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Preconcentration of Pb(II) by Graphene Oxide with Covalently Linked Porphyrin Adsorbed on Surfactant Coated C_{18} before Determination by FAAS

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ABSTRACT

A simple, highly sensitive, accurate and selective method for determination of trace amounts of Pb(II) in water samples is presented. A novel Graphene oxide with covalently linked porphyrin solid-phase extraction adsorbent was synthesized by covalently linked porphyrin onto the surfaces of graphite oxides. The stability of a chemically (GO-H_2P) especially in concentrated hydrochloric acid was studied which used as a recycling and pre-concentration reagent for further uses of (GO-H_2P). The method is based on (GO-H_2P) of Pb(II) on surfactant coated C_{18}, modified with a porphyrin-treated graphite oxides (GO-H_2P). The retained ions were then eluted with 4 ml of 4 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) at 283.3 nm for Pb. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions on chelation and recovery were investigated. 1.5 g of surfactant coated C_{18} adsorbs 40 mg of the Schiff's base which in turn can retain 15.2 ± 0.8 mg of each of the two ions. The limit of detection (3σ) for Pb(II) was found to be 3.20 ng l^{-1}. The enrichment factor for both ions is 100. The mentioned method was successfully applied on determination of lead in different water samples. The ions were also speciated by means of three columns system.

Keyword: Determination of lead; Preconcentration; Graphene oxide with covalently linked porphyrin (GO-H_2P); C18; Solid-phase extraction; FAAS.

1. INTRODUCTION

Trace amounts of metals are present in natural biosphere. Presence of some of these metals in very low concentrations and certain oxidation states are necessary. Higher concentrations and other oxidation states might be toxic and dangerous. Unfortunately the difference between these two levels is very small [1, 2]. Lead occurs in nature mostly as PbS. It is used in batteries, tetraethyl lead,

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(*) Corresponding Author - e-mail: alimoghimi@iauvaramin.ac.ir guns, solders and X-ray instruments [3]. Copper on the other hand occurs as CuS, CuS_2, $CuFeS_2$, $CuSO_4.5H_2O$ and other forms. More than 75% of copper production is used in electrical industries. It is also used in pigments, metallic blends and household. Hence determination of lead and copper in industry and environment are both very important. A preconcentration step is advisable in trace analysis. Lead and copper have been so far determined by various methods such as spectrophotometry [5, 6], liquid-liquid extraction [7-9], cloud point extraction [10, 11], and electrochemical measurements [12]. Some of these methods suffer from poor limit of detection and harmful solvents are being used in some others. On the other hand, effect of foreign ions on theanalyte is not negligible in many instances. In such cases, preconcentration of the analyte makes the determination easier and the composition of the sample less complicated. In recent years, solid phase extraction (SPE) has offered attractive possibilities in trace analysis. It has reduced the solvent and time consumption drastically [13, 14]. In order to increase the preconcentration or extraction power of SPE an organic or inorganic ligand is used in conjunction with the sorbont. Some of the ligands used for determination of lead and copper are: Amberlit XAD-2 with 3,4-dihidroxybenzoic acid [15], silicagel modified with 3-aminopropyl triethoxysilane [16], Levatit with di(2,4,4-trimethylpentyl)phosphinic acid [17], silicagel functionalized with methyl thiosalicylate [18], silicagel modified with zirconium phosphate [19] and C_{18} diskes modified with a sulfur containing Schiff's base [20, 28-32].

Comparing these examples with the presented method, they have either a lower enrichment factor or a higher limit of detection. On the other hand, the C_{18} disks can be used only a few times, while the proposed sorbent could be used more than 50 times without loss of efficiency.

Surfactant coated alumina modified with chelating agents has been used for extraction and preconcentration of environmental matrixes and metals [21, 22]. Here, the surfactant molecules have been associated on the alumina surface forming an admicell or hemimicell. Organic molecules attach themselves on the hydrophobe part and low concentration of metallic elements also on the hydrophobe part, which includes the chelating agent [22]. The Schiff's bases which are obtained from salisylaldelyde are known as multidentate ligands. These agents can form very stable complexes with transition metal ions [23, 24].

