Cadmium separation in human biological samples based on captopril-ionic liquid paste on graphite rod before determination by electrothermal atomic absorption spectrometry

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ABSTRACT

A mixture of captopril nanoparticles (CAP-NPs) and ionic liquid (IL, [HMIM] [PF6]) paste on micro graphite rod (CAP-IL-MGR) and was used for separation cadmium in human serum and urine samples by micro solid phase extraction (μ -SPE). 0.01 g of CAP-NPs and 0.1 g of [HMIM] [PF6] mixed with 1 mL of acetone and mixture passed physically on micro graphite rod (MGR) at 55°C. Then, the graphite probe placed on 10 mL of human biological samples with 5 min of sonication, then cadmium ions complexed by thiol group of captopril (CAP-SH) at pH=5.5. The cadmium ions on micro probe were back extracted with 0.25 mL of nitric acid (0.5 M) which was diluted with DW up to 0.5 mL and finally, the cadmium concentration determined by ET-AAS. By optimizing of amount of captopril, the absorption capacity and recovery were obtained 132.4 mg g⁻¹ and more than 96%, respectively. The limit of detection (LOD), linear range (LR) and enrichment factor (EF) were achieved 2 ng L⁻¹, 0.01-0.35 μ g L⁻¹ and 19.7, respectively (RSD %<5%). The validation was done by certified reference material (CRM, NIST) and ICP-MS analysis.

Keywords:

Cadmium

Human samples

Captopril

Ionic liquid

Micro graphite rod

Micro solid phase extraction

1. Introduction

Different chemical factories release toxic heavy metals such cadmium, lead and mercury in air, water, soil and also, it slowly enter to tissues of plants and animals by vary sources of erosion and abrasion of soils, forest fires and volcanic eruptions [1-3]. Cadmium with special properties such as, low melting temperature, corrosion resistance, rapid ion electrical exchange activity, high electrical and thermal conductivity can be used in battery factories [2]. Due to these properties is

used to make various products including, alkaline nickel-cadmium batteries, paints, alloys, plastics, electroplating protective coatings, solders, rods, television screens, lasers, pesticides, cosmetics and barrier in nuclear process [1, 2, 4-6]. Cadmium is an important industrial and environmental pollutant because it is widely used in many industrial activities (welding, smelting, mining, refining, soldering and etc.) [1, 2, 7]. So, many employments are in Cd exposure pollution. Approximately 512,000 workers in the United States have may a cadmium exposure in each year [8]. Cadmium is one heavy metal because relatively high density and its toxic effects even at low concentration. Cadmium has

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received considerable concern because its potential accumulation in the environment and in living organisms leading to long term toxic effects as a non-essential element [9-12]. It is classified as a human carcinogen by the north Carolina national toxicology program (NTP), international agency for research on cancer, (IARC), occupational safety and health administration (OSHA) and national institute of occupational safety and health (NIOSH) [2, 6, 10, 13, 14]. Cadmium occupational exposure to occurs primarily via respiratory tract [15] or ingestion and absorbed by the body and usually connected to metallothionein [4]. Cadmium mainly store in the liver and kidneys, but to a lesser degree rest stored throughout other organs of the body [2, 4, 16]. Toxic effects of Cd depend on enter rout, quantity, rate of exposure [4]. The values NIOSH and OSHA standard for Cd exposure ceiling limit is lowest feasible concentration and 0.005 mg m^{-3} respectively [17]. Long-term exposures to low levels of can result in renal disease but short-term Exposures to high levels of cadmium liver accumulation and hepatocellular damage. Exposures to cadmium also can produce many health effects such as lung irritation, testicular damage, pulmonary edema, renal, hepatic dysfunction, multiple sclerosis (MS) and osteomalacia and in some cases death. Various studies reported correlation between occupational Cd exposure and lung cancer and other cancers such as the prostate, renal, liver, hematopoietic system, urinary bladder, pancreatic, stomach and etc [3, 6, 10, 15, 18, 19]. In many studies, different techniques were used for cadmium analysis in water and human blood samples such as, automated anodic stripping voltammetry (ASV) technique with flow injection system, atomic absorption spectrometry (AAS), laser-induced breakdown spectrometry, hollow cathode excitation coupled to vidicon detection, atomic-fluorescence spectrophotometry, neutron activation analysis (NAA), non-flame atomic absorption spectrometry. [20-27]. Also, other methods were reported for separation and preconcentration of heavy metal in waters and blood urine of neuropsychological and multiple

