Simultaneous Determination of Trace Elements in River-water Samples by ICP-MS in Combination with a Discrete Microsampling Technique after Enrichment with a Chitosan-based Chelating Resin

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A new technique for the preconcentration of trace elements and matrix elimination with a chitosan-based chelating resin was proposed as a useful pretreatment prior to a measurement by inductively coupled plasma-mass spectrometry (ICP-MS). A small volume of the sample solution (80 µl) was discretely introduced into a nebulizer of ICP-MS using a segmented flow injection (SFI) system; a maximum of fifteen elements were simultaneously measured by a single injection. A chitosan-based chelating resin containing iminodiacetate (IDA) functional groups was used for matrix elimination and enrichment of analyte metal ions. Several metal ions, such as Al, Fe, Ni, Co, Cu, Zn, Ag, Cd, Pb and U, were quantitatively retained on the IDA chelating resin in a micro-column (resin: 1 ml) at pH 6, whereas Na, K, Mg and Ca were completely eluted from the column by washing with an ammonium acetate solution. The concentrations of 24 and 26 elements in river water certified reference materials, JAC 0031 and JAC 0032, respectively, were determined by the proposed SFI/ICP-MS system after pretreating the samples with the proposed technique, as well as without any pretreatment. The thus-obtained analytical data were evaluated by comparing them with the reference values, as well as with those obtained in other studies.

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Inductively coupled plasma-mass spectrometry is a powerful detection system for elemental analysis at trace and ultratrace levels.[1–4] Highly saline solutions, however, can cause some problems, such as clogging of the sampling orifice as well as spectroscopic and non-spectroscopic interferences.[5–9] Generally, sample dilution is an alternative method to alleviate matrix effects. However, sample dilution results in a difficulty in determining the analyte elements present at trace and ultratrace levels.[10] In order to avoid matrix effects and to eliminate interelement spectral interferences, ion chromatography (IC)[11,12] and high-performance liquid chromatography (HPLC)[13–15] have been used as effective techniques for sample pretreatment in ICP-MS, though they have some disadvantages, such as a long measuring time (more than 1 h per sample) and lowering the detection sensitivities. Flow-injection (FI) techniques coupled with ICP-MS have been investigated for the purpose of performing the on-line sample pretreatment of high-salt-content samples.[16–18] The FI/ICP-MS seems to be a promising technique when it can be coupled with an on-line pretreatment.[19–21] In FI/ICP-MS, however, the injected samples were diluted with a carrier solution in a long flow path, which resulted in band broadening of the analyte peaks and a deterioration of the detection sensitivity; thus the number of target elements was generally limited.

A few studies using flowing air as a sample carrier have been performed so far: the method is sometimes called segmented flow injection (SFI). Beauchemin and Craig used a mixture of air and argon gas through a silicagel column, and compared it with a water-flow method.[22–24] The sensitivity with the gas-flow method was higher than that with the water-flow method, though the gas-flow method showed a relatively large background. Coedo *et al*.[25] reported on the determination of ^{44}Ca in iron and steels using an FI/ICP-MS method based on a segmented air-water carrier. Stefanova *et al*.[26] showed an improvement of the detection limits by a factor of 3 by using an air-segmented discrete introduction (ASDI) coupled with ICP-MS, compared to a flow-injection technique with the same volume introduction. However, the application of a method using air flow as a carrier of sample solution to trace and ultratrace analysis by ICP-MS has hardly been examined so far. The method using air flow as a carrier has several advantages: (1) the system is very simple, (2) a special carrier is unnecessary, (3) the dispersion is very small, (4) the carry-over and the contamination is very low, (5) sample sizes are very small (~100 µl), and (6) detection sensitivity is relatively good.

For the reason that the abundance of trace elements in natural water samples is frequently below the detection limit of ICP-MS, a preconcentration step prior to the ICP-MS measurement is necessary. Chelating resins, such as an iminodiacetate (IDA) type of Chelex-100[27–31] and 8-hydroxyquinoline,[32–36] have been widely employed for preconcentration and matrix elimination in highly saline water analysis. In Chelex-100 resin, a volume change of the resin can occur by pH change, which causes the eluent flow to be irregular. Therefore, most of recent studies with Chelex-100 have been carried out by a batch method without a column.[27–31] Though an 8-hydroxyquinoline (8HQ) type chelating resin chemically bonded to silicagel does not exhibit swelling with a pH change, the stability constant of

Table 1 Standard operating conditions for a segmented-flow injection/ICP-MS system

ICP-MS	Model Seiko SPQ8000H Quadrupole type
Plasma conditions	
Forward power	1.1 kW
Reflected power	<5 W
Plasma gas	Ar 15 dm^3 min^{-1}
Carrier gas	Ar 0.45 dm^3 min^{-1}
Auxiliary gas	Ar 0.50 dm^3 min^{-1}
Sample uptake rate	1.0 ml min^{-1}
Interface conditions	
Distance from the load coil	10 mm from load coil
Sampling cone	Copper 1.1 mm ϕ
Skimmer cone	Copper 0.35 mm ϕ
Microsampling system	Seiko AT600 autosampler
Sample suction time	3 s (80 μl)
Rinse time with water	10 s
Rinse time with 0.1 M HNO_3	20 s
Delay time	30 s
Peak integration time	20 s
Dwell time	50 ms at each m/z
Repetitions	3 times

8HQ-Ca and 8HQ-Mg complexes are relatively close to those of some 8HQ-transition metal complexes. Therefore, most of the calcium and magnesium are recovered with transition metals, which can cause severe spectral interference with the determination of trace elements in sample solutions.

In this study, an IDA chelating resin of chitosan as a base material was investigated concerning how to eliminate major components, such as Na, K, Mg and Ca, and to enrich trace elements in solutions containing large amounts of salts. Also, the SFI method was examined in detail for evaluating whether the method is really useful as a convenient tool or not.

