Magnetic Solid Phase Extraction of Trace Lead and Copper on Chromotrope FB Impregnated Magnetic Multiwalled Carbon Nanotubes From Cigarette and Hair Samples for Measurement by Flame AAS

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INTRODUCTION

The levels of trace elements are an important component of safety and quality of the environment. Trace elements such as lead (Pb), arsenic (As), and cadmium (Cd) are generally recognized as pollutants and are harmful to the health of humans, plants, and animals (1-4). They are toxic when present in excessive amounts (5-8). Metals occur naturally in soil, plants, and air. However, their concentrations are usually increased due to anthropogenic activities such as from industry and traffic (9-12).

Lead is one of the toxic elements even at ultra-trace levels (13, 14) and is absorbed in humans through inhalation of air, dermal exposure, and ingestion of dust and soil. Other sources of lead are polluted water and lead-adulterated foods (15-18). Copper (Cu) is another critical, important and necessary trace element for humans, plants, and animals. It is an essential part of several enzymes, essential for human nutrition (19-20), and necessary for the synthesis of hemoglobin (21-23). Consequently, an analytical method to preconcentrate, separate, and determine trace elements in environmental samples including natural waters is very important.

Classical solvent extraction, micellar extraction, flotation, coprecipitation and membrane filtration are popular separation-preconcentration methods for trace elements from environmental and food sam-

ABSTRACT

A novel and simple magnetic-solid phase extraction procedure for the separation-preconcentration of lead(II) and copper(II) at trace levels has been established by using Chromotrope FB impregnated magnetic multiwalled carbon nanotubes as a new adsorbent. The influences of critical analytical parameters like pH, flow rates, eluent, and sample volume were optimized. Matrix effects were also examined. Analyte elements were quantitatively recovered at pH 6.0. The limit of detection values were $11.7 \mu\text{g L}^{-1}$ for lead and $3.7 \mu\text{g L}^{-1}$ for copper. The (%) RSD values were generally found at $< 7\%$. The validation was performed by the analysis of NCS-DC73349 Bush Branches and Leaves certified reference material. The method was applied to the FAAS determination of lead and copper concentrations in cigarette and hair samples.

ples (24-28). Solid phase extraction is a popular separation-enrichment technique using novel nanomaterials with a high adsorption capacity and high surface area with resistivity to concentrated acids and bases (29-31).

In the present work, Chromotrope FB impregnated magnetic multiwalled carbon nanotubes have been used for the preconcentration-separation of Pb(II) and Cu(II) in hair and cigarette samples.

EXPERIMENTAL

Instrumentation

For this study, a Model 3110 flame atomic absorption spectrom-

eter (PerkinElmer, Inc., Shelton, CT, USA) was used, equipped with air/acetylene flame with a 10 cm long slot burner head and hollow cathode lamps of Cu and Pb. The conditions for flame atomic absorption spectrometry (FAAS) are given in Table I. The calibration curve equations for Cu and Pb for FAAS determinations, respectively, were $(A = 0.0394 C (\text{Cu}) + 0.0056)$ and $(A = 0.0133 C (\text{Pb}) + 0.0011)$, where A is the absorbance and C is the concentration of the analyte. The correlation coefficients of the equations were 0.9992 and 0.99945 for Cu and Pb, respectively.

The pH values were measured using a Sartorius PT-10 pH meter (Sartorius, Germany) with a glass electrode. A neodymium magnet was used for the phase separations. A vortex mixer (Wiggen Hauser, Malaysia) was used for thoroughly vortexing and mixing of the solutions.