sclerosis patients [28-31]. Recently, the mesoporous silica nanoparticles, silver nanoparticles, nano carbon material, graphene and carbon nanotube were widely used for separation heavy metals in waters and human biological samples by different analytical technology such as ultrasound-assisted dispersive micro-solid-phase extraction (USA-D μ SPE) and ultrasound assisted-Ionic liquid trap-micro solid phase extraction (USA-ILT- μ SPE) [32, 33]. In this study, a new sorbent based on CAP-NPs passed on MGR with IL was used for separation of cadmium from blood and urine samples by micro solid phase extraction(μ -SPE).All samples analyzed by electro-thermal atomic absorption spectrometer (ET-AAS).

2. Experimental

2.1. Apparatus and Reagents

Cadmium was determined with electro-thermal atomic absorption spectrometer (ET-AAS Varian, USA) which was equipped with graphite furnace accessory (GFA). The current, wavelength and spectral bandwidth of multi hollow cathode lamp (MHCL) were tuned (wavelength 228.8 nm, slit 0.5 nm, lamp current 3.0 mA). All samples were analyzed by auto-sampler injector of GFA. In addition, the inductively coupled plasma mass spectrometers (Varian ICP-MS, 810-MS, 820-MS systems) with full PC control of all instrument settings and compatible accessories. Varian ICP-MS have gigahertz sensitivity (1000 Mc/s/mg/L) and low background and interferences. The Varian ICP-MS systems include a sample introduction system and solid state 27 MHz RF generators. Computer of Varian (ICP-MS) can be control of plasma positioning, triple stage vacuum system, all plasma gas flows, mass analyzer, and Discrete Dynode Electron Multiplier (DDEM) detector. To prepare the 1ppb multi-element test solution (1ppb), pipette 1mL of the 500ppb into a 500mL volumetric flask and dilute up to the mark using 1% HNO₃, other concentration from 0.05-0.9 ppb prepared by dilution of DW (LOD= 2 ng L^{-1} cadmium). The pH range of samples was determined by a digital pH meter (M 744, Metrohm). The samples

were shaken by a Vortex Mixer (Thermo USA). All reagents purchased from Sigma Aldrich and Merck Company from Germany. The nitric acid, hydrochloric acid, polyoxyethylene octyl phenyl ether, acetic acid, acetone and toluene (HNO_3 , HCl , TX-100, CH_3COOH , AC , $\text{C}_6\text{H}_5\text{-CH}_3$) were purchased from Merck, Darmstadt, Germany. The cadmium nitrate solution (500 mL , 1000 mg L^{-1} , 99.98%) as cadmium(II) nitrate stock solution (1% HNO_3) was purchased from Merck (traceable to SRM from NIST $\text{Cd}(\text{NO}_3)_2$ in HNO_3 0.5 mol L^{-1} , CAS N: 119777 Germany). Standard solutions (0.05 , 0.1 , 0.2 , 0.5 , $1\text{ }\mu\text{g L}^{-1}$) were prepared daily by dilution of DW with 1% nitric acid. The pH of the samples was adjusted with a phosphate buffer ($\text{HPO}_4\text{-H}_2\text{PO}_4$) for pH 5.5. Ultrapure water (DW) was obtained from Millipore Continental Water System (Bedford, USA). The CAP-NPs (CAP, CASN: 62571-86-2, $\text{C}_9\text{H}_{15}\text{NO}_3\text{S}$) were purchased from Sigma Aldrich (Germany). CAP as an antihypertensive agent that competitively inhibits angiotensin-converting enzyme (ACE; $\text{IC}_{50} = 23\text{-}35\text{ nM}$) act in human body. Also, ACP acts as a reversible and competitive inhibitor of LTA_4 hydrolase (Fig. 1). Ionic liquids are made up of charged species and imidazolium-based ionic liquids have one of the nitrogen atoms in the imidazolium ring in the cationic form. These are generally synthesized by alkylation of an N-alkylimidazole and further incorporation of the desired anion by anion metathesis. 1-Butyl-3-methylimidazolium hexafluorophosphate is an imidazolium-based, hydrophobic, room temperature ionic liquid (RTIL). 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF6] is an ionic liquid employed in many environmentally friendly analysis (CASN: 70956, Sigma, Germany). 1-Methyl-3-(3-cyanopropyl)imidazolium bis(trifluoromethylsulfonyl)amide (CASN: 38943 Sigma) as TSIL were purchased from Sigma, Germany. Graphite rod, L 150 mm (15 cm), diam. 3 mm, low density (CASN: 496537, 99.995% trace metals). Micro graphite rod as 5 cm was used (micro rod of graphite, MGR, Sigma Aldrich)

