

Multielement Analysis for Trace Metals in Natural Waters by On-Line Filtration-Concentration Flow Injection Method Coupled with Inductively Coupled Plasma-Mass Spectrometric Detection

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Abstract

A rapid and simple analytical method for the determination of transition metals and rare earth metals at sub-ppb (ppb = ng ml⁻¹) levels in the presence of alkali and alkaline earth metal matrices was developed. A solid phase filtration/concentration technique was utilized for the matrix separation and analyte preconcentration from river water samples. The flow injection system used was equipped with a chelating disk (0.5 mm of thickness and 5 mm of a diameter) made of an iminodiacetate resin. Detection of the metals was accomplished by inductively coupled plasma-mass spectrometry (ICP-MS), which allows simultaneous fifteen-element measurement at the same time. One milliliter of water samples (pH 5.5) was flowed through the chelating disk, and the enriched trace metals were eluted with 0.1 M nitric acid. The most important feature in this study is the possibility to work with the low adsorption efficiency, even less than 50%, which results in the improvement of sensitivity and precision. As a result, the measurable elements and the applicability of the method can be expanded compared with a batch-wise method. The proposed method was applied to the river certified reference materials (JAC0031 & JAC0032) for evaluating the accuracy and precision on the determination of several heavy metals. The analytical results obtained for such metals as V, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, and Pb, were in good agreement with the certified values and the literature values. The proposed method was applied to the determination of trace metals in river and seawater samples.

Keywords: Flow injection; ICP-MS; on-line pretreatment; solid-phase collection; matrix separation; trace elements; chelating resin disk; river water; certified reference materials

1. Introduction

It can be said that the detection power of inductively coupled plasma-mass spectrometry (ICP-MS) enables to measure trace elements at sub-ppb levels directly. However, polyatomic interferences and non-spectral interferences from the major ions in saline solutions make an ICP-MS analysis difficult [1-3]. Therefore, a sample pretreatment step is essential to obtain more reliable data and the desired detection limits. In recent years, flow injection (FI) technique has been increasingly used as an on-line preconcentration method for the determination of trace metals in such high-salt content samples by ICP-MS [4-8]. Generally, the on-line coupling of FI with ICP-MS requires the incorporation of a solid-phase column containing a chelating resin within the FI manifold.

Off-line pretreatment methods usually require large sample volumes (more than 500 ml) and laborious handling for low metal concentration samples. On the other hand, on-line column pretreatment method can overcome these disadvantages, and at the same time preserves the advantages of the off-line procedures, such as sensitivity improvement and effective matrix elimination.

As the packing materials for on-line pretreatment columns, silica-based immobilized 8-hydroxyquinoline (I-8HQ) [4, 9-11] and iminodiacetate (IDA) functional groups [8, 12-16] have been most widely used for on-line FI-ICP-MS systems. However, the I-8HQ-type resins have suffered from the release of trace impurities of the silica gel and the less stability of the immobilization. The IDA-type resins, such as Chelex-100, have suffered from the volume change of resins according to pH change of solutions.

In this paper, the use of an automatic chelation system is described for matrix elimination and on-line preconcentration of transition elements and rare earth elements (REEs) in river water samples and a seawater sample prior to the determination by ICP-MS. In the present on-line system, a disk-type filter is employed as a chelating solid instead of a beads-packed column, which can relieve back pressure from the column in the FI manifold and reduce the time for metal-ligand adsorption and desorption.

2. Experimental

2.1 Materials and Reagents

The chelating resin disk (3 M Empore™ Chelating Disk) was purchased from GL Science Inc. (Tokyo). A smaller size (5 mm

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i.d.) filter was prepared by cutting an original disk (47 mm i.d., 0.5 mm of thickness), and then rinsed twice with a 3 M HCl solution and ultrapure water alternately, followed by soaking in a 1 M ammonium acetate buffer solution for two days.

