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Research Article

SOLID PHASE EXTRACTION OF TRACE PB(II) IN INDUSTERIAL WASTE WATER SAMPLE USING NANO GRAPHENE OXIDE ON SURFACTANT COATED C_{18} BEFORE DETERMINATION BY FALME ATOMIC ABSORBTIONS

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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 ethylenediaminesolid-phase extraction adsorbent was synthesized by ethylenediamine onto the surfaces of graphite oxides. The stability of a chemically (GO–EDA) especially in concentrated hydrochloric acid which was then used as a recycling and pre-concentration reagent for further uses of (GO–EDA). The method is based on (GO–EDA) of Pb(II) on surfactant coated C_{18}, modified with a porphyrin -treated graphite oxides (GO–EDA). 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±0.8mg 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.

Keywords: *Determination of Lead, Preconcentration, Graphene Oxide with Ethylenediamine (GO–EDA), FAAS*

INTRODUCTION
Pb at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems (Izatt *et al.*, 1991; Izatt *et al.*, 1985; Izatt *et al.*, 1995; Blake *et al.*, 1996; Arca *et al.*, 2001; Hashemi *et al.*, 2001; Shcherbinina *et al.*, 1990). This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Pb can bind to the cell membrane and hinder the transport process through the cell wall. Pb at nearly 40ng mL^{-1} is required for normal metabolism of many living organisms (Gomes-Gomes, 1995; Unger *et al.*, 1979). On the other hand, Pb is an important element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Pb is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS). Boudreau *et al.*, (1989) as well as spectrometric methods (Bruening *et al.*, 1991; Mahmoud *et al.*, 1997).
Solid phase extraction (SPE) methods are the best alternatives for traditional classic methods due to selective removal of trace amounts of metal ions from their matrices. Solid phase extraction determinations can be carried out on different efficient ways. One of the most appropriative performation features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time (Mahmoud (a), Talata 1997; Mahmoud (b), Talata, 1997). The octadecyl silica membrane disks involves shorter sample processing time and decreased plugging due to the large cross-sectional area of the disk and small pressure drop which allows higher flow-rates; reduced channeling resulting from the use of sorbent with smaller particle size and a greater mechanical stability of the sorbent bed (Tong *et al.*, 1990).
In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium (Dadler *et al.*, 1987; Moghimi, 2007) and lead (Mahmoud, 1999). Meanwhile,

other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead (Leyden *et al.,* 1976; Moghimi *et al.*, 2009; Liu *et al.,* 1992), copper (Liu *et al.,* 1996; Mishenina *et al.*, 1996; Wang *et al.,* 1999), silver (Wang *et al.,* 1997; Zhang *et al.,* 1982), mercury (Zhou *et al.,* 1983; Zargaran *et al.*, 2008), cadmium (Tabarzadi *et al.,* 2010), palladium (Shin *et al.,* 2004), Ce (Nayebi *et al.*, 2006) and UO_2 (Mahmoud, 1998).

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 C18 modified with Graphene oxide with ethylenediamine (GO–EDA).

Such a determination has not been reported in the literature. The structure of Graphene oxide with ethylenediamine (*GO–EDA*) 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–EDA* 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.

Experimental

Reagents and Apparatus

Graphite oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30 lm) by the Hummers (Hummers *et al.,* 1958). 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 (Tabarzadi *et al.,* 2010). All solutions were prepared with doubly distilled deionized water. C_{18} powder for chromatography with diameter of about 50 µm obtained from Katayama Chemicals. It was conditioned before use by suspending in 4 M nitric acid for 20 min, and then washed two times with water. Sodium dodecyl solfate (SDS) obtained from Merck and used without any further purification.

Synthetic Procedures

Preparation of GO–EDA

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 EDA and the acyl chloride of GO, 15 mg of GO–COCl was treated under anaerobic, dry conditions with 7 mg of EDA dissolved in 6 ml of dry THF at room temperature for 72 h. The hybrid material, namely GO–EDA, was obtained as a brown-gray solidby 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 EDA and then with diethyl ether (2 × 20 mL) before being dried under vacuum.

Column Preparation

GO–EDA (40 mg) were 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.

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–EDA* were carried out 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.

