DETERMINATION OF TRACE ELEMENTS IN WATER SAMPLES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY CONNECTED WITH AIR FLOW- AND WATER FLOW- INJECTION TECHNIQUES

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Evaluation of an air-flow and a water-flow injection coupled with inductively coupled plasma - mass spectrometry (ICP-MS) was done for the determination of heavy metals including rare earth metals. In the air-flow injection (AFI) method, sharp and narrow peaks were obtained, whereas in the water-flow injection (WFI) method, broader peaks were obtained. The AFI method provided the sample throughput twice as many as WFI method. For most analytes, peak reproducibility in WFI method at sub-ppb levels was better than that in AFI method. The accuracy and precision of the two methods were evaluated by analyzing several heavy metals in river certified reference materials (JAC0032). The analytical results obtained by both methods were in good agreement with each other. These two microsampling techniques were applied to the determination of trace and ultratrace metals in four kinds of natural waters such as river water, seawater, lake water and mineral drinking water. More precise and reliable analytical data could be obtained by measuring the samples after the separation of matrices and enrichment of target elements with a chitosan-based chelating resin column.

Keywords: *ICP-MS, flow injection, air carrier, water carrier, segmented flow, microsampling, discrete injection, trace metal analysis, heavy metals, lanthanoids*

The development of a fast and reliable method for the determination of trace elements in environmental samples is urgently required. In these days, inductively coupled plasma - mass spectrometry (ICP-MS) has been widely used in trace and ultratrace analysis of various samples as a powerful tool for multielemental and isotopic analysis.[1-3] However, its application to the determination of trace metals in highly saline solutions, such as seawater, is essentially limited because of both spectral interferences and matrix effect.[4-6] Moreover, common continuous nebulization of solutions containing large amounts of salts is not suitable to ICP-MS because of the deposition of solids on the torch and the sampling cones.[7]

Flow injection (FI) techniques have been employed for ICP-MS to extend their specific capabilities such as minimal orifice blockage, minimal non-spectroscopic interference by concomitant salts, small sample consumption, high sample throughput and ease of automation. In addition, FI/ICP-MS allows contamination control, on-line sample pretreatment[8,9] and speciation analysis.[10,11]

An important aspect of discrete sampling in ICP-MS is that the signal profiles can vary as time[12], and depend on the dispersion produced by a particular FI introduction device.[13] One of the effective ways of decreasing the dispersion is to inject the sample into a gas as a carrier; some workers have investigated FI/ICP-MS by using air or air-water segmented carrier.[14-17] However, the multielement determination in natural water samples using an air-flow injection/ICP-MS (AFI/ICP-MS) has scarcely been studied so far.

An iminodiacetate (IDA)-type chelating resin of chitosan as a base material, which was investigated in previous work by Lee et. al,[18] was very useful when the abundance of trace and ultratrace metals in natural waters was lower than the detection limits of ICP-MS.

In this work, ICP-MS coupled with an air-flow and a water-flow injection technique was investigated to compare their performance, advantages and disadvantages of each method upon analyzing trace and ultratrace metals in natural waters.
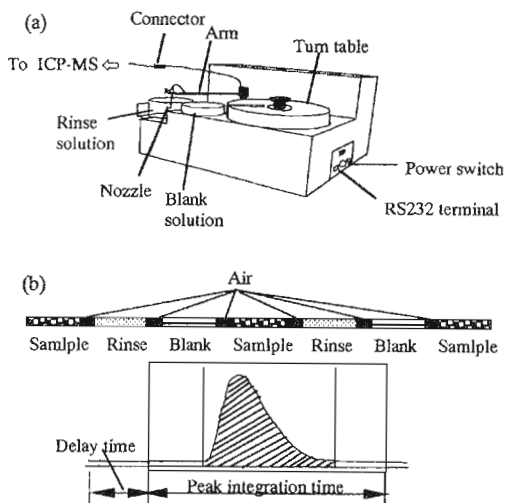
EXPERIMENTAL

Instrumentation

Fig. 1 Schematic diagram of air flow autosampler (a)
and its ICP/MS signal (b)