To secure the applicability and the reliability of the proposed methods involving both sample introduction by SFI/ICP-MS and the matrix elimination and preconcentration of analytes with the chelating resin column, the methods were applied to the determination of trace elements in river-water samples (reference materials issued from the Japan Society for Analytical Chemistry: JAC 0031 and JAC 0032). The analytical results obtained for JAC 0031 and JAC 0032 agreed closely with the certified values and other reference values obtained by the ICP-MS methods[27,37] and instrumental neutron activation analysis (INAA).[38]

Experimental

Instrumentation

The ICP-MS instrument used was a SPQ 8000H (Seiko Instruments, Tokyo, Japan), equipped with a glass concentric nebulizer (TR-30-C2, J. E. Meinhard Associates, CA, USA). A microsampling system mainly consisted of an AT-600 autosampler (Seiko Instruments) and MS software (trade name, Micro Suction ver. 1.8 M) for data acquisition and to control the ICP-MS instrument. The autosampler was composed of a nozzle tubing, a rinse solution tank, a blank solution tank, a turntable for sample suction (50 vials, 2 ml), a robotic arm for sample delivery and a cable RS232C connected to a personal computer (NEC Model PC9801 BA2) for ICP-MS operation. One end of a nozzle (PTFE tubing, 1 mm i.d. × 3 mm o.d.) of the autosampler was connected to suction tubing of the ICP-MS nebulizer. The standard operation conditions of the SFI/ICP-MS system and the data-acquisition parameters are summarized in Table 1. The suction times for rinsing the system, or the flow path for a blank solution (0.1 M HNO_3) injection and for sampling could be freely set by the MS software. A small volume of air was introduced through the nozzle while a robotic arm was moving from one tank to another.

River water certified reference materials

River water certified reference materials were examined to evaluate the proposed SFI/ICP-MS measurement method. The river water certified reference materials examined were those issued from the Committee of Reference Materials of the Japan Society for Analytical Chemistry. The preparation procedures were described by Akabane *et al.*[39] The reference samples, unspiked (JAC 0031) and spiked (JAC 0032), were both provided with adding nitric acid (about pH 1). Several elements, such as B, Al, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd and Pb, were spiked into JAC 0031 to prepare JAC 0032. The concentrations of such twelve elements in JAC 0032 ranged from 1 to 50 ng ml^{-1}. The concentration levels of the spiked elements were one fifth to one tenth of the regulatory limits of drinking water in Japan.[40]

Materials and reagents

A chitosan-based chelating resin (trade name: Chelate Chitopearl CI-03) was purchased from Fuji Spinning Co. (Tokyo, Japan). The CI-03 resin has a macroporous structure (the particle size of 0.3 mm) and a substantial metal-ligand exchange capacity (0.83 meq ml^{-1}). Before use, cleaning of the CI-03 resin was accomplished by removing the residual metal impurities: a 50 ml of wet resin was transferred to a 200 ml glass beaker, and mixed with 100 ml of 2 M HNO_3 and cautiously stirred at low speed (*ca.* 100 rpm) for 6 h, and rinsed with ultrapure water. Such a cleaning procedure was repeated twice. Small-size plastic columns (1 ml of volume) used for enrichment of trace elements and for matrix elimination were of polypropylene mini-columns with a controlling device for the flow rate (Muromachi Chemicals, Kyoto, Japan). An evaporation chamber (PTFE) and a clean-air supply pump, which were used to evaporate sample solutions to dryness on a PTFE-coating hot plate, were purchased from San-Ai Chemicals (Nagoya, Japan). All plastic labwares were used after being treated by soaking in 1 M HNO_3 for one week and then rinsing them with ultrapure water.

Analytical multielement standard solutions were prepared by diluting a mixed standard solution containing 10 μg ml^{-1} metal ions for ICP-MS (XSTC-13, Spex CertiPrep, NJ, USA). This mixed standard contains 31 elements (Li, Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Ag, Cd, In, Cs, Ba, Hg, Tl, Pb, Bi, Th and U). Other stock standard solutions containing 10 μg ml^{-1} of each metal (B, Ti, Mo, Zr, Sn, Sb, Te and W) were prepared from single-element standard solutions (1000 μg ml^{-1}) for atomic-absorption spectrometry (Wako Pure Chemicals, Osaka, Japan). These stock standard solutions were diluted with 0.1 M HNO_3 just before the SFI/ICP-MS measurement. The multielement standadards prepared in this way contained metal ions in concentrations ranging from 0.01 to 500 ng ml^{-1} (0.01, 0.1, 1, 10 and 500 ng ml^{-1}). To match the final acid concentrations of the working solutions to those of the sample solutions, 0.1 M HNO_3 was used as a diluent for preparing the working standard solutions. Ultrapure water (18.2 MΩ cm resistivity) was prepared with a Milli-Q Labo (Nihon Millipore, Tokyo, Japan). Nitric acid of ultrapure grade (60%, Cica-MERCK) from Kanto Chemicals (Tokyo, Japan) was diluted with ultrapure water to give

Table 2 Detection limits and total blank values obtained by segmented-flow injection/ICP-MS

