

# Flame Atomic Absorption Determination of Cd and Cu in Biological Samples After Solid Phase Extraction by Octadecyl Silica Membrane Disks Modified With a Schiff Base Ligand

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## Abstract:

A procedure for separation and preconcentration of trace amounts of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  from aqueous media is proposed. The procedure is based on the adsorption of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions on octadecyl bonded silica membrane disk modified with, Pyridine 2,6-diylbis{2,2'(azamethane-1-ylidene)4-bromophenol} (L) at pH = 8. The ligand has been synthesized by reaction of the 2,6-diamino pyridine and 5-bromo salicylaldehyde at ethanol under refluxing. The structure of the synthesized compound resulted from the Fourier-transform infrared spectroscopy (FTIR), Proton nuclear magnetic resonance ( $^1\text{H}$  NMR), Mass spectrometry (MS) and UV spectroscopy and elemental analysis data. The solid phase extraction experimental conditions were optimized by changing several parameters such as volume of eluting solvent, the effect of pH, limit of detection and maximum capacity of the disks for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  recovery. The retained  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions were then stripped from the disk with a minimal amount of  $0.7 \text{ mol.L}^{-1}$  nitric acid and  $1 \text{ mol.L}^{-1}$  hydrochloric acid solution as eluent respectively, and determined by flame atomic absorption spectrometry. The limit of detection of the proposed method was 7.6 and  $3.6 \text{ ng.mL}^{-1}$  for copper and cadmium ions, respectively. The method was successfully applied to determination of copper and cadmium in natural biological samples and the method was quantitative.

**Keywords:** copper; cadmium; solid phase extraction; octadecyl silica; Schiff base; atomic absorption spectrometry

## 1. Introduction

Heavy metals could be found naturally in soils, sediments, water and even in living organisms, anthropogenic releases can increase its concentration to unacceptable levels. Some of heavy metals like copper, cobalt are necessary for human life, while some heavy metals like lead, cadmium are problematic for human. Main sources of heavy metals in the environmental samples are industrial facilities and traffic [1, 2]. The direct determination of trace metals especially toxic metal ions such as copper, tin, arsenic, lead, antimony and cadmium from various samples requires mostly an initial and

efficient preconcentration step [3]. This preconcentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest [4].

Copper and cadmium ions have been determined by graphite furnace atomic absorption spectrophotometer (GFAAS) [5], differential pulse stripping voltammetry (DPSV) [6], X-ray fluorescence (XRF) [7], atomic emission spectrometry with inductively coupled plasma excitation (AES-ICP) [8], flame atomic absorption spectrometry (FAAS) [9], and fluorescence spectrometry [10]. But in most cases as a result of low concentrations of these

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analytes in real samples, a preconcentration step is usually necessary. It is necessary to utilize either very sensitive instrumental technique or enrichment - separation methods for the quantification of low concentrations of metals.

Preconcentrative separation techniques including coprecipitation [11], solvent extraction [12], membrane filtration [13], cloud point extraction [14] and ion exchange [15] have been used for determination of the traces heavy metal ions in environmental samples. Solid phase extraction has also emerged as a powerful tool for separation - enrichment of heavy metal ions [16]. Solid phase extraction based on adsorption is a recently used method that compensates solvent extraction disadvantages.

Solid phase extraction (SPE) is superior to the conventional extraction techniques [17] due to its simplicity, rapidity, renewability and eco-safety. Analytical- or process - scale selective separation using SPE technique requires a material which has (I) highly selective affinity to the target analyte in the matrix range requiring separation, (II) fast rate of analyte extraction from the loaded sample solution followed by effortless elution with the suitable solvent, (III) repeated usability and (IV) a wide range of accessibility [18-20].

Schiff base compounds have been extensively studied because of their biological and structural importance [21-23] and especially their specific and selective reactions with metal ions. Therefore, these compounds are able to form stable complexes with several transition metal ions [24, 25], among which the resulting  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  complexes are the most stable [26]. Pyridine 2,6-diylbis[2,2'(azamethane-1-ylidene)4-bromophenol] (L) ligand (Figure 1) was successfully applied to the direct determination of copper and cadmium ions in biological

samples.

