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Comparative Procedures for the Sample Decomposition of Rocks Used in Organic Agriculture and the Determination of Cu, Fe, Mn, and Zn by FAAS

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INTRODUCTION

For the proper development and growth, plants need essential elements such as nitrogen, phosphorus, potassium, copper, iron, manganese, and zinc which, based on their concentration, are classified as macro- or micronutrients. Copper, Fe, Mn, and Zn are usually classified as micronutrients. These elements are important because they impact the catalysis of enzymatic reactions; protein, carbohydrate, and chlorophyll synthesis; the biological fixation of N in leguminous plants; an increase or decrease in the plant's resistance to fungal and bacterial diseases; photosynthesis and the metabolic functions; make P and Ca available; and form auxins, which are the hormones that regulate vegetative development (1).

Normally, micronutrients are obtained from inorganic sources, synthetic chelates, organic complexes, and silicate oxides (2). Since for the organic approach to agriculture, use of soluble inorganic materials as nutrients are not acceptable (salts such as KCl, KNO_3, $NH_4H_2PO_4$, and others), and since there is a growing tendency to produce organically grown foods and plants, alternative nutrient sources have been proposed and are widely employed such as rocks, bovine dung, and some compounds produced by fermentation (3).

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ABSTRACT

The aim of this work was to develop an appropriate sample preparation procedure for the flame atomic absorption spectrometry determination of Cu, Fe, Mn, and Zn in rocks used in organic agriculture as a source of macro- and micronutrients.

Six different procedures were evaluated and are classified into three groups: (a) pressure digestion system with Teflon bombs, (b) conventional wet digestion in a digester heating block, and (c) closed microwave system with pressure and temperature control.

Two standard reference materials and two commercial samples were analyzed. It was found that the closed microwave system required low reagent consumption, less time, and resulted in low contamination.

Today, about $5 billion worth of organically grown products are shipped around the globe per year, and Brazil exports about $100 million per year, mainly coffee, cotton, sugar, and soy.

Ground rocks used in organic agriculture can vary in their chemical composition. They should be insoluble, and have as their main role the ability to gradually increase the soil's fertility by supplying the proper amounts of macro- and micronutrients (4).

In Brazil, some "organic producers" use and sell insoluble rocks for this purpose. Thus, the quantitative evaluation of inorganic minerals is necessary for quality control of these products.

There are several methods proposed in the literature for the treatment of rock samples for metals determination. Some of the methods employed include fusion (5,6), suspension of dry powders (7,8), acid decomposition (using Teflon® bombs) (9), pressurized Teflon vessels (6,10), microwave systems (11,12), hot plate (6,13,14), ultrasonic extraction (15), and chemical extraction (16). In general, methods that employ microwave as a source of energy are faster, less prone to contamination, consume less reagents, and offer better accuracy and precision.

The present paper aims to compare six different digestion procedures for the analysis of rock samples used in organic agriculture by employing Teflon bombs, glass digestion tubes, and a microwave oven for subsequent determination of Cu, Fe, Mn, and Zn by flame atomic absorption spectrometry (FAAS). The individual performance of each sample preparation procedure for each sample analyzed is described. As a result, a unique procedure is proposed for the determination of Cu, Fe, Mn, and Zn in single or simultaneous analysis.

EXPERIMENTAL

Instrumentation

The analyses were carried out with a PerkinElmer® AAnalyst™ 100 atomic absorption spectrometer, equipped with continuous

source background correction (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The instrumental parameters are given in Table I.

Household Teflon bombs, a Model TE-015 150 digester heating block with a 15-vessel capacity (Tecnal, Piracicaba, Brazil), and a Multiwave® microwave oven sample preparation system equipped with six 20-mL pressure decomposition TFM vessels (Anton Paar, Graz, Austria), were employed to dissolve the samples.

Reagents, Reference Solutions, and Samples

High-purity deionized water obtained with a Milli-Q™ water purification system (Millipore, Bedford, MA, USA) was used throughout the study. All inorganic acids were of analytical grade (HNO₃ 65%, HCl 37%, HClO₄ 70–72% from Merck, Darmstadt, Germany, and HF 48% from Jean Lab, Ribeirão Preto, Brazil). Hydrogen peroxide 30% (Merck, Darmstadt, Germany) was used in digestion procedure number 4. For preparing saturated solutions in order to remove excess HF, H₃BO₃ (99.5%, Synth, Diadema, Brazil) was used.

Analyte stock solutions (1000 mg L⁻¹) were prepared by appropriate dilution from standard atomic absorption solutions (Normex,, Carlo Erba, Milan, Italy). For calibration, the analytical solutions within the range of 0.5–8.0 mg L⁻¹ (Cu), 0.5–6.0 mg L⁻¹ (Fe), 0.2–2.5 mg L⁻¹ (Mn), and 0.1–0.8 mg L⁻¹ (Zn) were prepared in 1% HNO₃ by appropriate dilution of the stock solution.

Standard reference materials, used for evaluating the accuracy of the methods, included NIST 120c (Phosphate Rock) and GBW 07104 (Rock). Filter papers, medium filtration (Framex, Diadema, Brazil) were used.

TABLE I
Instrumental Parameters (AAnalyst 100 AA Spectrometer)

Element-specific Parameters	Cu	Fe	Mn	Zn
Light Source	HCL	HCL	HCL	HCL
Current (mA)	15	30	30	15
Wavelenght (nm)	324.8	248.3	279.6	213.9
Slit (nm)	0.7	0.2	0.2	0.7
Working Range (mg L⁻¹)	0.5–8.0	0.5–6.0	0.2–2.5	0.1–0.8

Instrument-specific Parameters	
Background Correction	Deuterium Lamps
Measurement Mode	Integrated Absorbance
Flame	Air/Acetylene (oxidizing)

The six decomposition procedures, listed in Table II, are as follows:

Procedure 1 used Teflon bombs and $1HNO_3 : 3HCl : 1HClO_4 : 4HF$ (v/v);

Procedure 2 used a digester heating block and $3HNO_3 : 1HCl$ (v/v);

Procedure 3 used a digester heating block and $1HNO_3 : 3HCl$ (v/v);

Procedure 4 used a digester heating block and $3HNO_3 : 1H_2O_2$ (v/v);

Procedure 5 used a microwave oven and $5.5 HNO_3 : 0.5 HF$ (v/v);

Procedure 6 used a microwave oven and $3HNO_3 : 1HCl : 2HF$ (v/v).

All measurements of integrated absorbance were made with at least three replicates.

RESULTS AND DISCUSSION

When hydrofluoric acid was used in the digestion procedure, a saturated solution of H_3BO_3 was added after dissolution to help removal of the remaining fluoride ions by formation of volatile tetrafluoboric acid. Otherwise, HF could damage the impact bed, the inside of the nebulizer, and other components of the nebulizer chamber (10,17,18). In some cases, a gelatinous precipitate of borosilicate was formed due to the high concentration of silicon in the samples. Rantala and Loring (19) observed that this precipitate has no adverse effects on trace element determination and removal of the bulk of the silicates is desirable.

According to the producer of MB-4 Rock (trade name for powdered rock), this rock consists of a mixture of serpentine and mica-schist, several silicates (total of 48%) such as magnesium, calcium, and iron, as well as P, K, and S, including micronutrients such as Co, Cu, Fe, Mn, and Zn. MB-4 is a calcareous substance, an important component of soil, and for best results should be applied to the soil together with organic compounds such as bovine dung.

The IPIRÁ Rock (also a trade name) is recommended for the enrichment of soil with macronutrients. It consists of volcanic minerals that suffered 1100–1300ºC heat, causing the chemical reduction of the elements P, Ca, and Mg into thermophosphate, CaO, and MgO, respectively. Its chemical composition is 11% CaO, 4% K_2O, 7% P_2O_5, and 3.5% MgO. Another advantage of this rock is that this elevated volcanic heating promoted better availability of the micronutrients to the plants.

TABLE II
Tested Decomposition Procedures

IDᵃ	Group	System	Sample Mass (g) / Final Volume (mL)	Reagents	Time/Power or Temperature
1	I	Teflon Bombs (17)	0.2 or 0.4 / 25	HNO_3 (1 mL) HCl (3 mL) HF (4 mL) $HClO_4$ (1 mL)	15 min / 65°C (opened bombs) 4 h / 120°C (closed bombs) near dry (opened bombs)
2	II	Digester Heating block	0.6 / 50	HNO_3 (3 mL) HCl (1 mL)	5 h / 120°C
3	II	Digester Heating Block	0.6 / 50	HNO_3 (1 mL) HCl (3 mL)	5 h / 120°C
4	II	Digester Heating Block	0.6 / 50	HNO_3 (3 mL) H_2O_2 (1 mL)	5 h / 120°C
5	III	Microwave Oven	0.2 / 25	HNO_3 (5.5 mL) HF (0.5 mL) H_3BO_3 (3 mL)	35 min ᵇ / 1000 W 20 min / 0 W 10 min / 1000 W 15 min / 0 W
6	III	Microwave Oven	0.2 / 25	HNO_3 (3 mL) HCl (1 mL) HF (2 mL) H_3BO_3 (12 mL)	40 min ᶜ / 1000 W 20 min / 0 W 10 min / 1000 W 15 min / 0 W

ᵃ Decomposition procedure identification, ᵇ 5 min (ramp) and 30 min (hold), ᶜ 40 min (hold).

It is interesting to note that although IPIRÁ Rock is generally used to increase the macronutrients in soil, the Cu, Fe, Mn, and Zn quantities are approximately equal or higher in comparison to the same elements in MB-4 Rock (see Tables III, IV, V, and VI).

Another experimental observation was that SRM 2 (NIST 120 c) is more easily soluble in any acid mixture than SRM 1 (GBW 07104), regardless of the procedure employed. The concentrations obtained for the four analytes in the SRM 2 sample were always in agreement with the corresponding certified values.

Table III illustrates the importance of using HF, and an increase in pressure and temperature for the accurate Cu determination in SRM 1 (GBW 07104). Similar results were obtained for the commercial MB-4 Rock sample regardless of the procedure used, whereas better results were observed for the commercial IPIRÁ Rock sample using HF in the closed systems (procedures 1, 5, and 6) or with aqua regia in an open system (procedure 3). Halicz and Brenner (8) studied the effects of grinding time for silicate rock slurries (as for MB-4 Rock) and their vitreous materials and suspensions of clay minerals using an inductively coupled plasma with high-solids nebulizer.

They verified that Cu was less affected by grinding time because its bonding strength in rock-forming silicates is exceptionally low and also does not form stable solid solutions with these minerals. For the elements Fe and Mn, an increase in grinding time was important for the response of intensity ratio of analyte : Sc internal standard (8).

Table IV illustrates the importance of HF in destroying the silicates present in MB-4 Rock for the accurate determination of Fe. It was found that digestion procedure 1 [Teflon, bombs and $1HNO_3$: 3HCl : $1HClO_4$: 4HF (v/v)] and procedure 6 [microwave oven and $3HNO_3$: 1HCl : 2HF (v/v)] were more

TABLE III. Cu Concentration (mg/kg) Determined in Four Rock Samples
Using Six Different Decomposition Procedures
The Certified and Recommended Values for Cu in SRM 1 (GBW 07104) and SRM 2 (NIST 120 c)
are 55.0 mg/kg and 12.8 mg/kg, respectively.

| Sample | Decomposition Procedures | | | | | |
| | No. 1 | No. 2 | No. 3 | No. 4 | No. 5 | No. 6 |
	Teflon bombs $1HNO_3$: 3HCl 4 HF: $1HClO_4$	Digester Heating Block $3HNO_3$: 1HCl	Digester Heating Block $1HNO_3$: 3HCl	Digester Heating Block $3HNO_3 : 1H_2O_2$	Microwave Oven 5.5 HNO_3 : 0.5HF	Microwave Oven $3HNO_3$: 1HCl : 2HF
SRM 1	54.3 ± 0.9	37.4 ± 1.0	37.2 ± 0.9	37.5 ± 1.3	55.3 ± 0.6	55.6 ± 0.1
SRM 2	12.1 ± 0.5	12.2 ± 0.4	12.5 ± 0.2	12. ± 0.6	10.1 ± 0.3	12.2 ± 0.7
MB-4	23.2 ± 0.6	19.2 ± 0.8	18.3 ± 0.8	21.1 ± 0.7	20.8 ± 0.2	22.1 ± 0.3
IPIRÁ	181.6 ± 3.6	131.9 ± 2.4	178.8 ± 1.6	147.2 ± 1.1	175.5 ± 6.5	172.2 ± 8.6

TABLE IV. Fe Concentration (mg/kg) Determined in Four Rock Samples
Using Six Different Decomposition Procedures
The Certified Values for Fe in SRMs 1 (GBW 07104) and SRM 2 (NIST 120 c)
are 3.0 mg/kg and 7554 ± 324 mg/kg, respectively.

| Sample | Decomposition Procedures | | | | | |
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
SRM 1	2.5 ± 0.2	3.1 ± 0.1	3.3 ± 0.2	1.6 ± 0.1	3.4 ± 0.2	3.6 ± 0.3
SRM 2	7431 ± 190	7449 ± 313	7837 ± 165	7585 ± 273	7286 ± 58,3	*
MB-4	44467 ± 978	437.2 ± 27.5	317.8 ± 25.2	316.9 ± 29.4	38177 ± 1832	47871 ± 2489
IPIRÁ	41038 ± 2298	40882 ± 1881	41825 ± 2635	37662 ± 942	34668 ± 2531	47695 ± 3052

* Lost sample.

TABLE V. Mn Concentration (mg/kg) Determined in Four Rock Samples
Using Six Different Decomposition Procedures
The Certified Values for Mn in SRM 1 (GBW 07104) and SRM 2 (NIST 120 c)
are 604 mg/kg and 209.1 ± 14.6 mg/kg, respectively.

| Sample | Decomposition Procedures | | | | | |
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
SRM 1	543.5 ± 19.6	610.4 ± 31.7	672.2 ± 32.3	534.8 ± 17.6	520.0 ± 24.4	540.7 ± 34.1
SRM 2	192.1 ± 4.2	219.6 ± 16.7	199.5 ± 15.5	199.2 ± 14.8	178.2 ± 13.4	173.3 ± 12.3
MB-4	776.8 ± 66.0	619.7 ± 21.7	561.9 ± 29.8	596.4 ± 37.6	666.7 ± 25.7	640.3 ± 17.3
IPIRÁ	3702 ± 248	1566 ± 119	1684 ± 108	1924 ± 94,3	2323 ± 57,9	2253 ± 46.5

TABLE VI. Zn Concentration (mg/kg) Determined in Four Rock Samples
Using Six Different Decomposition Procedures
The Certified and Recommended Values for Zn in SRM 1 (GBW 07104) and SRM 2 (NIST 120 c)
are 71.0 mg/kg and 72.3 mg/kg, respectively.

| Sample | Decomposition Procedures | | | | | |
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
SRM 1	76.5 ± 4.1	105.3 ± 5.7	76.2 ± 4.2	56.9 ± 3.8	74.0 ± 3.7	75.3 ± 5.4
SRM 2	77.9 ± 4.6	76.9 ± 3.3	70.3 ± 3.1	101.2 ± 4.9	69.4 ± 1.2	72.7 ± 1.6
MB-4	45.4 ± 1.7	55.8 ± 2.2	66.5 ± 1.3	51.7 ± 1.9	46.9 ± 2.4	44.8 ± 1.3
IPIRÁ	101.4 ± 2.7	69.2 ± 3.5	104.8 ± 5.6	102.8 ± 7.1	70.9 ± 1.2	76.3 ± 4.4

adequate; they provided the nearest values of Fe in comparison to procedure 5 [microwave oven and 5.5 HNO_3 : 0.5 HF (v/v)]. For this specific sample, HF addition is indispensable.

Table V shows the agreement results for Mn concentration in MB-4 Rock for procedure 2 [digester heating block and $3HNO_3$: 1HCl (v/v)], procedure 4 [digester heating block and $3HNO_3$: $1H_2O_2$ (v/v)], procedure 5 [microwave oven and 5.5 HNO_3 : 0.5 HF (v/v)], and procedure 6 [microwave oven and 3.0 HNO_3 : 1HCl : 2HF (v/v)] as well as the agreement results for Mn in IPIRÁ Rock using procedures 5 and 6. Contamination of these samples was observed when employing procedure 1 (Teflon bombs and $1HNO_3$: 3HCl : $1HClO_4$).

Table VI shows the importance of a closed system as the digestion procedure since open systems are very prone to Zn contamination. The contamination is aleatoric and can occur even with Teflon bombs. In this procedure, the bombs are initially exposed to ambient air for 15 minutes and then for an additional period of time for near dryness to eliminate all remaining HF (17) (Table II). Best results for the determination of Zn were obtained with procedure 5 [microwave oven and 5.5 HNO_3 : 0.5 HF (v/v)] and procedure 6 [microwave oven and $3HNO_3$: 1HCl : 2HF (v/v)].

Another experimental observation was that the studied rocks are not completely soluble in the absence of HF. In this case, it was necessary to filter the samples before analyzing the filtrates. The residue was always discarded.

CONCLUSION

In general, best results for the analytes Cu, Fe, Mn, and Zn were obtained when using HF for the acid mixture and employing a closed microwave system. This procedure demands less time, contamination is avoided, digestion is complete, and the results obtained are more accurate and precise than with the other techniques.

In cases of unknown rock samples routinely analyzed, it is recommended to employ procedure 6 [microwave oven and $3HNO_3$: 1HCl : 2HF (v/v)], since only 2 mL of HF is necessary for the determination of Fe and for the complete destruction of possible silicates and chromites - $FeCr_2O_4$ (11,18).

No optimization was performed to decrease the required time for the procedures involving the microwave system.

ACKNOWLEDGMENTS

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On-line Solid Phase Extraction Preconcentration of Ultratrace Amounts of Cobalt and Nickel in Soil and Human Hair Samples for Determination by Flow Injection Flame AAS

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INTRODUCTION

Cobalt is an essential micronutrient for man, animals, and plants, responsible for a range of metabolic processes (1,2). On the other hand, Ni is a moderately toxic element in comparison to other transition metals. It is known that inhalation of nickel and its compounds can lead to serious health problems, including respiratory cancer (3,4) or a skin disorder known as nickel eczema (5). This type of disease is characterized as an occupational disease (6,7) and is found in workers who handle great amounts of this element. Determination of Co and Ni by flame atomic absorption spectrometry (FAAS) often demands separation and preconcentration steps because of insufficient sensitivity or matrix interferences.

Over the years, several enrichment procedures were developed for Co and Ni determination involving analytical techniques such as coprecipitation (8,9) or liquid-liquid (10,11), cloud point (12), or solid phase (13,14) extraction. Solid phase extraction (SPE) has become the method of choice in many laboratories for the analysis of complex samples due to its ease of automation, low reagent consumption, absence of emulsion formation, flexibility, and for providing higher enrichment factors (15,16). Furthermore, SPE is environmentally friendlier than liquid-liquid extraction since it requires a low volume of solvents (16–19). However, in recent years the determina-

ABSTRACT

A flow injection on-line solid phase extraction (SPE) preconcentration system, coupled to a flame atomic absorption spectrometer (FAAS), was developed for the determination of cobalt and nickel at the μg/L levels. Cobalt and nickel were complexed with 2,3-dihydroxy naphthalene (DHN) in the pH range of 2.0–8.0 in the flow injection system and adsorbed onto a C_{18}-bonded silica gel microcolumn. The preconcentrated metal-DHN complexes were eluted with acidified methanol (pH ~2). The eluent was injected directly into the nebulizer of a FAAS for measurement.