The main goal of the present work is development of a fast, sensitive and efficient way for enrichment and extraction of trace amounts of Pb(II) from aqueous media by means of a surfactant coated C_{18} modified with, Graphene oxide with covalently linked porphyrin (GO-H_2P). Such a determination has not been reported in the literature. The structure of Graphene oxide with covalently linked porphyrin (GO-H_2P) (shown in Scheme 1). Such a determination has not been reported in the literature. The structure of Graphene oxide with covalently linked porphyrin (GO-H_2P) is shown in Figure 1. The chelated ions were desorbed and determined by FAAS. The modified solid phase could be used at least 50 times with acceptable reproducibility without any change in the composition of the sorbent, GO-H_2P or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C_{18} SPE mini-column.

2. EXPERIMENTAL

2.1. Reagents and apparatus

Graphite oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30 lm) by the Hummers [2]. Method and dried for a week over phosphorus pentoxide in a vacuum desiccators before use. 4-Isocyanatobenzenesulfonyl azide was prepared from 4-carboxybenzenesulfonyl azide via a published procedure [17]. All solutions were prepared with doubly distilled deionized water from Merck (Darmstadt, Germany). C_{18} powder for chromatography with diameter of about 50 μm obtained from Katayama Chemicals from supelco. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water. Sodium Dodecyl sulfate (SDS) obtained from Merck (Darmstadt, Germany) and used without any further purification.

2.2. Synthetic procedures

2.2.1. Preparation of GO-H_2P

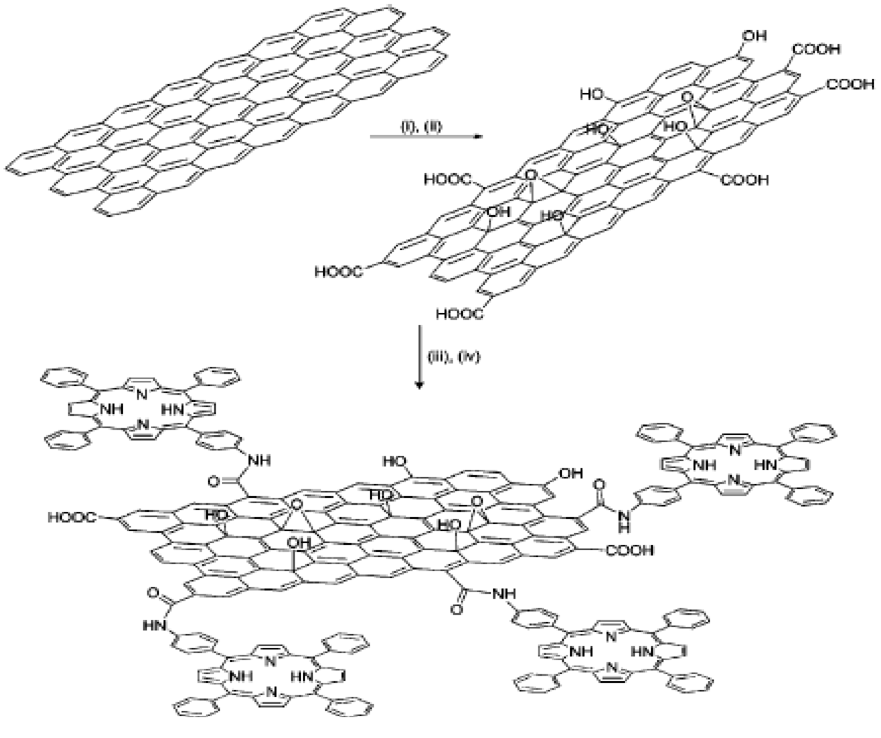
GO (15 mg) was stirred in 20 mL of oxalyl chloride at 80°C for 24 h to activate the carboxylic units by forming the corresponding acyl chlorides. Then, the reaction mixture was evaporated to remove the excess oxalyl chloride and the brownish remaining solid (GO-COCl) was washed with anhydrous tetrahydrofuran (THF). After centrifugation, the resulting solid material was dried at room temperature under vacuum. For the covalent coupling between the free amino function of H_2P and the acyl chloride of GO, 15 mg of GO-COCl was treated under anaerobic, dry conditions with 7 mg of H_2P dissolved in 6 ml of dry THF at room temperature for 72 h. The hybrid material, namely GO-H_2P, was obtained as brown-gray solid by filtration of the reaction mixture through 0.2 mm PTFE filter and the filtrate was sufficiently washed with methylene chloride (4×20 mL) to remove non-reacted free H2P and then with diethyl ether (2×20 mL) before being dried under vacuum.