The ICP-MS used was a SPQ 8000H (Seiko Instruments Co., Tokyo, Japan), fitted with a glass concentric nebulizer (TR-30-C2, J. E. Meinhard associates Inc., California, USA). An AFI/ICP-MS system was mainly consisted of an autosampler (Model AT-600, Seiko Instruments Co.) and a MS software (trade name, MicroSuction ver. 1.8 M) for controlling the ICP-MS operation and data acquisition. As is shown in Fig. 1 (a), one end of a nozzle (PTFE tubing, 1 mm i.d. x 3 mm o.d.) of the autosampler was connected to a suction tubing of ICP-MS main body. The autosampler was composed of a nozzle tubing, a rinse solution tank, a blank solution tank, a turntable for sampling (2 ml x 50 vials), a robotic arm for sample delivering and RS232C cable connected to a personal computer for ICP-MS operation. It was possible to select the intervals for rinsing the system and the flowing path, conditioning blank solutions and sampling arbitrarily by time setting.

A water flow injection/ICP-MS (WFI/ICP-MS) system was manually operated with a switching valve (model SVM-6M2L, Sanuki Kogyo, Tokyo), and the MS software was used to measure trace metals in a similar manner to AFI/ICP-MS system. Water carrier was propelled at 1.5 ml min⁻¹ (model DMX-2000, Sanuki Kogyo) into a nebulizer of ICP-MS. The switching valve was installed in the flow line as close as possible to the nebulizer in order to diminish the

dispersion of injected samples. Sample solution was loaded in a loop of the switching valve with a peristaltic pump (model ALITEA-XV, Sweden) at the flow rate of 1 ml min⁻¹.
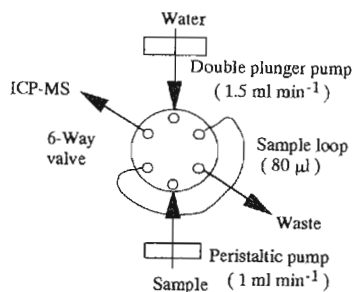

Fig. 2 Schematic diagram of water flow injection manifold

Standard operation conditions of AFI/ICP-MS system and WFI/ICP-MS system were summarized in Table 1. In the AFI/ and WFI/ICP-MS systems, maximum fifteen isotopes can be measured and their integrated peak areas were simultaneously obtained by one measurement. The principle of AFI/ICP-MS measurement was briefly illustrated in Fig. 1 (b). An optimal integration period of the flow signal for each analyte was determined by injecting a 10 ng ml⁻¹ multielement standard solution just before sample measurement. One milliliter was sufficient to obtain several replicates of the AFI/ and WFI/ICP-MS measurement. Total measuring time for one sample was 83 s in AFI/ICP-MS, and 155 s in WFI/ICP-MS. The integrated peak areas for metals were used to obtain the analytical results.

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 seawater sample collected at Shibukawa beach in Okayama Prefecture, a lake

Table 1. Standard operating parameters for air-flow injection and water-flow injection systems

ICP-MS	Seiko model SPQ8000H	Air-flow injection system	Seiko AT600 autosampler
Plasma conditions		Sample suction time (volume)	3 s (80 μl)
Forward power	1.1 kW	Rinse with water	10 s (270 μl)
Reflected power	<5 W	Rinse with 0.1M HNO_3	20 s (540 μl)
Plasma gas	Ar 15 l min^{-1}	Delay time*	30 s
Carrier gas	Ar 0.45 l min^{-1}	Peak integration time	20 s
Auxiliary gas	Ar 1.0 l min^{-1}	Dwell time	50 ms
Sample uptake rate	1.0 ml min^{-1}	Channel width	1
Interface condition		Water-flow injection system	Double-plunger type (manual)
Sampling depth	10 mm from load coil	Sample injection volume	80 μl
Skimmer cone	Copper 1.1 mm φ	Sample loading volume	30 s (500 μl)
Sampling cone	Copper 0.35 mm φ	Loop washing with 0.1M HNO_3	60 s (1000 μl)
		Carrier flow rate (water)	1.5 ml min^{-1}
		Delay time*	5 s
		Peak integration time	60 s
		Dwell time	50 ms
		Channel width	1

* Delay time means the interval necessary for the sample to move the turntable to the nebulizer.

water sample collected at Towada Lake in Aomori Prefecture, and a commercially available mineral water (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.