The enrichment factors were 725 and 600 for cobalt and nickel, respectively, with a 1-min preconcentration time and a sample throughput of 30/h. The detection limits, corresponding to three times the standard deviation of the blank, were found to be 0.1 μg/L with a precision of 2.5 and 2.6% (RSD) for five successive determinations of 10 μg/L of Co and Ni, respectively. No significant interference was observed from neutral electrolytes, Fe, Zn, and Cu.

In addition to testing the accuracy of the developed procedure for the analysis of nickel soil reference material (IAEA, Soil-7), the method was also applied successfully to the determination of Ni in soil and Ni and Co in human hair samples.

tion of trace elements with flow injection (FI) analysis techniques has received growing attention due to its simplicity, flexibility, high sampling rate, and versatility which allows the method to be used in conjunction with different spectrometry systems (20,21). The various FI-AAS procedures developed for Co and Ni up to 1998 are described elsewhere in the literature (14). The FI-AAS procedures subsequently developed for Co and Ni by various researchers (22–43) are summarized in Table I. Recently, we have described on-line SPE preconcentration FAAS procedures for the determination of Cu in seawater samples (44) and Zn in fractionated soil samples (45). This paper describes for the first time an on-line solid phase preconcentration with 2,3-dihydroxy-naphthalene (DHN) as the chelating agent and its subsequent sorption onto a C_{18}-bonded silica gel, followed by elution with methanol. The FI-FAAS procedure thus developed allows the analysis of 10 ng/g of human hair sample.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model AAnalyst™ 100 atomic absorption spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) was used, equipped with deuterium background corrector and PerkinElmer Lumina® hollow cathode lamps. Both lamps (Co and Ni) were operated at 10mA using a 0.7-nm slit width. The wavelength used was 240.7 nm for Co and 232.0 nm for Ni. A standard air-acetylene stainless steel burner and a 10-cm path length system were

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TABLE I. Summary of FIA-FAAS Procedures Developed Since 1998 for the Determination of Co and Ni

Analyte	Detection Technique	Chelating Agent	D.L.[a] (ng/mL)	Linear Range	Enrich-ment Factor[b]	Application	Ref.
Cobalt							
Co	FAAS	2-nitroso-1-naphthol	0.02	5–100	125	Water and Vitamin B_{12}	22
Co	FAAS	Nitroso-R-salt	1.25	1.25–220	79	Natural waters	23
Co	FAAS & ETAAS	Quinoline-8-ol & its derivatives	–	–	10–34	–	24
Co, Cu, Cd, and Zn	FAAS	Dithione	1.06	–	52	Biological CRMs	25
Co	Spectrom-etry	4-benzoylpiperidine-dithiocarbamate	0.1	0.6–100	–	Waters	26
Co	FAAS	1-nitroso-2-naphthol	3.2	0–250	17.2	CRMs of steels	27
Co	ETAAS	Nitroso-R-salt	5	–	15	Biological materials	28
Co, Cd, Pb, Cu, Mn, Bi, In, and Be	ICP-MS	8-hydroxyquinoline	–	–	300	Seawater	29
Co	FAAS	1-nitroso-2-naphthol	3.2	–	17.2	CRMs of steels	30
Co	FAAS	2-(2-thiazolylazo)-p-cresol	0.13	0.5–10	–	Natural waters	31
Co	ETAAS	Ammonium pyrollidine-dithio-carbamate	4	0.01–0.25	87	CRMs of water and mussel tissue	32
Nickel							
Ni	ETAAS	SP Sephadex resin	9	0.01–0.5	72	Human urine	33
Ni	ETAAS	SP Sephadex resin	10.2	0.01–0.5	71	Human urine & industrial waste	34
Ni	FAAS	2-(2-benzothiazolyl-azo)2-p-cresol	1.1	5–250	30	Biological CRMs	35
Ni	FAAS	Dimethylglyoxime	3	–	21	CRMs of steels & mussel	36
Ni	ICP-AES	Activated carbon	0.08	–	80	Natural waters	37
Ni	Spectrom-etry	Bis(acetylacetone)-ethylene-diiminite	–	Up to 25 000	–	Ni-Cu alloys	38
Ni and Zn	Spectrom-etry	1-(2-thiazolyl-azo)--2-naphthol	–	–	–	Cu-based alloys	39
Ni and Bi	ICP-MS	SP Sephadex resin	15	0.05–2.4	35	River sediment CRM	40
Ni, Cd, and Pb	ICP-OES	Cationic exchange resin	2	–	10	Food stuffs & vegetable materials	41
Ni, Pb, Cd, Cu, Zn, and Fe	IC	8-hydroxyquinoline	0.06	–	2	Natural waters	42
Cobalt and Nickel							
Co, Ni, Al, V, Mn, Cu, Zn, Mo, Cd, Pb, and U	ICP-MS	Muromac A-1	0.014 & 0.029	1–30	Co: 7.0 Ni: 6.0	Seawater CRMs	43
Co and Ni	FAAS	2,3-dihydroxy-naphthalene	0.1	0.5–20	Co: 725 Ni: 600	Human hair, soils	Present Method

[a] D.L. = Detection Limit.   [b] = Ratio of detection limits of Co and/or Ni with FAAS and FI-AAS.

operated at an air flow rate of 4.0 L/min and an acetylene flow rate of 1.0 L/min. The burner height was adjusted to about 30 mm from base for optimum sensitivity. The nebulizer uptake rate was adjusted to provide optimum response for conventional sample aspiration.

A PerkinElmer FIAS™-400 flow injection system connected to the spectrometer was used for on-line preconcentration of Co and Ni. The automatic operation of the injection valve and two multichannel peristaltic pumps were programmed using the spectrometer software (PerkinElmer AA WinLab™ V 3.0). Tygon® peristaltic tubing was used to pump the sample (11.6 mL/min) and reagent (4.0 mL/min); PTFE tubing of 0.3 mm i.d. was used for all connections in order to minimize dead volume. A commercially available conically shaped microcolumn of 50 μL capacity (PerkinElmer), packed with 20 mg of C_{18}-bonded silica gel (40–60 mm), was used. Time-resolved absorbance signals of Co and Ni were displayed on the computer monitor along with peak height and integrated absorbance values.

Reagents and Standard Solutions

All reagents used were of analytical reagent grade. 2,3-dihydroxy naphthalene (DHN) 0.1% (Aldrich, Milwauke, WI, USA) was prepared in 0.05 M ammonia solution because it is not soluble in pure water. Acidified methanol (pH ~2 with HNO_3) was used for elution of the Co and Ni adsorbed on the microcolumn. For all pH adjustments, 0.1 M (pH 5) sodium acetate-acetic acid buffer was used.

Stock standard solutions of Co and Ni (1 mg/mL) were prepared by dissolving approximate amounts of $CoCl_2 \cdot 6H_2O$ and $NiSO_4 \cdot 6H_2O$ (Aldrich, USA) in 250 mL of deionized water. These solutions were standardized by using the EDTA

titration procedure. The working solutions were prepared by suitable dilution.

Procedure

The FI manifold (0.3 mm i.d.) used for the on-line preconcentration and elution was described by Sperling et al. (46). The samples and ammoniacal DHN solutions were pumped simultaneously and mixed on-line. Preconcentration time was approximately 60 s and the sorbed Co and Ni was eluted at a rate of 5.0 mL/min with methanol, acidified to pH ~2. A linear calibration curve was obtained for 0 – 20 μg/L of Co and Ni using aqueous standard solutions in the sample stream.

Analysis of Soil Reference Material (IAEA Soil-7) and Soil Samples

A 0.5 g soil sample was weighed into a platinum crucible, 5 mL of HF and 1 mL of concentrated H_2SO_4 were added, the mixture heated to 150ºC on a hot plate. The process was repeated three times. The residue was cooled and fused with 2 g $KHSO_4$ at 800ºC in an electric muffle furnace for 30 min. The melt was cooled and dissolved in 50 mL deionized water and made up to 100-mL volume. Suitable aliquots were taken and subjected to preconcentration and analysis by the procedure described above. The Co and Ni content of the soil samples was established by reference to a calibration graph prepared in accordance with the above procedure.

Analysis of Hair Samples

The sampling protocol and washing procedures were carried out as described by Airey (47), Ryabukin (48), and Assarian and Oberleas (49). One gram of hair sample was dissolved in 10 mL concentrated HNO_3 + 30% H_2O_2 (4:2 v/v) and kept at 150ºC for 30 min

(50). The pH of the solution was adjusted to between 2 and 8 and subjected to FI-FAAS determination.

RESULTS AND DISCUSSION

The determination of Co and Ni was carried out by using air-acetylene flame. Background correction during method development was neccessary since separation by sorption did not effectively eliminate non-specific absorption by concomitant species.

Table II shows the absorbances obtained during the determination of 10 μg/mL each of Co and Ni by sorption with various ortho dihydroxy chelating agents such as catechol, 2,3-dihydroxynaphthalene (DHN), and 4,5-dihydroxy-1,3-benzene disulphonic acid onto C_{18}-bonded silica gel with subsequent determination by FI-AAS. It is clear from the Table II that sorption is maximum with DHN in comparison to catechol or 4,5-dihydroxy-1,3-benzene disulphonic acid.
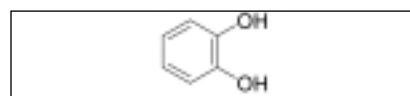
Catechol
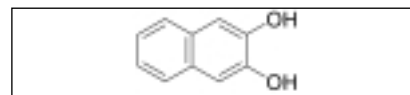
DHN
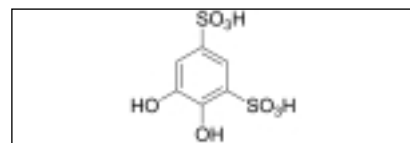
4,5-dihydroxy-1,3-disulphonic acid

The use of activated alumina column for sorption of the DHN complexes of Co and Ni gave absorbance signals of 0.133 and 0.100 compared to 0.200 and 0.160 with C_{18}-bonded silica gel, respectively. Hence, a C_{18}-bonded silica gel column was used for subsequent studies.

TABLE II
FI-FAAS Determination of Co and Ni with Catechol and
Related Compounds (µg/L)

S. No.	Chelating Agent	Absorbance	
		Co	Ni
1	Catechol	0.100	0.027
2	2,3-dihydroxy-1,3-naphthalene	0.200	0.160
3	4,5-dihydroxy-1,3 benzene disulphonic acid	0.017	0.014

TABLE III
Effect of Ammonia Concentration on FI-FAAS Analytical
Signals of Co and Ni (10 µg/L)

S. No.	NH_3 (M)	Absorbance	
		Co	Ni
1	0.05	0.200	0.160
2	0.075	0.195	0.160
3	0.100	0.197	0.062
4	0.500	0.067	0.050
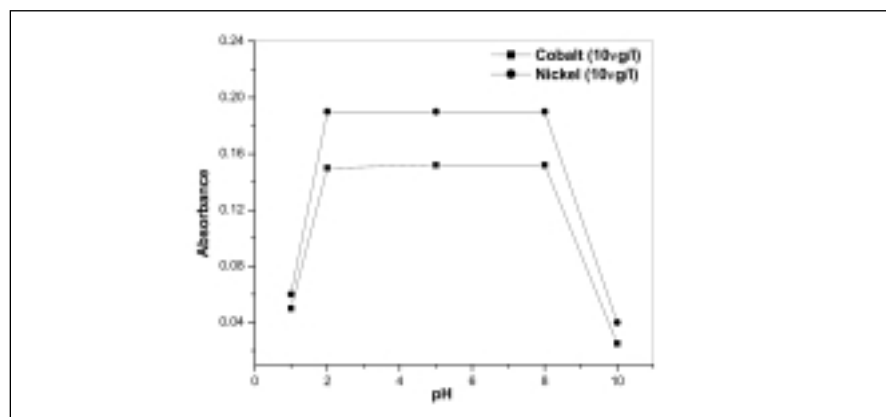
Fig. 1. Effect of pH on FI-FAAS signals of Co and Ni [(Co) or (Ni) = 10 µg/L, C_{18}-bonded silica gel, 0.2% DHN in 0.075 M NH$_3$].

Optimization of Analytical Parameters for the Determination of Co and Ni

The pH of the 10 µg/L Co and Ni samples was varied in steps of 1.0 over the range 1–10.0 after addition of the sodium acetate-acetic acid buffer. The SPE of Co and Ni onto C_{18}-bonded silica gel was found to be quantitative in the pH range of 2–8 (see Figure 1). At pH > 8.0, the formation of hydroxyl species results in a decrease in absorbance. Again, at pH < 2, the absorbances are lower due to insufficient formation of metal-DHN complexes lead-ing to low sorption. Therefore, the pH of the sample solution was adjusted to between 2 and 8 in subsequent studies after the addition of 0.1 M sodium acetate-acetic acid buffer.

The SPE of 10 µg/L of Co and Ni on C_{18}-bonded silica gel was studied at ammonia concentrations ranging from 0.05–0.5 M. The results listed in Table III show that maximum analytical signals were obtained with 0.05 – 0.1 M ammonia for Co and 0.05 – 0.075 M ammonia for Ni. Since the reagent is not soluble at ammonia concen-trations of less than 0.05 M, DHN was prepared in 0.075 M ammonia for subsequent studies. Varying the DHN concentration from 0.005% to 1.0% shows that sorption of Co and Ni was maximum when the DHN concentration is greater than 0.10%. Therefore, 0.2% DHN was used for subsequent studies.

Various miscible solvents (acidi-fied to pH ~2.0) such as methanol, dimethyl formamide, dimethyl sulphoxide, and acetonitrile were tested for the elution of previously sorbed DHN complexes of Co and Ni on C_{18}-bonded silica gel. Methanol gave the highest absorbance in comparison to other solvents and was selected for subse-quent studies. It was found that nitric acid in the range of 0.01–0.1 mol/L quantitatively elutes the Co- and Ni-DHN complexes (sorbed during the preconcentration step) on C_{18}-bonded silica gel.

Optimization of FI Analysis Flow Conditions

High sample loading flow rates are important for efficient precon-centration and high sample throughput. In general, FI sample flow rates are limited by the back pressure produced by the column and/or sorption efficiency. No degradation of sorption efficiency was observed up to a loading flow rate of 15.6 mL/min of sample and reagent. A higher flow rate through the peristaltic pump and the type of column used in this work will degrade precision. The reagent flow rate should not be too low in order to ensure good mixing of the reagent and sample solution. The optimum sample and reagent flow rates were found to be 11.6 and 4.0 mL/min, respectively, and these flow rates were used for subsequent studies.

An elution flow rate of 5.0 mL/min provided optimum sensitiv-ity and elution peaks with minimum tailing. No provision was

made to compensate for the lower flow rate delivered by the FI system; however, the transfer capillary to the nebulizer (PTFE, 0.3 mm i.d.) restricted the uptake rate to values close to the flow rates provided by the FI system. Operating the nebulizer at this flow rate does not lower the sensitivity relative to a decrease in the flow rate due to the potential improvement in nebulizer efficiency under starved conditions (14,46). The lower sample flow rate in the FI mode in comparison to the conventional free uptake rate of the nebulizer is also beneficial for droplet diameter distribution, which results in smaller droplets and is therefore less prone to vaporization interferences (46).

Performance of On-line Preconcentration System

The characteristic data for the performance of the on-line preconcentration system is summarized in Table IV. The efficiency of SPE was investigated by analyzing the previously collected column eluent from standard solutions of Co and Ni using the same preconcentration technique. From the results obtained by repeated preconcentration, a retention efficiency of > 99% was calculated for Co and Ni. The SPE elution sequence is highly reproducible, giving an overall pre-

cision of 2.5 and 2.6% (RSD) for five successive determinations of 10 µg/L of Co and Ni, respectively (Table IV). A linear relationship was observed between preconcentration time and an enrichment factor up to a 4-min loading time. With a loading time of 1 min, a 725- and 600-fold enhancement in sensitivity for Co and Ni, respectively, was observed as compared to conventional FAAS. The detection limits, corresponding to 3 times the standard deviation of the blank, were found to be 0.1 µg/L for Co and Ni. The linear equation with regression was as follows:

$$A_1 = 0.0035 + 0.0201C_1$$

$$A_2 = -0.0005 + 0.0160C_2$$

The correlation coefficients for Co and Ni were 0.99993 and 0.99999, where A_1 and A_2 are the absorbance and C_1 and C_2 are the concentrations of Co and Ni in µg/L. All statistical calculations were based on the average of triplicate readings for each standard solution in the given range. Furthermore, a 1-min loading time allows a sample frequency of 30/h. Higher sensitivities can be obtained by modifying the method, i.e., using longer preconcentration periods at the expense of lower sample throughput.

Interference Studies

The tolerance of maximum concentrations of coexisting ions usually present in human hair samples and the neutral electrolytes on the determination of 10 µg/L of Co and Ni were systematically studied using the FI-FAAS procedure described above. A deviation from the standard absorbance value greater than 3% was taken as interference. The maximum concentrations of neutral electrolytes and coexisting ions which do not cause reduction in the FI-FAAS signals of Co and Ni are: NaCl (1.0 M), NaNO$_3$ (1.0 M), Na$_2$SO$_4$ (1.0 M), Na$_2$O$_2$ (1.0 M), Fe, Zn, Cu, Cr or Mn (1 mg/mL). These observations suggest that the developed procedure can be used for the determination of Co and Ni in human hair samples.

Analysis of Standard Reference Material IAEA Soil-7

The accuracy of the developed preconcentration procedure was tested by analyzing a standard soil reference material (IAEA Soil-7) supplied by IAEA, Vienna, Austria. The Soil-7 sample was mineralized by using the dissolution procedure described, and was subjected to preconcentration and analysis by adopting the general procedure given in the Experimental section. The Ni content established by the present procedure agrees well with the reference values, whereas the Co content is below the detection limit as the certified Co content is 8.9 µg/g in soil (see Table V).

Analysis of Soil Samples

Soil samples collected from two stations in Trivandrum were mineralized and Ni was determined using the general procedure described. As can be seen in Table V, the SPE preconcentration method developed in the present paper enables simple and low-cost instruments such as FI-FAAS to analyze soil samples containing ultratrace amounts of Ni.

TABLE IV
Analytical Performance Data of FI On-line SPE and FAAS Determination of Co and Ni

	Cobalt	Nickel
Linear range	0.5–20 µg/L	0.5–20 µg/L
Sensitivity enhancement[a]	725	600
Concentration efficiency[a]	725	600
Precision (RSD[b]) (at 10 µg/L)	2.5	2.6
Sample consumption	11.6 mL	11.6 mL
Loading time	1 min	1 min
Sample frequency	30/h	30/h
Detection limit (3 σ)	0.1 µg/L	0.1 µg/L

[a] Compared to conventional nebulization.
[b] n = 5.

