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Preconcentration of Pb (II) on Micro Crystalline Naphthalene Modified with Organic-Solution-Processable Functionalized-Nano Graphene

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ABSTRACT

A selective method for the fast determination of trace amounts of Pb (II)ions in water samples has been developed. method has been developed for preconcentration of Pb on organic-solution-processable functionalized-nano graphene (SPFGraphene) adsorben in the pH range 5.0–10.0, prior to its spectrophotometric determination, based on the oxidation of bromopyrogallol red at λ = 517 nm. This method makes it possible to quantitize Pb in the range of 4.2×10^{-9} to 2.3×10^{-5} M, with a detection limit (S/N = 3) of 1.42×10^{-9} M. This procedure has been successfully applied to determine the ultra trace levels of Pb in the environmental samples, free from the interference of some diverse ions. The precision, expressed as relative standard deviation of three measurements is better than3.0%.

Introduction

The transition metals including cadmium, chromium and lead etc. are an important risk for humans and animals[1–3]. Also heavy metals at trace levels are components of the natural biosphere. Because the main sources of heavy metals for humans and animals are water, food and atmosphere[1,4,5], reliable and sensitive analytical methods and procedures have an important role to evaluate the impacts of metal pollutants. The determination of traces metal ions in these samples are continuously performed in the analytical chemistry laboratories around the world by using various instrumental techniques including atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) etc. Although, atomic absorption spectrometry and atomic emission spectrometry are among the most widely methods used for trace metal determination, their sensitivity is usually insufficient for monitoring the low level concentrations of metals in the environmental samples. The interfering effects of the matrix components of the samples are the one of the main problems in the determination of traces heavy metals by AAS and or ICP-AES. Also lower elements concentrations than the detection limits of the instrumental technique are another problem in the trace heavy metal determinations in environmental samples. Consequently, a preconcentration/ separation process is usually required[6–10].

Coprecipitation [11–13], membrane filtration [14,15], electrodeposition [16], cloud point extraction [17] and solvent extraction[18–21] are the popular methods for the preconcentration and separation of the traces transition metal ions. 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. SPE 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[15-16].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[17].

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium [18-19,35] and lead[20]. Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead[21-23], copper[24-26],silver[27-28], mercury[29-30] , cadmium[31] , palladium[32], Ce[33] and UO_2[34].

The used ligand is new and fairly selective and will not interfere in the determination process of Pb(II). Absorption spectrophotometry method (after preconcentration) was applied for determination of Pb based on the oxidation of bromopyrogallol red at 517 nm. Various effective parameters have been evaluated, and the developed procedure has been successfully employed for the quantitation of ultra trace amounts of Pb in water sample.

Experimental

Apparatus

The glass column with 10 mm i.d. and 200 mm height was used to make preconcentration column. An UV–Vis spectrophotometer WPA Cambridge UK (Diode Array, Model S2000) was applied for recording the absorption spectra. A spectrophotometer (Perkin-Elmer model 35) with 10mm glass cuvette was used to measure the absorbance at a fixed wavelength. Controlling the reaction temperature was done by a water bath thermostat (Gallenkamp Griffin, BJ-240-V) and a stopwatch was used for recording the reaction time. The synthesis of the TPP-NHCO-SPFNano graphene, is illustrated in Fig. 1.

Reagents

Doubly distilled water and analytical-reagent grade chemicals were used throughout.

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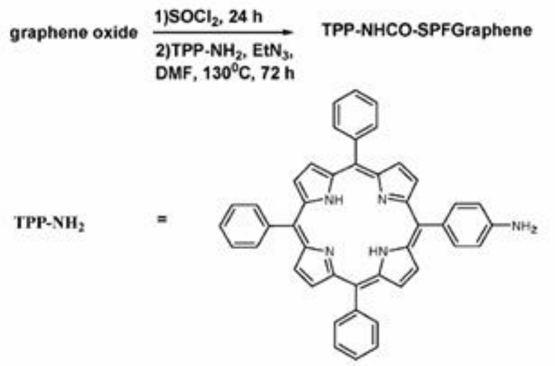
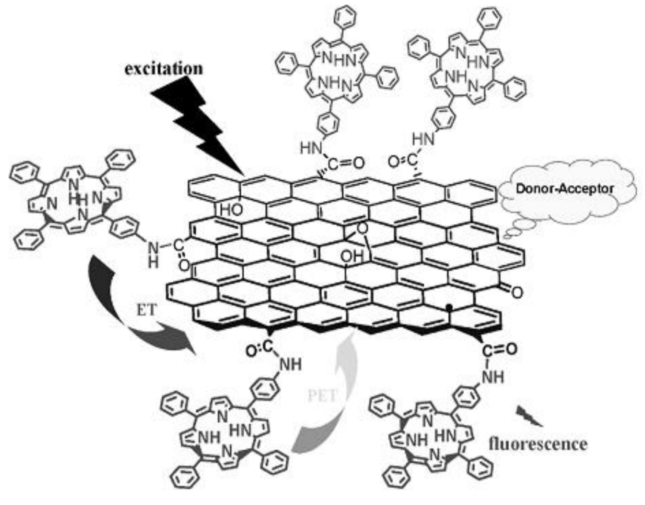
Synthesis of TPP-NHCO-SPFNano graphene

