

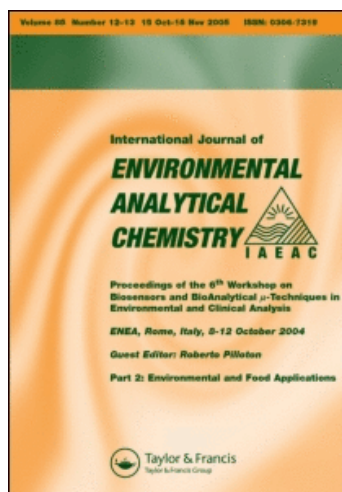
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Separation, pre-concentration and determination of trace amounts of lead(II) ions in environmental samples using two functionalised nanoporous silica gels containing a dipyridyl sub-unit

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Separation, pre-concentration and determination of trace amounts of lead(II) ions in environmental samples using two functionalised nanoporous silica gels containing a dipyridyl sub-unit

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In this study, two functionalised nanoporous silica gels containing dipyridyl sub-unit (SiL1 and SiL2) as selective solid-phase extraction materials for separation, pre-concentration and determination of trace levels of Pb(II) ions by inductively coupled plasma optical emission spectroscopy (ICP-OES) was investigated. The experimental parameters including pH, amounts and type of sorbent, sample volume, eluent type and interfering ions on the recovery of the target analytes were investigated, and the optimal experimental conditions were established. Under the optimised operating conditions with the SiL2 as sorbent, an enrichment factor of 300 was obtained. The detection limit based on three times standard deviations of the blanks was 150 ng L^{-1} . The proposed method was applied to the determination of lead in natural and wastewater samples with satisfactory results (recoveries greater than 96.5%, RSDs lower than 5.0%).

Keywords: solid-phase extraction; pre-concentration; lead; nanoporous silica gel; inductively coupled plasma

1. Introduction

Heavy metals are environmental pollutants, threatening the health of human populations and natural ecosystems alike. The increasing level of heavy metals in the environment represents a serious threat to human health, living resources and ecological systems. Removal of these species from the environment is thus a major focus of waste treatment and clean-up efforts. Lead is now known to be a poison absorbed into the bloodstream, from where, especially in the case of inorganic lead, it is distributed to soft tissue, bones and teeth. Organic forms of lead are fat soluble and therefore have a particular tendency to concentrate in the brain [1]. Thus, there has been an increasing interest in the development of sensitive, reproducible and accurate analytical methods for the determination of trace lead in environmental and biological samples [2,3].

Solid-phase extraction (SPE) is an attractive separation/pre-concentration technique for heavy metal ions with some significant advantages (simplicity, flexibility, economic,

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rapid, higher enrichment factors, absence of emulsion, low cost because of lower consumption of reagents, more importantly environment-friendly). Various SPE materials have been effectively used for the pre-concentration and separation of heavy metal ions at trace levels [4]. An efficient adsorbing material should consist of a stable and insoluble porous matrix having suitable active groups that interact with heavy metal ions. Silica-based organic-inorganic hybrids are ideal attractive composite materials. They combine in a single solid both the properties of a rigid three-dimensional silica network and the particular chemical reactivity of the organic component(s) [5–7]. These materials illustrate high surface area (surface areas in excess of $1000\text{ m}^2\text{ g}^{-1}$) silica frameworks, containing pore channels with diameters ranging from 2 to 10 nm. In particular, the design of silica-based adsorbents for the separation of toxic heavy-metal ions in aqueous solutions is a subject that has been intensively investigated [8]. For this purpose, a variety of organic functional groups were grafted or incorporated onto the surface of the nanostructured channels, for example 5-amino-1,3,4-thiadiazole-2-thiol [9], alizarin violet [10], thioacetamide [11], humic acid [12], thiosalicylic acid [13], p-dimethylaminobenzaldehyde [14], 2, 3-dihydroxybenzaldehyde [15], ofloxacin [16] and diaminothiurea [17]. Perhaps the greatest interest in these materials arises from the fact that most of them can be manufactured quite easily at room temperature by sol-gel processing. This processing involves the hydrolysis and condensation of silicon alkoxide precursors. The selectivity of the functionalised silica gels towards certain metal ions is attributed to several well-known factors such as the size of the organic modifier [18], the activity of the loaded surface groups [19], the type of the interacting donor atom and metal ion and the reported well-known phenomenon of hard–soft acid–bases [20].

