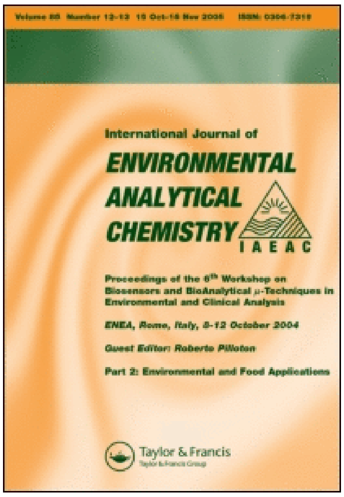

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Ultratrace determination of lead, cadmium and copper in environmental and biological samples by atomic absorption spectrometry after their separation and preconcentration using octadecyl silica membrane disks modified with a new n-s schiff base

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ULTRATRACE DETERMINATION OF LEAD, CADMIUM AND COPPER IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES BY ATOMIC ABSORPTION SPECTROMETRY AFTER THEIR SEPARATION AND PRECONCENTRATION USING OCTADECYL SILICA MEMBRANE DISKS MODIFIED WITH A NEW N–S SCHIFF BASE

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Pb(II), Cd(II) and Cu(II) ions were separated and preconcentrated by solid-phase extraction on octadecyl-bonded silica membrane disks modified with a new S–N-containing Schiff base (*bis*-2-thiophenal propandiamine) (BTPD) followed by elution and atomic absorption spectrometric detection. The method was applied as a separation and detection method for lead(II), cadmium(II) and copper(II) in environmental and biological samples. Extraction efficiency and the influence of sample matrix, flow rate, pH, and type and minimum amount of stripping acid were investigated. The maximum capacity of the membrane disks modified by 4 mg of BTPD was found to be 668 ± 10, 480 ± 8 and 454 ± 7 μg of lead, cadmium and copper, respectively. The limit of detection of the proposed method is 0.25, 0.01 and 0.02 ng/mL for lead, cadmium and copper, respectively.

Keywords: Copper(II); Cadmium(II); Lead(II); Solid-phase extraction; S–N Schiff base

INTRODUCTION

Lead, cadmium and copper are listed by the US Environmental Protection Agency (EPA) among the 129 priority pollutants [1,2]. Lead and cadmium are also listed among the 25 hazardous substances thought to pose the most significant potential

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threat to human health at priority superfund sites [3]. Lead and cadmium are listed by the EPA as class B2 and class B1 carcinogens, respectively [4].

Most of the lead, cadmium and copper in inner city soils and waters come from landfills and leaded paints. Landfills contain waste lead, cadmium and copper from mining, inorganic chemical, nonferrous metals and ammunition manufacturing, porcelain enameling, gum and wood chemicals, paint and ink formulations and from other industrial activities such as butter production and metal smelting. Humans absorb lead, cadmium and copper in small amounts from food, water and air. Lead(II) ions inhibit a select group of enzymes, including thiol-dependent enzymes involved in heme synthesis and mitochondrial energetics. The toxicological effect of lead may result from the ability of Pb^{2+} to uncouple oxidative phosphorylation and modify mitochondrial ion transport [4]. Lead also decreases glucose-6-phosphate dehydrogenase activity in humans, and thus decreases the glutathione level in red blood cells. When the blood lead concentration is near as above 80 µg/dL, basophilic stripping occurs in erythrocytes.

Cadmium can cause kidney and bone-marrow diseases and emphysema [5]. Ionic cadmium causes genotoxic effects in a variety of types of eukaryotic cells, including human cells. There is some evidence relating cadmium exposure to prostate cancer in men and animal studies [6]. An accumulation of cadmium in many tissues and a particularly long half-life, 10–30 years, have been reported for muscles, kidneys and liver [7].

Although copper in water is a hazard to many aquatic organisms, minute amounts of copper in the diet are needed for human, plant and animal enzymes (serving as enzyme activators) [8]. Thus, the determination of copper in water samples is warranted by the narrow window of concentration between essentialness and toxicity [9,10]. Copper is known to catalyze lipid peroxidation, possibly forming free radicals. However, copper is usually incorporated into stable complexes within cells or vascular fluids. Copper is essential for hemoglobin formation, carbohydrate metabolism, catecholamine biosynthesis, and cross-linking of collagen, elastin and hair keratin. In non-polluted areas, baseline concentration as low as 0.0003 mg/L have been recorded [11].