For the standard calibration of ICP-MS, a series of working standard solutions (blank, 0.001, 0.01, 0.1, 1, 10 and 100 ng ml⁻¹) were prepared by diluting multielement stock solution (1 µg ml⁻¹) with 0.05 M ammonium acetate buffer solution (pH 5.5, electronic industrial reagent grade, Kanto Chemicals, Tokyo). The stock solution (1 µg ml⁻¹) was prepared by mixing and diluting single element standards (1000 µg ml⁻¹, Wako Pure Chemicals, Osaka) and a multielement standard (10 µg ml⁻¹, XSTC-13, Spex CertiPrep, NJ, USA) with a 0.1 M nitric acid prepared from conc. HNO₃ (60 %, Cica-MERCK, Kanto Chemicals). Ultrapure water (18.2 MΩcm resistivity) used was prepared by a Milli-Q Element^{TR} (Nihon Millipore, Tokyo, Japan).

2.2 Instrumentation

A quadrupole-type SPQ 8000H (Seiko Instruments Co., Tokyo, Japan) ICP-MS was used for the determination of trace elements in eluates. The ICP-MS system was equipped with a glass concentric nebulizer (TR-30-C2, J. E. Meinhard Associates Inc., CA, USA). Data processing and acquisition for multi-flow signals were controlled by a MicroSuction^{TR} (software ver. 1.8 M, Seiko Instruments Co.). Standard operating conditions are given in Table 1.

The FI system used was of an in-house built device and the schematic diagram of FI system is shown in Fig. 1. Two sets of double plunger pumps (Flom Instruments Co., model dual pump 203) were used for propelling a sample carrier and an eluent at a flow rate of 1.5 ml min⁻¹, respectively. One six-way valve (Sanuki Kogyo, model SVA-6M 2HL) was used for switching sample load and sample injection. The chelating disk was fixed with PTFE filter holder (GL Science Inc., 2 mm of an effective filtering diameter) incorporated in the loop of the switching valve. An autosampler (System Instruments Co., model 23) equipped with a sample loop (1 ml), one six-way valve, and a turn table (1 ml vial x 50) was used for automatic sample introduction. PTFE tubings (0.5 mm i.d.) were used for all the connections in the FI manifold with the shortest length.

Table 1 Operating parameters for ICP-MS system

Frequency	27 MHz
Incident power	1.1 kW
Reflected power	<5 W
Plasma gas	Ar 15 L min ⁻¹
Carrier gas	Ar 0.45 L min ⁻¹
Auxiliary gas	Ar 1.0 L min ⁻¹
Sampling depth	10 mm from load coil
Sampling cone	Copper 1.1 mm φ
Skimmer cone	Copper 0.35 mm φ
Dwell time	50 ms
Acquisition time	30 s
Integration	Peak area

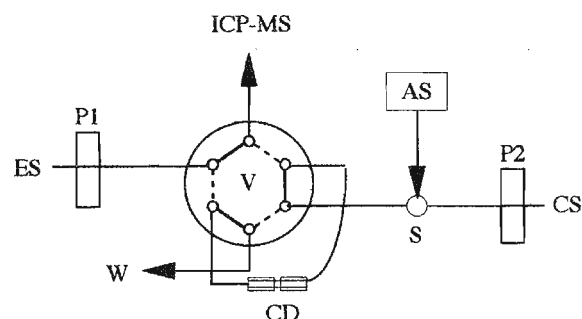


Fig.1 Schematic diagram of flow injection (FI) system. ES: eluent solution (0.1 M nitric acid), CS: carrier solution (0.05 M ammonium acetate buffer solution, pH 5.5), AS: autosampler, S: sample (1000 µl), V: six-way valve, CD: chelating resin disk, P1 and P2: pump (flow rate, 1.5 ml min⁻¹), W: waste, — : sample load state, - - - - : sample injection state.

2.3 Samples

A couple of the river certified reference materials (JAC0031 and JAC0032) were issued from the Committee of Reference Materials of the Japan Society for Analytical Chemistry.

River water samples examined in this study were collected at five points from upper to lower stream of Asahi River in Okayama Prefecture. A seawater sample was collected at Shibukawa Seashore in Tamano City (Okayama Prefecture). These samples were acidified to about pH 1 by adding conc. nitric acid (4 ml per one liter) before the filtration with a 0.45 µm membrane filter.

