

*Full Length Research Paper*

# Separation and determination of trace amounts of Pb(II) ions in water samples using organic solution-processable functionalized-nano graphene

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A novel and selective method for the fast determination of trace amounts of Pb(II) ions in water samples has been developed. The first organic solution-processable functionalized-nano graphene (SPFGraphene) hybrid material with porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin and its photophysical properties including optical triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together through an amide bond (TPP-NHCO-SPFGraphene) were used as absorbent for extraction of Pb(II) ions by solid phase extraction method. The complexes were eluted with HNO<sub>3</sub> (2M)10% V.V<sup>-1</sup> methanol in acetone and determined the analyte by flame atomic absorption spectrometry. The procedure is based on the selective formation of Pb(II) at optimum pH by elution with organic eluents and determination by flame atomic absorption spectrometry. The method is based on complex formation on the surface of the ENVI-18 DISK™ disks modified porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-TPP and grapheme oxide molecules covalently bonded together through an amide bond (TPP-NHCO-SPFGraphene) followed by stripping of the retained species by minimum amounts of appropriate organic solvents. The elution is efficient and quantitative. The effect of potential interfering ions, pH, TPP-NHCO-SPFGraphene, amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to about 1000 ml providing a preconcentration factor of 600. The maximum capacity of the disks was found to be 398 ± 3 µg for Pb<sup>2+</sup>. The limit of detection of the proposed method is 5 ng per 1000 ml. The method was applied to the extraction and recovery of Pb in different water samples.

**Key words:** Pb(II), Solid phase extraction (SPE), Octadecyl silica disks, flame atomic absorbtion spectrometry(FAAS), porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP), grapheme oxide molecules covalently bonded together through an amide bond (TPP-NHCO-SPFGraphene).

## 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. The direct determination of trace metals especially toxic metal ions such as Cobalt, tin, arsenic, lead, antimony, and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden et al., 1976). This pre-concentration is required to meet the detection limits

as well as to determine the lower concentration levels of the analyte of interest (Jones et al., 1983). This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar et al., 1998; Caroli et al., 1991). The application of solid phase extraction technique for preconcentration of trace metals from different samples results in several advantages such as the minimal waste generation, reduction of sample matrix effects as well as sorption of the target species on the solid surface in a more stable chemical form

(Alexandrova and Arpadjan, 1993).

The normal and selective solid phase extractors are those derived from the immobilization of the organic compounds on the surface of solid supports which are mainly polyurethane foams (Arpadjan et al., 1997), filter paper (Leyden and Luttrell, 1975), cellulose (Gennaro et al., 1983) and ion exchange resins (Saber et al., 2005; Shin et al., 2005; Mazlum et al., 2003; Mahmoud and Soliman al., 1997). Silica gel, alumina, magnesia, and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces (Unger and Porous, 1979) of which silica gel is the most widely used solid support due to the well documented thermal, chemical, and mechanical stability properties compared to other organic and inorganic solid supports (Boudreau and Cooper, 1989). The surface of silica gel is characterized by the presence of silanol groups, which are known as weak ion exchangers, causing low interaction, binding and extraction of the target analytes (Kvitek et al., 1982). For this reason, modification of the silica gel surface with certain functional groups has successfully been employed to produce the solid phase with certain selectivity characters (Bruening et al., 1991). Two approaches are known for loading the surface of solid phases with certain organic compounds and these are defined as the chemical immobilization which is based on the chemical bond formation between the silica gel surface groups and those of the organic modifier, and the other approach is known as the physical adsorption in which direct adsorption of the organic modifier with the active silanol groups takes place (Unger and Porous, 1979). Selective solid phase extractors and preconcentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen, and sulfur containing compounds (Mahmoud, 1997a, 1997b; Tong et al., 1990; Dadler et al., 1987). The most successful selective solid phases for soft metal ions are sulfur containing compounds, which are widely used in different analytical fields. Amongst these sulfur containing compounds are dithiocarbamate derivatives for selective extraction of Pb(II) (Mahmoud, 1998, 1999) and preconcentration of various cations (Leyden et al., 1976; Narin et al., 2000; Choi and Choi, 2003; Tabarzadi et al., 2010; Tahaei et al., 2008; Ohta et al., 2001; Cuculic et al., 1997; Tehrani et al., 2005; Thurman and Mills, 1998; Pawliszyn, 1997; Izatt et al., 1996; Hagen et al., 1990; Krueger and Fild, 1995; Yamini and Ashraf-Khorassani, 1994; Shamsipur et al., 1999; Shamsipur et al., 2001; Brunner et al., 2003; Zelder et al., 2004; Boll et al., 2005; Nayebi et al., 2006; Moghimi et al., 2007; Moghimi et al., 2008; Moghimi, 2007a, 2007b) and 2- mercaptobenzothiazol-modified silica gel for online preconcentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng et al., 1998; Taylor et al., 1995). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase preconcentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic

emission spectrometry (ICP-AES) was reported (Alexandrova and Arpadjan, 1993).

Mercapto-modified silica gel phase was used in preconcentration of some trace metals from seawater (Moghimi et al., 2010). Sorption of Pb (II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini and Moghimi, 2010) was also reported. 2-Amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA) for the extraction of silver(I), Pb(II), and palladium(II) (Moghimi et al., 2006), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin et al., 2000) as well as thiosemicarbazide for sorption of different metal ions (Campderros et al., 1998) and thioanilide loaded on silica gel for preconcentration of palladium(II) from water (Narin et al., 2000) are also sulfur containing silica gel phases.

