

Multielement Determination of Trace Metals in River Water (Certified Reference Material, JSAC 0301-1) by High Efficiency Nebulization ICP-MS after 100-fold Preconcentration with a Chelating Resin-Packed Minicolumn

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The determination of 34 trace metals in a river water certified reference material (CRM), *i.e.* JSAC 0301-1, which was issued by the Japan Society for Analytical Chemistry in January 2004, was performed by ICP-MS with a high efficiency nebulizer after preconcentration with a laboratory-made chelating resin-packed minicolumn, with which trace metals were concentrated 100-fold from 50 mL of a river water sample to 0.5 mL of the final analysis solution. Trace metals in JSAC 0301-1 were observed in the concentration range from 19 $\mu\text{g L}^{-1}$ of Al to 0.000053 $\mu\text{g L}^{-1}$ of Bi. It was found that most of the concentrations of trace metals, including rare earth elements (REEs), in JSAC 0301-1 were lower than those in JAC 0031, which was also a previously issued CRM prepared with water from the same river as that of JSAC 0301-1. The low concentrations of trace metals in JSAC 0301-1 might be attributed to the fact that there was a heavy rain before collecting the original water sample to prepare the present CRM. Furthermore, the REE distribution patterns of JSAC 0301-1, JAC 0031 and the average values of river water samples in Japan were parallel to each other. These results indicate that the distributions of REEs in JSAC 0301-1 and JAC 0031 were the typical ones of river water samples in Japan.

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Introduction

Certified reference materials (CRMs) were indispensable for evaluating the reliabilities of the analytical results,¹⁻⁴ especially when the concentrations of the analytes were at the trace or ultratrace level, because the results might be affected by spectral interferences and matrix interferences due to matrix elements in the samples as well as by contamination in pretreatment processes. Nowadays, many kinds of CRMs for trace metals in natural water were issued by various institutions, for example, the Japan Society for Analytical Chemistry (JSAC) and the National Research Council of Canada (NRC). Generally, the certified values were available only for a limited number of trace metals in CRMs, for which the concentrations were in the range from ppm (mg L^{-1}) to sub-ppb ($\text{sub-}\mu\text{g L}^{-1}$) levels. However, research on other trace metals, such as rare earth elements (REEs), in natural water samples, which generally exist at the ppt (ng L^{-1}) or sub-ppt level, have also attracted much attention,^{5,6} since the analysis of such trace metals in CRMs could be used to cross check different preconcentration and examination techniques, in addition to obtaining useful geochemical information from them.

There were two kinds of river water CRMs, namely JAC 0031 (unspiked) and JAC 0032 (spiked), issued by JSAC in 1995. The concentrations of trace metals, including REEs, in JAC 0032 and/or JAC 0031, were reported in some papers,^{4,7,8} which provided important information, especially about trace metals

for which certified values were not available. Recently, JSAC issued river water CRMs, *i.e.*, JSAC 0301-1 (unspiked), JSAC 0301-2 (unspiked), and JSAC 0302 (spiked), because the previously issued CRMs, *i.e.*, JAC 0031 and JAC 0032, were almost out-of-stock. Up to date, there have been few reports concerning trace metals in JSAC 0301-1, JSAC 0301-2, and JSAC 0302. Thus, in the present experiment the determination of 34 trace metals in JSAC 0301-1 was performed by ICP-MS with 100-fold preconcentration using a chelating resin-packed column. Then, many trace metals, whose certified values were not available because of their extremely low concentrations, could be determined with fairly good precision. In the preconcentration of trace metals in JSAC 0301-1, a chelating resin-packed minicolumn developed in the present laboratory was employed, where 50 mL of the sample was preconcentrated to 0.5 mL of the final analysis solution, followed by a measurement with a high efficiency nebulization ICP-MS.

Experimental

Instruments

An ICP-MS instrument (Model Agilent HP4500, Yokogawa, Tokyo, Japan) was used for the determination of trace metals, which consisted of a quadrupole mass spectrometer. The ICP-MS instrument was equipped with a high efficiency nebulizer, which allowed us to measure trace metals by the ICP-MS in 2 min with only *ca.* 0.2 mL of the analysis solution. The operating conditions for the ICP-MS instrument are given in Table 1, all of which were optimized for each instrumental parameter. A TWIN pH meter of Model B-212 (Horiba, Kyoto,

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Table 1 Operating conditions for the ICP-MS instrument

