Atomic Spectroscopy

July/August 2008 Volume 29, No. 4

In This Issue:

ASPND7 29(4) 115–156 (2008)
ISSN 0195-5373

Issues also available electronically.

(see inside front cover)

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Atomic Spectroscopy
Vol. 29(4) July/August 2008

Printed in the United States and published six times a year by:

PerkinElmer Life and Analytical Sciences
710 Bridgeport Avenue
Shelton, CT 06484-4794 USA
http://www.perkinelmer.com

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Stream Sediment and Soil Samples by Microwave Digestion Followed by ICP-MS Measurement

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ABSTRACT

A critical study has been made for the determination of rare earth elements (REEs) and eight other low level elements (Be, Ge, Mo, Sn, W, Hf, Ta and U) in stream sediment and soil samples by microwave digestion, followed by ICP-MS measurement. In this study, 0.1 g samples were decomposed in a microwave sample digestion system with 1 mL HF, 1.5 mL HNO_3, and 4 mL HCl at a pressure of 20 bar and a temperature of 200 °C for 30 minutes. The decomposition process was then repeated a 2nd time. After decomposition, the sample was transferred into a Teflon beaker, 1 mL $HClO_4$ was added, and the acids evaporated to near dryness. The residue was dissolved in dilute HNO_3, 10 mL of 100 ppb internal standard (indium) was added, and the solution transferred to a 100-mL volumetric flask. REEs and other trace elements were determined using a PerkinElmer SCIEX® Model ELAN® DRC™-e ICP-MS spectrometer.

Calibration of the instrument was performed with a Chinese stream sediment reference material, GSD-5. Sixteen stream sediment and soil reference samples were analyzed for 14 REEs and eight other trace elements; the values were compared with recommended values. It was found that the REE data were in close in agreement with the recommended values, and the data for Be, Ge, Mo, and U were generally good. However, the other four elements (Sn, W, Ta, and Hf) read either very low or high. The precision was generally better than 10% RSD for elemental concentrations >1 ppm and 0–20% RSD for elements present at <1 ppm. It can be concluded that the REEs, Be, Ge, Mo, and U could be determined by microwave digestion followed by ICP-MS measurement. However, Sn, W, Ta, and Hf could not be determined using this procedure.

INTRODUCTION

The Geological Survey of India (GSI) has embarked on an ambitious project of mapping the whole country geochemically during the next 10-15 years. Under the National Geochemical Mapping programme (NGCM), a large number of stream sediment and soil samples are being generated which are to be analysed for 68 constituents at their natural abundance level or below. XRF is being utilized for major and 16 trace elements determination in these samples (1). However, REEs and other elements present at very low levels (Be, Ge, Sn, Mo, W, Hf, Ta, and U) cannot be determined by XRF in these sample media.

ICP-MS has made tremendous progress in the field of geochemical analysis during the last 15 years. Its capability to determine low-level elements at their natural abundance level in various geological samples has been well recognized (2-4). However, complete dissolution of samples is a pre-requisite for obtaining good results. Unfortunately many geological samples, particularly stream sediment and soil, contain refractory minerals that are difficult to solubilize (5-7).

Open vessel digestion using different combinations of acids (including HF) for removal of silica is a common method for the decomposition of samples in geochemical laboratories. Often the refractory minerals remain undecomposed and require alkali fusion for complete decomposition (8). Closed vessel digestion has also been employed by some workers. Liang et al. (9) in their study used PTFE-lined stainless steel bombs for dissolution of 0.1 g stream sediment, soil, and rock samples in HNO_3 and HF at a temperature of 200 °C for 12 hours, followed by removal of acids on a hot plate at 140 °C, and dissolution in dilute HNO_3. The dissolution process described by the authors is very tedious and cannot be applied for routine analysis of samples.

For complete dissolution of geological samples, fusion employing $LiBO_2$ as fusion agent is commonly employed. The disadvantage of the alkali fusion technique is the high salt content in the solution, which will affect the detection limits, memory, and drift in instrumental response (3,7,10).

In recent times, microwave digestion has gained importance for the dissolution of various samples, including geological matrices (11-14). However, few attempts have been made for dissolution of stream sediment and soil samples by microwave digestion for ICP-MS analysis (5,15). Sengupta and Bertrand (13) in their study used a mixture of HF, HNO_3, and HCl for rapid dissolution of silicate rocks

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and stream sediment reference samples, followed by the addition of boric acid to mask fluoride prior to ICP-MS measurement of different elements, including REEs. Ivanova et al. (16) reported that REEs, Be, Bi, Tl, Th, and U could be successfully determined by ICP-MS in soil and sediment after treatment of the samples with HF+HNO_3 overnight, followed by stepwise microwave digestion with the addition of HF and H_3BO_3.

The microwave digestion procedure described by the above authors used boric acid for complexation of excess fluoride in digested solution. However, adding boric acid will increase the salt concentration of the solution and excess fluoride ions may create problems in measurement if they are not completely removed by complexation. Besides, these authors used only four stream sediment and soil samples for the analysis and only determined a limited number of elements (e.g., Ge and W were not studied). In the present paper, a detailed study has been made for the digestion of stream sediment and soil samples by microwave digestion employing HNO_3 and HF, followed by removal of HF in an open hot plate, dissolution in dilute HNO_3, and measurement of the REEs and eight other elements (Be, Ge, Mo, Sn, W, Hf, Ta, and U) by ICP-MS. Sixteen international standard reference stream sediments and soil samples were analyzed, and their data are presented. It was observed that the REE data are in good agreement with the recommended values. For Be, Ge, Mo, and U, comparable data were obtained. However, for Sn, W, Ta, and Hf, consistently low values were obtained, particularly for higher concentrations.

TABLE I
ICP-MS Instrumental Parameters and Measurement Conditions

RF Power	1100 KW
Lens Voltage	8.25
Plasma Argon Gas Flow Rate	15 L/min
Auxiliary Argon Gas Flow Rate	1.20 L/min
Nebulizer Argon Gas Flow Rate	0.86 L/min
Integration Time	1000 ms
Dwell Time	50 ms per amu
Acquisition Mode / No. of Sweeps	Peak hopping / 60
No. of Replicates	3
Washing Solution	2% HNO_3
Washing Time	30 sec

TABLE II
Microwave Digestion Operating Conditions

Power Supply	-	AC 230V and 50 Hz
Power Consumption	-	3680 VA
Microwave Power	-	1700 W delivered from 2 magnetrons
Rotor Speed	-	3 rpm
Sensor Probe	-	One reference vessel in Rotor 16 for precise temperature and pressure.
Magnetron		2455 MHz.
Rotor	-	16MF100
Sensor		Yes
Applied Power		650 W

EXPERIMENTAL

Instrumentation

A PerkinElmer SCIEX ELAN® DRC™-e ICP-MS instrument with a cross-flow nebulizer was used throughout this work (PerkinElmer SCIEX, Concord, Ontario, Canada). The spectrometer is optimized to provide minimal values (<3%) for the CeO^+/Ce^+ and Ba^{2+}/Ba^+ ratios, as well as optimum intensity for the analytes. The instrumental parameters and measurement conditions are given in Table I.

A Multiwave® 3000 microwave digestion system (Anton Paar, Austria) with a Rotor 16MF100 was used for the decomposition of the samples. The operating conditions of the microwave digestion system are given in Table II.

Reagents and Standard Solutions

Analytical reagent (AR) grade HF and $HClO_4$, and purified (subboiling) HCl and HNO_3 were used in this work. High purity water (18 MΩ) was prepared with a Milli-Q™ 116 apparatus (Millipore Corporation, Bedford, MA, USA) and used throughout the procedure.

The 8% acid mixture was prepared by mixing 300 mL concentrated HNO_3, 100 mL concentrated HCl, and 4600 mL high purity water.

High purity multi-element standards (100 ppm) were obtained from the manufacturer and diluted to 10 ppb for optimization and mass calibration of the instrument.

TABLE III
Isotopes Used and Interferences

Element	Mass (Amu) Selected	Abundances (%)	Interferences	Correction applied for:
Be	9.0122	100	Free	
Ge	73.9219	35.94	Se, ArS, Nd^{+2}, Sm^{+2}	Se
Mo	97.9055	24.13	Ru	Ru
Sn	117.902	24.20	MoO, U^{+2}	
La	138.906	99.9	Free	
Ce	139.905	88.5	Free	
Pr	140.907	100	Free	
Nd	142.91	12.18	Free	
Sn	146.915	15.00	Free	
Eu	150.92	47.8	BaO	
Gd	157.924	24.84	Dy, NdO, PrO, CeO,	Dy
Tb	158.925	100	PrO, NdO	
Dy	163.929	28.2	Er, SmO,NdO	Er
Ho	164.93	100	SmO	
Er	166.932	22.95	EuO, SmO	
Tm	168.934	100	EuO	
Yb	171.937	21.9	DyO, GdO, SmO	
Lu	174.941	97.4	GdO, TbO	
Hf	177.944	27.2	GdO, ErO, DyO	
Ta	180.948	99.9	Free	
W	181.948	26.3	Free	
U	238.05	99.3	Free	

Calibration

For quantitative analysis of the samples, calibration was done with a stream sediment reference material. It was found that calibration with pure standard solutions with matrix matching did not produce accurate results for standard reference materials (SRMs). After carrying out several experiments with a number of SRMs for calibration work, GSD–5 (Chinese Stream Sediment) was chosen for calibration standards.

Isotopes Used in Study

The isotopes used in this study are given in Table III. Interferences on the isotopes by oxides, doubly charged ions, and other elements are also listed. Oxides and doubly charged ion interferences are restricted to <3% by adjustment of the instrumental parameters. Elemental interferences (Se on ^{74}Ge, Ru on ^{98}Mo, Dy on ^{158}Gd, and Er on ^{164}Dy) are corrected by applying a specific equation for that particular element.

Standard Reference Material (SRM)

The SRMs used in this study are: GSD–2, GSD–3, GSD–4, GSD–6, GSD–7, GSD–8, GSD–9, GSD–10, GSD– 1, and GSD–12 (all Chinese Stream sediments); GSS–1, GSS–2, GSS–4, and GSS–8 (all Chinese soil); JSD–1 (Japanese Stream Sediment) and STSD– 1 (Canadian Stream Sediment).

Sample Dissolution by Microwave Digestion

A Multiwave® microwave sample digestion system (Anton Paar, Austria) with a Rotor 16MF100 was used for digestion of the samples. The digestion vessels consist of a liner made of trifluoromethane (TFM) and a ceramic outer jacket, which are closed with a screw cap. The rotor accommodates 16 vessels but for this study, only eight vessels were used for digestion. Eight samples were accurately weighed to 0.1000 g and placed into a clean TFM vessel to which 4 mL HCl, 1.5 mL HNO_3, and 1 mL HF were added. A built-in computer is used to specify the decomposition program and to control the Multiwave. The digestion program used by the microwave digestion system is given in Table II. The digestion system was run for 30 minutes at 20 bar pressure at a temperature of 200 °C. The system was allowed to cool and the process was repeated for another 30 minutes. After digestion, the vessels were opened and the contents transferred to Teflon® beakers. One mL $HClO_4$ was then added and the beakers placed on a hot plate. The acids were evaporated to a pasty mass. The mass was dissolved in 4 mL (1:1) HNO_3, and the solution transferred to a 100-mL volumetric flask with 25 mL of the 8% acid mixture. Ten mL of a 100-ppb indium solution (internal standard) was added to the flask, and the volume made up to volume with high purity water.

RESULTS AND DISCUSSION

Choice of SRMs

The chemical laboratories of the Geological Survey of India (GSI) use Chinese stream sediment and soil reference samples for calibration of various instruments for the determination of different elements in samples generated under the NGCM program. In addition, Canadian and Japanese standards are also used. For this reason, we selected 14 Chinese standards (10 stream sediments and four soils), one Canadian stream sediment, and one Japanese stream sediment standard.

Dissolution of Samples

Extensive investigations in the microwave digestion of stream sediment and soil samples show that most of the samples are not decomposed in a single digestion step (about 30 minutes). A second digestion step is required for complete digestion. Even then, a small residue is observed in some of the samples. After microwave digestion, the removal of fluoride provides a clear advantage so that fluoride ions do not create interferences during measurement. Besides, the TDS content of the solution is reduced due to removal of silica as SiF_4.

Instrumental Detection and Quantification Limits

The instrumental detection limit (3σ) for the elements is calculated from dilute nitric acid. The limit of quantification (10σ) is calculated from the reagent blank after taking the dilution factor into consideration. The detection and quantification limits are listed in Table IV.

Analytical Data

The results of our analysis are given in Tables V–VIII as the mean value ± standard deviation. Instrumental measurements were maintained at less than 3% RSD. These data were obtained after triplicate analysis of the samples. Along with our data, recommended values for the SRMs are also given. The precision of the measured data (determined by triplicate analysis of a single sample) is dependent on the concentration of the elements present. The precision is generally better than 10% RSD for elemental concentrations of >1 ppm but is 10–20% for elemental concentrations below 1 ppm.

TABLE IV
Instrumental Detection and Quantification Limits

	Detection Limit [a] (ng/mL)	Quantification Limit [b] (µg/mL)
Be	0.018	0.060
Ge	0.003	0.010
Mo	0.030	0.100
Sn	0.060	0.200
La	0.060	0.200
Ce	0.120	0.400
Pr	0.005	0.015
Nd	0.003	0.010
Sm	0.003	0.010
Eu	0.0004	0.001
Gd	0.0015	0.005
Tb	0.0016	0.006
Dy	0.0006	0.002
Ho	0.0006	0.002
Er	0.0009	0.003
Tm	0.0007	0.003
Yb	0.0002	0.004
Lu	0.0001	0.003
Hf	0.030	0.100
Ta	0.012	0.040
W	0.030	0.100
U	0.030	0.100

[a] 3σ (in solution);
[b] 10σ (in rock) – 1000 X dilution.

Rare Earth Elements

The REE data obtained in all the analyzed samples show close agreement with the recommended values. This indicates complete recovery of the REEs. Another way of checking the accuracy of REE values is to plot chondrite-normalized REE data. A plot of the REE concentrations normalized to their respective chondrite abundances should yield a smooth curve, with the exception of Ce and Eu. The chondrite-normalized REE plots for all of the 16 samples are shown in Figures 1–4, and the pattern is smooth for all of these samples. This further proves the accuracy of our REE data in the analyzed samples.

Eight Other Trace Elements

Besides the REEs, eight other trace elements were determined: Be, Ge, Mo, Sn, W, Ta, Hf. and U. Of these elements, four elements (Be, Ge, Mo, and U) show good agreement with the recommended values. The other four elements (Sn, W, Ta, and Hf), however, show inconsistent data. The probable reason is due to the instability of these elements in dilute nitric acid solution. The Sn values in only two samples (GSD-7 and GSD-10) were found to give good results. In the other samples, the Sn values were mostly in the lower range. In case of Hf, the results were either low or high except in five samples: GSD-3, GSD-6, GSD-10, GSD-12, and GSS-4) where the results are close to the certified values. Similarly for W, only three samples (GSD-9, GSD-10, and GSS-2) showed agreement with the recommended values. In other samples, the results were high or low. For Ta, the data were consistently low for the samples analyzed in this study.

TABLE V. Analytical Data of Stream Sediment and Soil Reference Samples (µg/g)

Element	GSD - 2		GSD – 3		GSD - 4		GSD – 6	
	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained
Be	17.1 ± 1.6	16.48±1.4	1.5 ± 0.3	1.10±0.2	2.4 ± 0.4	2.3±0.3	1.7 ± 0.4	0.93±0.3
Ge	1.7 ± 0.4	1.83±0.3	1.3 ± 0.4	1.10±0.2	1.4 ± 0.4	0.87±0.2	1.4 ± 0.4	0.82±0.2
Mo	2.0 ± 0.4	1.47±0.3	92 ± 7	85.0±6	0.86 ± 0.27	0.87±0.2	7.7 ± 1.2	4.26±1.3
Sn	29 ± 4	18.02±3.1	3.4 ± 0.9	13.54±2.0	4.0 ± 1.1	6.20±1.9	2.8 ± 1.0	8.14±2.1
La	90 ± 10	87.2±8	39 ± 7	35.2±6	40 ± 9	35.0±7	39 ± 8	31.2±5
Ce	192 ± 5	140.1±6	64 ± 6	59.0±5.5	78 ± 4	76.0±3	68 ± 8	65.0±6
Pr	18.6 ± 2.4	19.3±2.2	8.3 ± 0.8	8.40±1.2	9.3 ± 1.3	8.3±1.2	8.4 ± 0.6	7.80±0.5
Nd	62 ± 8	61.74±7	30 ± 4	26.0±3.7	32 ± 4	33.1±3	33 ± 6	28.0±4
Sm	10.8 ± 1.0	10.25±1.1	5.3 ± 0.4	5.1±0.6	6.2 ± 0.5	5.8±0.6	5.6 ± 0.6	5.20±0.5
Eu	0.49 ± 0.09	0.38±.08	1.3 ± 0.1	1.4±0.1	1.31 ± 0.13	1.40±0.14	1.5 ± 0.13	1.60±0.12
Gd	9.5 ± 1.4	10.07±1.2	4.7 ± 0.3	4.3±0.4	5.0 ± 0.8	4.2±0.7	5.5 ± 0.9	4.80±0.8
Tb	1.8 ± 0.3	1.70±0.2	0.7 ± 0.08	0.65±0.07	0.90 ± 0.16	0.72±0.15	0.69 ± 0.15	0.51±0.12
Dy	11 ± 2	9.98±1.8	4.0 ± 0.5	3.8±0.8	4.6 ± 0.4	4.2±0.3	3.8 ± 1.0	3.02±0.8
Ho	2.9 ± 0.4	2.8±0.3	0.9 ± 0.2	0.75±0.2	1.0 ± 0.2	0.78±0.2	0.76 ± 0.12	0.56±0.11
Er	8.2 ± 0.4	7.90±0.5	2.3 ± 0.3	2.1±0.2	2.5 ± 0.4	1.99±0.3	2.2 ± 0.5	1.80±0.4
Tm	1.55 ± 0.17	1.37±0.15	0.39 ± 0.07	0.30±0.5	0.46 ± 0.05	0.42±0.04	0.35 ± 0.07	0.30±0.06
Yb	11 ± 2	9.14±1.8	2.6 ± 0.2	2.7±0.2	2.9 ± 0.4	2.60±0.3	2.1 ± 0.4	1.80±0.3
Lu	1.6 ± 0.3	1.51±0.2	0.39 ± 0.04	0.31±0.02	0.47 ± 0.13	0.30±0.12	0.34 ± 0.08	0.28±0.07
Hf	20 ± 2	31.67±4	6.0 ± 1.3	7.45±1.4	5.8 ± 1.2	4.40±1.1	4.9 ± 1.0	4.34±0.8
Ta	15.3 ± 1.0	8.90±2	1.0 ± 0.2	0.17±0.1	1.4 ± 0.1	0.34±0.1	0.75 ± 0.08	0.27±0.07
W	24 ± 3	16.92±2	4.9 ± 0.7	2.97±0.6	2.5 ± 0.8	1.38±0.7	25 ± 3	13.67±4
U	17 ± 3	16.63±2.5	1.9 ± 0.5	1.55±0.5	2.6 ± 0.6	2.20±0.5	2.4 ± 0.5	1.80±0.4

* Geostandards Newsletter, Special issue of Geostandards Newsletter, Vol. XVIII, Special Issue, July 1994. Certificate of Certified Reference Material, Approved by State Bureau of Quality and Technical Supervision, The People's Republic of China (private communication).