Analysis of Human Hair Samples

The factors influencing the results in the trace element determination of hair samples are: (a) distance of the sample taken from the scalp, (b) age and sex of the donor, (c) geographical habit of the donors and their dietary supplements and medications. However, factor (a) was eliminated by the careful sampling procedure adopted in this study. We also eliminated factor (c) by choosing the hair samples from subjects of different ages and sex but from the same geographical region.

The samples were washed and analyzed using the FI-FAAS procedure described for the determination of Co and Ni. From the results listed in Table VI, the following conclusions can be drawn even though only 12 samples were analyzed, all collected in one city, i.e., from the same geographical region:

1. The cobalt content for samples 6–9 and 11–12 could not be determined by the present FI-FAAS procedure since it was below the detection limit.

2. Except for sample 10, all other subjects contained ~0.4–0.62 µg/g of cobalt.

3. The nickel content in samples 4–6 could not be determined by the developed FI-FAAS procedure.

4. The nickel content in the hair sample was ~0.97–1.70 µg/g, except for samples 4–6, which is in agreement with our earlier studies (9,50).

5. In case of male subjects, the nickel content increases with an increase in age. On the other hand, the nickel content in female subjects does not vary significantly with an increase in age. The increase in nickel content in male subjects with an increase in age can be attributed to occupational exposure.

TABLE V
Analysis of Soil Samples

S. No.	Samples	Amount of Ni, (µg/g) (95% confidence interval)	
		Present Method	Certified Value
1.	IAEA-Soil 7	24.7 (21–30)	26 (21–37)
2.	Soil sample from Station I	14.8 (14–18)	–
3.	Soil sample from Station II	62.2 (55–70)	–

TABLE VI
Analysis of Human Hair Samples (µg/g)

S. No.	Sex (age)	Cobalt	Nickel
1	F (20)	0.62±0.02	1.70±0.03
2	F (30)	0.55±0.02	1.45±0.03
3	F (35)	0.50±0.02	1.40±0.03
4	F (47)	0.45±0.01	< 0.01
5	F (74)	0.44±0.01	< 0.01
6	M (22)	< 0.01	< 0.01
7	M (25)	< 0.01	0.97±0.02
8	M (30)	< 0.01	1.00±0.02
9	M (36)	< 0.01	1.45±0.03
10	M (37)	1.93±0.02	1.70±0.03
11	M (48)	< 0.01	1.70±0.03
12	M (62)	< 0.01	1.69±0.03

CONCLUSION

On-line SPE preconcentration followed by FI-FAAS analysis allows the determination of Co and Ni as low as 0.01 µg/g of human hair sample with an overall enrichment factor of 725 and 600, respectively, and a 1-min preconcentration/ loading time. The precision of the procedure is good since the RSD values for five successive determinations of Co and Ni were < 3.0%. The procedure is simple and rapid (sample throughput = 30 /h) and allows the determination of 0.5–20 µg/L of Co and Ni by using DHN as the chelating/sorbent extraction agent.

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Determination of Cadmium by CVAAS Using Nebulous Phase Reaction Vapor Generation System

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INTRODUCTION

The interest in evaluating cadmium in the environment has increased due to its carcinogenic effects on human health. The determination of toxic trace cadmium in biological samples, such as tobacco leaves, is an important routine procedure in the study of environmental pollution and occupational exposure. When a cigarette is smoked, many of the toxic metals are inhaled which may become carcinogenic. Therefore, development of sensitive, simple, rapid, and accurate methods for the determination of trace cadmium in a variety of matrices is significant and imperative.

A number of techniques have been applied to the determination of cadmium, for example, flame atomic absorption spectrometry (FAAS) (1–2), electrothermal atomic absorption spectrometry (ETAAS) (3–4), inductively coupled plasma optical emission spectrometry (ICP-OES) (5–6), inductively coupled plasma mass spectrometry (ICP-MS) (7–8), and atomic fluorescence spectrometry (AFS) (9–10). Owing to the successful generation of cadmium volatile species from the reaction of acidified sample solutions using tetrahydroborate(III) reagent, vapor generation (VG) techniques are widely used for trace cadmium determination. These techniques offer significant advantages due to the rapid vapor generation of the elements in the sample matrix and provide a homogeneous vapor for cadmium determination. The main disadvantages of the conventional VG systems, in

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ABSTRACT

A new cold vapor atomic absorption spectrometry (CVAAS) method was developed for the determination of cadmium by nebulous phase reaction with a modified nebulizer. The sample solution was introduced by a peristaltic pump through the normal sample introduction channel of the nebulizer and then sprayed into the reaction tube. The KBH$_4$ solution was also introduced by peristaltic pump and then carried into the reaction tube by argon carrier gas through a second tube of the nebulizer. The aerosol of the sample was mixed with KBH$_4$ and reacted in the reaction tube in the nebulous state. After gas-liquid separation in a conventional nebulizer spray chamber, the volatile cadmium species was transported directly into quartz T-cells by carrier gas and determined by AAS at room temperature. This design effectively reduced the loss of volatile cadmium species in aqueous solution and in the transfer process. The reproducibility and sensitivity of Cd determination was greatly improved. The effects of several experimental parameters of the proposed system were optimized, and the interference of coexisting ions on the cadmium determination was investigated. A detection limit of 21 ng L^{-1} was obtained using the optimized experimental conditions, and the precision of the measurements (RSD) was 3.2% for 10 μg L^{-1} Cd. The accuracy of the method was verified by determining the cadmium concentration in certified reference materials.

The newly developed analytical procedure using microwave digestion has been successfully applied to the determination of cadmium in tobacco leave samples, and the recoveries of spike analytes in the studied samples ranged from 94 to 106%.

which the sample and reductant are continuously pumped into the hydride generator and the volatile species is then introduced into the detector (9–13), are loss of cadmium in the solution and in the transfer process, which results in lower precision and sensitivity.

Another vapor generation method is the use of a modified nebulizer system (14–18), in which both the analytes and reductant solutions are introduced into the nebulizer. After reaction of the analytes and reductant in the nebulizer, the volatile species generated are transferred to the detector.

In comparison to the determination of cadmium under higher temperatures, determination by atomic absorption spectrometry (AAS) at room temperature (19–21) has shown an enhancement in the sensitivity of cadmium determination.

However, to the best of our knowledge, no study has been published concerning the determination of cadmium in biological samples by CVAAS using the nebulous phase reaction vapor generation system.

In this paper, a modified nebulizer was used as both the volatile cadmium species generator and gas-liquid separator. The cadmium species generated was directly transferred to a quartz T-cell and determined by AAS at room temperature. This method reduces contact time in the liquid phase and reduces loss of the cadmium species in the solution and in the transfer process. The proposed method was successfully applied to the determination of cadmium in tobacco leave samples and certified reference materials.

EXPERIMENTAL

Instrumentation

A Model WFX-120 atomic absorption spectrometer (Rui-li Analytical Instruments Factory, Beijing, P.R. China) coupled to a Cd hollow cathode lamp was employed for Cd measurements using a lamp current of 1.4 mA. The wavelength and bandpass of the instrument were set at 228.8 nm and 0.2 nm, respectively. All measurements were carried out at room temperature. The instrument parameters are listed in Table I. IFIS-C peristaltic pumps (Rui-mai Electro. and Science and Technology Factory, Xi'an, P.R. China) carried the sample and KBH_4 solutions to the nebulizer. A microwave oven (Beijing Meicheng Science and Trade Co., Beijing, P.R. China) was used for sample digestion.

TABLE I
CVAAS Operating Parameters

Lamp Current	1.4 mA
Wavelength	228.8 nm
Bandpass	0.2 nm
Measured Signal	Time Average
Measuring Time	2.0 s
Measuring Temp.	Room Temp.
Argon Flow Rate	500 mL min^{-1}

Figure 1 is a schematic diagram of the vapor generation manifold using nebulous phase reaction. The sample solution was introduced into the reaction tube through the normal sample channel. The KBH_4 solution was pumped into the additional tube of the nebulizer and was then carried into the reaction tube by argon gas. The quartz T-cell was 150 mm long with an 8-mm i.d., and the side tube was 90 mm long with a 5-mm i.d. The reaction tube was 40 mm long with a 5-mm i.d.
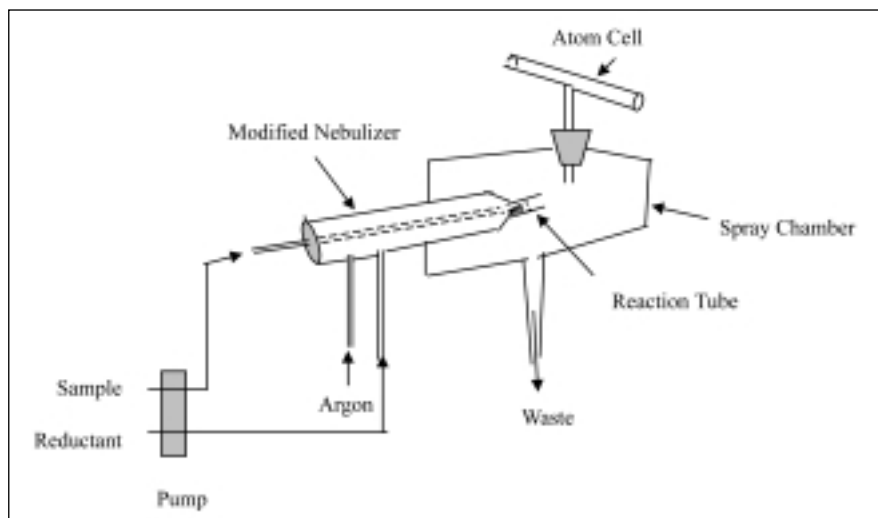
Fig. 1. Schematic diagram of vapor generation system.

Reagents and Standard Solutions

All reagents used were of analytical reagent grade or higher.

Ultrapure water obtained from a Milli-Q™ water purification system (Millipore, Bedford, MA, USA) was used throughout the experiments.

Cadmium standard solutions were prepared daily by serial dilution of a 1000 mg L^{-1} Cd stock solution (Shanghai Institute of Measurements, Shanghai, P.R. China).

KBH_4 (III) solutions were prepared fresh daily by dissolving appropriate amounts of KBH_4 powder (Shanghai Chemical Reagent Co., Shanghai, P. R. China) in 0.5% KOH solution (Shanghai Chemical Reagent Co., Shanghai, P. R. China).

7.5% (m/v) thiourea solution was prepared by dissolving thiourea powder (Shanghai Chemical Reagent Co., Shanghai, P.R. China) in ultrapure water.

100 mg L^{-1} Ni(II) stock solution was prepared by dissolving suitable amounts of $NiCl_2$ (Shanghai Chemical Reagent Co., Shanghai, P.R. China) in ultrapure water. Lower concentrations were obtained by stepwise dilution of the stock solution just before use.

Sample Pretreatment Procedure

Tobacco leaf samples were dried at 60°C for 48 hours prior to further preparation, then ground and stored in a desiccator. Approximately 0.2000 g of sample or reference material was accurately weighed and placed into PTFE vessels, then 2 mL concentrated HNO_3 and 1 mL 30% H_2O_2 were added. The vessels were sealed and placed into the microwave oven for digestion. The digestion program consisted of three stages: Stage 1 (50% power, 300 kPa, 5 min); Stage 2 (80% power, 500 kPa, 3 min); Stage 3 (80% power, 800 kPa, 5 min). Due to the strict requirements of acidity in Cd measurements, especially for HNO_3, which will inhibit Cd absorbance, the residual HNO_3 in the digestion solution had to be removed. After cooling, the digested solution was transferred to a 25-mL glass beaker, 1 mL of $HClO_4$ was added, and gently heated to near dryness. After cooling to room temperature, 10 mL of water was added and quantitatively transferred into a 25-mL calibrated flask. Then 5 mL of 7.5% (m/v)

thiourea and 1.25 mL of 1.0 mg L^{-1} Ni(II) solution was added to reach a final concentration of 1.5% (m/v) thiourea and 0.05 mg L^{-1} Ni(II), respectively.

Determination of Cadmium

The AAS instrumental parameters are listed in Table I. The flow rates of the sample and KBH$_4$ solution were 4.5 and 2.4 mL min^{-1}, respectively. The flow rate of the carrier gas (Ar) was 500 mL min^{-1}. The concentration of KBH$_4$ was 2.5%, and the amount of HCl, thiourea, and Ni(II) in the samples was 0.15 mol L^{-1}, 1.5% (m/v), and 0.05 mg L^{-1}, respectively. The aerosol of the sample and KBH$_4$ mixed and reacted in the reaction tube. After gas-liquid separation in the spray chamber, the generated volatile cadmium species was directly transported to a quartz T-cell and determined by AAS at room temperature. Then, 1 mol L^{-1} NaOH solution was added to waste to terminate the release of hydrogen and analyte gases.

RESULTS AND DISCUSSION

Evaluation of T-cell Material

T-cells of different materials were evaluated. All T-cells used were of the same size, i.e., 150 mm long with an 8-mm i.d. and the side tube 90 mm long with a 5-mm i.d. The results shown in Figure 2 indicate that the quartz T-cell provided highest response, while the aluminum T-cell produced a significantly smaller signal. However, it was noted that the response of the quartz T-cell decreased over time and this phenomenon was in agreement with Reference (6). Thus, the quartz T-cell should be dipped in 10% HNO$_3$ solution every day after the experiments are finished. Figure 2 shows the effects of the different T-cells (quartz cell, glass cell, PTFE cell, and aluminum cell) on 10.0 µg L^{-1} Cd absorbance.

Effect of Reaction Tube Length

The effect of reaction tube length on the absorbance signal was also studied. The experimental results shown in Figure 3 illustrate that the absorbance signal increased rapidly and showed a plateau between 35 and 45 mm. The absorbance decreased drastically as the reaction tube length increased further. This indicates that the reaction might not be completed in a shorter reaction tube, while a longer tube may cause additional loss of the volatile Cd species. Another advantage of using a reaction tube was that it effectively eliminates the influence of water aerosol on Cd absorbance. In light of these experimental results with blank solutions, it was found that a higher blank absorbance was exhibited without the reaction tube. Therefore, a reaction tube of 40 mm length was chosen for this work.

Effect of Sample and Reductant Flow Rate

In this work, both the sample and reductant solutions were introduced into the sample using a pump. As shown in Figure 4, an increase in sample flow rate results in higher absorbance. Considering the maximum pump speed, a sample flow rate of 4.5 mL min^{-1} was used for this study. As to the flow rate for KBH$_4$, 2.4 mL min^{-1} gave the best response and was used throughout this work.

Effect of Concentration of Reductant

The effect of KBH$_4$ concentration on the Cd absorbance signal is illustrated in Figure 5. As can be seen, the Cd absorbance increased rapidly up to 2.5% (m/v) KBH$_4$, while much higher KBH$_4$ concentrations reduced the Cd absorbance. The reason might be that excessive hydrogen gas dilutes the volatile Cd species. Therefore, 2.5% (m/v) KBH$_4$ was chosen for this study.

Effect of Acid and Acidity of Analytes

The effects of HCl, HNO$_3$, and H$_2$SO$_4$ and their concentration on the cadmium absorbance signal were studied with a series of 10.0 µg L^{-1} Cd solutions. The results in Figure 6 show that 0.1-0.2 mol L^{-1} HCl medium was of slightly higher sensitivity. Thus, 0.15 mol L^{-1} HCl was selected as the acid medium for the analysis.

Effect of Thiourea and Nickel

Some workers found that the generation efficiency of volatile Cd species was greatly enhanced in the presence of thiourea and Co(II) (9) or Ni(II) (21), which might act as the catalyzers. The effect of thiourea and Ni(II) was studied using a series of 10.0 µg L^{-1} Cd standard solutions and different concentrations of thiourea and Ni(II), respectively. The results shown in Figure 7(a) indicate that in the presence of 0.05 mg L^{-1} Ni(II) and by increasing the thiourea concentration, the absorbance signal increases rapidly up to 1.5% (m/v) thiourea. In the presence of 1.5% (m/v) thiourea, the Cd absorbance increases along with an increase of Ni(II) concentration up to 0.05 mg L^{-1} (Figure 7b). In this experiment, the combination of 1.5% (m/v) thiourea and 0.05 mg L^{-1} Ni(II) showed the maximum Cd absorbance signal and was therefore chosen for this study.

Effect of Carrier Gas Flow Rate

Figure 8 illustrates the effects of Ar carrier gas flow rate on absorbance. The best response was achieved when using 500 mL min^{-1} Ar. With a lower Ar flow rate, the volatile species cannot be transported effectively to the T-cell, while a higher flow rate (probably due to the dilution effect of argon on volatile species) results in a decrease in absorbance. Air was also tested as the carrier gas, but only one-tenth absorbance was
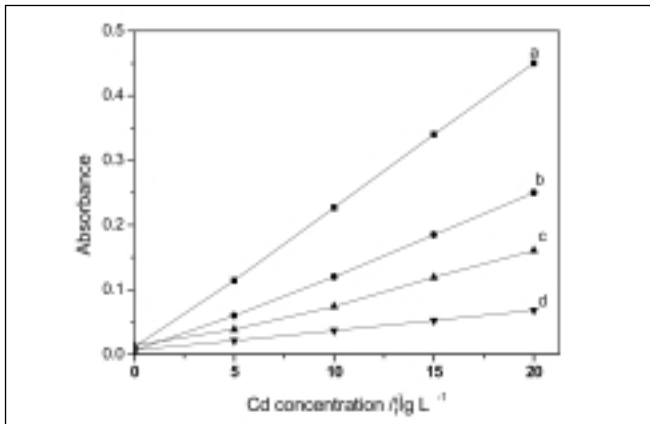
Fig. 2. Effect of T-cell of different materials on the 10.0 μg L⁻¹ Cd absorbance. (a) = quartz cell; (b) = glass cell; (c) = PTFE cell; (d) = aluminum cell.
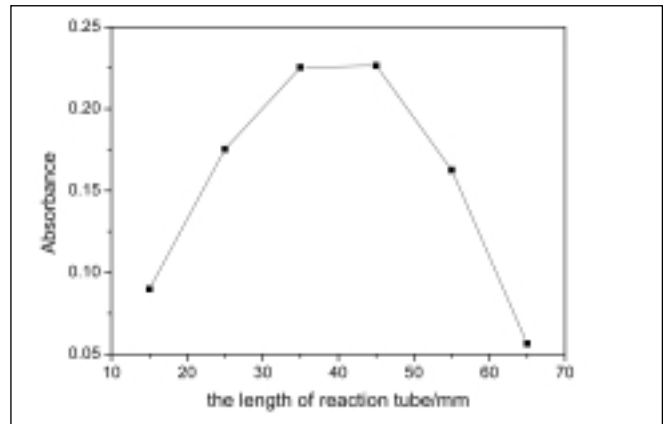

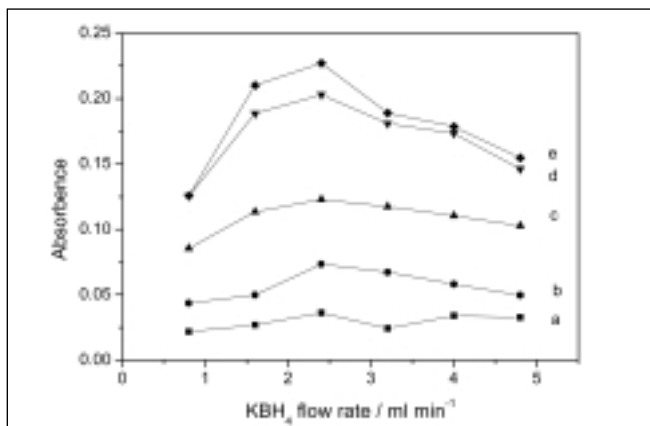Fig. 3. Effect of reaction tube length on the Cd absorbance. Cd concentration was 10.0 μg L⁻¹.