*Preparation of admicell column***:** to 40 ml of water containing 1.5 g of C_{18}, 150 mg of the above Graphene oxide was loaded after washing acetone, 1mol 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 transfered to a polypropylen tube (i.d 5 mm, length 10mm).

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.

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.

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.

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 (Yang *et al.*, 2009; Smith, 2009). 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 transferred 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-C18 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.

RESULTS AND DISCUSSION

The treatment of Graphene oxide with ethylenediamine (GO–EDA) can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides (Smith, 2009) or carbamate esters (Yang *et al.*, 2009), respectively.

The formation of GO–EDA 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 EDA with the acyl chloride activated GOES is evident from the presence of a band at 1630 cm^{-1}, which is characteristic for the carbonyl groups of the amide units (Zargaran *et al.*, 2008).

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–EDA material, is attributed to the decomposition of EDA (Figure 2).

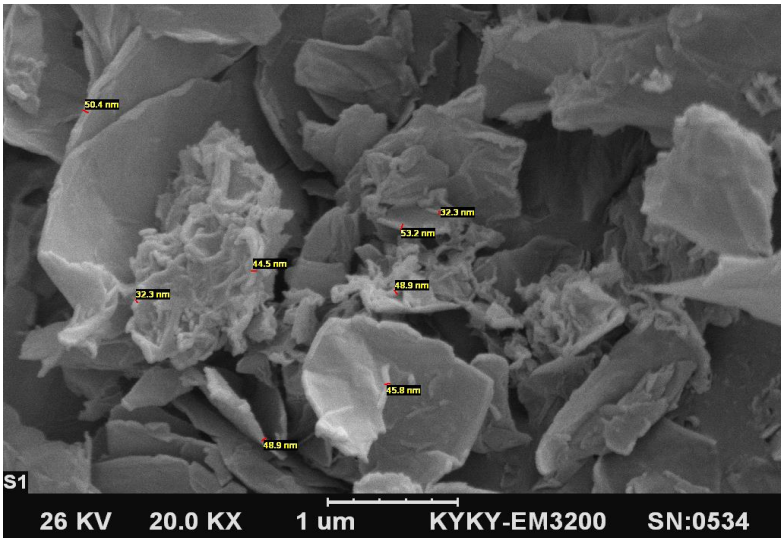

Figure 1: (a) Representative SEM image of GO–EDA and profile analysis showing a height of 1.77 nm for the enlarged region

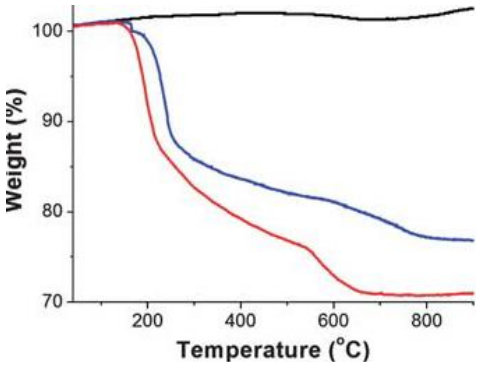

Figure 2: The TGA graphs of graphite (black), GO (blue) and GO–EDA (red), obtained under an inert atmosphere

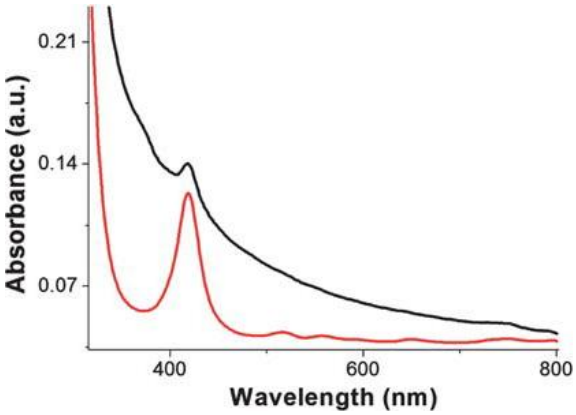

Figure 3: The UV-vis spectra of GO–EDA (black) and free EDA (red), obtained in DMF

The GO–EDA material forms a stable dispersion in DMF at a concentration not exceeding 1 mg mL^{-1}. The electronic absorption spectrum of GO–EDA 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 ethylenediamine EDA units (the Q-bands

at 516, 557, 589 and 648 nm were flattened to the base line in the GO–EDA material). Interestingly, the absorption of porphyrin in the GO–EDA material is broadened, shortened and bathochromically shifted (ca. 2 nm) as compared to that of the free EDA, 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 EDA) in the ground state. These results are in agreement with studies based on other hybrid systems consisting of ethylenediamine to Graphene oxide (Smith, 2009).