Materials and Reagents

A chitosan based chelating resin (trade name: Chelate Chitopearl CI-03) was purchased from Fuji Spinning Co. Ltd. (Tokyo, Japan). A small-size plastic column (a 1 ml of volume) for trace metal enrichment was a polypropylene mini-column (Muromachi Chemicals, Japan). A PTFE evaporation chamber and a clean-air pump used for preconcentration were purchased from San-Ai Kagaku (Nagoya, Japan). All plastic labwares were used after being treated by soaking them for a week in 1 M HNO_3 and then rinsing them by ultrapure water.

Analytical multielement standard solutions were prepared from single element standard solutions (1000 μg ml^{-1}) for atomic absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). A series of multielement standards were ranged from 0.01 to 100 ng ml^{-1} (0.1 M HNO_3). For matching the final acid concentration of the working solutions to that of sample solutions, 0.1M nitric acid was used as a diluent for preparing the working standard solutions. Ultrapure water (18.2 MΩcm resistivity) was prepared with a Milli-Q Labo (Nihon Millipore, Tokyo, Japan). Ultrapure grade nitric acid (60%, Cica-MERCK) from Kanto Chemicals (Tokyo, Japan) was diluted with ultrapure water to give various concentrations. Acetic acid (minimum 96%) and ammonia water (29%) used for preparing ammonium acetate buffer solutions were of electronic industrial reagent grade (Kanto Chemicals).

Column separation/preconcentration procedure

Chelate Chitopearl CI-03 resin packed in minicolumn (1 ml of volume, 5.0 ~ 5.5 mm of inner diameter, 50 mm of length) was washed with 5 ml of 2M nitric acid, and then washed with 10 ml of 0.1M nitric acid to lower the acidity of the column. After that, 5 ml of 0.2 M ammonium acetate buffer solution (pH 6) was added to the column adjusting pH. In case

of 50-fold concentration, 2ml of conc. ammonia water and 2ml of conc. acetic acid were added to 50 ml of water samples to adjust their pH to about 6, and the sample solutions were poured into the column. After the sample solutions were passed through the column, 5 ml of 0.2 M ammonium acetate buffer solution (pH 6) was added to the column for matrix elimination, and then 5 ml of ultrapure water was added to the column for rinsing the residual ammonium acetate. Finally, 10 ml of 1 M nitric acid was added to the column for recovering metal ions. While ultrapure water, diluted nitric acid, ammonium acetate buffer and sample solutions were passed through the column at the flow rate of 2 ml min^{-1}, no swelling and shrinking of the resin occurred. The eluates thus obtained were transferred to 100 ml of PTFE beakers and evaporated to dryness (120℃) using the evaporation chamber covered with a clear polyvinyl sheet to prevent the contamination. The residue was redissolved in 1 ml of 0.1M nitric acid added by using a micropipet.

RESULTS AND DISCUSSION

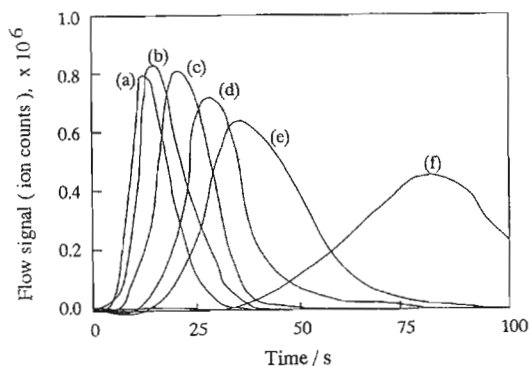### *Optimization of WFI/ICP-MS condition*

Fig. 3 Effect of carrier flow on flow signal in WFI/ ICP-MS

Sample: 10 ng ml^{-1} La solution; sample volume: 100 μl
(a) 1.8 ml min^{-1}; (b) 1.5 ml min^{-1}; (c) 1.25 ml min^{-1};
(d) 1.0 ml min^{-1}; (e) 0.5 ml min^{-1}; (f) 0.25 ml min^{-1}.

The optimum conditions of AFI/ICP-MS system were confirmed in the previous study.[18] In AFI/ICP-MS, the sample volume aspirated depended on both a suction time (1~10 s) and a suction flow rate (1.6 ml min^{-1}). The sample size (3s, 80 μl) in AFI/ICP-MS was adopted as a compromise to obtain lower

background, higher sensitivity and less measuring time. In this study, the optimization of WFI/ICP-MS system was investigated on three parameters (a carrier flow rate, nebulizer gas pressure and sample size).