Fig. 4. Effect of KBH_4 flow rate on Cd absorbance. Cd concentration was 10.0 μg L⁻¹. KBH_4 concentration was 2.5%(m/v). Sample flow rates: (a) = 1.0 mL min⁻¹; (b) = 2.0 mL min⁻¹; (c) = 3.0 mL min⁻¹; (d) = 4.0 mL min⁻¹; (e) = 4.5 mL min⁻¹.
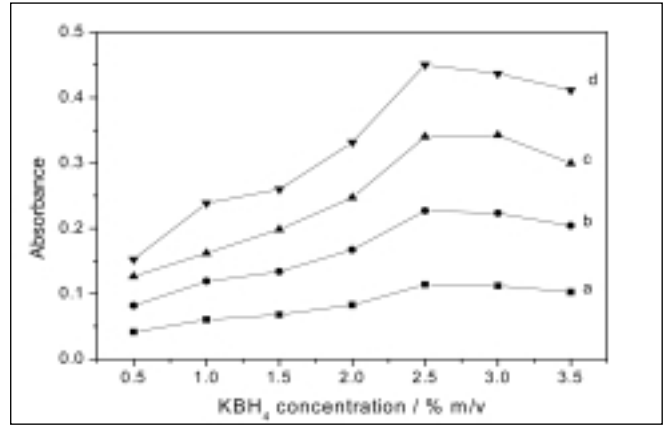
Fig. 5. Effect of KBH_4 concentration on Cd absorbance. Cd concentrations: (a) = 5.0 μg L⁻¹; (b) = 10.0 μg L⁻¹; (c) = 15.0 μg L⁻¹; (d) = 20.0 μg L⁻¹. The flow rate of KBH_4 was 2.4 mL min⁻¹.
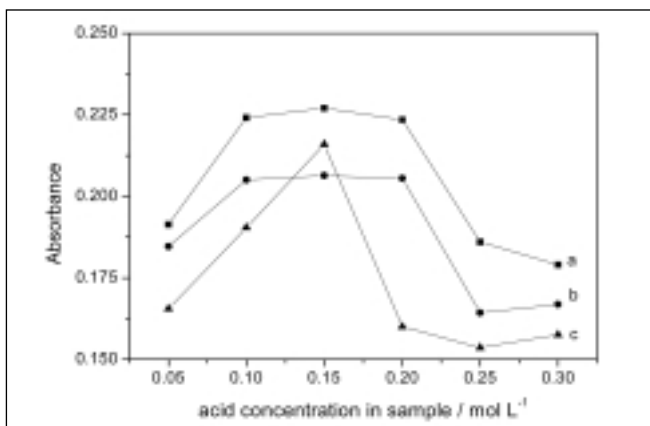
Fig. 6. Effect of different acid and their concentrations on 10.0 μg L⁻¹ Cd absorbance. (a) = HCl; (b) = HNO_3; (c) = H_2SO_4.
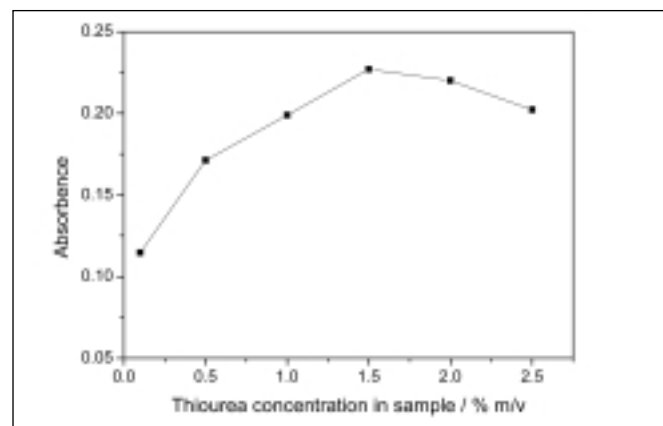
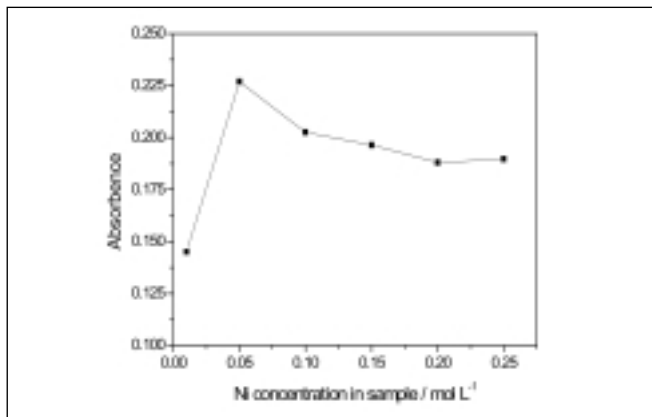Fig. 7(a). Effect of thiourea concentration on Cd absorbance in 0.05 mg L⁻¹ Ni(II). Cd concentration was 10.0 μg L⁻¹.

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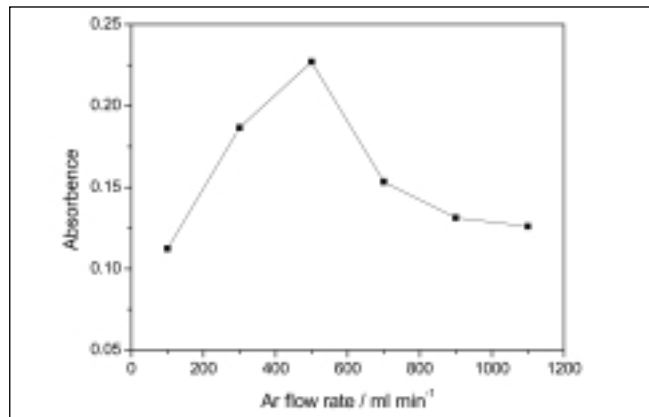*Fig. 7(b). Effect of nickel concentration on Cd absorbance in 1.5% (m/v) thiourea. Cd concentration was 10.0 μg L⁻¹.*

Fig. 8. Effect of argon flow rate on Cd absorbance. Cd concentration was 10.0 μg L⁻¹.

obtained in comparison to argon gas. Therefore, an argon flow rate of 500 mL min^{-1} was chosen for this study.

Interference Study

One major shortcoming associated with the KBH_4 acid system for conventional vapor generation is its susceptibility to transition metal ion interferences. In the present study, the effects of some concomitant ions and their concentrations on the determination of 10.0 μg L^{-1} Cd were investigated. The results listed in Table II show that alkali metals and alkaline earth metals had no effect on Cd absorbance; hydride generation ions such as Hg, As, Sb, Se, and Bi acted as gas phase interferences in the Cd determination; however, Cu and Pb were the most severe interference ions and reduced the Cd absorbance mostly in the liquid phase. Some transition ions of low concentrations, i.e., Sn(II), Cr(III), Mn(II), Fe(III), and Co(II) enhanced the sensitivity of Cd to a small degree. Since the existing concentrations of these concomitant ions are lower than their tolerance limit, it enabled the use of simple aqueous standard calibrations for Cd determination.

TABLE II
Effects of Coexisting Ions on Cd Determination (10.0 μg L⁻¹)

Species	Concn (mg L⁻¹)	Variation in Absorbance (%)
K(I)	1000	–
Ca(II)	100	–
Mg(II)	100	–
Al(III)	100	–
Zn(II)	1	–3
Hg(II)	0.3	–5
As(III)	0.5	–4
Sb(III)	0.5	–6
Se(IV)	0.2	–5
Bi(II)	0.1	–3
Cu(II)	1	–22
	0.1	–6
Pb(II)	1	–45
	0.1	–5
Fe(III)	1	+21
	0.1	+8
Cr(III)	1	+24
	0.2	+6
Mn(II)	1	+27
	0.3	+5
Co(II)	0.5	+10
	0.1	+4
Sn(II)	1	+18
	0.1	+3

Analytical Performance and Sample Analysis

Under optimal conditions, the calibration graphs were found to be linear up to at least 50 μg L^{-1} for Cd and the correlation coefficients were 0.9998. The limit of detection calculated as the concentration (giving the same signal with three times the standard deviation of the blank) was 21 ng L^{-1} for Cd. The precision, evaluated by the relative standard deviation, was 3.2% for 10.0 μg L^{-1} Cd.

To demonstrate the accuracy of the present method, it was applied to the determination of trace Cd in the following certified reference materials (National Center for Standard Materials, Beijing, P.R. China): GBW 07601 Human Hair, 07602 Bush Branch and Leaves, and GBW 08501 Peach Leaves. The results shown in Table III illustrate that the Cd concentrations in the various samples obtained by the present method were in good agreement with the certified values.

The proposed method was also successfully applied to the determination of Cd in a series of tobacco leaf samples. The analytical results and recoveries are shown in Table III. The Cd concentrations in tobacco leaves ranged from 1.633 to 2.015 μg g^{-1} with recovery values from 94–105%.

Table III
Analytical Results for Cd Determination in the Certified Reference Materials (CRMs) and Tobacco Leaf Samples

Sample	Certified Value (μg g^{-1})	Found Value (μg g^{-1})	Recovery (%)
GBW 07601	0.11 ± 0.02	0.106 ± 0.011	–
GBW 07602	0.078 ± 0.015	0.075 ± 0.010	–
GBW 08501	0.018 ± 0.004	0.019 ± 0.006	–
Tobacco Leaf 1	–	2.015 ± 0.003	102
Tobacco Leaf 2	–	1.633 ± 0.002	104
Tobacco Leaf 3	–	1.854 ± 0.003	95
Tobacco Leaf 4	–	1.794 ± 0.006	94

CONCLUSION

A study has been conducted to develop and optimize a rapid, sensitive, and reliable analytical method for the determination of Cd. The procedure, which is based on vapor generation using nebulous phase reaction atomic absorption spectrometry, proved to be feasible and effective. The detection limits and the precision of the measurements (RSD) obtained with the proposed method were 21 ng L^{-1} and 3.2% for 10 μg L^{-1} Cd, respectively. The method was successfully applied to the determination of Cd in biological samples.

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Ultrasound-assisted Acid Extraction of Trace Impurities From Quartz Samples Followed by ICP-OES Analysis

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INTRODUCTION

Quartz is widely used to produce high-performance lenses, prisms, and optical fibres, as well as for frequency control applications. Transition metal impurities are the most perturbing elements, which adversely affect the quality of the final products. However, alkali and alkaline earth impurities degrade the ultraviolet performance, shifting the UV cut-off (153 nm) to longer wavelengths (1).

Several techniques have been used to determine elemental impurities in quartz, such as inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) (2,3), GFAAS (4), and ion chromatography (5). The routinely used sample pre-treatment (2) involves complete dissolution of the matrix (SiO_2) using HF (48% m/v, 10 times the sample weight) and completely evaporating the silica matrix as SiF_4 before trace metals determination. This complete dissolution and subsequent evaporation step results in a long analysis time (7 hrs/sample), the possibility of contamination, and the requirements in containing/scrubbing the HF vapors. Dissolution using a high-pressure bomb (5) offers many advantages, but only one sample can be handled at a time. Methods such as ultrasonic solid liquid extraction (ULSE) are emerging as an alternative sample treatment method. El Azouzi et al. (6) developed an ultrasound-assisted leaching procedure to extract several elements from mussel samples, while Al-Merey et al.

ABSTRACT

A simple procedure was developed for the leaching of trace impurities (Zn, Fe, Mn, Cr, Mg, Cu, Ti, Al, Na, Li, K) from quartz samples by ultrasonic acid extraction, followed by ICP-OES analysis. Three different approaches were employed with the aim of extracting trace elements: (a) solid-liquid (dil. HF) extraction with ultrasonic bath; (b) solid-liquid (dil. HF) extraction using bath sonication after thermal treatment of the sample; and (c) solid-liquid (dil. HNO_3) extraction with an ultrasonic probe. Optimum performance of leaching for trace elements was achieved only in solid-liquid extractions involving dilute HF in bath sonication. The effects of sample mass, reagent leaching mixture, and sonication time on the extraction of elements were evaluated by comparison with those obtained by other established procedures.

The method described provides detection limits of 0.02 µg/g (Ti) and 0.2 µg/g (K). The application of the method to the determination of the above trace metals in two quartz samples is demonstrated. The advantages and drawbacks of ultrasound-assisted extraction with respect to total dissolution are discussed.

(7) have applied cold ultrasonic extraction to soil samples. Recently, Alvarez et al. (8) applied sonication to determine various elements in onion cultivars using TXRF. In another approach, Al-Masri et al. (9) reported an ultrasonic dissolution method to determine radio chemical metals from solid samples. Sonication of

sewage sludge samples with aqua regia-HF has been proposed for the determination of several elements in certified samples (10). Thus, ultrasound irradiation improves the sample preparation method as it facilitates and accelerates steps such as leaching and dissolution of trace elements from solid samples.

The aim of the present study was to investigate the efficiency of ultrasound-assisted acid extraction and compare it with total dissolution which is routinely used in the determination of trace impurities in quartz. The parameters influencing ultrasound-assisted extraction, such as sonication type, sonication time, and extractant composition, were investigated.

EXPERIMENTAL

Instrumentation

A Model JY2000 ICP-OES (Jobin Yvan, France) was used and the instrumentation and operating conditions are listed in Table I. An Imeco Model IS-250 ultrasonic cleaning bath (Imeco Ultrasonics, Mumbai, India) was used to induce the acid leaching process. This model is programmable for temperature and time, with a frequency of 35 kHz for the ultrasound energy. A 130 W, 20 kHz (Model No. CP130PB-1) ultrasonic processor (Cole Parmer, USA), equipped with a titanium micro tip, was also used. A Model EDAX scanning electron microscope (SEM), (Philips, The Netherlands), was used to examine the quartz particles before and after thermal pre-treatment. For SEM analysis, the quartz powder was embedded on a thin film of graphite paste.

TABLE I
Instrumentation and Operating Conditions of ICP-OES

RF Generator	900 W, Frequency 40.6 MHz
Monochromator	0.64 M, 2400 lines/mm, Czerny Turner Mounting
Torch	Jobin Yvon Demountable Quartz With Argon Sheathing Gas
Nebulizer	HF-Resistant PTFE Cross-flow Nebulizer
R.F. Forward Power	1.05 kW (<10 W reflected)
Plasma Gas Flow Rate	13 L/min
Aerosol Carrier Gas	1.2 L/min
Sample Uptake Rate	1.0 mL/min

Reagents

High purity deionized (DI) water with a resistance of 18 MΩ.cm^{-1} or greater was obtained through a Milli-Q™ water purification system (Millipore Corporation, Bedford, MA, USA). Hydrofluoric acid (48% m/w), nitric acid (69.5% w/w), and hydrochloric acid (36%w/w) were of GR grade, obtained from E. Merck, India. Stock standards (1000 mg/L) were prepared from reagent grade salts (E. Merck, India). Working standards were prepared by diluting the stock further to the range expected for the trace metals of interest.

Procedure for Ultrasound Extraction

Three different approaches were carried out for ultrasound-assisted extraction of trace metals from quartz:

(a) Leaching through bath sonication

0.5 g of quartz sample (mesh size –50 to +150) was weighed into a polypropylene (PP) centrifuge tube, 5 mL of 10% (m/v) HF was added, and ultrasonic treatment was performed with an ultrasonic bath for 60 min at a room temperature of 25ºC, with manual shaking every 15 min. After sonication, 5 mL of deionized (DI) water was added and centrifuged to separate the solid-liquid phase. The supernatant was analyzed for trace elements by ICP-OES.

(b) Bath sonication preceded by thermal treatment

0.5 g of sample was weighed into a cleaned platinum crucible. The sample was heated in air up to 700ºC on a Mecker burner for 10 min. After removing, the sample was immediately poured into a pre-cleaned platinum dish containing 5 mL of 5% HF (m/v); this was transferred into a polypropylene (PP) centrifuge tube. The leaching of trace elements was carried out by sonication in an ultrasonic bath for 30 min at 25ºC.

(c) Leaching through probe sonication

0.25 g of quartz was weighed into a PP centrifuge tube (25 mL) and 5 mL of 1% (m/v) HCl was added. Then the sample was sonicated for 3 min at 40% ultrasound amplitude. After sonication, 5 mL DI water was added and the supernatant liquid separated from the solid phase by centrifugation for three minutes at 4000 rpm. The trace elements were determined as described earlier.

Total Dissolution

The total dissolution method is normally used for routine analysis. A sample of 0.5 g was weighed into a 10-mL PFA vial (polyfluoroalkoxy, Cole Parmer, USA) to which 5 mL of HF (48% m/v) was added and left standing for 4 hrs for complete dissolution. The silicate matrix was evaporated as SiF_4 on an IR hot plate (3 hours), and

the analytes were determined as reported earlier (2).

RESULTS AND DISCUSSION

Analyte extraction from solid samples subjected to sonication is considered to be caused by the acoustic cavitations and consequent disruptive action (6,9). The aim of this study was to optimize/demonstrate a room temperature ultrasound-assisted extraction of relevant trace impurities from quartz samples. In this context, a series of parameters such as the nature of the leaching solution and the sonication time were evaluated in order to achieve quantitative recovery. Various acids (HCl, HF, HNO_3) and their mixtures were taken for ultrasound extraction using probe and bath sonication. The efficiency of probe sonication was evaluated in dilute HCl and HNO_3 as the use of HF would be unsuitable with the titanium-tipped ultrasonic probe. In an ultrasonic bath, extraction was carried out in the presence of single acids (HCl, HF, HNO_3) and their mixtures separately. To investigate the extraction efficiency by these extractants, the concentrations of the trace impurities were determined by the total dissolution method as described in the Experimental section. The extraction effect of individual acids and their mixtures was compared with the results of the total dissolution method.

Probe Sonication

The extraction efficiency of Mn, Cu, Na, and K was quantitative by probe sonication (3 min) in the range of 1–5% (m/v) HCl. For the rest of the elements (Zn, Fe, Cr, Mg, Ti, Al, and Li), the extraction efficiency was below 20%. Increasing the acid concentration and sonication time further shows no improvement in recovery. In the nitric acid medium (1 to 10% m/v), the recovery of all trace elements was below 20%.

