	0.033	0.0044 ± 0.0003	0.0046
La	139	0.46 ± 0.005	0.44	0.016 ± 0.001	0.016	0.0014 ± 0.0002	0.0012
Ce	140	0.35 ± 0.002	0.33	0.034 ± 0.002	0.030	0.0042 ± 0.0005	0.0029
Pr	141	0.092 ± 0.003	0.080	0.0037 ± 0.0002	0.0036	0.0003 ± 0.0001	0.00035
Nd	146	0.22 ± 0.005	0.22	0.020 ± 0.002	0.017	0.0011 ± 0.0002	0.0012
Sm	147	0.052 ± 0.002	0.050	0.0051 ± 0.003	0.0046	0.0003 ± 0.0001	0.00027
Eu	151	0.10 ± 0.005	0.11	0.0010 ± 0.0002	0.00091	0.0001 ± 0.0001	0.00010
Gd	157	0.081 ± 0.003	0.073	0.0056 ± 0.0003	0.0051	0.0003 ± 0.0001	0.00029
Tb	159	0.015 ± 0.002	0.010	0.0010 ± 0.0001	0.00095	0.00012 ± 0.00005	0.00011
Dy	163	0.039 ± 0.003	0.040	0.005 ± 0.001	0.0048	0.00044 ± 0.00002	0.00046
Ho	165	0.0084 ± 0.008	0.0069	0.001 ± 0.0005	0.0010	0.00015 ± 0.00002	0.00014
Er	167	0.022 ± 0.002	0.021	0.0028 ± 0.0002	0.0030	0.0038 ± 0.0003	0.0041
Tm	169	0.0023 ± 0.0002	0.0021	0.0005 ± 0.0001	0.00048	0.00012 ± 0.00002	0.00012
Yb	172	0.014 ± 0.001	0.013	0.0024 ± 0.0004	0.0025	0.00049 ± 0.00003	0.00048
Lu	175	0.018 ± 0.002	0.0017	0.0005 ± 0.0001	0.00042	0.00016 ± 0.00003	0.00013

a) AFI/ICP-MS coupled with filtration/concentration method using IDA-type chelating resin disk (50-fold preconcentration for REEs determination (n=3), and 10-fold preconcentration for remained seven trace elements (n=3)).

b) Cited from Ref. 11; AFI/ICP-MS with chitosan-based chelating resin column, mean values of three measurements (n=3).

The advantages of AFI method are rapid sample throughput, ease of automation, less band broadening and less sample consumption.

A microsampling system enabled to minimize sample sizes required for the AFI/ICP-MS measurement (less than 50 ml for preconcentration); therefore, high concentration ratio could be easily achieved with a small volume of samples. Lowering the sample volume required for the pretreatment is very useful because it diminishes amounts of reagents required and wastes.

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 various natural waters including seawater.

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