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On-line Flow Injection Flame AAS Determination of Cobalt in Soil and Sediment Samples With 5,7-Dichloroquinoline-8-ol-Embedded Polymeric Materials

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ABSTRACT

Dichloroquinoline-8-ol-embedded styrene-ethylene-glycol dimethacrylate polymer materials were prepared via the bulk, precipitation, and suspension polymerization methods using similar compositions. The polymerization was carried out by thermal means in the presence of 2,2'-azobisisobutyronitrile as initiator and 2-methoxy ethanol as porogen. The above synthesized polymeric materials were characterized physically and morphologically by using the FTIR, TGA, CHN, and SEM techniques. These polymeric materials were packed into homemade micro columns and used for on-line solid phase extraction (SPE) preconcentration

of trace amounts of cobalt. The preconcentrated cobalt species were eluted with 0.01 mol L⁻¹ of nitric acid and injected directly into the nebulizer of a flame atomic absorption spectrometer (FAAS) for quantification.

The enrichment factors for bulk, precipitation, and suspension polymerization materials, were 12.5, 12.5, and 6.0, respectively, with a 1-min preconcentration time and a sample throughput of 30 h⁻¹. The detection limits corresponding to 3 times the standard deviation of the blank were found to be 10, 10, and 80 µg L⁻¹ with a precision of 2.1, 2.5, and 2.6% (RSD) for five successive determinations of 80 µg L⁻¹ of cobalt. Furthermore, the retention

capacities determined by the batch method were 11.46, 11.42, and 8.52 mg of Co(II) per g of bulk, precipitation, and suspension polymerization materials, respectively. Thus, enrichment factor, detection limit, and retention capacities are in the order: precipitation ~ bulk > suspension. No significant interference was observed from neutral electrolytes and 100-fold amounts of Fe(III), Ni(II), Mn(II), Cu(II), and Zn(II). In addition to testing the accuracy of the developed procedure for the determination of cobalt in certified reference materials of soil and marine sediments, the method was applied successfully to the determination of cobalt in real soil and sediment samples.

INTRODUCTION

Cobalt is an essential micronutrient for a range of metabolic processes in man, animals, and plants (1,2). For the trace level determination of cobalt and other transition metals, environmental samples pose definite challenges to the analytical chemist since typical concentration levels are two orders of magnitude lower in geological samples than the detection limits of flame atomic absorption spectrometry (FAAS) analysis (3). Therefore, in the determination of trace and ultratrace amounts of cobalt in geological samples, a preconcentration procedure is often required. Con-

ventional off-line procedures for preconcentration and separation, although effective, are usually time-consuming, tedious, require large quantities of sample and reagents, and are vulnerable to contamination and analyte losses (4).

Flow injection (FI) on-line preconcentration and separation with a microcolumn has proved to be a suitable method and has been widely used in trace element analysis due to its simple automated operation and high reproducibility (5). FI-online preconcentration coupled with FAAS provides enhanced sensitivity, efficient removal of the matrix, low cost of the FAAS instrument, substantially higher sample throughput and, more importantly, employs a contamination-free closed system (5-7).

Many chelating sorbents have been reported in the literature for selectively sorbing cobalt from aqueous solutions, but only a limited number of them can be applied to FI-on line preconcentration (see Reference 8 and further references therein). This is perhaps due to the prime requirement that a sorbent in FI-AAS must have faster sorption and desorption. Hence, one has to be careful in choosing a sorbent material in on-line solid phase extraction (SPE) (9).

In this study, we developed a simple, sensitive, and selective flow injection on-line preconcentration and separation method for the routine determination of trace amounts of cobalt in geological samples based on 5,7-dichloro-quinoline-8-ol-embedded polymer materials.

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EXPERIMENTAL

Instrumentation

A PerkinElmer® AAnalyst™ 100 flame atomic absorption spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA) was used, equipped with deuterium background correction and a PerkinElmer Lumina™ cobalt hollow cathode lamp. This lamp was operated at 10 mA using a 0.7-nm slit width. The wavelength used was 240.7 nm. The system was equipped with a 10-cm air-acetylene burner head and a stainless steel nebulizer using flow rates of 4.0 L min⁻¹ (air) and 1.0 L min⁻¹ (acetylene). The burner height was adjusted to about 30 mm from base for optimum sensitivity. The nebulizer uptake rate was adjusted to provide optimum response for conventional sample aspiration.

A PerkinElmer FIAS™-400 flow injection system connected to the FAAS was used for on-line preconcentration of cobalt. The automatic operation of the injection valve and the two multichannel peristaltic pumps were programmed using the spectrometer software (PerkinElmer AA WinLab™ v. 3.0). Tygon® peristaltic tubing was used to pump the sample at 3.0 mL min⁻¹ and PTFE tubing of 0.3 mm i.d. was used for all connections in order to minimize dead volume. Homemade conically shaped micro-columns were used, packed with 20 mg of materials prepared by the bulk, precipitation, and suspension polymerization methods. Time-resolved absorbance signals of cobalt were displayed on the computer monitor along with the peak height and integrated absorbance values.

FT-IR spectra were recorded in the wave number range 4000–400 cm⁻¹ using a MAGNA FTIR-560 spectrometer (Nicolet, USA). The CHN analysis was carried out using a PerkinElmer elemental analyzer.

Thermo-gravimetric analysis studies were carried out using a Model TGA-50H (Shimadzu, Japan). The surface morphology of the 5,7-dichloroquinoline-8-ol-embedded polymeric materials was carried out using a JEOL Model JSM 5600LV scanning electron microscope (SEM). A Model Innova 4330 refrigerated incubation shaker (USA) was used for adsorption kinetic and adsorption isotherm studies. A Model LI-120 digital pH meter (ELICO, India) was used for pH measurements.

Reagents, Standard Solutions, and Samples

The polymeric materials 5,7-dichloroquinoline-8-ol (DCQ), styrene, ethylene glycol dimethacrylate (EGDMA), 2,2'-azobisisobutyronitrile (AIBN), and 2-methoxyethanol were obtained from Aldrich, Milwaukee, WI, USA. A cobalt stock solution (1000 µg mL⁻¹) (Aldrich) was prepared by dissolving 0.4039 g of CoCl₂·6H₂O in 100 mL of deionized water. A solution of 5% ammonium acetate (pH 7.0) was prepared to maintain the pH of the sample solution (7.0±2.0) during on-line flow injection solid phase extraction-preconcentration experiments.

Certified reference materials (CRMs) of soil and marine sediment were purchased from the International Atomic Energy Agency (IAEA, Soil 7) and the National Research Council, Canada (MESS-3), respectively. One sample each of house soil, river sediment, and marine sediment sample was collected in Trivandrum and after mineralization, each sample was subjected to the determination of cobalt.

Polymerization Studies

Bulk Polymerization

The 5,7-dichloroquinoline-8-ol (2 mmoles)-embedded polymer materials were prepared with 10 mmoles each of styrene as

monomer and EGDMA as cross-linking monomer. The polymerization mixtures were prepared in 2-methoxyethanol (10 mL) as porogen and 2,2'-azobisisobutyronitrile (AIBN) (0.05 g) as initiator, cooled to 0°C, purged with N₂ for 10 min, and then sealed in an R.B. flask. The bulk polymerization was carried out by keeping it in an oil bath at 80°C while stirring for 2–3 h. The polymer materials thus obtained were ground and sieved to get particle sizes ranging from 45–212 µm. These particles were washed thoroughly with water and 1.0 mol L⁻¹ HCl to remove the unembedded chelating agents and reactants.

Precipitation Polymerization

Synthesis of microspheres by precipitation polymerization was performed by using the same composition as used for the polymer materials for bulk polymerization, with the exception of using a 40-mL volume of porogen.

Suspension Polymerization

Synthesis of the beads by suspension polymerization was performed as follows:

Step 1: Polyvinyl alcohol (PVA, molecular weight ~400, 0.1 g) was dissolved in hot water (about 90°C, 30 mL), then cooled to room temperature. The solution was purged with N₂, placed in a water bath (60°C), and then stirred at 400 rpm for 30 min.

Step 2: The same composition as for the above bulk polymerization was used (porogen, DCQ, styrene, EGDMA, and AIBN) and subjected to N₂ purging. Then this solution was added dropwise to the above PVA solution and stirred for 2 h.

The polymerizing solution was put in an oil bath at 80°C for 24 h. The beads obtained were collected, washed with hot water, and dried.

Procedure for On-line Preconcentration

The FI manifold (0.3 mm i.d.) used in this study for on-line preconcentration and elution is described by Sperling et al. (10). The pH of the sample solution was adjusted to ~7.0 and pumped through homemade micro-columns packed with 20 mg of polymeric materials prepared by the bulk, precipitation, and suspension methods. The preconcentration time was approximately 1 min and the sorbed cobalt species were eluted with 0.01 mol L⁻¹ of nitric acid at a flow rate of 4 mL min⁻¹. Calibration curves were drawn by pumping 10–160 µg L⁻¹ of cobalt standard solutions through the micro-columns.

Analysis of Soil and Sediment CRMs, and Real Samples

A 0.5-g soil or sediment sample was weighed into a platinum crucible, 5 mL of HF and 1 mL of conc. H₂SO₄ were added, and the mixture was heated to 150°C on a hot plate. The process was repeated three times. The residue was cooled and fused with 2 g of KHSO₄ at 800°C in an electric bunsen burner for 30 min. The melt was cooled and dissolved in 50 mL of deionized water and made up to 100-mL volume. These sample solutions were subjected to preconcentration and analysis by the procedure described above. The cobalt content of the soil and sediment samples was established by reference to a calibration graph prepared in accordance with the above procedure.

RESULTS AND DISCUSSION

Characterization Studies

Characterization of 5,7-dichloroquinoline-8-ol-embedded polymer materials, synthesized by the precipitation, bulk, and suspension methods, was carried out as described below.

IR Spectra

The IR spectral studies of styrene-EGDMA and DCQ-embedded styrene-EGDMA, prepared by the different polymerization methods, indicate that the spectra contain a strong peak at 765 cm⁻¹ corresponding to the C-Cl bond. This shows the presence of DCQ in all of the materials except for the styrene-EGDMA polymeric material. This observation also indicates that 5,7-dichloroquinoline-8-ol is indeed embedded in the polymer matrix in all of the materials prepared by the precipitation, bulk, and suspension methods.

TGA Studies

The TGA studies of styrene-EGDMA and DCQ-embedded styrene-EGDMA polymers, prepared by the precipitation, bulk, and suspension methods, reveal an additional decomposition pattern starting at ~180°C in case of the latter polymer materials. These studies confirm the IR evidence that DCQ is indeed embedded in the polymer materials since the melting point of DCQ is 180°C.

Elemental Analysis

The elemental analysis data of styrene-EGDMA and DCQ-embedded styrene-EGDMA polymers, prepared by the precipitation, bulk,

and suspension polymerization methods, are listed in Table I. This table also shows the calculated / theoretical percentages of C, H, and N. The agreement between calculated and experimentally found values is quite good. Thus, the close similarity of % N in the polymer materials between the experimental and calculated values confirms that DCQ is indeed embedded in the styrene-EGDMA polymeric matrix.

SEM Studies

The morphology of the polymers prepared by the precipitation, bulk, and suspension polymerization methods was assessed by SEM (micrographs are shown in Figure 1). In all cases, the morphology was as predicted. For bulk polymerization, the morphology of the crushed polymer is shown. In the other two methods, microspheres and beads were produced by precipitation and suspension polymerization. As seen from the micrographs, there is a systematic morphological change in the material's shape and size of the polymers synthesized by the bulk, precipitation, and suspension methods. Bulk polymerization shows agglomerated polymeric materials in irregular shapes ranging from 1–20 µm. In the case of the precipitation method, the polymeric material shapes into regular

TABLE I
Elemental Analysis Studies

Polymerization Method	Calculated (%)			Experimentally Found (%)		
	C	H	N	C	H	N
A. Precipitation						
Styrene-EGDMA	71.52	7.28	-	71.50	6.99	-
DCQ-Styrene-EGDMA	68.90	6.67	0.80	68.70	6.70	0.84
B. Bulk						
Styrene-EGDMA	71.52	7.28	-	71.20	6.79	-
DCQ-Styrene-EGDMA	68.90	6.67	0.80	68.29	6.82	0.80
C. Suspension						
Styrene-EGDMA	71.52	7.28	-	71.40	6.85	-
DCQ-Styrene-EGDMA	68.90	6.67	0.80	67.98	6.68	0.88

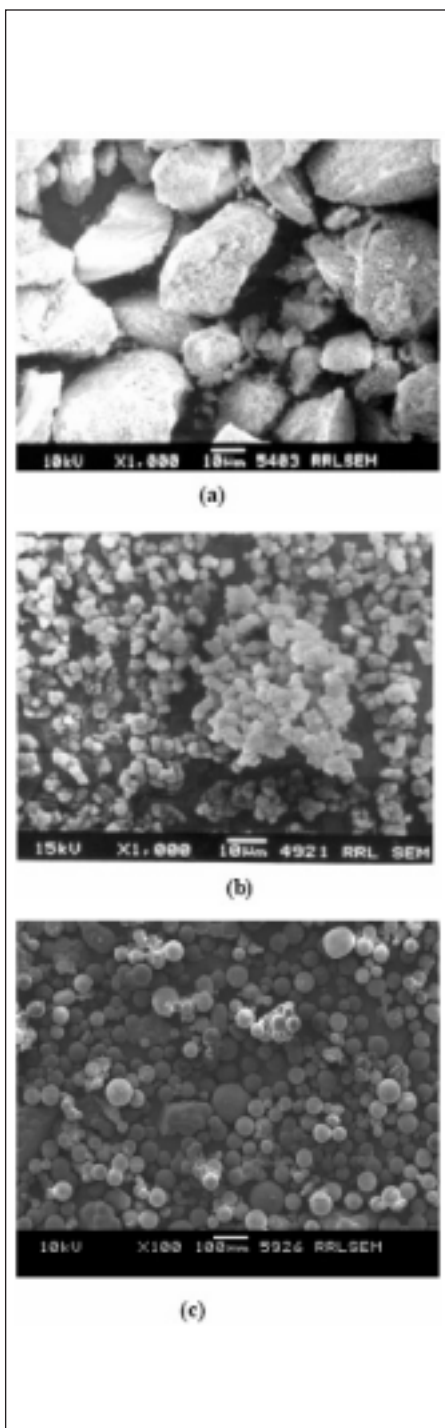


Fig. 1. SEM photographs of 5,7-dichloroquinoline-8-ol (DCQ)-embedded polymer materials synthesized by the (a) bulk, (b) precipitation, and (c) suspension methods.

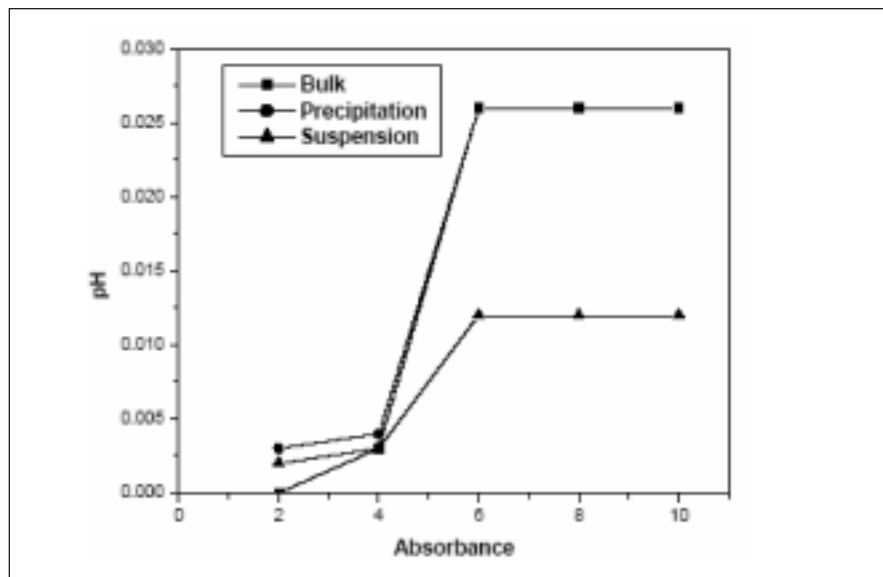


Fig. 2. Effect of pH on FI-FAAS signals of $80 \mu\text{g L}^{-1}$ of cobalt pumped through micro-columns packed with DCQ-embedded polymer materials synthesized by the bulk, precipitation, and suspension methods.

spherical particles of uniform sizes (300–400 nm). The roundness of the particles is not very perfect. In the suspension method, the material crystallizes into nanosized perfectly uniform spherical beads (~200 nm). Also, the materials organize into very regular shapes in case of the precipitation and suspension polymerization methods only.