Bath Sonication

In ultrasound-assisted extraction (6–10), generally dilute HNO₃, HCl, and their mixtures are used as extractants. From the probe sonication of quartz, it was observed that both HCl and HNO₃ were not effective for quantitative extraction of the desired trace impurities. Therefore, dilute HF was used as an extractant for bath sonication. This was not possible in probe sonication due to attack on the titanium tip. It was observed that the most critical parameters that influenced the extraction efficiency were HF concentration and sonication time.

Effect of HF Concentration

In this study it was found that quantitative extraction of the elements (Zn, Fe, Mn, Cr, Mg, Cu, Ti, Al, Na, Li, and K) can be achieved only when the HF concentration is equal to or more than 10% (m/v), except for calcium. Extraction of Ca has been observed up to 80%. A further increase in acid concentration (20% m/v) did not improve the extraction of Ca. Generally for other matrices, the presence of an oxidant in the reagent mixture improves the extraction. Therefore, a mixture of HF and HNO₃ was tried in bath sonication.

This mixture did not show any improvement in Ca recovery. From these observations it was concluded that only dil. HF (10% m/v) is ideal for the extraction of trace impurities (Figure 1).

Effect of Sonication Time

The effect of sonication time is very important for obtaining quantitative recovery. Extraction of trace analytes was carried out as a function of time for 10% (m/v) HF as extractant. It can be seen from Figure 2 that a minimum of 60 min is required for the quantitative extraction of trace analytes (except for Ca). By increasing the HF concentration further (20% m/v), no reduction in time for quantitative recovery was observed. When the acid concentration was reduced to 5%, the time required for quantitative extraction was around 90 minutes. Thus, optimum extraction efficiency for trace elements was achieved in 10% HF (m/v) with a bath sonication of 60 min.

Influence of Acid Volume and Sample Mass

Acid (10% m/v HF) volume was a factor that produced some effect towards the leaching of trace elements and the results in variable leaching of the matrix. As the volume of HF (10%) was increased to 10 mL, 960 µg/mL of silicon was leached into the solution, while no reduction in sonication time was observed. Another relevant finding was that the extraction efficiency was independent of mass when the mass-to-volume ratio was kept constant (0.5 g / 5 mL). The minimum amount of sample mass suitable for analysis was further limited by its homogeneity and sensitivity of the ICP-OES technique. In this case, a sample mass larger than 200 mg was used to minimize the influence of inhomogeneity on analytical variance. Homogeneity of the quartz samples used in this work was assessed by measuring the iron content in 10 extractions and determining the homogeneity factor (H_E) as suggested by Kurfurst et al. (12) in the following equation:

$$(H_E) = (RSD)m^{1/2}$$
$$m = \text{mass of the sample}$$

Materials with a homogeneity factor of less than 10 are said to be highly homogeneous. For iron, the homogeneity factor was between 7–8 in the range of 0.5 to 0.2 g. Thus, 0.5 g samples were taken for ultrasonic extraction.
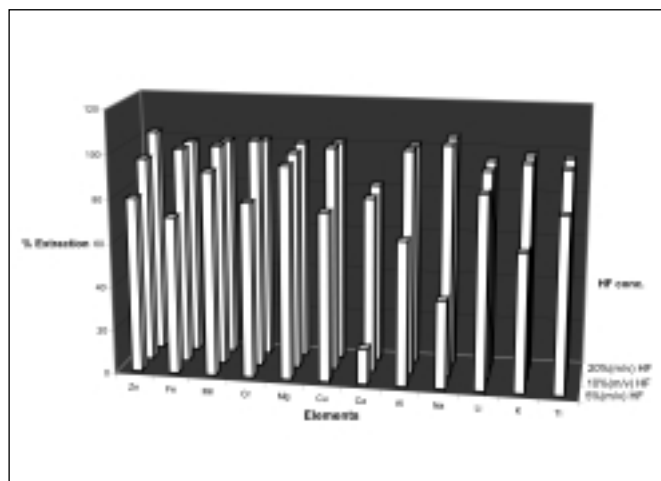

Fig. 1. Percent (%) extraction of each element against HF concentration at sonication time of 60 minutes.
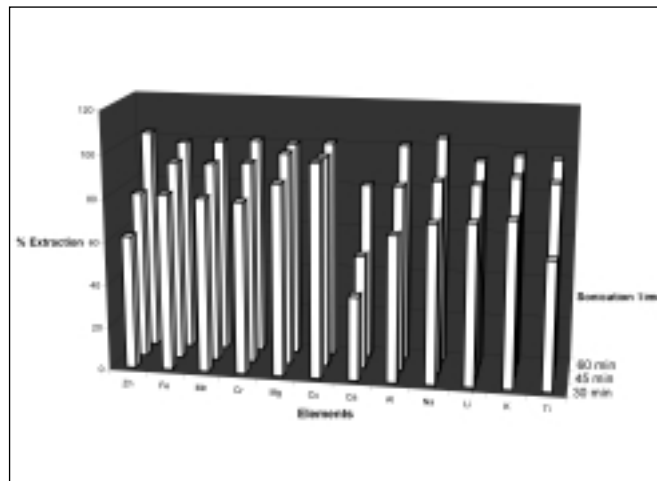

Fig. 2. Percent (%) extraction of each element against sonication time at 10% HF concentration.

Thermal Treatment - Bath Sonication

Particle size has been recognized as an important factor (6–10), which affects the analytical performance in ultrasonic solid-liquid extraction. When further reduction in particle size was attempted by mechanical grinding, it resulted in contamination of the ubiquitous elements Na, K, Fe, etc. Alternatively, the quartz sample was heated to 700°C and poured into 5 mL of 5% HF, then transferred to a clean platinum dish, and again transferred into a PP tube and bath-sonicated as described earlier. This process reduced the sonication time to 30 minutes. To investigate the physical changes that were taking place after inducing thermal shock, the SEM image of the air-dried sample was photographed (after decanting the HF and thoroughly rinsing with DI water). Figures 3(a) and 3(b) are the electron micrographs of quartz particles recorded before and after thermal treatment, respectively. A comparison between the two sets (a and b) of micrographs clearly indicates that extensive micro-cracking took place as a result of thermal shock. This micro-cracking increases the surface area, which is possibly responsible for fast extraction of analytes in combination with ultrasound-assisted extraction. However, incomplete extraction of calcium still persisted.

Leaching of Quartz Matrix

Usually any ultrasonic action will cause the matrix to be partially extracted into the liquid medium. Particularly in the present case, HF also attacks the quartz matrix. This might create a solution with high dissolved salt content that may affect the nebulization characteristics and excitation conditions in the plasma. It was, therefore, imperative to quantify the amount of silica that was leached into the extracting medium. An aliquot of the extractant was diluted and the
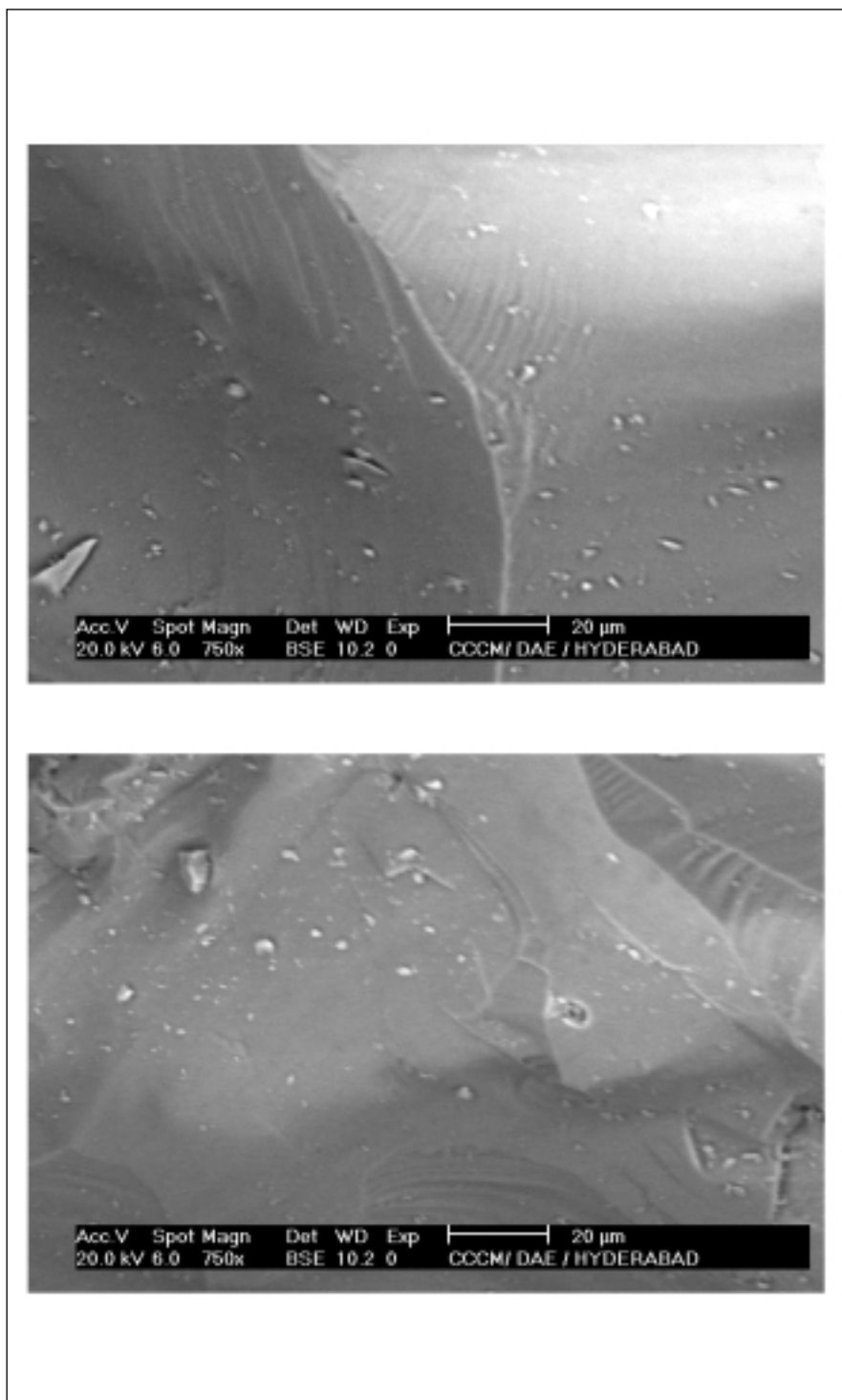

Fig. 3a. SEM images of individual quartz particles before thermal treatment (750 times magnification).
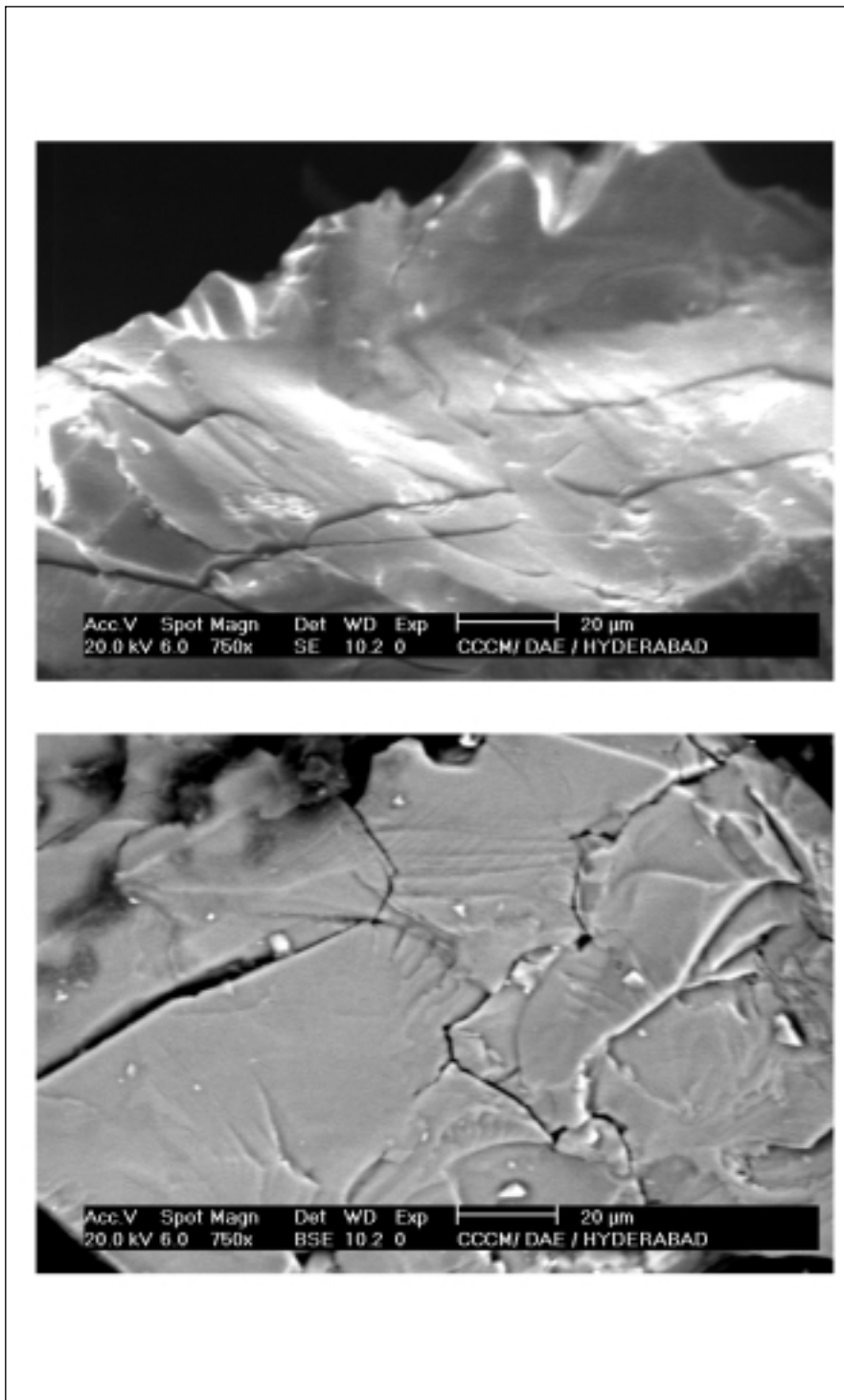
254

Fig. 3b. SEM images of individual quartz particles after thermal treatment showing micro-cracking (750 times magnification).

silica content was measured at 251.611 nm. It was found that at the recommended concentration of HF (10% m/v) during 60 min of sonication, the amount of silica leached was 320 µg/mL, which did not create any physical or spectral interference. Due to line overlapping of nickel with silicon at 221.647 nm, its determination was precluded by the present method. Even though an alternative line at 217.467 nm was used, the determination of nickel was not possible due to lack of adequate sensitivity at this emission line.

Sample Analysis, Accuracy, and Precision

The accuracy of the proposed ultrasound leaching method was evaluated by comparing the data obtained by the total dissolution method (2). The method was applied to the analysis of two quartz samples. Quantification of the analytes was obtained from calibrations with either aqueous standards or by the standard addition method. It was found that the results obtained by both methods were identical to each other. The results obtained on the two quartz samples by ultrasound-assisted extraction (6 replicate analyses of 10% m/v HF, 60 min) and by the total dissolution method are presented in Table II. The results for most of the analytes show no significant differences, indicating that the proposed ultrasound-assisted extraction provides fairly comparable results to the total dissolution method. The t-test was applied to examine whether the results obtained by ultrasound leaching differed significantly at the 95% confidence level. As the calculated 't' values were less than the critical 't' value of 2.571 (degree of freedom of 5), it shows that there are no statistically significant differences among the results obtained by the proposed ultrasound leaching and the routinely used total dissolution method (2). The quantification of

TABLE II
Comparison of Results Obtained by Sonication Method
and Total Dissolution Method (Concentrations in μg/g)

Analyte	Wavelength (nm)	Limit of Detection (μg/g)	Sample	Bath Sonication (10% m/v HF) Mean ± σ	Total Dissolution Method n=2
Zn	213.856	0.04	Qtz-1	0.30 ± 0.03	0.32
			Qtz-2	n.d	n.d
Fe	238.205	0.1	Qtz-1	94 ± 3	95
			Qtz-2	62 ± 2	63
Mn	259.610	0.05	Qtz-1	0.87 ± 0.07	0.86
			Qtz-2	3.2 ± 0.1	3.21
Cr	267.716	0.06	Qtz-1	2.2 ± 0.1	2.1
			Qtz-2	1.5 ± 0.1	1.4
Mg	279.553	0.02	Qtz-1	5.0 ± 0.2	5.05
			Qtz-2	8.0 ± 0.6	8.2
Cu	324.754	0.04	Qtz-1	1.12 ± 0.04	1.07
			Qtz-2	0.81 ± 0.05	0.82
Ti	334.941	0.02	Qtz-1	4.8 ± 0.2	5.2
			Qtz-2	6.2 ± 0.3	6.3
Al	396.152	0.05	Qtz-1	64 ± 2	62
			Qtz-2	77 ± 2	75
Na	588.995	0.08	Qtz-1	10.0 ± 0.7	9.5
			Qtz-2	5.1 ± 0.5	5.0
Li	670.784	0.03	Qtz-1	0.52 ± 0.04	0.55
			Qtz-2	0.43 ± 0.03	0.41
K	766.490	0.2	Qtz-1	12.8 ± 1.0	13.0
			Qtz-2	7.9 ± 0.6	8.2

calcium was not possible due to the variable extent of extraction. In one of the two analyzed quartz samples, the concentration of zinc was below the detection limits of ICP-OES. The detection limits for 11 elements (Table II) were calculated as three times the standard deviation of the blank values. The precision of the method, expressed as the relative standard deviation (%RSD) of five independent analyses of the sample, provided RSD values of less than 9% for most of the analytes.

CONCLUSION

The proposed ultrasound-assisted extraction either with 10% (m/v) HF bath sonication for 60 min or with 5% HF (m/v) bath soni-cation for 30 min with pre-thermal treatment provides a simple and fast approach for the ICP-OES determination of Zn, Fe, Mn, Cr Mg, Cu, Ti, Al, Na, Li, and K in quartz samples. The advantages are: (a) drastic reduction in sample pre-treatment time (one hour) compared to total dissolution (seven hours), (b) complete elimination of fume hood emission, (c) lower HF concentrations (10% or 5% vs. 48% m/v). The contamination risk for these ubiquitous elements is minimized since the complete sample preparation is carried out in closed conditions, and the lower process blanks are due to dilute reagents used for extraction.

Certain limitations of ultrasound extraction could be the non-quanti-tative extraction of certain elements (such as calcium) and unsuitability for certain analytical techniques (such as GFAAS), since HF is known to intercalate in graphite tubes, lead-ing to gas phase interference (13).