TABLE VI. Analytical Data of Stream Sediment and Soil Reference Samples (µg/g)

Element	GSD – 7		GSD – 8		GSD – 9		GSD – 10	
	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained
Be	2.7 ± 0.4	1.82±0.3	2.0 ± 0.3	1.85±0.2	1.8 ± 0.4	1.2±0.3	0.9 ± 0.3	0.47±0.2
Ge	1.4 ± 0.4	1.09±0.3	0.94 ± 0.27	0.62±0.25	1.3 ± 0.2	1.0±0.2	0.40 ± 0.06	0.36±0.05
Mo	1.4 ± 0.2	1.62±0.2	0.54 ± 0.19	0.67±0.18	0.64 ± 0.16	0.75±0.15	1.2 ± 0.2	0.90±0.1
Sn	5.4 ± 1.3	4.83±1.4	9.4 ± 1.5	4.50±1.3	2.6 ± 0.5	4.34±0.6	1.4 ± 0.4	1.54±0.03
La	45 ± 6	40.10±5	30 ± 5	27.2±4.2	40 ± 4	37.1±5	13 ± 1.4	14.3±1.12
Ce	78 ± 7	73.2±5.5	54 ± 6	49.3±5.5	78 ± 9	76.2±8	38 ± 5	36.1±4.5
Pr	9.6 ± 1.1	8.70±1.2	5.8 ± 0.5	5.4±0.6	9.2 ± 0.9	9.5±0.6	3.2 ± 0.4	2.90±0.3
Nd	37 ± 6	32.0±5.0	21 ± 2	22.2±3	34 ± 3	31.8±2	11.8 ± 1.6	11.2±1.5
Sm	6.1 ± 0.5	6.30±0.4	3.8 ± 0.3	3.50±0.2	6.3 ± 0.5	5.9±0.4	2.4 ± 0.2	2.7±0.2
Eu	1.3 ± 0.2	1.10±0.2	0.56 ± 0.08	0.53±0.07	1.33 ± 0.09	1.37±0.08	0.47 ± 0.05	0.37±0.06
Gd	5.8 ± 0.8	5.25±0.7	3.5 ± 0.6	2.8±0.5	5.5 ± 0.4	5.80±0.3	2.2 ± 0.3	1.9±0.2
Tb	0.76 ± 0.14	0.82±0.13	0.54 ± 0.09	0.48±0.08	0.87 ± 0.13	0.79±0.12	0.42 ± 0.11	0.37±0.12
Dy	4.2 ± 0.7	3.85±0.6	2.6 ± 0.4	2.21±0.3	5.1 ± 0.3	4.9±0.2	2.2 ± 0.3	2.30±0.2
Ho	0.96 ± 0.21	0.85±0.20	0.9±0.2	0.81±0.1	0.96 ± 0.08	0.85±0.07	0.45 ± 0.08	0.40±0.05
Er	2.3 ± 0.2	1.92±0.22	1.8 ± 0.3	1.60±0.2	2.8 ± 0.3	2.60±0.2	1.3 ± 0.2	1.40±0.2
Tm	0.44 ± 0.09	0.35±0.07	0.33 ± 0.06	0.27±0.05	0.44 ± 0.09	0.56±0.08	0.2 ± 0.04	0.17±0.03
Yb	2.6 ± 0.4	2.20±0.3	2.1 ± 0.4	1.80±0.3	2.8 ± 0.4	2.8±0.3	1.2 ± 0.3	0.99±0.2
Lu	0.39 ± 0.07	0.30±0.06	0.38 ± 0.07	0.33±0.05	0.45 ± 0.04	0.47±0.04	0.19 ± 0.04	0.16±0.03
Hf	4.9 ± 1.0	9.77±1.5	14.5 ± 1.8	8.62±1.9	9.7 ± 1.6	2.76±1.5	1.8 ± 0.4	2.18±0.2
Ta	1.35 ± 0.13	0.02	3.7 ± 0.5	0.62±0.2	1.3 ± 0.2	0.15±0.1	0.5	0.13±0.1
W	5.5 ± 1.0	3.38±0.8	2.0 ± 0.5	1.05±0.4	1.8 ± 0.3	1.71±0.2	1.6 ± 0.4	1.23±0.2
U	3.5 ± 0.5	2.90±0.4	3.0 ± 0.3	2.8±0.2	2.6 ± 0.6	2.20±0.5	2.1 ± 0.3	1.70±0.2

* Geostandards Newsletter, Special issue of Geostandards Newsletter, Vol. XVIII, Special Issue, July 1994. Certificate of Certified Reference Material, Approved by State Bureau of Quality and Technical Supervision, The People's Republic of China (private communication).

TABLE VII. Analytical Data of Stream Sediment and Soil Reference Samples (μg/g)

Element	GSD – 11		GSD – 12		STSD – 1		JSD – 1	
	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained
Be	26 ± 4	18.7±3	8.2 ± 1.1	7.45±1.2	1.6	1.5±0.11	1.3	1.12±0.11
Ge	1.81 ± 0.23	1.60±0.2	1.87 ± 0.13	1.68±0.12	<1	0.8±0.10	<	0.85±0.08
Mo	5.9 ± 0.8	4.9±0.7	8.4 ± 0.9	6.93±1.0	2	1.8±1.2	<	0.36±0.02
Sn	370 ± 68	18.22±3	54 ± 7	13.14±3.5	4	2±1.2	<	2.8±0.2
La	30 ± 3	33.0±2	32.7 ± 2.2	34.37±2.6	30	28±2.3	16.2[b]	17.9±2.1
Ce	58 ± 5	52.5±4.2	61 ± 5	61.44±4.3	51	48±4.3	32.4[b]	33.2±3.1
Pr	7.4 ± 0.6	6.9±0.9	6.9 ± 1.2	7.18±1.1	<10	8±1.5	4.09[b]	3.8±0.3
Nd	27 ± 3	31.2±2.8	26 ± 4	25.97±3.6	28	30±3.1	16.9[b]	18.2±1.8
Sm	6.2 ± 0.4	6.8±0.9	5.0 ± 0.5	4.89±0.6	6	5±0.5	3.45[b]	3.60±0.5
Eu	0.6 ± 0.08	0.66±0.06	0.61 ± 0.04	0.75±0.05	1.6	1.7±0.12	0.92[b]	0.85±0.08
Gd	5.9 ± 0.5	5.45±0.6	4.4 ± 0.4	4.62±0.5	6.5[a]	6.4±0.6	3.11[b]	2.45±0.12
Tb	1.13 ± 0.14	0.95±0.12	0.82 ± 0.08	0.81±0.07	1.2	1.1±0.05	0.44[b]	0.41±0.02
Dy	7.2 ± 0.8	8.20±0.9	4.8 ± 0.8	5.04±0.7	5.6	5.8±0.6	2.62[b]	2.52±0.3
Ho	1.4 ± 0.2	1.20±0.1	0.94 ± 0.09	1.05±0.08	1.2[a]	1.4±0.05	0.49[b]	0.53±0.04
Er	4.6 ± 0.6	4.20±0.5	3.1 ± 0.3	3.3±0.4	3.3[a]	3.7±0.3	1.43[b]	1.44±0.11
Tm	0.74 ± 0.11	0.72±0.12	0.53 ± 0.07	0.57±0.06	0.5[a]	0.6±0.03	0.20[b]	0.23±0.02
Yb	5.1 ± 0.8	4.56±0.7	3.7 ± 0.5	3.74±0.4	4	3.8±0.3	1.33[b]	1.50±0.10
Lu	0.78 ± 0.08	0.69±0.06	0.58 ± 0.08	0.62±0.05	0.8	0.65±0.06	0.19[b]	0.18±0.02
Hf	5.4 ± 0.5	7.08±0.6	8.3 ± 1.1	9.18±1.2	6.1	2.5±0.08	3.4	1.8±0.03
Ta	5.7 ± 0.5	0.16±0.2	3.2 ± 0.3	0.44±0.5	0.4	0.08±0.05	<	0.30±0.02
W	126 ± 13	25.76±5	37 ± 3	25.05±2.5	<4	1.2±0.05	<	-
U					8	7.8±0.5	<	1.05±0.04

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[a] Data from J.G. Sengupta et al., Talanta 42, 1947 (1995).

[b] Data from K. Yamamoto et al., Geochemical Journal, Vol. 39, pp 289 to 297, 2005.

CONCLUSION

The rare earth elements (REEs) including eight other elements (Be, Ge, Mo, Sn, W, Hf, Ta, and U) chosen for this study are of great importance for petrological studies. Additionally, these elements are not easily determined by other techniques (except NAA) due to their low abundance in the earth's crust. The accuracy of 14 REEs and four trace elements (Be, Ge, Mo, and U) are generally good. However, Sn, W, Ta, and Hf show very inconsistent results, although in some cases the Sn, W, and Hf values are close to the certified values. The Ta values are consistently low in all the samples. These experiments show that microwave digestion followed by the open digestion procedure can be utilized for the REE, Be, Ge, Mo, and U determination in stream sediment and soil samples. However, this method may not be suitable for Sn, W, Hf and Ta determination in these samples.

ACKNOWLEDGMENT

The authors thank Dr. D.K. Das, Dy. D.G (GC) and HOD, ER (Retired), for their keen interest in this work. The authors also thank the Director General, GSI, Kolkata, for the kind permission to publish this paper.

Received May 6, 2008.

TABLE VIII. Analytical Data of Stream Sediment and Soil Reference Samples (μg/g)

Element	GSS – 1		GSS – 2		GSS – 4		GSS – 8	
	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained	Recommended*	Obtained
Be	2.5 ± 0.4	2.20±0.3	1.8 ± 0.3	1.75±1.21	1.85 ± 0.53	1.62±0.40	1.9±0.3	1.80±0.22
Ge	1.34 ± 0.21	1.10±0.15	1.2 ± 0.2	1.22±0.15	1.9 ± 0.4	1.70±0.35	1.27±0.22	0.81±0.15
Mo	1.4 ± 0.2	1.43±0.22	0.98 ± 0.17	0.66±0.19	2.6 ± 0.4	2.80±0.32	1.16±0.15	1.40±0.12
Sn	6.1 ± 1.0	4.62±0.9	3.0 ± 0.4	1.41±0.31	5.7 ± 1.3	2.47±1.2	2.8±0.7	1.42±0.50
La	34 ± 3	35.0±2.5	164 ± 16	176.5±12	53 ± 6	58.2±4.2	36±4	29.33±3.2
Ce	70 ± 5	67.0±4.8	402 ± 25	380.5±18	136 ± 16	127.1±12	66±10	58.30±8.7
Pr	7.5 ± 0.5	6.9±0.6	57 ± 6	52.0±5.6	8.4 ± 1.9	6.80±1.6	8.3±0.9	7.80±1.1
Nd	28 ± 3	27.5±2.8	210 ± 22	189.0±18	27 ± 3	31.1±2.1	32±3	29.0±2.8
Sm	5.2 ± 0.4	4.90±0.4	18 ± 3	21.7±2.6	4.4 ± 0.5	3.92±0.4	5.9±0.6	5.80±0.6
Eu	1.0 ± 0.1	0.85±0.16	3.0 ± 0.3	2.85±0.25	0.85 ± 0.11	0.78±0.12	1.2±0.1	1.30±0.12
Gd	4.6 ± 0.3	5.10±0.21	7.8 ± 0.6	8.20±0.50	4.7 ± 0.6	4.20±0.5	5.4±0.5	4.90±0.4
Tb	0.75 ± 0.09	0.65±0.08	0.97 ± 0.40	1.05±0.30	0.94 ± 0.13	0.87±0.11	0.89±0.12	0.75±0.11
Dy	4.6 ± 0.3	4.20±0.25	4.4 ± 0.3	3.97±0.40	6.6 ± 0.7	5.9±0.60	4.8±0.5	4.30±0.4
Ho	0.87 ± 0.08	0.72±0.07	0.93 ± 0.15	0.82±0.15	1.46 ± 0.14	1.60±0.13	0.97±0.08	0.79±0.07
Er	2.6 ± 0.2	2.5±0.2	2.1 ± 0.4	1.80±0.30	4.5 ± 0.8	4.40±0.6	2.8±0.2	2.70±0.3
Tm	0.42 ± 0.07	0.37±0.06	0.42 ± 0.13	0.30±0.11	0.70 ± 0.12	0.62±0.13	46±0.08	0.37±0.05
Yb	2.7 ± 0.4	2.40±0.3	2.0 ± 0.3	1.80±0.15	4.8 ± 0.8	4.40±0.60	2.8±0.3	2.70±0.4
Lu	0.41 ± 0.06	0.38±0.05	0.32 ± 0.06	0.28±0.06	0.75 ± 0.09	0.62±0.06	0.38±0.07	0.31±0.04
Hf	6.8 ± 0.9	1.70±0.8	5.8 ± 0.9	2.03±0.07	14 ± 2	13.27±2.5	7.0±0. 8	4.50±0.4
Ta	1.4 ± 0.2	0.05	0.78 ± 0.18	0.08±0.15	3.1 ± 0.3	0.69±0.2	1.05±0.26	0.086
W	3.1 ± 0.4	2.07±0.15	1.08 ± 0.33	0.87±0.34	6.2 ± 0.7	3.11±0.4	1.7±0.5	2.77±0.6
U	3.3 ± 0.6	2.82±0.4	1.5 ± 0.4	0.89±0.2	6.7 ± 1.2	5.60±1.3	2.7±0.5	2.90±0.4

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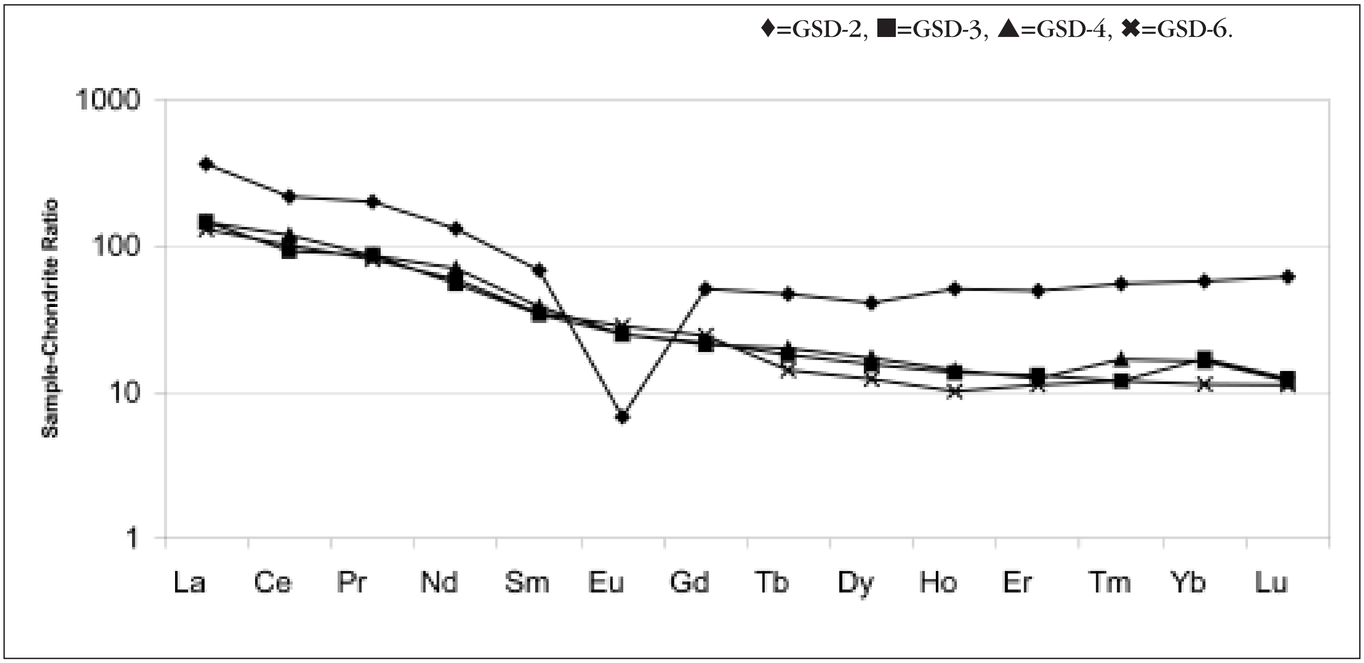

Fig. 1. Chondrite-normalized REE plot of stream sediment samples.

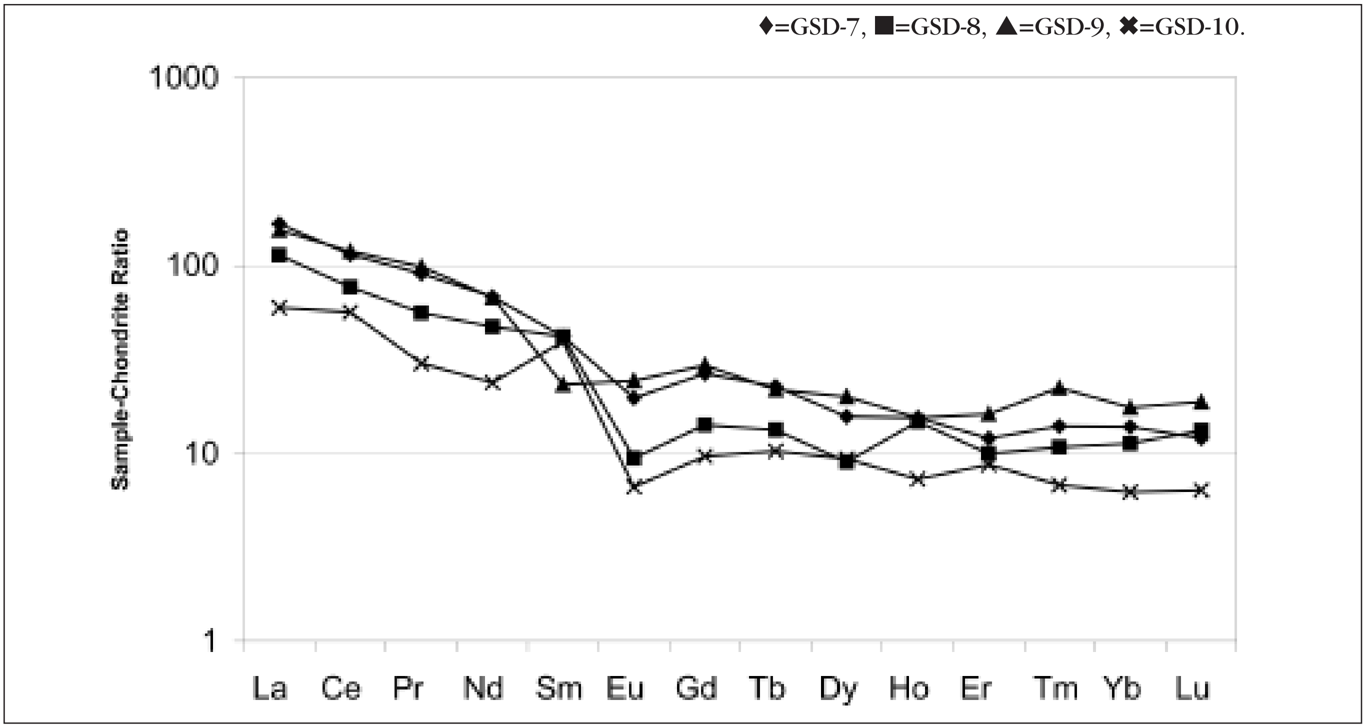

Fig. 2. Chondrite-normalized REE plot of stream sediment samples.

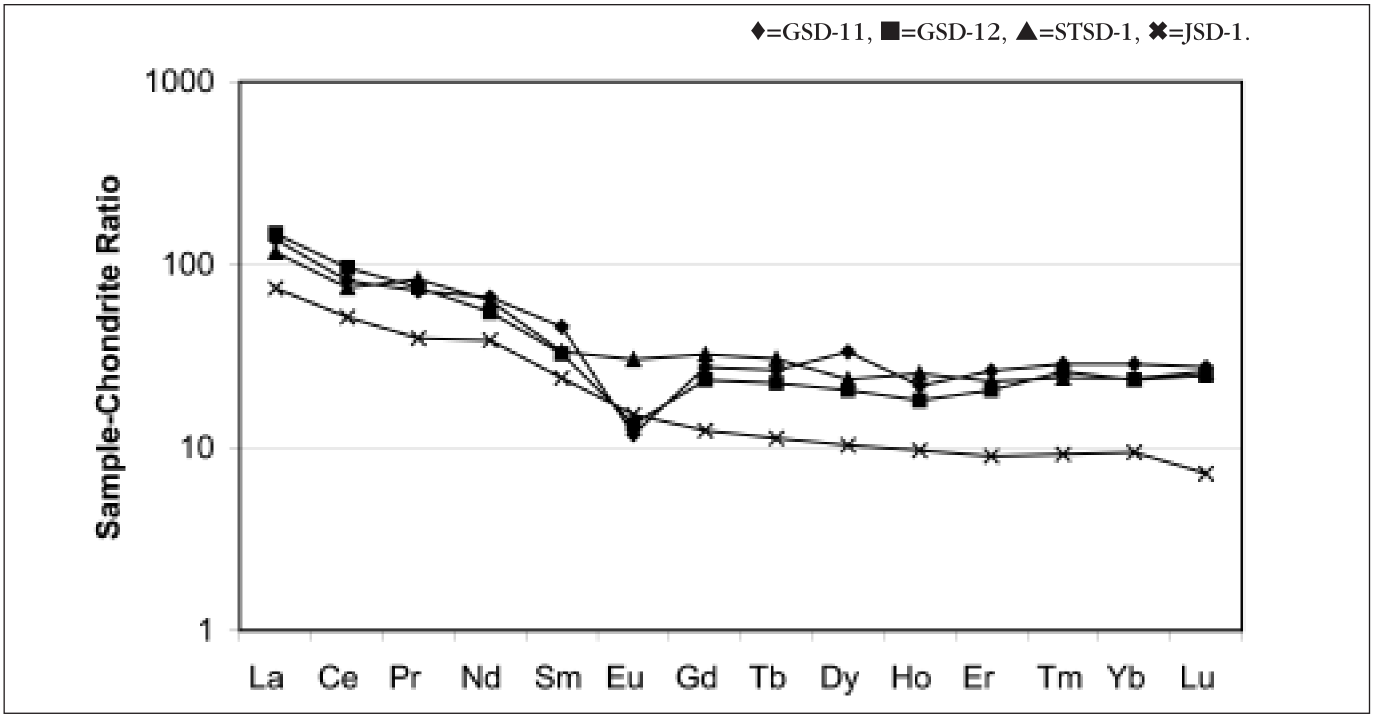

Fig. 3. Chondrite-normalized REE plot of stream sediment samples.

