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A Simplified Flow System for Inorganic Arsenic Speciation by Preconcentration of As(V) and Separation of As(III) in Natural Waters by ICP-MS

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ABSTRACT

The toxicity of certain elements is related to their organic constituents or oxidation states. As such, total elemental determinations do not always yield sufficient information for accurate risk assessment and therefore speciation, fractionation, or separation data is required. In order to obtain speciation for trace levels of arsenic, a flow system using the quaternary amine resin LC-SAX for As(V) preconcentration was coupled on-line with the ICP-MS. The flow network is comprised of a small resin column and a manual injector. While the sample was loaded through the resin column, the As(III) was determined. Moving the injector to the alternative position, elution takes place releasing the As(V) retained in the resin column. The elution with 200 mL of 1% (v/v) HNO_3 was adjusted to attain precise transient signals. An enrichment factor of approximately 4 for a sample volume of 1 mL was attained. The eluted band produced a transient peak with a width at half peak maximum of approximately 25 s, enough to determine As(V) by ICP-MS. The measurement precision for the 50 µg/L of As(V) and As(III) solutions was characterized by a RSD of 1.4 and 1.2%, respectively. The correlation coefficients for the calibration curves of As(V) and As(III) were 0.9997 and 1.000, respectively. The detection limits (DL) were 0.036 µg L^{-1} for As(III) and 0.094 µg L^{-1} for As(V). The feasibility of the proposed system was demonstrated by the determination of As(V) and As(III) in natural waters. In the samples, the As(V) and As(III) concentrations varied from 0.15 to 61 µg/L and 0.10 to 6 µg/L, respectively. Comparing the total As concentration with the results obtained after speciation, the recoveries were in the range of 99 to110%. The system was characterized by a sample throughput of 15 samples per hour.

INTRODUCTION

Arsenic (As) is a ubiquitous element found in the atmosphere, soils and rock, natural waters, and organisms. It is mobilized through a combination of natural processes such as weathering reactions, biological activity, volcanic emission, and anthropogenic activities (1). Arsenic occurs naturally in over 200 different mineral forms, of which approximately 60% are arsenates, 20% sulfides and sulfosalts, and the remaining 20% includes arsenides, arsenites, oxides, silicates, and elemental arsenic (2). In most rocks, arsenic ranges from 0.5 to 2.5 mg kg^{-1} (3) and is found in various types of metalliferous deposits. Arsenic is common in pyrite, galena, and chalcopyrite, and less common in sphalerite. The most common arsenic mineral is arsenopyrite, FeAsS. The level of arsenic in soils ranges from 0.1 to 50 mg kg^{-1} (mean around 6 mg kg^{-1}), but varies considerably among geographic regions (4). In fresh water, the As concentrations vary by more than four orders of magnitude depending on the source, the amount available, and the local geochemical environment (5).

Human activity has had an important additional impact on the environment through mining, combustion of fossil fuels, the use of arsenical pesticides, herbicides, crop desiccants, and other As sources, which contaminates numerous areas with this element and their compounds (5). Studies investigating the behavior of such contaminants in the environment have identified speciation as a key factor controlling their mobility, availability, and toxicity (6).

The Iron Quadrangle in the Minas Gerais State is one of the best known Brazilian mining regions, producing gold, topaz gems, and especially iron and manganese ores. Gold is often found in association with arsenopyrite. In 1999 and 2000, As determinations in surface water samples within this area showed concentrations varying from approximately 50–2300 µg L^{-1}, and thus above the limit allowed by the Brazilian legislation. In these investigations, the highest concentrations were found along a stream near the Passagem gold mine: 630 and 2300 µg L^{-1} (7). In the gold mining districts of Nova Lima and Santa Barbara, a study carried out in 2000 reports a mean As concentration of 30.5 µg L^{-1} in surface water samples (0.40 to 350 µg L^{-1}) (8). Another study in the same area in 2003 indicates that As concentrations in the water were up to 300 µg L^{-1} and in the range of 20 to

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4000 mg kg^{-1} in stream sediments. In this area, the As^{3+}/As^{5+} concentration ratios obtained for some water samples varied from 1.10^{-1} to 4.10^{-2} (9,10). The high As concentrations in this region also result from the mobilization of arsenic species to the hydrological system.

Following the accumulation of evidence for the chronic toxicological effects of As in drinking water, regulatory limits are being reduced. The WHO guideline value for As in drinking water was provisionally reduced in 2001 from 50 to 10 µg L^{-1} (11); this lower limit will be adopted by the U.S. EPA in 2006 (12). The new recommended value is based on the increased awareness of the toxicity of As, particularly carcinogenicity, and on the ability to measure it quantitatively.

The biological availability and the physiological and toxicological effects of arsenic depend on its chemical form and oxidation state (13). The naturally occurring organo-arsenic forms are generally found to be relatively nontoxic to aquatic life (14). However, the inorganic forms are highly toxic. Arsenic in the form of As(III) (arsenious acid, H_3AsO_3, and its dissociation products) is considered to be the most toxic form, followed by As(V) (arsenic acid, H_3AsO_4, and its dissociation products). Whether the arsenic is in the dissolved or the particulate state may also be very important from an ecotoxicological viewpoint, depending on the uptake form utilized by a particular organism. Additionally, the trivalent inorganic As is much more mobile than the pentavalent As (15,16).

For water samples, inorganic As speciation is an important tool due to the differences in toxicity, biochemical and environmental behavior of As species (17). Arsenic determination using on-line arrangements has the additional advantage of avoiding excessive sample handling, although some analysis schemes involve numerous steps while others are too costly to be recommended for routine use (18).

A flow injection system coupled to a GF-AAS was applied to As(III) pre-concentration and separation of total As in seawater samples. The As(III) was complexed with sodium diethyldithiocarbamate (NaDDTC) and retained on a C_{18} reversed phase packing column (19). A dual-column protocol for the sequential determination of As(III) and As(V) is described using inductively coupled plasma atomic emission spectrometry (ICP-AES) with ultrasonic nebulization (USN). This procedure employed a 16-way valve containing two different homemade mini columns for the selective preconcentration of As(III) and As(V) (20).

Arsenic speciation in environmental, geochemical, and hydrogeochemical studies has been made directly in the sampling field. The in situ sampling and As separation is performed with a syringe filled with the quaternary amine resin LC-SAX, which preconcentrates the As(V). However, the *in situ* procedure increases the possibility of contamination and sample loss. Therefore, the goal of this paper was to develop a rapid and simple flow injection system coupled to an ICP-MS for speciation of As(V) and As(III) in water samples from mining regions. To make this system feasible, the main parameters involved in coupling the preconcentration system to the ICP-MS were investigated in order to attain good sensitivity, accuracy, and stability.

EXPERIMENTAL

Instrumentation

The main flow system components were a peristaltic pump with six channels (Micronal B332 II, Piracicaba, São Paulo, Brazil), a Perspex homemade injector described elsewhere (21), Y-shaped connectors, Tygon® pumping tubing (Ismatec, Zurich, Switzerland) and polyethylene tubing.

The column filled with quaternary amine resin was made by placing a 400 mesh polyester screen (used in silk screen painting) covering the extreme of a 4-cm long and 3-cm wide Tygon tube with approximately 2.3 cm^3. The resin was loaded inside the column by pushing it with a syringe from one end, the other end being closed.

The flow system was connected to the cross-flow nebulizer of the inductively coupled plasma mass spectrometer (ICP-MS) with a 20 cm polyethylene tubing (0.86 mm i.d.). The measurements were carried out using an ELAN® 9000 ICP-MS instrument (PerkinElmer SCIEX, Concord, Ontario, Canada) under the conditions presented in Table I and a PerkinElmer AAnalyst™ 300 graphite furnace atomic absorption spectrometer (GF-AAS) (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA).

Reagents and Solutions

The quaternary amine resin LC-SAX (40-45 µm) from Supelco (Bellefonte, PA, USA) was used as

TABLE I
Instrumental and Operational Parameters of ICP-MS

RF (40 MHz), Power (W)	
Forward	1000
Reflected	< 5
Gas Flows (L min^{-1})	
Plasma	15
Auxiliary	1.2
Nebulizer	0.85
Measurement–^{75}As	Peak Jump
Sweeps	7
Reading/Replicate	1
Replicates	150
Dwell Time	100 ms

anionic exchanger to preconcentrate As(V). Purified water (18.2 MΩ.cm), produced with a Milli-Q™ system (Millipore, Bedford, MA, USA), and Suprapur® HNO_3 (Merck, Darmstadt, Germany) were used as the carrier and eluent, respectively.

External calibration analyses were carried out using standard solutions containing As(V) and As(III) in concentrations from 0 to 100 µg L^{-1}. A 1000 mg L^{-1} As(V) Certipur, standard solution (Merck, Darmstadt, Germany) and As(III) stock solution, prepared from As_2O_3 (Merck), were employed.

Flow System

As(V) preconcentration and separation of As(III) was achieved by employing a simplified flow injection system depicted in Figure 1. Firstly, the sample (S) was aspirated filling the sample loop L1 (1000 µL) following the scheme depicted in Figure 1-A, while the water carrier stream Ce was pumped (1.0 mL min^{-1}) through the resin column to the ICP-MS. Subsequently, in the preconcentration step, the injector was moved to the other position, Figure 1-B. In this position, the sample volume (L1) was pumped through the resin column to preconcentrate As(V), while As(III) was transported by the water carrier stream Cs (1.0 mL min^{-1}) to the ICP-MS. Also at this position, loop L2 (200 µL) was filled with the eluent. After the preconcentration step, the injector was again moved to the initial position (Figure 1-A), placing the column in the eluent pathway. The eluent solution held in loop L2 was carried by Ce through the resin column to elute the As(V) retained. The elution applying a reverse flow was employed to avoid the transport of eluted ions through the dead volume of the column, minimizing analyte dispersion (22).

RESULTS AND DISCUSSION

Flow parameters were established in order to reach high efficiency in the As(III) separation and As(V) preconcentration when coupling the flow system to the ICP-MS. The elution parameters were adjusted to attain the most efficient removal of As(V) from the resin column. In the elution step, the reverse flow elution mode was applied to prevent dispersion due to dead volume and resin compression in one side of the column (Figure 1). The eluent concentrations ranging from 0.5 to 3.0 mol L^{-1} of nitric acid were studied in order to achieve the best elution conditions for 50 µg L^{-1} As(V) solution, with a 1.0 mL sample loop, 4.0 mL min^{-1} loading and 1.0 mL min^{-1} elution flow rate. The results of five transient signals obtained for each eluent concentration are shown in Figure 2. According to the results, concentrations lower than 1.0 mol L^{-1} were not efficient to elute the As(V) retained in the resin column. In concentrations above 1.0 mol L^{-1}, the eluted signals were similar, but the higher standard deviation for concentrations varying from 1.0 to 2.0 mol L^{-1} indicates an incomplete removal of the element from the resin. Therefore, 2.5 mol L^{-1} was employed throughout the experiments. Peak profile comparing the direct determination and preconcentration of 50 µg L^{-1} of As(V) is depicted in Figure 3. The 1-mL

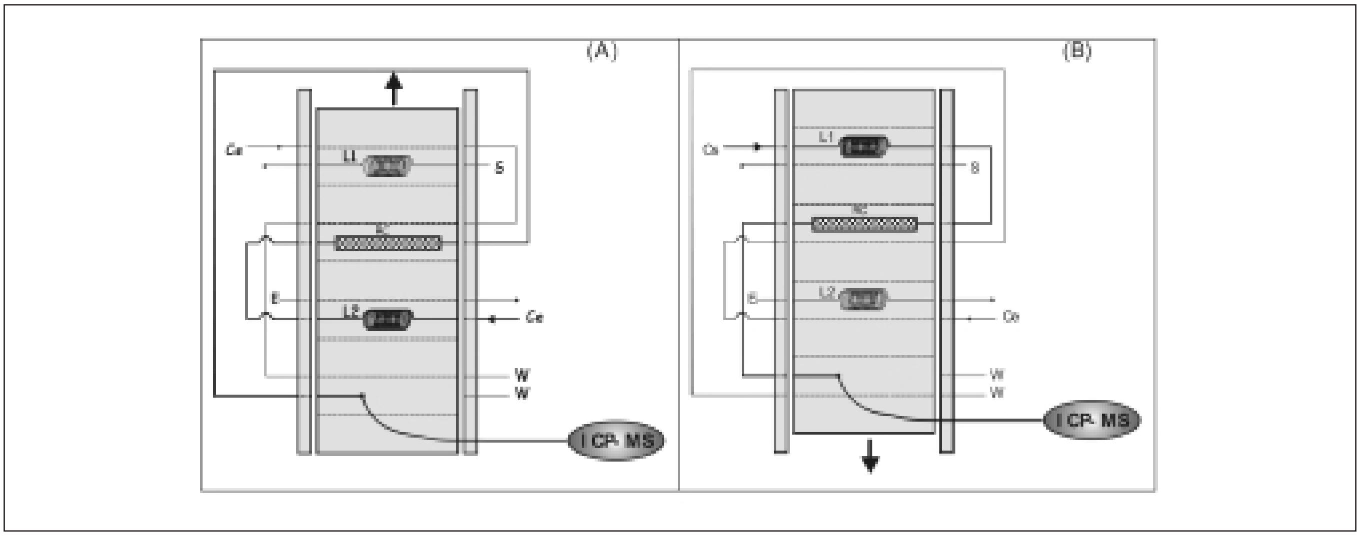

Fig. 1. Flow system for on-line preconcentration of As(V) and separation of As(III). The three rectangles represent the injector in the sampling and elution steps (A) and in the preconcentration step (B). Black arrows represent sites where pumping is applied for sample (S), eluent (E), and water carrier solution (C_s and C_e). L_1 and L_2 are the sample and eluent loops. The column (RC) is packed with ion exchange resin. W indicates the waste.

sample loop used in this system allows an enrichment factor of 4.

For solutions containing both inorganic arsenic species, in the sampling step, the As(V) was retained in the resin column while the As(III) flows through the column directly to the ICP-MS. Afterwards, in the elution step, the As(V) retained in the resin column is eluted and measured. The signal profile of a solution containing 100 µg L^{-1} of As(III) and 50 µg L^{-1} of As(V) is shown in Figure 4. Separation of As(III) and the preconcentration of As(V) takes approximately 3.5 minutes, since this system is characterized by a sample throughput of 15 samples per hour. For the sample measurements, the As was measured in two steps, where the acquisition time was 8 s for both in the maximum of the peak. In the first step, when the injector was in the pre-concentration position (Figure 1-B), the As(III) not retained by the resin was measured after a measurement delay of 60 s. Subsequently, to determine the As(V), the injector was moved to the elution position (Figure 1-A) using a 25 s delay.

The feasibility of the proposed system was demonstrated by the determination of As(V) and As(III) in water samples collected in a watercourse (Ribeirão Cardoso) located at Iron Quadrangle, Brazil. The samples were collected at three different locations on three different days. The detection limits (DL) calculated using 3σ of each blank solution are presented in Table II. The limits for all extracts were adequate to determine the target elements in all samples. The results of the determination of As(III) and As(V) using the preconcentration system, and also of the total arsenic content in the sample determined directly, are also presented in Table II. Comparing the concentration of As(III) plus As(V) with the As total, the overall recovery rates for the samples varies 75.6 to 100.8%, in which the lowest recoveries were obtained for the samples with lower concentrations (samples collected in local 1 – day 1 and local 2 – day 2). Currently, the only way to validate that only As(III) and As(V) are present is to sum the species and then measure total As.

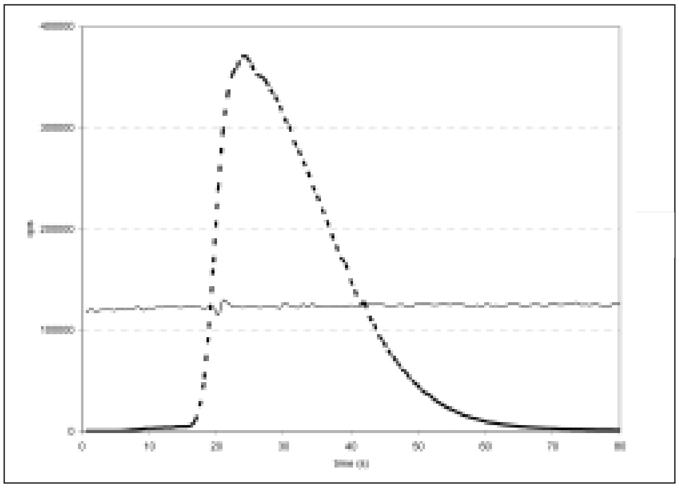

Fig. 3. As(V) signal profile after the pre-concentration and elution of 1.0 mL of 50 µg L^{-1} solution compared with the direct determination.