Since these water samples were acidified to about pH 1 and kept in a refrigerator, it was necessary to adjust their pH 5.5. To each sample, 1.2 ml of conc. ammonia water and 0.6 ml of glacial acetic acid were added to 50 ml of aliquots prior to on-line preconcentration procedure.

2.4 On-line separation/preconcentration procedure

On a load state, the sample solution (1 ml, pH 5.5) in a sample loop was injected in the stream of a buffer solution carrier, and then passed through a chelating resin disk. At that time, most of matrix ions were drained out with the buffer solution. On an injection state, metal ions adsorbing on the disk were eluted with 0.1M HNO₃ and introduced into the nebulizer of ICP-MS. The eluent stream containing the sample zone flowed in the opposite direction through the disk, thereby yielding sharper eluted peaks.

By the proposed system, maximum fifteen isotopes were simultaneously measured and their integrated peak areas were obtained in one measurement. Processing time for one cycle was 350 s including the time necessary for conditioning the pH of the disk with the pH 5.5 buffer (50 s), sampling a sample solution by the autosampler (60 s) and the loading the sample on the disk (90 s), the delay time of the eluate from the injection valve to the mass filter (30 s), the integration time for sample zone (30 s), and the washing time for the disk (90 s).

Since the standards used for calibrations are measured in the same manner as the samples, the correction for column efficiency was unnecessary, which results in the improvement of the

sensitivity and reproducibility, and can widen the measurable elements and applicability of the method, compared with the batch-wise method [19].

3. RESULTS AND DISCUSSION

3.1 Effect of the size of sample-carrier on flow signals

To examine the effect of the size of sample-carrier tubing on peak shape, three kinds of PTFE tubings (0.25 mm, 0.5 mm, and 1.0 mm i.d.) were tested at the constant eluent flow (1.5 ml min⁻¹). Only the line between the nebulizer and the switching valve was replaced in turn, whereas the other flow lines were fixed with 0.5 mm i.d. PTFE tubing.

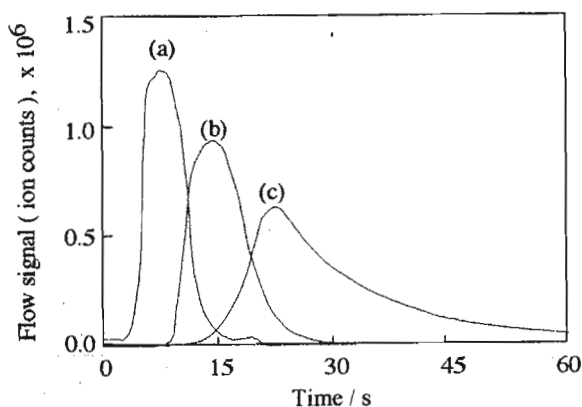


Fig. 2 Effect of the size of sample-carrier tubing on flow signal in on-line FI/ICP-MS

(a) 0.25 mm i.d.; (b) 0.5 mm i. d.; (c) 1.0 mm i.d.;
Sample: 10 ng ml⁻¹ of Mn solution (pH 5.5);
Sample volume: 1 ml;
Carrier: 1.5 ml min⁻¹ of 50 mM ammonium acetate buffer;
Eluent: 1.5 ml min⁻¹ of 0.1 M nitric acid.