Evaluation Of Main Experimental Variables

Effect of pH

A series of solutions containing 0 and $80 \mu\text{g L}^{-1}$ of cobalt solution were taken, the pH of the solutions was adjusted to between 2 and 10, and pumped through micro-columns packed with 20 mg of polymeric materials prepared by the precipitation, bulk, and suspension methods. The SPE of cobalt was found to be constant and maximum in the pH range of 6–10 (see Figure 2). The pH of the sample solution was adjusted to ~7.0 in subsequent studies after the addition of 1.0 mol L^{-1} of ammonium acetate solution. The analytical sig-

nal for on-line FIA-FAAS determination of cobalt lies in the order: precipitation ~ bulk > suspension.

Choice of Eluent

Various miscible solvents (acidified to pH ~2.0) such as methanol, dimethyl formamide, dimethyl sulphoxide, acetonitrile, and 0.01 mol L^{-1} of HCl and HNO_3 were tested for the elution of previously sorbed cobalt onto 5,7-dichloroquinoline-8-ol-embedded polymeric materials prepared by the precipitation, bulk, and suspension methods. It was found that nitric acid alone in the range of $0.01\text{--}0.1 \text{ mol L}^{-1}$ quantitatively elutes cobalt for the three materials. Again, the analytical signals obtained for FIA-FAAS determination of cobalt follow the order: precipitation ~ bulk > suspension for all eluents.

Optimization of FI Analysis Flow Conditions

High sample loading flow rates are important for efficient preconcentration and high sample throughput. In general, FI sample flow rates are limited by the back pressure produced by the column

and/or sorption efficiency. In this study, no degradation of sorption efficiency was observed up to a loading flow rate of 12.0, 3.0, and 6.0 mL min⁻¹ of sample in case of the precipitation, bulk, and suspension polymerization materials, respectively. The optimum sample flow rates, which do not result in back pressure, were found to be 12.0, 3.0, and 6.0 mL min⁻¹ for micro-columns packed with 20 mg of materials prepared by the precipitation, bulk and suspension methods, respectively. These flow rates were used for subsequent studies.

An elution flow rate of 4.0 mL min⁻¹ provided optimum sensitivity and elution peaks with minimum tailing. No provision was made to compensate for the lower flow rate delivered by the FI system; however, the transfer capillary to the nebulizer (PTFE, 0.3 mm i.d.) restricted the uptake rate to values close to the flow rates provided by the FI system. Operating the nebulizer at this flow rate does not lower the sensitivity relative to a decrease in the flow rate due to the potential improvement in nebulizer efficiency under starved conditions (10,11). The lower sample flow rate in the FI mode in comparison to the conventional free uptake of the nebulizer is also beneficial for droplet diameter distribution, which results in smaller droplets and is therefore less prone to vaporization interferences (11).

Performance of On-Line Preconcentration System

The characteristic data listed in Table II show the performance of the on-line FI preconcentration of cobalt with micro-columns packed with 20 mg of 5,7-dichloroquinoline-8-ol-embedded polymer materials obtained by the precipitation, bulk, and suspension methods. The efficiency of SPE was investigated by analyzing the previously collected column eluent from standard solutions of cobalt using the

same preconcentration technique. From the results obtained by repeated preconcentration, a retention efficiency of >99% was calculated for the precipitation and bulk materials. The SPE elution sequence for the three methods is highly reproducible and provides an overall precision of 2.1, 2.5, and 2.6% (RSD), respectively, for five successive/determinations of 80 µg L⁻¹ of cobalt passed through micro-columns packed with 20 mg of polymer materials. A linear relationship was observed between preconcentration time and an enrichment factor up to a 2-min loading time. Using precipitation-, bulk-, and suspension-based column materials and a 1-min loading time provided a 12.5-, 12.5-, 6.0-fold enhancement in sensitivity, while a 2-min loading time provided a 25-, 25-, 12-fold enhancement in sensitivity, respectively, in comparison to conventional FAAS. The detection limits corresponding to 3 times the standard deviation of the blank were found to be 10, 10, and 80 µg L⁻¹ of cobalt with precipitation-, bulk-, and suspension-based column materials, respectively. The linear equation with regression was as follows:

$$A_{\text{precipitation}} (A_p) = 0.0005 + 0.25 \times C$$

$$A_{\text{bulk}} (A_b) = 0.0005 + 0.30 \times C$$

$$A_{\text{suspension}} (A_s) = 0.0005 + 0.07 \times C$$

The correlation coefficients are 0.998, 0.999, and 0.996, where A_p, A_b, and A_s are absorbances and C is the concentration of cobalt in µg mL⁻¹. All statistical calculations are based on the average of triplicate measurements. Furthermore, a 1-min loading time allows a sample frequency of 30 h⁻¹. Higher sensitivities can be obtained by modifying the method, i.e., using longer preconcentration times at the expense of lower sample throughput. Under the optimal conditions described above, the role of DCQ-embedded polymer materials obtained by the precipitation, bulk, and suspension methods in on-line preconcentration of cobalt was investigated by adsorption kinetics and adsorption isotherm studies.

Adsorption Kinetics

The time required for loading cobalt onto DCQ-embedded polymeric materials prepared by the precipitation (Figure 3a), bulk (Figure 3b), and suspension (Figure 3c) methods was determined by agitating 20 and 60 mg (curves A and B in Figure 3) of cobalt in a refrigerated incubation shaker at 30°C for 0.5, 1, 2, 4, 8, 10, 20, 40, and 60 min. The amount of cobalt loaded onto DCQ-embedded polymer materials was determined by FAAS. The equilibrium time in which DCQ-embedded polymer materials attain 50% saturation with cobalt

TABLE II
Analytical Performance Data of On-line SPE-FIA-FAAS Determination of Cobalt Using Precipitation, Bulk, and Suspension Materials

Parameter	Precipitation	Bulk	Suspension
1 Linear Range (µg L ⁻¹)	10-160	10-160	80-160
2 Sensitivity Enhancement ^a	12.5	12.5	6
3 Concentration Efficiency ^a	12.5	12.5	6
4 Precision (RSD ^b) at 80 µg L ⁻¹ (%)	2.1	2.5	2.6
5 Sample Consumption (mL)	12	3	6
6 Loading Time (min)	1	1	1
7 Sample Frequency	30/h	30/h	30/h
8 Detection Limit (3σ) µg L ⁻¹	10	10	80

^a Compared to conventional nebulization; ^b n = 5.

(i.e., when the amount of metal ion sorbed on the SPE is half of its maximum sorption capacity) is called loading half-time ($t_{1/2}$). From curves A and B in Figure 3 it is clear that the loading half-time is <30 s. The kinetics of cobalt sorption on DCQ-embedded polymer materials follows the first order rate expression given by Lagergren (12):

$$\log (q_e - q) = \log q_e - K_{ads} t/2.303$$

where q and q_e are the amounts of cobalt adsorbed (mg per g) of DCQ-embedded polymer materials at time t (min), and equilibrium time (60 min), respectively, and K_{ads} is the rate constant of adsorption. Linear plots of $\log (q_e - q)$ versus t (Figure 4) show the applicability of the equation for the three DCQ-embedded polymer materials. The correlation coefficients and K_{ads} calculated from the slopes of Figure 4, are shown in Table III.

Adsorption Isotherms

The adsorption of cobalt was studied as a function of DCQ-embedded polymer materials obtained with the precipitation, bulk, and suspension methods by equilibrating for 60 min in a refrigerated incubation shaker. The amount of cobalt loaded onto the DCQ-embedded polymer materials was determined by FAAS. The Langmuir treatment (13) is based on the assumption that (a) maximum adsorption corresponds to saturated monolayer of adsorbate molecules on the adsorbed surface, (b) the energy of adsorption is constant, and (c) there is no transmigration of adsorbate in the plane of the surface. The equation is given as follows:

$$C_e / q_e = 1 / (q_0 b) + C_e / q_0$$

where C_e is the equilibrium concentration (mg L⁻¹), q_e is the amount adsorbed at equilibrium, and q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

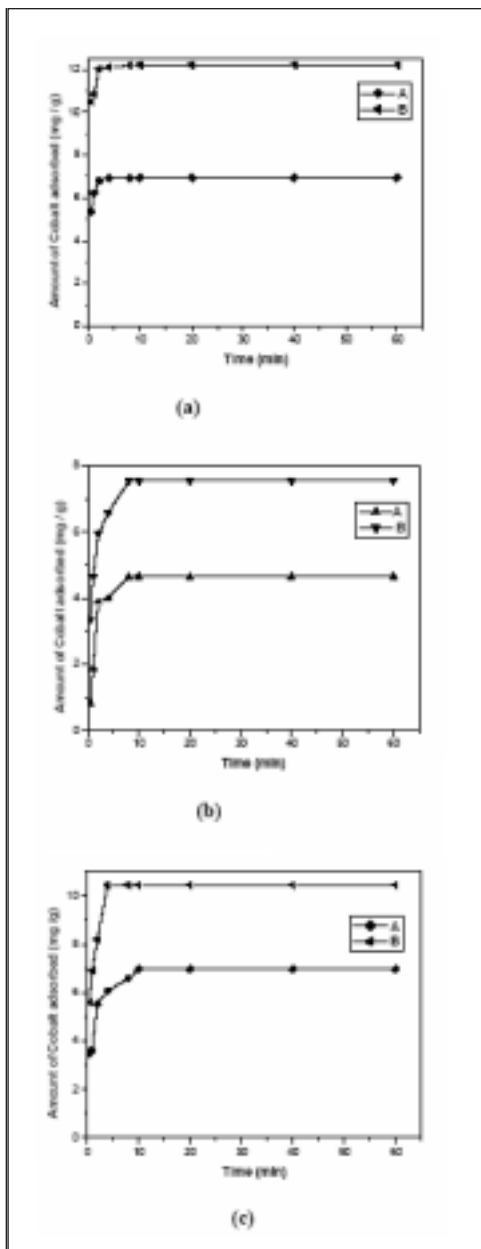


Fig. 3. Effect of agitation time on the adsorption of cobalt (a) bulk, (b) precipitation, and (c) suspension. Cobalt concentration (A) 20 mg L⁻¹ and (B) 60 mg L⁻¹, pH 7.0, adsorbent dose = 250 mg per 100 mL.

The linear plot of C_e/q_e versus C_e shows that adsorption obeys the Langmuir adsorption model (Figure 5). The correlation coefficient (R) for the linear fit of the Langmuir plots, q_0 and b values determined

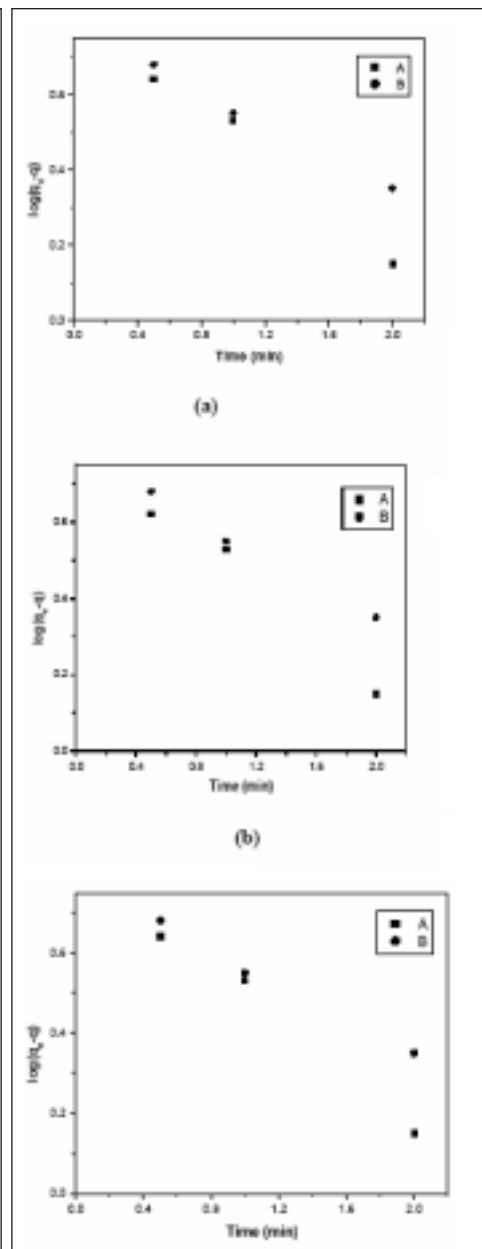


Fig. 4. Lagergren plots for the adsorption of cobalt: (a) bulk, (b) precipitation, and (c) suspension. Cobalt concentration (A) 20 mg L⁻¹, (B) 60 mg L⁻¹, pH 7.0, adsorbent dose = 250 mg per 100 mL.

from the linear regression fits of the Langmuir plots are shown in Table V. It can be seen that the binding capacities (q_0) are in the order: precipitation > bulk > suspension. The essential characteristics of the Lang-

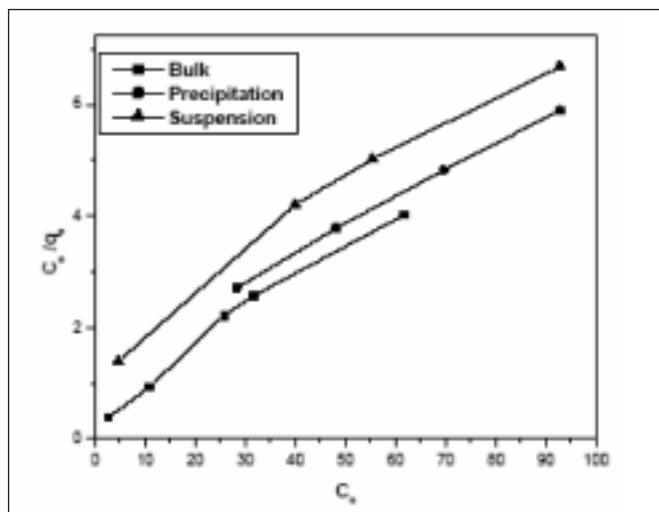


Fig. 5. Langmuir plots of bulk, precipitation, and suspension polymers for the adsorption of cobalt. Cobalt concentration: 20–100 mg L⁻¹, pH 7.0, equilibration time: 60 min, adsorbent dose = 250 mg per 100 mL.

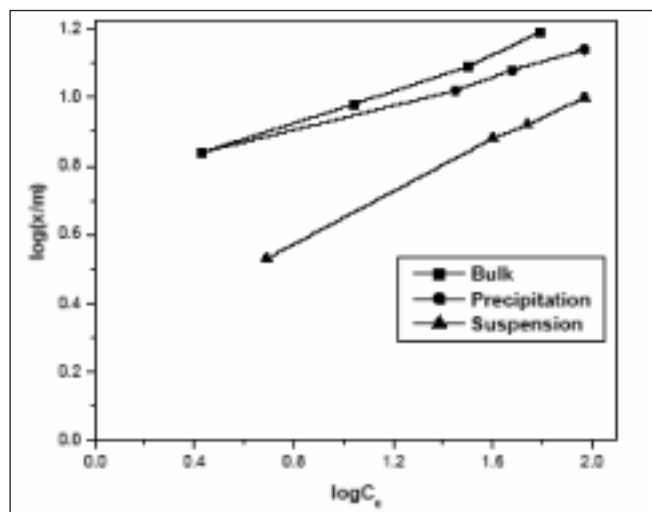


Fig. 6. Freundlich plots of bulk, precipitation, and suspension polymers for the adsorption of cobalt. Cobalt concentration: 20–100 mg L⁻¹, pH 7.0, equilibration time: 60 min, adsorbent dose = 250 mg per 100 mL.

TABLE III
Correlation Coefficient and K_{ads} Values of DCQ-Embedded Polymer Particles Obtained by Different Polymerization Methods

Cobalt (μg L ⁻¹)	Precipitation		Bulk		Suspension	
	Correl. Coeff. (R)	K _{ads} (L min ⁻¹)	Correl. Coeff. (R)	K _{ads} (L min ⁻¹)	Correl. Coeff. (R)	K _{ads} (L min ⁻¹)
20	0.993	1.01	0.980	1.04	0.991	1.10
60	0.997	0.50	0.990	1.21	0.997	0.62

TABLE IV
R, q₀, and b Values Determined From Langmuir Plots for the Adsorption of Cobalt

	Precipitation	Bulk	Suspension
R	0.999	0.988	0.990
q ₀	20.30	16.11	2.75
b	0.04	0.16	0.26

Langmuir isotherm can be expressed in terms of a dimensionless constant, equilibrium parameter, RL, which is defined by $RL = 1/(1+bC_0)$, where b is a Langmuir constant and C₀ is the initial concentration of cobalt (13). The RL values observed between 0 and 1 indicate favorable adsorption of cobalt onto the DCQ-embedded polymer materials (see Table V).