Human cannot exist without food and drinking water. Therefore, the development of accurate and rapid determination method for monitoring the level of copper, lead and cadmium in water and food is necessary and indispensable. Thus, the determination of trace amounts of these metals is becoming increasingly important because of the increased interest in environmental pollution.

The most common methods for determination of lead, cadmium and copper ions are flame and graphite furnace atomic absorption spectrometry [12] spectrophotometry [13] constant current stripping analysis [14] differential pulse anodic stripping voltammetry [15] and potentiometry [16,17] but their sensitivity is usually insufficient for the low concentrations in environmental samples. Consequently, a preconcentration and matrix elimination step is usually required. The most widely used techniques for the separation and preconcentration of trace amounts of these ions are liquid–liquid extraction (LLE) [18,19] precipitation and cation exchange resins [20], adsorption of their ion pairs on microcrystalline naphthalene [21] and solid-phase extraction (SPE) [22].

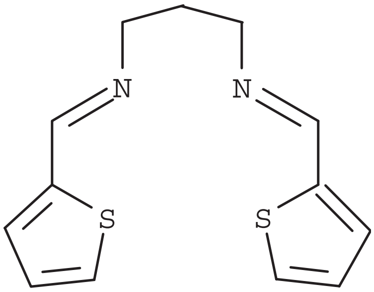
Solid-phase extraction is an alternative technique that reduces solvent usage and exposure, disposal cost and extraction time for sample preparation [23]. Recently, hydrophobic SPE disks have been used extensively for the determination of organic environmental polluents [24,25]. These disks, made of 90% (w/w) octadecyl silane in an inert polytetrafluoroethylene matrix, have a typical diameter of 47 mm and a thickness of 0.5 mm. The typical capacity of a disk for well-retained compounds ranges from 10 to 20 mg. The claimed major advantages of SPE disks include (1) shorter sample processing time due to the large cross-sectional area of the disk and decreased pressure drop, which allows sample processing at higher flow rates, (2) decreased plugging by particles due to large cross-sectional area of the disk and (3) reduced channeling resulting from the use of smaller diameter sorbent and greater mechanical stability of the sorbent bed [26].

In this work we wish to introduce a new reagent for preconcentration and separation of sub-part-per-billion levels of popular transition and heavy metal ions (copper, lead and cadmium) in food and water samples, by formation of relatively strong complexes between the reagent and transition and heavy metal ions, and their determination by AAS as an instrument available in most places. The preconcentration factor of the method is superior to any previously reported, and using this method very low level concentrations of copper, lead and cadmium, which cannot be detected by ICP-AES, could be determined.

EXPERIMENTAL

Reagents and Apparatus

Hydrochloric acid, citric acid, hydrobromic acid, acetic acid and nitric acid, high purity methanol, salicylaldehyde, ethylenediamine and ethanol (all from Merck) were used as received. Analytical-grade copper nitrate and other salts (all from Merck) were of the highest purity available and were dried in a vacuum over P_2O_5. BTPD (**1**) was prepared by condensation of stoichiometric amounts of salicylaldehyde and ethylenediamine in ethanol, as reported elsewhere [27]. The lead, cadmium and copper determination was carried out on a Perkin-Elmer 603 atomic absorption spectrometer with a hollow-cathode lamp and a deuterium background corrector. The AAS determination of all other cations was performed under the recommended conditions for each metal. Extractions were performed with 47 × 0.5 mm (diameter × thickness) Empore membrane disks containing octadecyl-bonded silica (8-μm particles 60-Å pore size, 3M Co., Paul, MN). The disks were used in conjunction with a standard Millipore 47-mm filtration apparatus.