2.2.2. Column preparation

GO-H_2P (40 mg) was packed into an SPE mini-column (6.0 cm × 9 mm i.d., polypropylene). A polypropylene frit was placed at each end of the column to prevent loss of the adsorbent. Before use, 0.5 mol L^{-1} HNO_3 and DDW were passed through the column to clean it.

2.3. Apparatus

The pH measurements were conducted by an ATC pH meter (EDT instruments, GP 353) calibrated against two standard buffer solutions of pH 4.0 and 9.2. Infrared spectra of GO-H_2P were carried out



Scheme 1: *A schematic illustration for the preparation of GO with covalently linked H_2P. (i) H_2SO_4/HNO_3 (2 : 1 v/v), (ii) $KClO_3$, 96 h, (iii) $(COCl)_2$, 80°C, 24 h, (iv) 5-(4-aminophenyl)-10,15,20-triphenyl-21,23H-porphyrin, THF, r.t., 72 h.*

from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions except Zn(II) were performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer. Zn(II) determinations were performed by a Varian Spect AA-10. Raman spectrophotometer analysis was performed with a Perkin-Elmer.

2.3.1. Preparation of admicell column

To 40 mL of water containing 1.5 g of C_{18}, 150 mg of the above Schiff base-chitosan grafted multiwalled carbon nanotubes was loaded after washing acetone, 1 mol L^{-1} HNO_3 solution and water, respectively, solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO_3 and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained C_{18} was washed three times with water, then with 5 mL of 4 M HNO_3 and again three times with water. The prepared sorbent was transferred to a polypropylen tube (i.d 5 mm, length 10 mm). Determination of Pb^{2+} contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hallow cathode lamp(HI-HCl) according to the recommendations of the manufacturers. These characteristics are tabulated in (Table 1). A metrohm 691 pH meter equipped with a combined glass calomel electrode was used for pH measurements.

Table 1: *The operational conditions of flame for determination of lead.*

Slit width	0.7 nm
Operation current of HI-HCL	10 mA
Resonance fine	283.3
Type of background correction	Deuterium lamp
Type of flame	Air/acetylene
Air flow	7.0 mL.min^{-1}
Acetylene flow	1.7 mL.min^{-1}

2.3.2. Procedure

The pH of a solution containing 100 ng of each Pb(II) was adjusted to 2.0. This solution was passed through the admicell column with a flow rate of 5 mL min^{-1}. The column was washed with 10 mL of water and the retained ions were desorbed with 1 mL of 4 M HNO_3 with a flow rate of 2 mL min^{-1}. The desorption procedure was repeated 3 more times. All the acid solutions (4 mL all together) were collected in a 10 mL volumetric flask and diluted to the mark with water. The concentrations of lead in the solution were determined by FAAS at 283.3.

2.3.3. Determination of lead in water samples

Polyethylene bottles, soaked in 1 M HNO_3 overnight, and washed two times with water were used for sampling. The water sample was filtered through a 0.45 μm pores filter. The pH of a 1000 mL portion of each sample was adjusted to 2.0 (4 M HNO_3) and passed through the column under a flow rate of 5 mL min^{-1}. The column was washed with water and the ions were desorbed and determined as the above mentioned procedure.

2.3.4. Speciation of lead in water samples

This procedure is reported in several articles. The method has been evaluated and optimized for speciation and its application on complex mixtures [26-29]. The chelating cation exchanger (Chelex-100) and anion exchanger, Dowex 1X-8 resins were washed with 1 M HCl, water, 1 M NaOH and water respectively. 1.2 g of each resin was transfered to separate polyethylene columns. Each column was washed with 10 mL of 2 M HNO_3 and then 30 mL of water. The C_{18} bounded silica adsorber in a separate column was conditioned with 5 mL of methanol, then 5 mL of 2 M HNO_3 and at the end with 20 mL of water. 5 mL of methanol was added on top of the adsorber, and passed through it until the level of methanol reached just the surface of the adsorber. Then water was added on it and connected to the other two columns. A certain volume of water sample was filtered through a 0.45 μm filter and then passed through the three columns system, Dowex 1X-8, RP-C_{18} silica adsorber and Chelex-100 respectively. The columns were then separated. The anion and cation exchanger columns were washed with 10 mL of 2 M HNO_3 and the C_{18}

column with 10 mL of 1 M HCl. The flow rate of eluents was 1 Ml min^{-1}. The lead content of each eluted solution were determined by FAAS.