Recently, we described the use of functionalised nanoporous silica gels for the assay of Cu(II) [21], Ag(I) [22], Hg(II) [23] and Ce(III) [24] in aqueous solutions. In this study, we examine the Pb-binding properties of two dipyriddy-functionalised nanoporous silica gels with different grafting moiety (Figure 1), $\equiv\text{Si}(\text{CH}_2)_3\text{N}=\text{C}(\text{C}_5\text{H}_4\text{N})_2(\text{SiL1})$ and $\equiv\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{N}=\text{C}(\text{C}_5\text{H}_4\text{N})_2(\text{SiL2})$. The applicability of these functionalised silica gel sorbent to selective solid-phase extraction of Pb(II) are described and discussed in detail. These sorbent materials contained dipyriddy groups covalently attached to the solid framework via an aminopropyl chain. The presence of rigid heterocyclic molecules such as dipyriddy, carrying hard N-donor atoms, has shown to have a marked influence on the coordination geometry at the metal centre [25].

2. Experimental

2.1 Apparatus

A Model Optima 2100 DV inductively coupled plasma optical emission spectrometer (ICP-OES) (PerkinElmer Instruments, USA) was used for the determination of lead. The operating conditions and analytical wavelength are summarised in Table 1. The pH values were measured with a Metrohm pH-meter (model: 713, Herisau, Switzerland) supplied with a glass combined electrode.

2.2 Reagents

All reagents used were of analytical grade. All solutions were prepared using distilled water. Organic solvents were of synthesis grade and were purchased from Sigma-Aldrich.

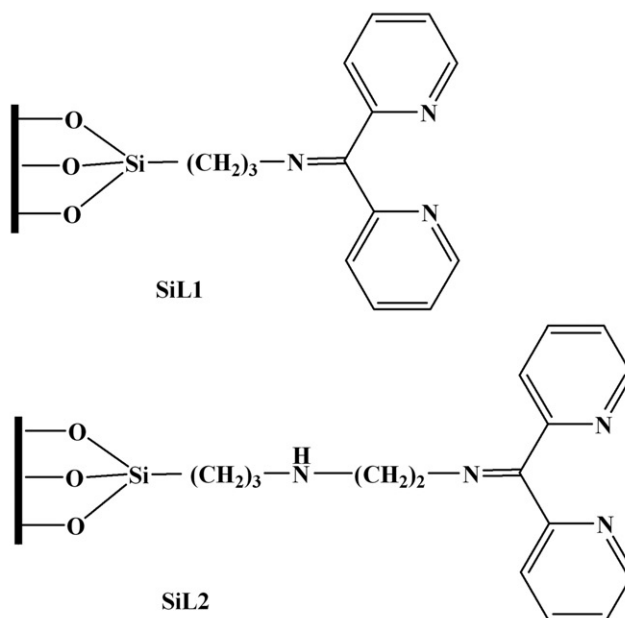


Figure 1. Chemical structures of SiL1 and SiL2.

Table 1. ICP-OES operating conditions.

Parameters	Values
RF generation power (W)	1300
Frequency of RF generator (MHz)	27.12
Coolant gas flow rate (L min ⁻¹)	5
Carrier gas flow rate (L min ⁻¹)	0.6
Auxiliary gas flow rate (L min ⁻¹)	0.2
Observation height (mm)	15
Solution uptake rate (mL min ⁻¹)	1.0
Max integration time (s)	15
Analytical wavelength (nm)	220.4

Working solutions were prepared from the stock solution by serial dilutions with distilled water. A stock standard acetic acid/acetate buffer solution (0.1 mol L⁻¹, pH 5.5) for adjustment of pH solutions was used. Silica gel 60 with specific surface area 500 m²/g and hydrochloric acid and 3-(triethoxysilyl)-propylamine were purchased from Merck company. 2,2'-dipyridyl ketone 99% was purchased from Sigma-Aldrich. The nitrate salts of the cations used (all from Merck). The standard reference material (GBW08301, river sediment) was provided as a gift by the Standard Research Center (Tehran, Iran).