ICP-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
Carrier gas flow rate	Ar 1.00 L min ⁻¹
Sampling depth	5.5 mm from load coil
Nebulizer: Micro-mist type	
Sample uptake rate	0.1 mL min ⁻¹
Data acquisition:	
Measurement mode	Peak hopping
Dwell time	50 ms/point
Data point	3 points/peak
Number of scans	100

Japan) was used for a pH adjustment. A magnetic stirrer (Model SR100, Advantec, Tokyo, Japan) was used to stir the solutions. A laboratory-made 8-port syringe pump was used to load the river water samples into a minicolumn with the syringes. A syringe pump of (Model KDS200, KD Scientific, MA, USA) was used to pass the rinsing solutions through the column. HPLC prefilters (Model DISMIC-13HP, Advantec, Tokyo, Japan, and Model Millex-LH, Nihon Millipore Kogyo, Tokyo, Japan) were used to construct a chelating resin-packed minicolumn. The pore size of the built-in membrane filters in both syringe filters were 0.45 μm . Single-use syringes of Terumo series (Terumo Corporation, Tokyo, Japan) were used for loading the samples, rinsing the column, and eluting the analytes with a nitric acid solution.

Chemicals and sample

Nitric acid, acetic acid and aqueous ammonia solutions 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 $\mu\text{g L}^{-1}$) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). The standard solutions for trace metals were prepared according to a paper by Itoh *et al.*⁹ Chelex 100 resin in 200–400 mesh was purchased from Bio-Rad Laboratories (Richmond, CA, USA). Before preconcentration, the chelating resin was cleaned by keeping it in 5 M HCl and changing the acid once every day for 5 days. After the resin was collected on a G4 glass filter, it was further rinsed with 2 M nitric acid and pure water, and kept in a 0.1 M of ammonium acetate at pH 6.0. The pure water used throughout the present experiment was prepared by a Milli-Q purification system (Model Element A-10, Nihon Millipore Kogyo, Tokyo, Japan).

The river water CRM sample (JSAC 0301-1) was purchased from Tama Chemicals (Kawasaki, Japan). According to an attachment to the CRMs provided by JSAC, the original river water from Doshi River (Kanagawa prefecture, Japan) for the preparation of JSAC 0301-1 was collected with a 1000 L polyethylene tank, and then filtered with a membrane filter with a pore size of 0.5 μm . The filtered sample was then homogenized and acidified to pH 1.0 by adding nitric acid. Finally, the sample was further filtered with a membrane filter with a pore size of 0.2 μm and bottled in PFA bottles (each 500 mL).

Preconcentration of trace metals in JSAC 0301-1

Trace metals in JSAC 0301-1 were preconcentrated with a chelating resin-packed minicolumn developed in the present

authors' laboratory.¹⁰ The minicolumn was constructed with two syringe filters (DISMIC 13HP and Millex-LH) for HPLC, and 0.088 \pm 0.004 g ($n = 10$) of the chelating resin (Chelex 100) in wet weight was packed into the space confined between the two filters. The method to prepare the chelating resin-packed minicolumn was similar to that of the reported one.¹⁰

The procedure used to preconcentrate trace metals in river water CRM was as follows. Firstly, 50 mL of a water sample, which was adjusted to pH 6.0 with an ammonia solution and acetic acid, was loaded into the minicolumn at a flow rate of 1.0 mL min⁻¹ with a 50 mL volume syringe. Secondly, 3 mL of 0.1 M ammonium acetate buffer (pH 6.0) and 5 mL of pure water were successively injected at a flow rate of 2 mL min⁻¹ for rinsing so as to minimize the amounts of the 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 to a 5 mL test tube, into which 0.05 mL of an internal standard solution (Ge, In, Re, Tl 100 $\mu\text{g L}^{-1}$ each) was added to correct for any matrix effects. The final analysis solution was subjected to a determination of trace metals by an ICP-MS equipped with a high efficiency nebulizer.

In the recovery test, trace metals were spiked in the river water sample, while taking into consideration their concentrations in the sample. The amounts of trace metals spiked in the sample are given in Table 2, along with the recovery values. The same preconcentration procedure as described above was carried out to estimate the recoveries for the trace metals.

All of the beakers, stirring bars, test tubes and pipettes used in the present experiment were soaked in 6 M nitric acid for more than one week and rinsed with pure water.