—— direct
----- As(V)

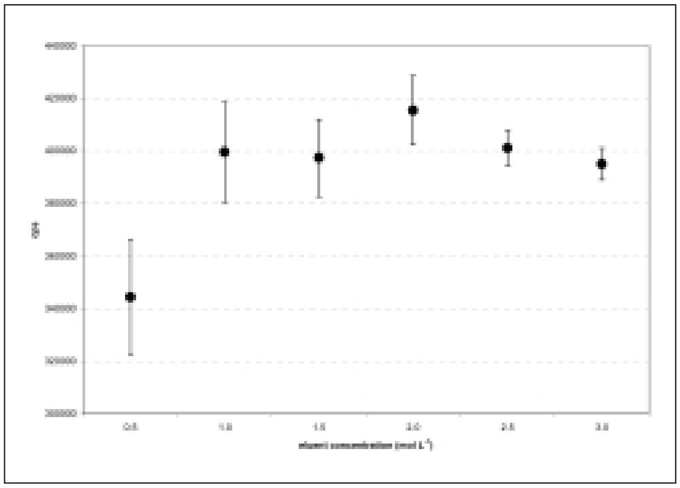

Fig. 2. Results obtained as a function of eluent concentration for 200 µL volume. A loading flow rate of 4.0 mL/min and an eluent flow rate of 1.0 mL/min were used. A solution containing 50 µg L^{-1} of As (V) was used to carry out the investigation of this parameter.

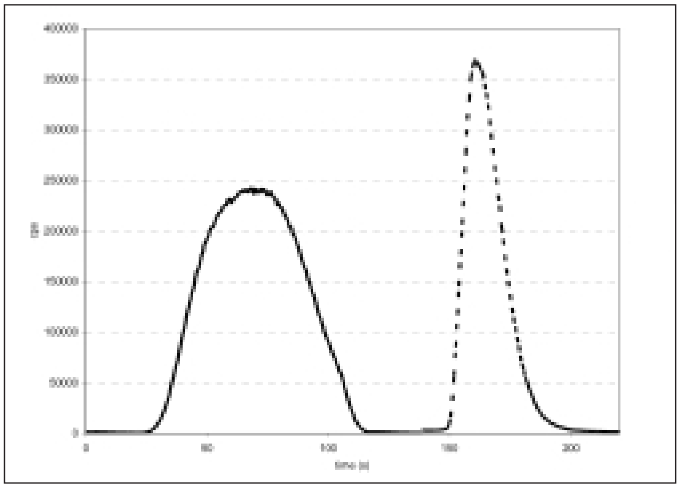

Fig. 4. Transient signal obtained at m/z 75 produced by injection of 100 µg L^{-1} of As(III) plus 50 µg L^{-1} of As(V).

—— As(III)
----- As(V)

TABLE II
As(III) and As(V) Concentration (μg L^{-1}) in the Water Samples
(Values correspond to the mean and standard deviation of three measurements.)

	As(III)	As(V)	Sum	Total	Recovery (%)
Local 1 – Day 1	0.224 ± 0.003	0.137 ± 0.015	0.361	0.477 ± 0.011	75.6
Local 2 – Day 1	0.046 ± 0.001	1.87 ± 0.07	1.92	2.18 ± 0.03	88.3
Local 2 – Day 2	0.062 ± 0.001	3.55 ± 0.04	3.61	3.95 ± 0.04	91.6
Local 3 – Day 1	0.133 ± 0.002	60.9 ± 0.6	61.1	64.5 ± 0.5	94.8
Local 3 – Day 2	0.062 ± 0.001	47.9 ± 0.4	48.0	47.6 ± 0.7	100.8
Local 3 – Day 3	6.3 ± 0.1	31.2 ± 0.3	37.5	38.8 ± 1.1	96.8
100 μg/L As(III) + 50 μg/L As(V)	100.9	48.3 ± 0.7	149.1	150 ± 1.2	99.4
50 μg/L As(V)		47.8 ± 1.1	47.8	50 ± 0.5	95.6
DL	0.036	0.094			

Although the concentrations of organic As species as monomethylarsonate (MMA) and dimethylarsinate (DMA) are very low in these samples, they are not retained by the LC-SAC resin. Therefore, organic As and As(III) flows through the system directly to the ICP-MS. However, due to the low concentration of organic As present in these samples, only the As(III) concentration is considered in the measurements.

To ensure the accuracy of the results, the total As concentrations of three samples used in the speciation and six other samples collected in the same location were determined by ICP-MS and GF-AAS. Comparison of the two data sets, shown in Table III, was assessed by testing the variances (F-test) and the means (paired *t*-test). For a confidence level of 95%, the $F_{calculated} = 1.08$ and $t_{calculated} = 0.32633$ were lower than the $F_{tab} = 3.44$ and $t_{tab} = 2.12$, which confirms that the analytical data obtained by the two methods are not significantly different for most of the results. The differences between the results for samples 1 and 4 may be ascribed to the uncertainty of the GF-AAS measurements in such low As concentrations, which are levels very close to the technique's detection limit.

TABLE III
Mean Concentration of Total As (μg L^{-1}) Measured by ICP-MS and GF-AAS

Sample	ICP-MS	GF-AAS
Sample 4	2.12	1.0
Sample 5	136.0	125.6
Sample 6	69.7	64.8
Sample 7	78.8	67.5
Sample 8	63.8	57.4
Sample 9	54.8	50.3
Local 2 - Sample 1	2.18	3.6
Local 3 - Sample 1	64.5	94.7
Local 3 - Sample 3	38.8	59.9

CONCLUSION

The simplified flow system using the quaternary amine resin LC-SAX coupled to an ICP-MS was efficient for the preconcentration of As(V) and its separation from As(III) in water samples containing low concentrations of organic As. The system is adequate for routine analysis of As(V) and As(III) since it allows a sample throughput of 15 samples per hour.

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Microwave-assisted Speciation Studies in Fly Ash by AAS and ICP-MS: Comparison Between Tessier and BCR Sequential Extraction Schemes

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ABSTRACT

The speciation of four environmentally important elements (copper, zinc, arsenic, and manganese) in terms of free ions, labile complexes, slowly labile complexes, and stable complexes has been investigated in fly ash. Microwave-assisted sequential extraction methodologies have been applied to two fly ash standards (NIST 1633b and NIES 38) in order to determine the comparative effects of the Tessier and BCR sequential extraction schemes. Both schemes were compared with respect to partitioning patterns of these elements, operation times, % recovery, and matrix effects.

FAAS was applied to study the individual leachates of manganese, zinc, and copper, while HGAAS was used for arsenic determination; ICP MS was used to check the validity of the results. Recoveries were found to be similar (difference of ~5%) for all elements, except for arsenic, where extraction by the Tessier scheme was about 10% higher than by the BCR scheme for the NIST 1633b standard fly ash. In order to estimate the effects of calibration by aqueous standards and the standard addition methods, the *t*-test (P= 0.95) was applied. It was found that interferences due to matrix effects are comparatively lower in the BCR extraction scheme. Microwave extraction time, taken for the total extraction of individual leachates, was about 21 min longer in the Tessier scheme.

INTRODUCTION

Coal fly ash is a rich source of a large number of trace elements in a complex alumino-silicate matrix and is one of the major pollutants emitted from coal-fired power stations. Large numbers of toxic trace elements carried by microscopic ash particles are emitted into the atmosphere (1) and vast amounts are generated as solid wastes. To study the environmental impact of coal-fired plants, an understanding of trace element migration is important (2). Hence, in order to obtain a thorough knowledge of the toxic actions of different species of an element (3), identification and quantification of the chemical forms of these elements are essential (4). To achieve this objective, various sequential extraction procedures have been designed and applied to different types of environmental samples (5–8).

The scheme developed by Tessier et al. (5) and its subsequent modifications (9–12) has been widely applied. To advance the scheme and make element partitioning more comparable, a group of European experts designed a standardized sequential extraction procedure known as the BCR scheme (13). Unlike the Tessier protocol, where partitioning of the elements is done in five fractions (exchangeable, carbonate-bound, iron/manganese oxide-bound, organic matter-bound, and residual fractions), the BCR protocol has four fractions: the acid-soluble, reducible, oxidizable, and residual fractions. This sequential extraction method has been successfully applied to different matrices, such as soils and sediments (14–16), bottom ash (17), sewage sludge (18), and wastewater sediments (19).

In most of the sequential extraction procedures applied to the Tessier and BCR schemes, the conventional technique has been used which involves shaking the individual fractions for a long time in order to ensure maximum leaching. As a result, the methods are comparatively tedious. However, previous studies on microwave-assisted extraction procedures are now being used on various matrices such as sewage sludge (20). In our earlier work (21), we had applied the microwave-assisted extraction procedure to the Tessier scheme and optimized the conditions for complete sequential extraction of copper, zinc, arsenic, and manganese in fly ash. Microwave-assisted techniques have been used in various fields of research for the benefit of maximum time savings and minimum contamination by reagents (22,23).

In the present work, the microwave-assisted technique was applied to two fly ash standards (NIST 1633b and NIES 38). The two extraction schemes were compared with respect to their extraction efficiency for particular elements, time of operation, and interference effects of the extractants and substances co-extracted with the analyte.

Extractable copper, zinc, and manganese were determined by

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flame atomic absorption spectrometry (FAAS), while arsenic was determined by hydride generation atomic absorption spectrometry (HGAAS). A comparative study of the results obtained with AAS was performed by inductively coupled plasma mass spectrometry (ICP-MS). The proposed method has proven to be extremely effective and rapid, especially for environmental samples such as fly ash (24-26).

EXPERIMENTAL

Instrumentation

A domestic microwave oven (Samsung CE 2933) with a 2450 MHz frequency magnetron and maximum power of 900 W was used as the microwave energy source. PTFE reactors with 115 mL internal volume, 1 cm cell wall thickness, and hermetic screw caps were used for sample digestion. The determination of elemental concentrations was done using a GBC Avanta atomic absorption spectrometer. Lamp intensity and slit widths were adjusted according to instrumental requirements. Hollow cathode lamps with resonance lines at 324.7, 213.9. 279.5, and 193.7 nm, respectively, for copper, zinc, arsenic, and manganese were used as the radiation sources. A Systronic 362 digital pH meter was used for pH measurements. An ULTRA MASS 700 inductively coupled plasma mass spectrometer (Varian, Australia) was employed for ICP-MS analysis, using yttrium as the internal standard. The instrumental operating conditions are given in Table I.

Reagents

All reagents used were of analytical reagent grade and of the highest purity available. Ammonium acetate and hydrogen peroxide were from E. Merck, Mumbai, India, and hydroxylamine hydrochloride was procured from SRL, India. Standard solutions for copper, zinc, arsenic, and manganese for calibration purposes in AAS measurements were prepared from 1000 g/mL stock solutions of each element (E. Merck, Germany).

Sequential Extraction Schemes

Sequential extraction schemes were applied to 0.2 g of coal fly ash standards S1 (NBS SRM 1633b) and S2 (NIES 38); the individual schemes of extraction are illustrated in Figure 1. For the first three fractions of the Tessier scheme and the first two fractions of the BCR scheme, the power was adjusted to stay below 180 W. The different stages of both schemes (as shown in Figure 1) ensure maximum extraction efficiency, while at the same time preventing excessive heating or partial leaching from the next phase. Hence, the temperature was constantly monitored so that it remained below 70°C. The time required for the BCR scheme was about 21 min less than that of the Tessier scheme (see Tables II and III).

TABLE I. ICP-MS Instrumental Operating Conditions

Instrumental Parameters		Scanning Parameters	
Plasma argon flow	0.01 L/min	Scanning mode	Segmented scan
Nebulizer argon flow	.8 L/min	Reading spacing	0.01 AMU
Auxiliary flow	1.0 L/min	Scans per replicate	30
Sampling depth	9.0 mm	No. of replicates	5
Extraction lens	–600V	Sample delay	30 seconds
First lens	–220V	Sample pump rate	5 mL/min
Photon stop	–13.2V	Analysis time	4 min/sample

TABLE II. Microwave Conditions for the Complete Leaching of Fly Ash in the Tessier Scheme

Fraction	Power (W)	Time (min)
Exchangeable	180	54 (6 × 9) [a]
Carbonate-bound	180	45 (5 × 9) [b]
Fe / Mn oxide-bound	180	45 (5 × 9) [b]
Organically bound	300	55 (5 × 2)+(5 × 9)] [c]
Residual	450	20 [(3 × 2)+(5 × 2)+4] [d]

[a] 6 minutes, 9 times;
[b] 5 minutes, 9 times;
[c] 5 minutes, 2 times; followed by 5 minutes 9 times;
[d] 3 minutes, 2 times followed by 5 minutes, 2 times followed by 4 minutes.

TABLE III. Microwave Conditions for the Complete Leaching of Fly Ash in the BCR Scheme

Fraction	Power (W)	Time (min)
Acid-soluble	180	78 (6× 13) [a]
Reducible	180	55 [(5× 2)+(5 x 9)] [b]
Fe/Mn oxidizable	180	45 (5 × 9) [c]
Residual	450	20 [(3 × 2)+(5 × 2)+4)] [d]

[a] 6 minutes, 13 times;
[b] 5 minutes, 2 times followed by 5 minutes, 9 times;
[c] 5 minutes, 9 times;
[d] 3 minutes, 2 times followed by 5 minutes, 2 times followed by 4 minutes.

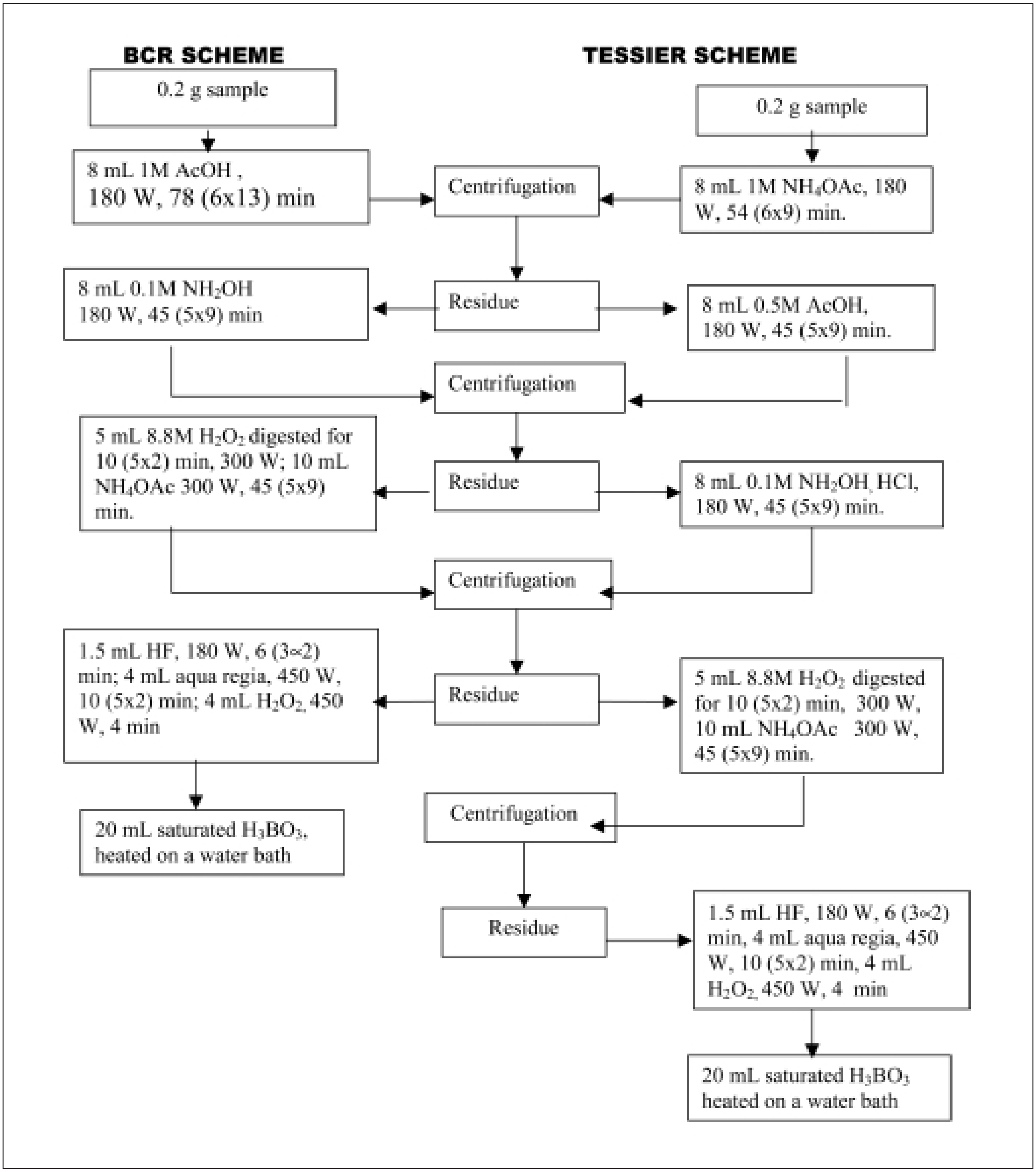

Fig. 1. Flow chart of BCR and Tessier schemes. Ac=acetate ion.

RESULTS AND DISCUSSION

Matrix Effects

Interference effects from substances co-extracted with the analyte in each stage of the extraction as well as from extraction solutions were investigated by comparing the slopes of the calibration curves (net absorbance versus element concentration) obtained from external standards and standard addition subjected to both extraction schemes. In the former case, the calibrant solutions contained the analyte in different concentrations in a 0.5 M HNO_3 medium. Hence, any significant change in the slope will be due to the influence of the extractants, as well as the fly ash matrix components, released at each stage in both sequential extraction procedures.