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Assessment of YPA$_4$ Chelating Resin for the Separation and Determination of Pt, Pd, Ru, Rh, and Au in Geological Samples by ICP-OES

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INTRODUCTION

Solid-phase extraction has extensively been used for the separation and preconcentration of trace elements (1,2) because of major advantages such as simplicity of operation, rapid phase separation, higher preconcentration factors, and low contamination risk in comparison to the classic liquid-liquid extraction technique. The main requirements for solid-phase extractants (3) include: (a) the possibility of extracting a large number of elements over a wide pH range, (b) fast and quantitative sorption and elution, (c) high capacity, regenerability, and accessibility. Numerous substances have been proposed and applied as solid-phase extractants such as modified silica (4), alumina (5,6), C$_{60}$-NaDDC (7), cellulose (8), nanometer-sized material (9), chelating resin (10), and microorganism (11).

Chelating resins are still one of the most effective materials among the above-listed sorbents. The use of chelating resins or chelating fibers in the extraction of trace metals has been described in a number of papers (12–15). Recently, chelating resins or fibers functionalized with groups containing sulphur or nitrogen donor atoms such as thiol (16), thiourea (17), dithizole (18), and thiohydrazide (19), have drawn the attention of researchers. These resins exhibit good kinetic properties, high adsorption capacity, and excellent adsorption selectivity towards the noble metal ions.

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ABSTRACT

A chelating resin (YPA$_4$) was used for the adsorption of metal ions, and their adsorption properties were studied. The effects of acid media, acidity, and equilibrium time on adsorption behavior of the analytes were examined. It was found that the YPA$_4$ resin showed different adsorption properties in HNO$_3$ vs. HCl media. In 3.5 mol L^{-1} HNO$_3$, the noble metal ions (Ag(I), Au(III), Ru(III), Rh(III), Pd(II), Pt(IV), and Bi(III)) could be quantitatively adsorbed by YPA$_4$ with the adsorption capacities ranging from 23.7 mg g^{-1} Bi(III) to 95.2 mg g^{-1} Au(III). In 3.2 mol L^{-1} HCl, Au(III), Ru(III), Rh(III), Pd(II), Pt(IV), Cu(II), Sn(II), and Bi(III) retained on the YPA$_4$ resin, and their adsorption capacities were in the range of 1.25 mg g^{-1} Cu(II) to 96.5 mg g^{-1} Au(III). The proposed method was successfully applied to the ICP-OES determination of Pt, Pd, Ru, Rh, and Au in geological standard reference materials.

Fibers containing the thiol groups for the extraction of trace noble metals have also been described (20–22). A chelating resin (YPA$_4$) of the aminoisopropylmercaptan type with a polythioether backbone with a total S and N content of 24.89% and 7.82%, respectively, was used (23). This resin should exhibit good adsorption properties towards noble metals and perhaps also other metals.

The aim of this work was to explore the possibility of YPA$_4$ for the adsorption of trace noble and other metals, and to investigate the adsorption characteristics of metal ions on the YPA$_4$ chelating resin in different inorganic acid media under static conditions. The effects of acid media, acidity, and equilibrium time on the adsorption rate and adsorption kinetic process of the analytes were investigated. At optimum conditions, the adsorption capacities of YPA$_4$ for the tested ions were also investigated. The kinetic characteristics and the adsorption mechanisms are briefly discussed.

EXPERIMENTAL

Instrumentation

A 2 kW power, 27±3 MHz ICP generator was used, equipped with a Model WPG-100 plane grating spectrometer with 1200 grooves mm^{-1} (Beijing Broadcast Equipment Factory, Beijing, P.R. China) and a conventional plasma silica torch. The inductively coupled plasma optical emission spectrometry (ICP-OES) operating conditions and the wavelength of the emission lines are summarized in Table I. The analytical lines were selected on the basis of freedom from spectral interferences.

Standard Solution and Reagents

The standard stock solutions (1.000 g L^{-1}) of the elements were prepared from AuCl$_3$, RuCl$_3$, RhCl$_3$, Pd(NO$_3$)$_2$, (NH$_4$)$_2$PtCl$_6$, AgNO$_3$, CuSO$_4$, SnCl$_2$, and Bi, respectively, by a conventional method. The reagents AuCl$_3$, RuCl$_3$, RhCl$_3$, Pd(NO$_3$)$_2$, (NH$_4$)$_2$PtCl$_6$, AgNO$_3$, and Bi were SpecPure® quality (supplied by the Shanghai First Reagent Factory, Shanghai, P.R. China). CuSO$_4$ and SnCl$_2$ (Beijing Chemical Plant, Beijing, P.R. China) were of analytical reagent grade. All other reagents used were also of analytical reagent grade.

TABLE I
ICP- OES Operating Conditions and Wavelengths of Emission Lines

Parameters	
Incident power	1.1 kW
Carrier gas (Ar) flow rate	0.8 L min^{-1}
Auxiliary gas (Ar) flow rate	0.4 L min^{-1}
Coolant gas (Ar) flow rate	16 L min^{-1}
Observation height	10 mm
Entrance slit width	20 mm
Wavelength	Cu 324.7 nm, Ag 328.1 nm, Au 267.6 nm, Ru 372.8 nm, Rh 343.5 nm, Pd 340.5 nm, Pt 299.8 nm, Sn 283.9 nm, Bi 306.0 nm

Fig. 1. The structure of YPA$_4$.

The analytical standard solutions were prepared by mixing and diluting the stock solutions. Doubly distilled water was used throughout.

Preparation of YPA$_4$

The YPA$_4$ chelating resin was purchased from the Department of Polymer Chemistry, Wuhan University, and the method preparation and the structural properties of the resin are described in reference (23). The structure of YPA$_4$ is shown in Figure 1. According to the information provided in reference (23), the band at 2425 cm^{-1} belonging to the SH group, and the band at 1610~1570 cm^{-1} belonging to the -NH- group, moved 10~21 cm^{-1} and 27~58 cm^{-1}, respectively, to the long wavelength, and became a broad peak after adsorbing the metal ions Au, Pd, and Pt. In addition, a new band at 438 cm^{-1} belonging to Pd-N was observed. The element analysis showed that the total content of S and N in YPA$_4$ was 24.89% and 7.82%, respectively (23). The YPA$_4$ resin, with a 100–140 mesh size, was immersed for 24 h in acetone and 1 mol L^{-1} HCl, respectively, then filtered and washed with doubly distilled water until neutral, and dried prior to storage for later use.

Recommended Procedure

To study metal ion adsorption under static conditions, a portion of the sample solution containing the ions investigated was transferred to a 10-mL flask and the acidity adjusted with 4 mol L^{-1} HNO$_3$ or 4 mol L^{-1} HCl. The final volume was diluted to 10 mL with doubly distilled water. Then, 50 mg of YPA$_4$ was added and the mixture stirred mechanically for 40 min to facilitate adsorption of the metal ions onto the YPA$_4$ chelating resin. This solution was allowed to stand for 60 min; however, for Ag(I), the mixture was kept standing for 60 min in the dark [Ag(I) was tested alone]. After centrifuging, the concentrations of the unsorbed ions in the liquid phase were directly determined by ICP-OES.

RESULTS AND DISCUSSION

Effect of Acid Media and Acidity on Adsorption

HCl and HNO$_3$ were selected as the adsorption media and the adsorption percentage of the analytes was evaluated at varying acidities. Figure 2 shows the effects of acidity on the adsorption percentage of the tested ions. As can be seen, the metal ions Au(III), Ag(I), Ru(III), Rh(III), Pd(II), Pt(IV), and Bi(III) were adsorbed quantitatively by the YPA$_4$ chelating resin in HNO$_3$ with a concentration of 3.5 mol L^{-1}. The adsorption percentages were over 90% for the metal ions investigated, except for Bi(III), whose adsorption percentage was 85% (see Figure 2-A). Similarly, the metal ions Cu(II), Au(III), Ru(III),
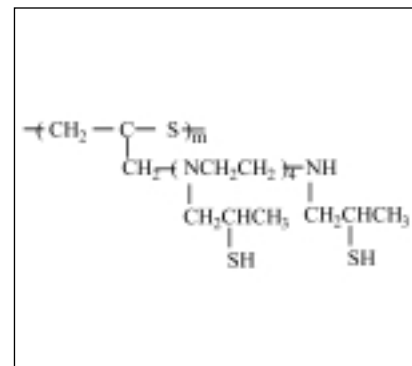
Rh(III), Pd(II), Pt(IV), Sn(II), and Bi(III) were adsorbed quantitatively by YPA4 resin in 3.2 mol L^{-1} HCl (see Figure 2-B). However, when comparing Figure 2-A with Figure 2-B, an adsorption difference can be seen between HCl and HNO$_3$. Firstly, Cu(II) and Sn(II) were not adsorbed by YPA$_4$ in HNO$_3$, but were adsorbed by the resin in HCl. Their adsorption properties strongly depend on the HCl concentration because the adsorption percentage of Cu(II) and Sn(II) increases rapidly with an increase in HCl concentration. This shows that the complexes (CuCl$_4$)$^{2-}$ and (SnCl$_4$)$^{2-}$ were formed, and a stronger ion exchange adsorption process may take place between the formed complex ions and the resin after treatment with HCl. Secondly, it was observed that in both acid media, Au(III), Ru(III), Pd(II), and Pt(IV) showed similar adsorption behavior to the YPA$_4$ resin and were quantitatively adsorped by the resin in a wide acidity range (0.5~4.0 mol L^{-1}). However, for Rh(III), the higher chloride concentration seems to be beneficial for its affinity to the resin. This can be attributed to the anionic chloro-complex formation (RhCl$_6$$^{3-}$), which may also undergo an ion exchange with the resin. Thirdly, the strong affinity of Bi to the S donor atom can perhaps explain the adsorption behavior of Bi(III) on the resin in both acid media.
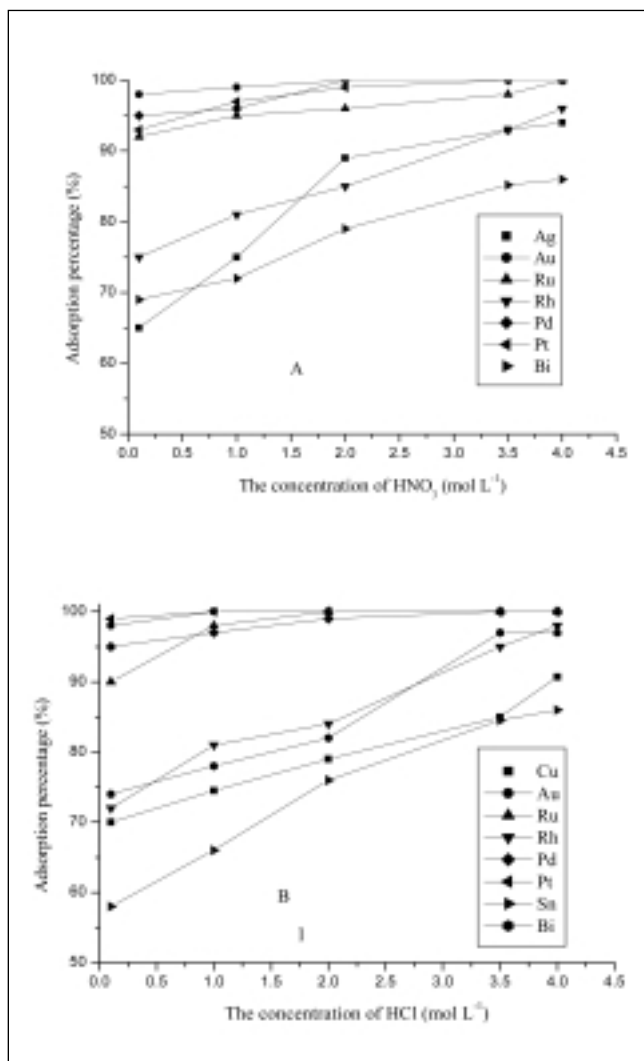
Fig. 2 (A-B) . Effects of acidity (HNO$_3$ and/or HCl) on the adsorption percentage of different metal ions.
Cu: 0.5 μg mL^{-1}; Ag, Pd: 1.0 μg mL^{-1}; Au, Ru, Rh: 2.5 μg mL^{-1};
Pt, Bi, Sn: 6.0 μg mL^{-1}. Sample volume: 10 mL.
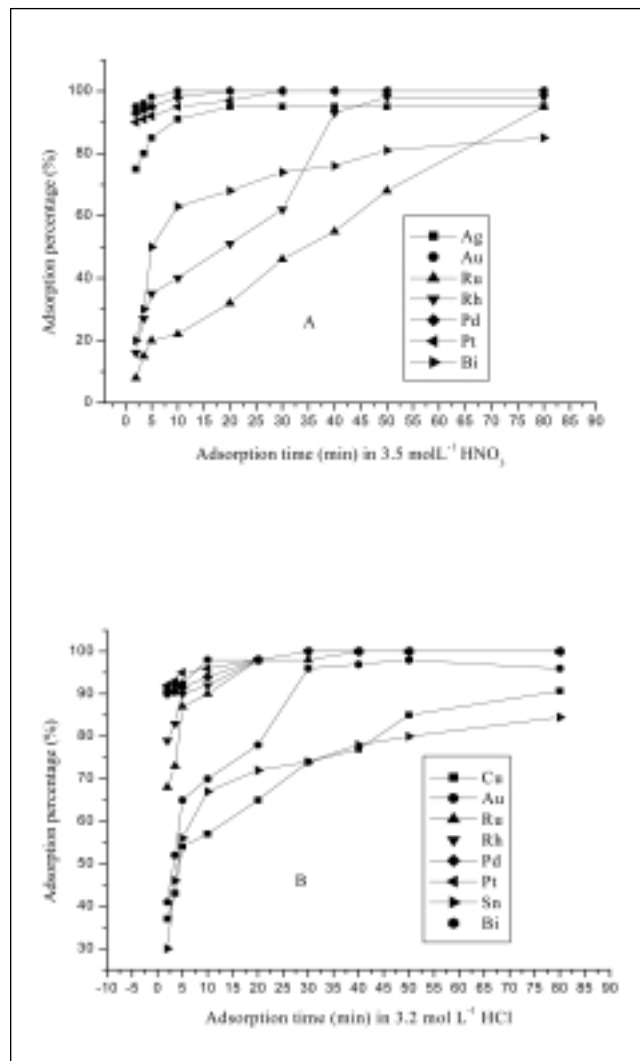

Fig. 3 (A-B). Effects of equilibrium time on the adsorption percentages of the studied ions on the resin
in 3.2 mol L^{-1} HCl and 3.5 mol L^{-1} HNO$_3$.
Cu: 0.5 μg mL^{-1}; Ag, Pd: 1.0 μg mL^{-1}; Au, Ru, Rh: 2.5 μg mL^{-1};
Pt, Bi, Sn: 6.0 μg mL^{-1}. Sample volume: 10 mL.

Adsorption Equilibrium

It is well recognized that rapid adsorption is of great importance for an ideal adsorption material. The adsorption kinetics of the resin were studied in 3.5 mol L^{-1} HNO$_3$ and 3.2 mol L^{-1} HCl. The dependence of the adsorption percentage of the metals on the YPA$_4$ chelating resin in both acid media on adsorption time are shown in Figure 3. From these data, the following can be concluded:

(a) In HNO$_3$, Au(III), Ag(I), Pd(II), and Pt(IV) were adsorbed quantitatively by the YPA$_4$ chelating resin within 5~10 min; but a much longer adsorption time of 35 min, 70 min, and 80 min was needed for Ru(III), Rh(III), and Bi(III) , respectively (see Figure 3-A).

(b) In HCl (Figure 3-B), Au(III), Ru(III), Rh(III), Pd(II), and Pt(IV) were adsorbed quickly (within 5~10 min) by the YPA$_4$ chelating resin; whereas, 30 min were

required for Bi(III) and over 60 min for Cu(II) and Sn(II).

(c) For Au(III), Pd(II), and Pt(IV), a quick adsorption process was observed both in HCl and HNO$_3$ media. However, a large difference was observed for the adsorption of Ru(III), Rh(III), and Bi(III) in both acid media. For example, for Ru(III), it took 80 min to be quantitatively adsorbed in HNO$_3$, but only 10 min in HCl. In other words, the adsorption of Ru(III), Rh(III), and

Bi(III) by YPA$_4$ resin was rapid in HCl. The possible reason is that the presence of chloride could shorten the equilibration time between Ru(III), Rh(III), Bi(III), and the resin.

(d) Ag(I) in HNO$_3$ and Cu(II) and Sn(II) in HCl all exhibited a slow adsorption process.

Repeated Use of Adsorbent

To test the long-term stability of the adsorbent, it must be subjected to successive adsorption and elution cycles. Several complexing agents were investigated to strip the metal ions from the resin. However, only Ag(I), Au(III), Pd(II), Pt(IV), and Cu(II) could be quantitatively desorbed with a 2.5% thiourea complexing agent. Thus, Ag(I), Au(III), Pd(II), and Pt(IV) were selected to investigate the stability of YPA$_4$ in 1.0 mol L^{-1} HNO$_3$. The procedure was carried out twice per day. The next two runs were made one day later, and so on, up to four days (with a total of eight adsorption-elution cycles). The adsorbent was stored in doubly distilled water overnight. The stability and potential re-use of the adsorbent were assessed by monitoring the change in the recovery of Ag(I), Au(III), Pd(II), and Pt(IV) at the end of eight adsorption-elution cycles. The recovery of the analytes was almost constant within the certainty limits. It seems that the adsorbent was relatively stable over the eight runs in the strong oxidizing acidic aqueous solutions.

Selectivity of the YPA$_4$ Chelating Resin

To characterize the selectivity of the resin, the adsorption studies of metal ions Cr(III and IV), Mn(II), V(V), Ba(II), Co(II), Ni(II), Al(III), Mg(II), La(III), Cd(III), Fe(III), Si(IV), Na(I), Ti(IV), Ca(II), Cu(II), Ag (I), Au(III), Ru(III), Rh (III), Pd(II), Pt(IV), Sn(II), and Bi(III) were carried out in both HNO$_3$ and HCl media at varying acidities. The

experimental results showed that the resin could selectively adsorb Cu(II), Au(III), Ru(III), Rh (III), Pd(II), Pt(IV), Sn(II), and Bi(III) in HCl, and Ag (I), Au(III), Ru(III), Rh (III), Pd(II), Pt(IV), and Bi(III) in HNO$_3$. However, Fe(III), Si(IV), Ca(II), Cr(III and IV), Mn(II), V(V), Ba(II), Co(II), Ni(II), Al(III), Mg(II), La(III), Cd(II), Na(I), and Ti(IV) could not be adsorbed by YPA$_4$ in either HNO$_3$ or HCl. It can clearly be seen that the YPA$_4$ resin exhibited excellent adsorption selectivity toward the noble metal ions Au(III), Ru(III), Rh(III), Pd(II), Pt(IV), and Bi(III) in both HCl and HNO$_3$ media. However, Cu(II) and Sn(II) could not be adsorbed in HNO$_3$, but could quantitatively be adsorbed in HCl. On the other hand, quantitative adsorption of Ag(I) was achieved only in HNO$_3$.