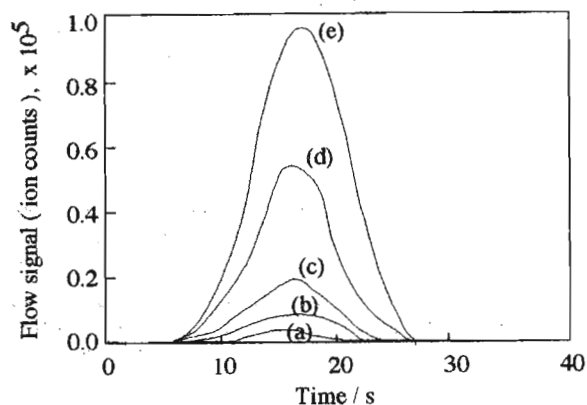


Fig. 3 Effect of sample size on flow signal in on-line FI/ICP-MS

(a) 50 µl; (b) 100 µl; (c) 200 µl; (d) 500 µl; (e) 1000 µl;
Sample: 10 ng ml⁻¹ of Cd solution (pH 5.5);
Carrier: 1.5 ml min⁻¹ of 50 mM ammonium acetate buffer;
Eluent: 1.5 ml min⁻¹ of 0.1 M nitric acid.

The effect of the tubing size on flow signals for a Mn standard solution, as an example, is shown in Fig. 2. The peak shape was broader and lower as the inner diameter of the tubing became larger. It was confirmed that the narrower the inner diameter is, the smaller the dispersion becomes. Therefore, 0.25 mm i.d. tubing was chosen as the flow line between the nebulizer and switching valve in this study.

3.2 Effect of sample size on flow signals

To examine the effect of sample sizes on peak intensity, several sizes of sample loops (50, 100, 200, 500, and 1000 µl) were tested at the constant eluent flow (1.5 ml min⁻¹). The signal profiles for a Cd standard solution (10 ng ml⁻¹), as an example, are shown in Fig. 3.

Good linear relationship was found between peak areas and sample volumes added. In this study, 1 ml of the sample size was chosen because the vial capacity of autosampler is 1 ml.

Table 2 Limits of detection and linearity obtained by the proposed on-line FI/ICP-MS

Isotope	m/z	LOD ^a (ng ml ⁻¹)	Linear range (ng ml ⁻¹)	Corr. coeff. ^b (r ²)
Li	7	0.1	1 - 100	0.9925
Be	9	0.05	0.1 - 100	0.9966
B	11	(c)	—	0.1073
Al	27	0.25	1 - 100	0.9970
V	51	0.042	0.1 - 100	0.9994
Cr	53	1.3	1 - 100	0.9801
Mn	55	0.093	0.1 - 100	0.9995
Fe	57	2.5	1 - 100	0.9964
Co	59	0.006	0.01 - 100	0.9999
Ni	60	0.034	0.1 - 100	0.9991
Cu	65	0.050	0.1 - 100	0.9992
Zn	66	0.12	0.1 - 100	0.9992
As	75	1.2	1 - 100	0.9969
Se	78	(c)	—	0.2447
Y	89	0.0012	0.001 - 100	0.9995
Mo	98	0.40	1 - 100	0.9984
Ag	107	0.01	0.1 - 100	0.9891
Cd	111	0.008	0.01 - 100	0.9985
In	115	0.05	0.01 - 100	0.9992
Ba	138	0.12	0.1 - 100	0.9996
La	139	0.0009	0.001 - 100	0.9999
Ce	140	0.0010	0.001 - 100	0.9999
Pr	141	0.0012	0.001 - 100	0.9999
Nd	146	0.0022	0.001 - 100	0.9998
Sm	147	0.0013	0.001 - 100	0.9999
Eu	151	0.0016	0.001 - 100	0.9997
Gd	157	0.0031	0.001 - 100	0.9998
Tb	159	0.0016	0.001 - 100	0.9999
Dy	163	0.0013	0.001 - 100	0.9999
Ho	165	0.0020	0.001 - 100	0.9999
Er	167	0.0030	0.001 - 100	0.9998
Tm	169	0.0014	0.001 - 100	0.9997
Yb	172	0.0020	0.001 - 100	0.9997
Lu	175	0.0017	0.001 - 100	0.9996
Pb	208	0.11	0.1 - 100	0.9977
U	238	0.007	0.01 - 100	0.9998

a: Limits of detection, 3σ (n = 10, ultrapure water; pH 5.5).

b: Concentration range of each metal solution is 0.01-100 ng ml⁻¹.

c: Not determined because these elements have no affinity to the chelating resin.