In order to estimate whether there was a significant difference between the concentration values obtained using either of the calibration methods, the *t*-test was applied (P= 0.95). Tables IV and V show the comparative results of the slopes of the calibration curves of the synthetic standards and the standard addition methods, in the Tessier and BCR schemes, respectively, for sample 1 (NIST 1633b standard fly ash). If the change in slope in the standard addition and aqueous standards is not greater than 5%, the aqueous standards can be safely used; otherwise the standard addition methods are recommended.

From the Tessier scheme it is evident that calibration by aqueous standards is feasible for copper in all stages; for zinc in the first, second, and fifth stages; and for manganese in the last four stages. Arsenic was found to be suffering significantly from matrix effects.

On the other hand, in the BCR scheme the interference due to matrix effects was found to be greatly reduced. The first four

TABLE IV. Comparison of Calibration Methods in BCR Sequential Extraction Scheme

	Element	Aqueous Standards (µg/g)$^{-1}$	Standard Addition (µg/g)$^{-1}$	% Change in slope
Fraction 1	Cu	1.55×10^{-4} (5.37×10^{-6})	1.57×10^{-4}(6.54×10^{-6})	+0.6
	Zn	2.83×10^{-4}(7.45×10^{-6})	2.79×10^{-4}(5.02×10^{-6})	-1.4
	As	0.034(1.03×10^{-3})	0.033(1.15×10-3)	+0.3
	Mn	1.15×10^{-4}(4.54×10^{-6})	1.19×10^{-4}(3.87×10^{-6})	+3.3
Fraction 2	Cu	1.55×10^{-4} (3.46×10-6)	1.54×10^{-4}(5.32×10^{-6})	-0.6
	Zn	2.80×10^{-4}(8.45×10^{-6})	2.77×10^{-4}(4.60×10^{-6})	-1.0
	As	0.034(0.65×10^{-3})	0.029(0.29×10^{-3})	-13.3
	Mn	1.16×10^{-4}(3.98×10^{-6})	1.15×10^{-4} (4.11×10^{-6})	-0.8
Fraction 3	Cu	1.49×10^{-4}(4.52×10^{-6})	1.54×10^{-4} (5.03×10^{-6})	+3.2
	Zn	2.82×10^{-4} (7.37×10^{-6})	2.78×10^{-4}(7.82×10^{-6})	-1.4
	As	0.033(0.93×10^{-3})	0.035(1.04×10^{-3})	+5.7
	Mn	1.18×10^{-4} (5.45×10^{-6})	1.20×10^{-4}(4.61×10^{-6})	+1.7
Fraction 4	Cu	1.48×10^{-4}(4.19×10^{-6})	55×10^{-4}(6.23×10^{-6})	+4.5
	Zn	2.81×10^{-4}(8.12×10^{-6})	2.84 (7.57×10^{-6})	+1.0
	As	0.032(1.02×10^{-3})	0.031(1.37×10^{-3})	-3.2
	Mn	1.19×10^{-4}(4.28×10^{-6})	1.17×10^{-4}(5.77×10^{-6})	-1.7

Average of three measurements. Standard deviations are given in parentheses.

TABLE V. Comparison of Calibration Methods in Tessier Sequential Extraction Scheme

	Element	Aqueous Standard (µg/g)$^{-1}$	Standard Addition (µg/g)$^{-1}$	% Change in Slope
Fraction 1	Cu	1.57×10^{-4} (3.34×10^{-6})	1.55×10^{-4}(4.86×10^{-6})	-1.3
	Zn	2.81×10^{-4}(6.87×10^{-6})	2.77×10^{-4}(7.49×10^{-6})	-1.4
	As	0.034(1.62×10^{-3})	0.028(1.03×10^{-3})	-21.42
	Mn	1.14×10^{-4}(5.12×10^{-6})	1.22×10^{-4}(6.04×10^{-6})	+6.5
Fraction 2	Cu	1.54×10^{-4} (4.92×10^{-6})	1.56×10^{-4}(6.26×10^{-6})	+1.3
	Zn	2.61×10^{-4}(5.34×10^{-6})	2.20×10^{-4}(8.40×10^{-6})	-18.6
	As	0.034(0.63×10^{-3})	0.030(0.72×10^{-3})	-13.3
	Mn	1.17×10^{-4}(3.65×10^{-6})	1.18×10^{-4}(2.19×10^{-6})	+1.9
Fraction 3	Cu	1.48×10^{-4}(2.39×10^{-6})	1.55×10^{-4}(5.82×10^{-6})	+4.5
	Zn	2.84×10^{-4}(4.97×10^{-6})	2.81×10^{-4}(5.11×10^{-6})	-1.06
	As	0.033(1.1×10^{-3})	0.029(1.50×10^{-3})	-13.7
	Mn	1.17×10^{-4} (3.52×10^{-6})	1.16×10^{-4}(4.03×10^{-6})	+0.8
Fraction 4	Cu	1.51×10^{-4}(6.01×10^{-6})	1.58×10^{-4}(7.93×10^{-6})	+4.4
	Zn	2.97×10^{-4}(5.48×10^{-6})	2.82×10^{-4}(8.35×10^{-6})	+5.3
	As	0.033(0.43×10^{-3})	0.032(0.75×10^{-3})	-3.1
	Mn	1.15×10^{-4}(4.75×10^{-6})	1.18×10^{-4}(5.03×10^{-6})	+2.5
Fraction 5	Cu	1.53×10^{-4}(4.93×10^{-6})	1.57×10^{-4}(5.88×10^{-6})	+2.5
	Zn	2.81×10^{-4}(8.12×10^{-6})	2.78×10^{-4}(8.03×10^{-6})	-1.1
	As	0.033(0.79×10^{-3})	0.031(1.04×10^{-3})	-6.3
	Mn	1.17×10^{-4}(5.67×10^{-6})	1.16×10^{-4}(6.41×10^{-6})	-0.9

Average of three measurements. Standard deviations are given in parentheses.

stages are safely recommended for calibration with aqueous standards, because for all elements a change in slope value is not more than 4.5%. The Fe/Mn oxide-bound step (second stage of the BCR scheme and third stage of the Tessier scheme) suffers from similar matrix effects in both extraction schemes.

On the whole, it can be concluded that elemental analysis by AAS is simpler with the BCR scheme than the Tessier scheme because there are fewer interferences due to the extractants as well as the substances co-extracted with the analyte in each stage of the extraction. However, arsenic, which was determined by HGAAS, was seriously affected by the matrix influences in both extraction schemes.

Comparative Partitioning of Elements in Either Scheme

The results for partitioning of certified samples are depicted in Figure 2 (BCR scheme) and Figure 3 (Tessier scheme). Following, the results for each element are discussed:

Copper

Both samples S1 (NBS SRM 1633b) and S2 (NIES 38) show that copper is well associated with the exchangeable phase of the Tessier scheme. It may be observed that the total concentration of the first two stages of the Tessier scheme is very close to the concentration of copper in the first stage of the BCR scheme. This effect is the same for both samples. A greater amount of copper is associated with the oxidize-able fractions in the Tessier scheme (third stage) compared to that of the BCR scheme (second stage). However, the overall % recovery in both schemes is very similar, i.e., the difference is not more than 3% in either case. Bodog et al. (11) reported a high % of copper in exchangeable form, suggesting high environmental mobility of copper.

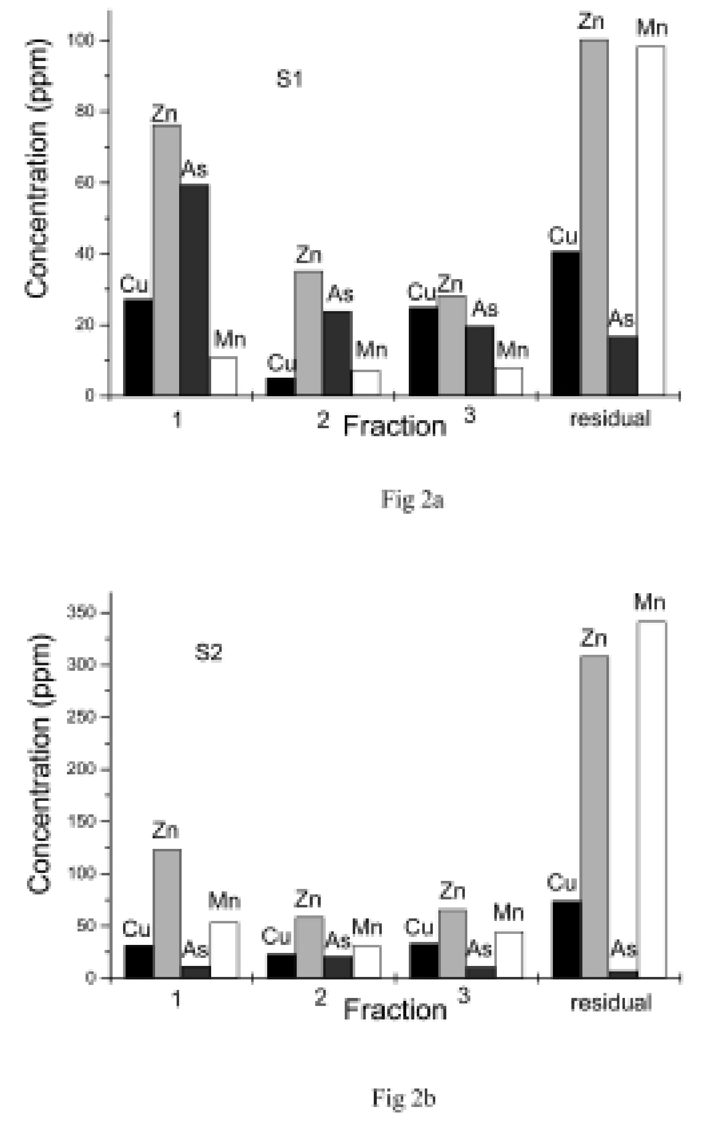

Fig 2a

Fig 2b

Fig. 2. Elemental concentrations of the different fractions of the BCR scheme (2a for sample S1 and 2b for sample S2).

Zinc

The recovery of zinc is much higher (117.3%) for sample S1 in comparison to the non-certified value, specified by NIST, in both extraction schemes. In case of sample S1, a higher % of zinc is present in the acid-soluble phase of the BCR scheme compared to that of the sum of exchangeable and carbonate-bound phases of the Tessier scheme. In both standards, the difference in the recovery of zinc was found to be about 3% in the two schemes. Zinc is associated with all phases in considerable quantities.

Arsenic

The recovery of arsenic for sample S1 was found to be higher in the Tessier scheme (99.6%) as compared to the BCR scheme (88.2%), and slightly higher for sample S2. However, for both standards, arsenic is mainly associated with the acid-soluble and oxidize-able phases. A lesser amount is associated with the residual phase. This suggests the higher mobility of arsenic.

Manganese

The recovery of manganese for sample S1 was found to be 5% higher in the BCR scheme and less than 1% greater for sample S2. Manganese is associated mainly with the residual phase. The other fractions are associated with very small amounts of manganese, suggesting its low bio-availability.

Hence for copper, zinc, and manganese, the recoveries of the BCR and Tessier schemes were very close, with the differences not greater than 5% for both standard fly ash samples. For zinc and manganese, higher extraction efficiencies could be seen in the BCR scheme than in the Tessier scheme for samples S1 and S2. The extraction efficiency of arsenic for sample S1 is 10.4% higher for the Tessier scheme in comparison to the BCR scheme and 2.9% lower for sample S2.

Intermethod Comparison for the Concentration of Selected Elements

The comparative data obtained from the two sequential extraction schemes were further checked by ICP-MS for Zn, Cu, and Mn (Figure 4). The results obtained from the sum of the individual fractions for the selected elements show that the error percentage in the BCR scheme is slightly lower than in the Tessier scheme (see Figure 4A). This may be due to a reduction in steps in the BCR scheme.

CONCLUSION

The application of the Tessier and BCR schemes on either of the fly ash standards shows a high recovery, ranging from 88.9–104.9% for copper, manganese, and arsenic.

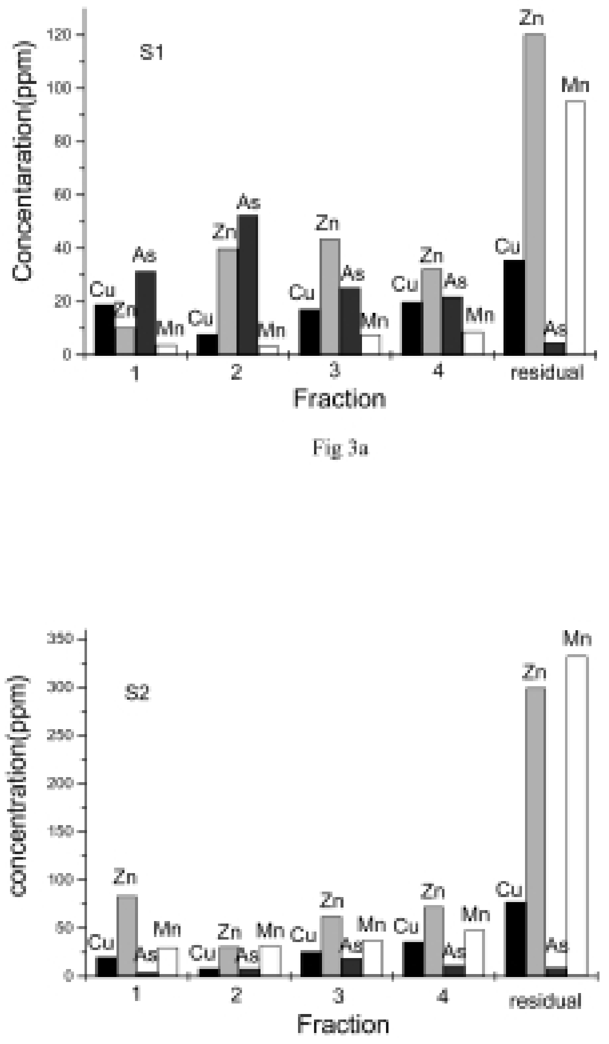

Fig 3a

Fig 3b

Fig. 3. Elemental concentrations of the different fractions of the Tessier scheme (3a for sample S1 and 3b for sample S2).

For zinc, the recovery ranges from 115 to 117% for the NIST 1633b certified coal fly ash sample (S1). The partitioning patterns indicate that arsenic has the largest potential mobility since a major part of it is associated with the non-residual phases (the first three fractions of the Tessier scheme and the first two fractions of the BCR scheme). Manganese has the least environmental mobility as more than 80% of it is in the residual phase. However, it may be inferred that on application of the microwave-assisted extraction, similar elemental concentrations have been obtained in both schemes, except for arsenic. Fewer stages are involved in the BCR scheme than in the Tessier scheme, though the first step of the former takes slightly longer. There are some minor but significant differences in the total extraction times and % recoveries.

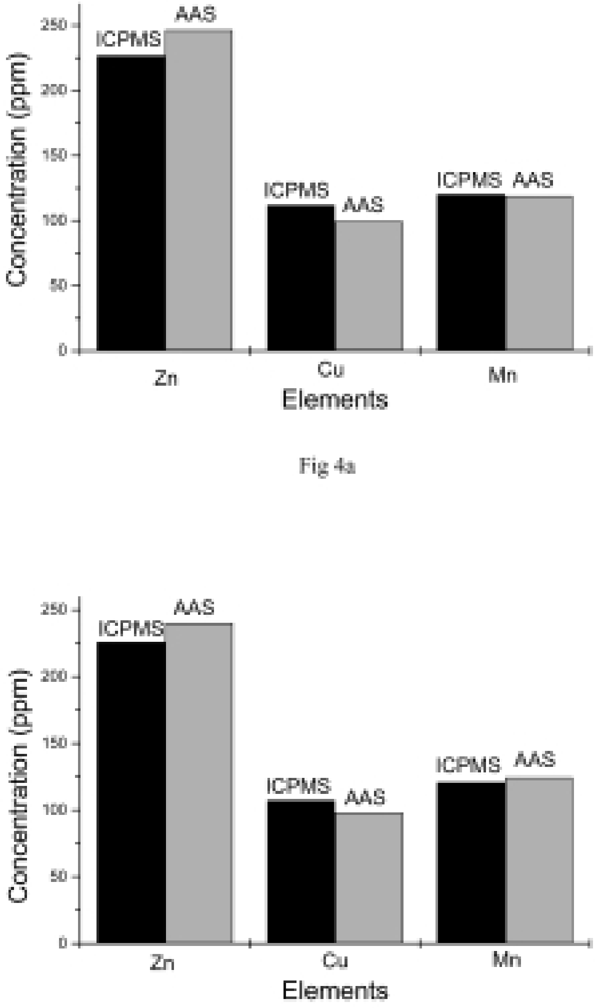

Fig 4a

Fig 4b

Fig. 4. Intermethod comparison for concentration of selected elements (4a for Tessier scheme sample S1 and 4b for BCR scheme sample S2).