In the present report, we wish to describe a proper concentrative method for the assessment of trace levels of Pb in different water samples. To the best of our knowledge, octadecyl silica membrane disks modified by (TPP-NHCO-SPFGraphene) have not been used for Pb isolation and preconcentration, previously this work was on the development of a rapid, efficient, and highly sensitive method for selective extraction and concentration of ultra trace amounts of Pb<sup>2+</sup> ions from aqueous media using octadecyl silica membrane disks modified by porphyrin-graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together through an amide bond (TPP-NHCO-SPFGraphene) and Flame Atomic Absorption Spectrometric (FAAS) determination.

## EXPERIMENTAL

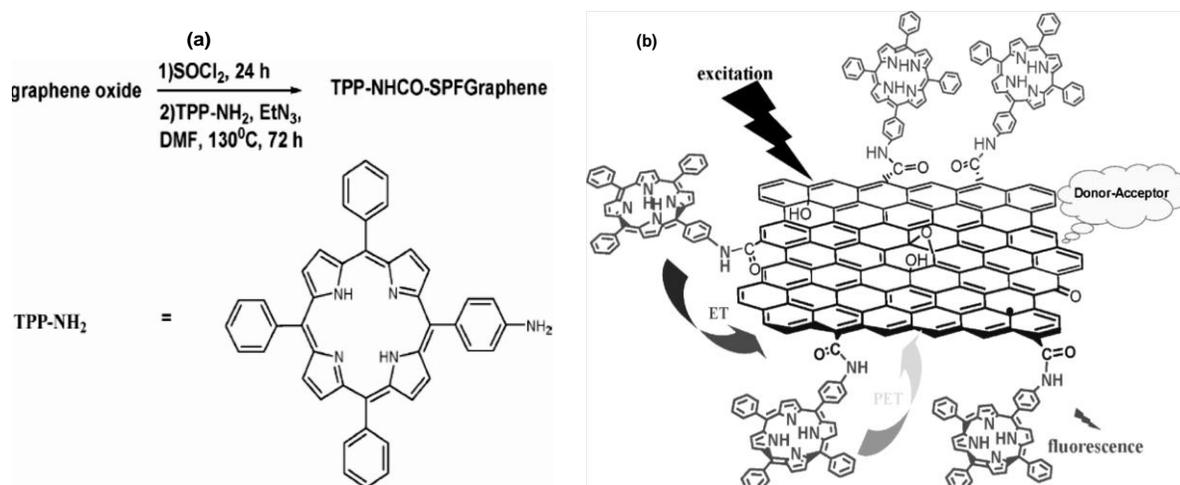
### Reagents

All acids were of the highest purity available from Merck and were used immediately when received. Methanol and Chloroform were of HPLC grade from Merck. Analytical grade nitrate salts of lithium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, cobalt (II), and Pb (II) were of the highest purity. Ultra pure organic solvents were obtained from Merck (Darmstadt, Germany), and high purity double distilled deionized water was used throughout the experiments.

The stock standard solution of Pb<sup>2+</sup> was prepared by dissolving 0.1000 g of the Pb powder in 10 ml concentrated nitric acid and diluted to 1000 ml with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution from Merck (Darmstadt, Germany). The synthesis of the TPP-NHCO-SPFGraphene, was illustrated in Figure 1a and b.

### Synthesis of TPP-NHCO-SPFGraphene

The first organic solution-processable functionalized-nano graphene (SPFGraphene) hybrid material with porphyrins. The synthesis of the porphyrin-Graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin and grapheme oxide molecules covalently bonded together through an amide bond (TPP-NHCO-SPF Graphene, Scheme 1 and 2) was carried out



**Figure 1.** (a) Synthesis scheme of TPP-NHCO-SPFGraphene, (b) Schematic representation of part of the structure of the covalent TPP-NHCO-SPFGraphene.

using an amine-functionalized porphyrin (TPP-NH<sub>2</sub>) and nano graphene oxide in N,N-dimethylformamide (DMF), following standard chemistry. Large-scale and water-soluble nano graphene oxide was prepared by the modified Hummers method (Becerril et al., 2008; Liu et al., 2008; Hummers and Offeman, 1958).

Results of atomic force microscopy characterization have confirmed that this grapheme material can be easily dispersed at the state of complete exfoliation, which consists of almost entire single-layered nano graphene sheets in H<sub>2</sub>O (Becerril et al., 2008; Liu et al., 2008; Hummers and Offeman, 1958).

TPP-NH<sub>2</sub> and Nano graphene oxide molecules are covalently bonded together by an amide bond. Much care had been taken to make sure all the unreacted TPP-NH<sub>2</sub> had been removed using extensive solvent washing, sonication, and membrane filtration. Details are given in the experimental part. The attachment of organic molecules to nano graphene oxide has made TPP-NHCO-SPFGraphene soluble in DMF and other polar solvents (Becerril et al., 2008; Liu et al., 2008; Hummers and Offeman, 1958).

### Apparatus

Determination of Pb<sup>2+</sup> 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. TPP-NHCO-SPFGraphene, (40 mg) were packed into an SPE ENVI-18 DISK™ disks. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK™ 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) obtained from Supelco in conjunction with a standard Millipore 47 mm filtration apparatus equipped with a vacuum pump. The pH measurements were carried out by an ATC pH meter (EDT instruments, GP 353).