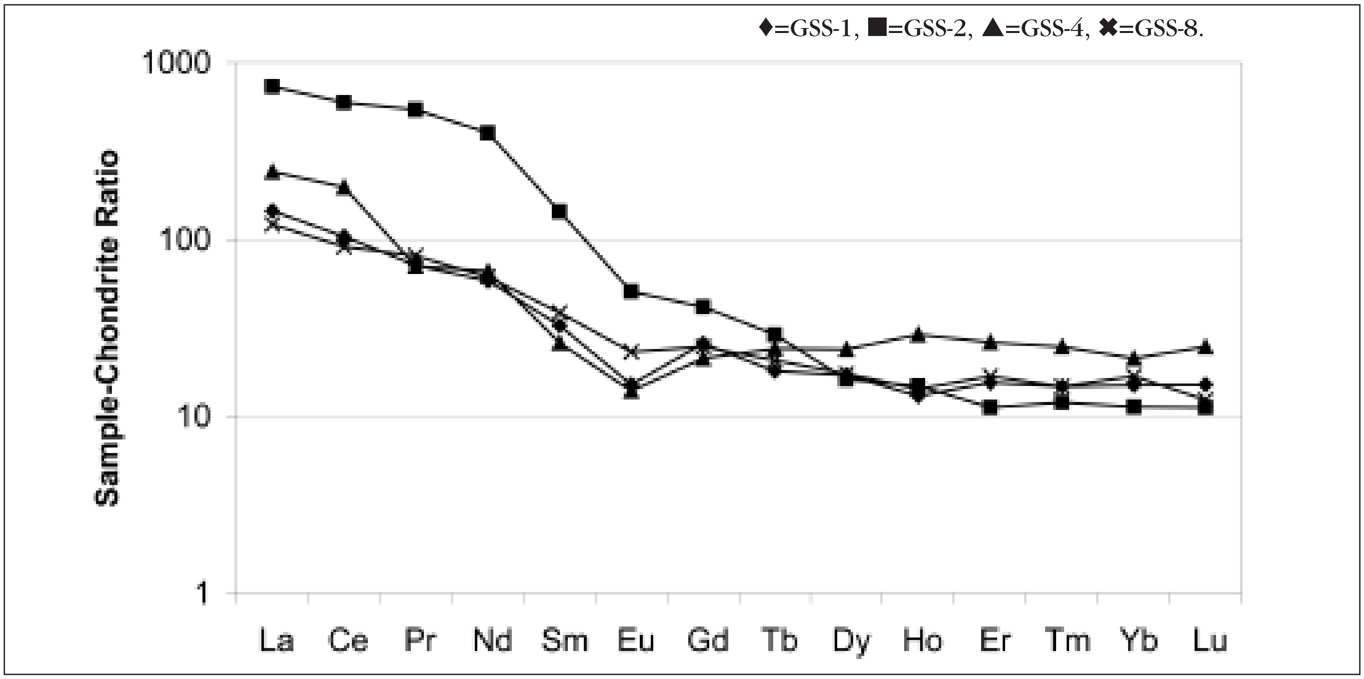

Fig. 4. Chondrite-normalized REE plot of stream sediment samples.

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Speciation of Cr(III) and Cr(VI) by Modified Carbon Nanofiber-Packed Microcolumn and Inductively Coupled Plasma Mass Spectrometry

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ABSTRACT

The possibility of using modified carbon nanofibers (CNFs) as solid phase extractants for the speciation of Cr(III) and Cr(VI) has been investigated by a microcolumn coupled with inductively coupled plasma mass spectrometry (ICP-MS). Experiments were performed to optimize conditions, such as pH, sample flow rate, sample volume and concentration of eluent, to achieve the quantitative separation of Cr(III) and Cr(VI). During all the steps of the separation, Cr(III) was selectively sorbed on the column packed with CNFs in the pH range of 3.25–4.0, while Cr(VI) was found to remain in solution. The retained Cr(III) was subsequently eluted with 1.0 mL of 1.0 mol L^{-1} nitric acid. A preconcentration factor of 100-fold was achieved for Cr(III). Under the optimized condition, detection limits (3σ) for Cr(III) and Cr(VI) were 0.015 ng mL^{-1} and 0.033 ng mL^{-1}. The relative standard deviations were 2.9% and 4.5%, respectively (n=9, c=0.5 ng mL^{-1}). The developed method was verified by analyzing the total chromium in certified reference materials and chromium species in water samples; recovery ranged from 97.0% to 104%.

INTRODUCTION

Due to different toxicities and reactivities of different forms of an element, chemical speciation is drawing growing attention in the fields of environmental, toxicological, nutritional, medical and analytical sciences (1). Chromium speciation is of great interest because its toxicity depends upon its oxidation state. Cr(III) is considered to be essential to mammals for the maintenance of glucose, protein and lipid metabolism (2,3). On the other hand, Cr(VI) is reported to be toxic for biological systems even at relatively low levels (4). This is mainly attributed to its high oxidation potential and easy penetration of biological cell membranes (5). Therefore, the separation and determination of the chromium species is of great importance.

It is well known that inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), and atomic absorption spectrometry (AAS) represent the most important routine methods for the determination of trace Cr in various samples. Unfortunately, the direct application of these techniques for the determination of trace Cr in real samples can only yield information on the total concentrations. Thus, in order to obtain information about its chemical form, separation and preconcentration are usually required before analysis. A variety of methods, including solvent extraction, coprecipitation, ion exchange, solid-phase extraction, chelating resin adsorption, chromatography and catalytic cathodic stripping voltammetry, have been developed for Cr speciation (6-12). Among these procedures, solid-phase extraction has attracted considerable practical interest in comparison with the traditional liquid-liquid extraction methods because of its major advantages: (i) simple operation; (ii) high concentration factor; (iii) rapid-phase separation, and (iv) ability to combine with different detection techniques (13). It should be noted that the adsorbent material for solid-phase extraction plays a fundamentally crucial role in the improvement of selectivity and sensitivity of the analytical method. In recent years, nanometer-size material has shown exceptional adsorption capability owing to its small size, large specific surface area, excellent mechanical strength, high chemical stability, and unique electrical properties. Some nanometer-size substances, such as carbon nanotubes (CNTs), nanometer-size titanium dioxide, and nanometer-size aluminum dioxide, have been successfully used as solid-phase extractants for preconcentration/separation of metal and non-metal ions, as well as adsorption of organic compounds (14-17).

Carbon nanofibers (CNFs), as a new type of carbon materials, have special surface morphology and steady structure characteristics, which make them promising candidates as adsorbers (18). Additionally, their surface properties can be modified through chemical treatments to satisfy special needs (19). CNFs have been found to be an ideal adsorbent for hydrogen storage (20). To the best of our knowledge, however, the application of CNFs to solid-phase extraction for the separation and determination of elements and their speciation has received little attention. In this work, the adsorption characteristics of CNFs for Cr(III) and Cr(VI) were investigated, and a novel method was developed for the speciation of chromium using a microcolumn packed with CNFs coupled with ICP-MS analysis. The proposed

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method has been applied to the determination of chromium in certified reference materials and chromium species in water samples with satisfactory results.

EXPERIMENTAL

Instrumentation

An X-7 ICP-MS system (Thermo Elemental Corporation, USA) was used for the determination. The optimum operation conditions for ICP-MS are summarized in Table I.

The pH values of the solutions were measured with a pH meter (Thermo Orion Corporation, USA) supplied with a combined electrode. An HL-2 peristaltic pump (Shanghai Qingpu Huxi Instrument Factory, P.R. China) coupled with a self-made polytetrafluoroethylene (PTFE) microcolumn (20 mm × 3.0 mm i.d.), packed with CNFs, were used for the preconcentration / separation process. A minimum length of PTFE tube with an inner diameter of 0.5 mm was used for all connections.

An Ethos T microwave digestion device (Milestone, Italy) was used for sample digestion. This device is pressure- and temperature-controlled so that on reaching maximum pressure and temperature the microwave energy input is automatically restricted.

Standard Solution and Reagents

The stock standard solution (1.0 mg mL^{-1}) of Cr(III) was obtained from the National Analysis Center of Iron & Steel (Beijing, P.R. China); Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ (Tianjin Reagent Factory, Tianjin, P.R. China) in 0.1 mol L^{-1} nitric acid. Working solutions were prepared daily by appropriate dilution of stock solutions. All reagents used were ultrapure or at least of analytical grade. High purity deionized water (18.2 MΩ) obtained from a Milli-Q™ A10 system (Millipore Corporation, USA) was used throughout this work.

CNFs were kindly provided by Shenyang Metal Institute of Chinese Academy (Shenyang, P.R. China). Before use, CNFs were oxidized with concentrated HNO_3 according to the literature (21). The treated CNFs were dried at 100 °C and stored for future use.

Sample Preparation

A 0.3000-g portion of sample (mussel or tea leaves) was accurately weighed into 100-mL Teflon® vessels; 6.0 mL of concentrated HNO_3 and 2.0 mL of 35% H_2O_2 (m/V) were then added. The solid particles which stick to the wall of the Teflon vessels should be rinsed with the digestion reagents. After about 5 minutes, when the first vigorous reaction had taken place, the digestion vessels were closed and placed into the microwave oven. Then, the samples were digested in the microwave oven at 180 °C (ramp, 10 min; hold, 15 min) with a power of 1.0 kW. After cooling and adding 0.5 mL of concentrated $HClO_4$, the solution was transferred into a Teflon beaker and heated to near dryness on a hot plate at 200 °C. The residues were dissolved with 1.0 mL of 0.1 mol L^{-1} HNO_3, and diluted to 10 mL with deionized water. The groundwater was collected in the vicinity of our laboratory, filtered through a 0.22-µm membrane filter, and analyzed as soon as possible after collection. The blank was prepared exactly as the samples.

TABLE I
ICP-MS Instrumental Operating Parameters

Plasma Power	1300 W
Plasma Argon Flow Rate	14.5 L min^{-1}
Auxiliary Argon Flow Rate	0.78 L min^{-1}
Nebulizer Argon Flow Rate	0.95 L min^{-1}
Sampler Orifice (nickel)	1.1 mm
Skimmer Orifice (nickel)	0.7 mm
Acquisition Mode	Peak-jumping
Number of Sweep	100
Dwell Time	10 ms
Acquisition Time	40 s
Number of Measurements per Peak	3
Isotopes	^{52}Cr and ^{115}In

Column Preparation

A PTFE microcolumn (20 mm × 3.0 mm i.d.), plugged with a small portion of glass wool at both ends, was filled with 20 mg of the treated CNFs. Before use, 1.0 mol L^{-1} HNO_3 solution and high purity deionized water were passed through the column in order to clean and condition it. Then, the column was conditioned to the desired pH value with 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} CH_3COONa.

General Procedure

An aliquot of aqueous sample solution containing Cr(III) and Cr(VI) was prepared. The pH value was adjusted to the desired pH with 0.1 mol L^{-1} HNO_3 and 0.1 mol L^{-1} CH_3COONa before use. The obtained solution was passed through the column by using a peristaltic pump at a desired flow rate. Cr(III) was retained on the column while Cr(VI) was collected in the effluent. Afterwards, the sorbed Cr(III) was eluted with 2.0 mL of 1.0 mol L^{-1} HNO_3. The Cr concentration was determined in the two fractions by ICP-MS.

RESULTS AND DISCUSSION

Surface Functionalization of CNFs

As a new carbon material, CNFs have attracted great attention in applications such as gas adsorption and catalyst support owing to their large specific surface, high chemical stability, and unique mechanical properties (20,22). The untreated CNFs, however, have a non-polar nature, low surface energy and, therefore, are usually unable to form a strong adhesion between their surface and polar substances (23). Fortunately, some investigations have shown that treatment of CNFs with oxidized acids can introduce many functional groups [such as carboxyl (—COOH), hydroxyl (—OH), and carbonyl (>C=O)] on the surface of CNFs (21,24). The oxygen-containing groups attached on the surfaces of CNFs can improve their adsorption capability of ions in solution.

In this work, CNFs were treated with concentrated nitric acid in accordance with the literature (21). The results of FTIR analysis indicate that the oxygen-containing groups form on the surface of CNFs, which is consistent with the result of the literature (21).

Effect of pH on Adsorption of Cr(III) and Cr(VI)

Due to the oxidization treatment with concentrated HNO_3, some acidic groups could form on the surface of CNFs. Thus, the adsorption of metal ions strongly depends on the pH of the solution, which affects the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbants. For these reasons, the effect of pH on the retention of Cr(III) and Cr(VI) on the column of CNFs was studied. The sample solutions were adjusted to a pH range of 1.0–7.0 with HNO_3 or CH_3COONa, and then passed through the microcolumn. The retained ions were stripped off from the column and measured by ICP-MS as described in the recommended procedure section. The effect of pH on the recovery of Cr(III) and Cr(VI) is shown in Figure 1. As can be seen, the quantitative recovery (>90%) for Cr(III) was found in the pH range of 3.25–4.0, whereas that of Cr(VI) was less than 4.0%. This suggests that it is possible to separate Cr(III) and Cr(VI): Cr(III) is retained on the column, while Cr(VI) is not. A pH of 3.5 was selected in this work.

Elution of Cr(III)

The pH profile experiments suggested that Cr(III) ions can be removed by increasing the strength of the acid. For this reason, the elution of Cr(III) from the microcolumn packed with CNFs was studied by using nitric acid solutions as stripping agent at different concentrations. The experimental results show that the elution of Cr(III) was quantitatively removed with 1.0 mL of 1.0 mol L^{-1} HNO_3; and good recoveries were obtained (>95%). Taking the required sampling volume for ICP-MS into account, a 2.0-mL eluent was adopted in the following experiments.

Influence of Sample Flow Rate

The flow rate of the sample solution is also a very important parameter for the quantitative separation of Cr(III) and Cr(VI) on CNFs and the length of time required for complete analysis. Therefore, the effect of the sample solution flow rate on the retention of Cr(III) on CNFs was examined under optimum conditions (pH, eluent, etc.). The flow rate was adjusted in the range of 0.5-2.0 mL min^{-1}. It was found that the retention of Cr(III) was practically unchanged up to 1.0 mL min^{-1}, but its retention decreased with higher flow rates due to a decrease in the adsorption kinetics. Accordingly, all subsequent experiments were performed at a flow rate of 1.0 mL min^{-1}.

Effect of Volume of Sample Solution

In order to explore the possibility of analytes from large volumes, the maximum applicable volume of sample must be determined. To study this effect, a series of solutions of increasing sample volumes (25, 50, 75, 100, 125, and 150 mL) containing 10 ng of Cr(III) were passed through the microcolumn under optimum conditions. As

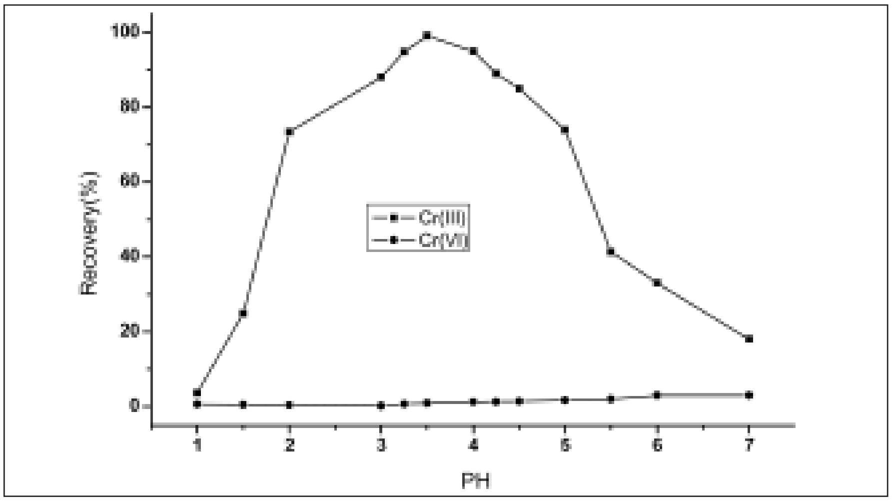

Fig. 1. Effect of pH on the adsorption of Cr(III) and Cr(VI) on CNFs. Cr(III) and Cr(VI): 5.0 ng mL^{-1}; sample volume : 20 mL.

shown in Figure 2, quantitative recoveries (>90%) were obtained for sample volumes up to 100 mL. In this work, because the elution volume was 1.0 mL, an enrichment factor of 100-fold was obtained for the ions studied by this method.

Adsorption Capacity

The capacity study used was based on one as recommended in the literature (25). For this purpose, 20-mL aliquots of a series of concentrations (0.1–0.6 μg mL^{-1}) were adjusted to the appropriate pH; then the preconcentration and separation procedure described above was applied. The breakthrough curves were obtained by plotting the metal ion concentrations (μg mL^{-1}) versus the milligrams of metal ions adsorbed on per gram of adsorbent. The adsorption capacity calculated from the breakthrough curve was 0.41 mg g^{-1} for Cr(III).

Effect of Interfering Ions

The effects of common coexisting ions on the separation and determination of Cr(III) were investigated. The tolerance limit of coexisting ions is defined as the largest amount that causes recovery of the analyte to be less than 90%. For this purpose, the interfering ion concentrations were varied, whereas the concentration of Cr(III) was kept constant at 5.0 ng mL^{-1}. The results for the effect of interfering ions on the recoveries of the analytes are presented in Table II. It can be seen that the presence of major cations and anions have no obvious influence on the determination under the selected conditions.

Column Reuse

In order to examine the long-term stability of CNFs, they were subjected to successive adsorption and desorption cycles by passing 20 mL of Cr(III) solutions through the column. The stability and potential regeneration of the column were assessed by monitoring the changes in the recoveries of Cr(III). The column can be reused after regeneration with 10 mL of 1.0 mol L^{-1} HNO_3 and 20 mL deionized water, respectively, and is stable up to 35 adsorption-elution cycles without obvious decrease in the recoveries for Cr(III).

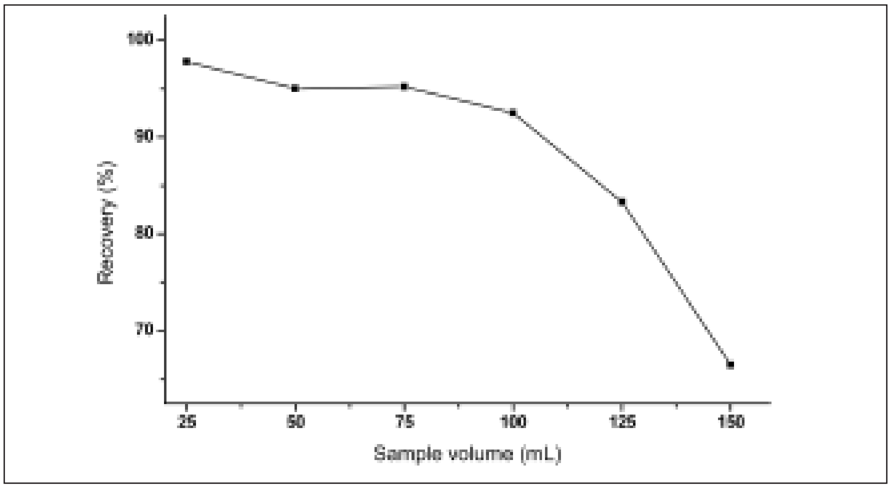

Fig. 2. Effect of sample volume on recovery of Cr(III) on CNFs. pH: 3.5; Cr(III): 10 ng.

TABLE II
Tolerance Limits of Coexisting Ions

Coexisting Ion	Concentration Ratio[a]
Na^+, K^+	10,000 [b]
Ca^{2+}, Mg^{2+}	2000 [b]
Fe^{3+}, Al^{3+}	100 [b]
PO_4^{3-}, SiO_3^{2-}, SO_4^{2-}	5000 [b]

[a] Concentration ratio: Foreign ion / Cr(III).

[b] Maximum concentrations tested.

Detection Limits and Precisions

According to the definition of IUPAC (3σ), the detection limits of this method for Cr(III) and Cr(VI), calculated from three times the standard deviation of the blank signal, were 0.015 ng mL^{-1} and 0.033 ng mL^{-1} with the relative standard deviations of 2.9% and 4.5% (n=9, c=0.5 ng mL^{-1}), respectively.

Application of Analysis

The accuracy of the proposed method was examined by analyzing total chromium in certified reference materials of mussel (GBW 08571) and tea leaves (GBW 07605). Table III shows that the analytical results are in agreement with the certified values of chromium in the standard reference materials. Furthermore, the proposed method was applied to the separation and determination of Cr(III) and Cr(VI) in water samples (groundwater collected from the vicinity of our laboratory and high purity water); the analytical data and recovery are listed in Table IV. The results indicate that the recoveries are reasonable for trace analysis ranging from 97.0–104%.

CONCLUSION

The adsorption behavior of Cr(III) and Cr(VI) on modified carbon nanofibers (CNFs) was investigated systematically. The experimental results indicate that Cr(III) was almost quantitatively retained in the pH range of 3.25–4.0, while Cr(VI) remained in the solution. The Cr(III) retained on CNFs can be easily desorbed and no carryover is observed in the next

TABLE III
Analytical Results of Chromium in Standard Reference Materials

Sample	Added $(\mu g\ g^{-1})$	Found[a] $(\mu g\ g^{-1})$	Certified $(\mu g\ g^{-1})$	Recovery (%)
Mussel (GBW 08571)	0	0.59 ± 0.07	0.57 ± 0.08	-
	0.7	1.28 ± 0.15	-	103
Tea Leaves (GBW 07605)	0	0.84 ± 0.02	0.80 ± 0.03	-
	0.7	1.49 ± 0.10	-	97.0

[a] Mean value ± standard deviation, n=3.

TABLE IV
Analytical Results and Recoveries of Cr(III) and Cr(VI) in Water Samples

Sample	Added $(ng\ mL^{-1})$		Found[a] $(ng\ mL^{-1})$			Recovery (%)	
	Cr(III)	Cr(VI)	Cr(III)	Cr(VI)	Total	Cr(III)	Cr(VI)
Groundwater	0	0	0.37±0.02	0.50±0.03	0.87±0.04	-	-
	5.0	5.0	5.32±0.11	5.70±0.19	11.02±0.32	99.0	104
	10	10	10.43±0.23	10.33±0.15	20.76±0.26	101	98.3
High Purity Water	0	0	nd[b]	nd	nd	-	-
	5.0	5.0	4.91±0.16	5.02±0.24	9.93±0.30	98.0	100
	10	10	9.95±0.34	10.13±0.18	20.08±0.37	99.0	101

[a] Mean value ± standard deviation, n=3.
[b] nd=Not detected.

analysis. An enrichment factor of 100-fold was achieved. Based on the high adsorption selectivity of CNFs for Cr(III) and Cr(VI), a simple, rapid, and reliable method was developed for the preconcentration, separation, and determination of chromium species in groundwater by the microcolumn packed with CNFs and coupled with inductively couled plasma mass spectrometry (ICP-MS). According to these results, it can be concluded that CNFs are likely to become an effective adsorbent of solid phase extraction for the speciation of chromium in various matrices other than water.