Interferences due to extractant solutions and elements co-extracted with the analyte are less in the BCR scheme than in the Tessier scheme, so that in most cases the standard addition calibration is not required. Nevertheless, both schemes depict the concentration of different species of metals viz. free ions plus labile complexes as well as weakly labile and stable species of fly ash.

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Determination of Palladium by Ultrasonic Nebulization Coupled to ICP-OES After On-line Preconcentration on Activated Carbon

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ABSTRACT

A system for the on-line preconcentration and determination of palladium by ultrasonic nebulization (USN) coupled to inductively coupled plasma optical emission spectrometry (ICP-OES) was studied. It is based on the chemical sorption of palladium-thiocyanate complex on a conical minicolumn packed with activated carbon (AC). The proposed procedure allowed the determination of palladium with a detection limit of 10 ng/L. The precision for 10 replicate determinations at the 500-ng/L Pd level was 2.9% relative standard deviation (RSD), calculated from the peak heights obtained. The calibration graph using the preconcentration system for palladium was linear with a correlation coefficient of 0.9995 at levels near the detection limits up to at least 100 µg/L. A total enhancement factor of 375-fold was obtained with respect to ICP-OES using pneumatic nebulization (15 for USN and 25 for preconcentration). A sampling frequency of 20 samples per hour was obtained. The effect of other ions in concentrations agreeing with water samples was studied. The addition/recovery experiments in the samples analyzed demonstrated the accuracy and applicability of the system for the determination of palladium in tap water samples.

INTRODUCTION

Noble metals, particularly palladium, find extensive use in the electrical industry as contacts in telephone relays and printed circuits, as grids for electronic tubes and electrodes for high quality spark plugs. The determination of traces and ultra-traces of palladium in the environment, as well as in body fluids of living species, at low concentrations is an urgent problem (1–5). Palladium affects the environment increasingly in the form of pollution, especially by its technical use in catalysts containing the active Pd metal. The use of catalytic converters has led to an anomalous increase in the concentrations of palladium in several natural matrices such as soil, water, and vegetation, in areas near intensive vehicle traffic, thus causing a new environmental risk (6–8). The effects of palladium, as well as of the other platinum group elements (PGE), on human health are still not clearly defined. Man comes in contact with this element directly, through inhalation of dust, and indirectly, through food and water. Palladium is currently the element of most concern for man and it is considered a powerful allergen (9). A critical evaluation of possible risks for human health can only be given if reliable analytical data are available.

The determination of trace amounts of palladium in geological, environmental, and biological samples requires modern instrumental techniques, among them flame atomic absorption spectrometry (FAAS) (10,11), electrothermal atomic absorption spectrometry (ETAAS) (12–14), inductively coupled plasma optical emission spectrometry (ICP-OES) (15–17), inductively coupled plasma mass spectrometry (ICP-MS) (18–21), neutron activation analysis (NAA) (22,23), capillary electrophoresis (CE) (24,25), X-ray fluorescence (XRF) (26), and spectrophotometry (27).

A separation/preconcentration step is often applied in order to remove matrix interferences and to preconcentrate the analyte to a level which can be reliably determined.

Various methods have been developed for palladium separation and preconcentration from diverse matrices such as anion exchange (20,22,28), precipitation (6,12), cloud point extraction (19), biosorption (13,14), co-precipitation (29) and sorption (5,10,15, 16,30), among others.

Activated carbon (AC) has been widely used for many purposes both in laboratory and industrial settings due to its ability to adsorb organic compounds and inorganic metal complexes. Since its introduction in analytical chemistry, enrichment of trace metals using AC has had favorably results resulting in very high concentration factors in different matrices (31–33).

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The mechanism of sorption on AC is still under investigation and the adsorption of metals on activated carbon could be explained using Langmuir and Freundlich equations. Adsorption equilibrium studies have revealed that the pH is the dominant parameter controlling the adsorption (34).

In the present work, a method for preconcentration and determination of palladium in spiked water samples at low concentration levels is proposed. It was based on solid phase extraction of palladium as thiocyanate complex onto activated carbon. The determination was carried out using ultrasonic nebulization associated with inductively coupled plasma optical emission spectrometry (USN-ICP-OES).

EXPERIMENTAL

Instrumentation

The measurements were performed with a Model ICP2070 sequential ICP spectrometer (Baird, Bedford, MA, USA). The 1-m Czerny-Turner monochromator had a holographic grating with 1800 grooves/mm. The flow injection (FI) system used is shown in Figure 1. A Model U 5000 AT ultrasonic nebulizer (CETAC Technologies, Omaha, NE, USA) equipped with a desolvation system was used. The ICP and ultrasonic nebulizer operating conditions are listed in Table I. A Minipuls™ 3 peristaltic pump (Gilson, Villiers-Le-Bell, France) was used. Sample injection was achieved using a Rheodyne® Model 50, four-way rotary valve (Cotati, CA, USA). A home-made conical minicolumn (40 mm length, 4.5 mm internal upper-diameter and 1.5 mm internal lower-diameter) was used as the activated carbon holder. Tygon®-type pump tubing (Ismatec, Cole-Parmer, Vernon Hills, IL, USA) was employed to propel the sample, reagent, and eluent. The 340.458-nm spectral line was used and flow injection system measurements were expressed as peak height emission, which was corrected against the reagent blank.

Reagents

Palladium standard solution was prepared by appropriate dilutions of a 1000-mg/L stock solution (Fluka, Switzerland) immediately before use. The palladium solution's pH was adjusted with hydrochloric acid solution.

The hydrochloric acid was Suprapur" grade (Merck, Darmstadt, Germany).

A 1×10^{-2} mol/L potassium thiocyanate (KSCN) solution was prepared by dissolving the reagent in water. Lower concentrations were prepared by serial dilution in water.

A 5% (w/v) thiourea (Fluka, Switzerland) solution was prepared by dissolving the reagent in 0.2 mol/L hydrochloric acid.

The activated carbon (Merck, Darmstadt, Germany, 50–70 mesh) was used after pretreatment with acid [activated carbon was heated to 60ºC with 10% (v/v) hydrochloric acid for 30 minutes and then with 10% (v/v) nitric acid for 20 minutes, and finally washed with deionized water until a neutral pH was reached].

Ultrapure water (18 MΩ cm) was obtained from an EASY pure RF (Barnstead, Iowa, USA). All other solvents and reagents were of analytical reagent grade or better, and the presence of palladium was not detected in the working range.

Column and Sample Preparation

The conical minicolumn was prepared by placing 100 mg of activated carbon into an empty column using the dry packing method. To avoid loss of activated carbon when the sample solution passes through the conical minicolumn, a small amount of quartz wool was placed at both ends of the conical minicolumn. The column was then connected to a peristaltic pump with PTFE tubing to form the preconcentration system. The average lifetime of the column is more than 300 cycles. All columns prepared in this way show good reproducibility, as proven by the precision of the signals obtained for the different columns.

The water samples were filtered through 0.45 µm pore size membrane filters immediately after sampling, adjusted to pH 3.0 with hydrochloric acid solution, and stored at 4ºC in Nalgene® bottles (Nalge Nunc International, Rochester, NY, USA).

TABLE I
ICP and Ultrasonic Nebulizer Instrumental Parameters

ICP Conditions	
RF Generator Power	1.0 kW
Frequency of RF generator	40.68 MHz
Outer Gas Flow Rate	8.5 L/min
Auxiliary Gas Flow Rate	1.0 L/min
Observation Height	15 mm
Ultrasonic Nebulizer Conditions	
Heater Temperature	140°C
Condenser Temperature	4ºC
Carrier Gas Flow Rate	1 L/min

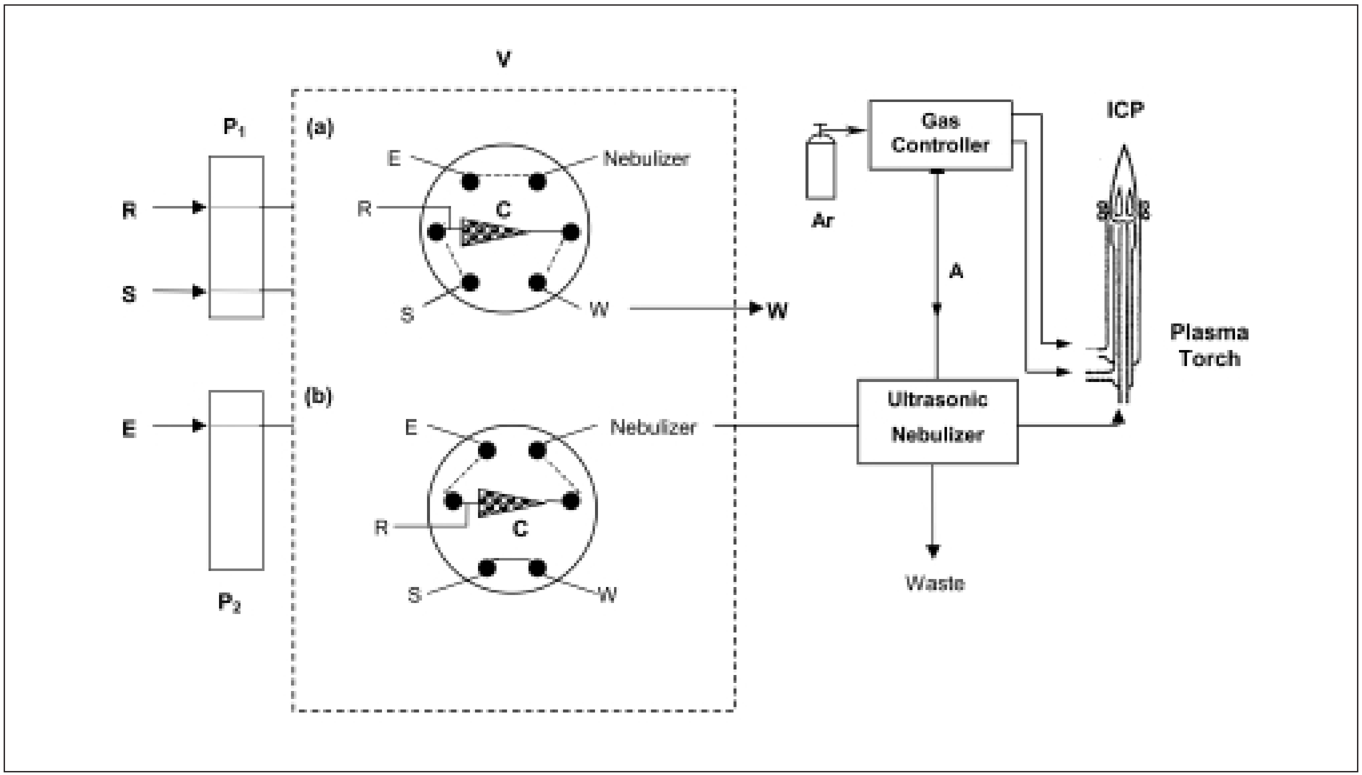

Fig. 1. Schematic diagram of the instrumental setup. S: Sample (flow rate: 10 mL/min); R: reagent (flow rate: 5.0 mL/min); E: eluent (flow rate: 1.5 mL/min); A: Ar (flow rate: 0.7 L/min); W: waste; P1, P2: peristaltic pumps; C: minicolumn packed with activated carbon; V: injection valve. Valve positions: (a) sample loading; (b) injection.

All glassware and plasticware used was previously washed with a 10% (v/v) HNO_3/water solution and then with ultrapure water.

Preconcentration Step

A 25-mL sample (buffered at pH 3.0) and the complexing reagent (potassium thiocyanate 1×10^{-4} mol/L) at 10.0 and 5.0 mL/min loading flow rates, respectively, were mixed on-line to form the metal complex. Palladium was retained by chemical sorption as the palladium-thiocyanate complex on the minicolumn packed with activated carbon and the remaining solution was discharged; valve V in load position (a) (Figure 1). Finally, the peristaltic pump was stopped, the injection valve V switched to the injection position (b), and the retained complex eluted with 5% (w/v) thiourea at a flow rate of 1.5 mL/min directly into the ultrasonic nebulizer and ICP-OES. The operating conditions were established and the determination was carried out.

Method Validation

A certified reference material of natural water with a certified value for Pd does not exist. However, using the method of standard addition, it is considered a validation method (35). In order to demonstrate the validity of this method, 125 mL of tap water was collected and divided into 5 portions of 25 mL each. Then, increasing quantities of palladium were added to the sample aliquots and palladium was determined by means of the preconcentration method (Table II).

RESULTS AND DISCUSSION

Sample Loading Variables

In order to optimize the sorption conditions for the retention of the metal complexes, the palladium signal was monitored by measuring with USN-ICP-OES while changing the pH of the solution that passes through the minicolumn. The procedure was similar to the Preconcentration step section, the optimum pH values were in the 2.5–4.0 range at the 500-ng/L Pd level (Figure 2). This phenomenon

TABLE II
Recovery Study (Tap Water)

Aliquots	Quantity of Pd Added (ng/L	Found (ng/L)	Recovery (%)
1	100.0	98.0	98.0
2	150.0	149.3	99.5
3	200.0	201.4	100.7
4	250.0	247.5	99.0
5	500.0	500.5	100.1

is understandable since better complexation occurs within this range. Based on these results, the final pH selected was 3.0.

The sample flow rate through the minicolumn packed with activated carbon is a very important parameter, since this is one of the steps that controls the analysis time. The influence of the sample loading rate on the analytical response obtained was studied between 1.0–15.0 mL/min. We could verify that the optimum sample loading flow rate was achieved at 10.0 mL/min, which, under optimum conditions, allowed us to reach an enhancement factor of 375-fold. At higher flow rates than 10.0 mL/min, the response decreased as is shown in Figure 3.

As regards the response variation with the molar concentration of the reagent potassium thiocyanate, the signal remained constant between 10^{-5} mol/L and 10^{-3} mol/L. A 1×10^{-4} mol/L potassium thiocyanate concentration was adopted for further experiments. The optimum load rate adopted was 5.0 mL/min.

Optimization of Elution Conditions

Thiourea has been successfully used to elute Pd, Pt, and Au from exchange resins and other types of sorbents (13–15,20,30). Thiourea also turned out to be a good eluent for the palladium-thiocyanate complex. Various concentrations of thiourea, thiourea + HCl, were used as the eluents. The results showed that Pd was quantitatively desorbed with 5% (w/v) thiourea solution prepared in 0.2 mol/L HCl. The effect of the flow rate of the eluent was studied and the best ICP-OES signal was achieved at 1.5 mL/min.

Interferences

The effects of potentially interfering species (at the concentration levels at which they may occur in the sample concerned) were tested under the optimum preconcentration conditions. Thus Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2}, and Fe^{3+} could be tolerated up to at least 2500 µg/L.

Analytical Performance

Under the optimum conditions described above, the performance data obtained for the on-line minicolumn preconcentration-USN-ICP-OES system for palladium determination are summarized in Table III. The overall time required for the preconcentration of 25 mL of sample (2.5 minutes, at a flow rate of 10 mL/min), conditioning (~0.3 minutes) and elution (~0.2 minutes, at a flow rate of 1.5 mL/min) was about 3.0 minutes;

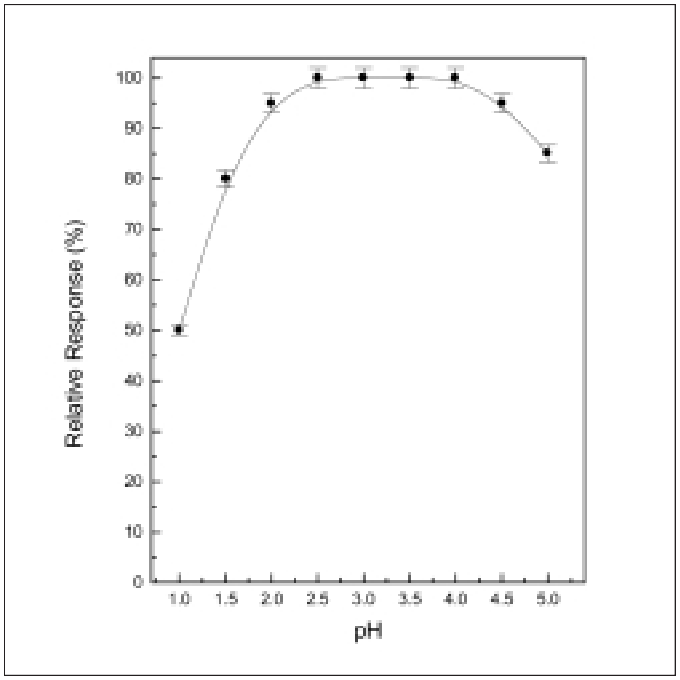

Fig. 2. Dependence of Pd preconcentration with pH of loading solutions. Sample loading volume 25 mL; loaded flow rate was 10.0 mL/min; the elution flow rate was 1.5 mL/min; Pd concentration was 500 ng/L.