### Sample extraction

Extraction were performed with glassy membrane disks, ENVI-18 DISK™ 47 mm diameter × 0.6 mm thickness containing octadecyl silica bonded phase (30 μm particles, 70 Å pore size) from Supelco. The disks were used in conjunctions with a standard

Millipore 47 mm filtration apparatus connected to water aspirator (Moghimi, 2007).

### Sample treatment

The water samples were filtered through 45 μm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 ml<sup>-1</sup> HNO<sub>3</sub> overnight and rinsed twice with deionized water. The analysis must be done within 2 days of sample collection to limit the risk of interconversion of Pb(II). Then, 5 ml of methanol was added to a 90 ml portion of each before analysis. The surface of the ENVI-18 DISK™ disks was modified with TPP-NHCO-SPFGraphene, and therefore could retain Pb<sup>2+</sup> ions properly. Instead of 10 mg of TPP-NHCO-SPFGraphene, an appropriate volume of an organic solvent (5 ml) was miscible with water. The most suitable solvent under the experimental conditions was HNO<sub>3</sub> (2M)10% V.V<sup>-1</sup> methanol in acetone.

### Disk cleaning and conditioning

A disk was placed in the apparatus and was washed with 10 ml of methanol to remove all contaminants arising from the manufacturing process and the environment. Then, the disk was dried by passing air through it for several minutes. To insure optimal extraction of the analytes of interest, the disk was again washed with 10 ml of methanol, immediately followed by 10 ml of water, without letting the surface of the disk to get dried. This step pre-wets the disk surface prior to extraction. Improper performance of this step causes slow flow-rate and poor analyte recoveries. It is important to avoid any air contact with the surface of the disk before the addition of the sample.

### Sample addition

After complete homogenization, accurate volumes of the sample solutions (100 ml portions) were transferred to the top reservoir of the disk apparatus. At the same time, the solution was drawn through the disk by applying a mild vacuum. Application of vacuum was continued until the disk was completely dried (about 5 min).

**Table 1.** The effect of presence of TPP-NHCO-SPFGraphene on extraction percent of Pb(II)<sup>a</sup>.

TPP-NHCO-SPFGraphene	pH	Extraction percent of Pb(II) <sup>a</sup>
Absence	2-6	0.03(7.5) <sup>b</sup>
Presence	2-6	98.9(2.1) to 65(2.8)

<sup>a</sup> Initial samples contained 10 µg of Pb(II) in 100 ml of water; <sup>b</sup> Values in parentheses are RSDs based on five individual replicate analyses.

**Table 2.** Effect of different eluting solvents on percentage recovery of Pb(II) adsorbed on the disk <sup>a</sup>.

Stripping solution	Recovery (%)		
	2 ml	5 ml	10 ml
HNO <sub>3</sub> (2M)10% V.V <sup>-1</sup> methanol in acetone	82.9 (2.6) <sup>b</sup>	92.8 (2.6)	98.7 (2.0)
Acidified methanol <sup>c</sup>	54.5 (2.3)	83.2 (2.2)	83.6 (2.9)
Ammoniacal methanol <sup>d</sup>	54.4 (2.5)	87.5 (2.6)	86.0 (2.8)
Nitric acid (1M)10% V.V <sup>-1</sup> methanol	82.7 (1.6)	99.6 (1.5)	99.8 (2.3)
Acetonitril	36.6 (4.8)	46.5 (5.5)	69.0 (2.9)
Formic acid (1M)10% V.V <sup>-1</sup> methanol	55.6 (1.2)	68.3 (2.0)	78.5 (2.8)
Hydrochloric acid (1M)10% V.V <sup>-1</sup> methanol	52.7 (1.9)	92.0 (2.6)	90.2 (2.0)
Hydrochloric acid (1M)10% V.V <sup>-1</sup> methanol	51.6 (2.5)	65.3 (2.5)	97.3 (1.6)
Methanol	52.8 (1.9)	85.2 (2.3)	82.4 (2.0)
Ethanol	64.0 (2.5)	85.6 (2.1)	86.9 (1.6)

<sup>a</sup> Initial samples contained 10 µg of each Pb in 100 ml water; <sup>b</sup> Values in parentheses are RSDs based on five individual replicate analysis; <sup>c</sup> Acidified solvents obtained by the addition of 0.1 M HCl; <sup>d</sup>Ammoniacal solvents obtained by addition of 0.1 M NH<sub>3</sub>.

### Analyte elution

In order to elute the analyte selectively, exactly 5 ml of acidified solvents 0.1 M HCl in methanol was passed through the disk and collected into a 5.0 ml volumetric flask under the extraction funnel. It was found that ultra pure alcoholic organic solvents were the best eluting agents. The concentration of Pb(II) in the eluates were then determined by FAAS using an external calibration graph.

## RESULTS AND DISCUSSION

### Evaluation of the role of the TPP-NHCO-SPFGraphene,

Some preliminary experiments were performed for investigation of absence or presence of TPP-NHCO-SPFGraphene, on the quantitative extraction of Pb(II). It was concluded that the membrane disk itself does not show any tendency for the retention of Pb(II), but introduction of 100 ml portions of aqueous Pb(II) samples containing 10 µg of Pb(II) and 10 mg of TPP-NHCO-SPFGraphene, which leads to its satisfactory retention (Table 1). The latter case is most probably attributed to the existence of a considerable interaction between Pb(II) and the TPP-NHCO-SPFGraphene. It should be mentioned that, the formation of stable complexes between Pb(II) and TPP-NHCO-SPFGraphene, at pH = 2 is probably due to an ion pair formation mechanism.