3. RESULTS AND DISCUSSION

The treatment of Graphene oxide with covalently linked porphyrin (GO-H_2P) can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides [20] or carbamate esters [21], respectively.

3.1. Morphology

Initially, the GO-based hybrid material was studied by AFM and TEM. Tapping mode AFM was applied to identify the morphology of the GO-H_2P material (Figure 1a). Analysis of numerous AFM images revealed the presence of graphene sheets with heights ranging between 1.5-3.5 nm and average lateral dimension of 150 nm. Considering the height of a single GO sheet as 0.8-1.0 nm [20] and the added contribution from the grafted porphyrin moiety, the obtained images are representative of single and/or bilayers of exfoliated modified GO sheets. Moreover, TEM images of GO-H_2P were obtained and compared with images of intact graphite, thus allowing the observation of multiple-layered GO sheets with various dimensions, most likely overlapped on the peripheral edges (Figure 1b).

The formation of GO-H_2P was followed by ATR-IR spectroscopy. Initially, in the spectrum of GO, the carbonyl vibration appears at 1716 cm^{-1}, while there are fingerprints at 3616 cm^{-1} and 3490 cm^{-1} due to the presence of hydroxyl species at the basal plane of graphene. The covalent linkage of H_2P with the acyl chloride activated GO is evident from the presence of a band at 1630 cm^{-1}, which is characteristic for the carbonyl groups of the amide units [23] (see Figure S2, Electronic supplementary information (ESI) available: Additional microscopy and spectroscopy data). (See DOI: 10.1039 /c0jm00991a).

The amount of porphyrin attached onto the graphene sheet was evaluated by thermogravimetric analysis. As compared with the TGA results of pure

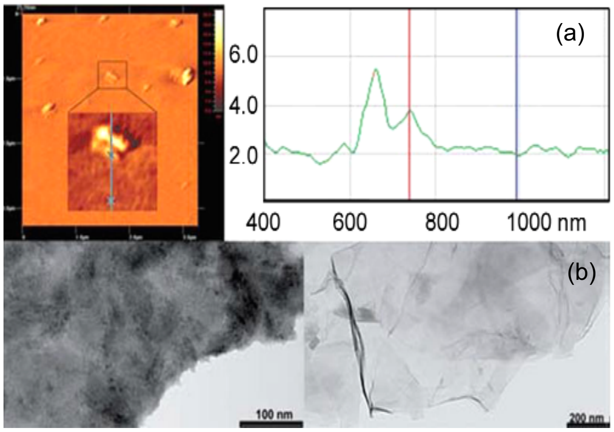


Figure 1: *(a) Representative AFM image of GO-H_2P and profile analysis showing a height of 1.77 nm for the enlarged region. Section analysis of other regions of the image show height ranges of 1.5-3.5 nm. (b) TEM images of the intact graphite (left panel) and GO-H_2P hybrid material (right panel).*

The amount of porphyrin attached onto the graphene sheet was evaluated by thermogravimetric analysis. As compared with the TGA results of pure graphite, which is thermally stable up to 900°C under nitrogen, and GO which decomposes above 600°C, after having lost the oxygenated species at 240°C (i.e. 14.7% weight loss), the 6% weight loss occurred in the temperature range 250-550°C for the GO-H_2P material, is attributed to the decomposition of H_2P (Figure 2). The GO-H_2P material forms a stable dispersion in DMF at a concentration not exceeding 1 mg mL^{-1}.