Element	*m*/*z*	Segmented FI with column pretreatment		Segmented FI without column pretreatment		Pneumatic nebulization	
		Total blank value[a]/ ng ml^{-1}	Analytical LOD[b]/ ng ml^{-1}	Blank value[d]/ ng ml^{-1}	Instrumental LOD[c]/ ng ml^{-1}	Blank value[d]/ ng ml^{-1}	Instrumental LOD[c]/ ng ml^{-1}
Li	7	0.13	0.06	0.022	0.014	0.018	0.002
B	11	1.4	0.3	0.26	0.09	0.22	0.015
Al	27	1.3	0.6	0.096	0.04	0.045	0.003
Ti	48	0.19	0.06	0.056	0.015	0.062	0.002
V	51	0.10	0.06	0.11	0.06	0.084	0.017
Cr	52	0.03	0.03	0.067	0.02	0.055	0.006
Mn	55	0.5	0.15	0.024	0.019	0.023	0.002
Fe	57	1.8	0.6	1.6	1.3	1.56	0.25
Ni	58	0.25	0.06	0.084	0.05	0.054	0.007
Co	59	0.02	0.009	0.016	0.008	0.012	0.002
Cu	65	0.70	0.6	0.090	0.054	0.077	0.013
Zn	66	0.95	1.5	0.066	0.11	0.048	0.016
Ga	69	0.04	0.018	0.035	0.013	0.022	0.002
As	75	0.4	0.15	0.13	0.039	0.14	0.025
Se	78	0.6	0.3	1.6	0.56	0.60	0.08
Rb	85	0.04	0.015	0.023	0.016	0.012	0.002
Sr	88	0.09	0.03	0.032	0.02	0.018	0.002
Zr	90	0.1	0.09	0.035	0.018	0.032	0.003
Mo	98	0.07	0.03	0.044	0.028	0.026	0.002
Pd	105	0.03	0.01	0.021	0.019	0.017	0.007
Ag	107	0.03	0.03	0.014	0.011	0.009	0.002
Cd	114	0.01	0.006	0.009	0.005	0.010	0.001
Sn	120	0.21	0.03	0.036	0.03	0.028	0.002
Sb	121	0.024	0.006	0.067	0.02	0.041	0.004
Te	130	0.02	0.006	0.024	0.014	0.037	0.007
Cs	133	0.002	0.001	0.0036	0.0012	0.003	0.0009
Ba	138	0.3	0.12	0.030	0.008	0.025	0.002
W	184	0.02	0.01	0.013	0.014	0.012	0.002
Pb	208	0.34	0.15	0.045	0.03	0.028	0.003
U	238	0.01	0.01	0.015	0.008	0.012	0.001

a. Total blank values include the contamination from the column preconcentration procedure (25-fold) and subsequent SFI/ICP-MS measurement (n = 6). b. Limit of detection for the whole procedure, 3σ (n = 6). c. Limit of detection for the 0.1 M HNO_3 solution, 3σ (n = 10). d. 0.1 M HNO_3.

adequate acid concentrations. Acetic acid (minimum 96%) and ammonia solution (29%) used for preparing an ammonium acetate buffer solution were of electronics industry reagent grade (Kanto Chemicals). A 4 M ammonium acetate solution for adjusting the pH of samples was prepared by mixing equimolar concentrations of an ammonia solution and an acetic acid solution. A 0.2 M ammonium acetate buffer solution used for column conditioning and for the matrix elimination from the column was prepared by diluting a 4 M ammonium acetate buffer solution and adjusting its pH to 6 by adding a small amount of nitric acid.

Column separation/preconcentration procedure

A chelating resin (CI-03) packed in a mini-column (1 ml of volume, 5.0 – 5.5 mm i.d., 50 mm long) was washed with 5 ml of 2 M HNO_3, followed by washing with 5 ml of 0.1 M HNO_3. After a 6 ml volume of 0.2 M ammonium acetate buffer solution (pH 6) was passed through the column for column conditioning, a mixture (pH 6) of 25 ml of a sample solution and 2.5 ml of 4 M ammonium acetate solution was passed through the column. After the sample solution was passed through the column, 5 ml of a 0.2 M ammonium acetate buffer solution (pH 6) was passed through the column to eliminate the matrix, such as alkali and alkaline earth metals. After that, a 5 ml volume of ultrapure water was passed through the column for rinsing the residual ammonium acetate in the column. Finally, 10 ml of 1 M HNO_3 were passed to recover any metal ions adsorbed on the resin. Throughout all of the column procedures, the flow rate was maintained at about 2 ml min^{-1}. 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 or shrinking of the resin occurred. The time required for column pretreatment was about 1 h. The eluate with 1 M HNO_3 was transferred to a 50 ml of PTFE beaker and evaporated to dryness on a hot plate (120˚C) in the evaporation chamber in which clean-air was flowing with the air-supply pump. The evaporation chamber was covered with a polyvinyl clear sheet to prevent the sample from contamination. The residue in the beaker was redissolved with 1 ml of 0.1 M HNO_3 and provided as a sample solution to the ICP-MS measurement. The thus-prepared sample solution was transferred into a sample vial of the autosampler, and 80 μl aliquots of the sample solution were used for the SFI/ICP-MS measurement.

Procedures for the measurement by SFI/ICP-MS

By the SFI/ICP-MS system, a maximum of fifteen isotopes were simultaneously measured and their integrated peak areas were obtained in one injection. Therefore, 30 analyte elements were classified into two groups, A and B. Group A was consisted of Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Ag, Cd,

Table 3 Reproducibility test for 14 heavy elements by segmented-flow injection/ICP-MS

Element	*m*/*z*	RSD^a, %				
		0.01 ng ml^{-1}	0.1 ng ml^{-1}	1 ng ml^{-1}	10 ng ml^{-1}	100 ng ml^{-1}
V	51	20	8.0	4.6	2.8	3.5
Cr	52	3.0	2.8	4.1	0.9	1.2
Mn	55	1.0	5.5	3.5	1.8	1.6
Fe	57	2.6	1.6	3.5	1.7	1.5
Ni	58	20	14	3.2	2.3	0.4
Co	59	11	7.0	3.1	2.4	2.1
Cu	65	6.3	1.7	4.0	2.9	1.5
Zn	66	2.7	7.6	4.2	1.9	2.7
As	75	30	15	3.6	4.2	2.0
Mo	98	25	21	7.0	3.2	2.6
Ag	107	20	8.4	2.9	1.8	1.7
Cd	114	24	11	4.8	1.7	1.6
Pb	208	6.1	3.8	3.9	4.3	3.7
U	238	38	11	4.8	2.5	1.9

a. Relative standard deviation ($n = 10$).

Pb and U (15 elements); Group B consisted of Li, B, Al, Ga, Rb, Sr, Zr, Mo, Pd, Sn, Sb, Te, Cs, Ba and W (15 elements). The optimal integration range of the transient signal for each analyte was determined by injecting a 10 ng ml^{-1} multielement standard solution just before the SFI/ICP-MS measurement. A measurement for each group was carried out by injecting the following solutions in this order: (1) a blank solution (0.1 M HNO_3), (2) the series of standard working solutions (0.01 – 500 ng ml^{-1} of each element), (3) a blank solution including the pretreatment with the chelating column and, (4) the samples. The time required for one measurement was within 90 s, including the rinsing time with ultrapure water (10 s), background conditioning with 0.1 M HNO_3 solution (20 s), the sample suction time (3 s), the delay time (30 s), the peak integration time (20 s) and the total arm moving time (about 3 s, three shifts per cycle). The delay time (30 s) in Table 1 means the interval necessary for the sample to move from the turntable to the nebulizer. Each sample was measured three times, and their averages of the integrated peak areas were estimated as the analytical results.