Fig. 1. The structural of captopril nanoparticles (CAP-NPs)

2.2. Preparing of solid phase

First, 50 micro gram of CAP, 100 micro liter of ionic liquid and 2 mL of acetone mixed with MGR by shaking at 5 min ($50\text{ }^\circ\text{C}$). After drying in oven ($120\text{ }^\circ\text{C}$), washing with DW at $25\text{ }^\circ\text{C}$ for 10 times and then drying for 10 min at $120\text{ }^\circ\text{C}$. The CAP physically passed on MGR based on IL was used as solid phase for extraction cadmium from blood samples.

2.3. Extraction Procedure

By $\mu\text{-SPE}$ procedure, the CAP-IL-MGR was used for separation and determination cadmium in of blood/serum/urine samples by ET-AAS. The procedure was developed as follows: 10 mL of blood samples and standard solution containing $0.05\text{-}0.35\text{ }\mu\text{g L}^{-1}$ of cadmium was used for further analysis after the pH adjusted up to 5.5 with phosphate buffer solution. Then, the graphite rod - IL/CAP was placed in real samples which were shaken for 5 min. Cd (II) ions were extracted from samples by thiol group of CAP. Then, the rod was taking out from samples and eluted with nitric acid (0.25 mL , 0.5 M) which was diluted with DW up to 0.5 mL . Finally, the obtained solution was determined by ET-AAS. The proposed method followed by MGR without CAP or IL at room temperature. The concentration of cadmium in DW as a blank sample was determined by $\mu\text{-SPE}$ method (Fig. 2).

3. Results and Discussion

3.1. Characterizations of CAP-NPs

The characterization of CAP nanomaterials on MGR were achieved by X-ray diffraction spectroscopy (XRD) (Fig. 3), scanning electron microscopy (SEM) (Fig. 4), Fourier transform

Fig. 2. The schema of cadmium extraction based on CAP-IL-MGR by μ -SPE procedure

Fig. 3. The X-ray diffraction spectroscopy (XRD) of CAP nanomaterials

infrared spectroscopy (FTIR) (Fig. 5) and UV spectrum analysis (UV-Vis) with absorption in 400 nm (Fig. 6). The X-ray diffraction (XRD) was used to determine the CAP-NP structure. Due to the XRD spectra of CAP-NPs, no change was seen after coating on MGR (Fig. 2). In the CAP-NP, the peaks at 2979 and 2877 cm^{-1} were assigned to the asymmetric CH_3 and CH_2 stretching vibration, and the peak at 2634 cm^{-1} was due to the symmetric CH_3 stretching mode. The peak at 2567 cm^{-1} corresponded to the SH stretching vibration. The peaks at 1747 and 1593 cm^{-1} were assigned to the $\text{C}=\text{O}$ stretching vibration of carboxylic acid and amide band, respectively. The peaks at 1471 and 1385 cm^{-1} were due to the asymmetric and

Fig. 4. The scanning electron microscopy (SEM) of CAP nanomaterials

Fig. 5. The Fourier transform infrared spectroscopy (FT-IR) of CAP nanomaterials

Fig. 6. The UV spectrum analysis (UV-Vis) of CAP in 400 nm

symmetric CH_3 bending vibrations, respectively. The peak at 1330 cm^{-1} was assigned to the OH bending vibration. The peaks at 1228–1200 cm^{-1} also corresponded to the $\text{C}-\text{O}$ and/or CN stretching vibrations (Fig 4). The SEM and TEM of graphite rod were showed in Figure 7(a) and 7(b) based

Fig. 7(a).The SEM of graphite rod - CAP/IL

Fig. 7(b).The TEM of graphite rod - CAP/IL

on nano lawyer of graphite (≈ 100 nm) which was coated with CAP/IL.

