Using a new ligand for solid phase extraction of mercury

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ARTICLE INFO

ABSTRACT

The octadecyl silica cartridge as a sorbent and 4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) as a ligand is a simple, rapid and reliable method for extracting and preconcentrating of Hg(II) in real samples prior to cold vapor atomic absorption spectrometry. Sample solutions were passed through a column at pH 4.5 then retained mercury ions on the column were eluted with minimal amount of 0.01 M nitric acid with 3 mL min^{-1} flow rate. The effect of pH, type of buffer, flow rate of sample and eluent, type and volume of the eluent were investigated and optimized. At optimum effective parameters, concentration factor and detection limit were achieved 128 and 1.87 ng L^{-1}, respectively.

1. Introduction

Mercury is one of the most toxic elements for plants and animals. This metal is so volatile that it can easily be exposed to human environment. Industrial wastes and mineral deposits are the major sources of mercury contaminations. Mercury hazards to living organisms such as marine samples are due to the accumulation and biomagnification characteristic of this toxic element that can influence the entire food chain and the humans who consume marine food [1].

Several methods have been applied for the separation and determination of mercury ion in real samples. They include: cold vapor atomic absorption spectrometry [2], complexation and spectrophotometric determination [3], coated magnetic nanoparticle adsorbents [4], inorganic sorbents and adsorbents [5,6], interaction with resins [7,8], solvent extraction [9], flame and graphite atomic absorption spectrometry [10], HPLC [11], high-performance thin layer chromatography (HP-TLC) [12], ion imprinted copolymers [13], and functionalized activated carbon [14].

Recently, solid phase extraction (SPE) cartridges and disks have widely and successfully been used for preconcentrating and separating of trace mercury ions from different matrixes [1,15–19]. The SPE has several important advantages over solvent extraction: faster operation, easier manipulation, not requiring large amounts of an organic solvent, less stringent requirements for separation,

higher preconcentration factor and easier linkage to analytical instruments such as ICP-MS, ICP-AES, HPLC and HP-TLC.

In the present work octadecyl silica cartridge as a sorbent and 4-bpdb (1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene) as a ligand is a simple, rapid and reliable method to separate and concentrate trace amounts of Hg(II) ions. This method was developed to separate Hg(II) ions from aqueous solution, fish sample, sausage and milk sample. Accordingly the determination of Hg(II) ions was conducted by cold vapor atomic absorption spectrometry.

2. Experimental

2.1. Apparatus

A flame atomic absorption spectrometer GBC 902 fitted with a mercury hollow cathode lamp, deuterium background corrector and an air/acetylene flame were used to perform atomic absorption measurements. The wavelength of 253.7 nm and spectral band pass of 0.5 nm were used throughout. A T-cell quartz tube (120-mm length and 5-mm i.d.) was placed directly on the nitrous oxide/acetylene burner which was equipped with T-cell tube holder. The measurement of LOD, RSD, LDR and calibration curve equation were based on turning off flame on cold vapor atomic absorption spectrometry and optimization of effective parameters fallowed to turning on flame. The operating parameters for working elements were recommended in the manufacturer's manual. A model 420A digital Orion pH meter equipped with a combined glass electrode was used for measuring pH. Microwave Lab Stations MLS-1200 (Milestone, Italy) was used in this research. A vacuum Pump

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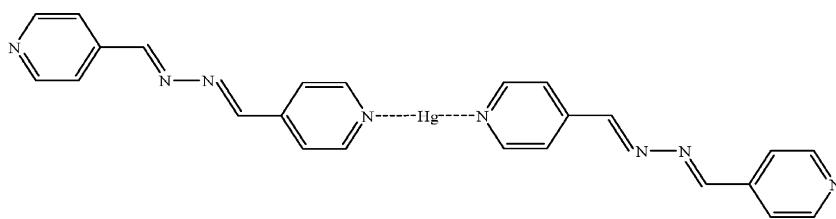*E-mail address:* m-soleimani@hotmail.com (M. Soleimani).

Fig. 1. Structure of 4-bpdb complex.

(MK2 Capex) and an adjustable vacuum gauge were allowed for flow-rate control during the extraction.

2.2. Reagents and materials

Methanol, ethanol, all acids, mercury acetate, sodium hydroxide, sodium chloride, potassium chloride, lithium sulfate, calcium nitrate, barium chloride, strontium chloride, ferric nitrate, sodium acetate, sodium formate, sodium phosphate and potassium nitrate were the highest purity available from Merck AG (Darmstadt, Germany). C_{18} cartridges containing 1000 mg octadecyl silica (50 μm particles size 60 Å pore size) were available from Macherey-Nagel Co. (Puren, Germany). The 4-bpdb was prepared according to the procedure in the literature [20]. The pH was adjusted by 0.5 M acetate/acetic acid buffer. Double distilled water was used throughout. The stock solution of mercury was prepared by dissolving an appropriate amount of mercury acetate in distilled water.