ACKNOWLEDGMENTS

Financial support from the Nature Science Foundation and the Education Department Foundation of Hubei Province, P.R. China, is gratefully acknowledged.

Received April 7, 2008.

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Determination of Selenium (IV) at Ultratrace Levels in Natural Water Samples by UV-assisted Vapor Generation - 'Collect and Punch' - Inductively Coupled Plasma Mass Spectrometry

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ABSTRACT

A UV-assisted vapor generation combined with a sensitive 'collect and punch'-inductively coupled plasma mass spectrometry (ICP-MS) method is described for the determination of Se(IV) at ultratrace levels in natural water samples. Volatile Se species were formed by UV irradiation in the presence of low molecular weight organic acids. The vapors were collected in a glass chamber before injection into the plasma in the form of a plug. This arrangement provided a 6–7 fold enhancement in sensitivity compared with continuous vapor injection. A detection limit (3σ) of close to 50 parts per trillion (0.05 µg/L) was achieved. A precision of 1.2% (RSD, n=6) was obtained for a 0.5 µg/L of Se(IV) solution. The method is specific for Se(IV) and was used for the determination of Se(IV) in tube well water samples of Punjab, India. The values obtained for Se(IV) by the UV assisted vapor generation method agreed well with the conventional HG-ICPMS method. The concentration of Se(IV) ranged from 0.5–5.0 µg/L in the water samples analyzed. However, the total selenium contents determined by HG-ICP-MS after reduction of Se(VI) to Se(IV) in many of these samples were greater than 50 µg/L, demonstrating that the major species in these water samples are Se(VI).

INTRODUCTION

There is a growing interest in the determination of chemical forms of selenium (Se) in environmental and biological matrices owing to their different beneficial or toxic effects. Selenium is an essential nutrient and has been known to be a necessary component of the human diet for many years. It is an important constituent of antioxidant enzymes like selenium glutathione peroxidase. The deficiency of Se in a diet causes Keshan disease in humans. However, a sustained higher intake of Se could also cause poisoning of livestock, known as alkali disease and blind stagers (1). At levels of only three to five times the bio-essential concentrations, selenium is considered toxic (2).

Selenium is introduced into the environment by both natural processes and human activity. Weathering of certain types of geological formations, such as calcareous shale rock, has been known to produce high levels of selenium in soils. As a result of rainfall interaction with surface rocks, the dissolved constituents are carried away through surface run-off into nearby ground water recharge areas. Water percolating through soil also transports soluble constituents into the local ground water (3). In India, elevated levels of selenium in agricultural soils have been found in the northeastern parts of Punjab. This has resulted in severe health problems to animals and humans. Deposition of seleniferous material transported through floodwaters from nearby hills of the Shivalik range over several decades has resulted in the accumulation of selenium in low-lying areas. Utilization of Se-contaminated underground water for irrigation purposes has further accentuated the problem of selenium toxicity in those regions. Total selenium concentration in these soils range from 0.32 to 4.55 mg kg^{-1} (4).

Drinking water is responsible for a significant fraction of the total intake of selenium by humans. Traces of selenium ranging from 0.00001–0.01 mg L^{-1} are commonly found in community drinking water. The major inorganic selenium species present in water are selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) anions, where Se is present in the (IV) and (VI) oxidation states, respectively. Little is known on the bioavailability of either form of selenium. The guideline level of selenium in drinking water set by the World Health Organization (WHO) is not to be more than 10 µg L^{-1} (5); recently this has been revised to 5 µg L^{-1} by the U.S. Environmental Protection Agency (USEPA) (6). Therefore, it is essential to determine the concentration of these selenium species at ultratrace levels in water samples.

For trace element analysis, inductively coupled plasma mass spectrometry (ICP-MS), in compari-

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son to other techniques, possesses advantages such as simultaneous and multi-element capability with low detection limits. However, selenium has a poor signal response as a result of its relatively high first ionization potential (9.75 eV). Also, the six available isotopes [^{74}Se (0.9%), ^{76}Se (9%), ^{77}Se (7.6%), ^{78}Se (23.6%), ^{80}Se (49.7%), and ^{82}Se (9.2%)] are subject to varying degrees of spectral interferences (7). Recently, ICP-quadrupole MS equipped with collision / dynamic reaction cell (DRC™) systems have been used to eliminate interferences from argide species. Similarly, High Resolution Sector Field-ICP-MS has been used at higher resolution (R = 9700) for separating the argide interference. Still, many laboratories use quadrupole mass spectrometers for selenium determination, where the lower abundant isotope (^{82}Se) is generally used, resulting in poor limits of detection. Direct solution nebulization, where only 1% of the solution nebulized enters the plasma, adds to the problem. Hence, for the determination of Se at ppb to sub-ppb levels in natural waters, special sample introduction methods are required for analysis by ICP-Quadrupole mass spectrometry.

Gaseous sample introduction into ICP-MS offers analyte transport efficiency (close to 100%) and improved limits of detection compared to solution nebulization. Hydride generation (HG) is the most widely utilized gas-phase sample introduction system in ICP-MS for selenium. The most frequently studied elements are As and Se and their species in river, sea-, ground, mineral, and tap water samples (8,9), which are analyzed without any sample pretreatment. By selectively forming the volatile species, hydride generation offers the unique advantage of separation of the analyte from complex matrices. Other methods of vapor generation include alkylation with Grignard reagents, formation of volatile chloride derivatives (10), cold vapor generation (11), and electrochemical hydride generation (12,13). The chemical method of vapor generation has certain limitations, such as interference from concomitant elements [notably transition metals such as Cu and Ni (14,15)], the purity of the reductant (such as $NaBH_4$), and other derivatization reagents used.

Recent publications (16,17) have shown that UV irradiation can induce photoreduction followed by production of volatile species. Guo et al. (18,19) have successfully demonstrated the generation and identification of volatile selenium species formed in the presence of low molecular weight organic acids by the action of UV light and its determination using atomic absorption spectrometry (AAS). A free radical mechanism has been proposed (18,20) for the generation of volatile Se species (SeH_2, SeCO, etc.) by UV irradiation of Se(IV) solution in a low molecular weight organic acid (formic acid, acetic acid, etc.) – nitric acid medium. Chen et. al. (21) studied in detail the photochemical stability of both inorganic and organic selenium species in various aqueous solutions. Guo et. al. (18) found a 3-fold enhancement in production of the volatile species in the presence of 30 mmol L^{-1} nitric acid along with formic acid. They also found that in the presence of nitric acid along with formic acid only SeCO was formed and not SeH_2. Only Se(IV) was observed to form the volatile species, while Se(VI) did not undergo photoreduction.

Sturgeon et. al. (22), in their recent communication, utilized a combined spray chamber/UV photolysis unit that has been shown to increase the sample introduction efficiency considerably for several elements. Figueroa et. al. (23) have reported a photo-assisted vapor generation method for the determination of Se at the pg/mL level by electrothermal atomic absorption spectrometry (ETAAS), following headspace single-drop microextraction. Nano-TiO_2 has been used as a semiconductor/catalyst (22,23) to increase the efficiency of selenium vapor generation in the presence of UV irradiation.

Earlier, a simple ‘collect and punch’ cold vapor inductively coupled plasma mass spectrometric technique, developed in our laboratory by Karunasagar et. al. (24), had shown a significant enhancement in sensitivity for the direct determination of mercury at the ng/L levels. In the present method, studies were carried out by coupling the UV vapor generation with the ‘collect and punch’ technique. The ‘collect and punch’ technique showed a significant enhancement in sensitivity for the determination of Se(IV) in ground water samples in comparison to the continuous vapor introduction method. The aim of this paper is to report a special sample introduction method for the determination of selenite [Se(IV)] in ground water at the ultratrace levels using ICP-MS. The method has been applied to ground water samples collected from the northeastern districts of Punjab, India.

EXPERIMENTAL

All of the experimental work was carried out at the Ultra Trace Analysis Laboratory (UTAL), C.C.C.M., which is equipped with class 100 clean room facilities and several class 10 clean workbenches having a vertical laminar flow and a once-through exhaust.

Instrumentation

ICP-MS: All measurements were performed using a Model Plasmatrace 2 inductively coupled plasma mass spectrometer (Micromass, UK) situated in a class 100 laboratory. The instrumental operating conditions are given in Table I. The Single Ion Monitoring (SIM) mode provided in the Prestige® software was used to monitor the selenium signal at mass 82 with respect to time. The instrument was operated in low-resolution mode.

Photoreactor: A flow-through photoreactor was constructed using a 4-m length of polytetrafluoroethylene (PTFE) tubing (1.6 mm o.d. X 1.0 mm i.d.) wound over an 8 W UV lamp (Philips, India).

A Minipuls™ 2 peristaltic pump (Gilson, Middleton, WI, USA) was used for pumping the sample solution.

The gas-liquid separator of a hydride generation unit (P.S. Analytical, Sevenoaks, Kent, UK) was used and the experimental setup is shown in Figure 1.

Reagents and Standards

All solutions were prepared with high purity de-ionized water (>18.2 MΩ.cm resistivity) obtained using a Milli-Q™ system (Millipore, Bedford, MA, USA). Sub-boiled nitric acid and hydrochloric acid were used in the experiments. These acids were purified in-house by sub-boiling in a quartz still located inside a laminar flow class 10 clean bench. Selenium stock solutions (1000 mg L^{-1}) were prepared from sodium selenite pentahydrate ($Na_2SeO_3 \cdot 5H_2O$, Analytical Reagent, CDH, New Delhi, India). Calibration solutions were prepared daily by diluting the stock solutions. Solutions of formic acid were prepared from 85% formic acid (E. Merck India Ltd., Mumbai, India).

TABLE I
ICP-MS Operating Parameters

ICP-MS System:	
Instrument	Micromass, Plasmatrace 2
Torch	Fassel
Plasma Forward Power	1400 W
Plasma Reflected Power	< 10 W
Sampler Cone	1.0 mm Nickel
Skimmer Cone	0.5 mm Nickel
Ion Lens Settings	Optimized for ^{82}Se
Peripump Speed	48.0 rev min^{-1}
Resolution	400
Gas Flow Rates:	
Coolant Gas	14 L min^{-1}
Auxiliary Gas	1.9 L min^{-1}
Nebulizer Gas	0.85 L min^{-1}
Gas-Liquid Separator:	
Carrier Gas (Ar) Flow	0.15 L min^{-1}
Sample Flow Rate	2.0 mL min^{-1}
UV Irradiation Time	1 min
Time of Vapor Collection	2 min
Data Acquisition-Single Ion Monitoring:	
Mass	^{82}Se
Dwell Time	80 ms
Number of Points	500
Acquisition Time	40s

Procedure

Sample Collection

Ground water samples were collected from six different tube wells (of 18–76 m depth) in the fields of Nawanshehar District, Ludhiana, Punjab. The samples were collected in 500-mL pre-cleaned polypropylene screw-capped vessels after thoroughly rinsing with the respective tube well waters. The samples were filtered through a G4 sintered glass crucible.

UV-assisted Vapor Generation Followed by 'Collect and Punch'

The conditions for UV-assisted vapor generation were similar to those reported by Guo et. al. (18). The Se(IV) standard and sample solutions were prepared in 1M formic acid and 30 mM HNO_3. The UV lamp was switched on and allowed to stabilize for 5 minutes before the sample solution was passed through. The solutions were then pumped through the polytetrafluoroethylene (PTFE) tubing using a peristaltic pump at a flow rate of 2 mL/min with a solution irradiation time of 1 minute. The effluent was transported into a gas-liquid separator.

'Collect and Punch' Apparatus

Argon gas (0.15 L/min) was introduced into the gas-liquid separator, and the volatile selenium species were transported by the Ar flow from the gas-liquid separator into the 'collect and punch' apparatus (24), see Figure 2(a), prior to injecting it into the plasma. The 'collect and punch' apparatus consisted of a chamber with a volume of 125 mL and three 3-way valves to control the flow paths. The Ar carrier gas for transporting the selenium vapor to the collection chamber and the Ar injector gas to 'punch' the vapor into the plasma were maintained as separate flows

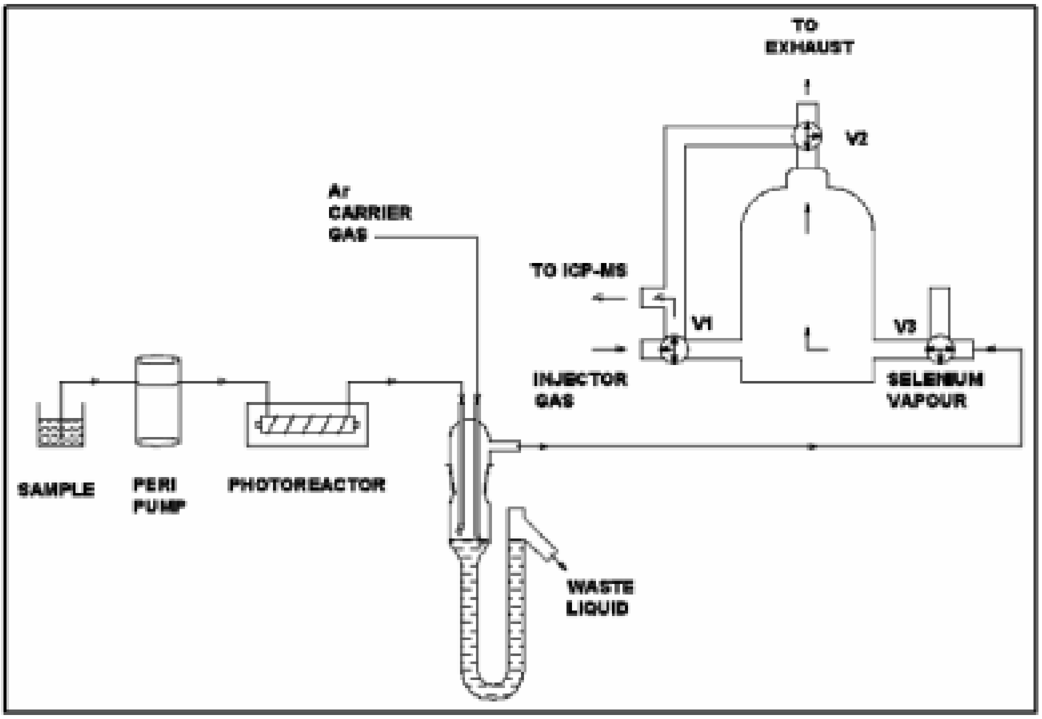

Fig. 1. Block diagram of the UV-Vapor generation-'Collect & Punch'-ICPMS instrument setup.

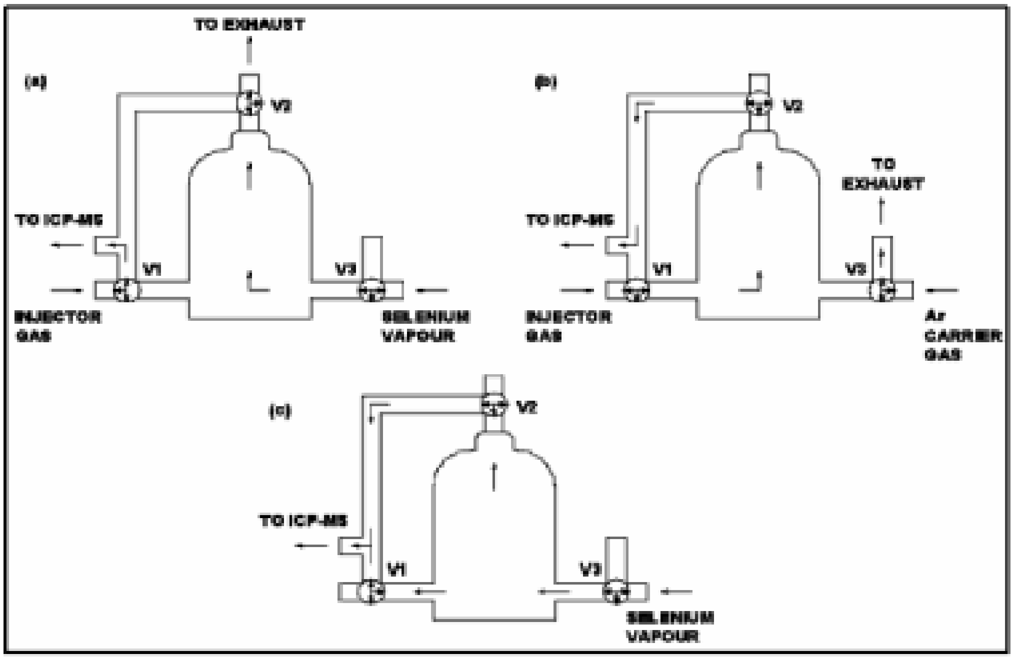

Fig. 2. Schematic diagram of the collection chamber used in the UV-Vapor Generation-'Collect and Punch'-ICP-MS method for the determination of Se(IV). Volume of the cell = 125 mL. Positions shown for (a) Collection of vapor, (b) Punching into the plasma, and (c) Optimization of Se-82 signal intensity.

to control filling up the collection chamber and punching into the plasma to optimize the selenium signal. The separate flows for the carrier and the injector gases help the independent optimization of the flow rates and prevent dilution of the selenium vapors generated.

As shown in Figure 2(a), valve V1 was closed initially to by-pass the cell and route the injector gas into the plasma, while valves V2 and V3 were turned on to allow collection of the vapor in the chamber. The reaction was started by pumping the sample solution through the photoreactor, which was continued for the desired length of time. Then valve V3 was switched to by-pass the chamber and route the carrier gas to the exhaust. The Single Ion Monitoring (SIM) mode of acquisition was initiated and valves V1 and V2 were turned to 'punch' the selenium vapor into the plasma, see Figure 2(b). The selenium vapor was carried through a Tygon™ tube which is attached to a socket that fits directly into the base of the plasma torch.

The relative enhancement in sensitivity between continuous vapor introduction and the 'collect and punch' method was determined in the following manner. The valves of the collection chamber were turned as shown in Figure 2(c) and the vapors sent directly into the plasma. A qualitative scan was performed for a 10-µg L^{-1} Se(IV) solution in the range of m/z 81–83. Then using the 'collect and punch' method, data was acquired for the same solution in SIM Mode.

RESULTS AND DISCUSSION

Optimization of ^{82}Se Signal Intensity

Before carrying out the 'collect and punch' experiment, the signal for Se (m/z = 82) was optimized as follows: A 50-µg/L solution of Se(IV) in a 1M HCOOH / 30 mM HNO_3 acid mixture was pumped through the PTFE tube wound around the UV lamp, with a peristaltic pump speed of 48 revolutions/min (sample uptake rate = 2 mL/min). The nebulizer gas (Ar injector gas) control on the instrument was set to zero. The Se vapors generated after UV irradiation were continuously passed from the gas-liquid separator into the plasma through the collection chamber, using the Ar carrier gas. As shown in Figure 2(c), the valves V1 and V2 of the collection chamber were closed and valve V3 was kept open to allow the Se vapors to pass directly into the plasma using the Ar carrier gas. The flow rate of the carrier gas was optimized to obtain the maximum signal for ^{82}Se on the rate meter display unit of the HR-ICP-MS instrument. This optimization was required to be performed daily. Figure 3 shows the change in peak height of selenium as the carrier gas flow is varied. In general, a flow rate of 0.8–0.85 L/min gave the best possible signal for selenium. The nebulizer control on the instrument was set to this flow rate for punching the selenium vapors into the plasma as a tight plug during the 'collect and punch' operation. This flow rate was very critical since the vapors are required to be sent into the plasma as a tight plug without any further dilution. A lower flow rate resulted in a prolonged time of transport during which dilution could occur, whereas a rapid flow could result in the 'plug' being pushed through the plasma quickly, thus reducing its residence time in the plasma.

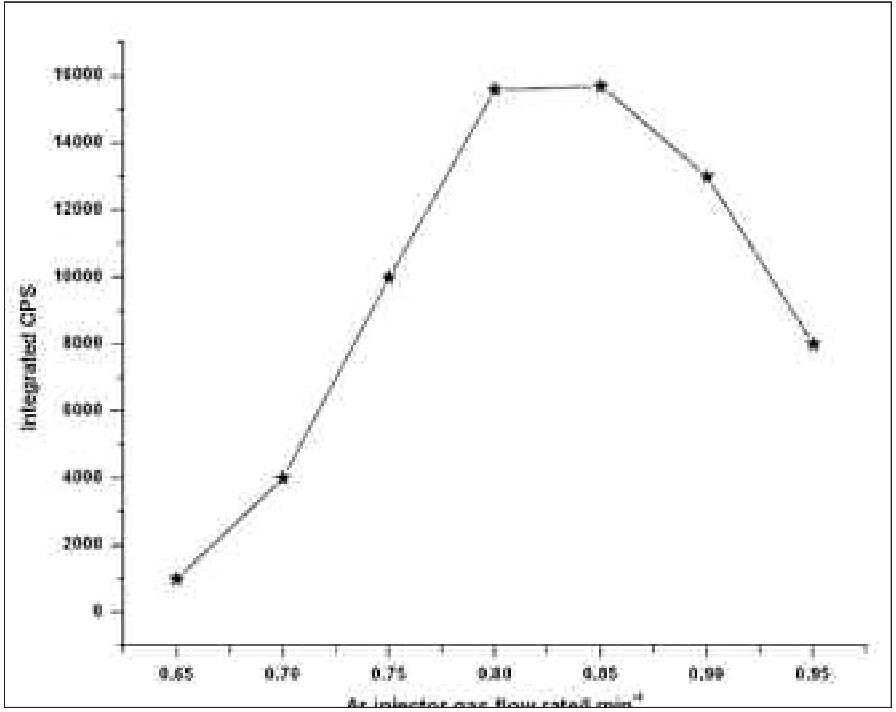

Fig. 3. Effect of the injector gas flow rate on the Se-82 signal. Concentration of Se(IV) = 10 µg L^{-1}.