2.3 Preparation and characterisation of SiL1 and SiL2

SiL1 and SiL2 were prepared according to the previously reported methods [21,22]. For the preparation of SiL1 and SiL2, a nanoporous silica gel was activated by refluxing

in hydrochloric acid (4 mol L^{-1}) for 24 h, where it was then washed with distilled water and dried completely. For the synthesis of SiL1, activated silica gel with N-(2-aminoethyl)-3-aminopropyl-trimethoxy silane was refluxed in dry toluene. The attained solid, aminopropyl silica gel (APSG), was filtered and washed with hot toluene and then dried. Then APSG was allowed to react with of 2,2'-dipyridyl ketone in refluxing toluene. The solid was filtered and washed with warm ethanol and dried in vacuum line. For the synthesis of SiL2, the APSG was washed with warm toluene and then was allowed to react with 2,2'-dipyridyl ketone in refluxing toluene under the argon atmosphere. The infrared spectrums of SiL1 and SiL2 showed bands at 1628 and 1632 cm^{-1} respectively, which are characteristic of $\nu_{\text{C=N}}$. The quantities of molecules, attached to the nanoporous silica after drying under vacuum, were calculated from the elemental analysis and were 0.18 and 0.13 mmol g^{-1} for SiL1 and SiL2, respectively.

2.4 Batch operation mode

Aliquots of 100 mL of sample solutions containing $10 \mu\text{g}$ of Pb(II) were prepared and the pH value was adjusted to 5.5 with 5.0 mL acetate buffer solution (0.1 mol L^{-1}). Then, 10.0 mg of dipyrldyl-functionalised nanoporous sorbent was added into the solution, shaken for the specific time and filtered through a cellulose acetate filter ($0.20 \mu\text{m}$ pore size, Advantec MFS Inc. CA, USA) and detected with ICP-OES. Blank experiments on non-functionalised silica gel were carried out and Pb(II) analysis were also performed to confirm Pb uptake by the materials.

3. Results and discussion

3.1 Type of modifier

The chemical and structural features of a ligand can be tuned by incorporating donor atoms in the chelating agent or, thereby promising the stability and selectivity of the resulting complexes, as well as forcing metal ions to adopt typical coordination geometry [26]. In this work we found out that two functionalised silica gels containing a dipyrldyl sub-unit (SiL1 and SiL2), recently synthesised in our laboratories, can act as excellent sorbent for selective complexation and SPE of low levels of Pb(II) ions. Some preliminary experiments were carried out in order to investigate the quantitative retention of Pb(II) ions by the proposed SPE protocol in the presence of SiL1, SiL2 and unmodified silica gel. It was found that, while the unmodified silica gel show very low tendency for the extraction of lead ions (i.e. some 18%), the SiL1 and SiL2 are capable to retain lead ions in the sample solution quantitatively (the test solution contained $10 \mu\text{g}$ of Pb(II) in 100 mL water). The extraction ability of Pb(II) ions was found to be dependent on the structure of the sorbent. Table 2 shows that, under similar experimental conditions, the efficiency of the extraction of Pb(II) ions decreased in the order $\text{SiL1} < \text{SiL2}$. This could be mainly due to the increased stability of the Pb(II) ion complex with SiL2, in comparison with the corresponding complex with sorbent SiL1. Therefore further experiments were carried by SiL2. SiL1 and SiL2 have difference in extension of the pendant ligand and presence of an extra secondary amino group in SiL2. Pb(II) is trapped by the appropriately oriented ring nitrogens of the dipyrldyl units. It is believed that the increased length of ethylene diamine arm with an addition of nitrogen donor atom may cause increasing efficiency of Pb(II) uptake. However, it is interesting to note that the coordinating properties of the dipyrldyl

Table 2. Effect of the sorbent structure on the recovery of 10 µg of Pb(II) in 100 mL water at pH 5.5.

Sorbent	Recovery (%)	RSD (%)
SiL1	64	4.8 ^a
SiL2	99.5	3.6
Unmodified SiO ₂	18	5.9

Note: ^aRSD of three replicate experiments.