However, in case of performing higher enrichment factor, a peristaltic pump was utilized to propel larger sample volumes into the disk.

The peak areas were linearly increased with increasing sample volumes up to 10 ml, even though the processing time became much longer. As a result, about 20-fold enrichment factor was accomplished by using 10 ml of the sample solution

3.3 Limits of detection (LODs) and linearity

LODs corresponding to 3 σ (σ : standard deviation) for trace metals contained in a blank solution (ultrapure water, the pH of which was adjusted with ammonium acetate buffer to 5.5) were obtained by performing the proposed on-line FI-ICP-MS method. The results for 36 elements are summarized in Table 2. As a result, the LODs for heavy metals were ranged from 6 pg ml⁻¹ (Co) to 2500 pg ml⁻¹ (Fe) and lanthanides from 0.9 pg ml⁻¹ (La) to 3 pg ml⁻¹ (Er), respectively. As a result, the LODs obtained by the present method are similar levels compared with the data obtained by a normal nebulization method. In addition, the linear range and the linearity (r^2) calculated from the calibration graphs for metals are listed in Table 2. Except for B ($r^2=0.1073$) and Se ($r^2=0.2447$), most of the elements showed good linearity (more than 0.99) over the calibration ranges from 0.01 to 100 ng ml⁻¹.

Table 3 Adsorption efficiency for trace elements on the chelating resin disk

Isotope	Recovery (%) ^a	Isotope	Recovery (%) ^a
Li	1 ± 0.5	In	92 ± 2
Be	22 ± 0.4	Ba	1 ± 0.1
B	—	La	100 ± 0.4
Al	102 ± 2	Ce	103 ± 2
V	97 ± 1	Pr	99 ± 0.2
Cr	3 ± 0.2	Nd	103 ± 2
Mn	45 ± 0.5	Sm	99 ± 1
Fe	95 ± 3	Eu	102 ± 2
Co	99 ± 1	Gd	101 ± 0.3
Ni	98 ± 2	Tb	99 ± 2
Cu	98 ± 2	Dy	98 ± 2
Zn	103 ± 2	Ho	99 ± 1
As	12 ± 0.5	Er	98 ± 2
Se	—	Tm	99 ± 0.2
Y	101 ± 2	Yb	98 ± 2
Mo	20 ± 1	Lu	98 ± 0.4
Ag	2 ± 0.2	Pb	100 ± 1
Cd	99 ± 1	U	38 ± 0.2

a: Obtained from an artificial seawater sample, 1 ml (n=5).

3.4 Recovery from artificial seawater sample

The adsorption and the elution behavior of trace elements in the on-line FI-ICP-MS system were investigated by using artificial seawater samples [17] which contains more than several hundreds ppm ($\mu\text{g ml}^{-1}$) levels of Na⁺, K⁺, Mg²⁺, Ca²⁺, and 1.0 ng ml⁻¹ of analytes elements. The ICP-MS measurement for the eluates was done by using the off-line system. The results obtained for the recovery of 36 trace elements using the proposed off-line procedure are listed in Table 3. Five runs were made to obtain mean values and their standard deviations. Six transition

metals (Ni, Co, Cu, Zn, Cd, and Pb) and all REEs showed complete adsorption and elution. On the contrary, the adsorption efficiency for Be, V, Cr, Mn, As, Mo, and U was not so high though their elution was almost completely done. However, the largest merit of the proposed method over the batch-wise method was that the standard deviations were much improved even if the adsorption efficiency of some metals was low. The improvement of the standard deviation of the adsorption efficiency lead to good reproducibility and better accuracy in trace metal determination.

Besides, four major elements in seawater (Na⁺, K⁺, Mg²⁺ and Ca²⁺) were almost completely removed from the chelating disk in on-line column pretreatment, and the amounts of such metals remaining in the eluate was less than 5 $\mu\text{g ml}^{-1}$. This result indicates that the proposed method is applicable to the determination of trace metals in seawater samples.