The Freundlich equation was also applied to the adsorption. This equation is basically empirical but often useful as a means of data description. It generally agrees quite well with the Langmuir equation and the experimental data over a moderate range of adsorbate concentrations. The Freundlich

TABLE V
Equilibrium Parameter, R_L

Initial Co Conc. (mg L ⁻¹)	R _L Value		
	Precipitation	Bulk	Suspension
20	0.58	0.23	0.13
40	0.41	0.13	0.09
60	0.32	0.09	0.06
80	0.26	0.07	0.05
120	0.19	0.05	0.03

isotherm is represented by the following equation (14):

$$\log(x/m) = \log K_f + (1/n) \log C_e$$

where C_e is the equilibrium concentration (mg L⁻¹) and x m⁻¹ is the amount adsorbed per unit mass of the DCQ-embedded polymer mate-

TABLE VI
K_f and n Values Deduced From Freundlich Plots for the Adsorption of Cobalt

	Precipitation	Bulk	Suspension
K _f	5.66	5.31	1.90
n	5.18	3.96	2.70

rials. A plot of log (x / m) versus log C_e (see Figure 6) is linear and the constants K_f and n obtained are shown in Table VI. The values of 1 < n < 10 show a favorable adsorption of cobalt onto the DCQ-embedded polymer materials (14). The correlation coefficients for the

TABLE VII
Analysis Of Certified Reference
Materials (CRMs)

CRMs	Cobalt Found ($\mu\text{g per g}$)	
	Present Method	Certified Value
IAEA Soil-7	8.8 \pm 1.1	8.9 \pm 1.0
MESS-3	14.3 \pm 2.0	14.4 \pm 2.0

Freundlich plots were found to be 0.997, 0.996, and 0.999 for the DCQ-embedded polymer materials prepared by the precipitation, bulk, and suspension methods, respectively, indicating a better fit for the experimental data in comparison to the Langmuir plot.

Effect of Neutral Electrolytes and Coexisting Ions

The tolerance of various neutral electrolytes and coexisting ions usually present in soil or sediment samples in the determination of 80 $\mu\text{g L}^{-1}$ of cobalt was systematically studied using the FIA-FAAS procedure described in a previous section. A deviation from the standard absorbance value greater than 3% was taken as interference. Thus, it can be stated that NaCl (5%), KCl (0.5%), CaCl_2 (0.1%), MgCl_2 (0.1%), and 2 mg L^{-1} of Fe(III), Ni(II), Mn(II), Cu(II), and Zn(II) do not interfere in the FIA-FAAS determination of cobalt. This observation suggests that the developed procedure can be used for the selective determination of cobalt in the presence of matrix elements which are likely to coexist in geological and environmental samples.

Analysis of Certified Reference Materials

Accuracy of the developed preconcentration procedure was tested by analyzing certified reference materials of soil (IAEA-Soil 7) and marine sediment (MESS-3). These soil and sediment samples were mineralized by following the

TABLE VIII
Analysis of Soil and Sediment Samples

Sample	Cobalt Added ($\mu\text{g of Co per g}$)	Cobalt Found ($\mu\text{g of Co per g}$)	Recovery (%)
House Soil, Trivandrum, India	-	9.20 \pm 1.2	-
	5.0	14.15 \pm 1.4	99.0
	10.0	19.20 \pm 2.0	100.0
Karamana River Sediment, Trivandrum, India	-	18.50 \pm 2.0	-
	15.0	33.50 \pm 3.0	100.0
	30.0	48.40 \pm 5.0	99.7
Arabian Sea Sediment, Trivandrum, India	-	17.60 \pm 1.8	-
	15.0	32.60	100.0
	30.0	47.40 \pm 5.0	99.3

dissolution procedure described in the Experimental section. The solution was subjected to preconcentration and analysis by adopting the on-line preconcentration procedure described in the Experimental section after adjusting the pH to 7.0 \pm 2.0. The cobalt content established by the present procedure agrees well with the certified values (see Table VII), verifying the accuracy of the developed procedure for the analysis of soil and sediment samples.

Analysis of Real Soil and Sediment Samples

Soil, river, and marine sediment samples were mineralized and the cobalt content was determined as described in the Experimental section. As can be seen from the results listed in Table VIII, the SPE on-line preconcentration method developed in the present study shows that the low-cost FIA-FAAS instrument used for the determination of trace amounts of cobalt in soil and sediment samples provides good analytical data.

CONCLUSION

This study shows that dichloroquinoline-8-ol-embedded polymeric materials, synthesized by the precipitation and bulk polymerization methods, results in quantitative sorption of trace amounts of cobalt,

unlike with the suspension method. However, as described elsewhere (14,15), the polymeric materials obtained by bulk polymerization lead to large and irregularly sized particles which have to be ground and sieved. The grinding and sieving operations performed either manually or mechanically are slow or produce irregular particles with rather limited control over particle size and shape. Hence, the bulk polymerization particles (though adequate for developing new on-line column materials and for use in mechanistic studies) are not suitable for large-scale sample throughput. On the other hand, precipitation polymerization leads to microspheres which can be directly used as on-line column materials. On-line solid phase extraction preconcentration with polymer materials prepared by precipitation polymerization followed by FIA-FAAS analysis allows the determination of cobalt as low as 10 $\mu\text{g L}^{-1}$. The enrichment factors for bulk, precipitation, and suspension polymerization materials, were 12.5, 12.5, and 6.0, respectively. The detection limits corresponding to 3 times the standard deviation of the blank were found to be 10, 10, and 80 $\mu\text{g L}^{-1}$ with a precision of 2.1, 2.5, and 2.6% (RSD) for five successive determinations of 80 $\mu\text{g L}^{-1}$ of cobalt. Furthermore, the retention capacities determined

by the batch method were 11.46, 11.42, and 8.52 mg of Co(II) per g of bulk, precipitation, and suspension polymerization materials, respectively. Thus, enrichment factor, detection limit, and retention capacities are in the order: precipitation ~ bulk > suspension.

The developed on-line FIA-FAAS procedure is simple and rapid (sample throughput = 30 h⁻¹) and allows the reliable analysis of soil and sediment samples for cobalt determination. Furthermore, the developed preconcentrative separation procedure when coupled on-line to the electrothermal AAS, ICP-AES, or ICP-MS techniques can offer better choices for the determination of cobalt in a variety of real samples such as seawater or biological samples.

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Characterization of Tire Bead Wire Coating With Special Emphasis on Tin Estimation Using an Atomic Absorption Spectrometer With a Flow Injection Analysis System (AAS-FIAS)^a

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INTRODUCTION

Bead wires of 0.965 mm and 1.60 mm are widely used in the tire industry. The function of bead wire is to hold the tire to the rim of the vehicle. Bead wire is made up of steel and is normally coated with copper and tin (bronze coating).

The first in-depth study on the effect of coating properties was done by Maeselle and Debruyne (1). In their study, the effect of copper concentration used for brass coating is discussed. They reported that a variation of plating conditions leads to different brass grain size, plating weight, mechanical deformation of the electro-deposit, thermal treatment, and compound composition. The optimum copper content of brass coating at constant plating weight was reported as 60%, 67–70%, or 75% copper, depending on the rubber compound used in adhesion tests.

The bonding mechanism of rubber to steel was extensively studied by W.J. van Ooij (2) and N.L. Hewitt (3). They reported that the adhesion is explained on the basis of an auto-catalytic effect of a thin film of cuprous sulfide formed on the brass surface by the combined action of sulfur and accelerators. The film transfers sulfur atoms to rubber molecules, which results in high rubber surface polarity. This sur-

ABSTRACT

Bead wires used by the tire industry are made up of steel and coated with a low level of copper and tin. The coating over steel is required for good adhesion between the rubber and the bead wire. Conventional flame atomic absorption spectrometer (FAAS) instrumentation cannot determine low levels (1–3%) of tin present in bead wire.

In this paper, an attempt has been made to estimate the tin content and also to characterize quantitatively the coating present in bead wire using a flame atomic absorption spectrometer (FAAS) in combination with a flow injection analysis system (FIAS). Repeatability and reproducibility of the measurements were found to be acceptable for this type of analysis and the results are reported here.

face bonds to brass by physical interaction.

The bead wire used by the tire industry normally contains 97–99 % copper (Cu) and 1–3% tin (Sn). The coating weight is generally found in the range of 0.15–0.65 g/kg. However, the tin content cannot be determined by FAAS since the detection limits for AA measurement in aqueous solution is approximately 10 mg/L (ppm) Sn even when using a high sensitivity nebulizer (4,5). Thus, if a 10-g sample is used for analysis, only µg/L (ppb) Sn will be available in solution.

There are different ways by which tin in µg/L (ppb) levels in solution can be estimated. For example, using an atomic absorption spectrometer with a flow injection analysis system (AAS-FIAS), inductively coupled plasma (ICP), or a graphite furnace atomic absorption spectrometer (GFAAS). Both ICP and GFAAS are used for tin estimation with low detection limits. These instruments are suitable for industries that require metal estimation for both hydride-forming and non-hydride-forming metals. However, these instruments are very costly. However, AAS-FIAS is economical and useful for the determination of metals that can form hydrides, such as Sn, Sb, As, Bi, Hg, Se, and Te.

Copper can be determined by conventional FAAS. In this study, special emphasis is given to tin determination by AAS in combination with FIAS.

EXPERIMENTAL

Instrumentation

A PerkinElmer® Model 3300 atomic absorption spectrometer, equipped with a FIAS™-400 flow injection analysis system, was used in this study (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The instrumental parameters are given in Table I.

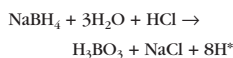
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The pump speed programming for the FIAS-400 is given in Table II. The reagents used are listed in Table III.

Estimation Principle of AAS-FIAS

The AAS-FIAS technique is based on the hydride generation principle (6). The hydride technique involves the reaction of an acidified aqueous sample with a reducing agent such as sodium borohydride. The sodium borohydride/acid reaction generates hydrides as shown in the following equation:



where E = the analysis of interest and m may or may not equal to n.

Calculation

The concentrations of copper and tin are given in Equations A and B (7,8), while Equation C calculates the plating weight.

Equation A:

$$\text{Tin concentration (\%)} = \frac{\text{Sn concentration (mg/L)} \times 100}{\text{Cu conc. (mg/L)} + \text{Sn conc (mg/L)}}$$

Equation B:

$$\text{Copper concentration (\%)} = \frac{\text{Cu concentration (mg/L)} \times 100}{\text{Cu conc. (mg/L)} + \text{Sn conc. (mg/L)}}$$

Equation C:

$$\text{Plating weight (g/kg)} = \frac{(\text{mg/L of Cu} + \text{mg/L of Sn}) \times \text{made up to volume in L}}{\text{Sample weight in grams}}$$

Preparation of Sample Solution

To estimate the tin content (%) in the coating of bead wire, the coating must first be extracted to enable the analysis by FIAS or any other technique (7,8). For this purpose, the bead wire was cut into approximately one-inch lengths and then cleaned with acetone and toluene to remove organic foreign matter from the surface. The wire

TABLE I
AAS-FIAS Instrumental Parameters

Parameters	Copper	Tin
Wavelength	324.8 nm	286.3 nm
Slit Width	0.7 nm	0.7 nm
Technique	Background-corrected atomic absorption using impact bead	Atomic absorption
Data Processing	Time average	Peak height with 37-point smoothing
Cell Temperature	-	900°C
Read Time	5 sec	15 sec
Flame Type	C ₂ H ₂ : Air	-

TABLE II
Pump Speed Programming for FIAS

Step	Time (s)	Pump 1 Speed	Pump 2 Speed	Valve
Prefill	15	100	120	Fill
1	10	100	120	Fill
2	15	0	120	Inject

TABLE III
Reagents Used

Reagent	Source
Suprapur® Hydrochloric Acid	Merck Ltd., Mumbai, India
Nitric Acid	Merck Ltd., Mumbai, India
Boric Acid	Merck Ltd., Mumbai, India
Sodium Borohydride	Sd Fine Chemicals, Mumbai, India
Sodium Hydroxide	Merck Ltd., Mumbai, India

was kept at 105°C for 30 min and then cooled in a desiccator. About 10 g of the sample was stripped with 10 mL conc. HNO₃. The solution was transferred to a 100-mL standard flask with double-distilled water. Concentrated HNO₃ was used to make iron passive as well to remove the coating. The sample solution was diluted to a 50-100 dilution factor (DF) and made up to 100-mL volume with a carrier solution, so that the matrix effect is nullified and at the same time the sensitivity is improved.

Preparation of Standard Solution

The standard solution was diluted to a measurable range with the carrier solution, using a dilution factor of 10. Therefore, the matrixes of the sample as well as the standard are the same.

Preparation of Carrier Solution and Reducing Agent

Preparation of the carrier and reducing solutions is very important. If these are not prepared properly, the signal may not be good or even be absent. Exactly 0.4% NaBH₄ in 0.05% NaOH was used as the reducing agent. Sodium hydroxide

was used for enhancing the stability of sodium borohydride. Saturated boric acid with 1% (v/v) HCl was used as the carrier solution. High purity chemicals were used throughout. All solutions were filtered to remove any suspended particle that might cause blockage in the FIAS. Gas bubbles formed in the reducing solution are disturbing as they may affect repeatability. Therefore, a freshly prepared reducing solution was used, which was stirred continuously with a magnetic stirrer. In case of tin estimation, the sensitivity can be improved by using argon carrier gas with 1% oxygen.

Carrier Gas Flow

Argon gas was used as the carrier gas, which carries hydrides from the mixing chamber to the quartz tube. The argon flow rate highly influences sensitivity. If the flow is too high, the metal atom or hydride cloud is dispersed too rapidly. If the flow is too low, the concentration of hydrides in the quartz tube is poor. To obtain the highest sensitivity, optimization of the flow rate is required. A 100 ± 10 mL/min flow rate was selected for our experiments.

Setting up of FIAS Instrument for Sn Determination

A tin hollow cathode lamp was used as the radiation source, installed into the spectrometer and aligned (6). The quartz cell was also aligned to get maximum energy to the spectrometer. The carrier and reductant fluid flow was adjusted so that the ratio of the carrier-to-reductant flow was about 2:1, with a carrier flow between 9 mL/min and 11 mL/min. The carrier gas flow was optimized. If a peak appeared too quickly, the carrier gas flow was slightly increased. If the peak maximum appeared too late, the carrier gas flow was slightly decreased. To condition the quartz cell, the cell was placed in a bath of concentrated hydrofluoric acid (40%) for 20 minutes. The cell was then thoroughly rinsed under running water, further rinsed with double-distilled water, and subsequently dried (9). After system optimization, the blank and standard were run and the signal was measured according to its peak height. Figure 1 shows how peak height varied with Sn concentration. The calibration graph obtained after the analysis is shown in Figure 2. The sample was subsequently analyzed.

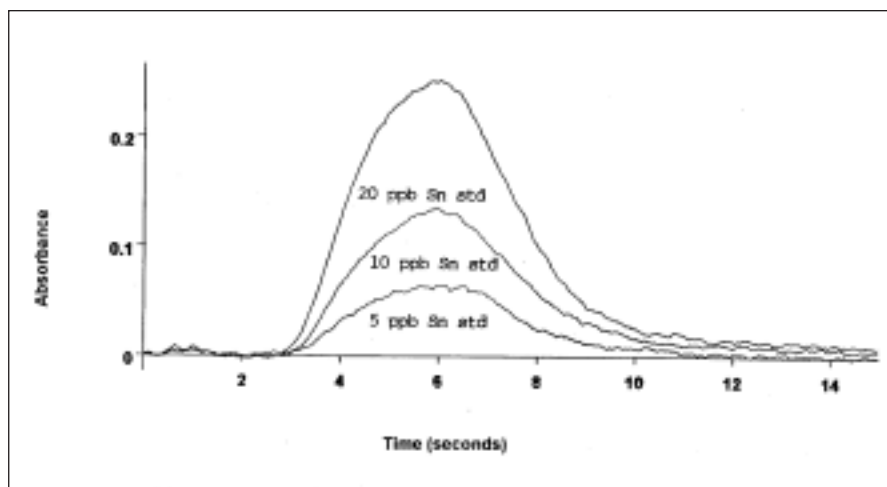


Fig. 1. Variation of peak height with concentration.

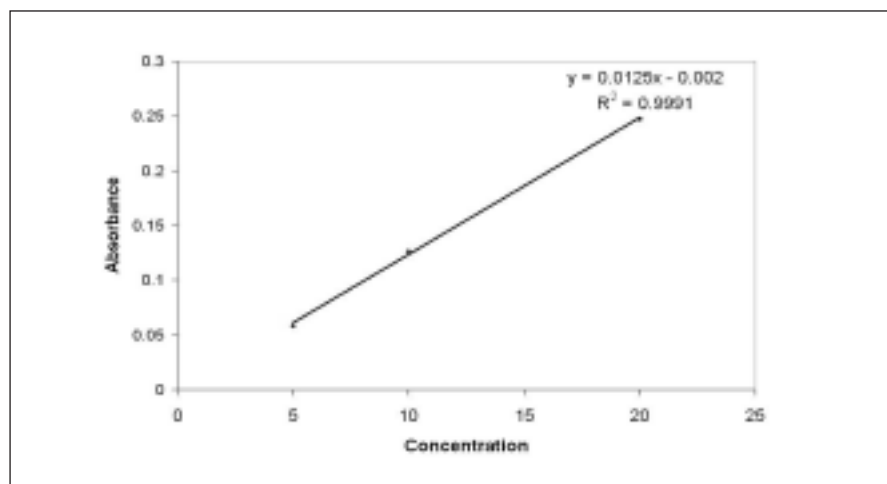


Fig. 2. Variation of absorbance with concentration.