BTPD **1**

Preparation of the SPE Membrane Disks

To remove potential interferences and to ensure optimal extraction of the analyte of interest, the disks should be cleaned and conditioned before use. Thus, after placing the membrane disk in the filtration apparatus, 10-mL of methanol was poured onto the disk and immediately drawn through the disk by applying a slight vacuum. After all of the solvent has passed through, the disk was dried by passing air through it for a few minutes. Disk conditioning was then begun by pouring another 10 mL of methanol onto the disk. Immediately, a low vacuum was applied and the solvent was drawn through the disk until the solvent surface almost reached the surface of the disk. The disk was not allowed to soak without vacuum, and air was not allowed to make contact with the surface of the disk. (It is preferable to have extra methanol above the disk rather than to allow any air to make contact with the surface of the disk.) Immediately, 10 mL of water was introduced onto the disk and drawn through. The disk was then dried under vacuum for 5 min; this was especially important for disks that were used for the first time. Finally, a solution of 5 mg of BTPD dissolved in 1 mL of methanol was introduced onto the disk so that the solution was spread over the whole disk surface. The solution was allowed to penetrate inside the membrane completely without applying any vacuum. After about 1 min, the filtration funnel containing the modified disk was transferred into an oven and the solvent was completely evaporated at 60°C. Then the sample solution containing Pb^{2+}, Cd^{2+} and Cu^{2+} was passed through the membrane. After the extraction, the disk was stripped from the membrane disk using appropriate amounts of acetic acid solution. The copper, cadmium and lead concentrations were determined by flame atomic absorption spectrometry.

RESULTS AND DISCUSSION

BTPD is a relatively lipophilic Schiff base bearing four donating atoms (two sulfur and two nitrogen atoms), which is insoluble in water at neutral pH. Our recent conductometric studies in acetonitrile revealed that it can form fairly stable and selective complexes with transition and heavy metal ions with the following selectivity pattern [28]:

$$Cu^{2+} > Co^{2+} > Ni^{2+} > Hg^{2+} > Pb^{2+} > Cd^{2+} > Zn^{2+} > Ag^{+}$$

Thus, we decided to examine its capability as a suitable reagent for pre-concentration and separation of sub-part-per-billion levels of copper, lead and cadmium ions via SPE, using octadecyl bonded silica membrane disks in various samples.

A literature survey revealed that in most reports specific reagents have been used for selective separation and preconcentration of metal ions [29–34]. For example, silica-immobilized 2-{[2-(triethoxysilyl)-ethyl]thiol} aniline as a selective sorbent for preconcentration of palladium [29], polymeric resins incorporating a chelating ligand (such as iminodiacetic acid) for the preconcentration of heavy metal ions [30], polystyrene resins containing azobenzyl phosphonic acid for selective separation of Pb^{2+}, Cu^{2+}, U^{6+}, Mn^{2+}, Zn^{2+} and Fe^{3+} [31], silica-bonded hydroxymate [32] and polyacrylic acid resins [33] for extraction of transition metal ions and calixarenes as efficient carrier for alkali metal ions extraction [34] have been reported in the literature.

Effect of Different Eluents on Stripping of Copper, Lead and Cadmium

For obtaining the maximum preconcentration factor, the volume of eluent that can completely strip the retained analytes from the modified disks is very important. Thus, some preliminary experiments were carried out in order to choose a proper eluent for the retained Pb^{2+}, Cd^{2+} and Cu^{2+} ions. After the extraction of 20 µg lead, cadmium or copper in 100-mL solutions by the modified disks, these ions were stripped with varying volumes of varying concentrations of different acids. From the data given in Table I, it is immediately obvious that, of the five different acid solutions used, 5 mL of 4.0 M acetic acid can accomplish the quantitative elution of lead, cadmium and copper from the membrane disk, while the other acids are ineffective for the complete elution of these ions. In a comparison with the other acids tested, acetic acid can easily penetrate into the modified disk, react with the BSTD (by porotonation of nitrogen atoms of BSTD and reduction of its complex-formation ability) and form water-soluble complexes with the metal ions, thus facilitating their diffusion into the eluent solution.

Influence of Flow Rates on the Extraction and Stripping of Pb^{2+}, Cd^{2+} and Cu^{2+} Ions

The influence of flow rates of the sample and stripping solutions from the modified membrane disk on the retention and recovery of Pb^{2+}, Cd^{2+} and Cu^{2+} ions was investigated. It was found that, in the range of 1–20 mL min^{-1}, the retention of lead, cadmium or copper by the membrane disk is not significantly affected by the sample solution flow rate. Similar results for the extraction of inorganic materials by octadecyl silica disks have already been reported [35,36]. On the other hand, quantitative stripping of Pb^{2+}, Cd^{2+} or Cu^{2+} ions from the modified membrane disks was achieved in a flow-rate range of 1.0–10 mL min^{-1}, using 5 mL of 4.0 M acetic acid as a stripping solution. At higher flow rates, larger volumes of 4.0 M acetic acid were necessary for quantitative stripping of Pb^{2+}, Cd^{2+}or Cu^{2+} ions.