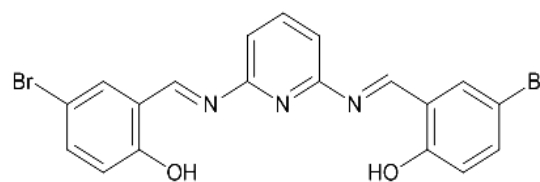


Figure 1. Chemical structure of (L).

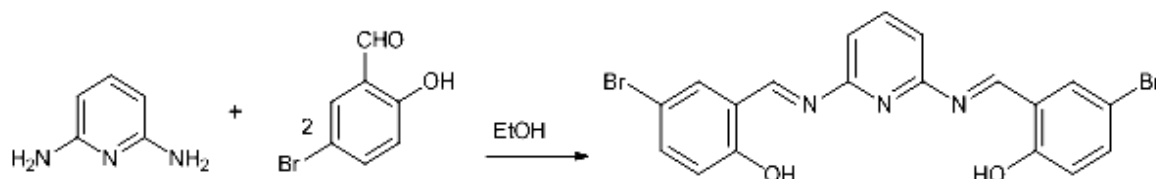
Membrane disk has been modified by chelating agents for selective extraction and determination of metal ions [27]. Schiff base compounds are able to form stable complexes with several transition metal ions [28]. These ligands have been applied as ionophore in construction of membrane electrodes [29], optical sensors [30], and as modifiers in solid phase extraction [31, 32].

In this work synthesis and application of a new Schiff base ligand (L) (Figure 1) as modifier of an octadecyl silica membrane disk for preconcentration and determination of copper and cadmium in various media by flame atomic absorption spectrometry have been reported. In order to optimize the experimental conditions, several parameters such as the volume of eluting solvent, the pH effect, the amount of ligand, limit of detection, maximum capacity of disks for  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  recovery and the recovery of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions in natural biological samples.

## 2. Results and Discussion

### Characterization of (L)

The Schiff base ligand (L) is formed in good yield by the condensation of the 2,6-diamino pyridine and 5-bromo salicylaldehyde at ethanol under refluxing [33, 34] (Scheme 1).



Scheme 1. Synthetic method for (L) ligand

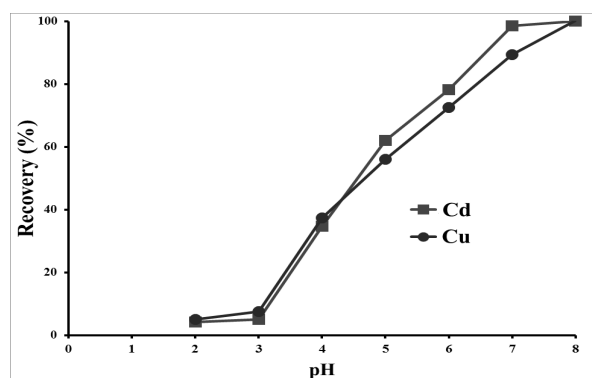
The structure of Schiff base was characterized by the spectroscopic data. The IR

spectrum of the ligand shows a broad band at  $3423\text{ cm}^{-1}$ , which can be attributed to the

phenolic OH group. Phenolic C-O stretch band is observed at  $1273\text{ cm}^{-1}$  in the Schiff base. However, the band due to the azomethine (C=N) group in this compound is observed at  $1607\text{ cm}^{-1}$ . The  $^1\text{HNMR}$  spectra of synthesized compound is consistent with its structure. The  $^1\text{HNMR}$  spectra of this compound is simple and consist of the aromatic proton signals and two singlet signals related to the resonance of the CH=N and OH proton, which appeared at 9.30 and 12.88  $\text{mg.L}^{-1}$ , respectively. The aromatic protons resonate as a multiple signal at 6.25-8.10  $\text{mg.L}^{-1}$ . The mass spectrum of this compound exhibited [M+] at  $m/z$  475 (55%) which elucidate the structure of the reaction product. The UV spectrum of the bis-Schiff base in ethanol, exhibited three absorption bands at 384, 316 and 295 nm assigned to  $n\rightarrow\pi^*$ ,  $\pi\rightarrow\pi^*$  and  $n\rightarrow\sigma^*$  transitions, respectively.

