

Extraction and Determination of Pb(II) by Organic Functionalisation of Graphenes Adsorbed on Surfactant Coated C₁₈ in Environmental Sample

A. Moghimi^{1*}, S. Yousefi Siahkalrodi²

¹Department of Chemistry, Varamin(Pishva)Branch, Islamic Azad University, Varamin, Iran

² Department of Biological Sciences, Varamin(Pishva)Branch, Islamic Azad University, Varamin, Iran

(Received: 10 June 2013

Accepted: 10 July 2013)

Abstract: A novel, simple, sensitive and effective method has been developed for preconcentration of lead. This solid-phase extraction adsorbent was synthesized by functionalization of graphenes with covalently linked *N*-methyl-glycine and 3, 4-dihydroxybenzaldehyde onto the surfaces of graphite. The method is based on selective chelation of Pb (II) on surfactant coated C₁₈, modified with functionalization of graphenes (*graphene-f-OH*). The adsorbed ions were then eluted with 4 ml of 4 M nitric acid and determined by flame atomic absorption spectrometry (FAAS) at 283.3 for Pb. The influence of flow rates of sample and eluent solutions, pH, breakthrough volume, effect of foreign ions were investigated on chelation and recovery. 1.5 g of surfactant coated C₁₈ adsorbs 40 mg of the functionalization of graphenes (*graphene-f-OH*) 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 the determination of Pb in different water samples.

Keywords: Determination of lead, Preconcentration, Graphene oxide with covalently linked *N*-methyl-glycine and 3, 4-dihydroxybenzaldehyde (*graphene-f-OH*), FAAS.

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 are very small [1-2]. Lead occurs in nature mostly as PbS. It is used in batteries, tetraethyl lead, guns, solders and X-ray instruments [3]. Copper on the other hand occurs as CuS, CuS₂, CuFeS₂, CuSO₄ .5H₂O 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[7,8], 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

Corresponding Author: A. Moghimi, Department of Chemistry, Varamin(Pishva)Branch, Islamic Azad University, Varamin, Iran. Email: alimoghimi@iauvaramin.ac.ir;kamran9537@yahoo.com

ions on the analyte 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]. In order to increase the preconcentration or extraction power of SPE an organic or inorganic ligand is used in conjunction with the sorbent. Some of the ligands used for determination of lead and copper are: Amberlit XAD-2 with 3,4-dihydroxybenzoic 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 C₁₈ disks 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 C₁₈ 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 salicylaldehyde 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 C₁₈ modified with graphene-*f*-OH (I, shown in Fig. 1).

Such a determination has not been reported in the literature. The structure of organic functionalization of graphenes (*graphene-f-OH*) is shown in Fig. 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, *graphene-f-OH* or SDS. On the other hand, in terms of economy it is much cheaper than those in the market, like C₁₈ SPE mini-column.

EXPERIMENTAL

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 *graphene-f-OH* were carried out from KBr pellet by a Perkin-Elmer 1430 ratio recording spectrophotometer. Atomic absorption analysis of all the metal ions was performed with a Perkin-Elmer 2380 flame atomic absorption spectrometer.

Reagents and Apparatus

All solutions were prepared with doubly distilled deionized water. C₁₈ 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 sulfate (SDS) obtained from Merck and used without any further purification.

Graphite oxide was prepared from purified natural graphite (SP-1, Bay Carbon, Michigan, average particle size 30 μm) 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]. Operation condition of AAS was presented in table 1.

Table 1: operation condition of AAS

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

Synthetic procedures

Preparation of graphene-*f*-OH

Pyridine dispersion was then mixed with 50 ml DMF affording a stable grey dispersion. An excess of *N*-methyl-glycine (50 mg) and 3, 4-dihydroxybenzaldehyde (50 mg) were then added in the DMF phase and the mixture was refluxed at 145–150 °C for 96 h. After completion of the reaction, the carbon material was separated from the mixture by filtration using a PVDF filter (diameter 0.45 mm), washed thoroughly with DMF, ethanol and dichloromethane and air-dried. The dried solid was then collected from the filter and fully dispersed in ethanol without leaving solid residues.