3.2. Optimization of methodology

The CAP-IL-MGR as a solid phased was used for separation and determination cadmium in of blood/serum/urine samples by μ -SPE procedure. Blood samples and standard solution containing 0.05 - $0.3 \mu\text{g L}^{-1}$ of cadmium was used at pH 5.5. The effects of parameters were studied and optimized for 10 mL of samples by CAP/IL/MGR.

3.2.1. The effect of pH

The pH is an important factor for cadmium extraction in blood/urine sample. By proposed

procedure, the formation of the cadmium–CAP as chelate agent (HS group) was evaluated for different pH range from 2 to 11 for 10 mL standard solutions containing 0.05 - $0.3 \mu\text{g L}^{-1}$ of Cd(II). Obviously, the efficient extraction for Cd(II) were achieved in the pH ranges of 5.0 – 6.0 by thiol group of CAP which was passed on MGR by butyl-3-methylimidazolium hexafluorophosphate [BMIM] [PF6]. Therefore, pH of 5.5 was selected as the optimum pH for cadmium extraction with CAP@IL in real samples (Fig. 8). The results showed, the cadmium extracted by IL@MGR up to 33% by amino acids (Cys) in serum and blood samples and lower extracted in urine up to 18%.

Fig. 8. The effect of pH on extraction of cadmium based on CAP by μ -SPE

3.2.2. The effect of concentration of CAP

The optimizing of CAP concentration was achieved by minimum reagent which was lead to total complex formation with highest extraction efficiency for cadmium. The effect of CAP concentration on the recoveries of cadmium was investigated using various amounts of CAP in the range of $0.1\text{--}1\ \mu\text{mol L}^{-1}$ for $0.35\ \mu\text{g L}^{-1}$ of Cd(II) at pH 5.5. By increasing of CAP concentration, the extraction recoveries of cadmium ions gradually increased and the total Cd(II) were extracted using $0.45\ \mu\text{mol L}^{-1}$ of CAP. However, the extraction efficiencies of Cd(II) were not increased more than $0.45\ \mu\text{mol L}^{-1}$ (Fig. 3). So, the $0.5\ \mu\text{mol L}^{-1}$ of CAP were selected as optimum concentrations (Fig. 9).

3.2.3. The effect of sample volume

Sample volume (SV) must be optimized for preconcentration and separation of cadmium from blood/urine/standard solutions. Under optimized conditions, the effect of sample volume was studied in the range of $1\text{--}20\ \text{mL}$ containing $0.35\ \mu\text{g L}^{-1}$ of Cd(II). The results showed, the cadmium ions can be extracted quantitatively up to $14\ \text{mL}$ of the sample. At higher volumes, the recovery values decreased. Also, in higher sample volumes (more than $14\ \text{mL}$), the CAP/ILs phase was partially

solubilized in sample solution and lead to non-reproducible results. So, the sample volume of $10\ \text{mL}$ was selected for further experiments (Fig. 10).

3.2.4. The effect of extraction time (CAP/IL-MGR)

For high precision and accuracy of results, the extraction time was optimized at pH=5.5. Under optimized conditions, the effects of shaking time on the recovery efficiency of cadmium were studied for $1\text{--}10\ \text{minutes}$. Based on obtained results, the cadmium ions were efficient extracted and separated from blood and urine samples after $5\ \text{min}$ of sonication.