Effect of Amount of Modifier on the Extraction of Pb^{2+}, $Cd^{2+}$and Cu^{2+} Ions

In order to investigate the optimum amount of BTPD for quantitative extraction by membrane disk, lead, cadmium and copper ion extraction was conducted using varying amounts of the ligand from 0 to10 mg. Table II shows that the extraction of all three

TABLE I Percentage recovery of copper from the modified membrane disks using different stripping acid solutions

Stripping acid solution	*Volume*, mL			
	5	*10*	*15*	*20*
Citric acid (3 M)	25.5	31.0	35.5	39.5
Nitric acid (3 M)	55.0	67.2	72.2	79.2
Acetic acid (4 M)	99.5	100.2	100.0	100.0
Acetic acid (3 M)	67.0	99.9	100.1	100.2
Acetic acid (2 M)	58.1	70.5	92.1	100.3
Acetic acid (1 M)	30.6	40.1	52.3	81.8
Hydrochloric acid (3 M)	45.3	77.3	79.6	81.6
Hydrobromic acid (3 M)	68.5	80.3	82.1	88.8

Initial samples contained 20 µg each of Pb^{2+}, Cd^{2+} and Cu^{2+} ions in 100 mL water.

TABLE II Effect of amount of BTPD on total Pb^{2+}, Cd^{2+} and Cu^{2+} ion extraction

Amount of BTPD, mg	*Recovery*, % *(RSD)*[a]
0	0
2	75 (1.5)
3	89 (1.4)
4	97 (1.1)
5	100 (1.0)
10	100 (1.0)

Initial samples contained 20 µg each of Pb^{2+}, Cd^{2+} and Cu^{2+} ions in 100 mL water.

[a] RSD values are based on three replicate analyses.

ions is quantitative using 5 mg of BTPD or more. Hence, subsequent extraction experiments were carried out with 5 mg of BTPD.

Effect of pH on the Extraction of Pb^{2+}, $Cd^{2+}$and Cu^{2+} Ions

The influence of the pH of aqueous samples on the extraction of 20 µg Pb^{2+}, Cd^{2+} and Cu^{2+} from 100-mL solutions was studied in a pH range 2.0 to 8.0. The pH was adjusted using 0.1 M solutions of either nitric acid or sodium hydroxide. The results obtained indicated that the modified membrane disk could retain the Pb^{2+}, Cd^{2+} and Cu^{2+} ions quantitatively in a pH range of 4.0–8.0. Higher pH values (>8.0) were not tested because of the possibility of hydrolysis of the octadecyl silica in the disks. At pH values lower than 4.0, the extraction efficiencies were reduced. This is most probably due to the protonation of the nitrogen donor atoms of BTPD, with consequent reduction of its complex-formation ability with the metal ions of interest.

Determination of Break-through Volume and Detection Limit

The break-through volume of sample solution was tested by dissolving 20 µg of lead, cadmium or copper ions in 25, 50, 100, 250, 500, 750, 1000, 1250, 1500, 1750 and 2000 mL of water and following the recommended procedure. In all cases, the extraction of metal ions by the modified membrane disk was found to be quantitative. Thus the break-through volume for the method should be greater than 2000 mL. Thus, the enrichment factor of the three metal ions tested should be at least 500.

In Table III the enrichment factor of the proposed method is compared with that of the best previously reported. As is immediately obvious, in term of concentration factor the proposed method is superior to the previously published methods [35–42].

The limit of detection (LOD) of the proposed method for the determination of lead, cadmium or copper was studied under the optimum experimental conditions. The LODs obtained from $C_{\mathrm{LOD}} = K_{\mathrm{b}} S_{\mathrm{b}} m^{-1}$ [43,44] for a numerical factor $K_{\mathrm{b}} = 3$ and a concentration factor of 400, are 0.25, 0.01 and 0.02 ng/mL for lead, cadmium and copper, respectively. It is interesting to note that the detection limits of the proposed SPE-AAS method are much lower than those of the ICP-AES and most other detection systems.