### Influences of pH

The pH of test solutions effect on the retention of  $5\mu\text{g Cd}^{2+}$  and  $10\mu\text{g Cu}^{2+}$  in 100mL solutions was studied at a pH range of 2.0 to 8.0 by using different buffer solutions pointed in the Experimental section. The pH was adjusted by using  $0.1\text{ mol.L}^{-1}$  of either nitric acid or sodium hydroxide solutions. As shown in Figure 2 the  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions can be retained quantitatively in the pH range of 7.0 - 8.0. For subsequent experiments, pH = 8 was chosen as a working pH. Higher pH values (>9) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks.



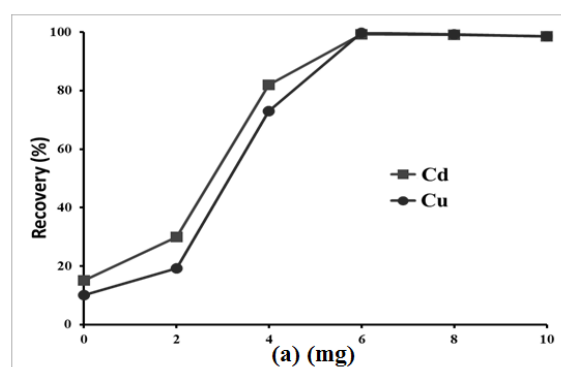
**Figure 2.** Influences of pH on recovery of metal ions,  $5\mu\text{g Cd}^{2+}$  and  $10\mu\text{g Cu}^{2+}$  in 100 mL solutions.

The recovery percentage depended on the

pH of the solution, which was nearly constant in the pH range of 7-8 indicate that the  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ion can be retained quantitatively at a pH range of 7.0 to 8.0. The pronounced decrease in solutions of  $\text{pH} < 7$  is due to the possible protonation of carrier ligand in acid solution. The quantitative recoveries (>98%) found for  $\text{Cd}^{2+}$  and (>89.5%) for  $\text{Cu}^{2+}$  at the pH 7.

### Effect of ligand amount

In order to investigate the amount of (L) on the quantitative recovery of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  by the membrane disk,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions extraction was conducted by varying the amount of ligand from 0 to 10 mg. It was found that the extraction of copper and cadmium by ligand modified disks was quantitative in the presence of 6-10 mg of the ligand. The amount of the ligand on recovery of copper and cadmium ions in 100 mL solution containing  $5\mu\text{g}$  metal ions was shown in Figure 3. The recoveries of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  increased by increasing the amount of the ligand and reached to 99.8% with at least 6 mg of the ligand. Therefore, 6 mg of the ligand was used for all the subsequent experiments.



**Figure 3.** Effect of (a) amount on recovery of metal ions,  $5\mu\text{g Cd}^{2+}$  and  $\text{Cu}^{2+}$  in 100 mL solutions at pH = 8.

### Eluent type and concentration of elution solution

In order to choose the most effective eluent for quantitative stripping of retained ions from the modified disk after extraction of  $5\mu\text{g Cu}^{2+}$  and  $\text{Cd}^{2+}$  from 100 mL sample (in the presence of 6 mg ligand in buffer solution  $\text{pH}=8$ ), the ions were stripped with 5 mL of different inorganic solutions such as HCl,  $\text{CH}_3\text{COOH}$ ,  $\text{HNO}_3$  and  $\text{HNO}_3$  in

methanol at different concentrations were used. It was found that 0.7 mol. L<sup>-1</sup> HNO<sub>3</sub> solution was the best eluent for desorption of cadmium and 1 mol. L<sup>-1</sup> HCl solution for copper ions from the modified disks (Table 1). The effect of eluent volume on the recovery of these ions was also studied.