However, at pH higher than 2 the retention and percentage recovery of Pb(II) are negligible.

### Choice of eluent

In order to select the most appropriate eluent for the quantitative stripping of the retained Pb(II) on the disks, 5 ml of various non organic (each containing 10% V.V<sup>-1</sup> methanol) and different organic solvents were tested. The results were tabulated in Table 2. As can be seen, the best eluting solvents were found to be 5 ml of HNO<sub>3</sub> (2M)10% V.V<sup>-1</sup> methanol in acetone, resulting in quantitative elution of Pb(II) from the disk. It should be emphasized that the presence of HNO<sub>3</sub> (2M)10% V.V<sup>-1</sup> methanol in acetone in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disk.

### The effect of the pH

The pH of the sample solutions were adjusted to different values between 2 to 9 by the addition of hydrochloric acid or a suitable buffer such as sodium acetate-acetic acid or sodium dihydrogen phosphate- disodium hydrogen phosphate, and then solutions passed through the disks. Eventually, the metal ions were stripped by pure

methanol or ethanol solutions followed by flame atomic absorption determination of the eluted Pb(II). Then, percentage recovery at various pH values was determined (Figure 2). According to the results shown in Figure 2, up to pH 4.0 to 4.5, complete recoveries are obtained. However, at higher pH values, percentage recovery decreases. This is due to fact that in an acidic solution, the protonation of TPP-NHCO-SPFGraphene occurs and there is a weak tendency for retention between Pb(II) and TPP-NHCO-SPFGraphene, whereas at higher values (pH > 5), Pb(II) reacts with hydroxide ions to produce Pb(OH)<sub>2</sub>. Therefore, sodium acetate-acetic acid buffer with pH = 4.5 was used for the preconcentration step. Other solvents used for dissolving TPP-NHCO-SPFGraphene, were methanol and ethanol.

The influences of these solvents on the recoveries as a function of pH are compared and shown in Figure 2. Meanwhile, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions, and incompatibility with flame having higher pH values (> 7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks (Moghimi, 2007). Pb (II) ions can be retained quantitatively by the modified membrane disk through the pH range from 4.0 to 4.5. However, at lower pH value (< 4.0), nitrogen atoms of the TPP-NHCO-SPFGraphene could be protonated and the stability of complex is reduced.

### Effect amount of counter anion

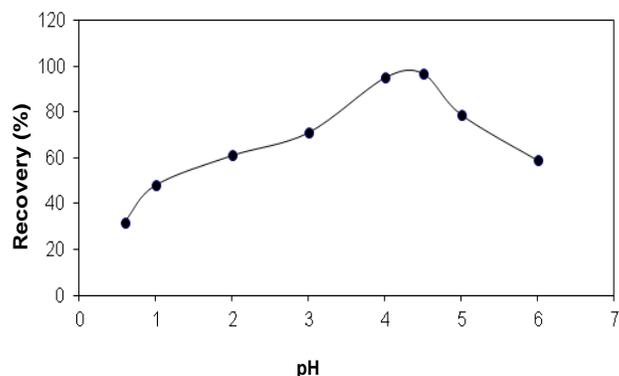
In order to investigate the effect of counter ion on the recovery Pb<sup>2+</sup> ions by the modified disks, different counter anions were tested (Table 3), it is immediately obvious that the nature of the counter anion strongly influences the retention of Pb ions by the disk. The results revealed that the TPP-NHCO-SPFGraphene, behaves in pH range of 4.0 to 4.5 (Moghimi, 2007) so that the Pb ions are retained as ion pair complexes by the membrane disks. As seen, acetate ion is the most efficient counter anion for the SPE of Pb(II) ions. The influence of the concentration of sodium acetate ion on Pb recovery was investigated, and the results are shown in Table 3.

As seen, the percent recovery of Pb<sup>2+</sup> increased with the acetate concentration until a reagent concentration of about 0.1 M is reached, beyond which the recovery remained quantitative.

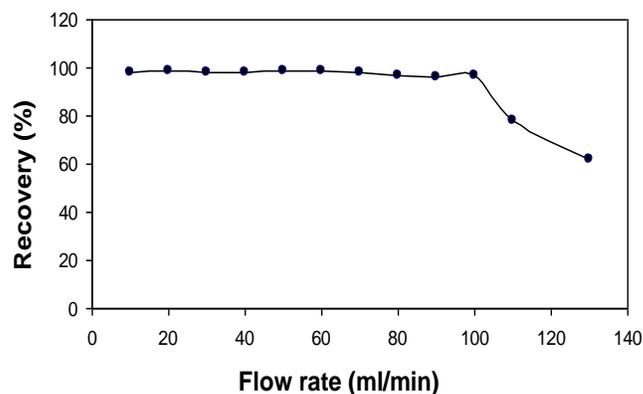
Moreover, acetate ion acts as a suitable buffering agent, while it effectively contributes to the ions pair formation; thus, in the Solid phase extraction (SPE) experiments, there was no need for the addition of any buffer solution.

### The influence of flow-rate

One of the most important parameters affecting solid



**Figure 2.** Influence of sample pH on the percentage recovery of Pb(II).



**Figure 3.** The effect of the flow-rate on extraction percent of Pb(II).

**Table 3.** Percent recovery of Pb from the modified membrane disk in the presence of 0.01 M of different counter anions <sup>a</sup>.