Optimization of the Parameters for the UV Vapor Generation and Collection

A 10-µg L^{-1} (10 parts per billion) Se(IV) solution in 1M HCOOH + 30 mM HNO_3 medium was used for the optimization of various parameters affecting the vapor collection in the cell and, consequently, the peak height of the signals.

Peripump Speed

The UV vapor generation was studied at different flow rates of 10 µg L^{-1} Se(IV) standard solution, based on the peristaltic pump speed. The peripump speed was varied between 25–55 rev/min. The vapor collection time in the chamber was kept constant at 5 minutes. The flow rate of the Ar carrier gas was maintained constant at 100 mL/min. As shown in Table II, maximum signal was obtained at 48 rev/min, which corresponded to a solution flow rate of 2 mL/min. For subsequent experiments, the sample solutions were transported with a peripump speed of 48 rev/min. At this speed, the sample solution is exposed to UV irradiation for one minute, depending on the length of the coil and its internal diameter.

Vapor Collection Time

The volatile Se vapors were collected in the 'collect and punch' apparatus for different time periods. The vapors were collected for 1, 2, and 4 minutes, and then punched into the plasma. The signal intensity was recorded. The flow rate of the Ar carrier gas (100 mL/min) and the peripump speed (48 rev/min) were maintained constant. As shown in Figure 4, the signal intensity increased up to two minutes and thereafter remained constant. Therefore, the vapors were collected for two minutes for the remaining experiments.

Carrier Gas Flow Rate

The flow rate of the Ar carrier gas was varied from 50–400 mL/min. The selenium vapors were collected for two minutes and then punched into the plasma. A maximum signal was obtained for a carrier gas flow rate of 150 mL/min. As the flow rate was increased beyond 150 mL/min, the signal dropped rapidly due to dilution of the selenium vapor in the collection chamber by the carrier gas. Hence, a flow rate of 150 mL/min was used to carry the volatile Se vapors from the gas-liquid separator into the collection chamber.

TABLE II
Effect of Peripump Speed on ^{82}Se Signal Intensity by UV-Vapor Generation-'Collect and Punch'-ICP-MS Method

Peripump Speed (rev/min)	Signal Intensity (cps)
25	60,000
30	68,000
40	80,000
48	110,000
50	95,000
55	80,000

A typical peak profile obtained for the Se(IV) is shown in Figure 5. As shown in the figure, the peak is sharp with a very short rinse time. Hence, peak heights were measured and used for calculations. The sharp rise at the leading edge indicates that the volatile selenium species collected in the cell was transported as a tight 'plug' with very little dilution due to the carrier gas. The asymmetry noted at the trailing edge indicates slight dilution with the carrier gas, which did not affect the calibration obtained by peak height measurements.

Figures of Merit

The peak height of the signal in the 'collect and punch' method was seven times higher than the continuous vapor introduction method. The developed method gave a peak height of ~ 4000 counts for the blank (1M HCOOH + 30 mM HNO_3). The blank equivalent concentration was close to 0.35 µg L^{-1}. This high blank could be due to the formation of $^{40}Ar_2{}^1H_2$, giving a signal at m/z 82.

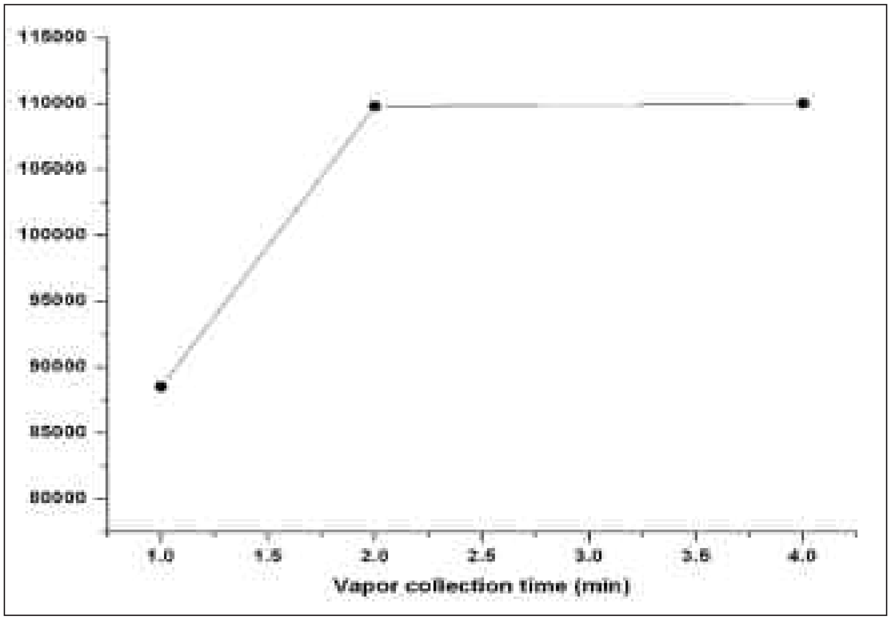

Fig. 4. Graph showing the variation in Se signal intensity with respect to vapor collection time.

The calibration plot showed good linearity, following the equation y = 105 + 10554x, in the range from 0.5 to 10 µg L^{-1} for the Se(IV) solution in 1M HCOOH and 30 mM HNO_3 mixture. The correlation coefficient (r) of the calibration curve was better than 0.999. The detection limit (defined as the concentration equivalent to three times the standard deviation of six measurements of the blank) was found to be 50 parts per trillion (0.05 µg L^{-1}). The relative standard deviation (%RSD, n = 6) was 1.2% at a concentration of 0.5 µg L^{-1}, showing good precision at such low concentration, even for the lower abundance Se-82 isotope. The RSD of the signal varied between 0.2–1.2% over the entire range for which calibration was obtained.

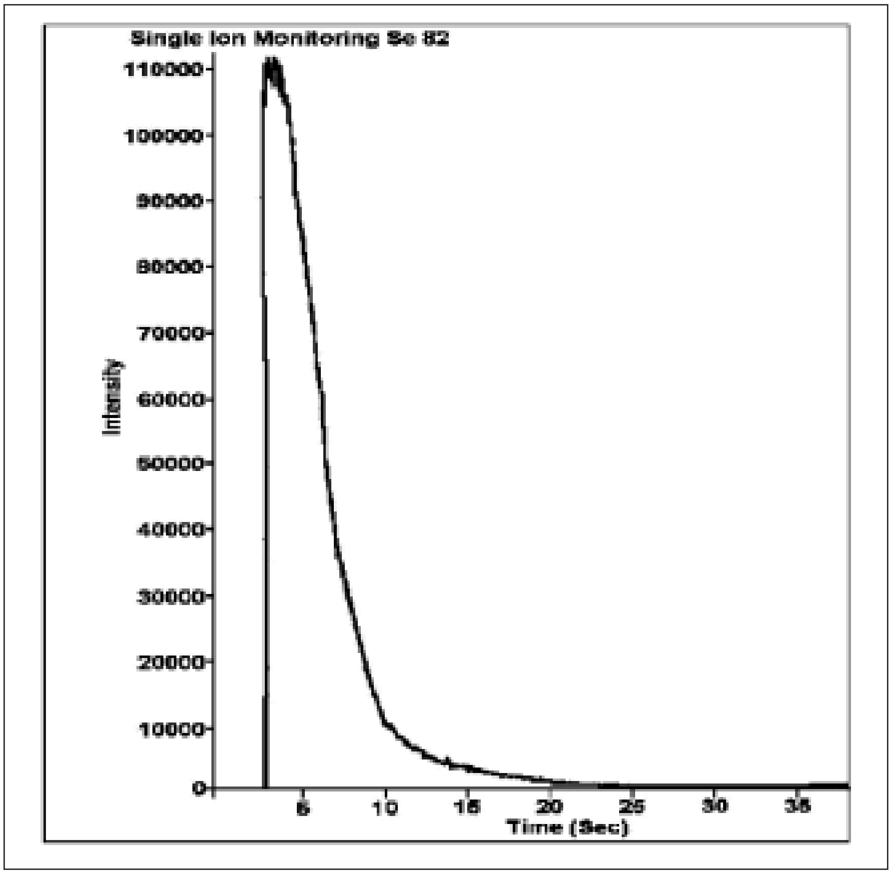

Fig. 5. Typical signal obtained for Se(IV) by UV-Vapor Generation-'Collect and Punch'-ICP-MS method. Se(IV) concentration = 10 µg L^{-1}. Experimental conditions as given in Table I.

Application of the Method

The method was applied to tube well water samples collected in Punjab, India. The samples were diluted 2-fold to reduce the salt content (18); formic acid and nitric acid of required concentration was added for UV vapor generation. The concentration of Se(IV) was determined applying the developed method; the results are shown in Table III. The concentration of Se(IV) obtained by the UV vapor generation–'collect and punch'-ICP-MS method matched well with the values obtained by the conventional HG-ICP-MS method. Applying the *t*-test (paired comparison) with multiple samples showed that the results of the two methods did not differ significantly at the 95% confidence level. The 2-fold diluted samples, when spiked with 10 µg L^{-1} of Se(IV), yielded quantitative recovery. The total selenium in the tube well water samples were determined by HG-ICP-MS after reduction of Se(VI) to Se(IV). The concentrations of total Se obtained by HG-ICP-MS were found to vary between 15–90 µg L^{-1} (Table III), suggesting that the major species in these tube well water samples was Se(VI). It appears that many of the tube wells in this region are contaminated with toxic levels of selenate [Se(VI)].

The concentration of total selenium cannot be determined by the 'collect and punch' method, as the method is specific for Se(IV). The complete conversion of Se(VI) to Se(IV) requires heating of the water sample in 5–6M HCl conditions. The present method has been found to be highly sensitive to the acidity of the sample and the formation of Se vapors by the UV-assisted vapor generation method was found to be negligible at such high acidities.

Guo et. al. (18) had earlier reported that as the concentration of nitrate was increased beyond 30 mM (1.86 g/L), the signal intensity decreased rapidly to almost zero. Hence, the concentrations of nitrate in these water samples were determined by ion chromatography prior to their analysis and were found to be below 50 mg L^{-1}.

CONCLUSION

The developed method using UV generation of Se species followed by 'collect and punch' introduction to ICP-MS offers good sensitivity for the determination of Se(IV) at ultratrace levels in ground water samples. This 'collect and punch' method of sample introduction into the ICP is very useful for quadrupole ICP mass spectrometers, where the lower abundant ^{82}Se isotope is generally used for quantifi-

TABLE II
Results for the Determination of Se(IV) in Tube Well Water Samples by UV Vapor Generation-'Collect and Punch'-ICP-MS Method

Sample Location	Concentration of Se(IV)		Spiked, Se(IV) (10 µg L^{-1})	Total Se
(Village)	UV-Vap-'C&P'-ICP-MS Concn[a] ± Std Dev[b] (µg L^{-1})	HG-ICP-MS Concn[a] ± Std Dev[b] (µg L^{-1})	UV-Vap-'C&P'-ICP-MS (% Recovery)	HG-ICP-MS Concn[a] ± Std Dev[b] (µg L^{-1})
Barwa	1.5 ± 0.1	1.7 ± 0.2	100	67.3 ± 0.1
Jainpur-1	3.0 ± 0.3	3.1 ± 0.2	96	14.7 ± 0.3
Jainpur-2	4.5 ± 0.5	4.0 ± 0.3	98	61.1 ± 0.2
Jainpur-3	0.9 ± 0.2	1.2 ± 0.1	101	92.7 ± 0.1
Jainpur-4	2.0 ± 0.4	2.3 ± 0.2	105	48.8 ± 0.2
Simbly	4.0 ± 0.2	3.5 ± 0.4	98	21.2 ± 0.1

[a] Values are means of three measurements ± standard deviation.
[b] Standard deviation of three replicates.

cation. The application of high resolution ICP-MS or collision cell / dynamic reaction cell ICP- MS to eliminate the argide interferences on the major isotopes (^{80}Se and ^{78}Se), enables the use of these isotopes for quantification, resulting in further improvement in sensitivity and the ability to measure lower levels. The only limitation of the method is that the nitric acid concentration and nitrate levels in the samples are very critical (should not exceed 30 mM NO_3^- = 1.86 g/L) for the generation of the volatile Se species.

Received April 7, 2008.

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Evaluation of Metal Ions and Nitrate Levels in Ground Water From Private Wells in Culturama (State of Mato Grosso do Sul, Brazil) by Flame AAS

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ABSTRACT

Nitrate and some metal ion levels (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Ca, K, Mg, and Na) were measured in 31 ground water samples from Culturama, a rural zone of Fátima do Sul city, Brazil. The fast-sequential multi-element flame atomic absorption spectrometry (FS-FAAS) method allowed the determination of these metals with quantification limits ranging from 1.36 µg L^{-1} (Mn) – 0.71 mg L^{-1} (Ca). Recovery values between 113–116% (Ca), 115–118% (Cd), 105–107% (Co), 98–102% (Cr), 95–98% (Cu), 88–89% (Fe), 84–89% (K), 93–99% (Mg), 97–103% (Mn), 86–93% (Na), and 108–110% (Zn) in three concentration levels were obtained with precisions, expressed as relative standard deviations (RSDs), below 2.2%. The results obtained indicated that concentrations of the elements were generally below the maximum allowed concentration (MAC), ranging from 0.19 to 22.46 mg L^{-1} for nitrate and from not detected to 40.9 mg L^{-1} for metal ions analysis. However, the concentrations of Cr, Mn, Cd, Fe, and nitrate in some water samples were above the maximum concentration allowed, set by Portaria MS No. 518/04 (March 25, 2004; Brazilian Regulations). A statistical analysis (as performed by Pearson and Cluster) was used to establish the probable sources of metal contamination. Activities such as agriculture and cattle raising, use of septic tanks, and influence of materials naturally originating in the soil of the Culturama area can all contribute to ground water contamination by these elements.

INTRODUCTION

The determination of heavy metals, especially some toxic metals that play important roles in the biological metabolism, has been receiving particular attention (1). Trace elements, and especially the inorganic species, are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources (2). The main natural sources of metals in waters are weathering of minerals. However, concentrations of metals and their actual impact can be greatly modified due to the interaction with natural water constituents.

Metals ions enter into the aquatic environment from a variety of sources. Although most metals occur naturally through biogeochemical cycles (3), they may also be added to the environment through anthropogenic sources, including industrial and domestic effluents, urban storms, water runoff, and atmospheric sources (4).

In most Brazilian states, agriculture and livestock are a very profitable business. It is known that the agricultural activities are potential sources of contamination, since agriculture requires a great amount of input, such as fertilizers, pesticides, and growth regulators. These may have a great impact in the ground water, as well as in lake and surface waters.

With an increasing concern about the degradation of the water environment, much research on water quality has been done over the past decade. Several techniques, including flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma optical emission spectrometry (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS), have been widely used for the determination of metal traces in different samples because the available data are highly precise and accurate (5).

The main water pollutant agents that come from agriculture are pesticides and nitrogen (6), and these are often heavy metals. Heavy metals are more easily found in agricultural areas as a result of the widespread application of fertilizers and animal supplements. The use of inorganic fertilizers is a very important contributing factor (7,8) to water quality degradation. In Brazil, there are many fertilizers that contain nitrogen in their chemical composition, resulting in nitrate loss into the soil and leaching into ground water (6).

In this context, it is apparent that data about water resources in our country is of vital importance. The objective of this study was to obtain first data for concentrations of nitrate and other inorganic species in the ground water of rural properties in the State of Mato Grosso do Sul, Brazil. The metal concentrations in 31 ground water samples from private wells in the district of Culturama was determined for the purpose of establishing a database, and

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to examine the quality of the water consumed by the rural population.

EXPERIMENTAL

Description of Sampling Site

Culturama, a rural zone of Fátima do Sul city (Mato Grosso do Sul State), is located at 22°18'16"S and 54°20'39"W (in mid-western Brazil, see Figure 1) and has a population of 3400 inhabitants. The district is at an altitude of 352 m and is inside the Fátima do Sul territorial unit (9). Agriculture is the major economy of the district, characterized mainly by the presence of small rural properties (on average 400,000 m^2), with emphasis on the seasonal production of cotton, peanuts, rice, beans, soya, and maize. The annual average temperature is 28 °C: maximum 35–36 °C and minimum 10–12 °C. The annual pluvial precipitation varies from 1400 to 1600 mm, with water surplus from October to May, and deficiency from June to September. The vegetation of Culturama is characterized by low vegetation, known as "Campos de Vacaria" (Vacaria Fields), typical of the Cerrado and consisting predominantly of herbaceous stratum and some small bush species. The main physical-chemical characteristics of the soil from Culturama are as follows:
4.6 (pH),
29 g dm^{-3} (organic matter),
4.0 (H+Al),
0.1 cmol$_c$ dm^{-3} (Al),
1.6 cmol$_c$ dm^{-3} (Ca),
0.4 cmol$_c$ dm^{-3} (K),
2.1 cmol$_c$ dm^{-3} (Cu),
123 cmol$_c$ dm^{-3} (Fe),
73 cmol$_c$ dm^{-3} (Mn), and
1.7 cmol$_c$ dm^{-3} (Zn).

Standards and Reagents

High purity water (resistivity 18.2 MΩ cm^{-1}), produced using a Milli-Q™ water purification system from Millipore (Bedford, MA, USA), was used to prepare all aqueous solutions.

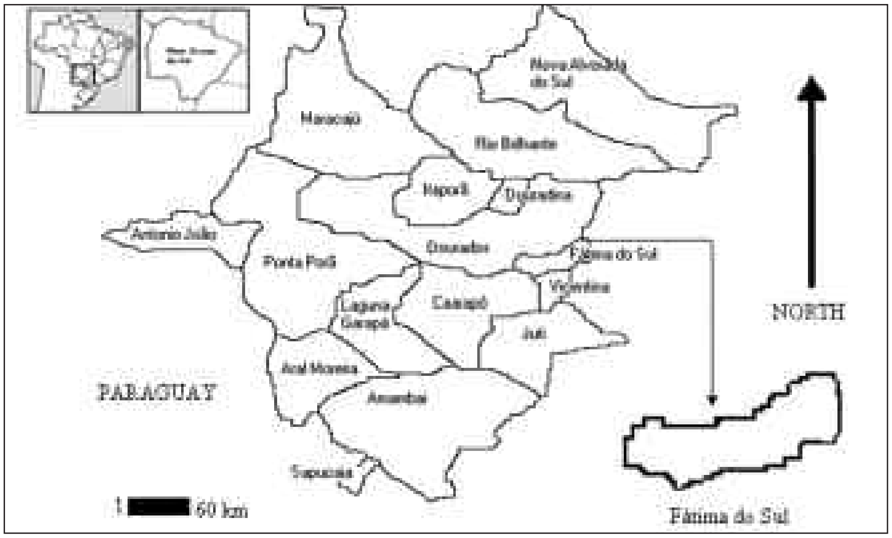

Fig. 1. Geographical location of Fatima do Sul, Brazil.

Individual stock standards (1000 mg L^{-1}) of Fe, Cu, Mn, Cr, Zn, Co, Cd, Ni, Ca, K, Mg, and Na for FAAS analysis were purchased from Aldrich (Milwaukee, WI, USA) and were in aqueous solutions containing 1% (v/v) nitric or hydrochloric acid (E. Merck, Darmstadt, Germany). HNO_3 (65%, v/v) was used for stabilization of the standard solutions and real samples. CsCl (99.5% purity) and KCl (99.5% purity) were both purchased from E. Merck, Darmstadt, Germany, and used as ionization suppression agents. $NaNO_3$ (99% purity) and HCl 37% (v/v) were also purchased from Merck and used to determine the nitrate concentrations in the samples.

Before use, all glassware was cleaned with 1:1 (v/v) HNO_3 (Merck) and deionized water; any residual water was dried by evaporation. The glassware employed during the measurements was thoroughly cleaned with distilled water, then washed, rinsed, and soaked overnight in 3–5% (v/v) Extran (MA 02 neutral, Merck, Darmstadt, Germany).

Sampling and Sample Preparation

A total of 31 ground water samples was collected from private wells in Colturama on the 22nd and 23rd of February, 2005. The average depth of the ground water in this area is 17 m (5–70 m). Plentiful ground water is available throughout the year. The water samples were collected from taps or, when possible, directly from the well in 1000-mL and 250-mL polyethylene bottles [washed with detergent, then with deionized water, HNO_3 (65%, 1:1, v/v), and again with deionized water]. The ground water samples were acidified with HNO_3 (65%, v/v) until obtaining a pH of < 2, then placed in an ice bath and brought to the laboratory. The samples were filtered through a 0.45-µm micropore membrane filter. After filtration, the water samples were stored in a refrigerator at 4 °C for a maximum of three days for nitrate analysis, and 180 days for metal ion analysis.

For metal ion analysis, 200 mL of each sample was transferred to a beaker. Then, 10 mL of HNO_3 (65%) was added and the samples heated to 90 °C on a hot plate for pre-concentration. The volume was reduced to approximately 30 mL and adjusted to 50 mL in a volumetric flask with deionized water. For Na, Ca, K, and Mg determination, dilutions of the samples were necessary, because these metal ions were in the samples in high concentrations. Then, 10 mL of each digested sample was taken and transferred to a 25-mL volumetric flask, the ionization suppressor agent (KCl or CsCl) was added, and the solutions brought to volume with deionized water. For nitrate determination, 50 mL of each ground water sample was transferred to a 125-mL Erlenmeyer flask and 1 mL of 1.0M HCl added (10). Blanks were prepared in the same way as the sample solution for both analyses.