2.3. Procedure for preconcentrating

Extraction was performed with C_{18} cartridges. The cartridges were used in conjunction with a proper vacuum apparatus. Before each extraction, the cartridge was washed with 5 mL methanol to remove all contaminants resulting from the manufacturing process and the environment. Having dried the cartridge by passing air through it for several minutes, 5 mL methanol was introduced to the cartridge and was allowed to drain through it. A thin layer of methanol was left on the cartridge and it was washed with 10 mL distilled water. This step pre-wets the cartridge before extracting the complex from water. For this purpose, 25 mL of the model solution containing 2 μg mL^{-1} of Hg(II) and 4.4 μg mL^{-1} ligand were prepared in double distilled water. The resulting solution was loaded on to the C_{18} cartridge in 6 mL min^{-1} flow rate. The retained Hg(II) ions were stripped with 2.5 mL 0.01 M HNO$_3$ and the concentrated mercury was determined by cold vapor atomic absorption spectrometry (CVAAS).

2.4. Sampling

The water samples were collected in pre-washed polyethylene bottles and were filtered through a filter paper (Whatman No.40) before use. Two fish samples, (Trout) and canned Tuna (Poolak) from Fadlak factory which were purchased from Qazvin local fish market were included in the study. The fish species were washed with distilled water, dried in filter paper, homogenized, packed in polyethylene bags and stored below −20 °C until analysis [21]. The milk sample was supplied from Vakil Dasht ranch (Qazvin-Kahak) and stored at −20 °C in laboratory until analysis. The sausage sample, Sotudeh from Behtoosheh Bonab Factory, was purchased from the local market in Qazvin and stored at −20 °C.

3. Results and discussion

The 4-bpdb is an electron-donating base which is soluble in mixture water/methanol (5.22×10^{-3} g in mixture 10:90 methanol–water). Recent studies revealed that it can form a fairly stable and selective 1:2 (M(4-bpdb)$_2$) complex with M^{2+} ions [20]. It has a pair of nitrogen atoms located in a position that allows each to form a covalent bond with M^{2+} ion. The structure of 4-bpdb complex is shown in Fig. 1.

The 4-bpdb ligand as a suitable reagent for solid phase extraction of Hg(II) ion was examined by using octadecyl silica cartridges. To measure accurately and preconcentrate of Hg(II), it was important that the 4-bpdb ligand can be produced stable complex with Hg(II). The UV–vis spectrums of three standard solutions including 0.1 mM of Hg(II), 0.1 mM of 4-bpdb ligand and mixture 0.1 mM of Hg(II) and 0.1 mM of 4-bpdb ligand were investigated (Fig. 2). The difference between mercury complex spectrum with mercury and ligand spectrums indicated the complex is formed.

Some preliminary experiments showed that while the cartridge did not show any tendency to retain of Hg(II) ion in the absence of ligand, it was capable of retaining mercury 4-bpdb complex in the sample solutions quantitatively (the test solution used contained 0.02 mM of Hg(II) and 0.02 mM of 4-bpdb ligand in 15 mL deionized water). To obtain quantitative recoveries of Hg(II) on cartridge, the preconcentration procedure was optimized for various parameters such as the sample matrix, the amount of ligand, the type of eluent for eluting, the flow rates and the break through volume.

3.1. Effect of pH

The pH of aqueous phase is an important factor in a liquid–solid adsorption procedure. Changes of pH can influence the reaction between Hg and the complexing agent. To determine the effect of pH, pH of Hg(II) sorption onto C_{18} cartridge was investigated within the range of 2–8 using the model solution. Fig. 3 shows that mercury ions were effectively adsorbed in the range of $4 \leq pH \leq 5$.
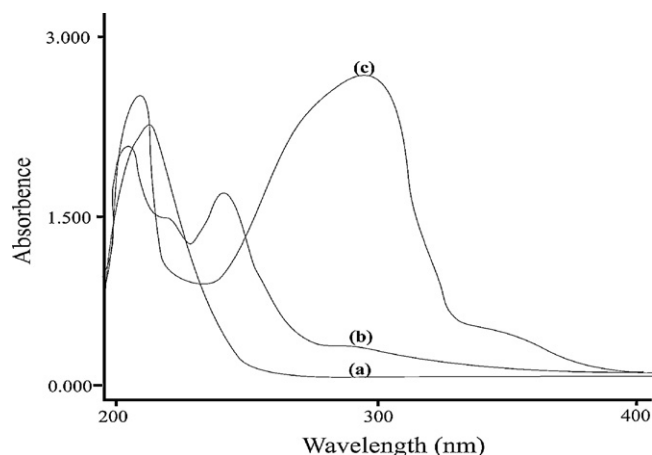

Fig. 2. Spectrums of (a) Hg(II); (b) ligand; and (c) complex.