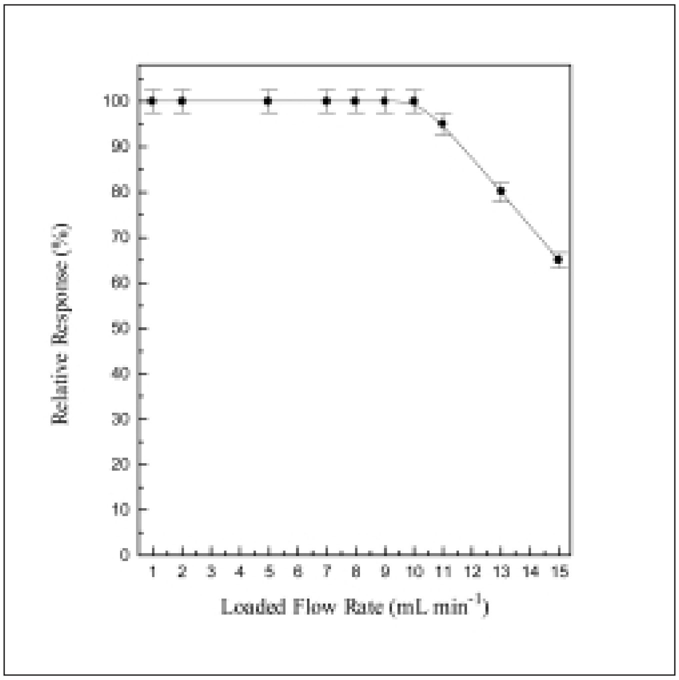

Fig. 3. Dependence of metal recovery with loading flow rate. Sample loading volume was 25 mL; the elution flow rate was 1.5 mL/min; Pd concentration was 500 ng/L.

the throughput was about 20 samples per hour. A sensitive enhancement factor of 375-fold was obtained with respect to ICP-OES using pneumatic nebulization (15 for USN and 25 for preconcentration).

The precision for 10 replicate determinations at the 500-ng/L Pd level was 2.9% relative standard deviation (RSD) calculated from the peak heights obtained. The calibration graph was linear with a correlation coefficient of 0.9995 up to at least 100 µg/L. The detection limit (DL) was calculated as the concentration of palladium required to yield a net peak that was equal to three times the standard deviation of the blank signal (3σ). The value of the detection limit obtained for the preconcentration of 25 mL of sample solution was 10 ng/L.

Application to Tap Water Samples

Finally, the results of the method applied to the determination of palladium in spiked tap water samples are shown in Table II. The recovery of palladium ranged between 98.0 and 100.7 %.

CONCLUSION

The methodology described above was successfully applied to the determination of palladium in spiked water samples. The developed manifold permitted high sample flow rates in order to achieve good sensitivity. This method proved to be rapid, reliable, and flexible with limited interference. The high enhancement factor (375-fold) obtained is a great advantage of this procedure in comparison to the many methods existing for palladium preconcentration.

TABLE III
Performance of the FI-On-Line Activated Carbon Sorption Preconcentration-USN-ICP-OES System Determination of Pd Under Optimized Conditions

Correlation Coefficient	0.9995
Working Range	0.01–100 µg/L
Sampling Frequency (f)	20 h^{-1}
Precision (at 500-ng/L Pd level)	2.9 %RSD, n=10
Detection Limit (3σ)	10 ng/L
Enhancement Factor	375

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Determination of Ag, Au, and Bi in Ethanol by ETAAS Using Zirconium as Permanent Modifier

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ABSTRACT

The determination of Ag, Au, and Bi in ethanol and 0.2% (v/v) nitric acid media by electrothermal atomic absorption spectrometry, with and without using a chemical modifier, was investigated. The modifiers tested were a mixture of Pd and Mg nitrates and a graphite platform treated with Zr. To treat the platform inside a graphite tube, a Zr solution is pipetted into and dried repeatedly on the platform. It is then submitted to various temperature programs in the electrothermal atomizer until 500 µg of Zr is delivered. Pyrolysis and atomization curves for different analytes under various conditions were obtained.

There is a three-fold increase in sensitivity for Bi in ethanol using the permanent modifier in comparison to the Pd and Mg modifier. The sensitivities for Ag and Au under these conditions are better. The atomization temperature utilized was lower than that recommended for the Pd and Mg modifier. Without a modifier, only Au can be properly measured in ethanol. In the nitric acid medium, the Zr-treated platform doubles the sensitivity for Bi, but does not affect the sensitivity for Ag and Au.

The method was applied to the analysis of two certified steel samples after on-line analyte preconcentration by complexation with O,O-diethyldithiophosphate, sorption on a minicolumn filled with C_{18} bonded to silica gel, and the elution with ethanol. The obtained concentrations agreed with the recommended values.

INTRODUCTION

The use of a chemical modifier, which is part of the stabilized temperature platform furnace (1) (STPF) concept, in electrothermal atomic absorption spectrometry (ETAAS) has been the subject of several investigations since its first proposal in 1975 by Ediger (2). The main purpose of a chemical modifier is to increase the volatility of the matrix or to thermally stabilize the analyte to higher temperatures for removal of the matrix during pyrolysis (3–6) without loss of the analyte. A mixture of Pd and Mg nitrates, applied in solution, has been proposed as a universal modifier since it stabilizes more than 20 analytes (3–5) according to the recommended conditions by the instrument manufacturers (7). In addition, other chemical elements have shown modifier properties, such as the platinum element group (6,8–20) (Pt, Pd, Ir, Rh, and Ru) or the carbide-forming elements (20–30) (Zr, Nb, Ta, and W). When the modifier solution is deposited onto the graphite tube or the platform surface and is submitted to a temperature program, a solid layer is formed. This layer acts as a permanent modifier, that is, the modifier does not need to be added for every determination.

As examples of this kind of modifier, Ir (6,9,11,14,17,18), Rh (11,13,14,17,18), Ir + Rh (18), Ru (14,16,19), Zr and W (21–24,26–28), W + Rh (29,30), and Zr plus noble metals (22,23,25–28) have been studied. Time-savings and lower analyte blank due to *in situ* cleaning of the modifier are additional advantages of the permanent modifiers (18-20,29,30). According to Tsalev et al. (20), the effect of these modifier surfaces may be associated with a very similar or a very different behavior of the analyte and modifier. When they are similar, the analyte may be strongly retained in the crystal lattice of the modifier by isomorphism, but if they are very different, a strong chemical bond between both may result.

Most of the determinations by ETAAS are performed in nitric acid. However, especially in Brazil, where ethanol itself or mixed with gasoline is widely used as an automotive fuel, the need to analyze ethanol is obvious because the copper presence, for instance, combines with the olefins and forms gums which can harm the motor.

In addition, ethanol is very often used as an eluent in preconcentration procedures based on sorbent extraction from C18 bonded silica gel (31–37), PTFE knotted reactors (38–42), amberlite XAD-16 (43), or activated carbon (44,45). A procedure based on liquid-liquid extraction also resulted in ethanolic medium (46). Mixed media have also been used, such as the matrix matching of ethanol in the calibration solutions to determine Pb in wines (47). Some authors (48–56) have claimed benefits in the use of ethanol for slurry procedures. Despite the need for analyzing ethanol samples, ethanol extracts, and slurries containing ethanol, little is known about the determination of analytes by ETAAS in this medium, especially concerning the right choice of modifiers and temperature programs.

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In this study, the thermal behavior of some metals (Ag, Au, and Bi) in an ethanolic medium is investigated by ETAAS. For comparison, their determination in an aqueous medium was also studied. As modifiers, a mixture of Pd and Mg nitrates in solution or Zr applied as a platform coating was tested. The best experimental conditions are applied to the analysis of steel solutions after preconcentration in a minicolumn filled with C_{18} bonded silica gel from which the analytes are eluted with ethanol.

EXPERIMENTAL

Instrumentation

The integrated absorbances were obtained using a Model AAnalyst™ 100 atomic absorption spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA), equipped with an HGA®-800 graphite furnace, an AS-72 autosampler , and a deuterium arc lamp continuum background corrector. Hollow cathode lamps from Hitachi (Mitorika, Ibaraki, Japan), operating at 13 mA for Ag and Bi and at 15 mA for Au, were used. Unless otherwise stated, the manufacturer's recommended conditions were employed. Argon 99.996% from White Martins (São Paulo, SP, Brazil) was used as sheath gas. A pyrolytically coated graphite tube (PerkinElmer Part No. B010-9322) containing a pyrolytic graphite platform (PerkinElmer Part No. B 010-9324) was used. The volume of the standard and sample solutions was 20 µL. The volume of the modifier in solution (15 µg of Pd plus 10 µg of Mg as nitrates) was 10 µL. The temperature program, shown in Table I, was optimized through pyrolysis and atomization curves. The samples were dissolved in a Model MLS-1200 MEGA microwave oven (Milestone, Sorisole, Italy).

Platform Coating With Zr

The tube platform was pretreated with Zr by dispensing 40 µL of a 500 µg/mL Zr solution onto the platform and submitting the tube to the following temperature program (ramp in s, hold in s):
90°C (ramp 5 s, hold 15 s);
140°C (ramp 5 s, hold 15 s);
1000°C (ramp 10 s, hold 10 s);
2000°C (ramp 0 s, hold 5 s).

This procedure, similar to the one used previously (18,19), was repeated 25 times in order to obtain a deposit of approximately 500 µg of Zr. Following, two temperature programs were applied to the tube in order to transform the oxides and oxicarbides into metallic carbide, as recommended for a W coating (29,30). Since, the thermal behavior of Zr and W is relatively similar, the same programs were applied for Zr.

For a low temperature conditioning (ramp in s, hold in s), the following program was run four times:
150°C (ramp 1 s, hold 10 s);
600°C (ramp 10 s, hold 15 s);
1100°C (ramp 10 s, hold 5 s);
1400°C (ramp 10 s, hold 10 s).

The following program was also run four times for a high temperature conditioning (ramp in s, hold in s): same steps as the previous program plus
1500°C (ramp 3 s, hold 5 s);
1600°C (ramp 1 s, hold 1 s);
1700°C (ramp 1 s, hold 1 s);
1800°C (ramp 1 s, hold 1 s);
1900°C (ramp 1 s, hold 1 s), and
2000°C (ramp 1 s, hold 1 s).

The gas flow rate used was 250 mL min^{-1} for all steps in all temperature programs.

Zirconium Mass

To investigate the effect of the Zr mass on the Bi signals for an aqueous Bi standard solution in 0.2% nitric acid, 2 µL of a 500-µg/mL Zr solution was deposited onto the platform and the tube was submitted to the following temperature program (ramp in s, hold in s):
90°C (ramp 5 s, hold 15 s);
140°C (ramp 5 s, hold 15 s);
1000°C (ramp 10 s, hold 10 s);
2000°C (ramp 0 s, hold 5 s);
20°C (ramp 1 s, hold 5 s).

Then, 20 µL of the standard Bi solution (1 ng of Bi) was transferred to the tube and the following temperature program was run (ramp in s, hold in s):
90°C (ramp 5 s, hold 10 s);
140°C (ramp 5 s, hold 20 s);
800°C (ramp 10 s, hold 5 s);
1300°C (ramp 10 s, hold 10 s);
2200°C (ramp 1 s, hold 5 s);
Read in this step and 20°C
(ramp 1 s, hold 5 s).

The gas flow rate used was 250 mL min^{-1} for all steps of all temperature programs, except during the read step of the second program, which was run under gas-stop conditions.

TABLE I
Temperature Program for the Determination of Ag, Au, and Bi in Ethanol Extracts

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar Flow Rate (mL min^{-1})
1	90	5	10	250
2	200	5	10	250
3	600 (Ag, Bi), 900 (Au)	10	20	250
4[a]	1300 (Ag, Bi), 1600 (Au)	0	5	0
5	2600	1	5	250
6	20	1	5	250

[a] Read in this step.

Reagents, Solutions, and Samples

All chemicals used were of analytical reagent grade, unless otherwise specified. The water was de-ionized in a Milli-Q™ system (Millipore, Bedford, MA, USA) with a final resistivity of 18.2 MΩ cm^{-1}. Nitric acid from Carlo Erba (Milan, Italy, No. 408015) and hydrochloric acid from Merck (Darmstadt, Germany, No. 102597) were further purified by sub-boiling distillation in a quartz still (Kürner Analysenteknik, Rosenheim, Germany). The ethanol was from Carlo Erba (No. 414629). The 1000 mg mL^{-1} stock solutions for Bi, Au, and Zr were from Aldrich (Milwaukee, WI, USA, atomic absorption standard solutions No. 20,699-7, No. 20,716-0, and No. 27,497-6, respectively). The 1000-mg mL^{-1} stock solution for Ag was from Fluka (Buchs, Switzerland, atomic spectroscopy standard solution No. 85137). The calibration solutions for the analytes and the standard solution for Zr were prepared by dilution of the stock solutions with 0.2% nitric acid. A 1.0% (m/v) solution of the ammonium salt of DDTP was prepared from the commercial reagent (Aldrich, No. 17779-2; 95% purity) by dissolution in water and purification by passing the solution twice through a minicolumn filled with ~100 mg of Chelex-100 resin (Merck, No. 101767).

Two certified reference steel samples (SRM 361 and 364) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were analyzed. An aliquot of 0.25 g of the steel sample was mixed with 4 mL of nitric acid and 2 mL of hydrochloric acid and submitted to four 5-min steps in the microwave oven at 250, 400, 600, and 250 W. After dissolution, the volume was made up to 100 mL.

Following, further dilutions with 1 mol L^{-1} hydrochloric acid were made:

1 + 49 for Ag in SRM 361;
1 + 1 for Ag in SRM 364;
1 + 1 for Au in SRM 36;
1 + 4 for Au in SRM 364;
1 + 19 for Bi in SRM 361; and
1 + 29 for Bi in SRM 364.

All glassware was previously washed with a detergent solution of Extran from Merck (No. 7553), rinsed with warm distilled water, and kept in a 50% (v/v) nitric acid solution for at least 48 h. It was then rinsed six times with deionized water.

Preconcentration Procedure

The FIA system and the basic procedure used for preconcentration was described elsewhere (45). For the FIA system, a peristaltic pump from Ismatec (Glattbrugg-Zürich, Switzerland, No.73315-15), equipped with Tygon® tubes of several diameters for aqueous solutions and solvent-flex tubes for alcohol solutions, was used. A homemade manual injector-commutator (45) and a PerkinElmer® minicolumn (Part Number B050-4047), filled with C_{18} bonded to silica gel, were employed. In the first step, with the injector-commutator in the loading position, the column is loaded with 10 mL of the calibration or sample solution containing 0.1% of DDTP and 1 mol L^{-1} hydrochloric acid, delivered by the peristaltic pump. The conditions (DDTP and hydrochloric acid concentrations) for the complexation were optimized elsewhere (45). Then the injector is manually changed to the second position, allowing 500 µL of ethanol to pass through the column, eluting the sorbed material in a reverse-flow mode. The eluate is collected in the autosampler cup of the spectrometer and immediately measured to avoid volatilization of the ethanol and changes in the solution. Finally, the column is washed with 2 mL of ethanol (while keeping the injector in the second position) and with 5 mL of water (after returning the injector to the first position). This cleaning step is efficient for Bi and Au, but not for Ag, for which the first cleaning solution is 3 mL of ethanol (reverse-flow mode) and the second is 5 mL of 1.0 mol L^{-1} nitric acid (direct-flow mode). All solutions are manually placed in the proper line of the pump, interspersed with a minimum volume of air that enters the tubing. The loading and elution flow rates were optimized at 1.2 mL min^{-1} and 0.36 mL min^{-1}, respectively.

RESULTS AND DISCUSSION

Pyrolysis and Atomization Curves

The pyrolysis and atomization curves for Ag, without modifier and with a mixture of Pd and Mg in solution and with a Zr-treated platform as modifiers, in aqueous 0.2% (v/v) nitric acid and in ethanol, are shown in Figure 1. These curves were obtained using atomization temperatures of 1500°C and of 1800°C for the Zr-treated platform and for the other conditions, respectively. Without a modifier, Ag is partially lost even at low pyrolysis temperatures since the pyrolysis curves decrease, especially in the ethanol medium for which no plateau in the curve is formed, while in the aqueous medium the losses only become more severe for pyrolysis temperatures above 600°C. The modifier in solution (Pd plus Mg) was quite effective, stabilizing the analyte in both media up to about 1100°C as demonstrated by the plateau in the pyrolysis curves. Also, the Zr-treated platform is a less efficient modifier, since severe losses start for pyrolysis temperatures above 800°C. It is interesting to note that when using the same modifier conditions, the sensitivity in the ethanol medium is always lower than that in the aqueous medium. However, best sensitivities were obtained for the Zr-treated platform. The sensitivities obtained

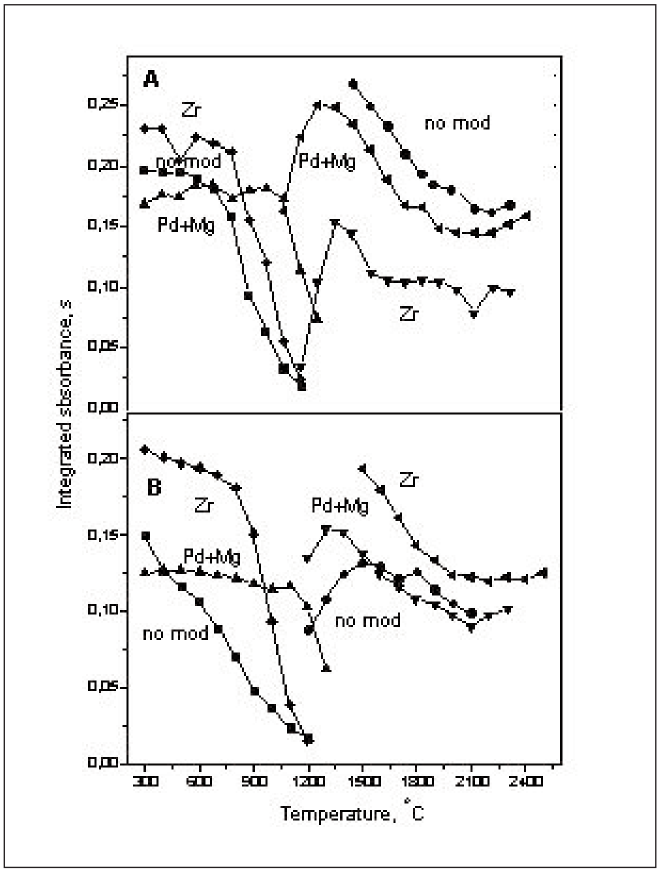

Fig. 1. Pyrolysis and atomization curves for 70 pg of Ag (a) in aqueous 0.2% (v/v) nitric acid and (b) in ethanol without modifier and with a mixture of 15 µg Pd plus 10 µg Mg in solution or a Zr-treated platform (500 µg of Zr). For the pyrolysis curves, the atomization temperature was 1500°C for the Zr-treated platform and 1800°C for the other conditions.