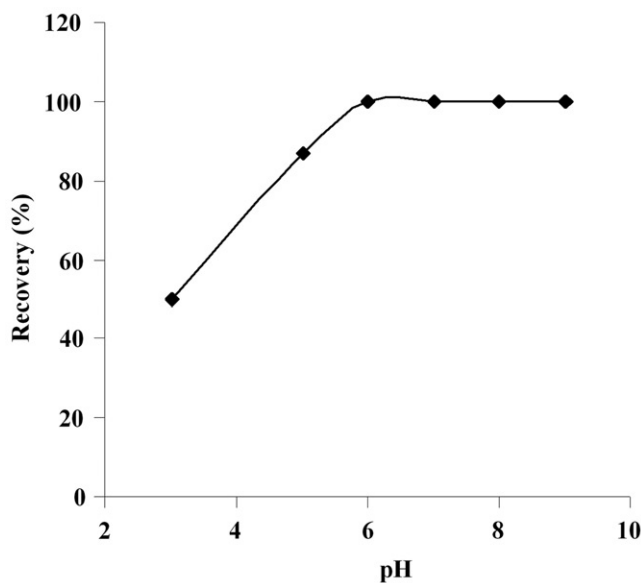


Figure 2. Effect of pH on adsorption of 100.0 µg L⁻¹ Pb(II) on SiL2. Experimental conditions: SiL2 sorbent: 10 mg, Shaking time: 5 min, pH: 5.5, Temperature: 25°C.

derivatives in their free form (in the solution) as well as in their bonded form on the silica surface are more or less different.

3.2 Effect of pH

In the solid-phase extraction studies, the influence of pH of the aqueous solution is one of the main factors for quantitative recoveries of heavy metal ions [15,27]. Due to this important point, the influences of pH on the recoveries of lead were investigated at the pH ranges 3–9 for 10.0 mg of the sorbents with the test solution contained 10 µg of Pb(II) in 100 mL water. The higher pH values were not studied because of the precipitation of lead ions in the test solution. Moreover, functionalised silica gels are not stable in high alkaline solutions due to the breaking of the Si–O–Si bonds by hydroxide ions attack [28]. pH of the solution was adjusted at the required value by adding 0.1 mol L⁻¹ sodium hydroxide and/or 0.1 mol L⁻¹ acetic acid. As can be seen in Figure 2, extraction was nearly constant

Table 3. Effect of the eluent on the recovery of lead.

Eluents	Volume (mL)	Recovery (%)
HCl 1 mol L ⁻¹	5	71.3 ± 3.5 ^a
HCl 1 mol L ⁻¹	10	91.3 ± 3.1
HNO ₃ 1 mol L ⁻¹	5	97.8 ± 3.8
HNO ₃ 1 mol L ⁻¹	10	99.6 ± 2.4
CH ₃ COOH 1 mol L ⁻¹	5	49.4 ± 2.3
CH ₃ COOH 3 mol L ⁻¹	10	62.4 ± 3.6
Na ₂ S ₂ O ₃ 1 mol L ⁻¹	10	48.1 ± 2.7

Note: ^aMean ± standard deviation ($n=3$).

and quantitative in the pH range of 6.0–9.0. At lower pH ($\text{pH} < 6$), the stability of complex formation between the sorbent and Pb(II) due to protonation of the amino and bipyridyl groups is reduced. Therefore, the extraction of lead decreased. Hence, pH of 5.5 (0.05 mol L⁻¹ acetate buffer) was chosen as the optimum pH for extraction.

3.3 Choice of eluent

In order to choose the most effective eluent for desorbing lead ion from the sorbent surface, aliquots of 100 mL of solution containing 10 µg Pb(II) was contacted with 5.0 mg of SiL2. A series of selected eluent solution such as nitric acid, hydrochloric acid, acetic acid and sodium thiosulfate was used. The amount of lead ion back-extracted into the liquid phase by each eluent was measured using ICP-OES. Percentage recoveries of lead ion were calculated for each sample. The results (Table 3) showed that recovery was the best when nitric acid was used as eluent. Therefore, 10 mL nitric acid (1 mol L⁻¹) was selected as eluent for further studies.

3.4 Effect of the sample volume

In order to investigate the possibility of concentrating low concentrations of lead from large volumes, the maximum applicable volume must be determined. For this purpose, the effect of the sample solution volume on the recovery was studied by keeping the total amount of Pb(II) uptake constant (10 µg). The quantitative recoveries were obtained for sample volume of 1500 mL. Therefore, the pre-concentration factor was 300 for Pb(II) since the final elution volume was 5.0 mL.