Results and Discussion

Analytical figures of merit for trace metals

The recovery values for trace metals obtained in the recovery test are summarized in Table 2 along with their spiked amounts. It can be seen in Table 2 that the recoveries for 25 elements, from Al to U, were larger than 80%, which are shown over the dashed line in the table. Although the recoveries for trace metals below the dashed line were smaller than 80%, it can also be seen that the reproducibilities of these recovery values were quite good, with a standard deviation of less than 4%. The analytical detection limits and blank values for the trace metals examined in the present method are given in Table 3, summarized as the analytical figures of merit. The analytical detection limits for trace metals examined in the present experiment were calculated from the instrumental detection limits, taking into account the concentration factor (100) and the recovery values. The instrumental detection limits were defined as the concentrations corresponding to 3-times the standard deviation of the background signal intensity, which was estimated from 10-times duplicate measurements of the 2 M nitric acid solution, with internal standard elements (Ge, In, Re, Tl 10 $\mu\text{g L}^{-1}$ each). The analytical detection limits for trace metals were in the range from 0.000006 $\mu\text{g L}^{-1}$ of Pr, Tb, and Lu to 0.008 $\mu\text{g L}^{-1}$ of Ti. In estimations of the blank values, 50 mL of 0.1 M nitric acid was used as the test solution, where the same preconcentration and measurement procedures as those for JSAC 0301-1 were performed. It can be seen from Table 3 that the blank values for most trace metals were not detected, which suggests that the determinations of these elements were not affected by the blank values. Although the blank value for Al was 0.33 $\mu\text{g L}^{-1}$, it is negligible compared to the concentration

Table 2 Results for the recovery test

Element	<i>m/z</i>	Amount spiked/ $\mu\text{g L}^{-1}$	Recovery ^b , %
Al	27	10	80 ± 6
Ti	47	1	82 ± 1
Co	59	1	105 ± 1
Ni	62	10	103 ± 2
Cu	65	10	88 ± 2
Zn	66	10	100 ± 1
Ga	71	0.1	99 ± 2
Y	89	0.1	96 ± 1
Cd	111	1	94 ± 1
La	139	0.1	96 ± 1
Ce	140	0.1	93.5 ± 0.8
Pr	141	0.1	93.2 ± 0.4
Nd	143	0.1	90 ± 3
Sm	147	0.1	94 ± 1
Eu	153	0.1	92.5 ± 0.6
Gd	157	0.1	93.9 ± 0.4
Tb	159	0.1	90.3 ± 0.9
Dy	163	0.1	89 ± 2
Ho	165	0.1	87 ± 1
Er	166	0.1	83 ± 4
Tm	169	0.1	83 ± 2
Yb	172	0.1	81 ± 3
Lu	175	0.1	80 ± 1
Pb	207	1	100.5 ± 0.7
U	238	0.1	92 ± 1

Sc	45	0.1	64.1 ± 0.9
V	51	10	34 ± 1
Mn	55	10	49 ± 2
Zr	90	1	36 ± 1
Nb	93	0.1	49.4 ± 0.9
Sn	118	1	69 ± 2
Hf	178	0.1	38 ± 2
Bi	209	0.1	76 ± 2
Th	232	0.1	66 ± 2

a. The amount of trace metals spiked in the 50 mL sample in the recovery test.

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

of Al in JSAC 0301-1, which was $19 \mu\text{g L}^{-1}$.

Analytical results for trace metals in JSAC 0301-1

The analytical results for trace metals in JSAC 0301-1 are summarized in Table 4, along with the available certified values. It can be seen in Table 4 that the concentrations of 32 trace metals were in the range from $0.000053 \mu\text{g L}^{-1}$ of Bi to $19 \mu\text{g L}^{-1}$ of Al, although those of Hf and Th were below their lower limits of determination, *i.e.*, $0.00023 \mu\text{g L}^{-1}$ and $0.00006 \mu\text{g L}^{-1}$, respectively. The results for Al, Cu, Zn, Cd, Pb, U, and Mn agreed well with the certified values or the information values issued by JSAC. These results indicate that the present method was effective for the preconcentration and determination of trace metals in river water. Neither certified values nor reference values for other 27 trace metals have been available until now. The observed values for Pb, Zr, Nb, Sn, and Bi are shown in brackets, because there might be some uncertainty for them caused by the relatively high blank values. Besides, the relatively larger standard deviation for the observed value of V might be attributed to $^{15}\text{N}^{36}\text{Ar}$ interference, because the matrix for analysis solutions was 2 M nitric acid; moreover, a 0.1 M ammonium acetate solution was used in the preconcentration procedure to minimize the amounts of matrix elements, such as