3.2.5. The effect of back extraction of MGR

After extraction process of cadmium by the proposed method, the MGR based on CAP/IL was back extracted with different acid solutions. By decreasing of pH, the cadmium–CAP complexes lead to the dissociation of complexing bond and released into the aqueous phase. In order to identify the best eluent for back-extraction of Cd(II) from the solid phase, $0.2\text{--}1.0\ \text{mL}$ of various mineral acids (HNO_3 , HCl and H_2SO_4) with different concentrations, $0.1\text{--}1.0\ \text{mol L}^{-1}$, were tested. The results show that HNO_3 ($0.25\ \text{mL}$, $0.5\ \text{M}$) provides higher recovery efficiency compared to the other acids (Fig.11).

Fig. 9. The effect of concentration of CAP on extraction of cadmium based on CAP by $\mu\text{-SPE}$

Fig. 10. The effect of sample volume on extraction of cadmium based on CAP by μ -SPE

Fig. 11. The effect of inorganic acids on back extraction of cadmium from CAP/IL/MGR

3.2.6. The Interference study

Matrix effects are a very problematic factor for cadmium extraction based on CAP/IL/MGR in blood samples and must be studied by different cations and anions. Since, the thiol group in CAP acted as good chelating agent for extraction of cadmium and other transition metals, so, the different concentration of transition metals was used and examined for evaluation of μ -SPE. By procedure, the recoveries of $0.35 \mu\text{g L}^{-1}$ of Cd(II) were studied in presence of individual interference ions. The deviation of the recovery by more than

5% was considered as the interference criterion. The results showed that many ions such as Co^{2+} , Cu^{2+} , Zn^{2+} and Pb^{2+} can be tolerated up to at least $0.6\text{--}1 \text{ mg L}^{-1}$ when determining the Cd(II) ions based on CAP/IL/MGR by ET-AAS. For concentrations of 1 mg L^{-1} of K^+ , Na^+ , Mg^{2+} , CO_3^{2-} and PO_4^{3-} which are usually found in human blood/serum samples, any interference was seen by proposed procedure. Moreover, Ni^{2+} and Hg^{2+} can be tolerated up to at least 0.03 mg L^{-1} and 0.045 mg L^{-1} for Cd(II) extraction by CAP.

3.3. Validation

Validity of the developed method was obtained by using standard reference materials (SRM,) from the national institute of standards and technology (NIST, Gaithersburg, USA). The procedure based on CAP-NPs passed on MGR by ionic liquid was used for cadmium extraction in human blood and urine samples by μ -SPE. The results showed a good agreement with SRM (Table 1). Also, the accuracy and reliability of the results were verified by spiking of blood and urine samples (10 mL). High efficient recovery between the added and measured amounts of cadmium was obtained by CAP-NPs (Table 2). Recovery and absorption capacity for CAP-NPs were achieved more than 95 % and 136.7 mg g⁻¹, respectively. In optimized conditions, the efficiency of extraction with IL, MGR, and CAP/IL/MGR were obtained 8.5%, 7.3% and more than 95%, respectively.

3.4. Comparing to published methods

Since 2010, the different techniques for extraction and determination cadmium in human biological fluids have been published. Different methodology such as liquid-liquid microextraction (LLME), micro solid phase extraction (μ -SPE), magnetic solid phase extraction (MSPE), column solid phase extraction (CSPE) have already used for extraction and speciation cadmium in liquid phase [33-37]. The figures of merit of the μ -SPE method compared to recently published methods for cadmium determination in human samples (Table 3).

4. Conclusions

A new method for the separation and determination of ultra-trace levels of cadmium in human blood, serum, plasma and urine samples were developed by CAP/IL/MGR sorbent. Cadmium was preconcentrated based on nanoparticles of CAP pure and determined by μ -SPE coupled with ET-

Table 1. Validation of cadmium results was performed by standard reference material (SRM) by μ -SPE