**Table 1.** Recovery of Cu<sup>2+</sup> and Cd<sup>2+</sup> from the modified membrane disk using 5 mL of stripping solutions.

stripping solutions	Recovery (%)	
	Cd <sup>2+</sup>	Cu <sup>2+</sup>
HNO <sub>3</sub> (0.3 mol.L <sup>-1</sup> )	59.0	53.0
HNO <sub>3</sub> (0.5 mol.L <sup>-1</sup> )	87.3	98.0
HNO <sub>3</sub> (0.7 mol.L <sup>-1</sup> )	100	99.8
CH <sub>3</sub> COOH (1 mol.L <sup>-1</sup> )	34.2	4.0
HCl (1 mol.L <sup>-1</sup> )	55.4	100
HNO <sub>3</sub> in CH <sub>3</sub> OH (1 mol.L <sup>-1</sup> )	81.9	80.0

### Analytical performance

#### Capacity of modified membrane disk

The maximum capacity of the modified membrane disk was determined by passing 100mL portions of a buffer solution containing 5000 µg of copper and cadmium, followed by determination of Cu<sup>2+</sup> and Cd<sup>2+</sup> ions using FAAS. The maximum capacity of the disk was found to be 4731±7.5 µg and 4256±0.5 µg of cadmium and copper ions, respectively. The reuse of a modified disk was tested for its ability to perform the SPE for more than one sample. It was found that the use of the same modified disk for at least three times resulted in no change in the recovery of the Cu<sup>2+</sup> and Cd<sup>2+</sup> ions. However, for the SPE

of trace amounts of copper and cadmium from real samples, it is recommended to use a new modified disk for every sample to protect the samples from possible contaminations.

#### Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction, because breakthrough volume represents the sample volume that can be preconcentrated without loss of analyte during elution of the sample. The breakthrough volume of the sample solution was tested by dissolving 5 µg of copper and cadmium in 100, 200, 400, 600, 800, 1000, and 1200 mL of buffer solution, and the proposed procedure was followed. In all cases, the extraction by the modified membrane disk was found to be quantitative. Thus, the breakthrough volume for the proposed SPE method should be greater than 1,000 mL. Hence, by considering the final elution volume of 10 mL and the breakthrough volume of 1200 mL, a preconcentration factor of 200 was easily achievable for both copper and cadmium ions.

#### Limit of detection

The limit of detection (LOD), of the proposed method for the determination of copper and cadmium ions was studied under the optimal experimental conditions. The LOD obtained from  $C_{LOD} = K_b S_b m^{-1}$  (for a numerical factor  $K_b = 3$ ) is 7.6 and 3.6 ng.mL<sup>-1</sup> for copper and cadmium ions, respectively. The LOD values of this method were compared with other methods (Table 2). Although the LODs do not show a high improvement, this method is faster and more conventional.

**Table 2.** LOD (ng.mL<sup>-1</sup>) comparison between this work and similar works.

sorbent	method	Cu <sup>2+</sup> (ng.mL <sup>-1</sup> )	Cd <sup>2+</sup> (ng.mL <sup>-1</sup> )	Ref.
Cresolphthalein - MWCNT	SPE	1.64	-----	[35]
1nitroso-2-naphthol-Diaion resin	SPE	0.26	0.18	[36]
Ammonium pyrrolidine dithiocarbamate - MWCNT	SPE	0.30	0.45	[37]
amine functionalized nanoporous silica	SBSE	13.8	1.6	[38]
-----	Membrane filtration	0.40	0.32	[39]
This work	SPE	7.6	3.6	----

### Influence of interference ions

The possible interferences of some alkaline and alkaline earth salts and some transition metals as sulfate salts on the retentions of copper and cadmium ions on modified membrane disk were also investigated. In order to selective separation and determination of copper and cadmium ions from its binary mixtures with diverse metal ions, a 100 mL buffer solutions with pH 8 containing 5  $\mu\text{g}$  of  $\text{Cu}^{2+}$  or  $\text{Cd}^{2+}$  and milligram amounts of other cations was taken, and the proposed procedure was followed. The results are summarized in Table 3.

**Table 3.** Effect of diverse ions on recovery of 5  $\mu\text{g}$   $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  ions.