Table 3 Analytical figures of merit for trace metals

Element	<i>m/z</i>	ADL ^a / $\mu\text{g L}^{-1}$	Blank ^b / $\mu\text{g L}^{-1}$
Al	27	0.001	0.33 ± 0.01
Ti	47	0.008	n.d. ^c
Co	59	0.00004	0.0022 ± 0.0005
Ni	62	0.001	0.005 ± 0.001
Cu	65	0.0003	0.0067 ± 0.0004
Zn	66	0.0006	0.057 ± 0.008
Ga	71	0.00004	n.d. ^c
Y	89	0.000009	0.00004 ± 0.00001
Cd	111	0.0007	n.d. ^c
La	139	0.00001	0.00007 ± 0.00001
Ce	140	0.00001	0.00011 ± 0.00002
Pr	141	0.000006	n.d. ^c
Nd	143	0.00006	n.d. ^c
Sm	147	0.00003	n.d. ^c
Eu	153	0.00001	n.d. ^c
Gd	157	0.00004	n.d. ^c
Tb	159	0.000006	n.d. ^c
Dy	163	0.00002	n.d. ^c
Ho	165	0.00001	n.d. ^c
Er	166	0.00004	n.d. ^c
Tm	169	0.000009	n.d. ^c
Yb	172	0.00003	n.d. ^c
Lu	175	0.000006	n.d. ^c
Pb	207	0.0001	0.0070 ± 0.0008
U	238	0.00002	n.d. ^c
Sc	45	0.0002	<0.0005
V	51	0.0001	0.0022 ± 0.0001
Mn	55	0.0007	<0.002
Zr	90	0.0003	0.006 ± 0.001
Nb	93	0.00005	0.0012 ± 0.0001
Sn	118	0.0002	0.0025 ± 0.0004
Hf	178	0.00008	n.d. ^c
Bi	209	0.00001	<0.00004
Th	232	0.00002	n.d. ^c

a. Analytical detection limit, calculated from instrumental detection limits, taking into account the concentration factor (100) and recovery values.

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

c. Not detected.

Mg and Ca, which were partly retained in the minicolumn.

In order to evaluate the present analytical results, the concentrations of trace metals in JSAC 0301-1 were compared to those in JAC 0031, which was prepared in 1995 with river water also collected from Doshi River. The correlation between the concentrations of trace metals in JSAC 0301-1 and those in JAC 0031 is shown in Fig. 1, where the results for JAC 0031 reported by Itoh *et al.* were used.⁸ It can be seen from Fig. 1 that the concentrations of most trace metals in JSAC 0301-1 were slightly less than those in JAC 0031. This may be due to the dilution by rain water that had fallen for several days before sampling of the river water for preparing JSAC 0301-1.

REE distribution patterns of river water samples

To evaluate the concentrations of REEs in the present CRMs, the shale normalized REE distribution patterns of JSAC 0301-1 (present work) and JAC 0031 (cited from Ref. 8) are shown in Fig. 2, together with those of the average values of river water in Japan (cited from Ref. 11) and SLRS-3 (cited from Ref. 12); SLRS-3 is a river water reference material for trace metals issued by NRC. In Fig. 2, the concentrations of the REEs were normalized to those in Post-Archean average Australian Shale (PAAS),¹³ where $[\text{REE}]_{\text{sample}}$ and $[\text{REE}]_{\text{PAAS}}$ mean the

Table 4 Analytical results for trace metals in a certified reference material (JSAC 0301-1)

Element	<i>m/z</i>	Concentration/ $\mu\text{g L}^{-1}$	
		Observed value ^a	Certified value
Al	27	19 ± 2	19.0 ± 0.9
Ti	47	0.148 ± 0.005	
Co	59	0.0080 ± 0.0003	
Ni	62	0.032 ± 0.002	
Cu	65	0.504 ± 0.006	0.57 ± 0.07
Zn	66	0.193 ± 0.005	0.19 ± 0.03
Ga	71	0.013 ± 0.003	
Y	89	0.00408 ± 0.00009	
Cd	111	0.0021 ± 0.0003	0.0023 ± 0.0007
La	139	0.00090 ± 0.00003	
Ce	140	0.00112 ± 0.00006	
Pr	141	0.00025 ± 0.00002	
Nd	143	0.00147 ± 0.00008	
Sm	147	0.00039 ± 0.00006	
Eu	153	0.00013 ± 0.00002	
Gd	157	0.00056 ± 0.00004	
Tb	159	0.000076 ± 0.000008	
Dy	163	0.00059 ± 0.00002	
Ho	165	0.00014 ± 0.00001	
Er	166	0.00053 ± 0.00001	
Tm	169	0.000080 ± 0.000006	
Yb	172	0.00068 ± 0.00006	
Lu	175	0.000186 ± 0.000003	
Pb	207	(0.004 ± 0.004)	0.005 ^b
U	238	0.0029 ± 0.0003	0.0029 ± 0.0002
Sc	45	0.0025 ± 0.0002	
V	51	9.0 ± 0.8	
Mn	55	0.117 ± 0.003	0.125 ± 0.007
Zr	90	(0.0091 ± 0.0006)	
Nb	93	(0.00028 ± 0.00006)	
Sn	118	(0.006 ± 0.003)	
Hf	178	<0.00023	
Bi	209	(0.000053 ± 0.000009)	
Th	232	<0.00006	

a. Mean ± standard deviation, $n = 5$ (There might be some uncertainty for values in bracket because of the relative high blank values).