RESULTS AND DISCUSSION

Repeatability of the method was carried out by analyzing five specimens of the same sample. To validate the technique, reproducibility was checked by analyzing two different samples after a one-week interval. All standards and samples were prepared fresh for each analysis. The short-term repeatability results of 25 replicates of tin and copper measurements are shown in Figures 3 and 4, respectively.

The repeatability of bead wire characterization is shown in Table IV. The results of the reproducibility study is shown in Table V.

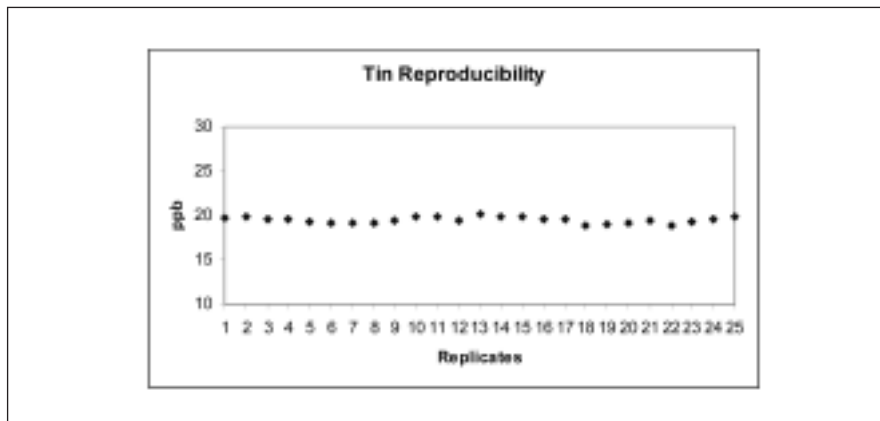


Fig. 3. Short-term repeatability of tin measurements.

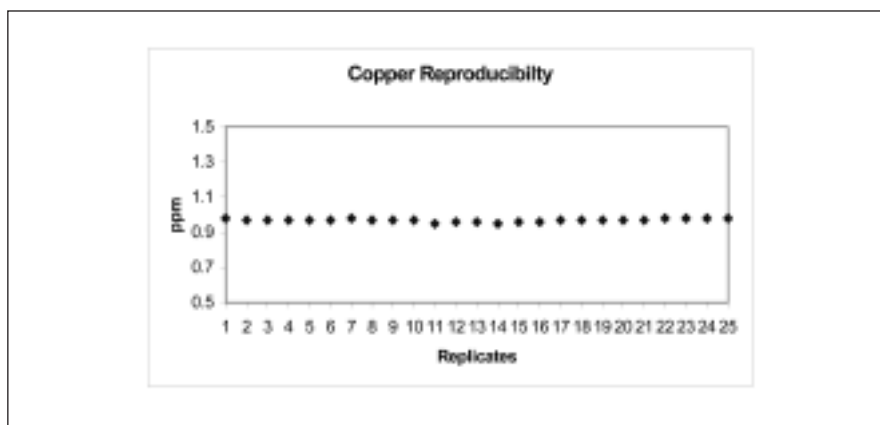


Fig. 4. Short-term repeatability of copper measurements.

TABLE IV. Repeatability of Tin Estimation

Replicates	Sample Weight(g)	Tin (%)	Copper (%)	Plating Weight (g/kg)
1	10.1353	1.0	99.0	0.49
2	10.0321	1.0	99.0	0.48
3	10.1531	1.1	98.9	0.48
4	10.0262	1.2	98.8	0.48
5	10.2074	1.1	98.9	0.49
Average		1.1	98.9	0.48
Standard deviation		0.07	0.07	0.003

TABLE V. Reproducibility

Sample ID	Parameters	Day 1	Day 2
Sample 1	Sn (%)	1.8	2.0
	Cu (%)	98.2	98.0
	Plating Weight (g/kg)	0.48	0.48
Sample 2	Sn (%)	1.2	1.5
	Cu (%)	98.8	98.5
	Plating Weight (g/kg)	0.48	0.48

CONCLUSION

In this study, tire bead wire coating including the estimation of tin content was quantitatively characterized using an atomic absorption spectrometer in combination with a flow injection analysis system (AAS-FIAS). The repeatability and reproducibility values of both copper and tin estimation were found to be acceptable and the method described appropriate for regular analytical laboratory use.

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Concentrations of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, and Zn in Uruguayan Rice Determined by Atomic Absorption Spectrometry

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ABSTRACT

The United Nations General Assembly declared the year 2004 the International Year of Rice and the concept "Rice is Life". The largest nutritional problems occurring globally are protein-energy malnutrition, and Ca, Fe, I, Zn, and vitamin A deficiency.

In this report, 49 rice samples (*Oryza sativa L.*) were digested by dry ashing in order to determine As, Cd, Cr, and Pb by ETA-AAS; while Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn were determined by FAAS; and Hg by CV-AAS using microwave-assisted decomposition. The following concentration ranges were obtained for Ca (9.1–15 mg/100 g), Cd (2.30–4.12 µg/kg), Co (41–60 µg/kg), Cu (1.33–180 mg/kg), Fe (4.41–7.15 mg/kg), K (167–217 mg/100 g), Mg (45–121 mg/100 g),

Mo (0.52–0.97 mg/kg), Mn (5.45–25.4 mg/kg), Na (0.95–2.50 mg/100g), Ni (0.53–0.72 mg/kg), and Zn (5.86–12.6 mg/kg).

Mean recoveries of elements from fortified rice were: 87±12% for As, 95.3±8.9% for Ca, 106.2±7.7% for Cd, 103.3±6.5% for Co, 89.4±8.1% for Cr, 99.3±4.6% for Cu, 103±10% for Fe, 96.3±9.3% for Hg, 95.4±12% for K, 98.3±8.0% for Mg, 93.4±7.8% for Mo, 95.3±9.9% for Mn, 89±12% for Na, 90.3±9.7% for Ni, 91.2±5.5% for Pb and 92.0±9.4% for Zn. The concentrations of the minerals and microelements studied fall within the typical range of rice grown around the world. Potassium was the most abundant mineral, followed by Mg and Ca; among microelements, the concentrations of Cu, Fe, Mo, Mn, Na, and Zn in rice were outstanding.

It was also found that the milling process highly affects the K, Mg, Mn, Na, and Zn concentrations, while it has little influence on Ca, Co, Cu, and Fe. On the other hand, there is a loss of Ca, Fe, and Mn during the parboiling process.

Recent studies have shown the potential to exploit the genetic variation of rice seeds with regard to the concentration of some minerals (Ca, Fe, Zn, etc.) without affecting yield or adding new traits.

All rice samples tested showed lower levels of As, Cd, Hg, and Pb in comparison to the maximum limit permitted by government organizations. Thus, the consumption of Uruguayan rice presents no health threat regarding the concentration of toxic elements such as As, Cd, Cr, Hg, and Pb.

INTRODUCTION

On December 16, 2002, the United Nations General Assembly (UNGA) declared the year 2004 the International Year of Rice (IYR) and the concept "Rice is Life". In declaring IYR, UNGA recognized that rice is the primary food source for more than half of the world's population, and that enhancing the sustainability and productivity of rice-based production systems will require the commitment of many parts of society as well as government and inter-governmental action (1).

Rice (*Oryza sativa L.*) is considered the main staple food for several

countries (Myanmar, Lao People's Democratic Republic, Vietnam, Cambodia, Bangladesh, Indonesia, Thailand, Philippines, Nepal, P.R. China) and is a major source of nutrients. In developing countries, rice accounts for 715 kcal/capita/day; 27% of dietary energy supply, 20% of dietary protein, and 3% of dietary fat. However, while rice provides a substantial amount of dietary energy, it has an incomplete amino acid profile and contains limited amounts of essential micronutrients. Today, more than 2,000 million people suffer from micronutrient malnutrition (Ca, Fe, I, Zn, and vitamin A deficiency). Malnutrition reduces the productivity of adults, reduces children's mental and physical development, and leads to premature death, particularly for

women and children. If food systems do not provide sufficient quantities and enough diversity of food on a continuous basis, malnutrition will ensue particularly for the poor, and their health and welfare will deteriorate. Nutritional considerations, therefore, were essential to the International Year of Rice and the concept that Rice is Life (2–5).

Currently, studies are also focused on the improvement of the nutritional quality by genetic manipulation and the fortification of rice.

Since rice is a staple food consumed worldwide, its nutritional vs. toxic composition is of special interest.

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Uruguay has emerged as a medium-size rice producer and is Latin America's major rice exporter, now listed as one of the world's top ten. Although it is a great producer of rice, dietary intake surveys in Uruguay list a consumption of 10 kg per capita/year, lower than the consumption in Asia (81 kg/year), but higher than that in Europe (3 kg/year), and far below Brazil which is the major consumer in the region with a consumption per capita of 39 kg/year (6,7).

Genetic factors, soil and weather conditions, and the use of fertilizers affect the final level of mineral and contaminant components in rice. The human food chain is linked through vegetable, fruit, and tuber consumption to the nature of the soil which supplies, for example, the mineral ions. These are in turn derived from the parent rock and from decaying plant and animal residues.

On the other hand, many industrialized processes give rise to environmental problems with increased levels of contamination from elements such as As, Cr, Hg, and Pb which can have profoundly deleterious effects on health. The joint FAO/WHO (Food and Agriculture Organization/World Health Organization) requires detailed information on the concentration levels of elements in agricultural crops to assess the toxicological and nutritional significance of human and animal intake of these elements. The normal "background" concentrations of toxic elements, such as Pb, Cd, Cr, and As, must be known to develop limitations on the intake of these elements from foods. Information on background levels provides guidance in evaluating the effect of soil additives, such as phosphatic fertilizers and sewage sludge (containing Pb, Cd, Cr, and As), as well as the effect of commercial food handling and processing steps which can result in

food contamination. Intake of relatively low doses of these elements over a long period can lead to malfunction of organs and chronic toxicity. Determination of base-line levels of Cd, Pb, Hg, and As in agricultural and horticultural crops is necessary to evaluate their toxicological significance and to establish action levels (8). These potentially toxic metals can be present in the environment from both natural and anthropogenic sources and enter the human body via the two main routes of ingestion and inhalation. The latter pathway is of minor importance except for industrial workers and people living close to emission sources. For the general population, ingestion is the major route of intake with food being the main contributor (9,10).

Cadmium

In the case of Cd, food serves as the major source for the general population. Concentrations of Cd in foods depend on soil contamination and the rate of uptake by plants from the soil. It is well known that among the cereal crops, Cd uptake from soil by rice is high and, therefore, rice is a major source of cadmium toxicity in rice-consuming countries. Approximately 40–60% of Cd intake in Japan comes from rice alone. Thus, rice serves as an index for environmental monitoring of Cd in rice-eating countries. However, the dietary intake of Cd from rice depends on the consumption level which varies for different occupational groups (11).

Chromium

Chromium is an essential element for the carbohydrate, cholesterol, and protein metabolism, while Cr toxicity depends on the metal's chemical form. Cr(VI) compounds show a toxic, mutagenic, and even carcinogenic character. Cr(III), which is the most frequently found form in foods and beverages, has low toxicity. Although humans can absorb Cr

by inhalation or dermal contact, Cr intake through diet is the primary route of entry into humans (12).

Arsenic

Arsenic toxicity also depends on the chemical form of the element, with As(III) being the most potent, followed by As(V), then monomethylarsenate, and finally dimethylarsenate. When ingested, inorganic arsenic may cause acute or chronic toxicity. Epidemiological evidence supports the conclusion that As is a human carcinogen associated mainly with lung, skin, and bladder cancer. These facts show the need for determining As concentrations in food (13).

Lead

Lead is a non-essential element that is toxic to biota at elevated concentrations. In nature, Pb commonly occurs in its monovalent (Pb^{+1}), divalent (Pb^{+2}), and tetravalent (Pb^{+4}) states, with divalent Pb being the most common. Lead can also form organometallic compounds, such as tetraethyllead, which was the largest single source of Pb contamination into the atmosphere in Uruguay prior to January 2004, when it was used as an antiknock additive in gasoline. Studies have shown the carcinogenicity of Pb in the gastrointestinal tract, respiratory system, and kidneys (13).

Mercury

Mercury occurs in different forms such as mercury 0 (liquid and vapor), inorganic mercury (I) and (II), alkylmercury, and phenylmercury. The antimicrobial actions of Hg have also been known for some time. Organomercurials, particularly the alkyl- and arylmercury compounds, are more active as bactericides or fungicides than the inorganic salts. The poisonous properties of Hg have been known throughout recorded history and are reported in ancient oriental and Roman literature (13).

Although the toxic effects of all of these elements have been known for a long time, studies are still ongoing to gain a better understanding of their effects within the biosystems.

Atomic Absorption Techniques for Metals Determination in Rice

For the determination of metal ions in rice, atomic absorption spectrometry (AAS) is the technique most widely used because of its versatility, precision, and accuracy. AAS determinations are usually made by flame atomic absorption spectrometry (FAAS) when metal concentrations are high enough (Cu, Zn, Fe, Ca, Mg, K, Na, Mn, Mo, Ni, and Co). For elements with low limits of detection (As, Cd, Cr, and Pb), the more sensitive electrothermal atomization atomic absorption spectrometry (ETA-AAS) technique is used, while cold vapor AAS (CV-AAS) is used for Hg determinations..

Sample Digestion

Prior to analysis, rice samples need to be brought into solution. The two most widely used techniques are based on dry ashing or wet digestion. Both techniques have advantages as well as limitations. The choice of technique should be based on the needs of the specific user. Dry ashing is cheap and provides good detection limits, but is time-consuming (strict temperature control should be observed to avoid metal losses) and sensitive to contamination.

Wet digestion is quick, requires little attendance, and is normally not as sensitive to contamination as dry ashing, but is labor-intensive and usually results in rather dilute solutions.

Since the introduction of microwave energy for wet digestion in 1975, microwave-assisted decomposition has been widely employed and numerous applications have been described both for open-vessel and closed-vessel digestions. Closed-vessel digestion has several advantages over open-vessel digestion: smaller quantities of reagent (no evaporation), less contamination, and a higher reaction rate. The most commonly used acid digestion of biological materials is nitric acid, but various different acid mixtures have also been used (14,15).

The aim of this study was the analysis for the first time in

Uruguay of four different forms of Uruguayan rice (brown, parboiled brown, milled, and parboiled milled) for the determination of As, Cd, Cr, and Pb by ETA-AAS in samples digested by dry ashing. However, microwave-assisted decomposition of the samples was used for the determination of Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn by FAAS, and Hg by CV-AAS.

EXPERIMENTAL

Instrumentation

A Perkin-Elmer® Model 5000 atomic absorption spectrometer was used, equipped with an HGA®-500 graphite furnace, MHS-10 hydride generation system, and deuterium background correction (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The graphite furnace and flame settings are listed in Tables I and II, respectively.

TABLE I
Instrumental Conditions and Furnace Program
for the Determination of As, Cd, Cr, and Pb

	As	Cd	Cr	Pb
Wavelength (nm)	193.7	228.8	357.9	283.3
Spectral Bandwidth (nm)	0.7	0.7	0.7	0.7
Drying (°C)	110	110	110	110
Ashing (°C)	900	250	1200	450
Atomization (°C)	2700	2100	2700	2300
Cleaning (°C)	2700	2700	2700	2700
Sample Injection (µL)	50	10	50	50
Background Correction	D ₂ Lamp	D ₂ Lamp	D ₂ Lamp	D ₂ Lamp
Measurement Mode	Peak Area/ Height	Peak Area/ Height	Peak Area/ Height	Peak Area/ Height

TABLE II. Instrumental Parameters for Flame AAS Determination

	Ca ^a	Co	Cu	Fe	Kb	Mg ^a	Mo	Mn	Na ^b	Ni	Zn
λ (nm)	422.7	240.7	324.8	248.3	769.9	285.2	313.3	279.5	589.0	231.1	213.9
H Slit (nm)	0.7	0.7	0.7	0.2	1.4	0.7	0.7	0.7	0.7	0.2	0.7
Flame Type	AAOF	AAOF	AAOF	AAOF	AAOF	AAOF	NOARF	AAOF	AAOF	AAOF	AAOF
Range (mg/L)	0.2-5.0	0.02-1.0	0.003-1.0	0.1-5.0	2.0-30	0.2-4.0	0.2-5.0	0.01-1.0	1.0-8.0	0.1-2.0	0.004-1.0
BG		D ₂ Lamp		D ₂ Lamp						D ₂ Lamp	D ₂ Lamp

AAOF=Air-acetylene oxidizing flame, NOARF=Nitrous oxide-acetylene reducing flame, BG= Background correction.

^a 0.1% La₂O₃ was used to control the depression of the signal caused by some elements.^b 0.1% CsCl was used as ionization buffer.