Table 4 Analytical results for the river water standard samples obtained by on-line FI/ICP-MS with chelating resin disk

Elem-ent	JAC0031		JAC0032	
	This study (ng/ml)	Certified (ng/ml)	This study (ng/ml)	Certified (ng/ml)
B	(n.d.) ^c	9.1±0.5	(n.d.) ^c	59±2
Al	9.8±1.6 ^a	13.4±0.7	65±3	61±2
V	7.5±0.05	(7.4) ^e	7.90±0.10	(7.5) ^e
Cr	(n.d.) ^d	0.14±0.02	14.8±1.5	10.1±0.2
Mn	0.45±0.1	0.46±0.03	5.4±0.2	5.4±0.1
Fe	(n.d.) ^c	6.9±0.5	61±5	57±2
Co	0.027±0.003	(0.022) ^e	0.024±0.002	(0.045) ^e
Ni	0.16±0.02	(0.38) ^e	10.3±0.2	10.2±0.3
Cu	0.95±0.06	0.88±0.03	10.6±0.1	10.5±0.2
Zn	0.86±0.04	0.79±0.05	11.6±0.3	11.3±0.4
As	(n.d.) ^d	0.28±0.04	5.4±0.2	5.5±0.3
Se	(n.d.) ^c	(0.1) ^b	(n.d.) ^c	5.2±0.3
Cd	(n.d.) ^d	(0.003) ^b	1.01±0.02	1.00±0.02
Pb	(n.d.) ^d	0.026±0.003	9.7±0.2	9.9±0.2
U	(n.d.) ^d	(0.0035) ^e	(n.d.) ^d	(0.0026) ^e

a: Mean±Standard deviation (n=5).

b: Not certified but only for information.

c: Not determined because of poor affinity to chelating resin.

d: Not determined because of insufficient sensitivity.

e: Cited from Ref. 18.

3.5 Evaluation of accuracy and precision

In order to evaluate the accuracy and the precision of the proposed method, two kinds of the river certified reference materials (CRMs) were analyzed. Several elements, such as B, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb, were spiked into JAC0031 to prepare JAC0032. The concentrations of these twelve elements in JAC0032 ranged from 1 to 50 ng ml⁻¹. The trace elements having certified or reference values in JAC0031 and JAC0032 were investigated, and five replicate runs were made for each CRM sample. The analytical results for fifteen trace elements obtained by on-line FI-ICP-MS proposed in this study are summarized in Table 4.

For JAC0032, the analytical data for nine trace elements, such as Al, V, Mn, Fe, Ni, Cu, Zn, Cd, and Pb, obtained by the proposed method agreed well with the certified values and the

literature values obtained by instrumental neutron activation analysis (INAA) [18]. The RSD for the 9 elements in JAC0032 were in the ranges of 0.94 – 8.2%. Analytical data for Co obtained by the proposed method, even though it was quite different from the literature value, can be considered to be reliable because Co is most precise and accurate in the present study.

On the other hand, the analytical results for five elements, such as V, Mn, Cu, and Zn, agreed well with the certified and literature values. The precision of these 5 elements in JAC0031 was in the ranges of 0.7 – 22%. It is found that higher enrichment factor is needed to determine the concentration for some heavy metals and REEs existing less than several ppt (pg ml⁻¹) levels. Especially, the concentrations for Fe, Cd, Pb, and U in JAC0031 were too low to determine when only one-milliliter of samples was used.

3.6 Application to natural water samples

Five river water samples, which were collected at the points of river source (Shiogama), upper stream (Katsuyama), middle stream (Asahi), middle-down stream (Takebe), and lower stream (Korakuen) of Asahi River, and a seawater from Seto Inland Sea were treated with the chelating resin disk in the proposed on-line preconcentration system. The metals were concentrated by 2-fold for the determination of 29 elements including Al, V, Mn, Fe, Co, Ni, Cu, Zn, As, Y, Mo, Cd, In, Pb, U, and fourteen REEs. In order to compare the analytical results obtained by the present study with the batch-wise method [19,20] using the same chelating resin disk, the samples described above was investigated. In the batch-wise system, the metal ions were concentrated by 10 fold for the determination of Al and heavy elements and 50 fold for the determination of REEs.