Interfering ion	Amount taken (ppm)	Recovery % for $\text{Cd}^{2+}$	Recovery % for $\text{Cu}^{2+}$
$\text{Na}^+$	100	85.3 $\pm$ 0.5	100.0 $\pm$ 0.5
$\text{Mg}^{2+}$	300	98.2 $\pm$ 0.8	99.0 $\pm$ 0.6
$\text{Ca}^{2+}$	1500	96.4 $\pm$ 0.3	92.1 $\pm$ 0.2
$\text{Mn}^{2+}$	100	98.0 $\pm$ 0.6	59.01 $\pm$ 0.4
$\text{Cu}^{2+}$	100	99.0 $\pm$ 0.1	99.2 $\pm$ 0.5

From the results obtained, it can be deduced that the presence of major cations have not significant effect on copper and cadmium determination by given procedure. Since, the ions that are commonly present in buffer samples did not interfere significantly; the method was applied to study the recovery of copper and cadmium in biological samples.

### Analysis of biological samples

In order to test the accuracy and applicability of the proposed method to the analysis of the real samples with different matrixes, it was applied to the separation and recovery of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions from different samples as unpasteurized milk fat, pasteurized milk (fat = 3%) and pasteurized milk (fat = 1.5%). The results are summarized in Table 4 and show that, in all cases, the copper and cadmium recovery is almost quantitative and the proposed method is suitable for the determination of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ions in real samples.

**Table 4.** Recovery of 5 $\mu\text{g}$  copper and cadmium from 100 ml solution of the milk samples.

Sample	Metal ions	Added ( $\mu\text{g.L}^{-1}$ )	Found ( $\mu\text{g.L}^{-1}$ ) N=3	RSD (%)
Unpasteurized milk fat	$\text{Cd}^{2+}$	0	258.1	0.4
		5	264.1	0.2
	$\text{Cu}^{2+}$	0	70.0	0.3
		5	75.4	0.2
Pasteurized milk (fat = 3%)	$\text{Cd}^{2+}$	0	361.0	0.2
		5	367.1	0.3
	$\text{Cu}^{2+}$	0	85.9	0.2
		5	86.5	0.3
Pasteurized milk (fat = 1.5%)	$\text{Cd}^{2+}$	0	330.2	0.2
		5	335.1	0.5
	$\text{Cu}^{2+}$	0	60.0	0.2
		5	67.0	0.5

The recovery of samples is satisfactory reasonable and was confirmed using addition method, which indicates the capability of the system in determination of ions. A good agreement was obtained between the added standards and measured analyte amounts.

## 3. Material and Methods

### Chemicals

All analytical grade reagents, inorganic acids and solvents were purchased from Merck

Company (Germany) and used as received. The new synthesized Schiff base (L) ligand with the highest purity was synthesized from 2,6-diamino pyridine and 5-bromo salicylaldehyde, as Scheme 1. Standard stock solutions of  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  ( $1\text{mg.mL}^{-1}$ ) were prepared by dissolving spectral pure grade chemicals in doubly distilled deionized water with the addition of nitric acid and further diluting daily prior to use. Working solutions were prepared daily from the stock solution by appropriate dilution with water. A buffer solution (pH 8.0) was prepared by mixing 0.1 mol.L<sup>-1</sup> potassium dihydrogen phosphate and

0.1 mol.L<sup>-1</sup> disodium hydrogen phosphate solutions in an appropriate ratio.

### Instruments

Melting point of synthesized ligand was determined by a Barnstead Electrothermal 9200 apparatus and can be uncorrected. FT-IR spectra were performed on a JASCO 4200 spectrometer using KBr discs. <sup>1</sup>HNMR spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts (ppm) were referenced to the internal standard tetramethylsilane (TMS). All UV-Vis Spectra recorded on a computerized double-beam 2550 Shimadzu spectrophotometer. The Mass spectrum was recorded on a Varian model Mat MS-311 spectrometer at 70 eV. Microanalyses were performed by the Elemental Analyzer (Elemental, Vario EL III).

Determination of Cu<sup>2+</sup> and Cd<sup>2+</sup> ions concentrations were on a GBC Sens AA flame atomic absorption spectrometer (air-acetylene flame) with Hollow Cathode Lamp (HCL) and equipped with a deuterium background corrector. Copper and cadmium hollow cathode lamps were used as the radiation sources with wavelengths of 324.8 and 228.8 nm, respectively. A Metrohm 827 pH meter was used to measure pH values. The Solid phase extractions were performed with 47 mm diameter 0.5 mm thickness 3M Empore membrane disks containing octadecyl-bonded silica (8 μm particles, 60 Å pore size). The formulation of the disks was 90% w/w octadecyl-bonded silica and 10% w/w polytetrafluoroethylene (PTFE). The disks were used in conjunction with a standard Scott Duran 47 mm filtration apparatus.