Rice Samples

Forty-nine commercial samples of long grain rice (*Oryza Sativa L.*), cultivated in Uruguay, were selected for this study. The samples were in the form of brown, milled, parboiled milled, and parboiled brown rice.

Prior to analysis, approximately 500 g of sample was ground in an analytical mill (Analytical Mill A10, Kinematica GAC, Luzern, Switzerland) and passed through a 1-mm sieve.

Reagents and Standard Solutions

All chemicals used in the sample preparation and analysis were of analytical grade or better.

Standard stock solutions of 1000 µg/mL were prepared for As, Ca, Cd, Co, Cr, Cu, Fe, K, Hg, Mg, Mo, Mn, Na, Ni, Pb, and Zn (Fluka Chemie GmbH, Germany, and AccuStandard Inc., New Haven, CT, USA), certified by the manufacturer to ± 1% (w/v) and traceable to NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA).

All solutions were prepared with ultrapure water with a specific resistivity of 18 MΩ·cm obtained by filtering distilled water through a Milli-Q™ Plus purifier system immediately before use (Millipore Corporation, Bedford, MA, USA).

Procedure of Sample Decomposition

Dry ashing of the rice samples for the determination of As, Cd, Cr, and Pb by ETA-AAS was performed in a multiplace mineralization block. The sample (~5 g) was weighed into a beaker resistant to high temperatures and, while continuously shaking the suspension, 5 mL ashing aid solution [10% w/v Mg(NO₃)₂ in ethanol] was added. Next, the following temperature program was used: heating at

125°C until nearly dry, then heating from 125–450°C for 2 hours, and holding at 450°C for 12–14 hours. If white ashes are not obtained after this temperature cycle, 1 mL HNO₃ should be added dropwise (brown fumes should be seen) and then 1 mL 30% H₂O₂ added; afterwards, repeat the heating cycle until white ashes are observed.

Once white ashes occur from the digestion cycle, 10 mL HNO₃ (10%) was added and the solution obtained was homogenized in an ultrasonic bath and then centrifuged.

Duplicate blanks were prepared by adding 5 mL ashing aid solution for the digestion procedure.

Microwave oven digestion was performed in order to determine Ca, Co, Cu, Fe, K, Hg, Mg, Mo, Mn, Na, Ni, and Zn by FAAS. Samples of 0.50 g were digested in Tetrafluoromethaxil (TFM) Teflon™ vessels with 5 mL HNO₃ using a Milestone MLS 1200 MEGA microwave oven (Milestone, Italy) and following the heating program listed in Table III.

For the determination of mercury by CV-AAS, analyte additions were performed before digestion and the microwave oven digestion as described above was followed.

TABLE III
Heating Program^a Used for the Determination of Ca, Co, Cu, Fe, Hg, K, Mg, Mo, Mn, Na, Ni, and Zn

Step	Power (W)	Time (min)
1	250	1
2	0	5
3	250	5
4	400	5
5	650	5

^a Caution: Digestion vessels must be cooled for an appropriate time before opening in order to avoid burns from hot and corrosive vapors and to eliminate sample loss.

Calibration and Accuracy Studies

Direct calibration against acidified standard solutions was carried out for Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn and by the standard additions technique for As, Cd, Cr, Hg, and Pb.

To ensure a high level of analytical reliability, recovery studies were included for each batch to estimate analytical accuracy. The rice samples were spiked with two different concentrations of a certified solution (Trace Metal Standard I and III, J.T. Baker Inc., Philipsburg, PA, USA) and then submitted to the digestion procedure. Each batch also contained a certified reference material (NIST CRM 1568a Rice Flour).

The limits of detection (LOD) obtained in this study are listed in Table III. These values were calculated on the basis of the concentration giving a reading equivalent to twice the standard deviation of the blanks.

The recommendations listed in the EURACHEM/CITAC guide (EuroAnalytical Chemistry/Co-Operation on International Traceability in Analytical Chemistry) were followed to identify and estimate the individual contributions to the total uncertainty of the method employed (16).

RESULTS AND DISCUSSION

The metal ion composition of brown, milled, parboiled milled, and parboiled brown rice is listed in Table IV and was calculated on the wet basis to allow a comparison with the literature data of the product when purchased.

The concentrations of all the elements studied (As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mo, Mn, Na, Ni, Pb, and Zn) in this survey fall within the typical range (as can be seen in Table IV) of rice from around the world (7,11,17–20).

Toxic Elements

All rice samples tested showed lower cadmium and lead concentrations than the maximum limit permitted by the Codex Alimentarius (0.1 mg/kg and 0.2 mg/kg, respectively) (21,22). Uruguayan legislation (23) regulates the levels of As and Hg in foodstuffs (2.0 mg/kg and 0.05 mg/kg, respectively). As can be observed in Table IV, As and Hg concentrations found in this work are far below the maximum concentrations allowed by this regulation. These low levels confirm that the rice growing areas as well as the groundwater employed for irrigation are situated in non-contaminated sites. It is well known that in some countries, i.e., Bangladesh, irrigation of the paddy fields with arsenic-contaminated groundwater has led to arsenic buildup in paddy soil, with subsequent elevations in

rice grain arsenic. P.N. Williams et al. (24) have recently reported high levels of As (up to 0.46 mg/kg) in rice from the United States. These high levels are attributed to the use of As herbicides in cotton fields in the early to mid-20th century and currently some of these areas are used for rice production.

Although the Cr content in rice is not yet regulated in Uruguay, it is important to know the Cr levels in foodstuff because of the element's toxicity. The presence of this metal can be attributed to the use of stainless steel equipment or contamination during processing.

The results of our study verify that the levels of As, Cd, Cr, Hg, and Pb concentrations found in commercially available rice are below the legislated limits. These low levels confirm the good agricul-

tural practices employed in the production of rice in Uruguay.

It has been demonstrated that under fasting conditions the gastrointestinal absorption of toxic metals can be significantly increased (13). For instance, Pb absorption in the human adult is in the order of about 10-15% (up to 50% for children) and under fasting circumstances it increases up to 45%. Studies have also shown that certain dietary factors such as milk fasting result in low calcium and vitamin D intake, causing iron deficiency and may enhance lead absorption from the gut (13). Since rice is considered a main staple food and a major source of nutrient for the poor who lack access to diverse foods, strict control should be enforced on the maximum level of toxic metals allowed in this important crop.

TABLE IV
Metal Content in Different Forms of Rice Produced in Uruguay

	Units	Brown	Milled	Parboiled Brown	Parboiled Brown	LOD	Typical Range	CRM (%)	Recovery (%)
As	µg/kg	< LOD	< LOD	< LOD	< LOD	50	0.01-0.61		87±12
Ca	mg/100 g	9.1±1.4	15±1.8	10±1.3	10±1.2	0.010	9-50	99±10	95.3±8.9
Cd	µg/kg	3.43±0.68	4.12±0.72	2.30±0.69	3.75±0.66	1.0	<1-230		106.2±7.7
Co	µg/kg	57±11	41±15	59.6±8.4	50±10	20	10-100		103.3±6.5
Cr	µg/kg	< LOD	< LOD	< LOD	< LOD	5.0	<1-100		89.4±8.1
Cu	mg/kg	1.80±0.16	1.52±0.16	1.45±0.15	1.33±0.16	0.010	1-6	95.2±8.4	99.3±4.6
Fe	mg/kg	7.14±0.64	7.15±0.66	5.90±0.71	4.41±0.77	0.050	2-50	89±11	103±10
Hg	µg/kg	< LOD	< LOD	< LOD	< LOD	1.0	<0.1-29		96.3±9.3
K	mg/100 g	217.3±4.9	167±5.6	210.6±3.7	167.2±5.8	0.10	60-280	99.4±8.4	95.4±5.7
Mg	mg/100 g	121±11	46.4±5.5	116±13	45.4±5.9	0.050	20-150	91.3±7.7	98.3±8.0
Mo	mg/kg	0.82±0.21	0.97±0.19		0.52±0.16	0.10	0.18-3.0		93.4±7.8
Mn	mg/kg	25.4±2.8	6.55±0.85	6.28±0.88	5.45±0.79	0.010	2-36	91±11	95.3±9.9
Na	mg/100 g	2.23±0.21	1.20±0.11	0.95±0.11	2.50±0.21	0.40	1.7-34	96.7±7.8	89±12
Ni	mg/kg	0.62±0.15	0.72±0.13	0.53±0.10	0.613±0.097	0.020	< 0.2-1.2		90.3±9.7
Pb	µg/kg	<LOD	< LOD	< LOD	< LOD	5.0	2-70		91.2±5.5
Zn	mg/kg	12.6±1.0	6.10±0.73	11.6±1.2	5.86±0.75	0.010	6-28	102.8±4.4	92.0±9.4

Minerals and Microelements

In addition to determining toxic elements in rice, the level of minerals and microelements was also studied. As listed in Table IV, potassium was the most abundant mineral (217, 211, 167, and 167 mg/kg for brown, parboiled brown, milled and parboiled milled rice) found in rice, followed by Mg and Ca. Among microelements, the presence of Cu, Fe, Mo, Mn, Na, and Zn in rice was outstanding (for milled rice, the values found were 1.5 mg/kg Cu, 7.25 mg/kg Fe, 0.97 mg/kg Mo, 6.55 mg/kg Mn, 1.2 mg/100 g Na, and 6.1 mg/kg Zn).

The concentration of most elements presented in Table IV were similar in brown and parboiled brown rice, except for Mn which was higher in brown rice (25.4 and 6.28 mg/kg, respectively).

It is generally accepted that as greater amounts of rice bran are removed from the grain during milling and polishing, more vitamins and minerals are lost. For all the samples analyzed in this work, milled rice shows a significantly lower content of K, Mg, Mn, Na, and Zn than brown rice. But the milling process seems to have little influence on the Ca, Co, Cu, Fe, and Ni levels. Similar results were reported in rice cultivated in Brazil (7).

The distribution pattern of metal ions in the rice grain is not yet clearly known. Some authors (4,7,26-27) point out that microelements (Cu, Fe, Mn, and Zn) are likely to be uniformly distributed in the grain and macroelements (P, K, Ca, and Mg) seem to be present chiefly in the external layers of the grain (aleurone, pericarp). Research has shown that element concentrations are highly affected by the milling process (25), while others have found a strong interaction between, for instance, iron content and milling, which suggests that

much of the iron concentration is in the outer layers (aleurone and pericarp) of rice (25).

The effects of rice grain processing with regard to the mineral levels in the edible product (i.e., milled and parboiled rice grain) are still being evaluated. On the other hand, the parboiling process seems to have little effect on the mineral content in rice (except for Ca, Fe, and Mn) as can be seen in Table IV. The high loss of these minerals was not expected. It is assumed that the minerals spread to the external layers of the grain when soaked and steamed and are subsequently removed by milling. R.J.B. Heinemann et al. (7) also observed significant losses of Ca and Mn in the parboiled milled rice cultivated in the south of Brazil.

It has been reported that parboiled rice is of superior nutritional value in comparison to milled rice, mainly due to the retention of minerals and water-soluble vitamins (26). The higher retention of micronutrients in parboiled rice has been assigned to their solubilization and migration to the center of the grain and their setting during the starch gelatinization process (26).

Nevertheless, the significance of the nutritional benefits of parboiled rice is still arguable, mostly due to the lack of uniform commercial processes applied in different countries. It is believed that the retention pattern of some minerals is the result of the interaction of different factors such as mineral location in the grain and their solubility during soaking, different ratios of migration, as well as variations in the hydrothermal process and milling resistance of the parboiled grain. Further studies need to be carried out to achieve a more complete understanding of mineral retention.

Staples are generally not considered an important source of minerals in the diet. However, because

rice is an important staple food, any increase in mineral concentration might well have a significant effect on human nutrition and health.

Genetic Alteration of Rice

Currently, several research institutions are working toward improving the nutrient content through greater utilization of rice genetic resources. Since 1995, researchers at the International Research Rice Institute (IRRI), Manila, Philippines, have been evaluating the genetic variability of Fe and Zn concentration in rice. Screening tests run to identify germplasm with high iron and zinc found a statistically significant correlation with phytate as the iron and zinc concentrations increased, so did phytate. But the nutritional implications with regard to the bioavailability of the increased Fe and Zn content counterbalanced with increased phytate are still under investigation (5,27).

Scientific programs are also focused on increasing the iron content of the grain and the element's bioavailability once ingested. A two-fold increase was achieved by transferring the coding sequence of ferritin from a bean (*Phaseolus vulgaris*) into rice endosperm (28). At the same time, to increase the bioavailability of iron, β -carotene was inserted, and the phytate gene from *Aspergillus fumigatus* was inserted to break down phytic acid which binds iron (5).

Yet, the controversy and questions remain concerning the advances in biotechnology. Specifically, there is uncertainty regarding the degree to which micronutrient levels can be increased, as well as the effect of this increase on yield, disease resistance, and palatability. The opportunities created through genetic alteration of the rice genome also create new imperatives for biosafety.

Enrichment and Fortification of Rice

As we mentioned previously, the complete milling and polishing that converts brown rice to white rice reduces the amount of vitamins and minerals in the final product. Studies have shown that rice enrichment and fortification techniques restore the levels of vitamins and minerals in milled rice at first removed from the grain during the milling process (7). Enriched rice is coated in a protective material which helps to prevent nutrient loss due to washing. The success of various fortification strategies, particularly those involving fortification with iron, is mixed. The fortification of foods with iron remains technically complex. Those iron compounds with the greatest bioavailability (ferrous sulphate and ferrous fumarate) significantly alter the palatability of food, whereas large declines in the uptake of iron are seen when a more palatable iron compound (elemental iron or ferric orthophosphate) is used (28).

Fortified rice holds great potential in reducing micronutrient deficiencies. Its success, however, will depend on making the enriched rice available, affordable, and palatable for the consumer (29).

CONCLUSION

Since rice is a staple food consumed worldwide, its nutritional vs. toxic composition is of special interest. Hence, the knowledge of the metal ion concentrations in rice is crucial to determine the amount of toxic elements and nutrients consumed with rice. It also helps to build up nutrition tables widely used to calculate food nutrient intake.

The report of the 16 elements (As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mo, Mn, Na, Ni, Pb and Zn) in Uruguayan rice here presented has no precedent in the country. Since Uruguay is one of the world's top ten rice producers, the awareness of toxic elements (As, Cd, Cr, Hg, and Pb) and mineral and microelements is vital for the trade market. This type of survey is very important since the determination of elements in rice may help prestigious rice producers from counterfeit rice and permit source confirmation for government certification.

The methodology employed for the determination of As, Cd, Cr, and Pb by ETA-AAS, and Ca, Co, Cu, Fe, K, Mg, Mo, Mn, Na, Ni, and Zn by FAAS, and Hg by CVAAS was appropriate and the results obtained were in general as expected.

The data generated show that the concentrations of the toxic elements As, Cd, Pb, and Hg in the rice samples tested are significantly lower than the maximum tolerance limits established by international organizations. These low levels confirm the good production practices employed in Uruguay and shows that the consumption of this rice presents no health threat.

In addition, the concentrations of all the elements determined in this survey fall within the range typical of rice grown around the world.

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Flame AAS Determination of Total Lead in Soil Sediments Near Highways in Maracaibo City, Venezuela

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INTRODUCTION

During the last decades, anthropogenic activities have increased the dispersion and accumulation of highly toxic compounds into the environment (1-4). Institutions and governmental agencies that investigate, legislate, and control environmental problems around the world have demonstrated that this type of contamination affects human health, particularly with regard to degenerative illnesses (3,5). Different international studies are available which have indexed the cases involving metals such as mercury, arsenic, cadmium, lead, aluminum, chromium, vanadium, and nickel (3,5,6).

Greater than 90% of the lead (Pb) contamination in Venezuelan cities is due to the combustion of gasoline with high concentrations of lead antiknock (tetraethyl lead) used in automobiles [>300 mg/L Pb (7)]. The high automobile density ($>10,000$ cars/day) in Maracaibo City, Venezuela, is responsible for the high levels of environmental Pb (up to 3000 mg/Kg Pb) (8). For this reason, the populations in our cities are exposed to the toxic actions of Pb by ingestion of polluted foods or by inhalation of lead compounds.

The economical growth of the Zulia State in particular is sustained by industries such as petrol companies, petrochemistry, polymers, and metal mechanics, which use a great

ABSTRACT

An FAAS-based method previously analytically developed for the total determination of Pb was employed to establish the Pb levels in 76 urban sediment samples collected near four highways in Maracaibo City, Venezuela. The proposed method is simple, uses controlled heating at 60-70°C, atmospheric pressure, and diluted acid media during treatment of the solid samples. These facts avoided the loss of Pb by volatility, which generally is responsible for experimental errors in the estimation of the real concentration of this analyte.

Accuracy of the FAAS method was evaluated by analyzing three certified materials, obtaining a mean relative error of 1.08% between the certified and experimental values. The average precision expressed as RSD was 1.93%. The detection limit (3σ) and characteristic concentration were 0.25 and 0.43 mg/L Pb, respectively.