Instrumentation and Chemical Analysis

A Hitachi Model U-1100 spectrophotometer (Tokyo, Japan) was used to determine the nitrate concentration in nitrogen form using the Standard Methods (4500 - NO^-_3 B) (10). The standard solutions and calibration curves were prepared by following the method strictly. Nitrate quantification was based on standard curves that were calibrated within the 0.2–7.0 mg L^{-1} range. For samples and standards, the absorbance reading at 275 nm was subtracted twice from the reading at 220 nm to obtain the absorbance due to the nitrate.

Samples with nitrogen concentrations higher than 7.0 mg L^{-1} were diluted with deionized water prior to measurement.

The determination of the metal ion concentrations in all samples was carried out by flame atomic absorption spectrometry using a Model 220 FS (Varian, Walnut Creek, CA, USA), operating in the fast-sequential mode, equipped with a dilution system and the SIPS 10 single pump to aid in the dilution of the bulk solutions for obtaining the required calibration curve. The wavelengths, lamp currents, band width, and flame type used were in agreement with the manufacturer's recommendations. An adjustable capillary nebulizer system (6–8 mL min^{-1}) and acetylene/air or acetylene/nitrous oxide was used for generation of aerosols and atomization during FAAS analysis. The total time required for three serial readings of each sample was 15 seconds, thus expressing the average value of the absorbances.

The calibration curves (external standard method) were constructed with five concentrations ranging from 0.10 to 15 mg L^{-1}. Linearity was evaluated by linear regression analysis, calculated by the least squares regression method. Correlation coefficients (R^2) within the range of 0.9941–0.9999 were obtained. Detection and quantification limits of the FAAS (LOD and LOQ) were calculated using Equations 1 and 2:

$$\text{LOD} = 3\, S_B/b \qquad \text{(Eq. 1)}$$

$$\text{LOQ} = 10\, S_B/b \qquad \text{(Eq. 2)}$$

where b is the angular coefficient of the straight line and S_B is the standard deviation of 10 blanks (11).

The accuracy of the FAAS method was determined in recovery tests carried out by spiking ultrapure water with standards of each metal ion in three levels of concentration (75, 100, and 125% of average value concentrations were obtained for the ions). The precision of the method was determined by the repeatability for three replicates of this test and the results were expressed as percentages to relative standard deviation (%RSD).

Statistical Analysis

Statistical analyses, including Pearson linear correlation and Cluster analysis, were performed using Minitab (12) software for Microsoft® Windows® Version 14. The Cluster analysis was performed with the average linkage between groups and correlation coefficient distance.

RESULTS AND DISCUSSION

The detection and quantification limits for the metal ions estimated by Eq. 1 and 2 are presented in Table I, as well as the mean recovery of the metal ions obtained at three levels of concentration.

Comparing the quantification limits with the maximum permissible amount of water for human consumption, as established by the Brazilian Regulations (13) presented in Table II, it is possible to observe that all quantification limits, except for chromium, are below the maximum permissible limits. For this reason, the FAAS technique can be used for this study. The recovery tests were accomplished for all metal ions, except for Ni, which showed concentration levels in the samples lower than the quantification limit of the method. Percentage recoveries between 84% and 102% were obtained for K, Na, Fe, Mg, Cu, Mn, and Cr, and between 105% and 118% for Co, Zn, Ca, and Cd. However, the recovery tests are above 100%, the concentrations of Zn, Ca, and Co in the real samples were below the maximum permissible limits in water for human consumption.

The results obtained for nitrate determination showed a range of 0.19–22.46 mg L^{-1}. Among the 31 water samples, approximately 19% had less than 1.0 mg L^{-1} of nitrate concentration, 50% between ≥1.0 mg L^{-1} and <5.0 mg L^{-1}, and 22% between ≥5.0 mg L^{-1} and <10.0 mg L^{-1}. In total, 9% of the samples had nitrate concentrations above 10.0 mg L^{-1}, the Brazilian drinking water standard (13). Figure 2 shows the values determined for each water sample.

TABLE I
Main Figures of Merit of Each Metal Ion in Three Concentration Levels

Metal Ions	C_0 (µg L^{-1})	LOQ (µg L^{-1})	Mean Recovery (%) Low[a]	Medium[b]	High[c]
Ca	100	710	115 ± 1.4	113 ± 1.9	116 ± 1.8
Cd	18	2.0	115 ± 2.0	118 ± 0.7	116 ± 1.5
Co	99	19	105 ± 1.9	106 ± 1.6	107 ± 1.9
Cr	91	73	102 ± 2.2	98 ± 2.0	99 ± 0.6
Cu	84	57	96 ± 0.63	98 ± 1.0	95 ± 2.0
Fe	130	90	88 ± 1.3	88 ± 1.3	89 ± 1.3
K	18	9.5	88 ± 1.6	86 ± 1.9	84 ± 1.4
Mg	7.6	182	99 ± 1.1	94 ± 1.3	93 ± 1.3
Mn	44	1.3	97 ± 2.0	98 ± 1.4	103 ± 1.1
Na	9.2	5.4	88 ± 1.4	86 ± 1.4	93 ± 1.3
Ni	150	314	-	-	-
Zn	16	4.0	110 ± 2.0	110 ± 1.7	108 ± 1.8

[a] 75%, [b] 100%, and [c] 125% of avarage values for each metal ions.
See avarage values in Table III.

TABLE II
Range of Metal Ion Concentrations Detected in the 31 Ground Water Samples of Culturama, Brazil

Metal Ions	Conc. Levels (µg L^{-1}) Min.	Max.	Braz.Reg. (µg L^{-1})
Ca	nd	40,900	*
Cd	nd	6.7	5.0
Co	< LOQ	87	-
Cr	nd	130	50
Cu	nd	83	2000
Fe	nd	170	300
K	nd	2600	-
Mg	nd	28,900	*
Mn	< LOQ	280	100
Na	210	2450	200,000
Ni	nd	< LOQ	-
Zn	< LOQ	47	5000

Conc. Levels: concentration levels
Braz. Reg.: Brazilian Regulations
nd: not detected
LOQ: limit of detection
*Expressed as hardness:
Ca + Mg = 500,000 µg L^{-1}

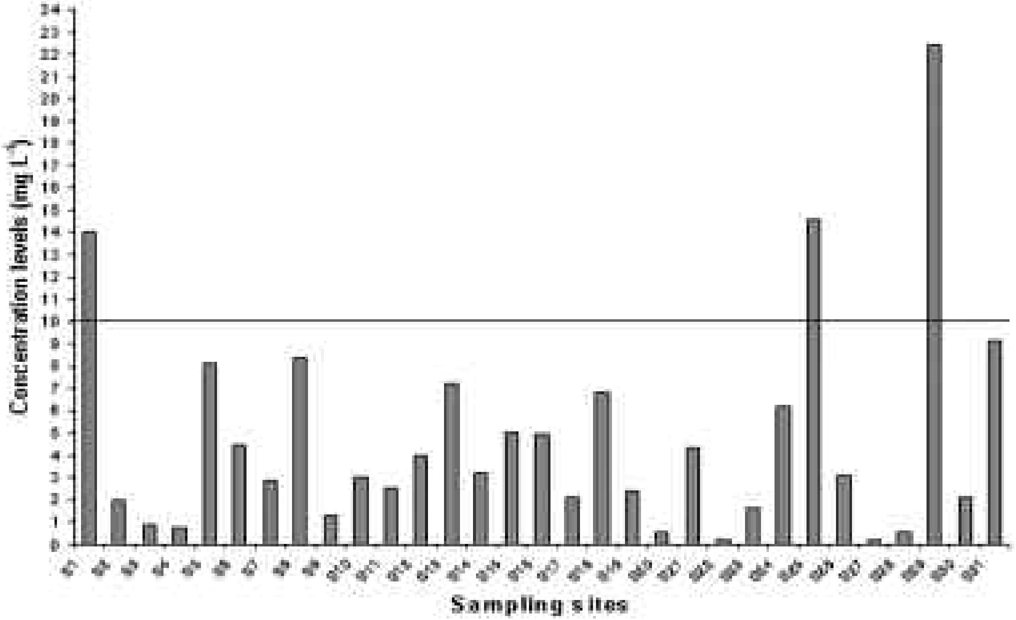

Fig. 2. Medium value of nitrate concentrations in the 31 ground water samples.

According to Liu et al. (14), nitrate concentrations above 1.0 mg L^{-1} indicate possible effects due to anthropogenic activities. The intensive use of fertilizers in agriculture, the presence of livestock, and the use of septic tanks by the rural population could be the probable sources of ground water contamination of the sampling site.

For the metal ions, the minimum and maximum values of concentration for each of the 31 ground water samples are summarized in Table II. Metal ions such as Mn, Zn, Mg, and K were determined in almost all of the samples, and other metal ions such as Cu and Cr were determined in a small number of samples. Among the inorganic ions studied, the ions Ca, K, Mg, and Na were the most abundant in the samples, while other ions showed low concentrations. The ion Ca, which was present at the highest concentrations, presented the maximum value of 40.95 mg L^{-1} for sample 15, while Cd and Cu were present at the lower concentrations. The ion Cu, specifically, was determined only in sample 24.

It is important to note that in most of the samples, Cr, Fe, Mn, and Cd were below the maximum permissible limits in water for human consumption as established by Brazilian Regulations:
Cr: 0.05 mg L^{-1}, Mn: 0.1 mg L^{-1},
Fe: 0.3 mg L^{-1}, Cd: 0.005 mg L^{-1}.
However, some samples were above the maximum permissible limits:
Samples 20, 22, 24, 29, 30, and 31 with Cr;
samples 1, 5, and 24 with Mn;
sample 11 with Fe; and
samples 20, 29, and 30 with Cd.

Metal ion occurrences in waters can be of natural or anthropogenic sources and due to industrial waste, domestic sewage, leaching of agricultural products and solid residues. According to Forstner et al. (4), it is difficult to establish global medium values of metal ions in bodies of water. This is due, firstly, to the variety of rock formations and, secondly, to various means of dissolution and transport of these elements in the water.

The metal ions more commonly found in the aquatic ecosystems coming from anthropogenic sources are: iron, manganese, copper, lead, zinc, chromium, nickel, cadmium, aluminum and, depending on the activities developed in the area, mercury.

The use of agrochemistry, mineral supplements, and agroindustrial (tannery) residues for fertilizing, can result in the contamination of soil, water courses, atmosphere, and food.

Agriculture and extensive cattle raising are activities developed at the sampling sites, as well as at other areas of the State of Mato Grosso do Sul. They represent the basis of their economy. These activities are intimately linked to the intensive use of agrochemistry and can pollute the environment. For instance, metal ions such as Fe, Mn, Co, Zn, and Cu are usually found in the mineral supplements for bovines. Chromium comes from being used in ruminant diets (15,16) mainly in stress situations (for treating diseases, during gestation and transport), and from the leather tanning processes (17–19). According to IBGE data, in the State of Mato Grosso do Sul, between January and March 2006, approximately 1,068,654 hides were tanned with chromium, 11.22% of the national production (20). However, Cr can also occur naturally from weathering of rock or soil as well as Fe, Mn, and other inorganic species.

Chromium is an element of considerable environmental and geological importance. The biochemical functions and the effects of this ion are related to its oxidation state. The hexavalent chromium (Cr^{6+}) is toxic as a carcinogenic agent, while the trivalent chromium (Cr^{3+}) is considered an essential nutrient for humans (21).

Cadmium is known as a potential pollutant because it is highly toxic and soluble in aquatic environments (22).

Iron and manganese are elements frequently found in the geological composition of the earth. As a result of their natural presence in the soil, these elements are easily found in aquatic bodies, even if only in very small concentrations. We collected samples in a large soya production area. According to Mann et al. (23), the application of manganese, independently of the means, increases the productivity of grains, germination, electric conductivity, index of emergency speed, and protein tenors in soya oil.

Table III shows medium values between the metal ion concentrations obtained in this study in comparison to other studies performed in Spain, Italy, and Poland.

Tamasi et al. (24) carried out studies of Al including some heavy metals such as V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in drinking waters from the Siena and Grosse to districts in Southern Tuscany, Italy. The results indicate that concentrations of these elements were generally far below the maximum allowed and set by Italian Law, and in a few samples some metal ions were in high concentrations. According to the authors, these effects are probably due to leaching from metal pipes. Ribicka et al. (25) determined the concentrations of nine metal ions (As, Cd, Cr, Cu, Ni, Pb, Zn, Fe, and Mn) in water from the Odra River, Olza town, Poland (close to the Czech Republic border), over the period from November 1997 to May 2000. According

TABLE III
Average Values of Concentration (mg L^{-1}) for Each Metal Ion in Different Studies

Metal	This Research		Italy (Ref. 24)		Poland (Ref. 25)		Spain (Ref. 26)	
	Mean* ± SD	CV(%)	Mean* ± SD	CV(%)	Mean* ± SD	CV(%)	Mean* ± SD	CV(%)
Cd	0.004 ± 0.002	50	0.003		0.13x10^{-3} ± 0.18x10^{-3}	138	0.09 ± 0.1	111
Co	0.05 ± 0.02	40	0.4 x10^{-3} ± 0.7x10^{-3}	175	nd		nd	
Cr	0.11 ± 0.02	18	0.64 x10^{-3} ± 0.2x10^{-3}	31	0.004 ± 0.006	150	nd	
Cu	0.08		0.005 ± 0.008	160	0.004 ± 0.003	75	0.03 ± 0.009	30
Fe	0.15 ± 0.06	40	0.17 ± 0.22	129	0.12 ± 0.25	208	2x10^{6} ± 1,2 x10^{6}	60
Mn	0.05 ± 0.05	100	0.014 ± 0.017	121	0.069 ± 0.081	117	0.5 ± 0.3	60
Ni	nd		0.003 ±0.005	166	0.005 ± 0.004	80	nd	
Zn	0.02 ± 0.01	50	0.1 ± 0.09	90	0.032 ± 0.029	90	0.35 ± 0.3	85
K	1.2 ± 0.7	58	nd		nd		9.1 ± 4.0	44
Mg	4.3 ± 5.5	127	nd		nd		nd	
Na	1.5 ± 0.7	46	nd		nd		134 ± 151	112
Ca	7.3 ± 8.3	113	nd		nd		nd	

SD = standard deviation;
nd = not detected value;
* = arithmetic mean;
(Ref. 24) = Tamasi et al., 2004;
(Ref. 25) = Rybicka et al., 2005;
(Ref. 26) = Alonso et al., 2004.

to the authors, the water samples were highly contaminated with Cd, Cu, and Zn, and the highest concentrations were found in the middle Odra section, at the Lubin–Glogów mining and processing region. Alonso et al. (26) carried out the determination of nine metals (Na, K, Zn, Cd, Pb, Cu, Mn, Fe, and Al) in surface waters from the Guadiamar River, Spain. According to these authors, the total concentrations in surface waters followed the trend Zn >Cu> Pb> Cd. The speciation study showed that Zn and Cd were present to a large extent in available forms (labile and H$^+$ exchangeable), while Pb and Cu were found mostly in the less available forms (highly inert). Moreover, the available forms were found in the northern section (mining pollution) and the highly inert forms in the southern section (urban, industrial, and agricultural pollution). These results could illustrate the potential value of speciation for discerning between different sources of pollution.

Comparing the average concentration of some metal ions obtained in this study, such as for Cd, Mn, Fe, and Cr (metal ions that presented concentrations above the limits set by Brazilian Regulations), the concentration of Cr and Cd were above those obtained by Tamasi et al. (24) and Ribicka et al. (25). This suggests probable anthropogenic sources in the contamination of the ground waters of Culturama. However, lower concentrations were observed for Fe in comparison to the findings by Tamasi et al. (24) and Alonso et al. (26), and for Mn as reported by Ribicka et al. (25) and Alonso et al. (26).

In order to diagnose and characterize possible sources of contamination, Pearson and Cluster used the normalized values of the metal ion concentrations to investigate possible correlations in the samples ($n = 31$) and among the inorganic ions. The Pearson statistical evaluations of the data showed moderate to strong correlations (12%) among the samples, 6% of this being positive ($0.595 \le r \le 0.934$, $p \le 0.05$) and 6% negative ($-0.595 \le r \le -0.831$, $p \le 0.05$); and among the individual analytes in 24% of the associations ($0.347 \le r \le 0.930$, $p \le 0.05$). Weak to moderate correlations were observed too, but only from sampling sites in 7.5% of the associations (positive and negative with p-values from 0.054 to 0.094). No significant correlations among the metal ions and among the samples were observed in 80% and 76% of the associations, respectively. The Cluster analysis was carried out to identify homogeneous groups of samples.

As shown in the dendrogram, Figure 3, the samples formed two major clusters revealing high similarity between them. The first cluster can be subdivided into two subgroups:
(1a) samples 1, 5, 8, 9, 14, 17, and 25;
(1b) samples 2, 3, 11, 13, 17, 18, 23, 26, and 31.
The second major cluster can be

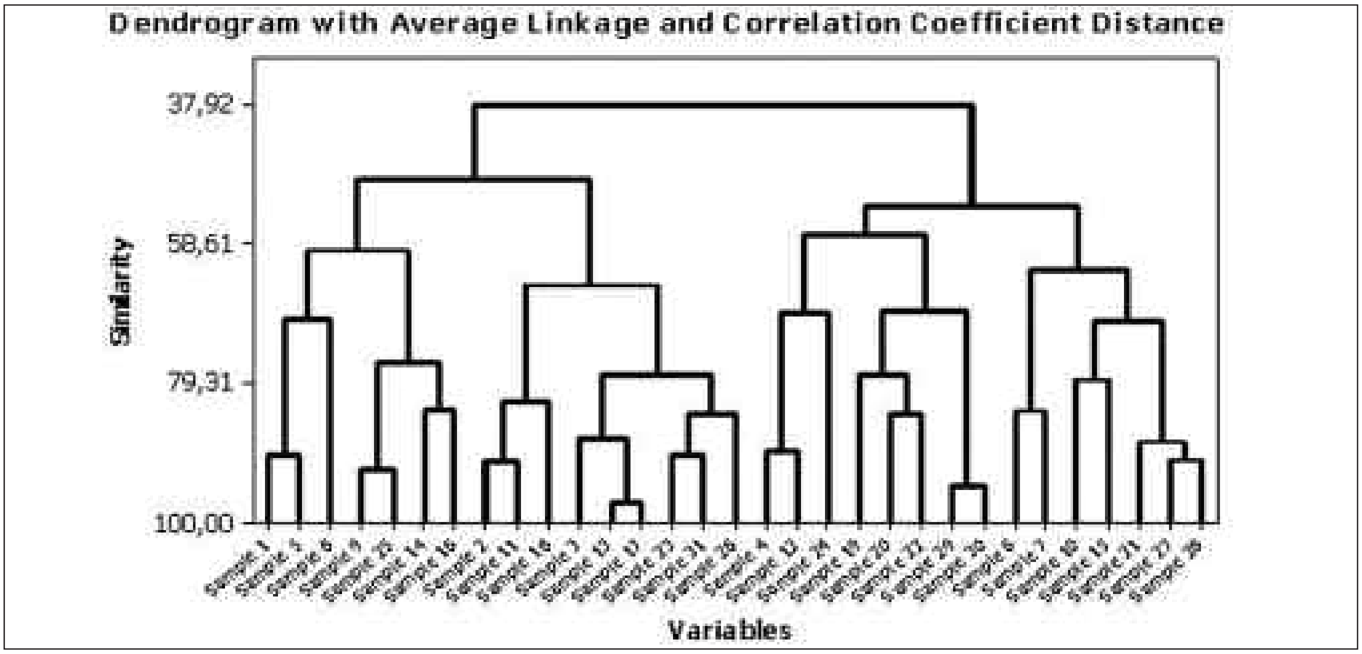

Fig. 3. Dendrogram showing relationships among the ground water sample sites.

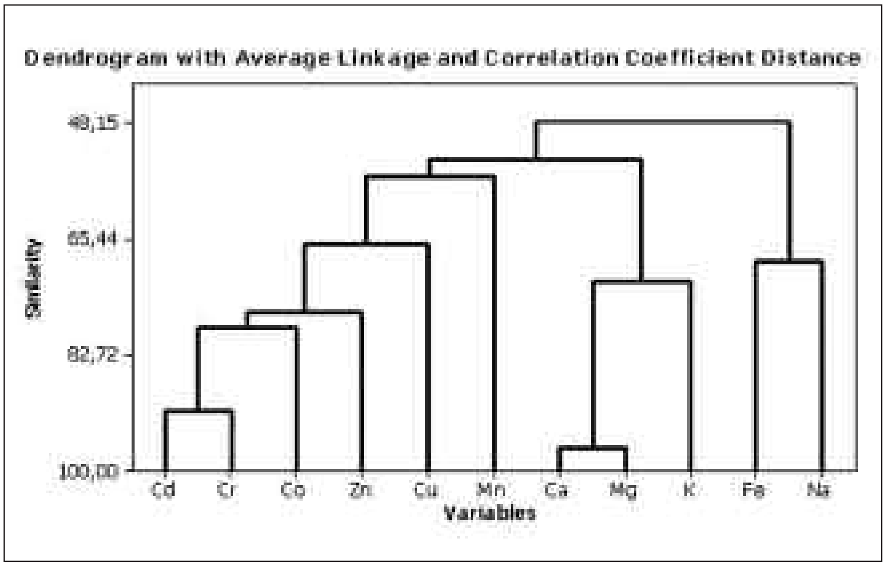

Fig. 4. Dendrogram showing relationships among the metal ions.

subdivided into two subgroups:
(2a) samples 4, 12, 19, 20, 22, 24, 29, and 30;
(2b) samples 6, 7, 10, 15, 21, 27, and 28.