3.5 Effect of the amount of SiL2

To check the effect of the amount of SiL2 on quantitative retention of analyte different amounts of sorbent (ranging from 2.0 to 30.0 mg) were added into the solution following the experimental method. The optimal amount of the sorbent which must be used for the quantitative recovery of 10 µg lead ion from aqueous sample solutions was found to be approximately 5 mg or more. The use of less than 5 mg of the sorbent, however, resulted in considerable decrease in the recovery of lead ions. The results showed that the extraction of Pb(II) was quantitative by using only 5.0 mg of sorbent. Subsequent extraction

Table 4. Tolerance limits of coexisting ions for 100.0 $\mu\text{g L}^{-1}$ Pb(II) solution at pH 5.5.

Coexisting ions	Tolerance limits (mg L^{-1})
Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+}	> 1000
Cd^{2+} , Ni^{2+} , Co^{3+}	300
Cr^{3+} , Al^{3+}	500
Tl^+ , Ag^+ , Fe^{3+}	40
Hg^{2+} , Cu^{2+}	25
NO_3^- , Cl^- , Br^- , CH_3COO^-	> 1000
PO_4^{3-}	200

experiments were carried out with 10.0 mg of SiL2 in order to achieve higher capacity and to account for other extractable species.

3.6 Adsorption capacity

The sorption capacity for lead ions was determined by shaking 10 mg of the SiL2 with a 100 mL of 10 $\mu\text{g mL}^{-1}$ Pb(II) ion solution at pH 5.5 for 5 min according to the recommended batch equilibrium procedure at room temperature. The loading capacity of the SiL2 for lead ions was calculated from the different batch experiments ($n=5$). The average value was 151 mg g^{-1} (RSD = 4.9%).

3.7 Effect of equilibrium time

In order to investigate the effect of shaking time on the extraction efficiency, extraction for a series of solutions containing 10 μg Pb(II) was carried out. The results showed that the shaking time from 1 to 20 min has no effect on the extraction efficiency of lead and the extraction was quantitative. Although the extraction process can be continued during the filtration, however, the results showed that extraction was quantitative and very fast in all cases. Thus, the mixtures have been shaken for 5 min to reach equilibrium in the subsequent experiments.

3.8 Effect of coexisting ions

In order to examine the effect of the various tested metal ions in the optimum conditions, extraction of lead ions in the presence of some selected metal ions was studied. In these experiments, 100 mL of solutions containing 10 μg of Pb(II) and various amounts of interfering ions were treated according to the recommended procedure. An ion was considered to interfere when its presence produced a variation in the extraction recovery of sample more than $\pm 5\%$. The results in Table 4 showed that except Hg(II) and Cu(II), in excess of 400-fold of all investigated ions had no significant interferences in the extraction and determination of Pb(II) and this high selectivity enables the method for accurate and precise determination of Pb(II) ions in real samples.

3.9 Reusability and stability of SiL2

A series of sorption/desorption experiments were performed to understand the reusability of the sorbent SiL2. After sorption, the sorbent was treated with 10 mL nitric acid (1 mol L^{-1}) to desorb Pb(II) and this sorption/desorption procedure was repeated four times. After each desorption step, the sorbent was washed with alkali (0.001 mol L^{-1} NaOH) to remove nitric acid and condition sorbent. It was determined that there was no decrease in sorption capacity after four consecutive uses of 10.0 mg of SiL2 ($\text{RSD} = 4.8$). On storing for six months under dark and dry conditions, the stability of sorbent was excellent and adsorption capacity did not change significantly.

3.10 Precision, limits of detection and quantification

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as the amount of analyte necessary to yield a signal equal to three times (3σ) and ten times (10σ) the standard deviation of the blank signals, respectively. In determining lead ion with ICP-OES, the value of LOD and LOQ and the range of linearity were 42, 145 and $100\text{--}800 \mu\text{g L}^{-1}$, respectively. In optimised conditions, using sample volume of 1500 mL and enrichment factor of 300, an LOD of 150 ng L^{-1} and an LOQ of $0.5 \mu\text{g L}^{-1}$ were obtained for the determination of lead. Ten replicate extractions and measurements of $10 \mu\text{g}$ of Pb(II) ion in 100 mL water solution gave a RSD of 4.2%. Comparable results were obtained from other solid phase extraction studies in literature (Table 5).