Effect of the flow rate of carrier on peak shape of 10 ng ml^{-1} of a La solution is shown in Fig. 3. As was expected, peak width was broader and peak height was lower as the flow rate of carrier became slower. To obtain more sensitive and sharper peak, 1.5 ml min^{-1} of water flow was employed. The peak height and peak area were both decreased over the flow rate of 1.5 ml min^{-1}. This phenomenon may be ascribed to the high transport rate of the sample solutions to a spray chamber, which results in relatively lower delivering ratio of fine aerosol into an ICP torch.
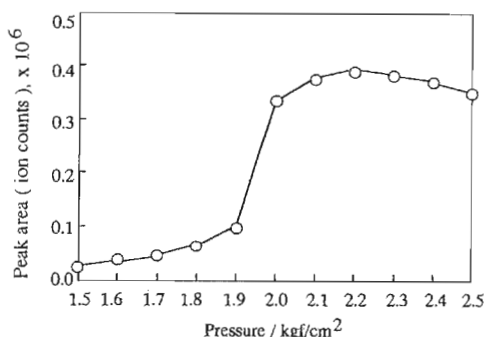

Fig. 4 Effect of nebulizer gas pressure on peak area in WFI/ ICP-MS

Sample: 10 ng ml^{-1} Y solution; sample volume: 100 μl;
carrier flow: 1.5 ml min^{-1}.

The most important parameter on sensitivity was to control the nebulizer gas pressure. The internal diameter (0.5 mm) of a PTFE tubing used in WFI/ICP-MS system was half of that in AFI/ICP-MS system (1.0 mm). Therefore, to maintain the same flow rate of the nebulizer gas (0.5 l min^{-1}, 1.8 kgf/cm^2) as AFI/ICP-MS system, it was necessary to increase the nebulizer gas pressure in WFI/ICP-MS system. As is shown in Fig. 4, the ion counts for Y was abruptly increased at 2.0 kgf/cm^2 and maximized at pressure around 2.2 kgf/cm^2 in WFI/ICP-MS system. The ion counts was gradually decreased at the pressure of more than 2.2 kgf/cm^2.

To examine the effect of sample sizes on peak shape and sensitivity, several sizes of loops (25, 50, 80, 100 and 200 μl) were tested under the constant
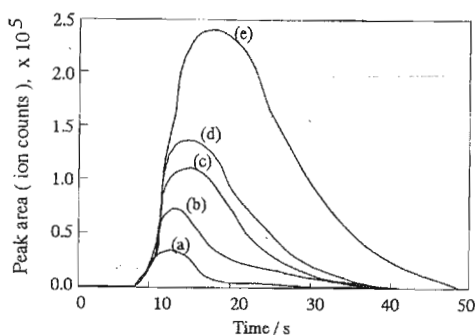
Fig. 5 Effect of sample size on flow signal obtained

by WFI/ ICP-MS

Sample: 10 ng ml^{-1} Cd solution;
carrier flow: 1.5 ml min^{-1};
sample size: (a) 25, (b) 50, (c) 80, (d) 100, (e) 200 μl.

carrier flow rate (1.5 mlmin^{-1}) and nebulizer gas pressure (2.2 kgf/cm^2). The signal profiles obtained by WFI/ICP-MS were shown in Fig. 5. The peak areas of the signals were proportionally increased with increasing sample volume. In this work, 80 μl of the sample size was adopted to compare their data with those obtained by AFI/ICP-MS.

Comparison of limit of detection (LOD)

Instrumental LODs, which were defined as the concentrations corresponding to three times of the standard deviations (σ) of blank intensity for trace metals contained in 0.1 M HNO$_3$, were obtained. They were summarized in Table 2. The instrumental LODs for 30 elements were obtained by both AFI and WFI methods. The average values and the standard deviations of 10 replicate measurements of the blank solution (0.1 M HNO$_3$) were obtained, and each limit of detection was calculated by putting the value corresponding to 3σ into the calibration graph for each metal. As a result, there was no significant difference in LODs for most elements between two methods. The LODs for common heavy metals were ranged from 10 to 100 pg ml^{-1} levels and lanthanoids from 0.1 to 1 pg ml^{-1} levels, respectively. The LODs of heavy metals obtained from AFI/ICP-MS and WFI/ICP-MS were at slightly higher levels than those obtained by using normal continuous nebulization method by a factor of 2-10 fold. However, LODs of lanthanoids were at almost the same levels in the three methods.