TABLE III Comparison of concentration factor of the proposed method and the best previously reported

Metal ion	*Concentration factor*	*Ref.*
Cu^{2+}	400	[35]
Ag^{+}	400	[36]
Ce^{3+}	200	[37]
Cu^{2+}, Zn^{2+}, Mn^{2+}	25	[38]
Co^{2+}, Cu^{2+}	100	[39]
UO_2^{2+}	100	[40]
Pb^{2+}	>100	[41]
Pb^{2+}	100	[42]
Pb^{2+}, Cd^{2+}, Cu^{2+}	500	This work

TABLE IV Separation of lead, cadmium and copper from binary mixtures

Second ion	*Amount taken*, mg	*Found, (RSD)*[a]	*Recovery, % (RSD)*
Na^{+}	20	NAPD[b]	100.1 (1.1)
K^{+}	20	NAPD[b]	100.1 (1.3)
Mg	20	NAPD[b]	100.2 (1.5)
Ca^{2+}	20	NAPD[b]	99.8 (1.3)
Sr^{2+}	20	NAPD[b]	99.9 (1.1)
Co^{2+}	4	0.1 (0.3)	99.2 (1.3)
Ni^{2+}	5	0.5 (0.5)	99.9 (1.1)
Zn^{2+}	5	0.3 (1.0)	99.5 (1.0)
Cr^{3+}	5	0.7 (0.2)	99.5 (1.5)
Ag^{+}	4	0.9 (0.5)	99.7 (1.2)
Fe^{3+}	100	0.7 (0.6)	99.7 (1.1)
Sn^{2+}	10	0.8 (1.1)	99.6 (1.2)
Hg^{2+}	10	0.5 (0.5)	99.7 (1.0)
Mo(VI)	10	0.4 (0.6)	99.8 (0.9)
Bi(III)	10	0.3 (1.1)	99.5 (1.1)

Initial samples contained 20 μg of Pb^{2+}, Cd^{2+} or Cu^{2+} ions in 100 mL water.

[a] RSD values are based on three replicate analyses.

[b] No adsorption, passes through disk.

Retention Capacity of the Modified Disk

The maximum capacity of the membrane disk modified by 4 mg of BTPD was determined by passing 50-mL portions of an aqueous solution containing 2000 μg lead, cadmium or copper through the disk, followed by determination of the retained metal ions using FAAS. The maximum capacity was found to be 668 ± 10, 480 ± 8 and 454 ± 7 μg of lead, cadmium and copper, respectively.

Separation of Pb^{2+}, Cd^{2+} and Cu^{2+} Ions from Synthetic Samples

In order to investigate the selective separation and determination of Pb^{2+}, Cd^{2+} and Cu^{2+} ions from their binary mixtures with other metal ions, an aliquot of aqueous solution (100 mL) containing 20 μg Pb^{2+}, Cd^{2+} or Cu^{2+} ions and various amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table IV and show that, while the cations of interest in the binary mixtures are retained almost completely by the modified membrane disk, retention of other cations by the disk is relatively low and they can be separated from Pb^{2+}, Cd^{2+} and Cu^{2+} ions almost quantitatively.

In order to assess the applicability of the method to real samples, with different matrices containing varying amounts of a variety of other ions, it was applied to the separation and recovery of lead, cadmium and copper ions from three synthetic samples (Table V). The results of three analyses of each sample show that, in all cases, the recovery of these ions is almost quantitative.

Determination of Pb^{2+}, Cd^{2+} and Cu^{2+} Ions in Water and Wastewater Samples

The proposed method was also applied to the determination of lead, cadmium and copper in two different wastewater samples (Calcimine and Dandy, Zanjan, Iran), (Tables VI and VII). The results obtained by the proposed method and inductively coupled plasma atomic emission spectrometry (ICP-AES) after a four-fold

TABLE V Recovery of 20 μg of copper, cadmium and lead added to 200 mL solution of synthetic water sample

Sample	*Recovery of Pb^{2+}, Cd^{2+} and Cu^{2+} ions, % (RSD)*[a]
Synthetic sample 1 (Co^{2+}, Ni^{2+}, Zn^{2+} and Ag^{+}, 5 mg of each cation)	98.9 (1.5)
Synthetic sample 2 (Na^{+}, K^{+}, Mg^{2+} and Ca^{2+}, 10 mg of each cation)	99.1 (1.1)

[a] RSD values are based on three replicate analyses.