Solutions and Reagents

Solutions were prepared with reverse osmosis purified water using a Milli-Q® system 18 MΩ-cm resistivity (Millipore Corporation, USA). All chemicals were of reagent grade. Stock solutions of the analyte elements were prepared from their nitrates as $1000 \mu\text{g L}^{-1}$, solutions in 0.02 M HNO_3 . Multi-walled carbon nanotubes (MWNT) (Sigma no: 636614-2G) were purchased from Aldrich, Milwaukee, WI, USA. A solution of Chromotrope FB (% 0.1 m/v) was prepared by dissolving of Chromotrope FB No. B22328 (Alfa Aesar, Germany) in small amounts of ethanol and diluting to 50 mL with water. Certified reference material (CRM) NCS-DC73349 Bush

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TABLE I
FAAS Instrumental Parameters

Element	Wavelength (nm)	Slit Width (nm)	Lamp Current (mA)	Flame Conditions*	
				(a)	(b)
Cu	324.8	0.7	15	9.5	2.3
Pb	283.3	0.7	15	9.5	2.3

* (a) Air (L/min), (b) Acetylene (L/min).

Branches and Leaves (National Research Centre for Certified Reference Materials, Beijing, P.R. China) were used in the experiments for validation of the procedure.

Phosphate buffer solution (0.1 mol L⁻¹) (pH 2.0–7.0), ammonia buffer solution (0.1 mol L⁻¹) (pH 8.0), and phosphate buffer solution (0.1 mol L⁻¹) (pH 9.0) were used in the experiments.

Preparation of Chromotrope FB Impregnated Magnetic Multiwalled Carbon Nanotubes

Magnetic multiwalled carbon nanotubes were obtained according to the procedure given in the literature (32) by using magnetite. To impregnate the Chromotrope FB to the surface of the magnetic multiwalled carbon nanotubes, 1.0 g magnetic multiwalled carbon nanotubes was added to 2 mL of Chromotrope FB solution and diluted to 30 mL with reverse osmosis water and stirring continuously for 20 minutes. Afterwards, the Chromotrope FB/magnetic multiwalled carbon nanotubes were filtered off, washed with reverse osmosis water, and dried overnight at 100 °C. The amount of Chromotrope FB deposited on the magnetic multiwalled carbon nanotubes was estimated by UV-Vis spectrophotometry from the residual amount of a Chromotrope FB in the solution. It was found that 66% of Chromotrope FB was retained on the adsorbent.

Test Procedure

A 10-mL aqueous sample solution containing Pb(II) and Cu(II) was adjusted to pH 6.0 using 2 mL

phosphate buffer solution. Then, 75 mg of Chromotrope FB impregnated magnetic multiwalled carbon nanotubes were added to this solution. After 5 minutes, it was vortexed with a revolution speed of 4000 rpm. After completion of the adsorption of the analytes onto the Chromotrope FB impregnated magnetic multiwalled carbon nanotubes, the adsorbent was separated at the bottom of the tube by using a neodymium magnet. The liquid phase was decanted. Then, 2 mL of 3.0 M HNO₃ in 10% acetone was added to the adsorbent for desorption of the analyte ions. Then the Chromotrope FB impregnated magnetic multiwalled carbon nanotubes were separated from the sample by using a neodymium magnet. An amount of 100 µL was aspirated into the nebulizer of the FAAS for absorbance measurements using the micro-injection system.

Analysis of CRM and Real Samples

The method was also applied to CRM NCS DC73349 Bush Branches and Leaves, and cigarette and hair samples. A wet ash procedure was

used for this purpose. One gram of a sample was transferred into a beaker and digested with 10 mL concentrated HNO₃ for 15 minutes at room temperature, then placed on a hot plate at 95 °C until a dry residue was obtained. The residue of each beaker was again digested with a mixture of HNO₃-H₂O₂ (2:1 v/v) until dryness. The residues in the beakers were then dissolved in 15 mL distilled water and filtered with a Whatman blue band filter paper. Then the procedure given in the “Test Procedure” was applied to these samples.

RESULTS AND DISCUSSION

Optimization

The pH is an important factor affecting quantitative adsorption of the analytes in the extraction studies (33-38). The effects of the pH on the recoveries of Pb(II) and Cu(II) ions on the Chromotrope FB impregnated magnetic multiwalled carbon nanotubes were tested at the pH range of 2.0–9.0. The results are depicted in Figure 1. The recoveries of Pb(II) and Cu(II) were found to be quantitative in the pH range of 3.0–8.0 and 5.0–7.0, respectively. For all further work, pH 6.0 was selected as optimal. The pH adjustments for pH 6.0 were done by using phosphate buffer solution.