Comparison of precision

To evaluate the reproducibility in the AFI and the WFI methods, two kinds of mixed solutions containing Y and fourteen rare earth elements (each metal concentration: 0.01 and 10 ng ml^{-1}) were measured and 10 replicates were obtained. The average values of RSDs (relative standard deviations) calculated from each element were compared with each other. In case of low-level concentration (0.01 ng ml^{-1}), more precise data were obtained in WFI method (5.8% RSD) than in AFI method (9.1% RSD). In high-level concentration (10 ng ml^{-1}), however, there was no remarkable difference in precision between AFI method (1.9% RSD) and WFI method (2.0% RSD).

Comparison of accuracy

In order to evaluate and compare the accuracy between two methods, the river certified reference material (JAC0032) was examined. No pretreatment was done before the measurement. An 80 μl of the sample was discretely injected, and eleven heavy metals of fifteen elements tested were determined. The analytical results by both methods were summarized in Table 3. The analytical data obtained by the AFI method and the WFI method agreed well with each other as well as with the certified values and the literature values obtained by instrumental neutron activation analysis (INAA).[23] Under the normal continuous nebulization method, a number of transition metals are substantially interfered from polyatomic ions derived from argon, oxygen, coexisting elements such as Na, Ca and Cl. The discrete microsampling method employed in this study was proved to be a useful technique for alleviating the spectral interferences even without pretreatment with a column. From the analytical data of V and As, it could be confirmed that WFI method was superior to AFI method because of less interferences from coexisting substances. In case of WFI method, the peak broadening by the dispersion of a sample zone was beneficial for diminishing spectral interferences.

Evaluation of chelating resin column performance

In order to evaluate the accuracy and the precision of the column pretreatment, two kinds of

Table 2 Instrumental detection limits for trace elements by AFI / ICP-MS and WFI / ICP-MS

| Element | m/z | LOD [a] (pg ml^{-1}) | | Element | m/z | | |
		Air carrier	Water carrier			Air carrier	Water carrier
Al	27	96	88	Y	89	0.36	0.26
V	51	60	24	La	139	0.38	1.48
Cr	52	20	34	Ce	140	0.43	1.15
Mn	55	19	15	Pr	141	0.12	0.20
Fe	57	1300	1150	Nd	146	1.1	0.17
Ni	58	50	29	Sm	147	0.74	0.25
Co	59	8	11	Eu	151	0.23	0.63
Cu	65	54	64	Gd	157	0.61	0.56
Zn	66	110	52	Tb	159	0.18	0.33
As	75	39	25	Dy	163	0.34	0.37
Mo	98	28	35	Ho	165	0.12	0.51
Ag	107	11	13	Er	167	0.29	0.41
Cd	114	5	13	Tm	169	0.15	0.69
Pb	208	30	63	Yb	172	0.27	0.61
U	238	8	9	Lu	175	0.17	0.66

a : limit of detection, which were corresponding to 3 σ (n = 10) obtained by measuring each trace metal contained 0.1 M HNO_3 solution.

Table 3 Analytical results of several trace elements in JAC 0032 by direct sample introduction with the AFI and the WFI systems

| Element | m/z | Found (ng ml^{-1}) | | | |
		AFI/ICP-MS	WFI/ICP-MS	Cert. values	INAA*
V**	51	8.9 ± 0.3	7.5 ± 0.1	-	7.5 ± 0.2
Cr	52	10.3 ± 0.2	9.9 ± 0.2	10.1 ± 0.2	10.4 ± 1.3
Mn	55	5.6 ± 0.2	5.3 ± 0.3	5.4 ± 0.1	5.4 ± 0.3
Ni	58	10.2 ± 0.3	10.3 ± 0.3	10.2 ± 0.3	11.2 ± 0.7
Co	59	0.036 ± 0.005	0.033 ± 0.01	-	0.045 ± 0.014
Cu	65	10.0 ± 0.2	10.6 ± 0.4	10.5 ± 0.2	10.8 ± 1.2
Zn	66	11.7 ± 0.2	12.0 ± 0.5	11.3 ± 0.4	10.7 ± 1.1
As**	75	6.2 ± 0.4	5.3 ± 0.4	5.5 ± 0.3	5.0 ± 0.4
Mo	98	0.39 ± 0.04	0.40 ± 0.02	-	0.40 ± 0.03
Cd	114	0.99 ± 0.02	1.00 ± 0.02	1.00 ± 0.02	0.99 ± 0.07
Pb	208	10.1 ± 0.5	9.9 ± 0.4	9.9 ± 0.2	-

* Cited from ref. 24.