The functionalized graphenes, here after denoted as graphene-*f*-OH, remained dispersed for at least 30 days. The formation of this stable brown dispersion (~0.5 mg ml⁻¹) provides a first indication for the successful functionalization of the graphenes according to the reaction scheme shown in Fig. 1 (note that the pristine, un-modified graphenes do not disperse at all in ethanol). The functionalized graphenes have similar dispensability in DMF, whereas the sodium salt (i.e. sodic phenolate) of this derivative is dispersible in water. [34]

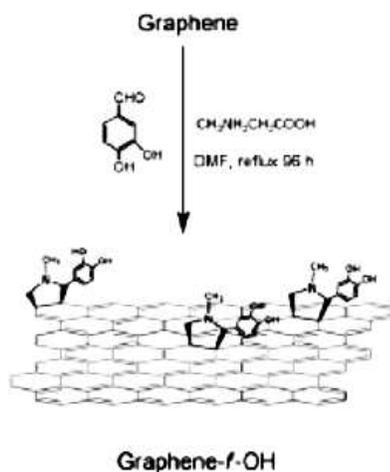


Figure 1. Schematic representation of the 1,3 dipolar cycloaddition of azomethine ylide on graphene.

Column preparation

graphene-f-OH (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 HNO₃ and DDW were passed through the column to clean it.

Preparation of admicell column: to 40 ml of water containing 1.5 g of C₁₈, 150 mg of the above Schiff base-chitosan grafted multiwalled carbon nanotubes was loaded after washing acetone, 1 mol l⁻¹ HNO₃ solution and water, respectively, solution was added. The pH of the suspension was adjusted to 2.0 by addition of 4 M HNO₃ and stirred by mechanical stirrer for 20 min. Then the top liquid was decanted (and discarded) and the remained C₁₈ was washed three times with water, then with 5 ml of 4 M HNO₃ and again three times with water. The prepared sorbent was transferred to a polypropylene tube (i.d 5 mm, length 10mm).

Determination of Pb²⁺ contents in working samples were carried out by a Varian spectra A.200 model atomic absorption spectrometer equipped with a high intensity hollow 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 solution containing 100 ng of each Pb(II) was adjusted to pH = 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 HNO₃ with a flow rate of 2 ml min⁻¹. The desorption procedure was repeated 3 and 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 HNO₃ 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 HNO₃) 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.

RESULTS AND DISCUSSION

Careful examination of a large number of TEM and AFM images reveals the presence of large plain or curved monolayer and few-layer graphenes with sizes ranging between 500 nm and 1 μm (Fig. 2). According to the AFM images (Fig. 2d), graphene-f-OH contains monolayer graphenes with thickness of 1.5 nm. Generally, the AFM thickness of unmodified monolayer graphenes is measured between 0.6–0.9 nm¹⁴. In our case, the increased thickness of 1.5 nm evidences the existence of functional groups across the graphene surface. Apart from the thickness criterion, the presence of functional groups across the graphene surface is further supported by the swollen appearance and surface roughness of the chemically modified monolayers, as clearly observed in the focus image (b). In contrast, unmodified monolayers display instead a smooth and flat surface [9].

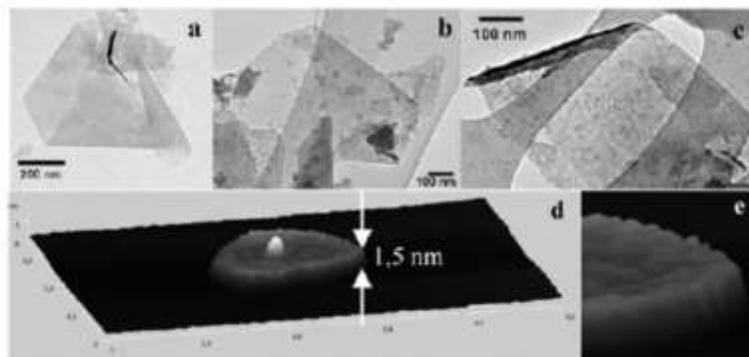


Figure 2. (Upper) Characteristic TEM and (lower) AFM images of the graphene-f-OH isolated from the ethanol dispersion.

The FT-IR spectrum of graphene-f-OH shown in Fig. 3 shows C-H stretch features at 2921 and 2855 cm^{-1} that are not present in the spectrum of starting graphenes, which is completely featureless. Also, apparent C=C stretch bands are observed around

1600 cm^{-1} . The C-O stretch band at 1250 cm^{-1} and the O-H stretch band at 3500 cm^{-1} are both attributed to the presence of phenols, providing additional support for successful functionalization.