Static Adsorption Capacities (Qs)

The adsorption capacity is an important factor to evaluate the adsorption performance of adsorption materials. A 20-mg portion of the resin was shaken with a 25-mL solution containing 5-1000 µg mL^{-1} of the corresponding metal ions under optimal acidity conditions for sorption (3.2 mol L^{-1} HCl or 3.5 mol L^{-1} HNO$_3$). After the distribution equilibrium was reached, the concentration of the metal ions in solution was determined by ICP-OES. The results of the varying concentrations of the analytes on the adsorption capacity are shown in Figure 4. As can be seen, the static adsorption capacities of the resin for Cu, Au, Ru, Rh, Pd, Pt, Sn, and Bi in 3.2 mol L^{-1} HCl were 1.25, 96.5, 27.2, 35.1, 78.8, 53.5, 10.5, and 42.2 mg g^{-1}, respectively (Figure 4-A). For Ag, Au, Ru, Rh, Pd, Pt, and Bi in 3.5 mol L^{-1} HNO$_3$, they were 59.8, 95.2, 25.4, 28.7, 89.3, and 23.7 mg g^{-1}, respectively (Figure 4-B), indicating that the resin possesses a much higher adsorption capacity for the tested ions

[except for Cu(II)] both in HCl and HNO$_3$. In comparing Figure 4-A with Figure 4-B, it can also be seen that the capacity of YPA$_4$ for a given ion varied with the change of acid media:

(a) The capacities of the resin for Pt(IV), Bi(III), Rh(IV), and Ru(IV) were slightly less in HNO$_3$ than in HCl.

(b) Contrary to Pt(IV), Bi(III), Rh(IV), and Ru(IV), the capacity for Pd(II) was more in HNO$_3$ than HCl.

(c) No obvious capacity difference for Au(III) between the two acid media was observed. This may be related to the different species of the analytes and the changeable structure of the resin in different inorganic acid media.

Adsorption Mechanisms

The resin-containing amino group can transform into R$_3$HN$^+$–Cl$^-$ in HCl. Like conventional anion exchange resins, the resin can exchange with anion complexes of the metals. Sn(II) and Cu(II) can form the chloro-complexes (CuCl$_4$)$^{2-}$ and (SnCl$_4$)$^{2-}$ in HCl media, and consequently can be adsorbed by the resin, but they cannot be adsorbed in HNO$_3$. The reason that Bi(III) can be adsorbed in both acid media is that Bi(III) has a high affinity to the S atom. This resin has a much higher S concentration (20%-25%); thus, formation of a coordination bond between Bi(III) and the S atom can be easily achieved.

In conformity with the hard and soft acids and bases theory (HSAB) (24), the functional groups containing S and N donor atoms interact strongly with the soft acid-like noble metals of silver, gold, and the platinum group metals. The resin containing the S and N atoms bearing a thio-ether backbone showed a strong adsorption capacity and selectivity for the noble metals [Ag(I), Au(III), Pd(II), Pt(IV),
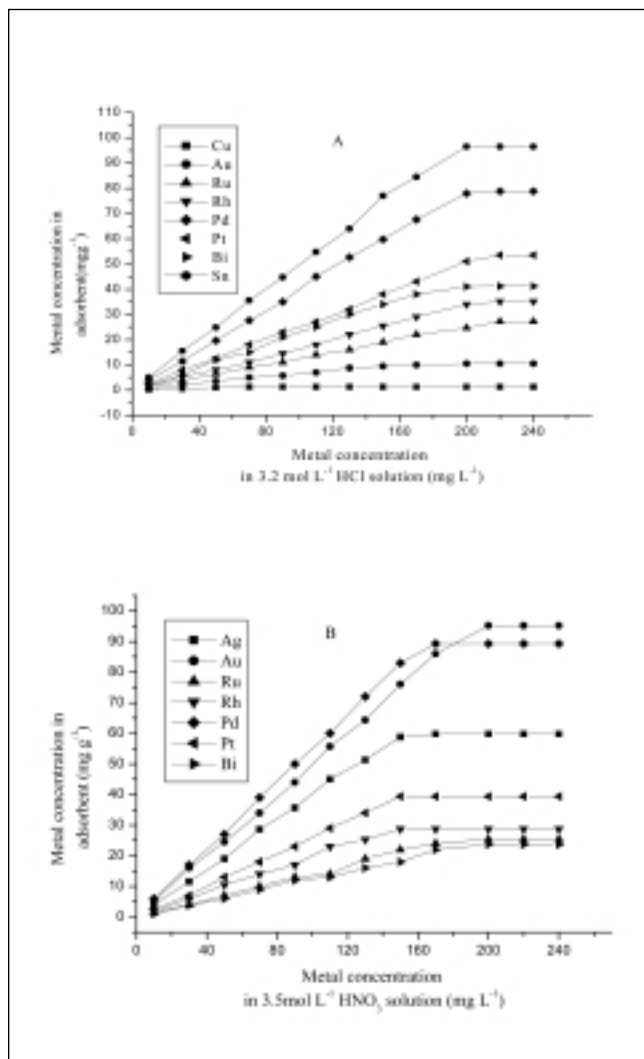
Fig. 4 (A-B). Adsorption isotherms of metals on the YPA$_4$ chelating resin (sample volume: 25 mL).

Rh(IV), Ru(IV)]. This may mainly be attributed to the formation of a coordination bond between the noble metals and the S and N atoms in the resin or perhaps an ion exchange progress may have taken place between them in the acid media.

Analytical Application

In order to establish the validity of the procedure, the method was applied to the determination of noble metals in geological standard reference material (GBW07293).

A 5.000 g sample of GBW07293 (provided by the Institute of Geophysical and Geochemical Prospecting, Langfang, P.R. China) and 25 g sodium peroxide were weighed into nickel crucibles and placed into a muffle furnace for 15 min at 700°C. The residue was dissolved in hot water in a beaker. The solutions were heated to near dryness, and the residue dissolved in dilute nitric acid. After the dissolved salts were centrifuged, the supernatant was heated to near dryness and the residue dissolved in 25 mL of 3.5 mol L^{-1} HCl. Then 50 mg of resin was added to the sample solution and treated as described previously. After centrifuging, the surfactant was removed and the resin washed three times with doubly distilled water. The resin was evaporated carefully to near dryness and placed into a muffle furnace for 15 min at 560°C. After cooling, the resin was transferred into a beaker and 10 mL of HNO$_3$ added. The mixture was heated on an electric hot plate to near dryness, then 2.5 mL of HClO$_4$ was added. The resultant solutions were heated to near dryness and dissolved in 10 mL of 10% (v/v) nitric acid.

The proposed ICP-OES method was applied to the determination of trace noble metals in geological standard reference material GBW07293. The analytical results are shown in Table II. As can be seen, the results agree very well with the certified values.

TABLE II
Analytical Results of Metals in Geological Material (GBW 07293)[a]

Element Value	Pt	Pd	Ru	Rh	Au
Certified (ng g^{-1})	440±37	568±51	13±1	22±3	45
Determined value (ng g^{-1})	375±29	513±47	11±1.3	20±2.1	41±2.8

[a] Average ± S.D. (n=3).

CONCLUSION

The adsorption properties of YPA$_4$ chelating resin towards metal ions were studied systematically. The results indicate that this resin has excellent adsorption selectivity, high adsorption capacity, good stability, and quick kinetic characteristics for noble metals. It also has great potential for the preconcentration and separation of Bi(III), Sn(II), and Cu(II).

ACKNOWLEDGMENT

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Isopiestic Distillation of Arsenious Chloride for the Determination of Trace Impurities in High Purity Arsenic by ICP-OES

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INTRODUCTION

High purity arsenic is used in the manufacture of compound semiconductors like GaAs (1) and the presence of impurities will affect its properties. Hence, raw materials need to be analyzed for trace and ultratrace levels of impurities before their conversion to the final product. For the analysis of high purity materials, the samples need to be treated minimally in order to achieve very low process blanks. Though analysis of solid materials by Spark Source Mass Spectrometry, Glow Discharge Mass Spectrometry, etc., eliminates the process blank problems, they often suffer from lack of suitable reference standards (2). Hence, solution-based techniques need to be adopted. Direct analysis of sample solutions by ICP-based techniques is difficult due to the presence of high concentrations of matrix elements. Moreover, for the accurate and precise determination of very low levels of impurities, the matrix elements need to be separated to enable pre-concentration of the impurities.

Reported matrix separation methods for arsenic are based on ion-exchange, solvent extraction, and volatilization (3-8). Matrix volatilization procedures gained much attention due to the high volatility of arsenic as chloride or bromide. Recently, Udas et.al. (9) reported an *in situ* volatilization of arsenic by GFAAS for the determination of trace impurities.

ABSTRACT

Isopiestic distillation of arsenic as arsenious chloride at room temperature is described. A matrix distillation of 98% has been achieved using *in situ*-generated HCl vapors in the presence of low concentrations of nitric acid added to the sample. In the present method, the generation of pure acid for sample dissolution, conversion of As to $AsCl_3$ and its volatilization are performed in a single step. The closed container volatilization using *in situ*-generated acid vapors resulted in lower experimental blanks (ng/g). The percentage recoveries of 10 analytes (Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, and Zn) added to the sample were 95–104%. The matrix-free solution in the sample container was diluted and analyzed for trace levels of impurities by ICP-OES. The values obtained were validated using the open volatilization method. The overall reproducibility of the method was 2–10%. The limits of detection of the analytes are in the ng/g levels.

However, these procedures are time-consuming and tedious as the temperature program needs to be optimized for every element. Isothermal distillation procedures were found to be suitable for the separation of volatile matrix elements due to their simplicity and lower process blanks (10,11). We reported isopiestic distillation of arsenic from arsenious oxide matrix in a closed container containing concentrated HCl, where arsenic is volatilized as $AsCl_3$ (12). However, the same procedure could not be applied for the analysis of arsenic

samples, because arsenic is not soluble in HCl and hence could not be volatilized as $AsCl_3$.

In this paper, we report the isopiestic distillation of arsenic as arsenious chloride from an arsenic matrix in the presence of low concentrations of HNO_3. The determinations were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES). The method was applied to the trace element analysis of high purity arsenic samples procured from the Special Materials Plant, Nuclear Fuel Complex, Hyderabad, India.

EXPERIMENTAL

Instrumentation

A Model JY-2000 ICP optical emission spectrometer (Jobin Yvon, France) was used for these studies, equipped with a 40.68 MHz R.F. generator. The operating parameters are given in Table I.

TABLE I
ICP-OES Operating Parameters

Power	1 kW
Plasma gas flow rate	12 L/min
Nebulizer gas flow rate	0.1 L/min
Slit width	20 µm/20 µm

Wavelengths (nm)	
Al: 396.152	Cd: 214.438
Co: 228.616	Cr: 357.869
Cu: 327.396	Fe: 238.204
Mg: 279.553	Mn: 257.610
Ni: 231.604	Zn: 213.856

Brand micro-pipettes and locally available HDPE and PTFE containers were used. The PTFE containers were cleaned by soaking in 20%

(v/v) HNO_3 for 8 hrs and rinsing with de-ionized water before use.

Reagents and Standard Solutions

Sub-boiled nitric acid and AR grade hydrochloric acid were used. Ultrapure water (18 MΩ.cm) was prepared by passing potable water through a deionization plant and then through a Milli-Q™ system (Millipore Corporation, Bedford, MA, USA).

All stock standard solutions were prepared using high purity metal/oxide (Leico, New York, USA) in ultrapure acids.

An experimental arrangement in which an HDPE container of 1-Litre capacity is used as the outer container for isopiestic distillation has been described previously (12).

Isopiestic Distillation of As With HNO_3

An arsenic sample (500 mg) was weighed into a Teflon® beaker to which different volumes (200–500 µL) of HNO_3 were added. This was kept in the outer container containing 50 mL of HCl and the container was closed. After 24 hrs, a 1-mL aliquot was removed from the outer container, diluted to the required volume, and As was determined by ICP-OES.

Isopiestic Distillation of As With Time

An arsenic sample (500 mg) was weighed into a Teflon beaker and 250 µL of HNO_3 was added. This beaker was placed in the outer container containing 50 mL of HCl and the container closed. A 1-mL aliquot was taken out of the outer container after 8, 16, 24, and 48 hrs and diluted to the required volume. Then, arsenic was determined by ICP-OES.

Analytical Procedures

An arsenic sample (500 mg) was weighed into a Teflon beaker, 250

µL of HNO_3 added and equilibrated with 50 mL of HCl as mentioned above. After 24 hrs, the contents of the sample container were diluted to 10 mL with deionized water and the impurities determined by ICP-OES. The procedure was repeated with known amounts standards added to the sample.

Open Volatilization Method

Arsenic (500 mg) was dissolved using 2 mL of aqua regia and evaporated to dryness. The residue was treated with 1 mL each of H_2SO_4 and HBr and evaporated to dryness. This procedure was repeated three times with three 1-mL additions of HBr. Excess H_2SO_4 was removed by heating. The final residue was diluted to 10 mL with 5% HNO_3 and the impurities determined by ICP-OES.

RESULTS AND DISCUSSION

Arsenic(III) chloride is volatile due to its high vapor pressure (1.29 kPa at 23°C). However, open volatilization of arsenious chloride is not suitable in a normal laboratory environment due to its toxicity and possible environmental contamination which increases the process blank values. Hence, matrix separation in a clean environment for both analytes and analyst is desirable. Previously we reported (12) an isopiestic distillation of arsenic as *in situ*-generated arsenious chloride from arsenious oxide samples in HCl vapors where exposure of the analyst to the matrix is minimized and process blank values are reduced drastically.

For the dissolution of arsenic, normally an oxidizing medium such as HNO_3 or H_2O_2 is required. Utilization of higher amounts of oxidizing agents will lead to the formation of As(V). In the present procedure, after dissolution, the major quantity of arsenic is expected to be present as As(III) chloride due to the presence of

excess HCl. However, it can also form As(V) chloride due to the presence of a low concentration of nitric acid. As(III) chloride is volatile whereas As(V) chloride is non-volatile. The ratio of As(III) to As(V) is decided by the volume of nitric acid added to the sample. Hence, it is necessary to optimize the minimum quantity of nitric acid required for complete dissolution of the sample. To 500 mg of arsenic, an amount of 200, 250, 300, 400, and 500 µL each of nitric acid was added and equilibrated with 50 mL of HCl. After 24 hrs, it was observed that the sample dissolution was not complete with 200 µL of nitric acid, possibly because the amount of nitric acid is not sufficient for matrix dissolution. However, in the remaining cases, the sample dissolution was complete, matrix removal was near quantitative (98%) when 250 µL of nitric acid was added. However, in the remaining cases, matrix removal was found to decrease with an increase in nitric acid, possibly due to the formation of higher amounts of As(V) chloride in the presence of higher amounts of nitric acid added. The results are shown in Figure 1.

It was found that arsenic is digested in a small amount of nitric acid (250 µL for 500 mg of arsenic) before equilibration with concentrated HCl present in the outer container; and arsenic is dissolved with *in situ*-generated HCl vapors in the presence of nitric acid. HCl vapors used for dissolution are generated *in situ*, which are very pure, and the whole process of sample dissolution and matrix volatilization takes place in closed containers, creating a clean environment within the container. As a result, the experimental blanks are found to be at ng/g level (Table II). The limits of detection for the elements of interest were calculated based on 3 σ variation in the measurement of blank (n=6).
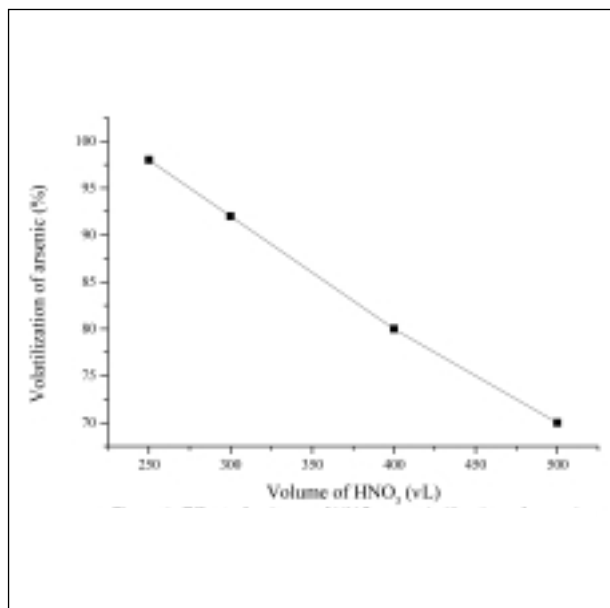
264

Fig. 1. Effect of volume of HNO₃ on volatilization of As.

TABLE II
**Comparison of Process Blank Levels
of Present Method and Open Volatilization Method
Along With Limits of Detection**

Element	Process Blank Values (µg/g)		Limits of Detection (µg/g)
	Present Method (n=6)	Open Volatilization Method (n=3)	
Al	0.55	7.50	0.30
Cd	<0.20	0.46	0.15
Co	<0.20	0.43	0.20
Cr	<0.30	0.46	0.30
Cu	<0.15	0.26	0.15
Fe	0.38	2.83	0.20
Mg	0.30	2.25	0.18
Mn	<0.18	0.21	0.18
Ni	<0.30	0.50	0.30
Zn	0.60	1.25	0.12

TABLE III
**Percentage Recoveries of Impurities
Added to 500 mg of As Sample
Diluted to 10 mL**

Element	Amount of Std. Added (µg)	Amolunt of Std. Recovered (n=3)	Recovery (%)
Al	4.0	3.60	95
Cd	2.0	1.94	97
Co	2.0	1.92	96
Cr	2.0	2.04	102
Cu	2.0	1.98	99
Fe	2.0	1.96	98
Mg	2.0	2.08	104
Mn	2.0	2.04	102
Ni	2.0	1.96	98
Zn	2.0	1.98	99

TABLE IV
**Comparison of Concentration of Impurities
Present in High Purity Arsenic Using
Present Method and Open Volatilization Method**

Element	Concentration of Impurities (µg/g)	
	Present Method (n=3)	Open Volatilization Method (n=3)
Al	2.9 ± 0.4	3.8 ± 1.0
Cd	<0.6	<0.6
Co	<0.6	<0.6
Cr	<0.6	<0.6
Cu	<0.5	<0.5
Fe	1.0 ± 0.1	1.3 ± 0.4
Mg	<0.55	<1
Mn	<0.6	<0.8
Ni	<0.5	<0.5
Zn	1.04 ± 0.1	1.30 ± 0.3

Uncertainties are given as 1σ variation of three independent experiments.

The rate of volatilization of arsenic was studied by removing 1-mL aliquots from the outer container after 8, 16, 24, and 48 hrs. After suitable dilution, arsenic was determined by ICP-OES. It was observed that there was an increase in volatilization of arsenic from 8 hrs to 24 hrs and reached a plateau after 24 hrs of equilibration. Beyond 24 hrs, there is no further volatilization of arsenic as reported in our earlier work (12). At optimum conditions, known amounts of standards added to the sample were also treated as mentioned in the Experimental section to evaluate the percentage recovery of the elements of interest. The percentage recoveries were found to be between 95–104% (Table III).

Application

Since the matrix volatilization and recovery of the impurities are near quantitative, the procedure can be applied to the analysis of

high purity arsenic. The method was applied for the separation and analysis of a 4N pure arsenic sample. In Table IV, the values obtained are compared with the values obtained using the open volatilization procedure. The higher uncertainty values in case of open volatilization are possibly due to contamination in a normal laboratory environment.