The amounts of Chromotrope FB impregnated magnetic multiwalled carbon nanotubes were also tested

Fig. 1. Relation between pH and (%) recovery for analyte ions.

in the range of 25–100 mg. Quantitative recoveries for lead and copper ions were obtained in the range of 50–100 mg of magnetic adsorbent. An amount of 75 mg Chromotrope FB impregnated magnetic

TABLE II
Effects of Various Eluents on the Recoveries of the Analytes (Volume of Eluent: 2 mL; N=3)

Eluent Type	Recovery (%)	
	Pb(II)	Cu(II)
0.25 M HNO ₃	92±2	81±4
0.5 M HNO ₃	96±3	82±4
1.0 M HNO ₃	91±2	84±3
2.0 M HNO ₃	94±1	88±2
3.0 M HNO ₃	96±3	90±1
0.25 M HCl	87±3	86±2
0.5 M HCl	98±3	91±3
1.0 M HCl	95±4	96±3
2.0 M HCl	96±2	90±1
3.0 M HCl	94±1	91±1
0.25 N HNO ₃ in 10% acetone	63±2	86±2
0.5 M HNO ₃ in 10% acetone	88±1	88±1
1.0 M HNO ₃ in 10% acetone	94±1	91±2
2.0 M HNO ₃ in 10% acetone	95±2	94±2
3.0 M HNO ₃ in 10% acetone	97±1	97±1

multiwalled carbon nanotubes was used for all other experiments.

The elution of the adsorbed analytes from the adsorbent is an important critical parameter (38–43). Different eluent solutions (as listed in Table II) were used to elute the adsorbed analyte elements from the Chromotrope FB impregnated magnetic multiwalled carbon nanotubes. Quantitative recoveries for both analyte ions were obtained when 2.0 mL of 3.0 M HNO₃ in 10% acetone was used as the eluent. For other elution solutions, the recovery of one analyte generally was quantitative; but the other ion was not recovered quantitatively. For all further studies, 2 mL of 3.0 M HNO₃ in 10% acetone was used as the eluent.

The volume of the samples is another key parameter for solid phase extraction studies to obtain a high preconcentration factor (44–49). The effects of the sample volume on the recoveries were examined by using 10–40 mL. The recoveries were quantitative for both Cu and Pb in the range of 10–30 mL. The recovery values were not quantitative for sample volumes higher than 30 mL. The preconcentration factor was 30 with a final volume of 2 mL.

TABLE III
Effects of Some Matrix Ions on the Recoveries of Pb(II) and Cu(II) (N=3)

Ions	Added as:	Concentration (µg/mL)	Recovery (%)	
			Pb(II)	Cu(II)
Na ⁺	NaNO ₃	1000	97±0	99±1
K ⁺	KCl	1000	97±1	97±3
SO ₄ ²⁻	Na ₂ SO ₄	2500	94±1	95±2
Fe ³⁺	Fe(NO ₃) ₃ ·9H ₂ O	5	91±2	92±1
Zn ²⁺	Zn(NO ₃) ₂ ·6H ₂ O	10	98±1	100±2
Mn ²⁺	Mn(NO ₃) ₂ ·4H ₂ O	10	100±2	102±1
Cu ²⁺	Cu(NO ₃) ₂ ·3H ₂ O	10	100±2	
Mg ²⁺	Mg(NO ₃) ₂ ·6H ₂ O	100	102±0	102±2

Matrix Effects

The negative and/or positive effects of alkali, alkaline earth metals, and some metal ions at high concentrations in real samples are a big problem in the determination of trace metals (50–56). The influences of matrix components were investigated, and the results are listed in Table III. The model solution containing analyte elements and matrix components were prepared and then applied to the developed procedure as described in the Experimental section. The results clearly demonstrate that the interfering ions did not interfere with the recovery values of the analyte elements, and that the proposed method was fairly free from matrix components as given in Table III.