In relation to metal ions, Figure 4 shows the presence of three big clusters. The first cluster was formed mainly by Cd, Cr, Co, Zn, Cu, and Mn. These elements probably originate from anthropogenic sources or come naturally from the soil. Metal ions such as Mn, Zn, Cu, and Co are usually found both in mineral supplements of bovines, chemical fertilizers, as well as Cd, Cr, Zn Cu, and Mn in agrotoxic formulations (27). The second and third clusters were formed by Ca, Mg, K, Fe, and Na. These associations can take place because of anthropogenic activity carried out in the area (soil correctives, chemical fertilizers) as well as be due to the influence of materials originating naturally in the soil.

CONCLUSION

A method for the multi-element determination of Ca, Cd, Co, Cr, Cu, Fe, K, Mn, Mg, Na, Ni, and Zn in ground water samples employing fast-sequential flame atomic absorption spectrometry (FS-FAAS) was demonstrated. Recovery values ranging from 84.6 to 118.2% for metal ions in three concentration levels were obtained with precision, expressed as relative standard deviations (RSD) of less than 2.2%. The results of this study show that, in general, the metal ions and nitrate concentrations in ground water samples of Culturama, Brazil, are lower than the maximum permissible limits of water for humans as established by Brazilian Regulations as follows: 10 mg L^{-1} for nitrate and 5 µg L^{-1} (Cd), 50 µg L^{-1} (Cr), 2000 µg L^{-1} (Cu), 300 µg L^{-1} (Fe), 100 µg L^{-1} (Mn), 200 000 µg L^{-1} (Na), 5 000 µg L^{-1} (Zn), and 500 µg L^{-1} (Ca+Mg).

The results obtained by the Pearson and Cluster analysis made it possible to infer probable sources of metal contamination. Activities such as agriculture and cattle raising, the use of septic tanks, and the influence of materials originating naturally in the soil can be contributing factors to the contamination by these elements in the ground water of Culturama, Brazil.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support for this research by FUNDECT and CAPES/PROP – UFMS for J.L.R.J., J.L.C.S., and N.R.P.

Received August 31, 2007.

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Preconcentration of Trace Copper in Environmental Water Samples With TiO_2 Nanotube Cartridge Prior to Flame Atomic Absorption Spectrometry

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ABSTRACT

This paper describes a new method using TiO_2 nanotubes, a new material, as solid-phase extraction adsorbent for the sensitive determination of trace copper prior to flame atomic absorption spectrometry (FAAS) analysis. Important parameters, which would affect the enrichment performance such as sample pH, the eluent and its volume, sample flow rate, sample volume, and concomitant ions have been optimized, respectively. The experimental results exhibited that copper could be adsorbed quantitatively on TiO_2 nanotubes at a pH of 7.0, and easily eluted with ethanol. Under optimal conditions, there was good linearity (R^2=0.9993) over the concentration range of 1 ~ 150 ng mL^{-1}; the detection limit was 0.94 ng mL^{-1} and the precision (RSDs) 2.3% (n=6).

This proposed method has been successfully applied to the determination of trace copper in real environmental samples and excellent results were achieved. All these facts indicate that TiO_2 nanotubes are an excellent adsorbent for the enrichment of metal ions and that the established method would be an important alterative in the environmental monitoring of metal ions.

INTRODUCTION

In recent years, environmental pollution due to heavy metals has received considerable attention worldwide; especially health and ecological problems (1) associated with environmental contamination continue to rise. Thus, the determination of trace heavy metals in environmental samples is becoming more important (2). Several sensitive methods have been developed for the determination of metal ions. Among them, flame atomic absorption spectrometry (FAAS) has been widely used for the determination of trace metal ions (3-5) due to the relatively simple and inexpensive equipment required. However, the direct determination of metal ions at trace levels by FAAS is difficult because of the lower concentrations and matrix interferences in real environmental water samples. For this reason, a preliminary preconcentration step is necessary (6-7) to improve the detection limit and selectivity.

The most widely used techniques for the preconcentration of trace elements include liquid–liquid extraction (8-9), solid-phase extraction (SPE) (10-12), precipitation and coprecipitation (13), flotation (14), ion exchange (15-16), cloud-point extraction (17-18), etc. The classical liquid–liquid extraction is usually time-consuming, labor-extensive, and requires relatively large volumes of organic solvents. As for the disposal of the organic solvent used, it also leads to a severe environmental problem. Among the various preconcentration methods, SPE is one of the most effective methods because it reduces consumption and exposure to organic solvents, disposal costs and extraction time, and it can provide more flexible working conditions and simple operation (19-22). The enrichment performance of SPE is related to the adsorbents, and the physical and chemical properties of the target analytes. The adsorbent is crucial for achieving the best performance and, in general, many materials have been proposed and applied as solid-phase extraction adsorbents, such as XAD resins (23-25), ion exchange resins, silica gel (26-27), cellulosic derivatives (28), polyurethane foam (29), active carbon (30), nanometer SiO_2 (31), and carbon nanotubes (32-34).

Copper is an essential micronutrient for the human body and plants; however, it is also a toxic substance to the organism when its concentration is over the allowable amounts. Meanwhile, superfluous absorption of Cu will affect the liver of goats, and the reports show (35) that a high supplement of copper results in an increase of γ-glutamyl transferase (GGT), glutomic oxaloacetic transaminase (GOT), and sorbitol dehydrogenase (SDH) which serve as an indicator of toxicosis. So it was very essential to establish a rapid and sensitive determination method of copper in environment. To date, some good methods based on various

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techniques have been successfully developed for the trace determination of copper. Narin et al. (36) reported a method for the determination of Cu using a 1-(2-pyridylazo) 2-naphtol (PAN) impregnated Ambersorb 563 resin as the solid phase extraction adsorbent in combination with atomic absorption spectrometry; the detection limit found was 0.67 µg L^{-1}. Soylak et al. (37-38) determined Cd(II), Co(II), Cu(II), Pb(II), Ni(II), Cr(III), and Fe(III) with flame atomic absorption spectrometry.

TiO_2 nanotubes are a new and excellent material that have attracted great attention. They have proved to have a larger surface area than multi-walled carbon nanotubes (39), and the surface area of TiO_2 nanotubes synthesized from hydrothermal treatment can reach 400 m^2/g (40), they have high chemical stability, durability, are corrosion-resistant, non-toxic, low cost, and have different band gap energies, excellent properties of photoelectricity, catalysis and gas sensitivity, etc. All of these features and merits mentioned above determined their extensive application such as catalysis (41), photocatalysis (42), and dye-sensitized solar cells. However, so far there are very few reported uses in the environmental field (43).

The main purpose of this work was to investigate the feasibility of TiO_2 nanotubes as SPE adsorbents for the extraction of trace copper and to enlarge the application of the use of TiO_2 nanotubes.

EXPERIMENTAL

Instrumentation

In this experiment, a Z-5000 Polarized Zeeman atomic absorption spectrophotometer (Hitachi Ltd., Tokyo, Japan), fitted with a copper hollow cathode lamp, was used for the determination of the target analyte. This apparatus was equipped with Zeeman-effect background correction. A SZ-93 ultrapure water apparatus was used for the preparation of ultrapure water in the laboratory (Yarong Ltd. Shanghai, P.R. China). A Model SHZ-3 (III) vacuum pump (Yuhua Instrument Co, Ltd., Zhengzhou, P.R. China) was used for concentrating the samples. The TiO_2 nanotube SPE cartridge was self-made in our laboratory.

Reagents and Standard Solutions

Hexane and dichloromethane, ethanol, and acetonitrile were obtained from Scharlau Chemie SA (Barcelona, Spain). Unless stated, all other reagents and chemicals used were of analytical grade.

Two stock standard solutions of $CuCl_2$ and DDTC (1000 µg $mL^{-1}$and 0.001 mol/L, respectively) were obtained by dissolving $CuCl_2$ and DDTC in ultrapure water. Working solutions were achieved by appropriate dilution of the stock standard solution. The pH of the working solution was adjusted with diluent hydrochloric acid (5%, v/v) and sodium hydroxide (1%, v/v).

Anatasephase TiO_2 nanotubes were synthesized with the hydrothermal treatment method in our laboratory; the specific surface area and medial aperture of TiO_2 nanotubes was 291 m^2/g and 3.66 nm determined with the linear portion of the BET plots, and JEM2011 scanning electron microscope (JEOL, Japan). The TEM image of the TiO_2 nanotubes at a magnification of 300,000 times is shown in Figure 1. The accelerating voltage was 200 kV. Before use, anatasephase TiO_2 nanotubes were dried for 2 hours at 70 °C, and then washed with methanol and ultrapure water in order to reduce the interferences of organic and inorganic contaminants.

General Procedure

Before preconcentration, the TiO_2 nanotube (200 mg) packed cartridge was prepared by modifying an Agilent ZORBAX SPE cartridge (Agilent, Santa Clara, CA, USA). The polypropylene upper and lower frit remained at each end of the cartridge to hold the TiO_2 nanotubes packing in place. Then the outlet tip of the cartridge was connected to a Model SHZ-3 (III) vacuum pump (Agilent). The inlet end of the cartridge was connected to a PTFE tube whose other end was inserted into the sample solution. Before starting the SPE procedure, 10 mL ethanol and 10 mL ultrapure water were used to wash the PTFE tube in order to remove contaminants. Then, the working

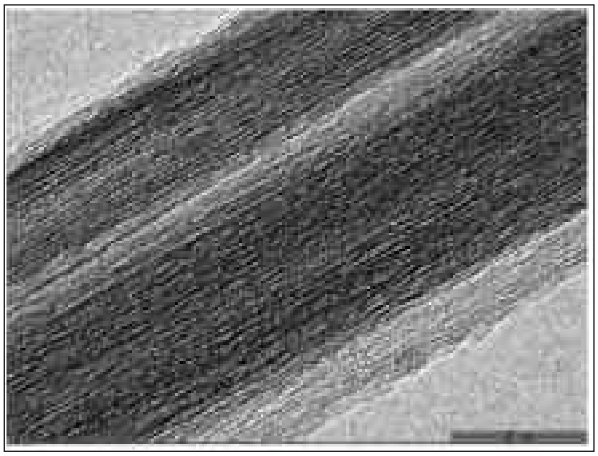

Fig. 1. The TEM image of the TiO_2 nanotubes.

solution containing Cu^{2+} ions chelated with DDTC of 120 ng mL^{-1} was passed through the minicolumn under vacuum conditions. When the preconcentration was completed, 10 mL ultrapure water was used to clean the impurity. Then the target analyte was eluted with an optimum volume of ethanol. Finally, the concentration of the Cu^{2+} was determined by FAAS. Between the extractions, the minicolumn was dried by passing air through it for 30 minutes.

Water Samples

In this experiment, four water samples were used for validating the proposed method. They were collected from 116 Factory of Xinxiang, Henan province (Sample 1), Battery Factory of Xinxiang, Henan province (Sample 2), Huanyu Battery Ltd. of Xinxiang, Henan province (Sample 3), and Jinlong Ltd of Xinxiang, Henan Province (Sample 4). All of the water samples were immediately filtrated through the 0.45 μm membrane after collection and were stored in brown reagent bottles at 4 °C.

RESULTS AND DISCUSSION

Choice of Eluent and Its Volume

The eluent is an important parameter in the SPE process which can influence the enrichment performance because it determines whether or not the analyte is eluted from the adsorbent completely. In order to ensure the target compounds to be eluted completely from the cartridge, four solvents such as ethanol, acetonitrile, nitric acid (1 mol L^{-1}), and a mixture of hexane and dichloromethane were investigated for eluting Cu^{2+} in this experiment, and it was found that ethanol was the most effective eluent for Cu^{2+}. For the sake of achieving better enrichment, a series of experiments in the range of 2–6 mL were designed for obtaining the optimal volume of ethanol. The results indicated that there was no decrease of extraction performance in the selected range and the recoveries were all over 90%. That was to say, 2 mL of ethanol was sufficient to elute the copper complex from the cartridge. Considering the cost and enrichment factor, 2 mL ethanol was adopted as the eluent throughout the experiments.

Effect of Sample pH

Usually, sample pH played an important role in the SPE step. It was an important parameter for the chelating reaction of metal ions. Generation of the complex determined whether it could be adsorbed onto the SPE adsorbent in most cases. To get excellent sensitivity, sample pH should be taken into account. In this experiment, it was investigated in the range of 3–10 and the results are exhibited in Figure 2. It can be seen that Cu^{2+} was adsorbed much better at a pH of 7 with a recovery over 90%. Hence, in the following experiments the sample pH was adjusted to 7.0.

Effect of Sample Flow Rate

Flow rate is another important factor that influences the enrichment efficiency. Because of the small size of TiO_2 nanotubes, the flow rate was optimized in the range of 0.2–0.8 mL min^{-1}. It was found that the flow rate in this range had no significant effect on the recoveries of the Cu^{2+} and the recoveries were all about 100%. Therefore, the maximum flow rate of 0.8 mL min^{-1} was selected as the optimal flow rate for further study.

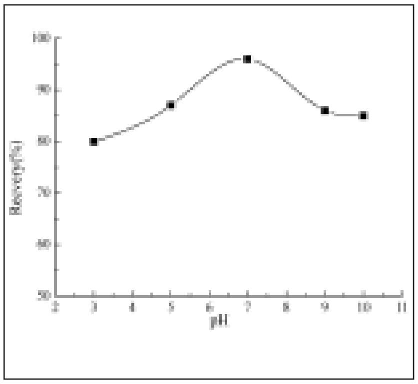

Fig. 2. Effect of pH on the recovery of Cu^{2+} on TiO_2 nanotubes.
Cu: 120 ng mL^{-1}.

Effect of Sample Volume

To obtain reliable and reproducible analytical results and a high concentration factor, sample volume is an important factor for SPE. Thus, it is necessary to investigate the influence of sample volume. For this purpose, a series of experiments ranging from 50–200 mL and spiked at the 120-ng mL^{-1} level were designed. The results are given in Figure 3. As can be seen, the recoveries of copper were between 95.8% and 97% when the volume was up to 200 mL. Finally, for the sake of saving analysis time, 150 mL was selected as the optimal sample volume.

Effect of Coexisting Substance

In general, coexisting substances will influence the determination of target ions by competing for the chelating reagent or the active sites of adsorbents. They were investigated in detail, and the working solution with the concentration of Cu^{2+} at 120 ng mL^{-1}, and different concentrations of different ions

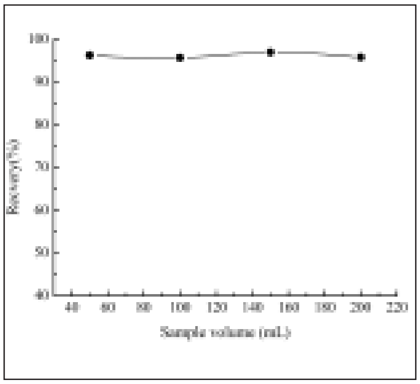

Fig. 3. Effect of sample volume on the recovery of Cu^{2+} on TiO_2 nanotubes.
Cu: 120 ng mL^{-1}.

were passed through the cartridge under the optimal conditions, and then the final eluent was analyzed by FAAS. The results in Table I show that the presence of large amounts of coexisting substances has very little influence on the enrichment of Cu^{2+}.

Analytical Performance

As a new method was established, some parameters such as linear range, correlation coefficients, and detection limit were crucial. A series of experiments were designed for obtaining such parameters and better analytical performance. These procedures were carried out under the optimal conditions. The results indicated that the proposed method earned an excellent linear range, detection limit, and precision. They were 1–150 ng mL^{-1}, 0.94 ng mL^{-1} (calculated based on three times the standard deviation of 11 runs of the blank samples) and 2.3% (n=6), respectively.

Analytical Application

Four real samples were used to evaluate the applicability and reliability of the proposed method. The results listed in Table II show that the total concentration of copper was detected in the blank real samples. In order to validate the applicability of proposed method, the spiked recoveries at two concentration levels (10 and 20 ng mL^{-1} of Cu^{2+} added) were investigated. The extraction procedure of the spiked solutions was carried out as described above. The recoveries of copper in the four samples were in the 94.6–103% range. The experimental results proved that the proposed method has good potential.

CONCLUSION

This paper investigated the enrichment power of TiO$_2$ nanotubes and developed a new method with TiO$_2$ nanotubes as the SPE adsorbents for the flame atomic absorption spectrometry (FAAS) determination of copper in environmental water samples. The experiments indicated that the proposed method was a simple, rapid and reliable method for the preconcentration of copper. Under optimal conditions, the developed method has a wide linear range over 1–150 ng mL^{-1} and high sensitivity with a low detection limit of 0.94 ng mL^{-1} Cu. The obtained recoveries of copper in the four environmental water samples ranged from 94.6–103%. These results demonstrate that TiO$_2$ nanotubes have great potential as an excellent adsorbent for the solid-phase extraction of copper in environmental water samples and could be applied for monitoring copper at trace levels in the environmental field.

ACKNOWLEDGMENTS

This work was supported by High-Tech Research & Development Planning (863 Plan) of P.R. China (2006AA06Z424), the Natural Science Foundation of Henan Province (072300460010), the Personal Innovation Foundation of Universities in Henan Province ([2005]126), the fund of Henan Normal University (No. 2006PL06), and the funds from the Henan Key Laboratory for Environmental Pollution Control.

Received March 18, 2008.

TABLE I
Effect of Coexisting Ions (Cu^{2+}: 120 ng mL^{-1})

Coexisting Ions	Conc. of Coexisting Ions (µg mL^{-1})	Recovery of Cu^{2+} (%)
Na^{+}	360	96.9
K^{+}	360	101
Zn^{2+}	3	94.7
Cd^{2+}	3	95.1
Ni^{2+}	3	90.4
Pb^{2+}	3	96.3
Cl^{-}	120	99.3

TABLE II
Results of Blank and Spiked Recoveries of Cu^{2+} in Real Environmental Samples

Sample	Blank (ng mL^{-1})	Added (ng mL^{-1})	Recovery (%)
1	2.76	10	103.0 ± 7.4
		20	99.8 ± 8.8
2	51.8	10	96.5 ± 1.5
		20	95.3 ± 3.1
3	35.2	10	99.4 ± 4.8
		20	99.8 ± 4.3
4	1.33	10	94.6 ± 1.7
		20	96.2 ± 1.4

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Solid Phase Extraction and Preconcentration of Nickel in Water Samples With Activated Carbon-PAR and Flame Atomic Absorption Spectrometry

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ABSTRACT

Preconcentration is commonly used if the concentration of trace elements in the sample is lower than the detection limit of the analytical technique. Furthermore, a number of interfering constituents can be removed by using preconcentration procedures. In this study, a simple, sensitive, accurate and selective method was optimized for determination of ultratrace levels of nickel. For this purpose, Ni was complexed with PAR and adsorbed on the activated carbon. It was found that reproducible recoveries up to 90% were achieved at the pH range of 4.0–7.0 with a contact time of 30 minutes. The adsorbed nickel was eluted by adding concentrated nitric acid and measured by flame atomic absorption spectrometry (FAAS). The optimized enrichment method was applied to the determination of nickel in natural water samples. The detection limit was found to be 0.6 ng mL^{-1}. The relative standard deviation (RSD) was found to be 9% by using 300 mL of 10 ng mL^{-1}Ni, for 10 replicate enrichment procedures. Nickel concentrations in the studied water samples were found to be in the ranges of 3.0–57 ng mL^{-1}.

INTRODUCTION

Nickel (Ni) is a metal component of the seven microbial enzymes which includes urease, hydrogenase, CO-dehydrogenase, methylcoenzyme M reductase, Ni-superoxide dismutase, glyoxylase I, and cis–trans isomerase. As such Ni is considered to be essential to plants, humans and some domestic animals. Some nickel-containing enzymes have also been studied with regard to their relationship to human diseases. For example, the bacteria *Helicobacter pylori* is suspected to cause ulcer and gastric carcinoma. However, basic dietary requirements of nickel for man have not been established. More attention has been focused on the toxicity of nickel in low concentrations since it has been found that nickel can cause allergic reactions and certain nickel compounds may be carcinogenic (1). In 1998, guidelines for maximum allowable Ni in drinking water were established at 20 ng mL^{-1} by international regulations such as WHO and other international and local authorities (2). In the literature, nickel concentrations were found to be in the range of 0.37-11.0 µg L^{-1} for tap, 0.11-19.3 µg L^{-1} for river and 0.1-12.2 µg L^{-1} for seawater (3-25). However, higher Ni concentrations were reported by some authors (16-17). As a result, there is a growing interest in the determination of Ni in the environment and in food samples (7,26-27). Due to the allowable low levels of Ni in foods and beverages and its very low concentration in natural water samples as described above, reliable and sensitive analytical methods are required for determination of this metal in those samples. For this purpose, the analytical methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES) (8-9), electrothermal atomic absorption spectrometry (ETAAS) (2-13,18,23), voltammetry (19-21), and inductively coupled plasma mass spectrometry (ICP-MS) (22), are generally used. However, the disadvantages of ETAAS analysis include interferences from matrix components, relatively long analysis times, and high level expertise of the analyst. It is interesting that graphite furnace atomic absorption spectrometry (GFAAS) and ICP-MS are also used with preconcentration procedures for Ni determination in water despite their high sensitivities (12-13,18,22-23). On the other hand, flame atomic absorption spectrometry (FAAS) in conjuction with preconcentration techniques and enrichment procedures is considered the best analytical method for Ni and other ultratrace metal determinations (3-7,14-17,24-35). There has been significant interest in recent years in solid-phase extraction (4, 6-10, 12-18,22-25) as well as liquid-liquid extraction (36) and the other similar preconcentration techniques (3, 5,11) to preconcentrate trace metals. The reported nickel levels in natural water samples are given in Table I. As can be seen from these values, amberlite XAD species and activated carbon (AC) were mostly used as the adsorbent for preconcentration of metals at the ng mL^{-1} level. Moreover, activated carbon was also used for speciation studies (37-38). An important strategy for metal enrichment is the incorporation of complexing reagents in solid supports. Thus, enrichment of trace elements onto AC from waters is usually carried out after chelation with organic reagents such as 8-hydroxyquinoline

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TABLE I
Nickel Concentrations Determined in Various Natural Water Samples in the Literature and in This Study
(The results in this study are mean values ± standard deviation; n = 3.)