3.11 Real sample analysis and analytical performance

The calibration curves used to determine metal ions with ICP-OES were made by measuring the emission of the working calibration solution (without any enrichment on the present matrix) at optimum operation parameters of the instrument and the solution conditions. To evaluate the capability of the method for real samples with different matrices containing varying amounts of diverse ions, the method was applied to the separation, pre-concentration and determination of lead from 100 mL of water samples. The suitability of the proposed method for the analysis of different water samples was checked by spiking samples with 50.0 and $100.0 \mu\text{g L}^{-1}$ of lead. For tap, mineral and waste water samples, the recoveries of the methods were in the ranges of 96.6–97.9%, 98.1–102.4% and 96.5–103.2%. In all experiments RSDs were lower than 5.0%. The data obtained with the proposed method were presented in Table 6. The lead content obtained from three replicate measurements in one certified reference material (GBW08301, river sediment) was $78.3 \pm 3.6 \mu\text{g g}^{-1}$, which was found to be in satisfactory agreement with the certified value of the sample ($79 \mu\text{g g}^{-1}$). The results indicate that the proposed method can be reliably used for the determination of lead in various natural water matrices.

4. Conclusion

In this work, two functionalised nanoporous silica gels containing a dipyriddy sub-unit, as new sorbents has been used for separation/pre-concentration purpose in the determination of lead. It is shown that the SiL2 has high capacity, good stability and fast adsorption and desorption kinetics. A high pre-concentration factor of 300 was obtained easily by this method. The proposed method can be applied to natural water, wastewaters and/or other

Table 5. Pre-concentration procedures using solid-phase extraction for the determination of lead.

Sorbent	Technique	LOD (ng L ⁻¹)	Enrichment factor	Real samples	Ref.
Pyrogallol red loaded active carbon Chromosorb 102	FAAS ^a	1.0	100	Wastewater	[29]
Dithizone co-crystallised with naphthalene	FAAS	2000	–	Soil and water samples	[30]
Naphthalene/alizarin red	ICP-OES ^b	47,000	13	Saline matrices	[31]
Sephadex A-25 loaded with thiocalix[4]arenetetrasulfonate	ICP-OES	53,000	40	Seawater	[32]
Octadecyl-bonded silica modified by [bis(2,4-dimethoxy benzaldehyde) ethylen diimine] (TDSE)	GF-AAS ^c	200	100	Certified reference seawater	[33]
<i>o</i> -Dihydroxybenzene anchored on silica gel	ICP-OES	150	500	Water, wastewater, black tea and hot pepper	[34]
Silica gel chemically modified with zirconium phosphate	FAAS	4000	250	River and tap water samples	[35]
Activated carbon	FAAS	6100	30	Industrial and river waters	[36]
Poly(aminophosphonic) acid	FAAS	3000	63	Water	[37]
Poly(8-HQ-SO ₃ H)	FAAS	6300	14	Alloy	[38]
Diphenylthiocarbazone-anchored on poly-meric microbeads	FAAS	1000	115	Drinking water	[39]
SiL2	GC-AAS ^d	280	180	Synthetic sample	[40]
	ICP-OES	151	300	Wastewater and Certified reference sediment	This work

Notes: ^aFlame atomic absorption spectrometry.
^bInductively coupled plasma optical emission spectrometry.
^cGraphite furnace atomic absorption spectrometry.
^dGas chromatography–atomic absorption spectrometry.

Table 6. The results for tests of addition/recovery for Pb(II) determination in some real samples (sample volume: 100 mL, final volume: 10 mL ($n = 3$)).

Sample	Amount added ($\mu\text{g L}^{-1}$)	Amount found ($\mu\text{g L}^{-1}$)	Recovery (%)
Tap water ^a	0	0	—
	50	48.3 (± 1.4) ^d	96.6
	100	97.9 (± 2.7)	97.9
Mineral water ^b	0	0	—
	50	51.7 (± 2.2)	102.4
	100	98.1 (± 3.5)	98.1
Wastewater ^c	0	24.1 (± 1.2)	—
	50	75.7 (± 3.7)	103.2
	100	120.6 (4.2)	96.5

Notes: ^aTap water samples of Tehran, Iran.

^bMineral water samples from the Damash Co. (Gilan, Iran).

^cWastewater samples from the Petrochemical Bandar Emam Company, Iran.

^dStandard deviation (S.D.) of three replicate experiments.

samples having lead levels higher than the detection limit of the method. The advantage of the proposed method was that it is a convenient and low cost one.

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