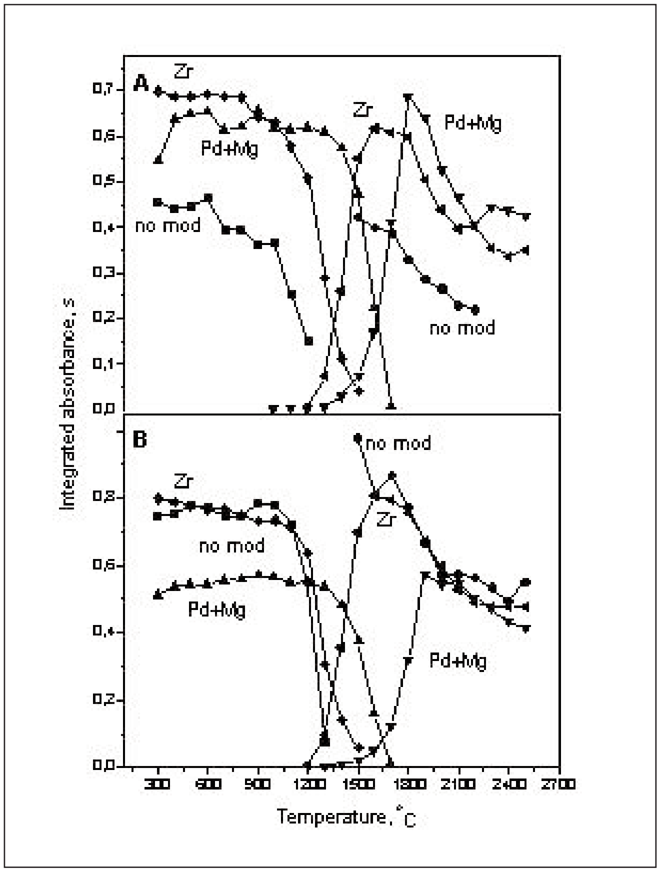

Fig. 2. Pyrolysis and atomization curves for 1.0 ng of Au (a) in aqueous 0.2% (v/v) nitric acid and (b) in ethanol without modifier and with a mixture of 15 µg Pd plus 10 µg Mg in solution or a Zr-treated platform (500 µg of Zr). For the pyrolysis curves, the atomization temperature was 1500°C for the Zr-treated platform and 1800°C for the other conditions.

for the different conditions are compared in Table II by providing the characteristic masses for the optimized temperature program. The recommended (7) atomization temperature of 1800°C does not lead to higher sensitivities as shown by the atomization curves for all conditions which have maxima around 1300–1500°C.

The pyrolysis and atomization curves for Au, in the same media as used for Ag, are shown in Figure 2. Without modifier, the analyte is stable up to around 1000°C in both media, but the sensitivity in ethanol is about twice that in the aqueous medium. This could be attributed to the lower solubility of Au in the nitric acid solution, but the curves obtained with the Zr-treated platform do not support this explanation. The mixture of Pd and Mg provides a more effective stabilization (in both media) up to around 1300°C with a sensitivity slightly lower in ethanol. The Zr-treated platform does not provide additional thermal stabilization since the maximum pyrolysis temperature is about the same as that without modifier (about 1000°C). In the aqueous medium, the sensitivity produced is much higher than that without a modifier but a similar sensitivity in ethanol in comparison to that without a modifier. As stated above, the characteristic masses shown in Table II give a comparison of the sensitivities for the different conditions. It was observed that there is a delay in the appearance temperatures when the Pd and Mg mixture was used as the modifier in comparison to the Zr-treated platform for both media (but even more in ethanol), which also indicates a more effective stabilization with the universal modifier. The higher appearance temperature in ethanol could indicate a higher and deeper penetration of the analyte in the graphite due to the more favorable physical properties of this solvent, confirming the stabilization mechanism proposed for Pd (19). The maximum temper-

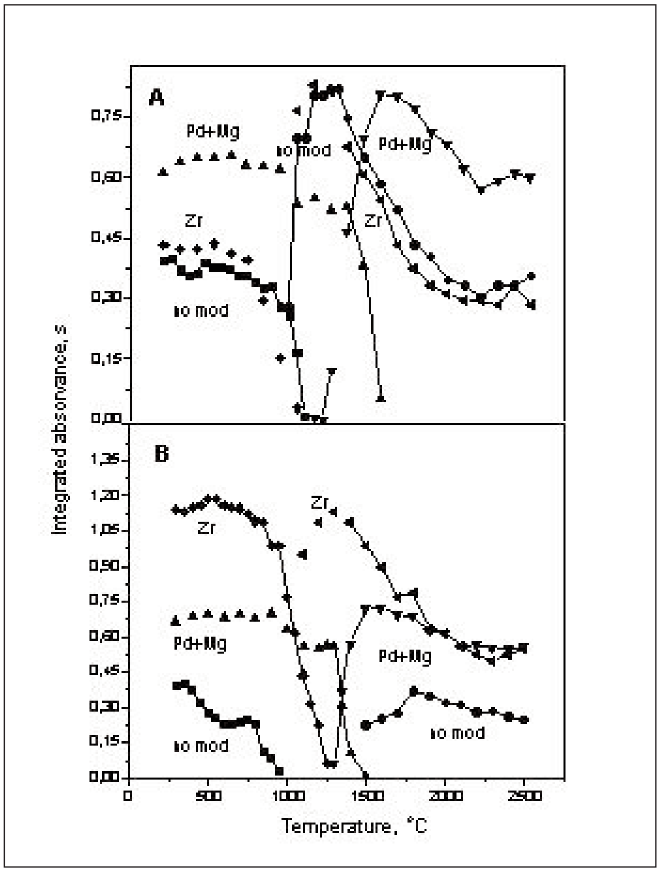

Fig. 3. Pyrolysis and atomization curves for 2.0 ng of Bi (a) in aqueous 0.2% (v/v) nitric acid and (b) in ethanol without modifier and with a mixture of 15 g Pd plus 10 µg Mg in solution or a Zr-treated platform (500 µg of Zr). For the pyrolysis curves, the atomization temperature was 1500°C for the Zr-treated platform and 2000°C for the other conditions.

Table II
Characteristic Mass (in pg/0.0044 s) for Ag, Au, and Bi Using 15 µg Pd plus 10 µg Mg or Zr-treated Platform (500 µg) as Modifiers in an Aqueous 0.2% Nitric Acid Solution and in Ethanol

Modifier	Medium	Ag	Au	Bi
Pd + Mg[a]	0.2% Nitric Acid	1.5	8.5	19.0
No Modifier	0.2% Nitric Acid	1.7	12.0	26.0
No Modifier	Ethanol	-	6.0	37.0
Pd + Mg	0.2% Nitric Acid	1.8	7.2	17.0
Pd + Mg	Ethanol	2.6	8.0	16.0
Zr-treated	0.2 % Nitric Acid	1.5	6.5	22.0
Zr-treated	Ethanol	1.7	5.6	8.0

[a] Recommended (7).

atures in the atomization curves are around 1500–1700°C for the Zr-treated platform, while for Pd plus Mg they are around 1800–1900°C.

The pyrolysis and atomization curves for Bi are shown in Figure 3. The most striking finding for this analyte is its much higher sensitivity in ethanol when the Zr-treated platform is used. However, the maximum pyrolysis temperature in this medium, about 900°C, is lower than with Pd plus Mg. In this same medium without a modifier, the pyrolysis curve decreases even at very low temperatures. The sensitivity is much lower than when Zr is utilized. Using Pd plus Mg as the modifier, the pyrolysis curves in both media are similar in sensitivity with a maximum pyrolysis temperature of about 1300°C in ethanol and about 1400°C in the aqueous solution. It is interesting to note that in the aqueous medium, Bi seems to be slightly more stable without a modifier than with the Zr-treated platform. As for Au, the appearance temperatures, as shown by the atomization curves, are much higher with Pd plus Mg as the modifier, in both media, with maximum temperatures in the atomization curves of around 1500–1600°C, while for the Zr-treated platform, the maximum is around 1200–1400°C.

The effect of the Zr mass on the Bi signal in aqueous acid solution can be seen in Figure 4. It was assumed that no Zr was lost from one determination to the other, since the maximum temperature used to clean the tube was 2200°C (see Experimental section) and the Zr boiling point is quite high. Blanks for 0.2% nitric acid were run between determinations and their values were taken into consideration. The curve increases steeply with the Zr mass up to 25 µg and remaining flat for higher masses. Thus, it appears that a mass of about 20 times less than the one used in the previous experiments would be sufficient to reach full sensitivity. Very long tube lifetimes were obtained using 500 µg Ru for 50% aqua regia extracts (19). It is conceivable that higher masses may provide longer tube lifetimes.

Analytical Figures of Merit and Results

The analytical characteristics of the method by ETAAS after preconcentration, using a Zr-treated platform and the temperature program given in Table I, are shown in Table III. The attained enrichment factors (calculated by the ratio of the slopes of the calibration curves with and without preconcentration) are quite good and the detection limits are at the ppt levels. The limit of detection (LOD) was defined as three

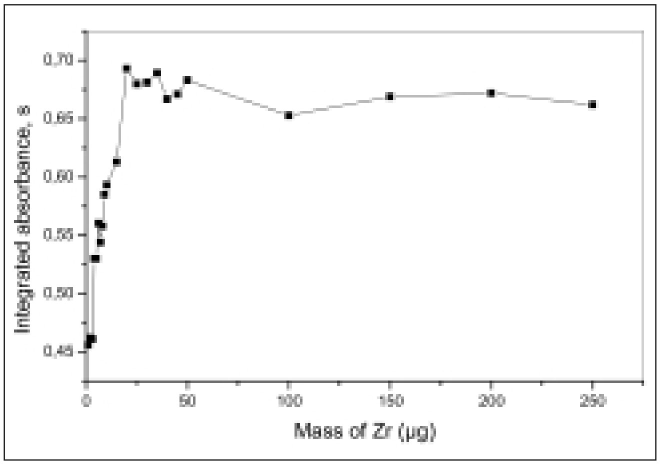

Fig. 4. Effect of the Zr mass deposited on the platform and submitted to a temperature program on the integrated signal of 1.0 ng of Bi in 0.2% (v/v) nitric acid.

times the standard deviation of 10 measurements of the blank. These results were based on preconcentrated solutions. The correlation coefficients are better than 0.99. As demonstrated in Table IV, the obtained concentrations were in excellent agreement with the recommended values. For calibration, the standard solutions were submitted to the same preconcentration procedure. The relative standard deviations ranged from 3–18%, showing a reasonable precision for a laboratory-made flow injection system.

CONCLUSION

Based on this study, it is possible to conclude that the mixed Pd/Mg modifier allows the use of higher pyrolysis temperatures, which may be desirable for complex samples. However, higher sensitivity is obtained with the Zr-treated platform, especially for Au and Bi in ethanol. In addition, the permanent modifier can be cleaned in situ, producing lower blanks and, consequently, lower detection limits. For ethanol extracts, resulting from separation procedures, the matrices are quite simple and the maximum pyrolysis temperatures (around 300–500ºC lower than with Pd plus Mg) are adequate, as demonstrated by the analysis of the steel sample solutions. It is possible that the tube lifetime is also longer with the Zr-treated platform as was confirmed for other permanent modifiers (19). The Zr-treated platform also saves time, since the treatment is only performed once and the modifier does not have to be added for each determination. Based on the above-stated advantages, we strongly recommend the use of a Zr-treated platform as the permanent modifier for the analysis of ethanol samples and extracts.

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TABLE III
Analytical Characteristics of Preconcentration Procedure Using Zr-treated Platform

Analyte	Slope[a] s (µg L^{-1})$^{-1}$	Slope[b] s (µg L^{-1})$^{-1}$	Enrichment (µg L^{-1})	Correlation Coefficient	Range (µg L^{-1})	LOD (µg L^{-1})
Ag	0.940	0.050	19.0	0.9933	01–0.5	0.029
Au	0.760	0.016	14.5	0.9949	0.1–1.0	0.020
Bi	0.600	0.015	15.5	0.9962	0.1–1.0	0.025

[a] After the preconcentration.
[b] In ethanol, no preconcentration.

TABLE IV
Obtained Concentrations (ppm) in Certified Steel Samples From NIST (n = 3)

Analyte	Sample	Obtained	Recommended
Ag	SRM 361	3.8 ± 0.7	4.0
	SRM 364	0.23 ± 0.04	0.2
Au	SRM 361	0.38 ± 0.01	<0.5
	SRM 364	0.95 ± 0.10	1.0
Bi	SRM 361	3.81 ± 0.35	4.0
	SRM 364	8.37 ± 0.43	9.0

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Electrothermal AAS Determination of Ni in Soft Drinks Using Co as the Internal Standard

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ABSTRACT

A method for the direct determination of Ni in soft drinks by graphite furnace atomic absorption spectrometry using a transversely heated graphite atomizer (THGA), Zeeman-effect background corrector, and Co as the internal standard (IS) is proposed. Magnesium nitrate was used to stabilize both Ni and Co. All diluted samples (1+1) in 0.2% (v/v) HNO_3 and reference solutions [5.0–50 µg L^{-1} Ni in 0.2% (v/v) HNO_3] were spiked with 50 µg L^{-1} Co. For a 20-µL sample dispensed into the atomizer, correlations between the ratio of absorbance of Ni to absorbance of Co and the analyte concentration were close to 0.9996. The relative standard deviation of the measurements varied from 0.5 to 3.4% and 1.0 to 7.0% (n=12) with and without IS, respectively. Recoveries within 98–104% for Ni spikes were obtained using IS. The characteristic mass was calculated as 43 pg Ni and the limit of detection was 1.4 µg L^{-1}. The accuracy of the method was checked for the direct determination of Ni in soft drinks and the results obtained with IS were better than those without IS.

INTRODUCTION

Graphite furnace atomic absorption spectrometry (GFAAS) is a suitable and widely used technique for trace element determinations due to its selectivity, sensitivity, and capability for direct analysis with minimal sample preparation and has been used in large-scale routine analyses (1). However, in some situations the complexity of the matrices may introduce errors in the analytical results (2). For example, the presence of gaseous bubbles in soft drinks may change the sample volume in the autosampler pipette, so the mass of the analyte inside the atomizer will change correspondingly to volume variation. As a consequence, the repeatability and/or accuracy of the measurements depreciates. The difficulties in the sampling process using the automatic sampler may be circumvented by adopting internal standardardization (IS) when working with complex samples (2).

Internal standardization (IS) is an attractive, simple, and efficient method to compensate for random and systematic errors in atomic emission or absorption spectrometric analysis (3). The basic principle of IS in chemical analysis is based on the addition of a known and fixed amount of one or more elements used as the internal standard to all blanks, reference solutions, and samples. For elements similarly affected by changes in the experimental conditions, the use of the ratio between the analyte and the internal standard signals may compensate for the fluctuations of analytical results, thus improving precision (4).

The IS technique has been successfully applied in atomic absorption spectrometry for the analysis of real samples and several benefits can be obtained in comparison to the conventional single determination. The literature lists eight references using IS with flame AAS (5–12) and five with GFAAS (13–17) in different matrices including steel (8), zinc die cast (9), steel, steel alloys and cement (10), steel, steel alloys, blood and cement (11), natural waters (12), serum (13), blood (14), blood, urine, and placenta (12), wines (13), blood (14), sparkling waters (15), milk (16–17). However, procedures involving the simultaneous determination of Ni and Co in soft drinks by internal standardization GFAAS are not described in the literature.