** These elemments, V and As, were subject to spectral interferences from ClO^+ and $ArCl^+$, respectively.

Table 4 Analytical results of Y and lanthanoids in river reference materials by AFI/ICP-MS

| | Found (pg ml^{-1}) | | | |
| | Total blank* | JAC 0031 | | JAC 0032 |
Element	AFI/ICP-MS	Ref. 24	AFI/ICP-MS	AFI/ICP-MS
Y	0.15 ± 0.01	8.10	7.67 ± 0.33	7.64 ± 0.30
La	7.51 ± 0.5	1.30	1.47 ± 0.08	1.22 ± 0.05
Ce	1.58 ± 0.1	1.80	1.62 ± 0.07	1.87 ± 0.18
Pr	0.20 ± 0.02	0.47	0.46 ± 0.03	0.48 ± 0.05
Nd	0.63 ± 0.05	2.40	2.29 ± 0.16	2.39 ± 0.18
Sm	0.16 ± 0.03	0.68	0.65 ± 0.06	0.57 ± 0.03
Eu	0.09 ± 0.01	0.27	0.27 ± 0.05	0.24 ± 0.03
Gd	0.15 ± 0.02	1.00	0.92 ± 0.04	0.93 ± 0.04
Tb	0.06 ± 0.01	0.13	0.18 ± 0.02	0.13 ± 0.02
Dy	0.13 ± 0.02	0.92	0.91 ± 0.06	0.81 ± 0.03
Ho	0.07 ± 0.01	0.24	0.26 ± 0.06	0.20 ± 0.03
Er	0.08 ± 0.01	0.73	0.73 ± 0.07	0.71 ± 0.04
Tm	0.07 ± 0.01	0.12	0.14 ± 0.03	0.10 ± 0.01
Yb	0.09 ± 0.01	0.82	0.87 ± 0.09	0.79 ± 0.05
Lu	0.07 ± 0.01	0.16	0.20 ± 0.05	0.11 ± 0.02

(n=5)
* These were obtained by measuring the solutions prepared according to the column pretreatment
procedure by using 50 ml of 0.1 M HNO$_3$.

river certified reference materials (JAC 0031 and JAC 0032) were investigated. The concentrations of Y and 14 lanthanoids in these reference materials were too low (sub-pg ml^{-1} ~ pg ml^{-1} level) to detect in direct sample introduction. The preconcentration (50-fold) was carried out at the same time as follows; five 50-ml aliquots of the samples were treated with the five independent chelating columns and the analytical results were obtained by the AFI/ICP-MS method. Since the certified values for Y and 14 lanthanoids in JAC 0031 and JAC 0032 have never been determined yet, the data by the present study were compared with the literature values[24] obtained by another ICP-MS in combination with the preconcentration using Chelex - 100. Analytical results of Y and 14 lanthanoids in river reference materials were listed in Table 4. As a whole, the analytical results in JAC0031 obtained by the method with the chelating column pretreatment procedure were in good agreement with the literature values.

Analysis of natural waters

In the column pretreatment, the effect of matrix components in seawater, such as Na$^+$ (0.5 M), Cl$^-$ (0.5 M), K$^+$ (0.01 M), Mg^{2+} (0.05 M), Ca^{2+} (0.01 M) and SO$_4^{2-}$ (0.02 M), on the recovery of metal ions was examined by using artificial seawater samples. The recovery of each metal obtained according to the proposed procedures using the chelating column was almost the same as that of artificial river samples.[18] Four major elements were almost removed from the sample solutions in the column pretreatment, and the