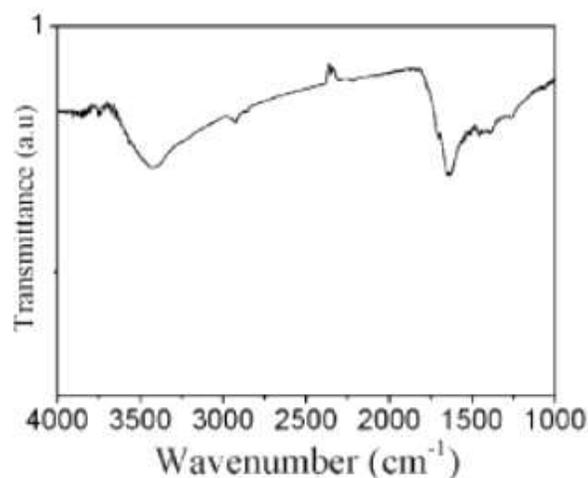


Figure 3. (Left) FT-IR and (right) UV-Vis spectra of graphene-f-OH in ethanol at moderate concentrations.

Stability studies

The stability of the newly synthesized *graphene-f-OH* 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), this ion was used to evaluate the stability measurements for the *graphene-f-OH* phase [14]. The results of this study proved that the *graphene-f-OH* 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 *graphene-f-OH* phases were also found to be stable over a range of 1 year during the course of this work. Primary investigations revealed that surfactant coated C₁₈ could not retain Pb(II) cations, but when modified with the *graphene-f-OH* retains these cations selectively. It was then decided to investigate the capability of the *graphene-f-OH* as a ligand for simultaneous preconcentration and determination of lead on admicell.

The C₁₈ surface in acidic media (1<pH<6) attracts protons and becomes positively charged. The hydrophil part of SDS(-SO₃⁻), is attached strongly to these protons. On the other hand, the *graphene-f-OH* are attached to hydrophobe part of SDS and retain small quantities of metallic cations[22].

Effect of pH

The effect of pH of the aqueous solution on the extraction of 100 ng of each of the cations Pb(II) nitrate was studied in the pH range of 1-10. The pH of the solution was adjusted by means of either 0.01 M HNO₃ 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 2-10 and are shown in Fig. 4. It is probable that at higher pH values, the cations might be hydrolysed and complete desorption does not occur. Hence, in order to prevent hydrolysis of the cations and also keeping SDS on the C₁₈, pH=2.0 was chosen for further studies.

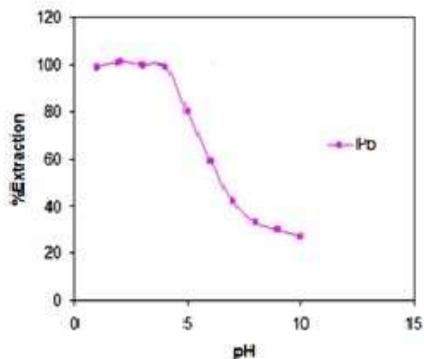


Figure 4. Extraction percentage of Pb(II) against pH.

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 C₁₈ with SDS and a *graphene-f-OH* 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 HNO₃ 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.

Effect of the graphene-f-OH quantity

To study optimum quantity of the *graphene-f-OH* 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 *graphene-f-OH*. The best result was obtained on the sorbent which was modified with 40 mg of the *graphene-f-OH*.

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 replicates was found to be $15.2 \pm 0.8 \mu\text{g}$ of each cation. The limit of detection (3σ) for the cations [30] were found to be 3.20 ng l^{-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

Effects of foreign ions were 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.

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, it is possible to preconcentrate and at the same time separate the neutral metal complexes of *graphene-f-OH*, anionic complexes and free ions from each other by this method[27]. Water samples were passed through the three connected columns: anion 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 *graphene-f-OH* in the second, and the free ions in the third. We have proposed a method for determination and preconcentration of Pb in water samples using surfactant coated C_{18}

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 Pb²⁺ 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 ₃ COO ⁻	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.

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
Tap water(100mL)	Pb	0.100	0.094(2.60)	97
		-	0.017(3.0)	-
Snow water(50mL)	Pb	0.050	0.066(2.42)	96
		-	0.045(2.25)	-
Rain water(100mL)	Pb	0.100	0.152(2.30)	98.0
		-	0.042(2.25)	-
Synthetic sample 1 Na ⁺ , Ca ²⁺ , Fe ³⁺ , Co ²⁺ , Cr ³⁺ , Hg ²⁺ , 1 mg l ⁻¹	Pb	0.100	0.143(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

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.

ACKNOWLEDGMENTS

The author wish to thank the Chemistry Department of Varamin branch Islamic Azad University for financial support.

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