Water Type	Enrichment Technique	Measurement Technioque	Ni Found (ng mL^{-1})	Ref.
Tap	[a]SPE-XAD-2	FAAS	76 (1.3 µM)	16
River			447 (7.6 µM)	
Tap	SPE-XAD-2	FAAS	3.1	6
River			2.6-3.6	
Tap	SPE-XAD-2	FAAS	1.2	25
River			73-112	
Fresh	SPE-XAD-2	FAAS	0.19-1.53	24
Tap	SPE-XAD-2	ICP-AES	0.96	9
River			6.34	
Tap	SPE-XAD2	FAAS	0.74	4
River			7.63	
Tap	SPE-XAD-4	UV-Vis.Spect.	0.46-0.94	10
Well Water			1.6	
River	SPE-XAD-4	GFAAS	5.1-19.3	23
Tap	SPE-activated carbon (XAD-4)	FAAS	6.0-10.4 (5.9-11.0)	15
Tap	SPE-activated carbon	FAAS	1.0-5.0	7
Stream			1.0-8.0	
Lake			15	
Dam Lake-River			2.0	
Tap	SPE-activated carbon	ICP-AES	3.1-4.25	8
River			1.49-1.80	
Tap	SPE-activated carbon	FAAS	2.2-8.1	14
Delta	SPE-pore glass	GFAAS	0.2-2.5	13
Tap	SPE-C18 cartridge	HPLC(AAS)	31.5(30.2)	17
River			48.4(49.8)	
River	SPE-poly(N-isopropyl-acrylamide)	ICP-MS	2.05	22
Mineral	SPE-poly vinyl pyrrolidinone	GFAAS	25	18
Sea			43	
Sea	SPE-silicagel	ETAAS	2.34	12
Tap	Cloud point	FAAS	5.19	3
River			0.11	
Sea			0.10	
Tap	Cloud point	FAAS	2.87	5
River			4.88	
Sea			4.51	
Tap	Cloud point	UV-Vis.Spect.	Not detected	11
River			10.4	
Sea			12.2	
Tap		Voltammetry	0.51-3.02	19
Tap		Voltammetry	0.37 (6.3 nM)	20
River			0.48 (8.2 nM)	
Tap		Voltammetry	0.53 (8.9 nM)	21
River			0.94 (16 nM)	
Underground			1.77 (30 nM)	

[a] SPE = Solid Phase Extraction.

Table I continued on next page....

(oxine), ammonium pyrrolidine dithiocarbamate (APDC) and cupferron (26-35). 4-(2-pyridyl-azo) resorcinol (PAR) is a versatile organic chromogenic reagent and it forms complexes with a variety of transition metals at different pH ranges and different adsorbents. The other advantage of PAR is the absence of its affinity for alkali and alkaline-earth ions.

In this study, a preconcentration method based on adsorption of nickel- PAR complexes on the activated carbon was modified for the determination of nickel at the ng mL^{-1} level by FAAS. The optimized method was applied to nickel determination in different natural waters.

EXPERIMENTAL

Instrumentation

An ATI UNICAM Model 929 flame atomic absorption spectrophotometer, equipped with an ATI UNICAM hollow cathode lamp, was used for the determinations (UNICAM, Cambridge, England). The optimum conditions for FAAS are given in Table II. The pH was measured with a Schlott Lab-Star pH meter (Schlott Lab Tech GmbH, Vienna, Austria). In the enrichment procedure, magnetic stirrers and a centrifuge were used.

TABLE II
Operating Parameters for FAAS

Parameters	
Wavelength	232 nm
HCL Current	7.5 mA
Type of Flame	Air - C_2H_2
Background Correction	D_2 Lamp
Slit Width	0.2 nm
Air Flow Rate	4.0 L min^{-1}
Acetylene Flow Rate	0.6 L min^{-1}

TABLE I (continued from previous page)

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Water Type	Enrichment Technique	Measurement Technique	Ni Found (ng mL^{-1})	Ref.
Elazig City Tap	SPE-activated carbon	FAAS	3.0±0.4	This study
Elazig-Harput Tap	“		14±1	
University Tap	“		3.0±0.3	
Keban Dam Lake	“		3.0±0.4	
Karakaya Dam Lake	“		4.0±0.5	
Mineral Water	“		10.0±1.0	
Dicle River - polluted	“		57±5	
Dicle River - unpolluted	“		9.0±1.0	
Hazar Lake	“		12±1	
Hazar Lake + 5.0 ng mL^{-1} Ni	“		16.7; Rec: 94%	
Hazar Lake + 10 ng mL-1 Ni	“		21.6; Rec: 92%	
Hazar Lake + 15 ng mL^{-1} Ni	“		26.8; Rec: 96%	
Std. Ref. Material (SPS-SW2 Batch 113)	“		Cert: 50.0±0.3 Found: 49±0.4 Rec: 98%	

Cert = Certified; Rec = Recovery.

Reagents and Standard Solutions

All glassware (Pyrex®) was kept permanently full of 1M nitric acid when not in use. In the digestion work, concentrated HNO_3 was used for decomposition of adsorbed Ni-PAR complexes on the activated carbon. The standard diluted solutions were prepared from stock standard nickel solution of 1000 mg L^{-1} (Merck, Darmstadt, Germany).

The citrate buffer solutions of pH of 3.0–8.0 were prepared by adding 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions to 0.1 mol L^{-1} sodium citrate solutions. The phthalate buffer solutions of pH of 3.0–8.0 were prepared by adding 0.1 mol L^{-1} HCl or 0.1 mol L^{-1} NaOH solutions to 0.1 mol L^{-1} potassium hydrogen phthalate solutions. The PAR solution of 0.05 % was prepared by dissolving 0.05 g of 4-(2-pyridyl-azo) resorcinol in 100 mL of 0.1M NaOH.

The activated carbon (Merck) was purified by pretreating with concentrated HCl (Merck) for 3 hours, washing with distilled water, drying at 110 °C and treating with aqua regia (hydrochloric acid-nitric acid (3+1)) for 24 hours, as described elsewhere with slight modification (28). The mixture was filtered through filter paper (Advantec Toyo 5 B, white ribbon, Advantec Tokyo Kaisha Ltd., Tokyo, Japan), washed with water and dried at 110 °C. A suspension of 25 mg mL^{-1} in distilled water was prepared from this dried activated carbon.

Enrichment Procedure

In the optimization studies, 60 mL of a 100 ng mL^{-1} nickel solution including the matrix components: Ca 100 mg L^{-1}, Mg 50 mg L^{-1}, Fe and Al 2 mg L^{-1}, were used as model solutions. The pH of this solution was adjusted to desired value by adding the solutions of diluted HCl and NaOH. After adding the necessary buffer solution (10 mL), PAR as complexing agent (20 mL of 0.05%) was added. Then, the activated carbon suspension of 25 mg mL^{-1} was added and pH of the mixture was again adjusted to the studied pH, if necessary. The mixture was stirred mechanically for 30 min and filtered through a filter paper (Advantec Toyo 5 B, white ribbon). The residue was dried at 105 °C for 1 hour. After transferring the residue to a glass beaker, 4 mL of concentrated HNO_3 was added and the mixture evaporated to near the dryness. The steps of enrichment scheme are given in Figure 1.

RESULTS AND DISCUSSION

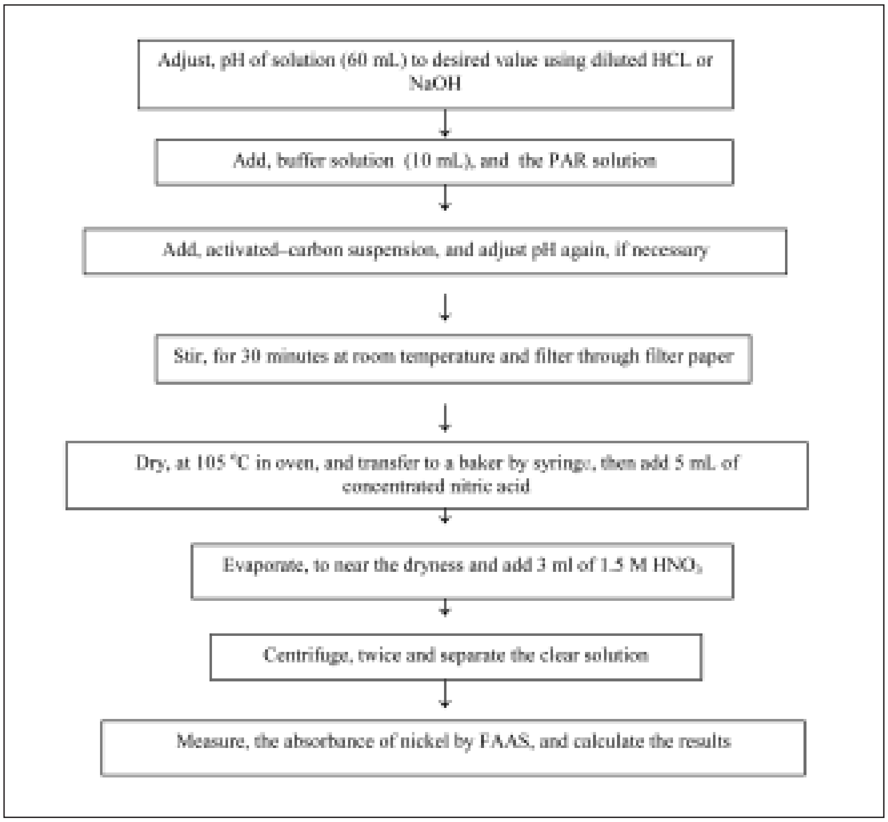
All parameters that were thought to affect the enrichment and measurement steps in the analytical scheme were examined. These parameters were investigated by using the model nickel solutions of 100 ng mL^{-1}. The effect of each parameter was tested three times.

Influence of pH on Recovery

The model Ni solutions were preconcentrated as shown in Figure 1 by using pH values ranging from 3.0 to 8.0 to determine if preconcentration yield is dependent upon the pH. The recoveries obtained are given in Figure 2. It can be seen that maximum recoveries (up to 90%) were found in the pH range of 4.0–7.0 for the phthalate buffer and 4.0–7.0 for the citrate buffer. Therefore, in all subsequent studies, citrate buffer was used at the pH of 4.5± 0.2.

Effect of the Amount of PAR on Recovery

In order to determine the optimum amount of PAR, the recoveries of nickel at the optimum pH (4.5 ± 0.2) were examined by using different volumes of 0.02% PAR and phthalate buffer, and adding 125 mg of activated carbon suspension (5 mL of 25 mg mL^{-1}). It can be seen from Figure 3 that the recoveries increase up to 90% by using PAR of 15 mL and do not change by adding up to 30 mL. Thus, 20 mL of 0.05% PAR was used in the subsequent studies. The slight decrease in the recovery after adding 40 mL of PAR may be attributed to desorption of the adsorbed Ni-PAR complex or the dissociation of the formed Ni-PAR complex.



Adjust, pH of solution (60 mL) to desired value using diluted HCL or NaOH

Add, buffer solution (10 mL), and the PAR solution

Add, activated–carbon suspension, and adjust pH again, if necessary

Stir, for 30 minutes at room temperature and filter through filter paper

Dry, at 105 °C in oven, and transfer to a baker by syringe, then add 5 mL of concentrated nitric acid

Evaporate, to near the dryness and add 3 ml of 1.5 M HNO_3

Centrifuge, twice and separate the clear solution

Measure, the absorbance of nickel by FAAS, and calculate the results

Fig. 1. Steps of analytical scheme in the enrichment procedure.

Effect of Amount of Activated Carbon on Recovery

In order to determine the optimum amount of the activated carbon (AC), different amounts of the AC were added to the model nickel solutions described above.

The enrichment procedure at the other optimum conditions (pH=4.5 and 20 mL of PAR) was applied. It was found (see Figure 4) that the recoveries increased up to 90% by adding 4 mL AC (100 mg) and it does not change by increasing up to 6 mL (150 mg). Thus, 125 mg of AC was used in all subsequent studies.

Effect of Stirring Time on Recovery

The enrichment procedure was applied to the model nickel solutions by using different stirring times at the other optimum conditions. Figure 5 shows that a contact time of 25 minutes was sufficient for maximum recovery (up to 90%), and the recoveries do not change by stirring up to 60 minutes. The obtained optimum stirring time is significantly shorter in comparison to? the rather long contact time of 4 hours as reported for maximum

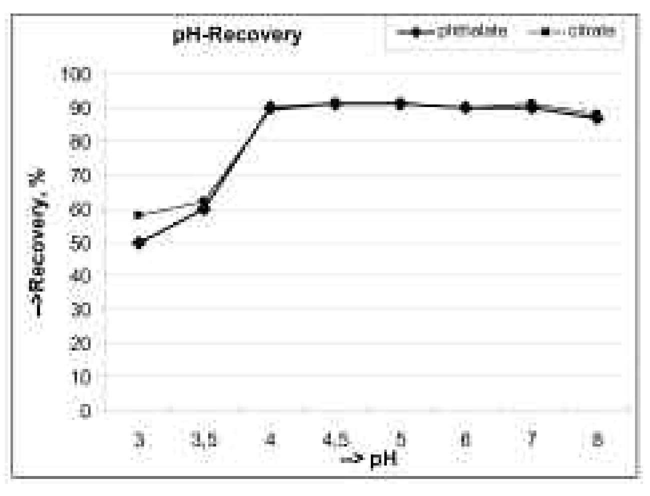


Fig. 2. Influence of pH on recovery of Ni with AC-PAR.

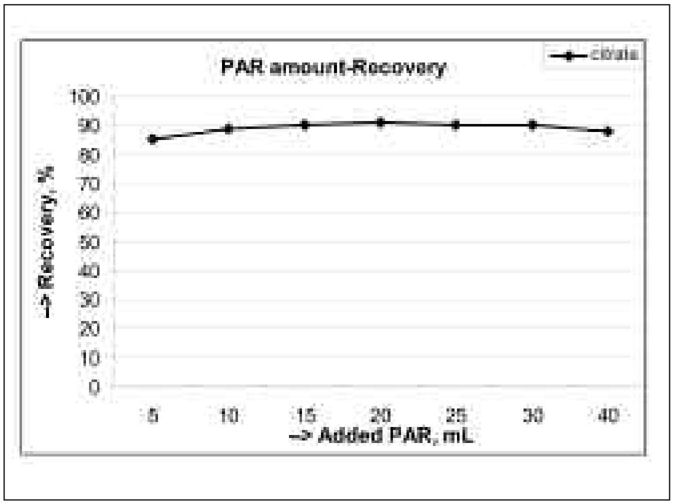


Fig. 3. Influence of amount of PAR on recovery of Ni.

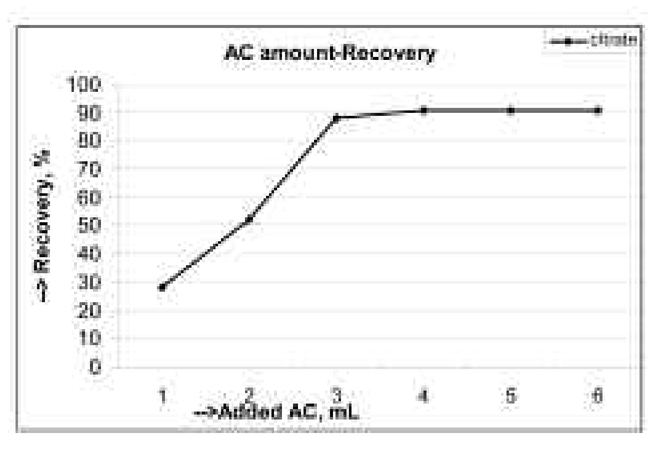


Fig. 4. Effect of amount of AC on recovery of Ni.

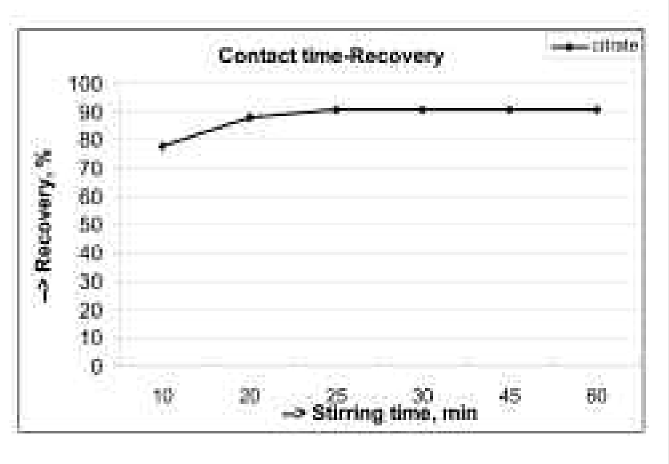


Fig. 5. Effect of stirring time on recovery of Ni with AC-PAR.

recovery in the literature (39). So, the stirring time of 30 minutes was used in all studies.

Effect of Elution Volume on Recovery

The efficiency of the eluant (1.5M HNO_3) was studied by taking different volumes (1.5–4.0 mL). It was found that 2.5 mL of 1.5M HNO_3 was sufficient for maximum recovery (90%) of Ni. Therefore, 3.0 mL of 1.5M HNO_3 was used for the complete desorption of the adsorbed nickel.

Analytical Performance

The calibration curve was observed to be linear at the concentration range of 2–20 ng mL^{-1} by bringing 300 mL of solution to a final volume of 3.0 mL. As a result, the enrichment factor of 100-times was achieved. The equation of the curve was as follows:

$$y = 6.7411 X + 0.8407; R^2 = 0.9998$$

The relative standard deviations (RSD) were 9% for 300 mL of 10.0 ng mL^{-1} for 10 replicate enrichment procedures. The level of Ni in the blank was found to be 0.6 ng mL^{-1} with a standard deviation of 0.2 ng mL^{-1}. Therefore, the detection limit (LOD) defined as three times the standard deviation of the blank was 0.6 ng mL^{-1} when 300 mL of solution was preconcentrated to a final volume of 3.0 mL.

The accuracy of the method was studied by examining the Standard Reference Material (reference material for measurement of elements in surface waters) SPS-SW2 Batch 113 (Spectrapure Standards As, Oslo, Norway). The results in Table III show that the recovery value for Ni is 98%. In addition, the accuracy of the method was studied by examining the recoveries of nickel from water samples fortified with this element. The results in Table I show that, at least, 92% of the nickel added to the water samples was recovered.

Applications

The studied water samples were obtained from the vicinity of Elazig city at the east coast of Turkey. Considering the concentration of Ni ions in the studied samples, a 300-mL of water sample was transferred into a 600-mL beaker. The optimized enrichment method was applied to this sample. The obtained results are given in Table I. The values given are the mean values of three different portions of the same sample. The nickel concentrations in the studied water samples were found to be in the range of 3.0–57 ng mL^{-1}. These results are in agreement with the many values found in the literature (Table I). The concentrations observed are lower than the maximum allowable Ni (20 ng mL^{-1}) in drinking water by WHO, except the Dicle river water which has been polluted by an abandoned copper mine.

CONCLUSION

A sensitive, selective, and reliable preconcentration method was modified by adsorption of nickel-PAR complexes on AC for the determination of Ni at ultratrace levels. Matrix components were characterized and upper concentration levels of the matrix components were added to all standard Ni solutions. Sensitivity and reproducibility were examined considering the probability of chemical interferences in natural waters where some metals in the studied water samples are at higher levels than in tap and natural surface waters. The relative standard deviation (RSD) was found to be 9% by using 300 mL of 10 ng Ni mL^{-1} for 10 replicate preconcentration procedures. The sensitivity of flame atomic absorption spectrometry (FAAS) was increased up to 100-times by using the optimized method, resulting in a detection limit of 0.6 ng Ni mL^{-1}.

Received April 12, 2008.

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Atomic Spectroscopy
Vol. 29(4), July/August 2008

Practical Guide to ICP-MS: A Tutorial for Beginners - Second Edition

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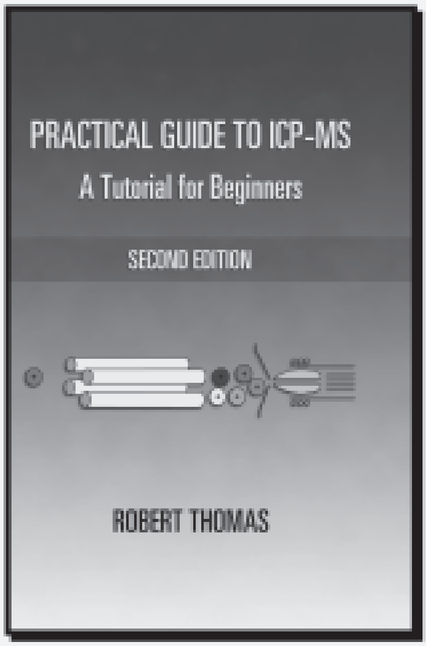

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Publisher: CRC Press/Taylor and Francis

Catalog No. 67869, ISBN:978-1-42006-786-6 at $109.95/£57.99 each. June 2008, 365 pages.

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