Table 1
Effect of sample matrix on recovery of Hg(II)–4-bpdb complex on the C_{18} cartridge.

Sample matrix	Recovery%					
	Concentration (M)					
	0.00	0.0025	0.005	0.01	0.035	0.05
Acetate buffer	34	57	87	91	91	90
Formate buffer	34	57	87	92	91	90
Phosphate buffer	34	31	31	31	31	30
Potassium chloride	34	32	31	33	31	32

Conditions: mercury, $2\,\mu g\,mL^{-1}$; sample volume, 25 mL; sample pH, 4.5; eluent, 2.5 mL $0.01\,mol\,L^{-1}$ nitric acid; sample flow rate, $6\,mL\,min^{-1}$; and eluent flow rate, $3\,mL\,min^{-1}$.

The determination of mercury was carried out at pH 4.5. The pH of the analytical procedure was adjusted with a buffer solution of acetic acid–sodium acetate at 4.5. At these conditions, the determination of mercury had a good recovery. The recovery of adsorption decreased at pH higher than 6 due to forming mercury hydroxides.

3.2. Effect of sample matrix

The effect of sample matrix on the retention of mercury complex was investigated by adding acetate, formate and phosphate buffers and potassium chloride salt within the range of 0.0–0.05 M. The percentage of the recovery of the mercury ion was nearly constant with increasing or decreasing potassium chloride salt and phosphate buffer concentration while their pH was adjusted at 4.5 because the tendency of chloride and phosphate anions for the formation of non-charge ion pair with Hg(II)–4-bpdb complex was weak. But the percent recovery increased when acetate or formate buffers were added and reached a constant value over 91% in 0.005 M buffers (Table 1).

3.3. Effect of choosing eluent

To choose a proper eluent, 25 mL Hg(II) ion solution with 0.01 M acetate buffer were passed onto the column then the retained Hg(II) was stripped with 3 mL of methanol, ethanol, acetonitrile and 0.01 M solutions of hydrochloric, sulfuric and nitric acid (Table 2). Results showed that nitric acid solution was a proper elution solvent. As seen, all the experiments were carried out with 0.01 M nitric acid solution. To choose a suitable concentration of acid, the concentration of acid was investigated within the range of 0.001–0.1 M. The proper concentration of acid was 0.01 M HNO_3. To choose the proper volume of eluent, the retained Hg(II) ions on the column were stripped with varying volumes (1–6 mL) of 0.01 M HNO_3. The suitable volume of the elution solvent was 2.5 mL of 0.01 M HNO_3. Hence, the subsequent elution experiments were carried out with 2.5 mL of 0.01 M HNO_3.

Table 2
Effect of type and amount of eluent on extraction efficiency.

Eluent	% Recovery				
	Volume (mL)				
	1.5	2	2.5	3.5	4.5
HNO_3	68	88	91	90	90
HCl	15	22	21	20	21
H_2SO_4	28	35	44	42	44
Methanol	10	12	10	10	10
Ethanol	10	10	10	10	10
Acetonitrile	10	12	10	10	10

Conditions: mercury, $2\,\mu g\,mL^{-1}$; sample volume, 25 mL; sample pH, 4.5; concentration of all acids, $0.01\,mol\,L^{-1}$ nitric; sample flow rate, $6\,mL\,min^{-1}$; and eluent flow rate, $3\,mL\,min^{-1}$.
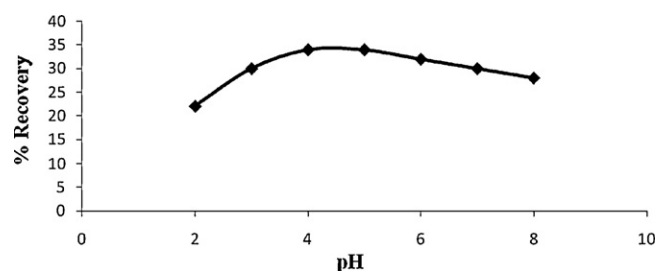

Fig. 3. Effect of pH on the recovery of mercury. Conditions: mercury, $2\,\mu g\,mL^{-1}$; sample volume, 25 mL; eluent, 2.5 mL $0.01\,mol\,L^{-1}$ nitric acid; sample flow rate, 6 mL min; and eluent flow rate, $3\,mL\,min^{-1}$.