The analytical results for 23 elements, such as Al, Ni, Co, Fe, Cu, Zn, Y, Cd, Pb and 14 REEs, obtained by both the methods showed good agreement with each other, because the adsorption

Table 5 Analytical results for trace elements in river waters and seawater by the proposed on-line FI-ICP-MS method using an IDA-type chelating resin disk.

Element	Asahi River										Seawater	
	Source water		Upper stream		Middle stream		Mid.-down stream		Lower stream		Seto Inland Sea	
	On-line ^a (ng ml ⁻¹)	Batch ^b (ng ml ⁻¹)	On-line (ng ml ⁻¹)	Batch (ng ml ⁻¹)	On-line (ng ml ⁻¹)	Batch (ng ml ⁻¹)	On-line (ng ml ⁻¹)	Batch (ng ml ⁻¹)	On-line (ng ml ⁻¹)	Batch (ng ml ⁻¹)	On-line (ng ml ⁻¹)	Batch (ng ml ⁻¹)
Al	19.4	17.5	66.3	60.5	11.6	12.2	39.5	35.5	34.0	30.3	2.53	2.32
V	24.5	23.7	14.5	18.0	24.9	21.5	17.3	17.0	20.1	19.2	0.92	1.05
Mn	0.17	(0.1) ^d	20.2	(18) ^d	4.10	(4) ^d	51.9	(49) ^d	18.1	(17) ^d	5.5	(5) ^d
Fe	190	200	360	340	570	590	400	420	430	430	36	28
Co	0.08	0.07	0.16	0.18	0.15	0.14	0.16	0.16	0.15	0.14	0.052	0.050
Ni	1.16	1.36	2.09	1.45	1.27	1.40	1.38	1.35	1.50	1.60	0.73	0.90
Cu	1.65	1.66	1.12	1.05	1.23	0.99	0.95	0.88	2.38	2.22	1.8	2.1
Zn	4.08	3.69	2.53	2.42	0.95	1.09	1.41	1.28	2.76	2.68	2.6	2.9
As	1.96	(2) ^d	1.45	(1) ^d	2.92	(3) ^d	2.08	(2) ^d	2.17	(2) ^d	2.4	(3) ^d
Y	0.010	0.0096	0.106	0.110	0.046	0.043	0.095	0.095	0.071	0.075	0.035	0.031
Mo	(n.d.) ^c	(0.2) ^d	(n.d.) ^c	(0.4) ^d	(n.d.) ^c	(0.5) ^d	(n.d.) ^c	(0.4) ^d	(n.d.) ^c	(0.6) ^d	9.7	(10) ^d
Cd	0.020	0.017	0.021	0.018	0.016	0.016	0.017	0.018	0.031	0.036	0.055	0.062
In	1.87	1.6	3.80	3.6	1.72	1.8	2.47	2.5	1.71	1.7	(n.d.) ^c	0.008
La	0.024	0.022	0.12	0.12	0.064	0.059	0.106	0.098	0.077	0.070	0.022	0.020
Ce	0.036	0.037	0.16	0.15	0.075	0.075	0.160	0.156	0.127	0.120	0.047	0.032
Pr	0.0070	0.0059	0.030	0.028	0.013	0.013	0.028	0.028	0.020	0.019	0.0065	0.0054
Nd	0.018	0.017	0.099	0.098	0.034	0.033	0.095	0.087	0.066	0.058	0.021	0.023
Sm	0.0045	0.0042	0.027	0.026	0.011	0.011	0.023	0.020	0.017	0.015	0.0034	0.0044
Eu	0.0028	0.0030	0.012	0.011	0.0052	0.0049	0.0091	0.010	0.0069	0.0044	0.0012	0.0019
Gd	0.0058	0.0053	0.029	0.028	0.012	0.013	0.025	0.025	0.018	0.019	0.0062	0.0083
Tb	0.0030	0.0031	0.0099	0.0092	0.0053	0.0065	0.0071	0.0082	0.0060	0.0061	0.0017	0.0023
Dy	0.0068	0.0064	0.026	0.0024	0.012	0.011	0.020	0.019	0.015	0.015	0.0065	0.0082
Ho	0.0029	0.0026	0.0089	0.0077	0.0064	0.0059	0.0068	0.0067	0.0055	0.0049	0.0015	0.0023
Er	0.0046	0.0045	0.016	0.014	0.0096	0.0090	0.011	0.013	0.0097	0.0089	0.0051	0.0075
Tm	0.0023	0.0024	0.0091	0.0090	0.0063	0.0059	0.0056	0.0056	0.0045	0.0038	0.0010	0.0017
Yb	0.0066	0.0067	0.016	0.015	0.011	0.0094	0.014	0.013	0.010	0.0091	0.0056	0.0065
Lu	0.0025	0.0026	0.0084	0.0078	0.0072	0.0070	0.0057	0.0054	0.0049	0.0049	0.0015	0.0014
Pb	0.57	0.54	0.32	0.31	0.38	0.25	0.18	0.16	0.47	0.49	0.57	0.61
U	0.12	(0.1) ^d	0.034	(0.03) ^d	0.030	(0.03) ^d	0.027	(0.03) ^d	0.019	(0.02) ^d	2.74	(3) ^d