CONCLUSION

High vapor pressure of HCl and $AsCl_3$ were utilized for the purification of reagent, dissolution, and isopiestic distillation of arsenious chloride from arsenic samples for the determination of trace impurities. In the present procedure, problems in the open volatilization, namely exposure of the analyst to toxic arsenic, and utilization of higher quantities of reagents, namely H_2SO_4 and HBr, were eliminated. The method reported was found to be simple, cost-effective, and can be used for the routine analysis of arsenic samples of ~4N (99.99%) purity with minimum process blanks.

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Determination of Trace Impurities in High Purity Tellurium (7N Pure) Using ICP-MS and Transversely Heated Electrothermal AAS

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INTRODUCTION

The purity of tellurium (Te) is very important in the manufacture of compound semiconductors such as CdTe and CdHgTe (1) which have a strategic application in night vision equipment and in infrared and γ-ray detectors. For such applications, high purity Te is required. The semiconductor industry currently requires the level of metal impurities at 5.0×10^9 atoms/cm^2 (2). Analyzing such high purity samples is very difficult in normal laboratories because of contamination from sources such as the environment, containers, reagents, and the analyst (3). Methods to prevent sample contamination from these sources are now well documented (4) and include a metal-free, clean environment where contamination from the surroundings is minimized by cleaning the room air through an HEPA filter; the use of plastic containers such as PFA, PTFE, etc.; the use of high purity reagents; and the use of clean lab garments by the analyst.

Methods for the determination of trace impurities in Te have been reported in the literature (5–7). Most of these involve ion exchange separation, precipitation of Te, solvent extraction, and matrix volatilization. These methods require a number of chemical processing steps and the use of various reagents which increase the process blank, and hence, are only suitable for analyzing 4N (99.99%) – 5N (99.999%) pure samples. The analysis of 7N (99.99999%) pure

ABSTRACT

A rapid method for the determination of trace impurities in 7N pure (99.99999%) tellurium (Te) metal is described. In this method, Te is precipitated as the oxide in a solution containing 1:1 nitric acid; while trace impurities remain in solution. The amount of acid required for precipitation has been optimized. The quantification of trace impurities such as Al, Cd, Co, Cr, Cu, Fe, In, Ni, and Pb is possible by this precipitation method.

Accuracy of the procedure was obtained by comparing the results of both ICP-MS and TH-ETAAS, whose results agree well. The one-step matrix separation procedure described reduces the process blank by enabling the characterization of 7N pure Te. Using this method, a number of high purity Te samples were analyzed.

samples requires a procedure with a minimum number of sample preparation steps and also using a minimum amount of analytical reagent (high purity) along with clean lab protocols. The process blanks must be at the 1–10 ng/g levels for quantification of these samples.

Solid analysis techniques (8) such as Spark Source Mass Spectrometry (SS-MS) and Glow Discharge Mass Spectrometry (GD-MS) have also been used for analyzing high purity Te, but the lack of appropriate reference standards is a problem. Therefore, the results obtained are only semi-quantitative in nature.

Techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with powerful detection limits and Transversely Heated Electrothermal Atomic Absorption Spectrometry (TH-ETAAS) with effective Zeeman background correction are highly suitable for the analysis of high purity materials. However, the sample has to be brought into solution for analysis by these techniques. For ICP-MS, additional chemical processing is needed for the removal of major amounts of matrix; this means that for analyzing materials that are 6N–7N pure, single-step matrix separation and pre-concentration procedures using minimum amounts of reagents would be preferred. This lowers the process blank and hence improves confidence on the final results.

In this work, the suitability of ICP-MS and TH-ETAAS is examined for the characterization of 7N pure Te inside metal-free class 100 clean rooms with a class 10 laminar workbench. The method described uses a simple chemistry for the separation of the matrix, and the results obtained by ICP-MS and TH-ETAAS analysis are compared.

EXPERIMENTAL

Instrumentation

A Model VG Plasma-Quad3 ICP-MS (VG Elemental, U.K.) and a PerkinElmer® Model 4100 ZL TH-ETAAS with Zeeman background correction (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) were the instruments used. An Inductively Coupled Plasma Optical Emission (ICP-OES) Model JY-2000 (Jobin Yvon, France) was used for direct analysis of 3N to 4N

Te. The instruments were operated under the conditions recommended by the manufacturer, except that the drying step in TH-ETAAS was modified to 50 s.

Reagents and Standard Solutions

Nitric acid was purified by sub-boiling distillation. Deionized water was purified by passing tap water through a reverse osmosis (R.O.) system (from BARC, Mumbai), then through a deionization system, and finally through a Milli-Q™ (Millipore Corporation, Bedford, MA, USA) water purification system to get better than 18 MΩ.cm^{-1} pure water. The water was collected in a class 100 environment. All stock standards were prepared by dissolving 99.99% pure metals in nitric acid. The working standards were prepared by subsequent dilution.

Procedure

Tellurium metal chunks weighing 1.0–1.2 g were dissolved in 4 mL (1:1) nitric acid diluted with Millipore water and warmed with an infrared (I.R.) lamp in a class 10 clean workbench. After 30 minutes, the reaction ceased and the supernatant solution was taken into a PTFE evaporation disk with Eppendorf pippettes. The white precipitate was washed 2 times with 2-3 mL cold water, and the washing was added to the evaporation disk. Excess nitric acid was removed by heating on an I.R. lamp in the class 10 clean workbench, and the volume was made up to 2-mL volume. Half a mL of the above solution was taken for analysis by TH-ETAAS.

RESULTS AND DISCUSSION

Optimization of (1:1) Nitric Acid for Maximum Precipitation of Te

Initially, different amounts of Te in the range of 0.2–1.5 g were added to 4 mL (1:1) nitric acid by diluting concentrated sub-boiled nitric acid with equal volumes of deionized water. Major amounts of Te precipitated as tellurium oxide (TeO$_2$). The amount of Te remaining in the solution was determined and the results are illustrated in Figure 1, curve-a. It was observed that with 0.2–0.4 g Te, nearly 28% of Te remained in the solution, while with larger amounts of 0.8–1.2 g, only 2–3% remained in the solution; the remaining Te precipitated. Tellurium appears to have some solubility in (1:1) nitric acid medium. Therefore, by reducing the amount of acid, the quantity of Te in solution could be reduced. Figure 1, curve-b, shows the Te remaining in the solution by maintaining the Te to acid ratio constant, i.e., by reducing the volume of acid for smaller amounts of samples. However, suf-

ficient acid should be present in the solution to dissolve all of the Te. Therefore, 1.0–1.2 g Te was dissolved in 4 mL (50%) nitric acid.

Optimization of TH-ETAAS Temperature Program and Interferences

The instrumental operating parameters were optimized and found to be the same as those recommended by the manufacturer, except that the drying time was increased from 30 s to 50 s. With a 30-s drying time, a 25–50% lower absorbance signal was observed for all elements due to incomplete drying at the recommended temperature of 130ºC. Adding various amounts of standard to the matrix checked the interference due to residual Te. Recovery obtained for the elements Al, Cd, Co, Cu, In, Ni, Pb, and Zn was nearly 90–100% (see Table I). This indicates that matrix interference was negligible for these elements. For Mn, Cr, and Fe, a 70–85% recovery was observed, while only a 50% recovery was obtained for Na, K, and Ca in comparison to the aqueous
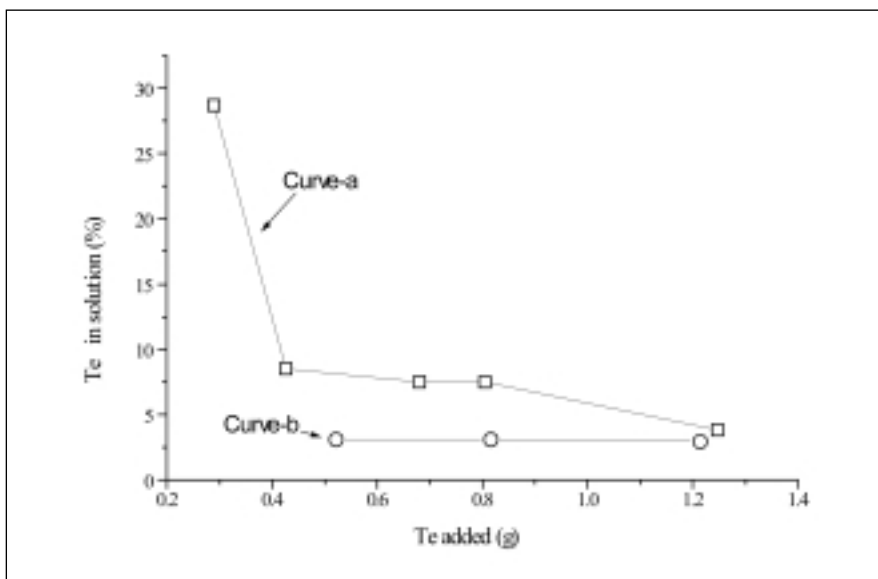

Fig. 1. Amount of Te (%) retained in the solution.
Curve-a: Adding different amounts of Te to 4 mL (50%) nitric acid.
Curve-b: Ratio of Te to nitric acid fixed by reducing the total volume.

standard. Therefore, the standard addition curve was used to quantify these elements.

Optimization of ICP-MS Operating Conditions and Interferences

The ICP-MS operating parameters were optimized using a tuning solution containing 10 µg/L each of ^{9}Be, ^{59}Co, ^{115}In, and ^{209}Bi. At first, the parameters such as nebulizer gas flow and position of the Ni sampler cone were adjusted by changing the x, y, and z axis of the plasma torch. Then the voltages of the ion lenses (extractor and collector) were varied to get optimum counts for these elements. In order to check the interferences due to residual Te and the nitric acid matrix, a spectrum of one of the samples in scan mode was obtained. Spectra in the region m/z 7.4–26.6, 27.4–43.6, 55.4–56.6, 79.4–81.6, and 120–130 were not acquired (to protect the detector from high counts due to ionization of gases present in the atmosphere and due to Ar$^+$, ArO$^+$, Ar^{2+}, and 120–130 Te$^+$). Due to nitric acid in the matrix, large peaks at m/z 52, 54, and 55 were observed. These were due to ^{38}Ar^{14}N$^+$, ^{40}Ar^{14}N$^+$, and ^{40}Ar^{15}N$^+$, which will interfere in the determination of Cr and Mn. Peaks observed between m/z 136–146 were due to the formation of $^{120-130}$Te^{16}O$^+$.

Recovery After Spiking the Solution Before Precipitation With Known Standards

In order to check the loss of trace elements from the solution during precipitation, known amounts of standards were added to 4 mL (1:1) nitric acid before adding the Te metal. Reaction started almost immediately after Te was added. The mixture was warmed with an I.R. lamp to enhance the reaction, and precipitation was started. The solution was analyzed after removing excess

acid, then made up to 2-mL volume for TH-ETAAS and to 20-mL volume for ICP-MS analysis. These experiments were carried out separately. The results obtained by both ICP-MS and TH-ETAAS are listed in Tables IIa and IIb. In both cases, recoveries between 90–110% were obtained for most of the elements (Al, Cd, Co, Cr, Cu, Fe, In, Ni, and Pb); Fe was only determined by TH-ETAAS. The higher values obtained for Ni by ICP-MS are due to the Ni sampler cone. For Bi, Ge, Sb, Sn, Ti, and V, a recovery between 1–26% was observed by ICP-MS analysis, indicating a loss of these elements from the solution. Sb was also not recovered by TH-ETAAS, confirming the findings of ICP-MS. A 65% recovery for As and an 81% recovery for Zn was obtained by ICP-MS. The high value of 123% obtained for Cr by TH-ETAAS may be due to contamination. Good recovery for 9–10 elements without adding any complexing agent such as EDTA was found indicating that these elements can be determined using this procedure.

TABLE I
Recovery of Trace Elements in the Presence of Te Matrix by TH-ETAAS

Elements	Amount of Matrix Added (µg)	Amount of Analyte Added (pg)	Recovery (%)
Al	200	600	93
Ca	200	25	50
Cd[a]	380	75	100
Co	200	100	92
Cr	100	450	75
Cu	200	800	93
Fe	40	100	86
In	200	500	104
K	200	50	50
Mn	200	250	71
Na	40	10	50
Ni	200	500	90
Pb[a]	200	650	95
Zn[b]	20	75	89

[a] 5 µg Mg(NO$_3$)$_2$+50 µg PO$_4$
[b] 5 µg Mg(NO$_3$)$_2$

TABLE IIa
Recovery of Spiked Solution Obtained With TH-ETAAS to Assess the Loss of Trace Elements During Precipitation

Elements	Amount of Analyte		Recovery (%)
	Spiked (ng/mL)	Recovered (ng/mL)	
Al	6	6.5	108
Cd	1	0.98	98
Co	5	4.5	90
Cr	8.5	10.5	124
Cu	8	8.2	103
Fe	5	5.3	106
In	10	10.5	105
Ni	5	4.9	98
Pb	10	10	100
Sb	20	0	0
Zn	2	2	100

TABLE IIb
Recovery of Spiked Solution Obtained with ICP-MS to Assess the Loss of Trace Elements During Precipitation

Elements	Amount of Analyte		Recovery (%)
	Spiked (ng/mL)	Recovered (ng/mL)	
Al	6.3	6.8	108
As	5.0	3.4	68
Bi	8.0	1.8	23
Cd	7.7	7.5	98
Co	5.1	5.0	98
Cr	8.8	8.0	91
Cu	8.0	7.6	95
Ge	5.0	0.15	3
In	5.0	4.6	92
Ni	8.8	8.5	97
Pb	6.5	6.2	95
Sb	5.2	0.2	3.9
Zn	4.8	3.9	81

TABLE III
Comparison of Process Blanks Obtained by Proposed Method and Precipitation and Ion Exchange Procedure Reported in the Literature[a]

| Elements | Proposed Method | | TeO$_2$ Precipitation (5) at pH 4.5[b] | Ion Exchange Separation (5) |
	TH-ETAAS	ICP-MS		
Al	2	2	–	–
Ca	30	–	–	–
Cd	<0.05	1.8	50	40
Co	<5	1.8	–	–
Cr	<3	120	500	160
Cu	<2	<2	1000	560
Fe	25	–	–	–
In	<10	2.0	–	–
Mn	>0.5	–	300	160
Na	<5	–	–	–
Ni	3	–	850	160
Pb	<3	<3	650	200
Zn	10	10	–	–

[a] Based on ng/g in normal laboratory conditions.
[b] In normal laboratory conditions.

TABLE IV
Comparison of Limit of Detection by TH-ETAAS and ICP-MS

| Elements | Limit of Detection (ng/g) | |
	TH-ETAAS	ICP-MS
Al	1	1.2
Ca	5	–
Cd	0.05	0.1
Co	5	1
Cr	3	3
Cu	2	3
Fe	5	–
In	5	0.5
K	5	–
Mn	0.5	0.5
Na	5	–
Ni	3	3
Pb	3	3
Zn	3	3

Process Blank and Limit of Detection

The process blank obtained by this procedure and the one involving the precipitation of TeO$_2$ in the pH 4–5 range are compared in Table III. In the latter case, the blank was recalculated in ng/g. The low blanks obtained by this procedure are due to the minimal chemical processing steps which are precipitation, evaporation of excess nitric acid, and minimal use of reagents (nitric acid and high purity water, both of which can be obtained in highly pure form). Additional processing steps such as pH adjustments and addition of complexing agents such as EDTA are completely avoided as in the TeO$_2$ precipitation method (5). The limits of detection, based on three times the fluctuation in the blank

values, are given in Table IV. By using TH-ETAAS, Cd shows a two times lower detection limit compared to ICP-MS because of lower dilution; In shows 10 times higher detection limits with TH-ETAAS in comparions to ICP-MS because of loss of In as InO in the graphite furnace.

RESULTS

In order to check the accuracy of the method, a Te sample with 3N–4N purity was analyzed by direct dissolution as well as by precipitation using the proposed method. The results are given in Table V. The elements Al, Ag, Cd, and Cu were determined by ICP-OES, while Co, Cr, Mn, Ni, Pb, and Zn were determined by TH-ETAAS. It can be seen that the results are in agreement within experimental error.

TABLE V
Results of Trace Impurities in 3N to 4N Te Samples (n=3) (μg/g) Obtained by Direct Dissolution and Proposed Precipitation Methods Using ICP-OES and TH-ETAAS

| Elements | Sample | |
	Direct Method	Proposed Method
Al[a]	7±2	10±2
Ag[a]	3.3±0.2	3.3±0.1
Cd[a]	82±6	98±8
Co[b]	0.02±0.01	0.02±0.01
Cr[b]	0.4±0.2	0.3±0.1
Cu[a]	6.3±0.4	6.3±0.4
In[b]	<0.1	<0.1
Mn[b]	0.94±0.08	0.86±0.06
Ni[b]	3±1	2.5±0.5
Pb[b]	10±2	10±2
Zn[b]	1.6±0.2	1.4±0.3

[a] Determined by ICP-OES.
[b] Determined by TH-ETAAS.

The results obtained on three 7N samples by both techniques (ICP-MS and TH-ETAAS) are presented in Table VI and the values agree well. However, the results for Cr and Ni were higher by ICP-MS. In the case of ^{52}Cr, the higher values obtained are due to the interference of $^{38}Ar^{14}N^+$, even though the spiked samples showed good recovery. This may be due to the differences in the residual nitric acid in the process blank and sample. For the spiked samples, the process blank is the unspiked sample; hence, residual nitric acid is the same, resulting in good recovery. For Ni, the contamination in ICP-MS measurements are due to the sampler cone. All remaining values are in good agreement with both techniques, thus indicating the accuracy of the proposed method.

CONCLUSION

A fast and simple method for the characterization of trace elements in 7N pure Te samples is reported. The values obtained with both ICP-MS and TH-ETAAS analysis agree well, except in the case of Cr and Ni. The difference is due to isobaric interferences; therefore, the ICP-MS values must also be cross-validated by TH-ETAAS.

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TABLE VI
Results of Trace Impurities in Te Samples (n=3) (ng/g)

Ele-ments	Sample 1		Sample 2		Sample 3	
	ICP-MS	TH-ETAAS	ICP-MS	TH-ETAAS	ICP-MS	TH-ETAAS
Al	18±3	15±2	7.4±2	6±2	5.3±2	5±1
Ag	9.3±0.8	8±1	11±1	9±1	8.5±0.9	10±1
Cd	2±0.2	1±0.5	0.5±0.2	1±0.5	–	–
Co	2.5±1	<5	1.6±1	<5	1.5±1	<5
Cr	60±4	<5	60±6	<3	50±6	<3
Cu	8.0±1	<10	6±2	<10	6±2	<10
In	1.0±0.5	<10	–	<10	1.0±0.5	<10
Mn	<1	<0.5	<1	<0.5	<1	<0.5
Ni	350±15	<3	430±13	<3	470±20	<3
Pb	<3	<3	<3	<3	<3	<3
Zn	<5	<5	<5	<5	<5	<5

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