Results and Discussion

Limits of the detection (LODs) of metals obtained by SFI/ICP-MS

Instrumental LODs were estimated as the concentrations corresponding to three-times the standard deviations (σ) of the intensities of the blank signals at *m*/*z* for each analyte, where a 0.1 M HNO_3 solution was used as a blank; they are summarized in Table 2. The instrumental LODs for 30 elements were obtained by SFI/ICP-MS and by pneumatic nebulization/ICP-MS under the same conditions, except for using the SFI system. The average values and the standard deviations of the blank signals were obtained by using the results of 10 replicate measurements of 0.1 M HNO_3. The LODs for most of the elements ranged from 10 to 100 pg ml^{-1} levels, which were slightly higher than those obtained by a pneumatic nebulization method. This indicates that the standard deviations obtained by SFI/ICP-MS are slightly worse than those obtained by pneumatic nebulization/ICP-MS. The total blank values, which mean the blank values of the blank solution obtained throughout the entire pretreatment procedure, such as the column pretreatment procedure, evaporation and redissolution, are also listed in Table 2; the total blank values for 30 metals were obtained by using 25 ml of 0.1 M HNO_3 as a blank solution and by treating it with the column according to the 25-fold preconcentration procedure. To obtain the total blank values, six replicate preconcentration procedures were performed. Most of the total blank values were less than 25-times the blank values of 0.1 M HNO_3. This indicates that the contamination occurring in the pretreatment with the column was negligibly small compared with that from nitric acid. The content of Cr in a 0.2 M ammonium acetate buffer solution was 12 ng ml^{-1}, while the total blank value of Cr was very low (0.03 ng ml^{-1}). This is because Cr^{6+} is not retained in the column by chelation with the IDA-group, and most of the Cr in sample solution can be removed from the column during the sample pretreatment.

Precision of the simultaneous multielement measurement by SFI/ICP-MS

Reproducibility tests for 14 elements were performed by SFI/ICP-MS measurements. To evaluate the reproducibility of a SFI/ICP-MS measurement, five kinds of the multielement standard solutions (0.01, 0.1, 1, 10 and 100 ng ml^{-1}) were measured 10 times per sample in succession from the lowest concentration to the highest one. Table 3 gives the results of the reproducibility at each concentration for each element. For most of the elements examined, the relative standard deviations (RSDs) decreased with increasing the metal concentrations, and their RSDs were smaller than 5% at the concentrations higher than 1 ng ml^{-1} for each metal concentration. As a result, we found that precise and stable flow signals for multielements in sample solutions could be obtained simultaneously using the microsampling technique by the SFI/ICP-MS.

Effect of the pH on the recoveries of elements in the column pretreatment

Artificial standard solutions of river water were used to investigate the recoveries of trace elements in a pretreatment with the chelating resin column. The artificial standard solutions contained major elements, such as Na (20 μg ml^{-1}), K (10 μg ml^{-1}), Ca (50 μg ml^{-1}) and Mg (15 μg ml^{-1}), the concentrations of which were higher by several times those in usual Japanese river-water samples, and also contained 30 elements at the same concentrations of 1 ng ml^{-1}. In order to examine the pH effect on the recoveries of trace elements in the column pretreatment, seven different artificial sample solutions with the same multielemental composition at the same

Table 4 Recoveries of trace elements at pH 6 in the preconcentration procedures with chitosan-based IDA chelating resin column

Element	m/z	Recovery[a], %	Element	m/z	Recovery[a], %
Li	7	< 0.1	Rb	85	< 0.2
B	11	4 ± 1	Sr	88	< 0.2
Al	27	101 ± 3	Zr	90	3 ± 0.3
Ti	48	48 ± 4	Mo	98	13 ± 2
V	51	90 ± 2	Pd	105	5 ± 2
Cr	52	4 ± 0.5	Ag	107	99 ± 2
Mn	55	50 ± 5	Cd	114	100 ± 2
Fe	57	96 ± 3	Sn	120	14 ± 1
Ni	58	99 ± 2	Sb	121	13 ± 2
Co	59	98 ± 2	Te	130	2 ± 0.2
Cu	65	100 ± 3	Cs	133	< 0.1
Zn	66	98 ± 5	Ba	138	< 1.0
Ga	69	85 ± 3	W	184	11 ± 3
As	75	52 ± 4	Pb	208	95 ± 6
Se	78	20 ± 4	U	238	98 ± 3

a. These are the average values obtained by using seven different columns, and the figures with ± are the standard deviations.

concentrations were prepared, and their pHs were varied from 1 to 7. The recovery changes with changing the pH of the solutions for 25 elements were observed. Their results are summarized in Fig. 1. For most of the elements examined, except for Fe, Al and As, the recovery increased with increasing the pH of the samples, and the maximum recovery was obtained at a pH above 4. Nearly 100% of the recovery was obtained for Al, Fe, Ni, Co, Cu, Zn, Ag, Cd, Pb and U at pH 4 – 6. The recoveries of elements such as V, Ti, Mn, As, Se, Mo, Sn, Sb and W were about 10 – 90% above pH 4, while those of B, Cr, Zr and Pd were about 1 – 10%. Most of the Li, Rb, Sr, Cs and Ba were lost (>99%) during the preconcentration procedure. At pH 7, the recovery of Fe abruptly decreased. This phenomenon may result from the formation of hydroxide. As a result, the pH of the sample solution was adjusted to 6, while taking into consideration the efficient and reproducible recoveries of as many elements as possible. In addition, as a compromise, 10 ml of 1 M HNO_3 were chosen as an eluent in this study. The results as the percentage of the recoveries of 30 trace elements obtained under the optimized column preconcentration conditions are summarized in Table 4. These data show the average values obtained by using seven independent columns packed with 1 ml of the chelating resin.