3.4. Effect of flow rate of sample and eluent solutions

The flow rate of the sample and eluent affected the retention of mercury on adsorbing and desorbing. To investigate the effect of flow rate, 15 mL test solution was passed through the column at the optimum conditions (pH, eluent, etc.) with a peristaltic pump. The flow rates were adjusted within the range of $0.5–6.0\,mL\,min^{-1}$. It was found that the retention of the mercury ion did not change up to $6.0\,mL\,min^{-1}$ flow rate of sample practically. The recoveries of the analytes decreased slightly when the flow rate was over $6.0\,mL\,min^{-1}$. Thus, $6.0\,mL\,min^{-1}$ flow rate of the sample was employed in this work. Also the recoveries of the analytes decreased slightly when the flow rate of the eluent was over $3.0\,mL\,min^{-1}$, so a $3.0\,mL\,min^{-1}$ flow rate of the eluent was suitable.

3.5. Effect of amount of ligand on the recoveries

To investigate the effect of the amount of ligand on recovery, the amount of 4-bpdb was changed within the range of $0.5–5\,\mu g\,mL^{-1}$ in a $2\,\mu g\,mL^{-1}$ mercury solution. The recovery values of mercury ions increased with increasing amount of 4-bpdb (Fig. 4). The recovery of mercury was constant above $4.2\,\mu g\,mL^{-1}$ ligand. Hence, subsequent extraction experiments were carried out on $4.2\,\mu g\,mL^{-1}$ ligand.

3.6. Interference studies

To investigate the effect of interfering ion on recovery, 15 mL solutions which contained $2\,\mu g\,mL^{-1}$ Hg(II), $4.4\,\mu g\,mL^{-1}$ ligand, 0.01 M buffer and amounts of other ions were passed on column then the recommended procedure was followed (Table 3). The interfering species did not interfere with Hg(II) retention at the optimum effective parameters. The obtained results indicated that the C_{18} cartridge can be successfully used to extract Hg(II) from
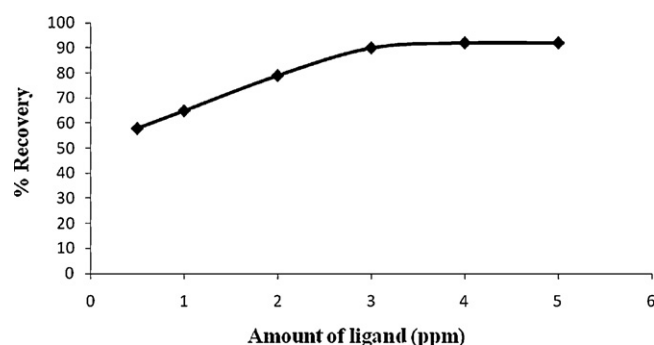

Fig. 4. Effect of the amount of ligand on the recovery of mercury. Conditions: mercury, $2\,\mu g\,mL^{-1}$; sample volume, 25 mL; sample pH, 4.5; eluent, 2.5 mL $0.01\,mol\,L^{-1}$ nitric acid; sample flow rate, $6\,mL\,min^{-1}$; and eluent flow rate, $3\,mL\,min^{-1}$.

Table 3
Effect of foreign ion on extraction efficiency.

Foreign ion	Foreign ion (mg L^{-1})	Recovery%
K$^+$	350	90
Na$^+$	15.9	91
Li$^+$	6.32	88
Ca^{2+}	1.12	88
Ba^{2+}	4.32	89
Sr^{2+}	28.1	88
Fe^{3+}	3.14	88
CH$_3$COO$^-$	5160	92
HCOO$^-$	257	91
Cl$^-$	8.31	90
PO$_4^{2-}$	384	90
NO^{3-}	15.3	91
Cu^{2+}	558	88
Cd^{2+}	281	89
Pb^{2+}	5.31	90
UO$_2^{2+}$	14.3	87

Conditions: mercury, 2 mg L^{-1}, other effective parameters are optimum.

Table 4
Determination of Hg(II) in water samples.