The aim of the present paper is to evaluate cobalt as an internal standard for the direct determination of nickel in soft drink samples by simultaneous multi-element atomic absorption spectrometry using $Mg(NO_3)_2$ as the chemical modifier. The performance of the proposed method was checked after analyzing soft drink samples.

EXPERIMENTAL

Instrumentation

A PerkinElmer® SIMAA 6000 simultaneous multielement atomic absorption spectrometer was used equipped with a longitudinal Zeeman-effect background correction system (PerkinElmer Life and Analytical Instruments, Shelton, CT, USA). The standard PerkinElmer

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THGA® Transversely Heated Graphite Furnace Atomizer (Part No. B050-4033) was used. Hollow cathode lamps (HCL) were used for Ni (232.0 nm, 25 mA, and slit 0.7 nm; Perkin Elmer Part No. N305-0152) and Co (242.5 nm, 30 mA and slit 0.7 nm; PerkinElmer Part No. N305-0118), respectively. These were operated according to the conditions recommended by the manufacturer. Atomic signals were measured in peak area mode. High–purity argon (99.999%, White Martins, Brazil) was used as the protective and purge gas. A PerkinElmer AS-72 autosampler was used for taking and delivering solutions from polypropylene cups to the graphite tube. It should be pointed out that the experiments were carried out using the stabilized temperature platform furnace, the so-called STPF conditions (2), including Zeeman-effect background correction.

The measurements of each analytical solution and the samples were carried out in three replicates.

Reagents, Reference Solutions and Samples

High purity water was obtained using a Millipore Rios 5 Reverse Osmosis® and a Millipore Milli-Q™ Academic® system (resistivity 18.2 MΩ cm) (Millipore Corporation, Bedford, MA, USA), together with Suprapur® nitric acid (Merck, Darmstadt, Germany), were used throughout to prepare the solutions.

Analytical reference solutions containing 0.0, 5.0, 10, 20, 40, and 50 µg L^{-1} Ni plus 50 µg L^{-1} Co were prepared daily by dilution of the 1000 mg L^{-1} Ni and Co stock solutions (Normex®, Carlo Erba, Italy) and then acidified to 0.2% (v/v) with HNO_3. The autosampler washing solution was 0.1% (v/v) of Triton® X-100 in 0.2% (v/v) HNO_3.

The 0.03% (m/v) Mg solution was prepared by appropriate dilution of a 10-g L^{-1} Mg stock solution (PerkinElmer Part No. BO19-0634).

The soft drinks were purchased at a local market in Araraquara City, São Paulo State, Brazil. For the direct determination, the samples were diluted (1+1 v/v) with 0.2% (v/v) HNO_3 and spiked with 50 µg L^{-1} Co. This dilution factor was selected as a compromise between the required sensitivity and the minimum organic matter dispensed inside the graphite tube.

Methods

The electrothermal behavior of Ni and Co was investigated in the presence of $Mg(NO_3)_2$ as the chemical modifier. The pyrolysis and atomization curves were obtained for diluted soft drink (1+1) samples in 0.2% HNO_3 and spiked with 50 µg L^{-1} Ni plus 50 µg L^{-1} Co. Although GFAAS with Zeeman-effect background corrector is a potentially efficient technique for the determination of Ni at trace levels with a simple dilution of the sample prior to analysis, the large amount of carbonaceous residue from organic matrices generated after a few firings impaired the adequate performance of the spectrometer. This drawback was circumvented using an air-assisted pyrolysis step at 600°C for 40 s. The optimized heating program used for the simultaneous measurements of Co and Ni is shown in Table I.

TABLE I
Heating Program for the Determination of Ni in Soft Drink Samples

Step	Temp. (°C)	Time (Ramp, Hold)	Gas Flow (mL min^{-1})
1	110	5, 20	250 (Ar)
2	130	10, 15	250 (Ar)
3	600	20, 40	250 (air)
4	20	1, 40	250 (Ar)
5	1500	10, 20	250 (Ar)
6	2300	0, 5	0 (Read)
7	2550	1, 4	250 (Ar)

The efficiency of cobalt as the internal standard for Ni determinations in soft drink samples was also evaluated by means of correlation graphs (18). Twenty consecutive measurements of a solution containing 25 µg L^{-1} Ni plus 50 µg L^{-1} Co in soft drink samples in the presence of $Mg(NO_3)_2$ as the chemical modifier were tested. The absorbance values were normalized with respect to these consecutive measurements. The correlation graph was plotted from the normalized absorbance signals (n = 20) of internal standard (axis y) versus analyte (axis x). Parameters such as correlation coefficient, intercept, and slope were evaluated in order to verify the resemblance between simultaneous measurements obtained for the analyte and the internal standard.

The influence of the sample matrix on the Ni and Co absorbance signals was investigated by evaluating the accuracy and precision from addition-recovery tests and the analysis of samples with and without IS. All samples were spiked with 25 µg L^{-1} Ni and 50 µg L^{-1} Co and three replicates were performed for each sample. The absorbance corresponding to each original sample was adopted as the blank signal.

RESULTS AND DISCUSSION

Electrothermal Behaviors of Ni and Co

Using the heating program of the atomizer as shown in Table I, the electrothermal behavior of Ni and Co in diluted nitric acid and sample was studied in the presence of $Mg(NO_3)_2$ as the chemical modifier. The pyrolysis and atomization curves were built up in order to determine the optimal pyrolysis and atomization temperatures (Figure 1). All measurements were based

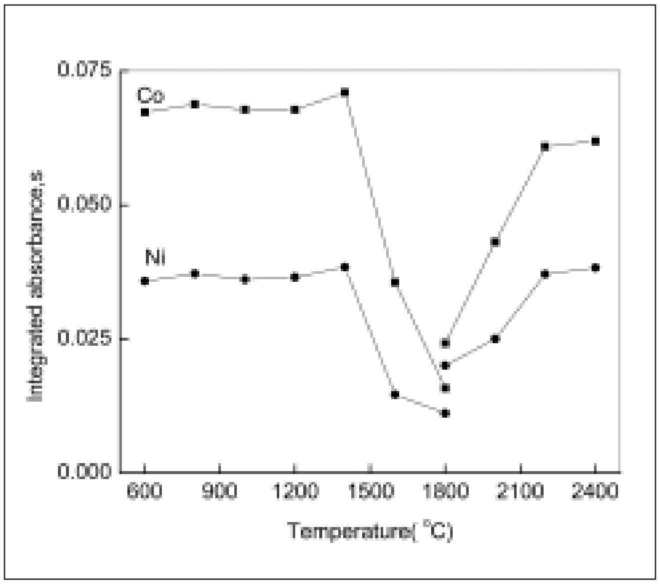

Fig. 1. Pyrolysis and atomization temperature curves for nickel and cobalt. Integrated absorbance refers to 50 µg L^{-1} Ni and Co in diluted soft drink samples (1+1) in 0.2% (v/v) nitric acid.

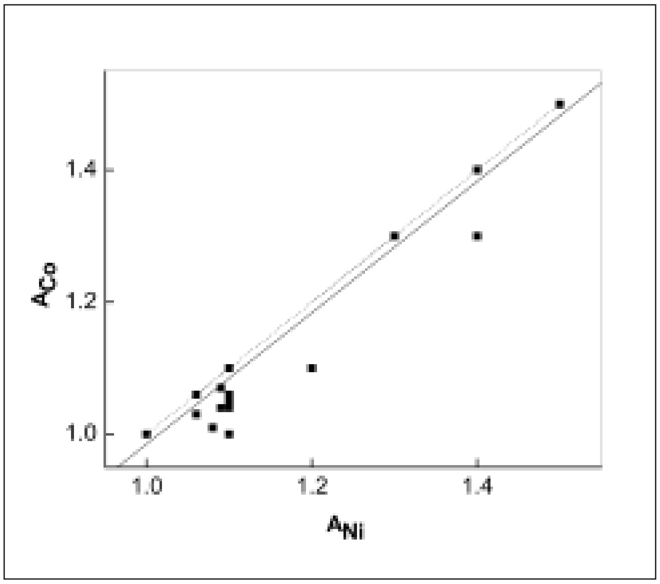

Fig. 2. Correlation graph between 50 µg L^{-1} Co (IS) and 25 µg L^{-1} Ni (analyte). The dotted line indicates the ideal straight correlation.

on integrated absorbance. Since the modifier stabilized Ni and Co at temperatures up to 1500ºC, this was the pyrolysis temperature selected for further experiments. The optimum atomization temperature for the determination of Ni and Co in soft drink samples was close to the 2300°C range, which resulted in best signal profile and good repeatability of measurements. Thus, the atomization temperature was fixed at 2300ºC.

Correlation Graph

The correlation graphs used to verify the similarity among simultaneous measurements by inductively coupled plasma optical emission spectrometry (ICP-OES) (18,19) were applied here for GFAAS. The correlation graph for Co-Ni was obtained after 20 successive simultaneous measurements of a soft drink sample spiked with 25 µg L^{-1} Ni and Co by plotting the normalized absorbance of analyte vs. normalized absorbance of Co. It was observed that the absorbance of the Ni solution varied similarly to that of Co. This suggests the potential application of cobalt as an internal standard for nickel. The plot of the normalized absorbance of cobalt vs. normalized absorbance of Ni was built up in order to obtain the correlation graph (Figure 2). The linear fit equation for the pair Co-Ni was: $A^{Co}=-0.106\pm0.06+1.06\pm0.05\ A^{Ni}$, $r=0.9797\pm0.038$. The performance of Co can be observed by comparing the obtained correlation coefficient to the ideal correlation, that is, the perfect matching between the analyte and IS (r=1, a=0, b=1). The obtained correlation graph suggests Co as a suitable IS for Ni determination in soft drink samples using $Mg(NO_3)_2$ as the chemical modifier.

Figures of Merit

Precision and accuracy studies were carried out using addition-recovery experiments for 10 commercial soft drink samples. The results obtained with and without Co are shown in Table II. It is interesting to note that the relative standard deviations ranged from 0.5–7.0% with and without Co, respectively (n = 12, sample spiked with 25 µg L^{-1} Ni). Recoveries in the 98–104% interval range for Ni spikes were obtained by using IS. The limit of detection (LOD) was calculated as 1.4 µg L^{-1} Ni and the characteristic masses obtained using aqueous reference solutions containing Ni were close to 43 pg.

CONCLUSION

Cobalt was effective as an internal standard to minimize the problems of sampling associated with samples containing high concentrations of gases and matrix effects for the Ni determination in soft drink samples by simultaneous GFAAS.

The use of internal standardization to minimize random and systematic errors and to improve the performance of simultaneous AAS techniques can be beneficial and is very practical in simultaneous detection spectrometers.

TABLE II
Results for Nickel (n = 3) in Soft Drink Samples (mean ± standard deviation) and Comparative Recoveries (in %) With and Without IS. Numbers in Parentheses Represent % RSDs. (Heating program of Table I was employed throughout.)

Sample	Ni (µg L^{-1})	Recoveries (%)	
		With IS	Without IS
1	6.4 ± 0.8	101 (1.5)	91 (2.0)
2	6.0 ± 0.5	104 (1.0)	88 (3.5)
3	6.9 ± 1.0	99 (0.7)	87 (4.0)
4	14.5 ± 1.5	100 (2.0)	90 (6.5)
5	13.2 ± 0.7	101 (3.4)	85 (4.8)
6	15.6 ± 0.8	102 (0.5)	80 (1.0)
7	7.7 ± 1.2	102 (0.8)	85 (3.0)
8	7.2 ± 0.3	98 (2.1)	80 (5.0)
9	10.1 ± 1.0	98 (1.7)	81 (7.0)
10	4.2 ± 1.6	100 (1.0)	78 (6.8)

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FAAS Determination of Palladium After FI On-line Micro-column Preconcentration and Separation With Dicyandiamide-formaldehyde Resin Immobilized Silica Gel

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ABSTRACT

A simple and selective method was developed for the routine determination of trace palladium in metallurgical samples using flow injection (FI) on-line preconcentration and separation with flame atomic absorption spectrometry (FAAS). Pd was selectively preconcentrated on a micro-column packed with a dicyandiamide-formaldehyde resin immobilized silica gel in a wide range of sample acidity (0.1–5.0 mol L^{-1}). It was then effectively eluted into the FAAS with a thiourea solution. Coexisting anions with a concentration of 20.0 mg mL^{-1} and common metal ions of 5.0 mg mL^{-1} did not interfere with the determination of 0.1 μg mL^{-1} of Pd at a sample flow rate of 4.8 mL min^{-1} for 60s. The limit of detection for Pd was 1.1 ng mL^{-1} with a relative standard deviation of not more than 3.0%. The proposed method was successfully applied for the determination of Pd in metallurgical samples and the results were in good agreement with the certified values.

INTRODUCTION

In the preconcetration and separation of noble metals, adsorbents immobilized with the chelating groups with many nitrogen atoms were usually used. Zhang et al. (1) investigated the adsorption of Au on a guanidine resin based on polystyrene. Li et al. (2) determined Au, Pd, and Pt in anode slime with guanidine resin as the group reagent. Chen et al. (3) investigated the adsorption mechanism and thermodynamic properties of a resonance diamine resin for platinum. Although, dicyandiamide was often used as the curing reagent (4) for epoxy resins because of the reactive groups in its structure, it should be possible for dicyandiamide to be used as the chelating group for metal ions since it has similar structural characteristics with the guanidine mentioned above. Gong et al. (5) prepared a dicyandiamide-epoxy resin and used it as chelating adsorbents for the preconcentration and separation of metal ions from sample solution.

The flow injection (FI) on-line preconcentration and separation technique coupled with flame atomic absorption spectrometry (FAAS) has proven to be a suitable method for the determination of trace metal ions due to enhanced sensitivity, lower consumption of reagents, high efficiency, and reproducibility (6-8) in comparison to off-line preconcentration and separation. In our previous work, several small chelating group modified silica gels (9–14) or glass beads (15) and dendrimer-like molecule modified silica gels (16–17) were prepared and applied to on-line separation and preconcentration coupled with flame atomic absorption spectrometry (AAS) determination of noble metals.

In the present paper, a polymer (dicyandiamide-formaldehyde resin) was immobilized onto the surfaces of silica gel for the first time and used as micro-column packing for the determination of Pd, coupled with the flow injection (FI) on-line preconcentration and separation FAAS method. The accuracy of the proposed method is demonstrated by the determination of Pd in metallurgical standard reference materials.

EXPERIMENTAL

Instrumentation

A 180-80 polarized Zeeman-effect background corrected atomic absorption spectrometer (Hitachi, Japan), equipped with a 180-0205 data processing unit (Hitachi, Japan), was employed. Zeeman-effect background correction was used for all measurements in the view of precision. The instrumental settings of the spectrometer are provided in Table I. A Model 056 recorder (Hitachi, Japan) was used for monitoring the peak shape. Peak area absorbance mode (integrated absorbance) was used for evaluating the results throughout.

The FI on-line separation and preconcentration system consisted of two LP-1 peristaltic pumps (KYKY Eastern Instrument Corp., Beijing, China), a 16-way rotary injection valve, and a micro-column (3 cm × 3 mm i.d., Zhaofa Institute for Laboratory Automation, Shenyang, China). PTFE tubing (0.8 mm i.d.) was used for all connections and was kept as short as possible to minimize dead volumes.

Reagents and Standard Solutions

Silica gel of chromatographic grade (Shanghai Institute of Inor-

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ganic Chemistry, Shanghai, China) was of 60–80 mesh and its surface area was 250 m^2 g^{-1}. γ-aminopropyltriethoxysilane (Shuguang Chemicals Factory, Nanjing, China) was purified by distillation at 123°C under 10 mm Hg. The dicyandiamide used was of analytical reagent grade and required no further treatment. All other reagents used were of the highest purity available or at least of analytical reagent grade. Distilled water was used throughout.

A standard stock solution of Pd(II) (1000 mg L^{-1}) was prepared by dissolving pure $PdCl_2$ in 1 mol L^{-1} HCl solution. Standard solutions of Pd(II) were prepared by dilution of the stock solution with distilled water and HCl just before use.

FI Procedures

The FI manifold is shown in Figure 1, and details of the operation sequence of the FI on-line separation and preconcentration of Pd(II) are given in Table II. As reported previously (13), in step 1 (Figure 1A), the injection valve was in the Fill position and pump 1 was activated whereby the blank solution (0.2 mol L^{-1} HCl solution) was pumped through the micro-column at a flow rate of 4.8 mL min^{-1} for 30 s to eliminate the eluent from the last elution. In step 2 (Figure 1A), the sample solution 0.100 µg mL^{-1} Pd(II) in 0.2 mol L^{-1} HCl solution was loaded onto the micro-column at a flow rate of 4.8 mL min-1 for 60 s. Pd(II) was adsorbed onto dicyandiamide-formaldehide resin immobilized silica gel (DFSG), while all other ions flowed off to waste. In step 3 (Figure 1A), the blank solution was driven through the micro-column at the same flow rate for 20 s to remove the sample matrix remaining in the micro-column. In step 4 (Figure 1B), pump 2 started to work, while pump 1 stopped. The valve was turned to the Injection position. The eluent solution was introduced through the micro-column in the reverse direction to AAS at a flow rate of 1.8 mL min^{-1} for 20 s and peak area absorbance was read (Figure 1B). The complete cycle of preconcentration and elution required 130 s with a sample loading time of 60 s.