Counter anion <sup>a</sup>	Recovery (%)
Cl <sup>-</sup>	15.9
Br <sup>-</sup>	20.8
ClO <sub>4</sub> <sup>-</sup>	35.7
SCN <sup>-</sup>	47.6
Picrate	74.7
Acetate	98.8

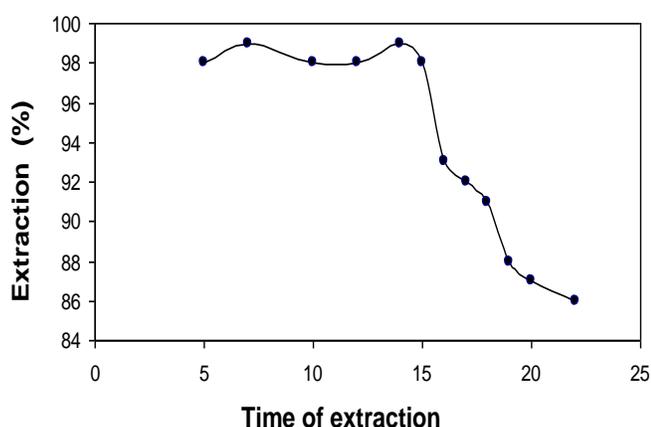
<sup>a</sup>Initial samples contained 10 µg of Pb(II) in 100 ml of water.

phase extraction is the speed of the process. Hence, the effect of flow-rates on extraction efficiencies was investigated. It was found that in the range of 10 to 100 ml.min<sup>-1</sup>, the retention of Pb(II) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Figure 3). Thus, the flow-rate was maintained at 89 ml.min<sup>-1</sup> throughout the experiment.

**Table 4.** Influence of the TPP-NHCO-SPFGraphene amount on the recovery of Pb(II) ions <sup>a</sup>.

TPP-NHCO-SPFGraphene amount (mg)	Recovery of Pb(II) (%)
2	32.20(2.3) <sup>b</sup>
5	45.40(2.0)
8	83.24(2.8)
10	95.7(2.8)
15	98.5(2.0)
20	98.6(2.8)

<sup>a</sup>Initial samples contained 10 µg of each Pb in 100 ml water; b Values in parentheses are RSDs based on five individual replicate analysis.

**Figure 4.** Influence of eluent (5 ml of HNO<sub>3</sub> (2M)10% V.V<sup>-1</sup> methanol in acetone) type on disk efficiency.

### Quantity of the TPP-NHCO-SPFGraphene

The optimum amount of TPP-NHCO-SPFGraphene for the quantitative extraction of Pb(II) was also investigated by adding various amounts of it to the solution (between 2 to 20 mg). The results are listed in Table 4. The experimental results revealed that the extraction of Pb(II) was quantitative using a sample solution containing more than 10 mg TPP-NHCO-SPFGraphene. Hence, subsequent extractions were performed with 15 mg of TPP-NHCO-SPFGraphene.

### Disk efficiency

Undoubtedly, one of the major parameters affecting the SPE determinations is the efficiency of the used membrane disks. However, to the best of our knowledge this case has not been discussed elsewhere in similar reports. Under the optimum experimental conditions, it was found out that, each ENV-18 DISK<sup>TM</sup> disk could

perform at least 14 replicate analyses if organic eluting solvents are used. On the other hand, acidic, eluents practically decrease the number of time a disk could be used to perform 10 replicates. These observations are presented in Figure 4.

### Analytical performance

When solutions of 10 µg Pb in 10, 50, 100, 600, 1000, 2000, 2500, and 3000 ml solutions under optimal experimental conditions were passed through the disks, the Pb(II) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500 ml, providing a concentration factor of > 600. The limit of detection (LOD) of the method for the determination of Pb(II) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank (5 ml of methanol) is 5 ng per 1000 ml.

The capacity of the modified disks (5 mg TPP-NHCO-SPFGraphene) was determined by passing 50 ml portions of sample solutions containing 8 mg of Pb and 0.1 M sodium acetate-acetic acid buffer with pH 4.0 to 4.5, followed by the determination of the retained metal ions in the eluting solution using AAS. The maximal capacity of the disk obtained from three replicate measurements was 398 ± 3 µg of Pb<sup>2+</sup> on the disk.

In order to investigate the selective separation and determination of Pb<sup>2+</sup> ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions (50 ml) containing 10 µg Pb<sup>2+</sup> and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 5. The results show that the Pb(II) ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100 mg of various ions. Meanwhile, retention of other cations by the disk is very low and they can be separated effectively from the Pb<sup>2+</sup> ion. It is interesting to note that, in other experiments, we found that in the presence of high enough concentrations, NH<sub>2</sub>OH.HCl is a suitable reducing agent (> 0.5 M) (Moghim, 2007; Tuzen et al., 2005).

### Analysis of water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Pb from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20 January, 2012), snow water (Tehran, 16 February, 2012) and Sea water (taken from Caspian Sea, near the Mahmoud-Abad shore) samples were analyzed (Table 6). As can be seen from Table 3, the added Pb ions can be quantitatively recovered from the water samples used. As it's seen, the recovered Pb ion revealed that the results are quite reliable and are in satisfactory agreement with those obtained by ICP-AES.