The Pb mean concentrations ($\pm 1SD$, mg/kg) of the different sampling points were: A-5: 3,385 \pm 2,503; A-L: 3,554 \pm 1,712; C-1: 2,252 \pm 2,224; and C-2: 2,457 \pm 1,666. These concentrations were approximately 300% higher than the values found in a study carried out between 1984 and 1985. High concentrations of Pb found in Maracaibo City are related to the high automobile traffic, which consumes exorbitant volumes of leaded gasoline.

The developed analytical method for the FAAS-determination of Pb in urban sediment samples was accurate, precise, and free of interferences, constituting an analytical tool for the evaluation of this toxic element in environmental samples.

variety of metals and chemical compounds for obtaining their products. Most of these compounds can be toxic when they exceed the safe threshold values for the environment and the human organism (7-9). Over the last 50 years, Maracaibo City has experienced drastic urban growth, changing from a small city of 250,000 inhabitants to a metropolis of more than 2,000,000 (8). The subsequent urban activities resulted in an increase in automobile traffic and, consequently, a high consumption of leaded gasoline. Nowadays, high levels of lead are found in the urban sediment of the main avenues and streets of this city (≥ 3000 mg/Kg Pb) (7,8).

In early 1999, the Venezuelan government implemented the sale of unleaded gasoline in order to reduce the high Pb contamination of the country's main urban areas. However, due to the fall of purchasing power of the Venezuelan population, use of cheaper leaded gasoline persists (8).

It is important to point out that Pb is one of the most important toxic metals studied around the world due to its dispersion through the oceans, the high concentrations found in the urban environment, and the pathological effects on human beings (10). Lead in combination with other heavy metals such as mercury, cadmium, and aluminum forms a group of highly toxic elements that do not perform any metabolic functions in tissues, organs, and fluids of the organism (10). Whole blood lead concentrations above 400 mg/L are dangerous, damaging organs and vital systems, even causing death (11).

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The clinical risk for children has increased due to Pb intoxication and produces irreversible health damage (11).

Previous works (12-16) reported the concentrations of deposited total lead in heavy traffic and school areas as well as the geographical distribution of Pb in the urban areas of Maracaibo City. In these investigations, relatively high levels of deposited total lead were found in the urban areas. The largest concentrations were obtained for the central (1517±396 mg/kg Pb) and northern (1954±555 mg/kg Pb) regions (16). In general, the concentrations of Pb in the urban sediment samples were between 220 and 1954 mg/kg (16).

Analytical methods for Pb determination have been developed due to the environmental relevance of this metal (7,8,17-19). Flame atomic absorption spectrometry (FAAS) is one of the techniques more widely used for this type of analysis because it provides adequate detection limits (i.e., in mg/L), sensitivity, and selectivity (8,17-19). In order to provide reliable and reproducible results, FAAS requires appropriate pretreatment procedures of the solid environmental samples due to the volatility of Pb using acid digestion with atmospheric pressure and controlled temperatures (60-70°C) (7,8).

In this work, we determined the Pb levels of 76 urban sediment samples collected near four highways of Maracaibo City using an FAAS-based method previously analytically developed (15-17). The novelty of the proposed method is based on the control of Pb loss during digestion of the solid samples. This analytical aspect can be ignored by some chemists but it is generally responsible for important experimental errors in the estimation of the real concentration of this analyte.

EXPERIMENTAL

Instrumentation

The determination of lead was carried out using a PerkinElmer® Model 460 flame atomic absorption spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA). The operating parameters of the instrument are shown in Table I.

Reagents and Standard Solutions

All chemical reagents used were of analytical grade. The concentrated solution of lead (~1000 mg/L) was prepared using a concentrated Titrisol® solution of Pb (Merck, Darmstadt, Germany). The standard solutions for the calibration curves were performed daily by serial dilution of the concentrated solution of the analyte in 0.01 M nitric acid (Merck). For each sample, the lead concentrations were determined using 7-point calibration curves, and aqueous standard solutions of 0.0, 5.0, 10.0, 15.0, 25.0, 35.0, and 50.0 mg/L Pb.

The evaluation of the accuracy of the method was carried out through the analysis of standard reference materials: Buffalo River Sediment NIST SRM 2704 (National Institute of Standards and Technology, Gaithersburg, MD, USA), and two certified reference materials: Pond Sediment NIES No. 2 and Vehicle Exhaust Particulates NIES No. 8 (National Institute for Envi-

ronmental Studies, Ibaraki, Japan). In addition, the accuracy of the employed method was evaluated through recovery studies of the spiked samples.

Sampling of Urban Vial Sediment

The urban sediment samples (USS, n = 76) were collected near four heavily traveled highways in Maracaibo City: "Av. 5 de Julio" (A-5), "Av. La Limpia" (A-L), "Circunvalación 1" (C-1), and "Circunvalación 2" (C-2). The samples were obtained in March and May 2001 from areas adjacent to the main roads during the regional dry season with high temperatures and winds of appreciable magnitude. Samples ranging from 500-1000 g were obtained in triplicate taken from the surface of the terrestrial layer and placed into polypropylene bags with hermetic seals. Along each avenue, different samples were collected; each sampling point was located about 200 or 300 m from the next, depending on the road longitude. The number of samples collected was 21, 22, 14, and 19 for A-5, A-L, C-1, and C-2, respectively.

Treatment of the Samples

Each sample was sifted to eliminate strange bodies (i.e., stones, glass pieces and/or wood, withered leaves from trees, cigarette butts, etc.) and then size-grain homogenized. Once sifted, the samples were dried in a convection oven for graveness at 60±2°C. Temperature control was necessary to avoid loss due to volatilization of the metal. The volatile character is a well-known physicochemical property of this analyte. This drying step was also applied to the three certified test sample materials to evaluate the accuracy of the analytical method.

The dry solid samples were previously acid-digested in triplicate employing atmospheric pressure

TABLE I
Operating Parameters for
Flame AA Determination of
Total Pb in Urban Sediment
Samples

Parameter	Value
Wavelength	283.3 nm
Spectral bandwidth	0.7 nm
Type lamp	Hollow cathode
Lamp current	8 mA
Gases in the flame	Air-acetylene

and controlled heating by convection at temperature intervals between 60 and 70°C (7,8). A 2.0000-g dry soil sediment sample (or a predetermined weight of the certified material) and 4 mL of concentrated nitric acid free of Pb were placed in a 250-mL beaker with a clock glass and digested for 10 min at 65 ± 5°C. The samples were then diluted with 25 mL of deionized water and digested for 50 min; thus, the total digestion time for each sample was 1 hour. The resulting solution was transferred to a 25-mL volumetric flask and brought to volume with deionized water. The representative blank solutions were prepared using the same digestion conditions.

RESULTS AND DISCUSSION

Analytical Figures of Merit

The linearity of the calibration curve was obtained up to 50 mg/L Pb. For each sample, the Pb concentration was determined using 7-point calibration curves with aqueous standard solutions of 0.0, 5.0, 10.0, 15.0, 25.0, 35.0, and 50.0 mg/L Pb, as shown in Figure 1(A). Absorbance (A) was found to be linearly related to the concentration (c) using the equation: $A = 0.0093c + 0.0025$ (the standard deviations of intercept and slope were 0.00002 and 0.00008, respectively; $r = 0.9999$, $p < 0.001$). These graphs allowed the analytical determination of Pb in urban sediment samples.

The within- and between-run precision of the method proposed was evaluated by determining Pb in three real samples of 20-fold diluted sediment (Table II). Three aliquots of each real sample were analyzed (five runs each) using the instrumental and operating parameters provided in Table I. The obtained results show an RSD average of <5% (~1.93%), resulting in mean RSD values of 2.20 and 1.66%, respectively. These results demon-

strate that the analytical method developed for Pb was adequately reproducible and appropriate for this type of analysis.

The accuracy of the proposed spectrometric method for the determination of Pb was verified by analyzing three certified materials: Buffalo River Sediment NIST SRM 2704 (NIST, Gaithersburg, MD, USA), Pond Sediment NIES No. 8 (NIES, Ibaraki, Japan), and Vehicle Exhaust Particulates NIES No. 8 (NIES; Ibaraki, Japan) (Table III). The results indicate that the measured concentrations obtained using the FAAS-based method for Pb did not differ significantly with respect to certified values. It verifies the appropriate accuracy in the analytical determination of the metal considered in this investigation. This parameter was also evaluated by means of recovery studies resulting in an average Pb recovery of $100.8 \pm 3.5\%$ (Table IV), demonstrating the appropriate reliability of the proposed method.

Due to the lack of a background corrector in the spectrometer used for the determination of Pb in the digested sediment samples, a spectral interference study could not be carried out. It is important to note that due to the digestion process carried out with the samples, an acid matrix comparable to the simple matrix of the aqueous solutions was obtained. In consequence, the digested certified samples, having a matrix similar to the real samples, showed a statistical correspondence between the certified and experimental metal concentrations. Therefore, it can be assumed with a high grade of reliability that spectral interferences did not exist.

The study of non-spectral interferences was carried out by comparing the slopes of the working curves with those obtained by the method of standard addition. The slopes obtained for the calibration and standard addition curves were

0.0093 ($r = 0.9999$, $p < 0.001$), and 0.0092 ($r = 0.9996$, $p < 0.05$), respectively [Figure 1(B)]. The mean relative error between slopes was 1.08%, which indicates an absolute parallelism. These results implied the absence of non-spectral interferences in the FAAS analyses for the developed Pb method and permitted the use of either the calibration graphs or the standard additions methods for metal quantification.

The detection limit and the characteristic concentration were 0.25 mg Pb/L and 0.43 mg Pb/L, respectively. The experimental value for the characteristic concentration was near to the theoretical value reported for the instrument: 0.55 mg Pb/L (20). This similarity was expected because the characteristic concentration is independent of the matrix under study, if the analyses using FAAS are free from interferences. In consequence, the experimental values indicated the appropriate sensitivity of the described methodology; therefore, these findings allowed the determination of lead in the environmental samples listed.

Levels of Pb in Urban Sediment Samples of Maracaibo City

The concentration of Pb (mean ± SD, mg/Kg) in the different samples were: A-5: $3,385 \pm 2,503$; A-L: $3,554 \pm 1,712$; C-1: $2,252 \pm 2,224$; and C-2: $2,457 \pm 1,666$. These high concentrations found at the studied avenues have increased when compared to the values found in a previous study carried out between 1984 and 1985 (i.e., A-5: 1822 ± 476 ; A-L: 792 ± 421 ; C-1: 764 ± 253 ; and C-2: 758 ± 292) (16,17). These high Pb concentrations in Maracaibo City are associated with the high traffic, which consumes high volumes of leaded gasoline. Table V shows the average Pb concentrations in mg/kg at the different avenues in the two sampling periods in 1985 and 2001. The percentage increase for Pb concentrations near these highways is also indicated.

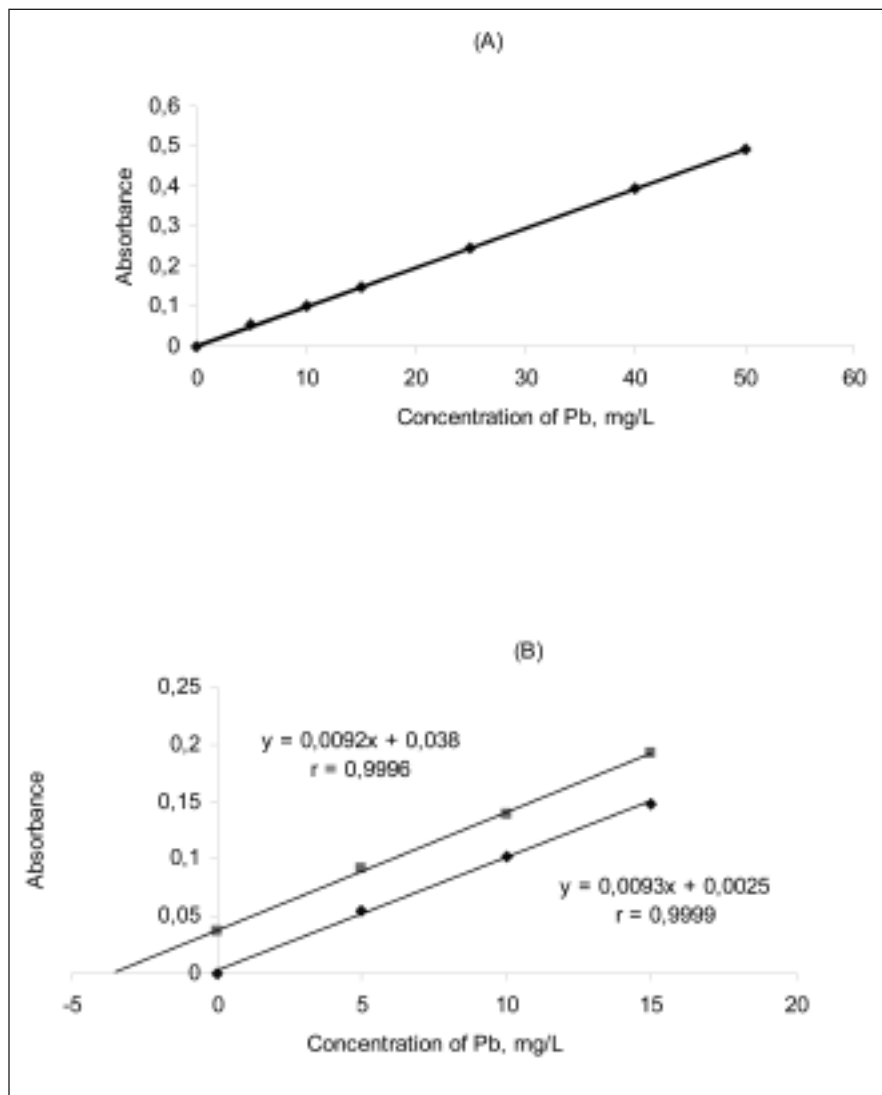


Fig. 1. Calibration curve (A) and study of non-spectral interferences (B) for the FAAS determination of Pb in soil sediments near highways in Maracaibo City (Zulia State, Venezuela), showing adequate parallelism between calibration (◆) and standard addition (■) curves.

TABLE II
Within-run and Between-run Precision Studies for the Determination of Pb by FAAS in Urban Sediment Samples of Maracaibo City

Sample	Mean Conc. ^a (mg/L)	Within-run		Between-run	
		SD	RSD (%)	SD	RSD (%)
A-5	3.12	0.02	0.64	0.03	0.96
A-L	3.85	0.15	3.90	0.10	2.60
C-1	4.44	0.09	2.03	0.07	1.58
C-2	5.38	0.12	2.23	0.08	1.49

^a In 20-fold diluted sample, prepared in triplicate, and five replicate absorbance readings.

The percentage increase of total lead was high (i.e., between 186 and 449%), which is reliable proof of the elevated levels of environmental contamination of Maracaibo City during the last 16 years. The residential and commercial buildings located in the studied areas act as physical barriers, avoiding the free displacement of lead by means of wind and thus favoring their sedimentation (17). It is important to note that in 1985, the concentration of deposited total lead in the A-5 area was statistically different ($p < 0.05$) with respect to the others; but by 2001, the Pb values were found to be the same as for the four areas tested.

CONCLUSION

High concentrations of Pb found in Maracaibo City, Venezuela, are due to the high automobile traffic where exorbitant volumes of leaded gasoline are used (about >300 mg/L Pb). The percentage increase in total lead concentration reveals the high grade of lead contamination of Maracaibo City. These concentrations is a potential health danger for the population of this Venezuelan city.

The developed analytical method for the FAAS determination of Pb is based on using controlled heating at 60–70°C, atmospheric pressure, and diluted acid media for the treatment of the solid samples. The method is accurate, precise, and free from interferences. This analytical approach employed in the treatment of the solid samples reported in this work would be of benefit to other laboratories worldwide.

As a final commentary, the authors would like to mention that in August of 2005, the Venezuelan government implemented the sale of only the unleaded gasoline. This step will provide new and future variants of investigations regarding this toxic element and allow to

TABLE III
Accuracy Studies for the Determination of Pb by FAAS Employing Standard Reference Materials

Material	Mean Concentration \pm SD ($\mu\text{g/g}$)		Relative Error (%)
	Certified Value	Measured Value	
NIST SRM 2704 a	161 \pm 17	160.2 \pm 5.4 n = 7	0.50
NIES No. 2 b	105 \pm 6	103.5 \pm 2.8 n = 7	1.43
NIES No. 8 c	219 \pm 9	221.9 \pm 6.2 n = 5	1.32

^a Buffalo River Sediment (NIST, Gaithersburg, MD, USA).

^b Pond Sediment (NIES, Ibaraki, Japan).

^c Vehicle Exhaust Particulates (NIES, Ibaraki, Japan).