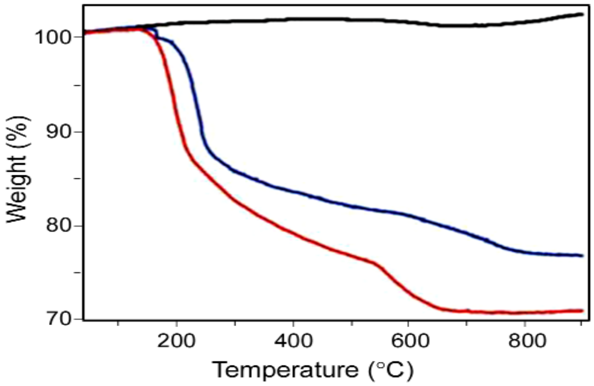


Figure 2: *The TGA graphs of graphite (black), GO (blue) and GO-H_2P (red), obtained under an inert atmosphere.*

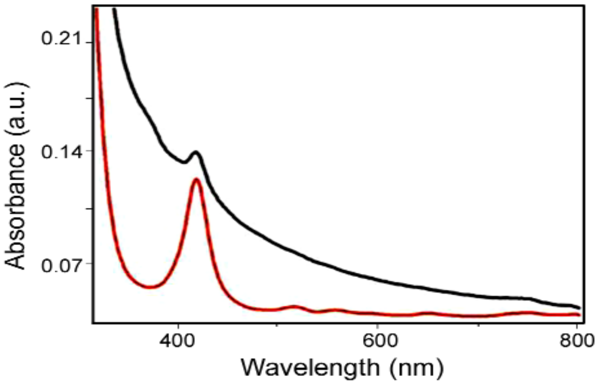


Figure 3: *The UV-Vis spectra of GO-H_2P (black) and free H_2P (red), obtained in DMF.*

The electronic absorption spectrum of GO-H_2P in DMF (Figure 3), shows (i) a broad signal monotonically decreasing from the UV to the visible region, which is attributed to GO and (ii) a characteristic band at 420 nm (Soret-band) corresponding to the covalently grafted H_2P units (the Q-bands at 516, 557, 589 and 648 nm were flattened to the base line in the GO-H_2P material). Interestingly, the absorption of porphyrin in the GO-H_2P material is broadened, shortened and bathochromically shifted (ca. 2 nm) as compared to that of the free H_2P, a result that corroborates not only the linkage of porphyrin with the GO sheets but also electronic interactions between the two species (i.e. GO and H_2P) in the ground state. These results are in agreement with studies based on other hybrid systems consisting of porphyrins covalently grafted to carbon nanotubes and nanohorns [20].

3.2. Stability studies

The stability of the newly synthesized GO-H_2P phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1 M sodium acetate) in order to assess the possible leaching or hydrolysis processes. Because the metal capacity values determined in Section 3.2 revealed that the highest one corresponds to Pb(II)s, this ion was used to evaluate the stability measurements for the GO-H_2P phase [14]. The results of this study proved that the GO-H_2P is more resistant than the chemically adsorbed analog especially in 1.0, 5.0 and 10.0 M hydrochloric acid with hydrolysis percentage of 2.25, 6.10 and 10.50 for phase, respectively. Thus, these stability studies indicated the suitability of phase for application in various acid solutions especially concentrated hydrochloric acid and extension of the experimental range to very strong acidic media which is not suitable for other normal and selective chelating ion exchangers based on a nano polymeric matrix [9]. Finally, the GO-H_2P phases were also found to be stable over a range of 1 year during the course of this work. The IGO is insoluble in water. Primary investigations revealed that surfactant coated C_{18} could not retain Pb(II) cations, but when modified with the GO-H_2P retains these cations selectively. It was then decided to investigate the capability of the GO-H_2P as a ligand for simultaneous preconcentration and determination of lead on admicell. The C_{18} surface in acidic media (1<pH<6) attracts protons and becomes positively charged. The hydrophyl part of SDS ($-SO_3-$) is attached strongly to these protons. On the other hand, the GO-H_2P is attached to hydrophobe part of SDS and retains small quantities of metallic cations [22].