**Table 5.** Separation of Pb from binary mixtures<sup>a</sup>.

Diverse ion	Amount taken (mg)	Found (%)	Recovery of Pb <sup>2+</sup> ion (%)
Na <sup>+</sup>	92.5 <sup>s</sup>	1.15 (2.4) <sup>b</sup>	97.5 (2.7)
K <sup>+</sup>	92.4	1.32 (2.3)	98.7 (2.2)
Mg <sup>2+</sup>	24.23	0.70 (2.2)	97.5 (1.7)
Ca <sup>2+</sup>	26.4	2.25 (3.0)	98.7 (1.8)
Sr <sup>2+</sup>	2.45	2.85 (2.1)	98.7 (2.0)
Ba <sup>2+</sup>	3.66	3.16 (2.1)	97.7 (2.3)
Mn <sup>2+</sup>	2.64	1.75 (2.2)	96.3 (2.8)
Co <sup>2+</sup>	2.13	6.40 (1.8)	95.0 (1.9)
Ni <sup>2+</sup>	1.64	2.23 (2.4)	99.5 (2.4)
Zn <sup>2+</sup>	2.76	4.97 (2.1)	98.7 (2.6)
Cd <sup>2+</sup>	2.57	2.90 (2.0)	98.2 (2.5)
Hg <sup>2+</sup>	1.65	2.81 (2.1)	97.7 (2.3)
Ag <sup>+</sup>	2.34	3.45 (2.9)	98.6 (2.5)
UO <sup>2+</sup>	2.85	2.80 (2.1)	97.3 (2.6)

<sup>a</sup>Initial samples contained 10µg Pb<sup>2+</sup> and different amounts of various ions in 100 ml water(0.1 M acetate ion); <sup>b</sup> Values in parentheses are RSDs based on five individual replicate analysis.

**Table 6.** Recovery of Pb added to 1000 ml of different water samples (containing 0.1 M acetate at pH = 4.0-4.5).

Sample	Pb <sup>2+</sup> added (µg)	Pb <sup>2+</sup> determined (ng.ml <sup>-1</sup> )	ICP-AES
Tap water	0.0	1.65 (2.8) <sup>a</sup>	ND
	10.0	11.90 (2.5)	11.8
Snow water	0.0	4.84 (2.3)	ND
	10.0	14.96 (2.3)	14.5
Rain water	0.0	2.85 (2.5)	ND
	10.0	12.82 (2.4)	12.9
Sea water	0.0	12.43 (2.3)	12.5
	10.0	22.70 (2.2)	23.6

<sup>a</sup>Values in parentheses are RSDs based on five individual replicate analysis; <sup>b</sup> Not detected.

## Conclusion

Results presented in this work demonstrate very well the tremendous possibilities offered by the solid phase extraction of trace amounts of Pb(II) in water samples using Octadecyl Silica membrane disks modified by (TPP-NHCO-SPFGraphene) and its determination by FAAS. The method developed was simple, reliable, and precise for determining Pb in water. Also, the proposed method was free of interference compared to conventional procedures to determine Pb. (Moghimi, 2007; Shamsipur et al., 1999; Soylyak et al., 2002; Saracoglu et al., 2001; Melek et al., 2006). The method can be successfully applied to the separation and determination of Pb in binary mixtures.

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## REFERENCES

- Alexandrova A, Arpadjan S (1993). Elimination of sulfide interference by sodium hypochlorite solution in the cold vapor atomic absorption spectrometric determination of mercury using tin(II) reduction in alkaline medium. *Analyst* 118:1309-1313.
- Arpadjan S, Vuchkova L, Kostadinova E (1997). Study of the adsorption