Matrix elimination by washing with ammonium acetate buffer

The removal of alkali and alkaline earth metals from the resin by washing with ammonium acetate solutions has been reported in many papers with Chelex-100.[41–43] Since there are no data concerning the chitosan-based IDA chelating column, the removal of alkali and alkaline earth metals was investigated using an artificial standard solution according to the chelating column pretreatment procedure. After the artificial sample was passed through a chitosan-based chelating column, the column was washed by passing 0.2 M ammonium acetate (pH 6) through it. The results obtained by varying the volumes of the ammonium acetate buffer showed that 5 ml were sufficient to eliminate the residual matrix components. The removed rates (%) of four elements, such as Na, K, Ca and Mg, were obtained by measuring the concentrations in the eluents eluted with 10 ml of 1 M HNO_3. The results are listed in Table 5. The removed rates were over 99.9% for these elements.

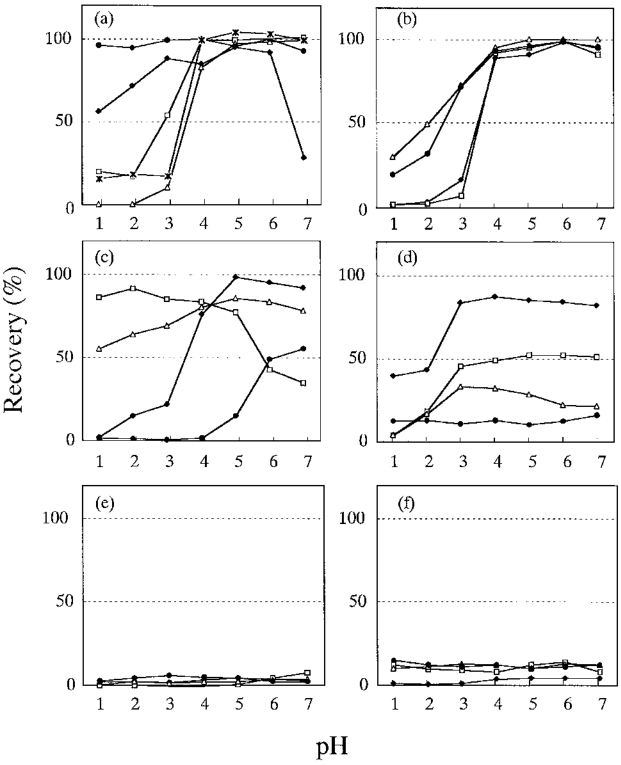

Fig. 1 pH dependence of the recovery of elements in the preconcentration with a chitosan-based chelating resin column. (a) ◆: Fe, □: Ni, △: Co, ●: Cu, ∗: Zn; (b) ◆: Ag, □: Cd, △: Pb, ●: U; (c) ◆: Al, □: Ti, △: V, ●: Mn; (d) ◆: Ga, □: As, △: Se, ●: Mo; (e) ◆: B, □: Cr, △: Zr, ●: Te; (f) ◆: Pd, □: Sn, △: Sb, ●: W.

Analysis of river-water samples by SFI/ICP-MS

In order to evaluate the accuracy and precision of the proposed method, two kinds of river-water certified reference materials were examined. In direct sample introduction by SFI/ICP-MS without any pretreatment, each river-water sample was measured 5 times and data for 5 replicate measurements were obtained. Such measurements were carried out for each set of 15 elememts. In the case of measurements of the samples obtained by SFI/ICP-MS with the chelating column pretreatment, three similar chelating resin columns were employed for a 25-fold preconcentration procedure for each river-water sample; three 25 ml aliquots of the sample were treated with three chelating resin columns, and the final analytical results were obtained by making a correction of the measured value for each element using the recovery value given in Table 4. The thus-obtained analytical results by the present methods, as well as the certified values, are summarized in Table 6 for JAC 0031 and in Table 7 for JAC 0032. The analytical results obtained by other workers are also listed in both Tables 6 and 7 for a comparison of the present data with reference values obtained by other methods, such as ICP-MS[27,37] and INAA.[38]

In an analysis of JAC 0031 by SFI/ICP-MS without any column pretreatment procedures, the results for B, Al, Cr, Mn, Cu and Zn agreed well with the certified values, whereas the results for Fe, Ni, Co and As deviated positively from the certified and/or reference values. Such positive errors in $^{57}Fe^+$ and $^{75}As^+$ were possibly caused by spectral interferences from $^{40}Ca^{16}OH^+$ and $^{40}Ar^{35}Cl^+$, respectively. The large differences in the concentration between the two methods with and without the column pretreatment procedures were seen in Ni and Co.

Table 5 Removal of Na, Mg, K and Ca after rinsing the resin with and without ammonium acetate buffer in the chitosan-based IDA resin column preconcentration procedure

Element	*m*/*z*	Added conc./ μg ml^{-1}	Remained conc.[a]/μg ml^{-1}		Removed rate[b], %	
			with buffer	without buffer	with buffer	without buffer
Na	23	20	0.018	0.25	99.91	98.8
Mg	24	15	0.004	1.5	99.97	90.0
K	39	10	0.008	0.20	99.92	98.0
Ca	43	50	0.089	7.3	99.82	85.4

a. Concentrations in the eluents eluted with 10 ml of 1 M HNO_3. b. Removed rate (%) = {(added conc. – remained conc.)/added conc.} × 100.