b. Information value, issued by JSAC.

concentrations of the REEs in the sample and those in PAAS, respectively. It can be seen from Fig. 2 that the REE distribution patterns of JSAC 0301-1, JAC 0031 and river water samples in Japan provide similar shapes to one another. The similarities of the REE distribution patterns for these samples may indicate that the present CRM, JSAC 0301-1, is one of the typical river water samples in Japan. This conclusion may agree with that reported by Itoh *et al.* in terms of JAC 0031.⁸ It can also be seen from Fig. 2 that the distribution patterns of REEs in JSAC 0301-1, JAC 0031 and river water samples in Japan showed relatively larger enrichments of heavy REEs compared to light REEs. Such characteristic behaviors of dissolved REEs were often found in natural water, such as river water and seawater. Henderson summarized that the relative enrichment of heavy REEs may reflect the higher abilities of heavy REEs to form soluble complexes in water.¹⁴ On the other hand, SLRS-3 showed a REE distribution pattern with a horizontally smooth line, along with generally higher REE concentrations in it than those in other Japanese river water samples. These results may indicate that there was some possibility for the existence of suspended particulate materials in SLRS-3, which had a similar REE composition to those of

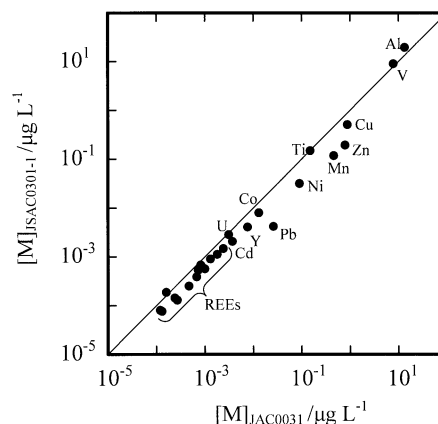


Fig. 1 Correlation between the concentrations of trace metals in certified reference materials JSAC 0301-1 and JAC 0031.

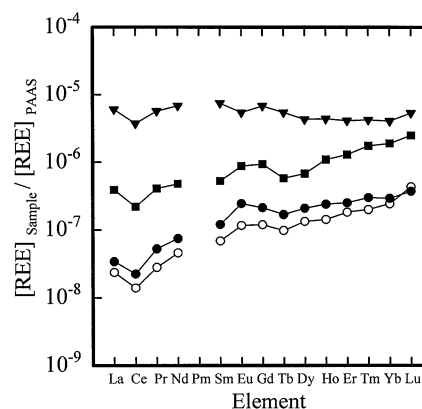


Fig. 2 Shale normalized REE distribution patterns of certified reference materials. ○, JSAC 0301-1; ●, JAC 0031, cited from Ref. 8; ▼, SLRS-3, cited from Ref. 11; ■, average values of river waters in Japan, cited from Ref. 12.

shale.¹⁴ Moreover, it can be seen from Fig. 2 that the concentrations of REEs in JSAC 0301-1 and JAC 0031 were 2–3 orders of magnitude lower than those in SLRS-3. Such lower concentrations of ultratrace metals in JSAC 0301-1 and JAC 0031 indicate that the determinations of REEs in the former ones require much lower detection limits for REEs, which require larger concentration factors.

Conclusion

The concentrations of 34 trace metals in river water certified reference material (JSAC 0301-1) were obtained by high efficiency nebulization ICP-MS after 100-fold preconcentration with a chelating resin-packed minicolumn. Trace metals in JSAC 0301-1 were observed in the concentration range from 19 $\mu\text{g L}^{-1}$ of Al to 0.000053 $\mu\text{g L}^{-1}$ of Bi. Most of the concentrations for trace metals, including rare earth elements (REEs), in JSAC 0301-1 were lower than those in JAC 0031. The present analytical method allows the determination of ultratrace metals at the sub-ppt (sub- ng L^{-1}) level in only 50 mL of sample with preferable precision, and will find further applications.

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