The first organic-solution-processable functionalized-nano graphene (SPFGraphene) hybrid material with porphyrins. The synthesis of the porphyrin–Nano graphene nanohybrid, 5-4 (aminophenyl)-10, 15, 20-triphenyl porphyrin (TPP) and grapheme oxide molecules covalently bonded together vi a an amide bond (TPP-NHCO-SPF Nano graphene, Scheme 1 and 2) was carried out using an amine-functionalized prophyrin (TPP-NH_2) 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.[53-55] 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_2O.[53,54] TPP-NH_2 and Nano graphene oxide molecules are covalently bonded together by an amide bond. Much care has been taken to make sure all The unreacted TPP-NH_2 has 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- SPFNano graphene soluble in DMF and other polar solvents. [53,54]



Scheme 1. Synthesis scheme of TPP-NHCO-SPFNano graphene



Scheme 2. Schematic representation of part of the structure of the covalent TPP-NHCO-SPFNano graphene

Standard Pb solution

A standard solution of Pb(II), 1.0×10^{-3} M was prepared by dissolving 0.1111 g Pb nitrate (Merck) in water containing a drop of concentrated HCl and diluting to the mark in a 250-ml volumetric flask. All working solutions of Pb(II) were prepared by serial dilution of the stock solution.

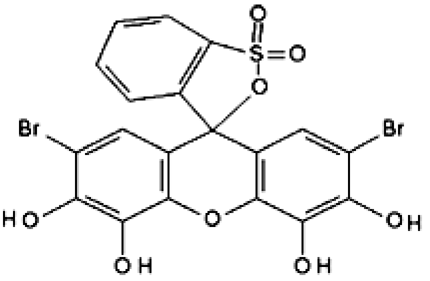


Fig 1. Structure of Bromopyrogallol red structure

Standard bromopyrogallol red solution

An aqueous solution of (1.0×10^{-4} M) bromopyrogallol red (Merck) was prepared by dissolving of 0.0140 g bromopyrogallol red in water and diluting to the mark in a 250-ml volumetric flask. Universal buffer solutions in the range from 2.0 to 10.0 were prepared with acetate, phosphate, and borate. Glycine/HCl buffer was used for pH 1.0. Stock solutions (5.0×10^{-3} M) of interfering ions were prepared by dissolving suitable salts in water, hydrochloric acid or sodium hydroxide solutions.

General procedure

The column was packed with 3.0 g adsorbent and was conditioned with 1.0–2.0 ml of pH 5.0. Then, 10.0 ml of Pb solution (5.0×10^{-5} M) was passed through the column at 0.1 ml min^{-1}. The analyte was eluted from the column by 1.0 ml of HCl, 1.0 M. A sample solution was prepared by pouring 0.5 ml of buffer solution (pH 1.0) in a 10.0 volumetric flask and 3.0 ml of 1.0×10^{-4}M bromopyrogallol red was added. The mixture diluted to ca. 8ml with water then 1.0 ml of Pb(II) (5.0×10^{-5} M) (eluted solution from column) was added and the solution diluted to the mark with water. The reaction mixture as agitated and then an appropriate amount of the solution was transferred to the spectrophotometric cell and variation in absorbance was recorded for the first 0.5–5.0 min from initiation of the reaction at 517 nm. A calibration graph was plotted with absorbance change ($\Delta A = A_5 - A_{0.5}$) versus Pb concentration.

Results and discussion

organic-solution-processable functionalized-nano graphene (SPF Graphene) with the following structure (Scheme 1) is a new chelating agent which can form stable complex with Pb(II). By immobilizing this tridentate bisamide ligand on microcrystalline naphthalene, Pb(II) can be adsorbed. Then desorption of Pb is carried out by using a strong inorganic acid. The Pb(II) concentrations were determined spectro photometrically after passing solution through the column. Therefore, first the optimum conditions for spectro photometric procedure should be studied.