TABLE V
Increase of Total Sedimented Lead Between 1985 and 2001 Near Four Highways in Maracaibo City

Avenue	Mean Concentration \pm SD (mg/kg^{-1} Pb)		Increment (%)
	1985	2001	
A-5	1822 \pm 476 ^a	3385 \pm 2503	186
A-L	792 \pm 421	3554 \pm 1713	449
C-1	763 \pm 255	2252 \pm 2224	295
C-2	758 \pm 292	2457 \pm 1666	324

A-5: Av. 5 de Julio, A-L: Av. La Limpia, C-1: Circunvalación 1; C-2: Circunvalación 2.

^a $p < 0.05$.

study and evaluate whether or not Pb will remain permanently in the urban atmosphere of Maracaibo City.

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TABLE IV
Recovery of Pb Added to Sediment Samples

Concentration (mg/L Pb) Added	Concentration (mg/L Pb)		Recovery (%)
	Expected	Found	
5	7.15	7.09	99.2
5	8.70	8.60	98.9
5	10.08	10.23	101.5
10	12.15	13.00	107.0
10	13.70	13.35	97.4
10	15.08	14.96	99.2
15	17.15	18.00	105.0
15	18.70	18.05	96.5
15	20.08	20.64	102.8
Average recovery \pm SD =			100.8 \pm 3.5

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Chelating Resin Micro-column Separation/ Preconcentration and Electrothermal Vaporization ICP-OES Determination of Trace Bismuth in Environmental and Biological Samples

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INTRODUCTION

Due to its chemical and physical properties, bismuth and its compounds are widely used in semiconductors, cosmetics, pharmaceuticals, and metallurgical additives, as well as in the preparation and recycling of uranium nuclear fuels (1). A number of toxic health effects in humans and animals, such as osteoarthropathy, hepatitis, and neuropathology (2), have been attributed to Bi compounds. Since the use of Bi in different areas of industry has increased, Bi has now excessively spread into the environment. As a result, the chance of exposure of organisms to bismuth has risen significantly. These cases underline the necessity for methods to determine Bi concentrations in environmental, biological, and other systems (3–15).

However, concentrations of Bi in real samples are usually at the $\mu\text{g g}^{-1}$ – ng g^{-1} levels, and could not be determined directly by conventional techniques owing to insufficient sensitivity and matrix interference. Hence, an efficient separation and preconcentration procedure is usually necessary prior to determination.

The most widely used techniques for the separation and preconcentration of trace bismuth include coprecipitation (14), hydride generation (6,8,10), liquid-liquid extraction (3), and ion-exchange and sorption (9–11,16–20). Among these tech-

ABSTRACT

A new method for the determination of trace Bi in environmental and biological samples by chelating resin YPA_4 microcolumn separation/preconcentration in conjunction with electrothermal vaporization-inductively coupled plasma optical emission spectrometry (ETV-ICP-OES) has been developed. The resin loaded with Bi was prepared by slurring and then directly introduced into the graphite furnace without any pretreatment. The factors affecting the adsorption and vaporization behavior of Bi were investigated in detail. It was found that chelating resin YPA_4 is not only an effective solid phase extractant for the quick adsorption of Bi in a wide acidity range of 0.1–3.5 mol L^{-1} HCl, but also a chemical modifier to vaporize Bi quantitatively from the furnace at the low vaporization temperature of 1000°C. With the use of YPA_4 as a chemical modifier, the sensitivity was increased by a factor of 6. Under optimum conditions, the adsorption capacity of YPA_4 for Bi was 63.5 mg g^{-1} ; the detection limit (3σ) of the instrument for Bi was 300 pg, with the relative standard deviation (RSD) of 3.5% ($n=8$, $C=2 \mu\text{g mL}^{-1}$). The proposed method was applied to the ETV-ICP-OES determination of trace Bi in environmental and biological reference materials, and the determined values were in good agreement with certified values.

niques, the methods using ion-exchange resin or sorbent extraction, such as modified silica (17), ion exchange resin (9), chelating resin (18–20), metal oxide (21), and activated carbon (22) have proved to be effective (9–11,16–22). In addition, the use of chelating resin for separation and preconcentration is especially simple and less time-consuming than other methods (19).

Using Muromac A-1 chelating resin, Sung et al. (19) simultaneously determined the concentration of bismuth, cadmium, and lead in urine by ETAAS. Yamini et al. (9) successfully determined ultra-trace Bi in water samples by ETAAS using C_{18} loaded with Cyanex 301 as the solid phase extractant. However, all of these methods involved elution with nitric acid as the eluant which is a laborious process and prone to contamination. Therefore, techniques for solid phase extraction, which could directly analyze the adsorbent loaded with the analytes without any complicated elution process, are much more attractive.

Electrothermal vaporization (ETV), as an alternative sampling device for inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS), possesses several benefits over conventional nebulization (e.g., small sample size requirements, the capability for solid and slurry analysis, ashing-matrix separation, etc.) (23). However, ETV-ICP-OES or ETV-ICP-MS does have limitations which include severe memory effects, incomplete vaporization, and transport loss. The use of

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chemical modifiers has been proven to be very effective to prompt the vaporization of analyte, suppress transport loss, eliminate memory effects, and therefore to improve the analytical performance of the method.

In recent years, various chemical modifiers, such as halogenating reagents [especially polytetrafluoroethylene (PTFE)] (24), DDTC (diethyldithiocarbamate) (25), and Pd (12) have been reported for ETV plasma spectrometry determination of refractory elements. Chang et al. (12) employed the salt of platinum group Rh and Pt/Pd as chemical modifiers to determine trace Bi in steel-making flue dust and in sea reference water samples by ETV-ICP-MS, respectively. Coedo et al. (26) developed a method to determine As, Sn, Sb, Se, Te, Bi, Cd, V, Ti, and Mo in steelmaking flue dusts. Slurry samples were analyzed directly by ETV-ICP-MS, and an added quantity of Rh acting as the modifier resulted in an increase for the same analytes in matrix-slurry solutions. However, a very high vaporization temperature (2900°C) was used which is unfavorable for the ETV device, especially, the graphite tube.

The aim of this work was to explore the possibility of using YPA₄ resin (aminoisopropylmercaptan type with a polythioether backbone, which a total content of S and N in the resin of 24.89% and 7.82%, respectively) as both an adsorbent and a chemical modifier for ETV-ICP-OES determination of Bi, and to develop a new method that possesses good selectivity and excellent sensitivity for the determination of trace Bi. YPA₄ resin loaded with the analyte was directly introduced into the ETV device without any pretreatment, and thus the complicated elution process was avoided. The factors affecting the adsorption and vaporization behavior of Bi were investi-

gated in detail. Finally, the proposed method was applied to the determination of trace Bi in environmental and biological reference materials to validate the accuracy of the method.

EXPERIMENTAL

Instrumentation

The graphite furnace sample introduction device (Beijing Second Optics, Beijing, P.R. China) and ICP-OES instrument (Beijing Broadcast Instrument Factory, Beijing, P.R. China) used in this work were identical with that reported previously (27). The ICP spectrometric system was equipped with a 2-kW plasma generator and a conventional silica plasma torch. A WF-1B type heating device with a matching graphite furnace was used for analyte vaporization. Radiation from the plasma was focused as a 1:1 image on the entrance slit of a WDG 500-1A type monochromator (Beijing Second Optics, Beijing, P.R. China) with a reciprocal linear dispersion of 1.6 nm mm⁻¹. The transient emission signals from the plasma were detected with a R456 type photomultiplier tube (Hamamatsu, Japan), fitted with a laboratory-built direct current amplifier, and recorded by a U-135C recorder (Shimadzu, Japan). The instrumental operating conditions and wavelengths are listed in Table I.

Standard Solutions and Reagents

The bismuth stock solutions (1.000 mg mL⁻¹) were prepared by dissolving high-purity Bi (The First Reagent Factory, Shanghai, P.R. China) in 1 mol L⁻¹ nitric acid. The working standard solutions of bismuth were prepared by diluting the stock solution with 0.5 mol L⁻¹ HCl. All other reagents used were of analytical reagent grade. Doubly distilled water was used throughout.

Preparation of YPA₄

The chelating resin YPA₄, as indicated above, is an aminoisopropylmercaptan type with a polythioether backbone, having a total S and N content in the resin of 24.89% and 7.82%, respectively (produced at and purchased from the Department of Polymer Chemistry, Wuhan University). The synthesis, IR spectroscopy characterizations, and elemental analysis have been described previously (28-29). The chelating resin YPA₄ with a 140 mesh size was immersed in acetone and 1 mol L⁻¹ HCl for 24 h, respectively, then filtered and washed with doubly distilled water, and dried prior to storage for use for the adsorption of bismuth.

Separation and Preconcentration Procedure

HCl was selected as the adsorption medium. A 0.5~10.0 µg amount of sample solution containing Bi was transferred to a 1-mL centrifuge tube, the acidity adjusted to the desired value with 4 mol L⁻¹ HCl, and the final volume diluted to 1.0 mL. Then, 10 mg of the YPA₄ chelating resin was added, and the mixture was stirred mechanically for 5 min to facilitate adsorption of

TABLE I
ETV-ICP-OES Instrumental
Operating Conditions

Wavelength	Bi: 306.7 nm
Incident Power	1.0 kW
Carrier Gas (Ar)	0.6 L min ⁻¹
Coolant Gas (Ar)	16 L min ⁻¹
Plasma Gas (Ar)	0.8 L min ⁻¹
Observation Height	12 mm
Entrance Slit Width	25 mm
Exit Slit Width	25 mm
Drying Temp.	100°C, ramp 10 s, hold 20s
Vaporization Temp.	1000°C, 4 s
Clearing Temp.	2500°C, 2s
Sample Volume	10 mL

Bi onto the chelating resin. After centrifugation, the supernatant was removed. The resin loaded with Bi was evaporated carefully to near dryness and then prepared to a 1.0-mL slurry by adding 0.1% (m/v) agar.

Recommended Procedure for ETV-ICP-OES

After selecting the analytical wavelength and using a pneumatic nebulization system, the sample introduction system was disconnected from the plasma torch, and replaced by the graphite furnace device. After plasma stabilization, 10 μL of the prepared sample was pipetted into the graphite furnace with a micro-syringe, and the sample inlet hole sealed with a graphite cone. Under the optimized conditions, the analytes loaded onto YPA₄ were quickly vaporized from the graphite furnace and introduced into the ICP by Ar carrier gas. The emission signal was recorded and peak height was measured for quantification.

RESULTS AND DISCUSSION

Effect of Acidity on Adsorption of Bi

HCl was selected as the adsorption medium and the adsorption percentage of Bi on YPA₄ was evaluated at varying acidities. Figure 1 shows the effects of acidity on adsorption percentage of Bi.

As can be seen, the metal ion Bi was adsorbed quantitatively by the chelating resin YPA₄ at an HCl acidity ranging from 0.1 mol L⁻¹ to 3.5 mol L⁻¹. The adsorption percentages were over 90%, which showed that the resin possesses the possibility of extracting Bi over a wide acidity range. For this study, 0.5 mol L⁻¹ HCl was selected as the acidity for separation and preconcentration of Bi.

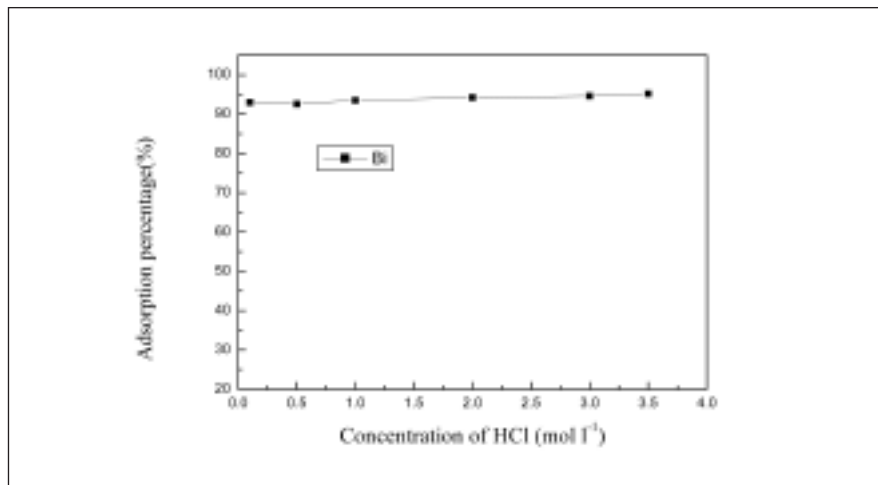


Fig. 1. Effect of acidity (HCl) on adsorption percentage of Bi (%). Bi: 6.0 $\mu\text{g mL}^{-1}$; Sample volume: 10 mL.

Effect of Equilibrium Time

It is well known that a rapid adsorption is of great importance for an ideal adsorption material. The adsorption kinetics of the resin was studied in 0.5 mol L⁻¹ HCl. The results of the dependencies of the adsorption time of Bi on the chelating resin YPA₄ in HCl show that Bi was adsorbed quantitatively within 2–5 min, which can be considered a fast adsorption kinetics process. The 20–25% content of S in the resin and a strong affinity of Bi to the S donor atom may easily explain the rapid adsorption behaviors of Bi on the resin in HCl medium.

Static Adsorption Capacities (Q_s)

The adsorption capacity of materials is an important factor to evaluate the adsorption performance. Using 0.5 mol L⁻¹ HCl and a 5-min stirring time, a 20-mg portion of the resin was shaken with 25 mL aqueous solution containing 5–2000 μg of Bi. After the distribution equilibrium was reached, the concentration of Bi in solution was determined. The results showed that the static adsorption capacity of the resin for Bi was 63.5 mg g⁻¹, which indicates

that the resin possesses a high adsorption capacity for Bi.

Interference Effects

The effects of common co-existing ions in environmental and biological samples on Bi(III) were examined. Using 0.5 mol L⁻¹ HCl and a 5-min stirring time, different concentrations of the metal ions were added to the solution containing 5 μg Bi. The tolerances of the coexisting ions are given in Table II. It can be seen that the YPA₄ chelating resin showed excellent selectivity toward Bi and thus is an ideal material to separate and preconcentrate Bi in complicated samples.

TABLE II
Tolerance Limits for Coexisting Ions in the Adsorption of the Studied Elements

Coexisting Ions	Tolerance Limit of Ions
K ⁺ , Na ⁺	50,000 mg L ⁻¹
Mg ²⁺	40,000 mg L ⁻¹
Ca ²⁺ , Sn ²⁺	15,000 mg L ⁻¹
Cu ²⁺	10,000 mg L ⁻¹
Pb ²⁺	5,000 mg L ⁻¹
SO ₄ ²⁻	160,000 mg L ⁻¹

Vaporization Behaviors of Bi in ETV-ICP-OES

As described above, the chelating resin YPA₄ showed good adsorption selectivity, high adsorption capacity, excellent stability, and fast kinetic characteristics for Bi. However, our preliminary experimental results showed that it is very difficult to desorb Bi from the resin even by using strong complexing agents such as thiourea. Additionally, the elution process is tedious and time-consuming. Thus, in this work, the resin loaded with Bi was directly introduced into the electrothermal vaporizer in the form of a slurry without desorption.

Figure 2 shows the typical signal profile of Bi without the addition of YPA₄ and also after adsorption by YPA₄. As can be seen, the presence of YPA₄ greatly changed the vaporization behaviors of Bi. An intense and sharp emission signal profile was obtained for Bi after adsorption by YPA₄, and Bi was quantitatively vaporized at the low temperature of 1000°C (Figure 2-D). In addition, no obvious memory effect was observed at a temperature of 2500°C (Figure 2-E), indicating that Bi had been vaporized completely. On the other hand, using the same conditions but without YPA₄, a weaker emission signal for Bi was obtained and peak height was just one sixth of that obtained by Bi loaded on YPA₄ (Figure 2-A). Although no memory effect existed at 1000°C (Figure 2-B), a severe memory effect was found at 2500°C (Figure 2-C). These results indicated that (a) the chelating resin YPA₄ is an effective chemical modifier for ETV-ICP-OES determination of Bi at a low temperature of 1000°C and (b) when compared to the results obtained without use of YPA₄, the presence of YPA₄ not only remarkably enhanced the sensitivity of Bi, but also greatly lowered the vaporization temperature of Bi (from the conventional 1600°C to 1000°C). The explanation

is based on the assumption that the complexes formed between Bi and the function group of YPA₄ are stable and easily volatile, and that the analyte was vaporized and transported from the graphite furnace into ICP in the form of a complex. Thus, the transport efficiency of Bi from ETV to the plasma was greatly increased (3). Without YPA₄, a higher vaporization temperature is required for Bi. A possible reason may be that although BiCl₃ possesses good volatility (boiling point at 441°C) and excellent chemical stability in acid media, BiCl₃ can be hydrolyzed at the drying stage and transformed into BiOCl, and finally into Bi (boiling point at 1564°C) or Bi₂O₃ (boiling point at 1887°C). Thus, a higher vaporization temperature is required to vaporize Bi from the graphite furnace.

Optimization of ETV Conditions

Pyrolysis Temperature and Time

In general, the selection of an appropriate pyrolysis temperature is very important for removing the organic matrix of the resin and preventing analyte loss during pyrolysis.