- behavior of heavy metal ions on nanometer-size titanium dioxide with ICP-AES. *Analyst* 122:243-250.
- Becerril HA, Mao J, Liu ZF, Stoltenberg RM, Bao ZN, Chen YS (2008). Evaluation of solution-processed reduced graphene oxide films as transparent conductors *ACS Nano*. 2:463-469.
- Boll I, Kramer R, Brunner J, Mokhir A (2005). Oligonucleotide-Templated Reactions for Sensing Nucleic Acids *J. Am. Chem. Soc.* 27:7849-7855.
- Boudreau SP, Cooper WT (1989). Analysis of thermally and chemically modified silica gels by heterogeneous gas-solid chromatography and infrared spectroscopy. *Anal. Chem.* 61:41-48.
- Bruening ML, Mitchell DM, Bradshaw JS, Izatt RM, Bruening RL (1991). Removal of cesium from alkaline waste solution: Part II – Column ion exchange study. *Anal. Chem.* 63:21-27.
- Brunner J, Mokhir A, Kramer R (2003). Copper(II)-Quenched Oligonucleotide Probes for Fluorescent DNA Sensing. *J. Am. Chem. Soc.* 125:12410-12415.
- Campderos ME, Acosta A, Marchese J (1998). Selective separation of copper with Lix 864 in a hollow fiber module. *Talanta* 47:19-23.
- Caroli C, Alimanti A, Petrucci F, Horvath Z (1991). Selective pre-concentration and solid phase extraction of mercury(II) from natural water by silica gel-loaded dithizone phases. *Anal. Chim. Acta* 248:241-247.
- Choi YS, Choi HS (2003). Studies on Solvent Sublation of Trace Heavy Metals by Continuous Flow System as Ternary Complexes of 1,10-Phenanthroline and Thiocyanate Ion. *Bull. Korean Chem. Soc.* 24:222-228.
- Cuculic V, Mlakar M, Branica M (1997). Synergetic adsorption of copper(II) mixed ligand complexes onto the SEP-PAK Cl8 column. *Anal. Chim. Acta* 339:181-189.
- Dadler V, Lindoy LF, Sallin D, Schlaepfer CW (1987). Selective pre-concentration and solid phase extraction of mercury(II) from natural water by silica gel-loaded dithizone phases. *Aust. J. Chem.* 40:1557-1563.
- Gennaro MC, Baiocchi C, Campi E, Mentasti E, Aruga R (1983). Undesirable and harmful metals in wines-Determination and removal. *Anal. Chim. Acta* 151:339-344.
- Hagen DF, Markell CG, Schmitt GA (1990). Enhanced biosensor performance for on-site field analysis of explosives in water using solid-phase extraction membranes. *Anal. Chem.* 67:3363-3369.
- Hummers WS, Jr. Offeman RE (1958). Preparation of graphitic oxide. *J. Am. Chem. Soc.* 80:1339-1339.
- Izatt RM, Bradshaw JS, Bruening RL (1996). Non-destructive separation of metal ions from wastewater containing excess aminopolycarboxylate chelant in solution with an ion-selective immobilized macrocyclic. *Pure Appl. Chem.* 68:1237-1242.
- Jones JS, Harrington DE, Leone BA, Bramdstedt WR (1983). Determination of trace elements in analytical-reagent grade sodium salts by atomic absorption spectrometry and inductively coupled plasma atomic emission spectrometry after pre-concentration by column solid phase extraction. *Atom. Spectrosc.* 4:49-57.
- Krueger CJ, Fild JA (1995). Method for the analysis of triadimefon and ethofumesate from dislodgeable foliar residues on turfgrass by solid-phase extraction and in-vial elution. *Anal. Chem.* 67:3363-3369.
- Kvitek RJ, Evans JF, Carr PW (1982). Denaturation of purple membranes at the air/water interface studied by SEM. *Anal. Chim. Acta* 144:93-98.
- Leyden DE, Luttrell GH (1975). Comparison of chelating agents immobilized on glass with chelex 100 for removal and pre-concentration of trace copper(II). *Anal. Chim.* 47:1612-1616.
- Leyden DE, Luttrell GH, Nonidez WK, Werho DB (1976). Adsorption of Co(II) and Cu(II) on silica gel surface modified with pyridinium ion from acetone and ethanol solutions. *Anal. Chem.* 48:67-72.
- Leyden DE, Luttrell GH, Sloan AE, DeAngelis NJ (1976). Automated separation and pre-concentration of copper(II) from natural waters using a column treatment. *Anal. Chim. Acta* 84: 97-102.
- Liu ZF, Liu Q, Zhang XY, Huang Y, Ma YF, Yin SG, Chen YS (2008). Substrate effect on the electronic structures of CuPc/graphene interfaces. *Adv. Mater.* 20:3924-3928.
- Mahmoud ME (1997a). Silica gel-immobilized Eriochrome black-T as a potential solid phase extractor for zinc (II) and magnesium (II) from calcium (II). *Talanta* 45:309-314.
- Mahmoud ME (1997b). Silica-immobilized formylsalicylic acid as a selective phase for the extraction of iron(III). *Talanta* 44:15-21.
- Mahmoud ME (1998). Proceeding of the 25th FACSS Conference, Austin, TX, USA, 11–15 October. pp. 297-303.
- Mahmoud ME (1999). Selective solid phase extraction of mercury(II) by silica gel-immobilized-dithiocarbamate derivatives. *Anal. Chim. Acta* 398:297-302.
- Mahmoud ME, Soliman EM (1997). Study of the selective extraction of iron (III) by silica-immobilized 5-formyl-3-arylazo-salicylic acid derivatives. *Talanta* 44:1063-1069.
- Mazlum AM, Ensafi AA, Naeimi H, Dastanpour A, Shamelli A (2003). Synthesis and analytical application of a novel tetradentate N<sub>2</sub>O<sub>2</sub> Schiff base as a chromogenic reagent for determination of nickel in some natural food samples. *Russ. J. Electrochem.* 39:269.
- Melek E, Tuzen M, Soylak M (2006). Flame Atomic Absorption Spectrometric Determination of Cadmium(II) and Lead(II) after their Solid Phase Extraction as Dibenzyldithiocarbamate Chelates on Dowex Optipore V-493. *Anal. Chim. Acta* 578:213-219.
- Moghimy A (2006). Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Isopropyl 2- [(isopropoxy carbothioyl)disulfanyl]ethane thioate and determination by flame atomic absorption spectrometry. *Oriental J. Chem.* 22(3):527-532.
- Moghimy A (2007a). Solid Phase Extraction of Trace Copper(II) Using Octadecyl Silica Membrane Disks Modified with *N,N'*-Disalicylideneethylenediamine. *Chin. J. Chem.* 25(10):1536-1542.
- Moghimy A (2007b). Preconcentration and Determination of Trace Amounts of Heavy Metals in Water Samples Using Membrane Disk and Flame Atomic Absorption Spectrometry. *Chin. J. Chem.* 25(10):640-645.
- Moghimy A (2008). Preconcentration of Copper(II) Using Mesoporous Organo-Silicas and Determination by Flame Atomic Absorption Spectrometry. *Chin. J. Chem. J. Korean Chem. Soc.* 52(2):155-163.
- Nambiar DC, Patil NN, Shinde VM (1998). Effects of Mercuric Chloride on the Immunological, Hematological, Biochemical Parameters and Diseases Resistance of Nile Tilapia Challenged with *Aeromonas hydrophila*. *Fresenius J. Anal. Chem.* 360:205-212.
- Narin I, Soylak M, Elic L, Dogan M (2000). Solid Phase Extraction of Copper(II) from Aqueous Solutions by Adsorption of its 2-propylpiperidine-1-carbodithioate Complex on Alumina Column. *Talanta* 52:1041-1047.
- Nayebi P, Moghimy A (2006). Preconcentration of mercury by adsorption of its diphenylthiocarbazono complex on an silica gel-immobilized Schiff base diphenylthiocarbazono (DPC) column and spectrophotometric determination. *Oriental J. Chem.* 22(3):507-512.
- Ohta K, Tanahasi H, Suzuki T, Kaneco S (2001). Degradation of Reactive Yellow 86 with photo-Fenton process driven by solar light. *Talanta* 53:715-722.
- Pawliszyn J (1997). *Solid-Phase Microextraction, Theory and Practice*, Wiley-VCH, New York. pp. 233-254.
- Qiaosheng P, Qiaoyu S, Zhide H, Zhixing S (1998). Application of 2-mercaptobenzothiazole self-assembled monolayer on polycrystalline gold electrode as a nanosensor for determination of Ag(I). *Anal.* 123:239-243.
- Saber TM, Rastegar F, Parchehbaf A, Rezvani Z (2005). Preconcentration and Determination of Copper(II) AND zinc(II) Using Octadecyl Silica Membrane Disks Modified by 1,5-Diphenylcarbazide and Flame Atomic Absorption Spectrometry. *Chin. J. Chem.* 23:1437-1442.
- Saracoglu S, Soylak M, Elci L (2001). Enrichment and Separation of Traces of Cadmium, Chromium, Lead and Manganese Ions in Urine by Using Magnesium Hydroxide Coprecipitation Method. *Trace Elem. Electrolytes* 18:129-133.
- Shamsipur M, Ghiasvand AR, Sharghi H (2001). Electrochemical oxidation of Catechol derivatives in presence of 4-Hydroxycoumarin *Int. J. Environ. Anal. Chem.* 82:23-29.
- Shamsipur M, Ghiasvand AR, Yamini Y (1999). Preconcentration, Determination and Speciation of Chromium(III) Using Solid Phase Extraction and Flame Atomic Absorption Spectrometry. *Anal. Chem.* 71:4892-4897.
- Shin DH, Ko YG, Choi US, Kim WN (2005). Synthesis and Properties of some Transition Metal Complexes with Water Soluble Hydroxy Functionalized Polyacrylonitrile. *Ind. Eng. Res.* 43:2060.