Stability Studies

The stability of the newly synthesized *GO–EDA* phases was performed in different buffer solutions (pH 1, 2, 3, 4, 5, 6 and 0.1M 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–EDA* phase (Zargaran *et al.*, 2008). The results of this study proved that the *GO–EDA* 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 (Yang *et al.*, 2009). Finally, the *GO–EDA* 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–EDA* retains these cations selectively. It was then decided to investigate the capability of the *GO–EDA* as a ligand for simultaneos 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–EDA* are attached to hydrophobe part of SDS and retain small quantities of metallic cations (Smith, 2009).

Effect of pH

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 H NO_3 or 0.01M 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 Fig. 4. It is probable that at higher pH values, the cations might be hydrolysed and complete desorbeption does not occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the C_{18}, pH=3.5 was chosen for further studies.

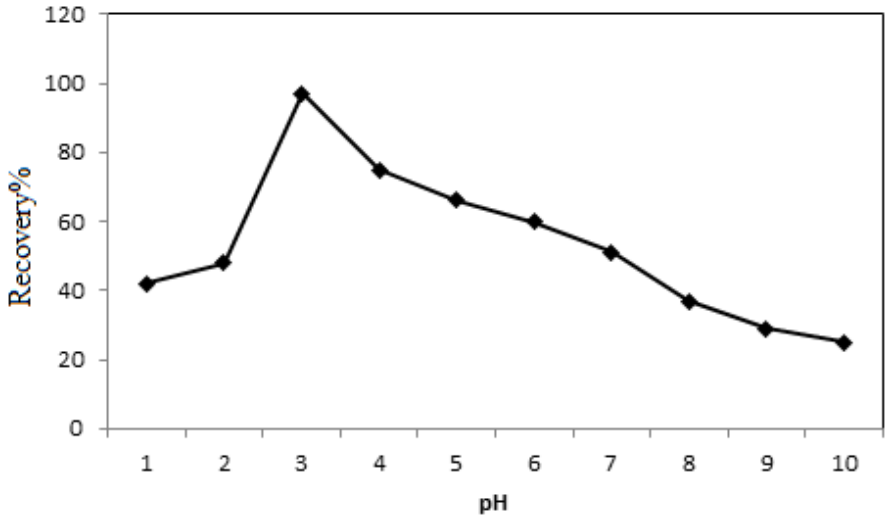

Figure 4: Extraction percentage of Pb(II) against pH

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}

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)
$CH3COO^{-}$	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

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–EDA* has been reported in literature (Smith, 2009; Yang *et al.*, 2009).

Flow rate of 1-2 ml min^{-1}for desorption of the cations with 4 ml of 4 M HNO_3has 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.

Effect of the GO–EDA Quantity

To study optimum quantity of the *GO–EDA* on quantitative extraction of lead, 50 ml portions of solutions containing 100 ng of each cation were passed through different columns the sorbent of which were modified with various amounts, between 10-50 mg of the *GO–EDA*. The best result was obtained on the sorbent that was modified with 40 mg of the *GO–EDA*.

Table 3: Recovery of Pb contents of water samples

		Amount added(µg)	Found(µg)	%Recovery
Sample Distilled water (100mL)	Pb	-	-	-
		0.050	0.043(2.40)[a]	96
		0.100	0.094(2.60)	97
Tap water(100mL)	Pb	-	0.015(3.0)	-
		0.050	0.068(2.42)	96
Snow water(50mL)	Pb	-	0.048(2.25)	-
		0.100	0.155(2.30)	98.0
Rain water(100mL)	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

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 limit of detection (3σ) for the catoins (Yang *et al.*, 2009) was 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 ml solution was examined. As the results of seven individual replicate measurements indicated, they were 2.85% and 2.98% for Pb(II).

Effect of Foreign Ions

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 3.5. 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.

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, 2014), Snow water (Tehran, 7 February, 2014), 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. Water samples were passed through the three connected columns: anoin exchanger, C_{18}-silica adsorber and chelating cation exchanger. 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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