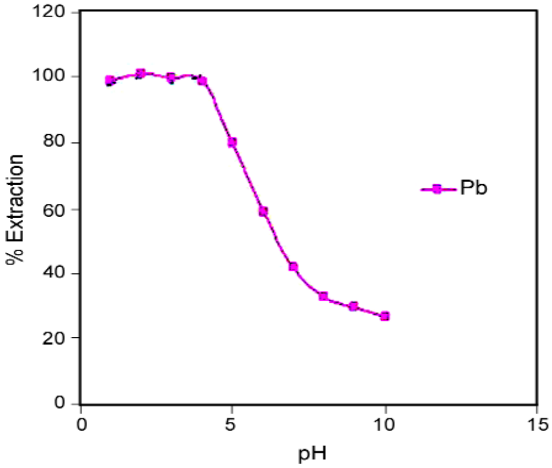


Figure 4: *Extraction percentage of Pb(II) against pH.*

3.3. Effect of pH in does not occur

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Pb(II) was studied in the pH rang of 1-10. The pH of the solution was adjusted by means of either 0.01 M HNO_3 or 0.01 M NaOH. The results indicate that complete chelation and recovery of Pb(II) occurs in pH range of 2-4 and that of in 2-8 and are shown in Figure 4. It is probable that at higher pH values, the cations might be hydrolysed and complete desorption occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the C_{18}, pH= 2.0 was chosen for further studies.

3.4. Effect of flow rates of solutions

Effect of flow rate of the solutions of the cations on chelation of them on the substrate was also studied. It was indicated that flow rates of 1-5 mL min^{-1} would not affect the retention efficiency of the substrate. Higher flow rates cause incomplete chelation of the cations on the sorbent. The similar range of flow rate for chelation of cations on modified C_{18} with SDS and a GO-H_2P has been reported in literature [21, 22]. Flow rate of 1-2 mL min^{-1} for desorption of the cations with 4 mL of 4 M HNO_3 has been found suitable. Higher flow rates need larger volume of acid. Hence, flow rates of 5 mL min^{-1} and 2 mL min^{-1} were used for sample solution and eluting solvent throughout respectively.

3.5. Effect of the GO-H_2P quantity

To study optimum quantity of the GO-H_2P on quantitative extraction of lead, 50 mL portions of solutions containing 100 ng of each cation were passed through different columns the sorbent of

Table 2: *Effect of foreign ions on the recovery of 100 ng of Pb.*

Diverse ion	Amounts taken (mg) added to 50 mL	% Found	% Recovery of Pb^{2+} ion
Na^+	92.2	1.19(2.9)a	98.6s(1.9)
K^+	92.2	1.38(2.1)	98.7(2.2)
Mg^{2+}	13.5	0.8(1.8)	96.9(2.7)
Ca^{2+}	23.3	1.29(2.0)	95.4(1.9)
Sr^{2+}	3.32	2.81(2.2)	98.2(2.1)
Ba^{2+}	2.26	3.16(2.4)	98.3(2.0)
Mn^{2+}	2.44	1.75(2.3)	98.5(1.8)
Co^{2+}	2.37	1.4(2.3)	98.1(2.2)
Ni^{2+}	2.25	2.0(2.14)	98.4(2.4)
Zn^{2+}	2.44	1.97(2.1)	98.7(2.2)
Cd^{2+}	2.63	1.9(2.0)	98.8(2.6)
Bi^{3+}	2.30	2.7(1.4)	98.4(2.7)
Cu^{2+}	2.56	2.81(2.3)	97.7(2.5)
Fe^{3+}	2.40	3.45(2.4)	97.6(2.8)
Cr^{3+}	1.30	2.92(2.2)	96.3(2.4)
UO^{2+}	2.89	1.3(2.2)	97.3(2.2)
NO^{3-}	5.5	2.3 (2.3)	96.4(2.6)
CH_3COO^-	5.3	2.2(2.6)	95.5(2.2)
SO_4^{2-}	5.0	2.9(3.0)	98.4(2.1)
CO_3^{2-}	5.4	1.8(2.5)	96.3(2.5)
PO_4^{3-}	2.6	2.1(2.0)	98.9(2.0)

a: Values in parenthesis are CVs based on three individual replicate measurements.

which were modified with various amounts, between 10-50 mg of the GO-H_2P. The best result was obtained on the sorbent which was modified with 40 mg of the GO-H_2P.