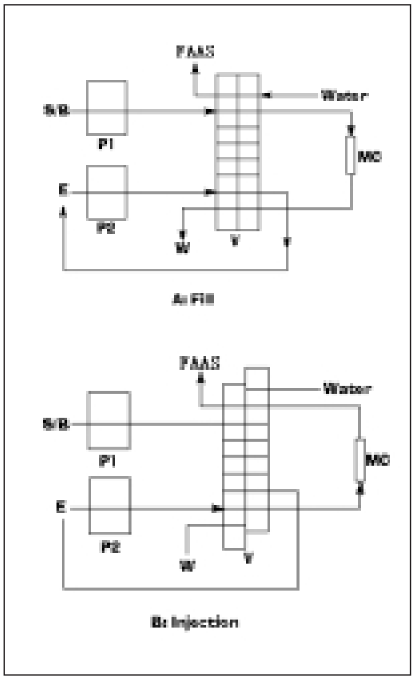

Fig. 1. FI manifold.
P1 and P2, peristaltic pumps;
MC, microcolumn packed with PMDSG; V, injection valve;
S, sample solution; B, blank solution;
E, elution solution; W, waste.

Preparation of DFSG

The pretreatment of silica gel and synthesis of aminopropyl silica gel (APSG) was performed as described previously (13). DFSG was prepared as follows: 3.0 g APSG, 10 mL H_2O, 8.4 g dicyandiamide, and 8.9 mL 37% formaldehyde solution were added to a three-neck flask with a reflux condenser and an agitator. The pH of the mixture was changed to 8–9 with 0.1 mol L^{-1} NaOH solution. Then the flask was put into a water bath whose temperature was controlled; the temperature was raised to 90°C and agitated for 8 hours. After pouring off the above reactive solution, the resulting solid silica gel was washed several times with N,N-dimethylformamide (DMF); it was then extracted with DMF for 10 hours. After extracting and washing several times with acetone, a yellow-white DFSG was obtained and dried for later use. The synthesized routine for the preparation of DFSG is shown schematically in Figure 2.

Sample Pretreatments

An accurately weighed 0.5-g sample, secondary nickel alloy sample (65.17% Ni, 14.64% Cu, and

TABLE I
Instrumental Settings

Current of Pd Hollow Cathode Lamp	10 mA
Absorption Line	247.6 nm
Slit Width	0.4 nm
Position of Burner	5.0 mm
Air Pressure	1.6 kg cm^{-2} (9.4 L min^{-1})
Acetylene Pressure	0.1 kg cm^{-2} (2.2 L min^{-1})

TABLE II
Operating Sequence of the FI On-line Separation and Preconcentration System for FAAS Determination of Pd(II)

Step	Valve Position	Pump Active	Pumped Medium	Flow Rate (mL min^{-1})	Time (s)	Function
1	Fill	1	Blank	4.8	30	Eliminate the eluent
2	Fill	1	Sample	4.8	60	Preconcentrate
3	Fill	1	Blank	4.8	20	Remove matrix
4	Injection	2	Eluent	1.8	20	Elute

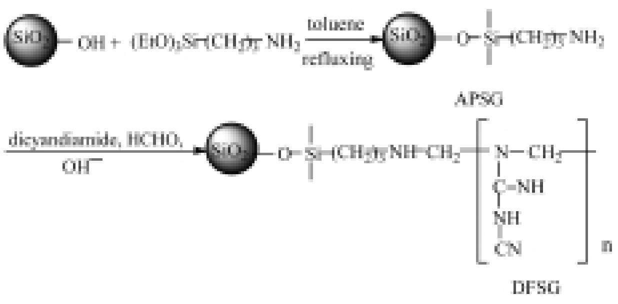

Fig. 2. Preparation of DFSG.

8.03% Fe), and anode slime (more than 90% Cu), with 1.0 g of Na_2CO_3-Na_2O_2 was put into a porcelain crucible, fused at 700ºC for 30 min. Then 20 mL aqua regia was added to the crucible while heating on an electric hot plate. When only a little liquid was left in the crucible, 5 mL concentrated hydrochloric acid was added to remove the nitric acid remaining during the heating cycle. Then, 5 mL 0.5 mol L^{-1} HCl was added into the crucible and the solution filtered into a 25-mL calibrated flask. The filter paper and residue were washed several times with 0.5 mol L^{-1} HCl and the washings added to the same flask. The volume of the filtrate was adjusted to the mark with 0.5 mol L^{-1} HCl solution. The stored sample solutions were diluted and adjusted to proper concentration and acidity before analysis.

RESULTS AND DISCUSSION

Characterization of DFSG

In the Fourier Transmission Infra-red (FT-IR) spectra of DFSG, the -CN group absorption at 2177 cm^{-1}, the methylene group absorption at 2945 cm^{-1}, and the C=N absorption at 1606 cm^{-1} were found. The appearance of these absorption peaks indicated that the dicyandiamide-formaldehyde resin was successfully grafted onto the amino silica gel. The results of the elemental analysis showed that the percentages of N, C, and H were 6.96%, 9.87%, and 1.65%, respectively.

Effect of Acidity

The influence of HCl concentration of the sample solution on peak area absorbance of Pd(II) is shown in Table III ranging from 0.1~ 5.0 mol L^{-1}. It shows that in this acidity range the peak area absorbances of Pd were over 95%, which would be of advantage for preconcentration and separation. The maximal peak area absorbance of Pd was achieved when 0.2 mol L^{-1} HCl solution was used as the medium. Thus, 0.2 mol L^{-1} HCl was used as the optimal sample medium for Pd(II) determination in further experiments.

TABLE III
Effects of HCl Concentration of Sample Solution on Peak Area Absorbance of Pd(II)[a]

HCl Conc (mol L^{-1})	Relative Peak Area Absorb. (%)
0.1	96.1
0.2	99.7
0.5	95.2
1.0	95.4
2.0	95.2
5.0	95.1

[a] Pd(II) concentration: 0.100 mg mL^{-1}. Eluent: 2.0% thiourea. Sample solution flow rate: 4.8 mL min^{-1}. Eluting flow rate: 1.8 mL min^{-1}. All data points are averages of at least 3 parallel measurements.

TABLE IV
Effects of Thiourea Concentration in the Eluent on the Absorbance of Pd(II)[a]

Thiourea Conc. (%)	Relative Peak Area Absorb. (%)
0.1	89.2
0.5	95.4
1	96.3
2	99.8
5	96.6
10	92.1

[a] HCl concentration of the sample solution: 0.20 mol L^{-1}. Other details as in Table III.

Desorption of Pd(II)

Thiourea (TU) was usually used as the eluent for Pd(II) from chelating adsorbents. The influence of the concentrations of TU on the peak area absorbance of Pd(II) was investigated in the range of 0.1 ~ 10.0 % (Table IV). It showed that Pd(II) could be eluted efficiently when the TU concentration in the eluting solution was equal to or more than 2.0% with which the peak area absorbance of Pd(II) reached its maximum. Thus, 2.0% was selected as the TU concentration in the eluting solution.

The actual eluent at the beginning period was a mixture of HCl and TU. This was due to the HCl solution remaining in the micro-column after the washing period with the blank HCl solution to remove the co-existing ions. Therefore, the influence of acidity of the eluting solution was also investigated. Table V shows that 0.1–5.0 mol L^{-1} HCl in the eluting solution had little influence on the elution and determination of Pd. However, when the amount of

TABLE V
Effects of Eluent Acidity on Elution

Acidity	Rel. Peak Area Absorb. (%)
0.1 mol L^{-1} HCl	100
0.2 mol L^{-1}HCl	98.8
0.5 mol L^{-1} HCl	99.1
1.0 mol L^{-1} HCl	99.6
2.0 mol L^{-1} HCl	99.8
5.0 mol L^{-1} HCl	99.5
0.1 mol L^{-1} HNO_3	99.6
0.2 mol L^{-1} HNO_3	97.4
0.5 mol L^{-1} HNO_3	96.6
1.0 mol L^{-1} HNO_3	94.4
2.0 mol L^{-1} HNO_3	91.7

TABLE VI
Effects of Co-existing Ions on Peak Area Absorbance

Species Added	Conc. (mg mL^{-1})	Relative Error	Species Added	Conc. (mg mL^{-1})	Relative Error(%)
Na^+	5.0	1.9	Zn^{2+}	5.0	–2.7
K^+	5.0	–1.5	Mn^{2+}	5.0	0.0
Mg^{2+}	5.0	–0.4	Cr^{3+}	5.0	0.4
Ca^{2+}	5.0	–3.1	Cd^{2+}	5.0	–0.1
Pb^{2+}	0.3	–3.3	SO_4^{2-}	20.0	0.8
Al^{3+}	5.0	–2.3	PO_4^{3-}	20.0	0.7
Cu^{2+}	5.0	–0.5	Cl^-	20.0	–0.1
Ni^{2+}	5.0	0.0	NO_3^-	20.0	–1.6
Fe^{3+}	5.0	–2.8	ClO_4^-	20.0	0.4
Co^{2+}	5.0	1.3			

TABLE VII
Analytic Performances of the Proposed System

Precision (% RSD, n = 7)	2.3 (0.1 μg mL^{-1} Pd)
Limit of detection (ng mL^{-1}, 3σ, n=9)	1.1
Sample frequency (samples h^{-1})	27
Linear range (μg mL^{-1})	0.1 - 0.5
Regression equation (5 standards, n=3, C in μg mL^{-1})	A=0.8649C+0.0005
Correlation coefficient	0.9998

HNO_3 in the eluting solution was increased, the peak area absorbance of Pd decreased, which might result from the fact that TU was oxidized by HNO_3. A 2.0% TU solution was used as the eluent for Pd(II) for further experiments.

Effect of Flow Rate

A high flow rate is favorable for sample loading and elution. The response increases with an increase in sample loading flow rate. The high flow rate of the eluent will shorten the elution period and give a sharper peak signal. In the studied eluting flow rate range of 1.8–3.8 mL min^{-1}, the analyte was eluted completely where peak area absorbance decreased in accordance with the increase. The flow rate nearest to the nebulization aspiration flow rate (2.1 mL min^{-1}), 1.8 mL min^{-1}, was used as the eluting flow rate.

In the studied sample loading flow rate range of 1.8–4.8 mL min^{-1}, the peak area absorbance of 0.100 μg mL^{-1} Pd increased with an increase in the sample loading flow rate according to the linear equation, which can be stated as follows:

$$A = 0.01789 * Fr\ (mL\ min^{-1}) + 0.0004\ (r = 0.9996)$$

where A=peak area absorbance; Fr=flow rate. A flow rate of 4.8 mL min^{-1}, the highest flow rate our pumps could provide, was used as the sample loading flow rate for Pd(II).

There was no obvious difference between the absorbance obtained after a 20-s period and a 30-s period of matrix removal. For further experiments, a 20-s period of matrix removal was adopted.

Interference of Co-existing Ions

The effects of the anions Cl^-, NO^{3-}, SO_4^{2-}, PO_4^{3-}, and ClO_4^-, and co-existing metal ions were investigated when Pd(II) was determined at 0.100 μg mL^{-1}. In addition, each cation was investigated without other cations present. The results in Table VI show that 5.0 mg mL^{-1} of the co-existing metal ions [except Pb(II) was 0.3 mg mL^{-1}] and 20.0 mg mL^{-1} of the anions mentioned above (added as sodium salts) did not interfere with the preconcentration and determination of Pd. This demonstrates that DFSG is a very suitable material for the on-line preconcentration and separation of Pd from complex samples.

Analytical Performance

After 300 adsorption and desorption cycles, the adsorption properties of DFSG did not change. The saturated adsorption capacity of DFSG for Pd(II) was 0.2274 mmol g^{-1} calculated from the break-through curve. The characteristic data for the analytical performance of the proposed FI on-line micro-column separation and preconcentration system for FAAS determination are summarized in Table VII. The relative standard deviation (RSD) was 2.3% for 0.100 μg mL^{-1} of Pd(II).

The limit of detection (LOD), calculated as the amount of Pd(II) required to yield a net peak area absorbance and equal to three times the standard deviation of the background signal (3σ) of the blank solution, was 1.1 ng mL^{-1}, with a sample loading flow rate of 4.8 mL min^{-1} and a 60-s sample loading time.

In order to test the accuracy and applicability to the analysis of real samples, the proposed method was used to analyze an alloy sample and an anode slime sample. The results, as the average value of three separate determinations, are shown in Table VIII. The analytical results are in good agreement with the certified values.

TABLE VIII
Determination of Pd in Metallurgical Samples (n=3)

	Found (g t^{-1})	Certified (g t^{-1})	Relative Error(%)
Nickel alloy	160.7	161.0	–0.2
Anode slime	91.2	91.0	0.2

CONCLUSION

The FI on-line preconcentration and separation of Pd(II) for its determination by FAAS was investigated using a dicyandiamide-formaldehyde resin immobilized silica gel (DFSG) as the micro-column packing. Pd(II) was adsorbed in a wide range of sample acidity (0.1–5.0 mol L^{-1}) and the adsorbed Pd(II) was eluted completely with thiourea solution. The co-existing ions with higher concentrations had no influence on the preconcentration and determination of Pd. The limit of detection for Pd was 1.1 ng mL^{-1} with a relative standard deviation of not more than 3.0%. The proposed method was successfully applied to the FI preconcentration and separation of Pd in real samples.

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2006 Winter Conference on Plasma Spectrochemistry

Tucson, Arizona, January 8–14, 2006

Plasma Spectrochemistry for Trace Element, Stable Isotope, and Elemental Speciation Analyses

The 2006 Winter Conference on Plasma Spectrochemistry, fourteenth in a series of biennial meetings sponsored by the *ICP Information Newsletter*, features developments in plasma spectrochemical analysis by inductively coupled plasma (ICP), dc plasma (DCP), microwave plasma (MIP), glow discharge (GDL, HCL), and laser sources. The meeting will be held Monday, January 9 through Saturday, January 14, 2006, in Tucson, Arizona (www.visitTucson.org) at the Hilton Tucson El Conquistador Golf and Tennis Resort (www.hiltonelconquistador.com). Continuing education short courses at introductory and advanced levels and manufacturers' seminars will be offered Friday through Sunday, January 6-8. Spectroscopic instrumentation and accessories will be shown during a three-day exhibition from January 10 to 12, and a Workshop on New Plasma Instrumentation will be presented on Tuesday, Wednesday, and Thursday afternoons. A golf tournament will be held on Sunday, January 8.

Objectives and Program

The continued growth in popularity of plasma sources for atomization and excitation in atomic spectroscopy and ionization in mass spectrometry and the need to discuss recent developments of these discharges in spectrochemical analysis stimulated the organization of this meeting. The Conference will bring together international scientists experienced in applications, instrumentation, and theory in an informal setting to examine recent progress in the field. Approximately 600 participants from 30 countries are expected to attend.

Over 300 papers describing applications, fundamentals, and instrumental developments with plasma sources will be presented in lecture and poster sessions by more than 200 authors. Symposia organized and chaired by recognized experts will include the following topics: 1) Sample introduction and transport phenomena; 2) Micronebulization and flow processing spectrochemical analysis; 3) Elemental speciation and sample preparation for speciation; 4) Plasma instrumentation, including chemometrics, expert systems, on-line analysis, microplasmas, software, and remote-system automation; 5) Sample preparation, treatment and automation, 6) Excitation mechanisms, plasma phenomena and modeling; 7) Spectroscopic standards and reference materials, and high-purity materials; 8) Plasma source mass spectrometry, 9) Glow discharge atomic and mass spectrometry, 10) Stable isotope analyses, and 11) Laser-assisted plasma spectrometry. Six plenary and 24 invited lectures will highlight advances in these areas. Four afternoon poster sessions will feature applications, automation, and new instrumentation. Six panel discussions will address critical development areas in sample introduction, instrumentation, elemental speciation, plasma source mass spectrometry, and novel software and hardware. Plenary, invited, and submitted papers will be published in Fall 2006 after peer review as the official Conference proceedings.

Schedule of Activities

Call for Papers, Abstracts Due, Early Bird Registration	Friday, July 15, 2005
Exhibitor Booth Reservation and Pre-Registration Due	Friday, September 16, 2005
Final Abstracts for All Paper Due	Friday, October 14, 2005
Exhibitor Reservation Deadline	Friday, October 14, 2005
Conference Pre-Registration Deadline	Friday, October 14, 2005
Hotel Reservation Deadline	Monday, December 5, 2005
Late Pre-Registration Deadline	Friday, December 9, 2005
2006 Winter Conference Short Courses	Friday - Sunday, January 6 - 8, 2006
2006 Manufacturers' Seminars	Friday - Sunday, January 6 - 8, 2006
2006 Winter Conference on Plasma Spectrochemistry	Monday, - Saturday, January 9 - 14, 2006
2006 Workshop on New Plasma Instrumentation	Tuesday - Thursday, January 10 - 12, 2006
2006 Instrument Exhibition	Tuesday - Thursday, January 10 - 12, 2006
Conference Manuscripts Submission Deadline	February 17, 2006

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