Analytical Features

The detection limits (LODs) of the present method for lead and copper, calculated based on 11 determinations of the standard deviation of the blank, were 11.7 µg L⁻¹ and 3.7 µg L⁻¹, respectively. The relative standard deviation (RSD) determined from 11 analyses was below 5%.

Application to CRM Sample

The present method was applied to CRM NCS-DC73349 Bush Branches and Leaves to verify the validity of the method for copper and lead levels after the wet digestion procedure as given in the Experimental section. The results in Table IV show that the presented solid phase extraction method is in good agreement with the certified values of the certified reference material.

The correctness of the present procedure was also verified by analyzing the concentration after addition of known amounts of Cu and Pb onto a cigarette and a hair sample. The results listed in Table V for the cigarette sample and in Table

VI for the hair sample show that good agreement was obtained between the added and found analyte content using the present solid phase extraction system.

In addition, the analyte elements of Cu and Pb in cigarette samples (purchased at a local market in Kayseri, Turkey) and in hair samples

TABLE IV
Application of Present Method to CRM NCS-DC73349 Bush Branches and Leaves for the Determination of Pb and Cu (N=3)

	Lead	Copper
Certified value (µg/g)	47	6.6
Found (µg/g)	45.2±3.0	6.1±0.8
Recovery (%)	96	93

TABLE V
Addition-Recovery Tests for Cigarette Sample (N=3) Using Solid Phase Extraction

	Added (µg)	Found (µg)	Recovery (%)
Pb	0	1.14±0	
	4	5.2±0.3	95
	8	8.8±0.3	95
Cu	0	3.0±0.1	
	2	5.1±0.2	102
	4	7.0±1.0	98

TABLE VI
Addition-Recovery Tests for Hair Sample (N=3) Using Solid Phase Extraction

	Added (µg)	Found (µg)	Recovery (%)
Pb	0	0	
	16	15.2±2	95
	24	22.7±1	94
Cu	0	0.4±0.1	
	8	8.2±0.1	97
	12	12.2±1	98

(from healthy subjects living in Kayseri, Turkey) were determined by flame atomic absorption spectrometry. The results are listed in Table VII.

Comparison of Proposed Procedure With Preconcentration Methods in Literature

A comparison between the figures of merit of the proposed method with other solid phase extraction methods used for the preconcentration/separation of copper and lead is given in Table VIII (55-62).

TABLE VII
Application of Present Procedure Using Flame AAS Analysis of Cigarette and Hair Samples (N=3)

Sample	Concentration (µg/g)	
	Pb	Cu
Cigarette 2	BDL	13.2±0.3
Cigarette 3	BDL	7.7±0.1
Cigarette 1	BDL	10.2±0.4
Hair 2	BDL	14.6±1.0
Hair 3	BDL	5.8±1.0

BDL: below the detection limit.

TABLE VIII
Comparison of Proposed Method With Some Methods in the Literature

Adsorbent	PF ^a	LOD ^b (µg/L)	Ref.
Magnetic allylamine modified graphene oxide-poly(vinyl acetate-co-divinylbenzene) nanocomposite	40	Pb: 2.39, Cu: 2.34	32
Fe ₃ O ₄ /graphene magnetic nanoparticles	-	Pb: 0.87, Cu: 0.22	42
Core-Shell magnetic chitosan biopolymer	25	-	52
Oxidized single-walled carbon nanotubes	50	Pb:5.4, Cu: 3.9	57
Multiwalled carbon nanotubes	50	Pb:5.5, Cu:2.3	58
Chromotrope FB impregnated magnetic multiwalled carbon nanotubes	15	Pb: 11.7, Cu: 3.7	This work

^a PF: Preconcentration factor.

^b LOD: Limit of detection.

CONCLUSION

A simple and novel procedure based on magnetic solid phase extraction of lead and copper at trace levels on Chromotrope FB impregnated magnetic multiwalled carbon nanotubes in hair and cigarette samples from Kayseri, Turkey, has been established. The advantages of the presented magnetic solid phase extraction method include time savings for adsorption and elution steps, low use of organic solvents, and the magnetic adsorbent can be used at least five times without loss of its adsorption properties.

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