Table 5 Analytical results of trace elements in several water samples by AFI/ICP-MS with and without preconcentration (50-fold) using a chitosan-based chelating resin column

element	m/z	Found (ng ml^{-1})*							
		Rhein River		Shibukawa		Towada Lake		Evian	
		direct	column	direct	column	direct	column	direct	column
Al	27	23.7	25.8	2.4	2.3	13.4	11.8	1.35	1.96
V**	51	10.8	6.8	n.d.	1.5	15.8	9.9	n.d.	2.94
Cr	52	0.91	n.d.	0.15	n.d.	0.28	n.d.	3.78	n.d.
Mn	55	32.2	34.0	5.63	5.50	2.45	2.40	0.43	0.44
Fe**	57	n.d.	58.3	n.d.	10.8	15.2	7.5	n.d.	0.60
Ni	58	1.94	1.60	0.86	1.07	0.57	0.52	0.50	0.49
Co**	59	0.33	0.09	5.31	0.05	0.06	0.013	0.12	0.01
Cu	65	2.11	2.43	4.42	4.55	1.55	1.65	0.63	0.66
Zn	66	2.56	2.16	3.66	3.70	11.6	11.3	1.30	2.70
As**	75	4.08	3.82	n.d.	2.50	n.d.	1.10	n.d.	1.56
Mo	98	0.87	0.68	3.62	3.02	0.28	0.38	0.60	0.48
Ag	107	n.d.	0.016	n.d.	0.08	n.d.	0.013	n.d.	0.011
Cd	114	0.06	0.05	0.07	0.06	0.02	0.03	0.01	0.01
Pb	208	1.38	1.43	0.64	0.67	n.d.	0.45	n.d.	0.39
U	238	0.74	0.68	0.94	1.67	n.d.	0.005	1.05	1.13
Y	89	0.21	0.20	0.030	0.032	0.041	0.033	0.0049	0.0046
La	139	0.45	0.44	0.024	0.018	0.014	0.016	n.d.	0.0012
Ce	140	0.36	0.33	0.028	0.029	0.052	0.030	n.d.	0.0029
Pr	141	0.093	0.080	0.008	0.0056	0.0042	0.0036	n.d.	0.00035
Nd	146	0.23	0.22	0.018	0.021	0.021	0.017	n.d.	0.0012
Sm	147	0.059	0.050	n.d.	0.0011	0.0028	0.0046	n.d.	0.00027
Eu**	151	0.42	0.11	n.d.	0.0021	0.0041	0.00091	n.d.	0.00010
Gd	157	0.080	0.073	n.d.	0.013	0.0058	0.0051	n.d.	0.00029
Tb	159	0.019	0.010	n.d.	0.0024	n.d.	0.00095	n.d.	0.00011
Dy	163	0.038	0.040	n.d.	0.012	0.0057	0.0048	n.d.	0.00046
Ho	165	0.010	0.0069	n.d.	0.0026	n.d.	0.0010	n.d.	0.00014
Er	167	0.024	0.021	n.d.	0.0078	n.d.	0.0030	n.d.	0.0041
Tm	169	n.d.	0.0021	n.d.	0.0013	n.d.	0.00048	n.d.	0.00012
Yb	172	n.d.	0.013	n.d.	0.0069	n.d.	0.0025	n.d.	0.00048
Lu	175	n.d.	0.0017	n.d.	0.0014	n.d.	0.00042	n.d.	0.00013

* Mean values of three determinations (n=3).
** These elements were susceptible to be interfered from polyatomic ions of matrix elements.

amount of each metal remaining in the final solutions (1 ml of 0.1M HNO_3) was less than 1 $\mu g\ ml^{-1}$. This result indicates that the proposed method can be applied to the determination of trace metals in seawater samples. Four kinds of natural water samples were treated with the proposed chelating resin columns, and the metal ions were concentrated by 50-fold according to the proposed procedures. The sample solutions containing concentrated metal ions were measured by the AFI/ICP-MS method, and the data obtainrd by the direct sample introduction method without the pretreatment were also summarized in Table 5. For several heavy metals, it was proved that more reliable analytical data could be obtained only after removing concomitant salts or major components; for example, the concentration of V, Fe, Co, As and Eu could not be determined accurately by the direct sample introduction method because of spectral interferences from $^{35}Cl^{16}O^+$ ($^{51}V^+$), $^{40}Ar^{16}OH^+$ ($^{57}Fe^+$), $^{43}Ca^{16}O^+$ ($^{59}Co^+$), $^{40}Ar^{35}Cl^+$ ($^{75}As^+$) and $^{135}Ba^{16}O^+$ ($^{151}Eu^+$).