Table 6 Analytical results for the certified reference material of unspiked river water (JAC0031) obtained by SFI/ICP-MS with and without sample pretreatment

Element	*m*/*z*	SFI/ICP-MS[a]/ng ml^{-1}		Certified value/ ng ml^{-1}	ICP-MS[e] (ICP-AES)/ ng ml^{-1}	INAA[f]/ ng ml^{-1}	ICP-MS[g]/ ng ml^{-1}
		No pretreatment (*n* = 5)	Pretreatment (*n* = 3)				
Li	7	0.034 ± 0.001	n.d.[c]				0.032 ± 0.001
B	11	9.3 ± 1	(10)[d]	9.1 ± 0.5	8.3 ± 0.2		
Al	27	13.8 ± 0.9	13.5 ± 0.6	13.4 ± 0.7	14 ± 1		13.6 ± 0.8
Ti	48	[40.6 ± 1.1][b]	(0.6)[d]		0.15	< 8.4	
V	51	[9.0 ± 0.4][b]	7.4 ± 0.5		7.8 ± 0.5	7.4 ± 0.4	7.80 ± 0.05
Cr	52	0.17 ± 0.03	(0.1)[d]	0.14 ± 0.02	0.27 ± 0.01	0.139 ± 0.009	
Mn	55	0.45 ± 0.02	(0.5)[d]	0.46 ± 0.03	0.50 ± 0.5	0.45 ± 0.04	0.45 ± 0.01
Fe	57	[68 ± 5][b]	6.3 ± 1.5	6.9 ± 0.5	7.2 ± 0.9	7.2 ± 0.9	
Ni	58	[0.38 ± 0.02][b]	0.13 ± 0.02		0.090	0.38 ± 0.19	0.122 ± 0.002
Co	59	[0.035 ± 0.001][b]	0.012 ± 0.002		0.013	0.022 ± 0.007	0.024 ± 0.001
Cu	65	0.90 ± 0.02	0.89 ± 0.05	0.88 ± 0.03	0.83	< 4.7	0.91 ± 0.02
Zn	66	0.89 ± 0.12	0.75 ± 0.09	0.79 ± 0.05	0.64	0.81 ± 0.12	0.94 ± 0.01
Ga	69	0.038 ± 0.005	0.036 ± 0.002			< 1.3	
As	75	[1.4 ± 0.7][b]	(0.3)[d]	0.28 ± 0.04		0.23 ± 0.01	0.26 ± 0.01
Se	78	n.d.[c]	(0.1)[d]	(0.1)[d]		0.076 ± 0.002	
Rb	85	0.52 ± 0.04	n.d.[c]			0.51 ± 0.05	0.52 ± 0.02
Sr	88	21.0 ± 0.1	n.d.[c]		19.4 ± 0.3	20 ± 1	19.2 ± 0.7
Zr	90	0.063 ± 0.005	(0.06)[d]			< 0.12	
Mo	98	0.39 ± 0.03	(0.4)[d]		0.50 ± 0.008	0.41 ± 0.05	0.43 ± 0.02
Pd	105	0.37 ± 0.08	(0.4)[d]				
Ag	107	n.d.[c]	0.004 ± 0.0002			< 0.0014	
Cd	114	n.d.[c]	0.003 ± 0.001	(0.003)[d]	0.0037	< 0.02	0.003 ± 0.001
Sn	120	(0.03)[d]	(0.05)[d]			< 0.098	
Sb	121	0.074 ± 0.006	(0.070)[d]			0.073 ± 0.003	0.077 ± 0.001
Te	130	n.d.[c]	(0.03)[d]			< 0.011	
Cs	133	0.0063 ± 0.0005	n.d.[c]			0.0058 ± 0.0006	0.0059 ± 0.0001
Ba	138	0.79 ± 0.03	n.d.[c]		0.77 ± 0.009	0.88 ± 0.07	0.883 ± 0.006
W	184	(0.02)[d]	n.d.[c]			0.0143 ± 0.0019	0.015 ± 0.001
Pb	208	(0.05)[d]	0.024 ± 0.004	0.026 ± 0.003	0.025		0.026 ± 0.002
U	238	n.d.[c]	0.0025 ± 0.0005		0.0027 ± 0.0002	0.0035 ± 0.0008	0.003 ± 0.001

a. These analytical data were those corrected by using the recovery values (%) for corresponding metal ions shown in Table 4. b. These values are possibly interfered from polyatomic ions of matrix elements. c. Not determined. d. Information value. e. Cited from Ref. 27. f. Cited from Ref. 38. g. Cited from Ref. 37.

$^{58}\text{Ni}^{+}$ and $^{59}\text{Co}^{+}$ might have been interfered with by $^{42}\text{Ca}^{16}\text{O}^{+}$ and $^{43}\text{Ca}^{16}\text{O}^{+}$, respectively. Spectral interference from $^{48}\text{Ca}^{+}$ (natural abundance 0.19%) with $^{48}\text{Ti}^{+}$ was also seen. The result of $^{51}\text{V}^{+}$ obtained by SFI/ICP-MS without any pretreatment, which could be interfered from $^{35}\text{Cl}^{16}\text{O}^{+}$, was slightly higher than the data of other reference values. For determining these elements, no correction was made in direct sample introduction by SFI/ICP-MS without a pretreatment. However, the method in combination with the chelating resin-column pretreatment method, which can eliminate matrix components and enrich analytes, can solve such problems, as can be seen from Tables 6 and 7.

The concentrations of Ag, Cd and U were not determined by SFI/ICP-MS without a pretreatment, because their concentrations were below the detection limits, whereas more accurate and reliable concentrations of these elements were obtained by SFI/ICP-MS using the 25-fold column preconcentration procedure with a chitosan-based chelating resin column. However, the concentrations of alkali and alkaline earth metals could not be obtained by SFI/ICP-MS with a pretreatment, because their recovery was less than 1%. In the case of elements such as Li, Rb, Sr, Cs and Ba, the data obtained by SFI/ICP-MS without a pretreatment were adopted; they are in good agreement with the reference values.

Although Cd and Pb in the case of JAC 0031 could not be determined by SFI/ICP-MS without a pretreatment, they could be easily determined by SFI/ICP-MS without a pretreatment in JAC 0032, because these elements were spiked.