TABLE VI Determination of copper, lead and cadmium in Sarcheshmeh River water

Sample	*Cu*, $\mu g\,g^{-1}$ *(RSD)*[a]		*Pb*, $\mu g\,g^{-1}$ *(RSD)*[a]		*Cd*, $\mu g\,g^{-1}$ *(RSD)*[a]	
	(SPE-AAS)	*(ICP-AES)*	*(SPE-AAS)*	*(ICP-AES)*	*(SPE-AAS)*	*(ICP-AES)*
1	0.15 (0.3)[a]	0.14 (1.5)	0.22 (1.2)	0.21 (0.5)	0.05 (1.1)	0.05 (0.8)
2	0.09 (1.3)	0.09 (1.0)	0.19 (1.1)	0.20 (0.7)	0.04 (1.0)	0.04 (0.5)

[a] RSD values are based on three replicate analyses.

TABLE VII Determination of lead, cadmium and copper in wastewater samples

Sample		*Found*, $mg\,mL^{-1}$ *(RSD)*[a]	
		(SPE-AAS)	*(ICP-AES)*
Pb[b]	1	35.6 (0.6)	35.2 (0.5)
	2	33.3 (0.5)	33.1 (0.3)
Cd	1	11.3 (0.5)	11.5 (0.4)
	2	11.4 (0.5)	11.5 (0.3)
Cu	1	10.2 (0.7)	10.7 (0.2)
	2	10.3 (0.5)	10.6 (0.2)

[a] RSD values are based on three replicate analyses.
[b] Measurements for lead were done after four-fold concentration of samples by evaporation.

preconcentration (by evaporating the solution) are in satisfactory agreement. Concentration of the sample solution before detection by ICP-AES is necessary because the concentration of lead is lower than the detection limit of this technique.

Analysis of Lead, Cadmium and Copper in Black Tea, and Hot and Black Pepper Samples

The proposed method was also applied to the determination of lead, cadmium and copper in two black tea samples. The procedure used for the extraction of these metals from tea samples was similar to that reported in the literature [45]. One gram of the dry tea sample (dried at 110°C) was placed in a 50-mL beaker, followed by the addition of 7 mL of concentrated nitric acid, and the beaker was covered with a watch glass. The beaker was allowed to stand overnight, than the contents were heated on a hotplate (150°C), for 15 min. The sample was cooled, 8 mL of perchloric acid was added, and the mixture was heated again at 200°C until the solution became clear (about 1 h). The watch glass was removed and the acid evaporated to dryness at 150°C. The residue was completely dissolved in 5 mL of 1 M nitric acid and the solution was transferred to a 100-mL calibrated flask. The solution was neutralized with NaOH solution and diluted to the mark, and the recommended procedure was followed. The results are shown in Table VIII. As can be seen, the amounts of lead, cadmium and copper in black tea, and hot and black pepper samples can be accurately determined with the proposed method.

Analysis of Lead, Cadmium and Copper in Standard Biological Samples

The accuracy and applicability of the proposed method was also tested by its application to the determination of manganese in standard biological samples provided by the National Institute for Environmental Studies: NIES No. 1 Pepperbush; NIES, No. 3 Chlorella; NIES, No. 5 Human Hair and NIES, No. 7 Tea Leaves. A 0.1-g sample was taken in a beaker and dissolved in 5 mL concentrated nitric acid with heating. The solution was cooled, diluted and filtered. The filtrate was neutralized with NaOH and diluted to 100 mL with water in a calibrated flask. An aliquot of the sample solution was taken and Pb^{2+}, Cd^{2+} and Cu^{2+} ions were determined by the recommended procedure. The results given in Table IX show a satisfactory

TABLE VIII Determination of lead, cadmium and copper in black tea samples

Sample	*Metal*	*Found*, mg mL^{-1} *(RSD)*[a]	
		(SPE-AAS)	*(ICP-AES)*
Iranian black tea (Lahijan)	Cu	46.80 (0.3)	46.70 (0.2)
	Cd	0.75 (0.8)	0.72 (0.8)
	Pb[b]	5.25 (1.1)	5.15 (1.1)
Indian black tea (Seylon)	Cu	37.55 (0.3)	38.61 (0.2)
	Cd	0.54 (1.0)	0.52 (0.9)
	Pb[b]	3.35 (1.8)	3.28 (1.0)

[a] Values in parentheses are RSD values are based on three replicate analyses.