### Synthesis of (a)

A solution of 5-bromo salicylaldehyde (2 mmol), 2,6-diamino pyridine (1 mmol) in ethanol (10 mL) was refluxed for 2 h. The reaction mixture was cooled in an ice bath to give the precipitate. The crude product was collected, washed with water (5 mL) and then recrystallized from ethanol to give the pure (L) Schiff-base.

### Spectroscopic data of (a)

Yellow solid, Yield 81%, M.p. 227-229 °C, IR (KBr,  $\nu_{\max}$ ): 3423 (OH), 3048 (C-H), 1607, 1542 (C=N), 1474, 1273 (C=C), 1168 (C-OH), 817 (C-Br) cm<sup>-1</sup>; <sup>1</sup>HNMR (DMSO-d<sub>6</sub>),  $\delta$ : 6.25-8.10 (m, 7H, H-Ar), 9.30 (s, 2H, CH=N), 12.88 (s, 2H, OH) ppm; MS (m/z, %): 475 (M<sup>+</sup>, 55), 460 (25), 291 (60), 277 (70), 201 (70), 201 (70), 94 (100); UV/vis  $\lambda_{\max}$  (EtOH) 295, 316, 384 nm. Anal. Calcd. For C<sub>19</sub>H<sub>13</sub>Br<sub>2</sub>N<sub>3</sub>O<sub>2</sub>: C, 48.03; H, 2.76; Br, 33.63; N, 8.84%. Found: C, 48.34; H, 2.73; Br, 33.57; N, 8.91;

### Sample Extraction

After placing the membrane in the filtration apparatus, it was washed with 10 mL methanol and then with 10 mL deionized water to remove all contaminations arising from the manufacturing process and the environment. After drying the disk by passing air through it for several minutes, a solution of 6 mg (L) ligand dissolved in 3 mL acetonitrile was introduced to the reservoir of the apparatus and was drawn slowly through the disk by applying a slight vacuum. The filtration step was repeated until the passed solution was completely clear. Finally, the disk was washed with 25 mL deionized water and dried by passing the air through it. The membrane disk modified by the ligand was then ready for sample extraction. It is important to note that the surface of the disk was not left to become dry from the methanol was added until the extraction of Cu<sup>2+</sup> and Cd<sup>2+</sup> ions from water were completed [40]. Then 100 mL of the sample solution containing 10 μg Cu<sup>2+</sup> (or Cd<sup>2+</sup>) was passed through the membrane (flow rate = 5 mL.min<sup>-1</sup>). After the extraction, the disk was dried completely by passing air through it for a few minutes. The extracted copper was stripped from the membrane disk using appropriate amounts of suitable eluent (the best eluent was 1 mol.L<sup>-1</sup> nitric acid). This step was done with 5 ml eluent solution and the Cu<sup>2+</sup> (or Cd<sup>2+</sup>) was determined with flame atomic absorption spectrometer.

## 4. Conclusions

The proposed solid phase extraction procedure based on octadecyl silica membrane disks modified with (a) is a convenient, accurate and precise technique for the determination of copper and cadmium by flame atomic absorption

spectrometry. A high preconcentration factor of 200, achieved by this method, makes it a very sensitive procedure in comparison with the previously reported SPE methods. The preparation of the modified disk is very simple. The modified disk is reusable and can be used at least 10 times without any significant change in the recovery. The elution was easily performed with  $0.7 \text{ mol.L}^{-1} \text{ HNO}_3$  and  $1 \text{ mol.L}^{-1} \text{ HCl}$  for cadmium and copper, respectively. The elution of the complex does not involve strong acids or toxic organic solvents, in fact that it is noninflammable, inexpensive and nontoxic. The matrix effects with the method were reasonably tolerable. The important features of the proposed method are its higher adsorption capacity with good preconcentration factor. The developed method is sensitive in detecting  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$  at ppb levels. The method can be successfully applied to the preconcentration and determination of copper and cadmium in biological samples without the risk of contamination

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