SEM	ICP-MS ($\mu\text{g L}^{-1}$)	Added ($\mu\text{g L}^{-1}$)	Found by μ -SPE * ($\mu\text{g L}^{-1}$)	Recovery (%)
SRM ^a	0.032 $\pm$ 0.005	-----	0.031 $\pm$ 0.002	96.9
		0.03	0.062 $\pm$ 0.003	103.3
SRM ^b	0.211 $\pm$ 0.013	-----	0.206 $\pm$ 0.013	97.6
		0.1	0.303 $\pm$ 0.018	97.0
SRM ^c	0.262 $\pm$ 0.038	-----	0.255 $\pm$ 0.012	97.3
		0.1	0.351 $\pm$ 0.019	96.0

* Mean value $\pm$ standard deviation based on three replicate measurements

^a Concentration Values for SRM 955c Caprine Blood, Level 1 (0.032 $\pm$ 0.006)

^b Concentration Values for SRM 955c Caprine Blood, Level 2 (2.140 $\pm$ 0.240, Dilution with DW, 1:10)

^c Concentration Values for SRM 955c Caprine Blood, Level 3 (5.201 $\pm$ 0.038, Dilution with DW, 1: 20)

ICP-MS: Inductively Coupled Plasma Mass Spectrometer (ICP-MS)

Table 2. Evaluation of cadmium extraction based on CAP by μ -SPE method in human biological samples by spiking of cadmium standard

Samples	Added (ng L ⁻¹)	Found * (ng L ⁻¹)	Recovery (%)
Serum	-----	68.76 $\pm$ 3.45	-----
	50	117.53	97.5
Blood	-----	179.54 $\pm$ 8.32	-----
	100	280.03 $\pm$ 15.11	100.5
Urine	-----	234.32 $\pm$ 12.24	-----
	150	379.75 $\pm$ 18.36	96.9
Plasma	-----	148.66 $\pm$ 6.87	-----
	150	291.82 $\pm$ 14.55	95.4

* Mean value $\pm$ standard deviation based on three replicate measurements

Table 3. Comparing of proposed method based on μ -SPE with other publisher works

Techniques	preparation	Matrixes	*LOD	*EF/PF	*RSD (%)	Ref.
^a VAM-DLLME	APDC-IL	water	0.048	76.9	4.1	33
SPE-F-AAS	^b WMCNT-BCBATT	biological	0.2	100	3.2	34
CSPE-F-AAS	^c sorbent of Am 15	water	0.23	20.0	3.0	35
^D FIA-TS-FF-AAS	^E IIP	Hair	0.024	165	5.0	36
SPE-F-AAS	M-MWCNT	Blood	0.04	120	1.2	37
^F DLLME-ET-AAAs	^G TOMAS-X100	Blood, Urine	0.005	10.4	2.3	38
μ -SPE-ET-AAS	^H CAP-IL-MGR	Blood, Urine	0.002	19.7	2.4	This work

* Linear rang (LR, $\mu\text{g L}^{-1}$); Detection limit (DL, $\mu\text{g L}^{-1}$), the *relative standard deviation* (RSD%)

^a Vortex-assisted modified dispersive liquid-liquid microextraction (VAM-DLLME)

^b Multi wall carbon nanotube- benzyl-4-[chlororbenzylidene amine]-4H-1,2,4-triazole-3-thiol (BCBATT)

^c Amberlyst 15 as sorbent

^D Thermospray flame furnace atomic absorption spectrometry (FIA-TS-FF-AAS)

^E Ion imprinted polymer (IIP)

^F Dispersive liquid-liquid microextraction coupled by electrothermal atomic absorption spectrometer

^G Trioctylmethyl ammonium thiosalicylate (TOMAS, TSIL)

^H Captopril nanoparticles - ionic liquid ([HMIM] [PF6]) paste on micro graphite rod

AAS. The developed method provides relatively lower LOD, LOQ and RSD ($< 2\%$, $n=10$) with favorite enrichment factor (19.7) and recoveries (more than 95 %). As low cadmium concentration in blood and serum samples ($< 0.2 \mu\text{g L}^{-1}$), a good linear range from $0.01 \mu\text{g L}^{-1}$ to $0.35 \mu\text{g L}^{-1}$ was used for a 10 mL sample by μ -SPE. In optimized conditions, the accurate / precise results with simple sample treatment and high efficient extraction were obtained with CAP/IL/MGR sorbent before cadmium concentration determined by ET-AAS.

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