[b] Measurements for lead were done after four times concentration of samples by evaporation.

TABLE IX Analysis of cadmium, copper and lead in biological samples

Sample[a]	*Composition*,[b] μg g^{-1}	*Found*,[c] μg g^{-1}
NIES, No. 1 Pepperbush	K, 1.51 ± 0.06; Mn, 0.203 ± 0.107; Mg, 0.408 ± 0.020; Ca, 1.38 ± 0.07%; Cd, 6.7 ± *0.5;* Ni, 8.7 ± 0.6; Fe, *205* ± 17; Co, 23 ± 3; Pb, *5.5* ± *0.8;* Cu, 12 ± 1; Zn, 340 ± 20; Ba, 165 ± 10; Na, 106 ± 13; Rb, 75 ± 4; Sr, 36 ± 4; As, 2.3 ± 0.3; P, (1100); Cr (1.3); Cs, (1.2); Ti, (0.13); Hg, (*0.056*)	Cd, 6.7 ± *0.5* Pb, *5.5* ± *0.8* Cu, 12 ± 1.0
NIES, No. 3 Chlorella	K, 1.24 + 00fr; Mg, 0.33 ± .002; Ca, 0.46 ± 0.03; Fe, 0.185 ± 0.010; P, (1.7)%; Zn, 205 ± 10; Sr, 40 ± 3; Co, 0.87 ± 0.05; Cd, (0.026); Mn, 69 ± 5; Cu, 3 *5* ± 03; Sc, (0.013)	Cd, 0.024 ± 0.002 Pb, 0.60 ± 0.03 Cu, 3 *5* ± 1.0
NIES, No. 5 Human Hair	Pb, 6.0; Cd, 0.20; K, 34; Rb, 0.19; Sb, 0.07; Zn, 169; Al, 240; Fe, *225*; Mg, 208; Hg, 4.4; Sc, 0.05; Se, 1.4; Na, 26; Sr, 2.3; Ti, 3.2; Ca, 728; Cr, 1.4; Ba, 2.2; Co, 0.10; Mn, 5.2; Cu, 16.3; Ni, 1.8	Cd, 0.19 ± 0.02 Pb, 5.9 ± 0.2 Cu, 16.1 ± 0.3
NIES, No. 7 Tea Leaves	Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; Cr, *0.15;* Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, *15.5;* Sr, 3.7; Ca, 3200; Cs, 0.22; Co, 0.12; Mn, 7.00; Ni, *6.5;* Cu, 7.0	Cd, 0.028 ± 0.02 Pb, 0.81 ± 0.03 Cu, 6.9 ± 0.2

[a] NIES: National Institute of Environmental Studies reference materials.
[b] Values in parentheses were approximate and not certified.
[c] Average of three determinations ± standard deviation.

agreement with the certified values. It is interesting to note that, for the analysis of biological samples by the recommended procedure, direct determination of components and particularly of lead by ICP-AES is impossible, because the detection limit of ICP-AES is much higher than the concentration of lead in the final solutions. The amount of sample needed for direct monitoring of lead (NIES, No. 3 Chlorella) by ICP-AES is about 17 g.

CONCLUSIONS

The proposed method has the following advantages. The method is rapid; the time taken for the separation analysis of lead, cadmium and copper in a 500-mL water sample is at the most 30 min. It can selectively separate Pb^{2+}, Cd^{2+} or Cu^{2+} ions from other associated metal ions, even at much higher concentrations. The method can be successfully applied to the separation and determination of lead, cadmium and copper in environmental and biological samples. The detection limits of the method are lower than those of ICP-AES. The concentration factor of the method for lead and cadmium is superior to all previously reported values.

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