- Soylak M, Uzun A, Elci L (2002). Sorbent Extraction of Copper, Lead, Nickel and Cadmium Ions in Dialysis Concentrates before their Atomic Absorption. Spectrometric Determinations, Trace Elem. Electrolytes 19:15-19.
- Tabarzadi M, Abdouss M, Hasani SA, Shoushtary AM (2010). Mat.-wiss. u. Werkstofftech 41:4-221.
- Tahaei P, Abdouss M, Edrissi M, Shoushtari AM, Zargaran M (2008). Mat.-wiss. u. Werkstofftech. 39:839.
- Tajodini N, Moghimi A (2010). Preconcentration of Mercury by Adsorption from Natural Water by Silica Gel -Loaded Schiff's Base Diphenylthiocarbazone (DPC) phases. Asian J. Chem. 22(7):4994-5000.
- Taylor KZ, Waddell DS, Reiner EJ (1995). Direct Elution of Solid Phase Extraction Disks for the Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in Effluent Samples. Anal. Chem. 67:1186-1192.
- Tehrani MS, Moghimi A, Waqif HS (2005). Preconcentration and determination of trace amounts of heavy metals in water samples using membrane disk and flame atomic absorption spectrometry. Mater. Sci. Res. India 3(2):135-142.
- Thurman EM, Mills MS (1998). Solid-Phase Extraction, Principles and Practice, Wiley, New York. pp. 344-352.
- Tong A, Akama Y, Tanaka S (1990). Selective preconcentration of Au(III), Pt(IV) and Pd(II) on silica gel modified with  $\gamma$ -aminopropyltriethoxysilane. Anal. Chim. Acta 230:179-185.
- Tuzen M, Soyak M, Parlak K (2005). Cadmium and Lead Contamination in Tap Water Samples from Tokat, Turkey. Bull. Environ. Contam. Toxicol. 75:284-289.
- Unger K, Porous S (1979). Comparison of an ordered mesoporous aluminosilicate, silica, alumina, titania and zirconia in normal-phase high-performance liquid chromatography. Elsevier, Amsterdam. pp. 156-166.
- Yamini Y, Ashraf-Khorassani M (1994). Solid-Phase Extraction and Determination of Trace Amounts of Lead(II) Using Octadecyl Silica Membrane Disks Modified with a Recently Synthesized Anthraquinone Derivative and Atomic Absorption Spectrometry. High Resolut. J. Chromatogr. 17:634-639.
- Zelder FH, Brunner J, Kramer (2005). A fluorogenic and chromogenic probe that detects the esterase activity of trace copper(II)s. R. Chem. Commun. pp. 902-911.