During the pyrolysis stage, the temperature was ramped from 100°C to the desired final temperature; thereafter, the furnace was kept at that temperature for 20 s to ensure that the charred resin was sufficiently vaporized from the furnace. It was found that the analyte loss during pyrolysis occurred when the pyrolysis temperature was ≥500°C. Thus, a pyrolysis temperature of 300°C was selected. However, when the resin was directly vaporized after drying at 100°C for 20 s without adopting the pyrolysis stages, the emission signal intensity of Bi was almost the same as that obtained by adopting the pyrolysis stage. To avoid the loss of Bi caused by the resin pyrolysis, the resin loaded with Bi was directly vaporized from the graphite furnace after maintaining the temperature of 100°C for 20 s without the pyrolysis stage.

Under the selected drying temperature of 100°C, the effect of drying time on Bi signal intensity was investigated. The results showed that there were no obvious differences in signal intensity of Bi when the drying time was changing

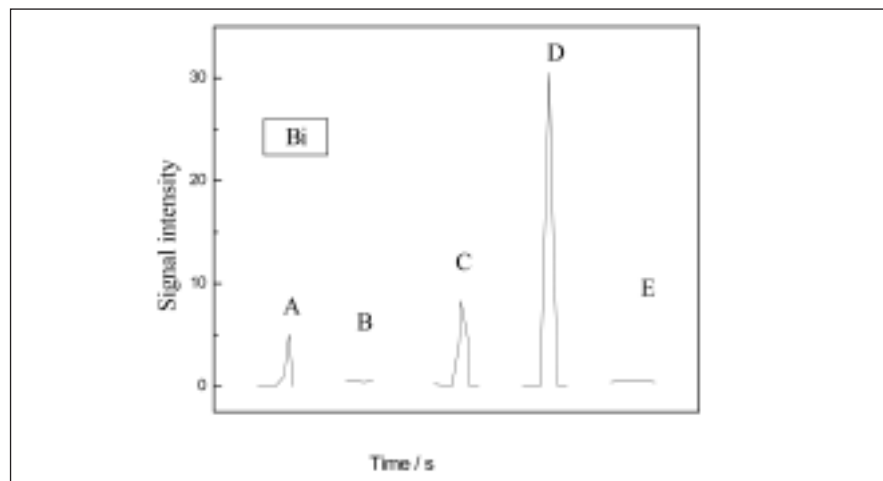


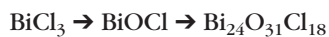
Fig. 2. Signal profiles for Bi.
 A: Only 20 ng Bi at 1000°C;
 B: Residual signals of empty firing at 1000°C after A;
 C: Residual signal of empty firing at 2500°C after A;
 D: 20 ng Bi with YPA₄ at 1000°C;
 E: Residual signals of empty firing at 2500°C after D;
 Conditions: Drying 100°C, ramp 10 s, hold 20 s.

from 5 s to 40 s. Therefore, a drying time of 20 s was chosen.

Effect of Vaporization Temperature

Using a drying temperature of 100°C and a drying time of 20 s, the influence of vaporization temperature on signal intensity of Bi adsorbed by YPA₄ was studied and the results are shown in Figure 3. As can be seen, the emission signal of Bi was observable over the temperature range of 500°C and was enhanced with an increase in temperature up to 1000°C. The maximal signal was obtained at about 1000°C and remained unchanged in the temperature range from 1000 to 1600°C. However, the analytical signal of Bi slightly decreased with an increase in temperature from 1600 to 1800°C. A vaporization temperature of 1000°C was therefore selected for Bi.

Figure 3 also shows the effect of vaporization temperature on the signal intensity of Bi in 0.5 mol L⁻¹ HCl medium (without YPA₄). As can be seen, the emission signal of Bi was observed at the temperature of 600°C, the emission signal enhanced with an increase in temperature, and reached a plateau at about 1600°C. The results indicated that Bi was not vaporized from the electrothermal vaporizer as the compound of BiCl₃. The reason may be that, on the one hand, the volatilization of HCl took place at the drying stage, or, on the other hand, BiCl₃ was hydrolyzed at this stage. The simple hydrolysis process may be presented as follows (30):



The compound Bi₂₄O₃₁Cl₁₈ may finally transform into Bi₂O₃ or Bi during the ETV heating cycle, and Bi was vaporized as the form of Bi₂O₃ or Bi. Bi₂O₃ and Bi have a relatively high boiling point of 1887°C and 1564°C, respectively, and a higher vaporization temperature is

required for its complete vaporization.

Using the same conditions, dependence of the blank signal of the resin YPA₄ on the vaporization temperature was also examined and the results are also shown in Figure 3. No obvious blank signal of the resin YPA₄ was found over the whole temperature range tested.

Effect of Vaporization Time

Under the selected vaporization temperature of 1000°C, the effect of vaporization time on signal intensity of Bi was studied. The results showed that there were no obvious differences in signal intensity of Bi when the vaporization time was changed from 3 s to 10 s. However, when the vaporization time was less than 3 s, vaporization of Bi was not complete. Thus, a vaporization time of 4 s was required.

Effect of Amount of YPA₄

In this work, YPA₄ was used as an adsorbent for Bi. As described above, under the optimized conditions, the adsorption capacity of the resin for Bi is 63.5 mg g⁻¹. On the other hand, YPA₄ was also tested as a chemical modifier for

ETV-ICP-OES determination of Bi. Thus, the effect of the amount of YPA₄ in the slurry on the emission signal intensity of Bi in ETV-ICP-OES was examined. For this purpose, the following experiment was designed: The slurry of 6% YPA₄ loaded with the analyte was prepared by mixing the YPA₄-loaded analyte with 0.1% (m/v) agar as the stabilizer. The slurry series (1%, 0.5%, 0.2%) were obtained by diluting 2% YPA₄-loaded analyte slurry with 0.1% agar solution. By this treatment, the analyte in the resin slurry was diluted 2-, 4-, and 10-fold, respectively.

Figure 4 shows the results obtained for the above experiment. It can be seen that the signal intensity of the analyte increases linearly with an increase of YPA₄ from 0.2% to 1% (corresponding to an increase in analyte concentration linearly). It can also be seen that the amount of YPA₄ ranging from 0.2% to 1% has almost no obvious effect on the signal intensity of the analyte. However, when the content of YPA₄ was increased to 2%, the signal intensity of Bi decreased rapidly. For this reason, a 1% YPA₄ was chosen for this work.

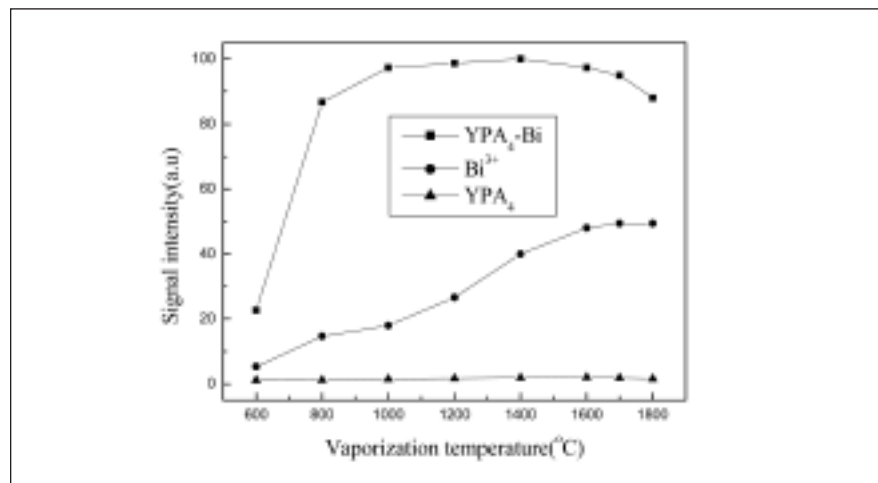


Fig. 3. Effect of evaporation temperature on signal intensity. Conditions: Bi 20 ng adsorbed by YPA₄; Drying 100°C, ramp 10 s, hold 20 s; Vaporization time 4 s.

Detection Limit and Precision

According to the definition of IUPAC, the detection limit (3σ) (calculated as three times the standard deviation of the background noise signal intensity) of the instrument for Bi was 300 pg and the relative standard deviation (RSD) was 3.5% ($n=8$, $C=2 \mu\text{g mL}^{-1}$).

Sample Analysis

In order to establish the validity of the procedure, the method described above was applied to the determination of Bi in biological and environmental standard reference materials (GBW07605 Tea Leaves and GBW07406 Soil, obtained from the Institute of Geophysical & Geochemical Exploration, CAGS, P.R. China).

A 0.8510-g of GBW07605 Tea Leaves sample was weighed into a quartz beaker, dissolved in 15 mL of $\text{HNO}_3\text{-HClO}_4$ (4:2, v/v); then using mild heating conditions (approximately 400°C), the sample solution was vaporized to near dryness, and finally dissolved in 10 mL of 0.5 mol L⁻¹ HCl.

Then, 10 mg YPA_4 was added to the above digested tea leaves sample solution and then prepared according to the procedure described above. The average results of five replicate determinations and the certified results are given in Table III. As can be seen, the analytical results obtained were in good agreement with the certified values.

A 0.020-g sample of GBW07406 Soil was weighed into a PTFE (polytetrafluoroethylene) beaker, dissolved in 10 mL of $\text{HNO}_3\text{-HClO}_4\text{-HF}$ (4:2:1, v/v/v); then using mild heating conditions, the sample solution was vaporized to near dryness, and finally dissolved in 10 mL of 0.5 mol L⁻¹ HCl.

A 10-mg amount of YPA_4 was added to the digested soil sample solution, and then prepared according to the procedure described

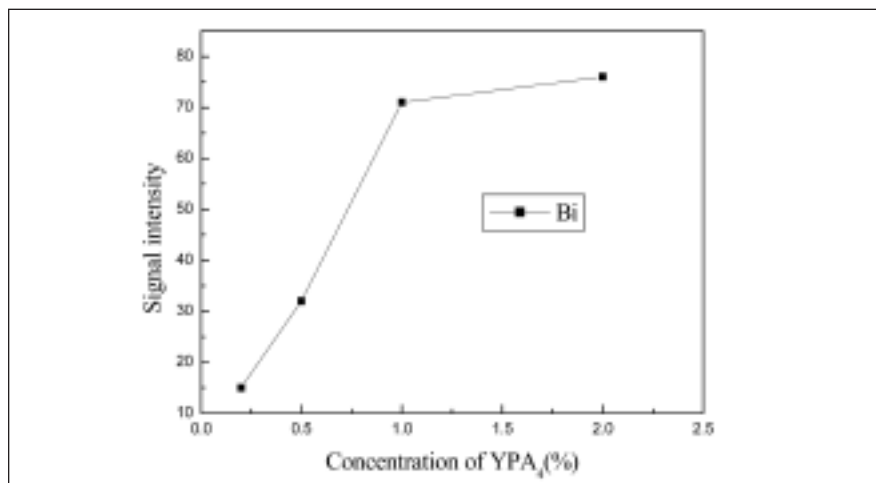


Fig. 4. Effect of concentration of YPA_4 resin on signal intensity. Conditions: Bi 20 ng adsorbed by YPA_4 ; Drying 100°C, ramp 10 s, hold 20 s; Vaporization 1000°C, 4 s.

TABLE III
Analytical Results of Bi in Tea Leaves and Soil Reference Materials^a

Element	GBW07605 Tea Leaves		GBW07406 Soil	
	Determined	Certified	Determined	Certified
Bi	0.055±0.001 $\mu\text{g g}^{-1}$	0.063±0.008 $\mu\text{g g}^{-1}$	51.8 ±3.9 $\mu\text{g g}^{-1}$	49±7 $\mu\text{g g}^{-1}$

^a Average ± s.d. (n=5).

above. The average values of five replicate determinations and the reference values are also given in Table III. Good agreement between the determined values and the reference values was obtained.

CONCLUSION

In this study, the chelating resin YPA_4 containing the S and N donor atoms was used as both an adsorbent and a chemical modifier for ETV-ICP-OES determination of Bi. The double effects of YPA_4 resin provide a new effective strategy for the separation/preconcentration and determination of trace/ultra-trace elements. In the presence of YPA_4 , Bi was quantitatively vaporized at the low vaporization temperature of 1000°C. Compared with the conventional vaporization temperature of 1600°C, a decrease of 600°C in vaporization temperature is beneficial in prolonging the lifetime of the evaporator. In addition,

the sensitivity was increased by a factor of 5–6 with YPA_4 as the chemical modifier. Since no elution and no pretreatment (slurring) of the eluant are required, the whole analytical operation is simplified. Therefore, it is possible to concentrate analytes from a small sample volume with a higher enrichment factor. The proposed method is applicable to the determination of trace/ultra-trace Bi in complicated matrixes, such as in biological, environmental, and geological samples.

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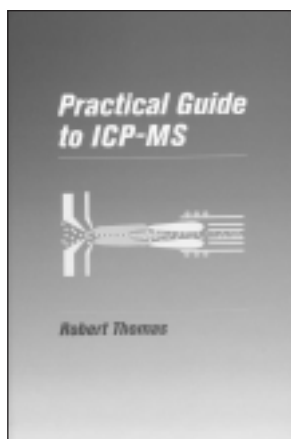
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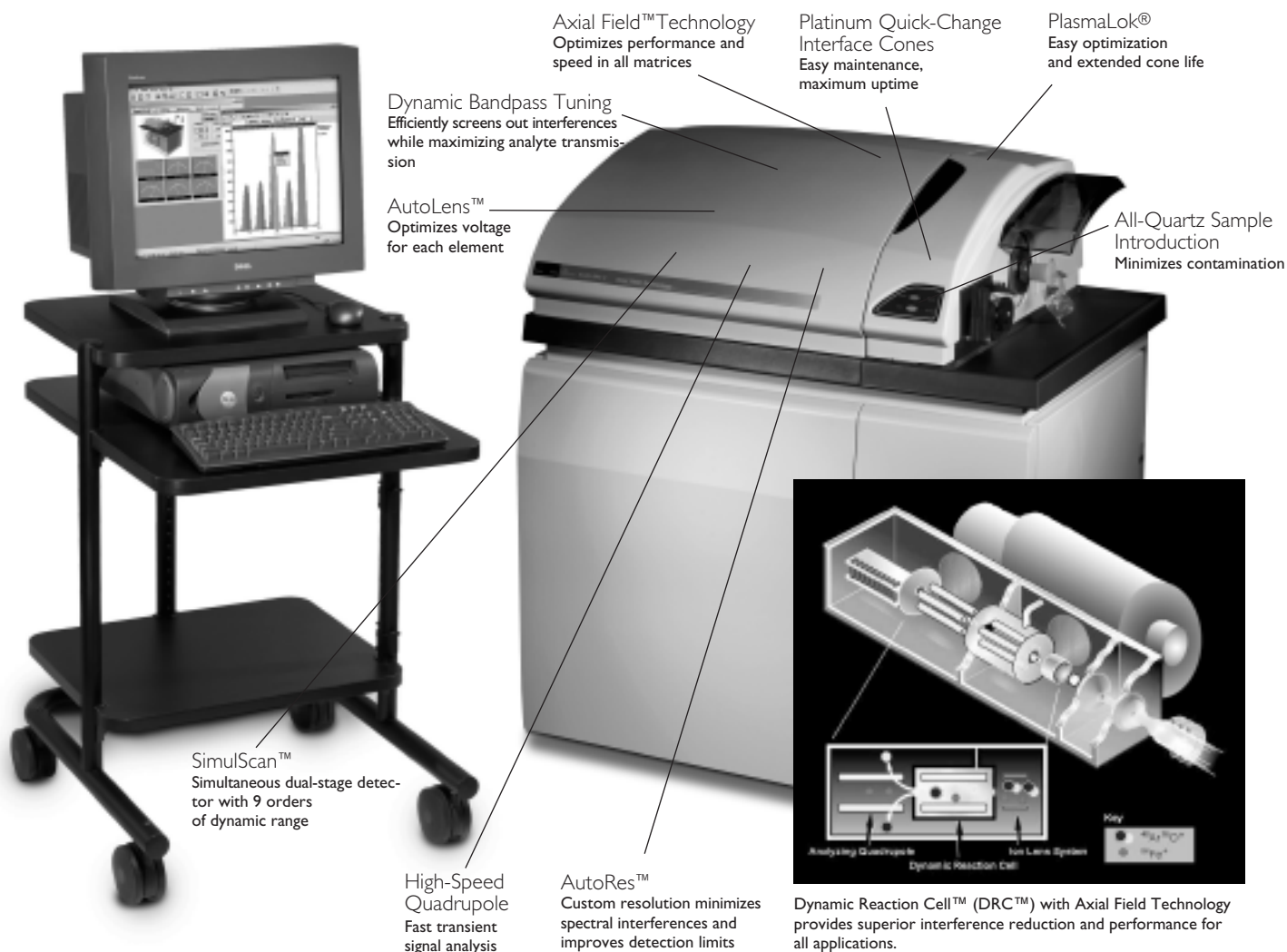
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