a: Mean values of two determinations (n=2) obtained by the proposed FI-ICP-MS method.

b: Mean values of three determinations (n=3) obtained by air flow injection (AFI)/ ICP-MS after metal enrichment with a chelating resin disk.

c: Not determined because of insufficient sensitivity.

d: Determined by correction of recovery (less than 50%).

efficiency for these elements on the chelating disk is almost 100% and can lead to the most precise and accurate performance among the analyte metals. Other elements, such as V, Mn, As, Mo, In, and U, which can not retained on the chelating disk, were also determined by both the methods.

The most interesting and important difference between the two methods is that the correction of the column efficiency for each metal was not necessary in the proposed on-line method. The recovery ratio for each element on the chelating disk could be compensated in on-line FI pretreatment procedure because standard samples and the real samples are treated similarly.

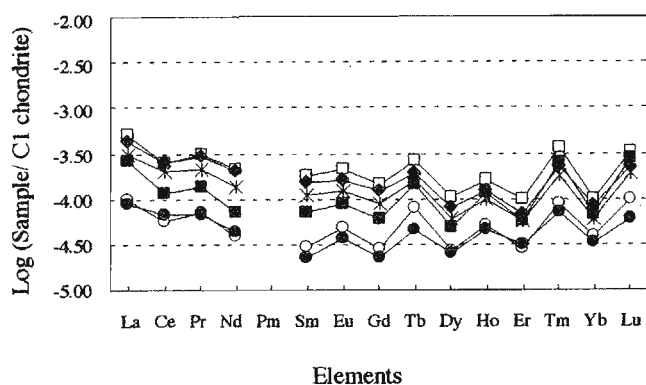


Fig. 4 REEs patterns of river waters and seawater
 ○ :Shiogama; □ :Katsuyama; ■ :Asahi;
 ◆ :Takebe; * :Korakuen; ● :Seto Inland Sea.

As is shown in Fig. 4, the REEs patterns obtained by normalizing with C1-chondrites [21] for six water samples gave very similar shape even though the metal abundances in the samples were different from one another. We can explain the two things by this result; one is that at least REEs in this area are not contaminated by human activity, and the other is that the unique REEs pattern from aqueous samples is closely related with topographical effect, such as rocks and sediments around the river streams.

4. Conclusion

The determination of 28 elements in river waters and seawater was successfully achieved by the proposed on-line FI-ICP-MS with the chelating resin disk. The most important observation in this study is that Mn, Cr, As, Mo, Ba, and U, of which recovery was less than 50% in a batch-wise method, showed good linearity in each calibration graph and good reproducibility. Such results indicate that metals with the recovery of less than 50% can be determined by the on-line method with good accuracy and precision.

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