3.6. Figures of merit

The breakthrough volume is of prime importance for solid phase extractions. Hence, the effect of sample volume on the recovery of the cations was studied. 100 ng of each cation was dissolved in 50, 100, 500 and 1000 mL of water. It was indicated that in all the cases, chelation and desorption of the cations were quantitative. It was then concluded that the breakthrough volume could be even more than 1000 mL. Because the sample volume was 1000 mL and the cations were eluted into 10 mL solution, the enrichment factor for both cations is 100, which is easily achievable. The maximum capacity of 1.5 g of the substrate was determined as follow; 500 mL of a solution containing 50 mg of each cation was passed through the column. The chelated ions were eluted and determined by FAAS. The maximum capacity of the sorbent for three individual replecates was found to be 15.2 ± 0.8 µg of each cation. The limits of detection (3σ) for the catoins [30] were found to be 3.20 ngl^{-1} for lead ions. Reproducibility of the method for extraction and determination of 100 ng of each cation in a 50

Table 3: *Recovery of Pb contents of water samples.*

Diverse ion		Amounts taken (mg) added to 50 mL	% Found	% Recovery of Pb^{2+} ion
Sample Distilled water (100 mL)	Pb	-	-	-
		0.050	0.043(2.40)[a]	96
		0.100	0.094(2.60)	97
Tap water (100 mL)	Pb	-	0.015(3.0)	-
		0.050	0.068(2.42)	96
Snow water (50 mL)	Pb	-	0.048(2.25)	-
		0.100	0.155(2.30)	98
Rain water (100 mL)	Pb	-	0.045(2.25)	-
		0.100	0.143(2.40)	98
Synthetic sample 1 Na^+, Ca^{2+}, Fe^{3+}, Co^{2+}, Cr^{3+}, Hg^{2+}, 1 mg L^{-1}	Pb	-	-	-
		0.100	0.104(2.40)	98
Synthetic sample 2 K^+ Ba^{2+}, Mn^{2+}, Cd^{2+} , Ni^{2+}, Zn^{2+}, 1 mg L^{-1} of each cation	Pb	-	-	-
		0.100	0.105(2.70)	99

a: Values in parenthesis are CVs based on three individual replicate measurements.

Table 4: *Results of speciation of Pb in different samples by three columns system.*

	Tap water (1000 mL)	Water sample (1000 mL)[a]	River water (50 mL)
Column	Pb(μg)	Pb(μg)	Pb(μg)
Dowex 1X8	-	-	-
Silica C-18	-	-	-
Chelex-100	0.012(4.0)[b]	0.104(2.9)	0.103(2.8)

[a]: This was a solution containing 0.1 μg of each cation in 1000 mL of distilled water.

[b]: Values in parenthesis are CVs based on three replicate analysis. The samples are the same as those mentioned in Table 4.

mL solution was examined. As the results of seven individual replicate measurements indicated, they were 2.85% and 2.98% for Pb(II).

3.7. Analysis of the water samples

Effect of foreign ions was also investigated on the measurements of lead. Here a certain amount of foreign ion was added to 50 mL of sample solution containing 100 ng of each Pb(II) with a pH of 2.5. The amounts of the foreign ions and the percentages of the recovery of lead are listed in Table 2. As it is seen, it is possible to determine lead without being affected by the mentioned ions.

3.8. Analysis of the water samples

The prepared sorbent was used for analysis of real samples. To do this, the amounts of lead were determined in different water samples namely: distilled water, tap water of Tehran (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 25 January, 2013), Snow water (Tehran, 7 February, 2013), and two synthetic samples containing different cations. The results are tabulated in Table 3. As it is seen, the amounts of lead added to the water samples are extracted and determined quantitatively which indicates accuracy and precision of the present method.

Separation and speciation of cations by three columns system is possible to preconcentrate and at the same time separate the neutral metal complexes of GO-H_2P, anionic complexes and free ions from each other by this method [27]. Water samples were passed through the three connected columns: anoin exchanger, C_{18}-silica adsorber and chelating cation exchanger. Each species of lead is retained in one of the columns; anionic complexes in the first column, neutral complexes of GO-H_2P in the second, and the free ions in the third. The results of passing certain volumes of different water samples through the columns are listed in Table 4. According to the results, it is indicated that lead present only as cations. On the other hand the t-test comparing the obtained mean values of the present work with those published indicate no significant difference between them. We have proposed a method for determination and preconcentration of Pb in water samples using surfactant coated C_{18} impregnated with a Sciff's base. The proposed method offers simple, highly sensitive, accurate and selective method for determination of trace amounts of Pb(II) in water samples.

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