The analytical results obtained for unspiked elements (18

Table 7 Analytical results for the certified reference material of spiked river water (JAC0032) obtained by SFI/ICP-MS with and without sample pretreatment

Element	m/z	SFI/ICP-MS[a]/ng ml^{-1}		Certified value/ ng ml^{-1}	ICP-MS[e] (ICP-AES)/ ng ml^{-1}	INAA[f]/ ng ml^{-1}	ICP-MS[g]/ ng ml^{-1}
		No pretreatment (n = 5)	Pretreatment (n = 3)				
Li	7	0.034 ± 0.001	n.d.[c]				0.034 ± 0.001
B	11	58 ± 2	(60)[d]	59 ± 2	59 ± 3		
Al	27	61 ± 2	59 ± 2	61 ± 2	59 ± 3		58 ± 1.1
Ti	48	[40.6 ± 1.1][b]	(1)[d]		0.15	< 8.3	
V	51	[8.9 ± 0.3][b]	7.3 ± 0.5		7.9 ± 1.0	7.5 ± 0.2	7.64 ± 0.02
Cr	52	10.3 ± 0.2	10.1 ± 0.5	10.1 ± 0.2	9.61 ± 0.07	10.4 ± 1.3	
Mn	55	5.6 ± 0.2	(5)[d]	5.4 ± 0.1	5.3 ± 0.1	5.4 ± 0.3	5.1 ± 0.1
Fe	57	[108 ± 8][b]	53 ± 4	57 ± 2	56 ± 4	58 ± 5	
Ni	58	10.2 ± 0.3	10.4 ± 0.3	10.2 ± 0.3	10.3 ± 0.1	11.2 ± 0.7	10.3 ± 0.2
Co	59	[0.036 ± 0.005][b]	0.011 ± 0.002			0.045 ± 0.014	0.023 ± 0.001
Cu	65	10.0 ± 0.2	9.81 ± 0.3	10.5 ± 0.2	11.2 ± 0.8	10.8 ± 1.2	10.8 ± 0.1
Zn	66	11.7 ± 0.2	12.0 ± 1.1	11.3 ± 0.4	11.7 ± 0.3	10.7 ± 1.1	12.5 ± 0.2
Ga	69	0.040 ± 0.003	0.041 ± 0.002			< 1.3	
As	75	[6.2 ± 0.4][b]	(5)[d]	5.5 ± 0.3		5.0 ± 0.4	5.8 ± 0.1
Se	78	4.6 ± 0.5	(5)[d]	5.2 ± 0.3		5.2 ± 0.2	
Rb	85	0.56 ± 0.04	n.d.[c]			0.53 ± 0.03	0.50 ± 0.01
Sr	88	20.2 ± 0.1	n.d.[c]		19.6 ± 0.2	24 ± 2	18.5 ± 0.4
Zr	90	0.072 ± 0.006	(0.1)[d]			< 0.21	
Mo	98	0.41 ± 0.04	(0.4)[d]		0.49 ± 0.01	0.40 ± 0.03	0.40 ± 0.01
Pd	105	1.3 ± 0.1	(1)[d]				
Ag	107	n.d.[c]	0.004 ± 0.0002			< 0.0019	
Cd	114	0.99 ± 0.02	1.01 ± 0.02	1.00 ± 0.02	1.08 ± 0.02	0.99 ± 0.07	1.05 ± 0.05
Sn	120	0.18 ± 0.03	(0.2)[d]			< 0.17	
Sb	121	0.15 ± 0.01	(0.2)[d]			0.145 ± 0.010	0.171 ± 0.002
Te	130	n.d.[c]	(0.04)[d]			< 0.018	
Cs	133	0.0056 ± 0.0004	n.d.[c]			0.0061 ± 0.0004	0.0063 ± 0.0002
Ba	138	0.94 ± 0.06	n.d.[c]		0.79 ± 0.01	0.86 ± 0.05	0.918 ± 0.012
W	184	(0.03)[d]	(0.02)[d]			< 0.03	0.014 ± 0.001
Pb	208	10.1 ± 0.5	9.87 ± 0.3	9.9 ± 0.2	10 ± 1		10.4 ± 0.1
U	238	n.d.[c]	0.0023 ± 0.0007		0.0026 ± 0.0007	0.0026 ± 0.0005	0.003 ± 0.001

a. These analytical data were those corrected by using the recovery values (%) for corresponding metal ions shown in Table 4. b. These values are possibly interfered from polyatomic ions of matrix elements. c. Not determined. d. Information value. e. Cited from Ref. 27. f. Cited from Ref. 38. g. Cited from Ref. 37.

elements: Li, Ti, V, Co, Ga, Rb, Sr, Zr, Mo, Pd, Ag, Sn, Sb, Te, Cs, Ba, W and U) in JAC 0032 obtained by SFI/ICP-MS without a pretreatment were almost the same as those of JAC 0031; exceptions were observed in the results of Pd, Sn and Sb. The concentrations of these elements in JAC 0032 were 2 – 3 times higher than those in JAC 0031. Iwashita *et al*.[37] explained the difference in the Sb concentration between JAC 0031 and JAC 0032. They proposed two possibilities: one was contamination from the spiking procedure; the other was a concentration change by a short-time variation. However, the former possibility is unlikely considering the total amounts of spiked metals. The latter is possible at present. As a whole, the analytical results for trace elements obtained by the SFI/ICP-MS with pretreatment are in good agreement with the certified values and those obtained by INAA; also the analytical results for alkali and alkaline earth metals obtained by SFI/ICP-MS without a pretreatment are in good agreement with the reference values.

In conclusion, 24 elements in JAC 0031 and 26 elements in JAC 0032 were determined by SFI/ICP-MS with a pretreatment procedure using a chitosan-based chelating resin column, as well as without a pretreatment. A microsampling system enabled us to minimize the sample volume required (25 ml) for the SFI/ICP-MS measurement. The use of a small sample volume required for the pretreatment is very helpful to reduce the amounts of reagents and wastes. It was found, for the first time, that the chitosan-based IDA chelating resin is very useful for the pretreatment of river-water samples, prior to an ICP-MS measurement. The main advantages of the chitosan-based chelating resin are: (1) no swelling and shrinking of the resin, (2) relatively high flow-rate compared with Chelex-100 resin, and (3) relatively strong retention of heavy metal ions and easy elution with 1 M HNO_3 compared with Chelex-100 resin using 2 M HNO_3. The combination of the chitosan-based chelating resin column with the SFI/ICP-MS method, which allowed at the same time the preconcentration of analytes and the elimination of matrix elements, was found to be very useful for the determination of trace elements in a wide variety of natural-water samples.