CONCLUSION

In this study, the comparison of the performance of ICP-MS connected with the flow introduction of samples using an air flow carrier (AFI method) and a water flow carrier (WFI method) was done in detail. The advantages of AFI method were: (1) rapid sample throughput, (2) ease of automation, (3) less band broadening and (4) less sample consumption, whereas the advantages of WFI method were: (1) simplicity of detection system, (2) better precision for measurement at sub-ppb level, (3) less spectral interferences. Direct sample introduction by the AFI and the WFI method were proved to be very useful for the determination of trace metals in aqueous samples. The determination of thirty trace elements in natural waters was successfully achieved by AFI/ICP-MS with the pretreatment procedure using the chitosan-based chelating resin column. 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.

Acknowledgment

References

1. H. Kumagai, M. Yamanaka, T. Sakai, T. Yokoyama,T. M. Suzuki and T. Suzuki, *J. Anal. At. Spectrom.*, **13**, 579 (1998).
2. A. Itoh, T. Hamanaka, W. Rong, K. Ikeda, H. Sawatari, K. Chiba and H. Haraguchi, *Anal. Sci.*, **15**, 17 (1999).
3. S. A. Pergantis, E. M. Heithmar and T. A. Hinneers, *Anal. Chem.*, **67**, 4530 (1995).
4. T. H. Zhang, X. Q. Shan, R. X. Liu, H. X. Tang and S. Z. Zhang, *Anal. Chem.*, **70**, 3964 (1998).
5. M. Bettinelli and S. Spezia, *J. Chromatogr.A*, **709**, 275 (1995).
6. E. Fujimori, H. Sawatari, A. Hirose and H. Haraguchi, *Chem. Lett.*, **1994**, 1467.
7. D. J. Douglas and L. A. Kerr, *Anal. At. Spectrom.*, **3**, 749 (1988).
8. A. G. Coedo, M. T. Dorado, I. Padilla and F. Alguacil, *Anal. Chim. Acta*, **340**, 31 (1997).
9. P. Becottehaigh, J. F. Tyson, E. Denoyer and M. W. Hinds, *Spectrochim. Acta, Part B*, **51**, 1823 (1996).
10. J. J. Tomson and R. S. Houk, *Anal. Chem.*, **58**, 2541 (1986).
11. M. J. Powell, D. W. Boomer and D. R. Wiederin, *Anal. Chem.*, **67**, 2474 (1995).
12. E. R. Denoyer, *At. Spectrosc.*, **15**, 7 (1994).
13. J. F. Tyson., *Spectrochim. Acta Rev.*, **14**, 169 (1991).
14. D. Beauchemin, *Analyst*, **118**, 815 (1993).
15. J. M. Craig and D. Beauchemin, *Analyst*, **119**, 1677 (1994).
16. A. G. Coedo, M.T. Dorado, I. Padilla and F. J. Alguacil, *J. Anal. At. Spectrom.*, **11**, 1037 (1996).
17. V. Stefanova, V. Kmetov and L. Futekov, *J. Anal. At. Spectrom.*, **12**, 1271 (1997).
18. K. H. Lee, M. Oshima, T. Takayanagi and S. Motomizu, *Anal. Sci.*, in contribution.
19. K. H. Lee, M. Oshima, M. Yamada, S. Motomizu, *Separation Sciences '99 (Tokyo)*,

Abstract, 37 (1999).

20. K. H. Lee, Y. H. Gao, S. Motomizu, *Analytical Chemistry Tokyo Symposium '99 · Tokyo Conference on Instrumental Analysis (Makuhari), Abstract*, 175 (1999).

21. K. H. Lee, M. Oshima, S. Motomizu, *The 48th Annual Meeting of the Japan Society for Analytical Chemistry (Kobe), Abstract*, 28 (1999).

22. K. H. Lee, M. Oshima, M. Yamada, S. Motomizu, *The 36th Semiannual Meeting on Flow Injection Analysis (Yamanashi), Abstract*, 4 (1999).

23. S. Suzuki, Y. Okada and S. Hirai, *Bunseki Kagaku*, **46**, 223 (1997).

24. A. Itoh, K. Iwata, S. Ji, T. Yabutani, C. Kimata, H. Sawatari and H. Haraguchi, *Bunseki Kagaku*, **47**, 109 (1998).