Sample	Added Hg(II) (ng mL^{-1})	Found (ng mL^{-1})	Eluent (mL)	Recovery%	P.f.	RSD%
Tap water	–	0.28	2.5	–	128	4.31
Tap water	4	4.25	2.5	89	128	4.28
Seawater	–	0.85	2.5	–	128	3.86
Seawater	4	4.76	2.5	89	128	3.22

Conditions: The measurement was performed at optimum effective parameters.

water sample before their determination by cold vapor atomic absorption.

3.7. Analytical performance

To investigate the effect of volume on the adsorption of sample solution, 50 μg of Hg(II) ion and 110 μg of 4-bpdb ligand in 100, 200, 300 and 320 mL water were dissolved and the recommended procedure was followed. The experiments showed that the break-through volume for the method was greater than 320 mL. To investigate the maximum capacity of the cartridge, 25 mL of sample solutions containing 4.5–15.2 μg mL^{-1} of Hg(II) ion and 9.9–33.44 μg mL^{-1} of 4-bpdb were passed through the cartridge

Table 5
Determination of Hg(II) in fish samples.

Sample	Added Hg(II) (ng mL^{-1})	Found (ng mL^{-1})	Eluent (mL)	Recovery%	RSD%
Ton	–	1.89	2.5	–	3.10
Ton	2	3.85	2.5	94	2.98
Trout	–	ND	2.5	–	–
Trout	2	1.97	2.5	98	3.28

Conditions: The measurement was performed at optimum effective parameters.

Table 6
Determination of Hg(II) in milk and sausage.

Sample	Added Hg(II) (ng mL^{-1})	Found (ng mL^{-1})	Eluent (mL)		RSD%
Milk	–	0.16	2.5	–	4.21
Milk	2	2.13	2.5	86	3.54
Sausage	–	ND	2.5	–	–
Sausage	2	1.98	2.5	98	4.45

Condition: The measurement was performed at optimum effective parameters.

and the recommended procedure was followed. The maximum capacity of the cartridge was found to be 9.86 μg mL^{-1} of Hg(II) ion. The calibration graphs were constructed with five standard solutions containing Hg(II) ion complex according to the general procedure and the calibration curve equation for mercury was $A = 0.1022C + 0.0232$ (μg L^{-1}), $R = 0.994$. The dynamic linear range of the method was from 6.25×10^{-3} to 3.1×10^{-1} μg L^{-1}.

4. Applications

4.1. Analysis of water samples

The present method was applied for preconcentrating and determining Hg(II) ions in water samples. Two water samples from Khazar and tap water (Karaj city) were subjected to the recommended procedure. The pH of the samples was adjusted to optimum pH level before the standard addition then Hg(II) ions were preconcentrated and determined. In the standard addition method, 500 mL samples were spiked with 4 ng mL^{-1} of Hg(II) ions then the added samples were loaded onto the cartridge (Table 4).

Table 7
The comparison of the proposed method with other extraction methods.

Method	DOL (ng mL^{-1})	LDR (ng mL^{-1})	RSD (%)	Ads capacity (mg g^{-1})	Reference
The proposed method	1.87×10^{-3}	0.0062–0.31	2.98–4.45	0.49	–
C$_{18}$ modified-SPE	2.5×10^{-3}	–	–	–	[25]
Silica modified-SPE	4.75×10^{-3}	0.02–1	1	200	[26]
C$_{18}$ modified-membrane	3.8×10^{-3}	–	3.1	–	[27]
Functionalized silica gel-SPE	0.90	1–1500	3	8	[28]
Chelating resin-SPE	6.00×10^{-3}	0.1–30	3.5	–	[29]
Silica modified-SPE	–	–	–	340–700	[30]
Functionalized silica gel-SPE	–	–	–	3.652	[31]
C$_{18}$-SPE	10.92	32.9–263.9	3.2	0.52	[15]
Microextraction	0.01	–	6.1	–	[32]
Gold-wire microextraction	0.006	–	4.6	–	[33]
Functionalized silica gel-SPE	0.90	1–1500	3	–	[28]
Solid phase spectrophotometry	0.024	0.062–250	2.4	–	[34]
Membrane	4	–	0.1–2	–	[35]
Cloud point extraction	4.00×10^{-3}	–	3–5	–	[36]
Cloud point extraction	4.00×10^{-3}	–	3.4	–	[37]
Ionic liquid based-preconcentration	2.3	–	2.8	–	[38]
IIP	0.39	–	–	4.46	[39]
IIP	0.006	0.02–1	5–9	6.4	[40]
IIP	2.875			25	[41]
IIP	0.05	0.13–25	2.4	41	[42]

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