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References

1. S. A. Pergantis, E. M. Heithmar, and T. A. Hinners, *Anal.*

Chem., **1995**, *67*, 4530.
2. A. Stroh and U. Völlkopf, *J. Anal. At. Spectrom*., **1993**, *8*, 35.
3. M. J. Bloxham, S. J. Hill, and P. Worsfold, *J. Anal. Proc*., **1993**, *30*, 159.
4. E. Fujimori, R. Wei, H. Sawatari, K. Chiba, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **1996**, *69*, 3505.
5. T. J. Hwang and S. J. Jiang, *Analyst*, **1997**, *122*, 233.
6. J. W. McLaren, D. Beauchemin, and S. S. Berman, *Anal. Chem*., **1987**, *59*, 610.
7. J. J. Thompson and R. S. Houk, *Appl. Spectrosc*., **1987**, *41*, 801.
8. A. L. Gray and J. G. Williams, *J. Anal. At. Spctrom*., **1987**, *2*, 599.
9. S. H. Tan and G. Horlick, *J. Anal. At. Spctrom*., **1987**, *2*, 745.
10. J. W. McLaren, J. W. H. Lam, S. S. Berman, K. Akatsuka, and M. A. Azeredo, *J. Anal. At. Spctrom*., **1993**, *8*, 279.
11. K. Kawabata, Y. Kishi, O. Kawaguchi, Y. Watanabe, and Y. Inoue, *Anal. Chem*., **1991**, *63*, 2137.
12. Y. Inoue, H. Kumagai, Y. Shimamura, T. Yokoyama, and T. M. Suzuki, *Anal. Chem*., **1996**, *68*, 1517.
13. A. Itoh, T. Hamanaka, W. Rong, K. Ikeda, H. Sawatari, K. Chiba, and H. Haraguchi, *Anal. Sci*., **1999**, *15*, 17.
14. T. Hamanaka, A. Itoh, S. Itoh, H. Sawatari, and H. Haraguchi, *Chem. Lett*., **1995**, 363.
15. A. Itoh, C. Kimata, H. Miwa, H. Sawatari, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **1996**, *69*, 3469.
16. A. Malahoff, I. Y. Kolotyrkina, and L. K. Shpigun, *Analyst*, **1996**, *121*, 1037.
17. M. R. Plantz, J. S. Fritz, F. G. Smith, and R. S. Houk, *Anal. Chem*., **1989**, *61*, 149.
18. A. Seubert and G. Petzold, *J. Anal. At. Spectrom*., **1995**, *10*, 371.
19. X. P. Yan, R. Kerrich, and M. J. Henry, *J. Anal. At. Spectrom*., **1999**, *14*, 215.
20. S. N. Willie, H. Tekgul, and R. E. Sturgeon, *Talanta*, **1998**, *47*, 439.
21. D. Beauchemin and A. A. Specht, *Can. J. Anal. Sci. Spectrosc*., **1998**, *43*, 43.
22. D. Beauchemin, *Analyst*, **1993**, *118*, 815.
23. J. M. Craig and D. Beauchemin, *Analyst*, **1994**, *119*, 1677.
24. J. M. Craig and D. Beauchemin, *J. Anal. At. Spectrom*., **1994**, *9*, 1341.
25. A. G. Coedo, M. T. Dorado, I. Padilla, and F. J. Alguacil, *J. Anal. At. Spectrom*., **1996**, *11*, 1037.
26. V. Stefanova, V. Kmetov, and L. Futekov, *J. Anal. At. Spectrom*., **1997**, *12*, 1271.
27. A. Itoh, K. Iwata, S. Ji, T. Yabutani, C. Kimata, H. Sawatari, and H. Haraguchi, *Bunseki Kagaku*, **1998**, *47*, 109.
28. A. Itoh, C. Kimata, H. Miwa, H. Sawatari, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **1996**, *69*, 3469.
29. H. Haraguchi, A. Itoh, C. Kimata, and H. Miwa, *Analyst*, **1998**, *123*, 773.
30. S. Ji, C. Kimata, T. Yabutani, A. Itoh, E. Fujimori, K. Chiba, and H. Haraguchi, *Biomed. Res. Trace Elem*., **1997**, *8*, 37.
31. H. Sawatari, T. Toda, T. Saizuka, C. Kimata, A. Itoh, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **1995**, *68*, 3065.
32. J. W. McLaren, J. W. Lam, S. S. Berman, K. Akatsuka, and M. A. Azeredo, *J. Anal. At. Spectrom*., **1993**, *8*, 279.
33. K. Akatsuka, J. W. McLaren, J. W. Lam, and S. S. Berman, *J. Anal. At. Spectrom*., **1992**, *7*, 889.
34. V. Dupont, Y. Auger, C. Jeandel, and M. Wartel, *Anal. Chem*., **1991**, *63*, 520.
35. D. Beauchemin and S. S. Berman, *Anal. Chem*., **1989**, *61*, 1857.
36. D. Beauchemin, J. W. McLaren, A. P. Mykytiuk, and S. S. Berman, *J. Anal. At. Spectrom*., **1988**, *3*, 305.
37. T. Shimamura and M. Iwashita, *Anal. Sci*., **1997**, *13*, 177.
38. S. Suzuki, Y. Okada, and S. Hirai, *Bunseki Kagaku*, **1997**, *46*, 223.
39. I. Akabane, J. Yoshinaga, M. Matubara, A. Kawase, and K. Okamoto, *Proceedings of 57th Symposium of the Japan Society for Analytical Chemistry*, **1996**, 73.
40. *Ministry of Health and Welfare (Japan)*, Notification No. 69, December **1992**.
41. S. C. Pai, P. Y. Whung, and R. L. Lai, *Anal. Chim. Acta*, **1988**, *211*, 257.
42. C. J. Cheng, T. Akagi, and H. Haraguchi, *Bull. Chem. Soc. Jpn*., **1985**, *58*, 3229.
43. H. M. Kingston, I. L. Barnes, T. J. Brady, T. C. Rains, and M. A. Champ, *Anal. Chem*., **1978**, *50*, 2064.