Effect of variables on the determination of Pb

Bromopyrogallol red with following structure Fig. 1 is oxidized by Pb and the absorbance of the solution decreases with time, at $\lambda = 517$ nm. The change in the signal is proportional to Pb concentration. Fig. 3 shows the absorption spectra of bromopyr- ogallol red-Pb system at different times. Experiment (spetrophotometric determination) on eluted Pb solution was done at different pH values (1.0–5.0). Fig. 2 shows the effect of pH on the net absorbance (ΔA). The maximum net absorbance is at pH 1.0; whereas higher pH values cause decreasing in the signal. At higher pH values, oxidation potential of Bromopyrogallol red increases, thus the reaction rate and ΔA decreased. Therefore the pH of 1.0 was selected for this study. The influence of bromopyrogallol red concentration on the reaction rate was tested at pH 1.0 with 1.0×10^{-5} M, Pb(II) at 30

◦C (Fig. 3). It can be seen that the best concentration for bromopyrogallol red is 3.0×10^{-5} M. At higher values the aggregation of bromopyrogallol red causes the reaction rate to be decreased. Effect of temperature on the maximum signal (ΔA) was studied for the range of 10–50 ◦C, under optimum conditions otherwise as previously described. Fig. 4 shows that with increasing temperature up to 30 °C, ΔA signal or the rate of reaction increases. So temperature was fixed at 30 °C. At higher temperature bromopyrogallol red can be decomposed.

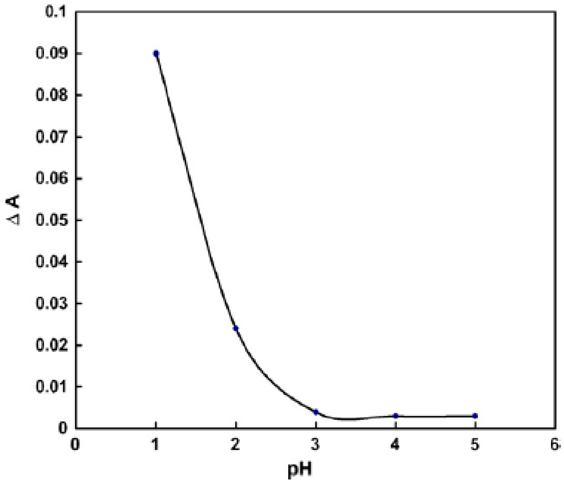


Fig 2. Effect of pH on the reaction rate.
Conditions: bromopyrogallol red, 1.0×10^{-5} M; Pb(II), 1.0×10^{-5} M; temperature, 30 °C; measuring time, 5.0 min from initiation of the reaction

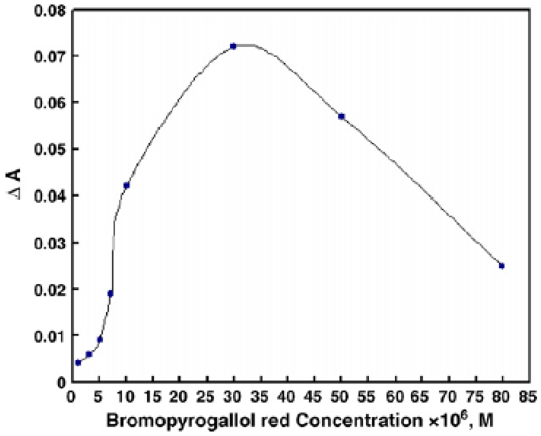


Fig 3. Effect of bromopyrogallol red concentration on the reaction rate. Conditions: pH 1.0; Pb(II), 1.0×10^{-5}M; temperature, 30 °C; measuring time, 5.0 min from initiation of the reaction

Effect of variables on the preconcentration

The effect of pH on preconcentration of Pb(II)was examined in range of 1.0–10.0, and the results are shown in Fig. 5. The results show that in the pH range of 5.0–10.0, the analyte was adsorbed on microcrystalline naphthalene quantitavely and the recoverywas more than 90%. For pHlower than 5.0 the complex will not be formed on adsorbent (at acidic media, active sites of ligand will be protonated) and at high pH values, Pb will precipitate on the column (precipitating instead of adsorption will occur). In order to obtain the best conditions for determination after preconcentration and to prevent the precipitation of Pb (especially at high concentrations), the most acidic pH from this range of buffers (5–10), was selected. The influence of analyte retention time was investigated by passing 10.0 ml of Pb(II) (5.0×10^{-5} M) solution in the pH 5.0 with different flowrates, and performing the experiment with the passed solution. The results show that in the higher flow rates, Pb cannot be adsorbed on microcrystalline naphthalene quantitavely. The best flow rate was selected to be 0.1 ml min^{-1}. As the Pb complex is unstable in high acidic solutions, hydrochloric acid was selected to desorb the adsorbed analyte. Fig. 6 shows that Pb(II) can be desorbed from the adsorbent by elution with 1.0 ml, HCl, 1.0 M. For investigating the ability of microcrystalline naphthalene to adsorb Pb(II) after sequential elutions, the preconcentration process was repeated for many times. It was indicated that the results were satisfactory, even by using one column for 10 times, with out changing the packing. The different volumes of Pb solution, 1.0×10^{-8} M in the range of 10–1000 ml were passed through the column and the signal of each eluted solution was compared with calibration curve data which is achieved from determination method. The obtained signals of concentrated Pb solutions presented that a preconcentration factor of 100 can be achieved by this method. The effect of ionic strength on the sensitivity was studied. The sensitivity would be slightly changed with increasing the ionic strength of the reaction mixture.

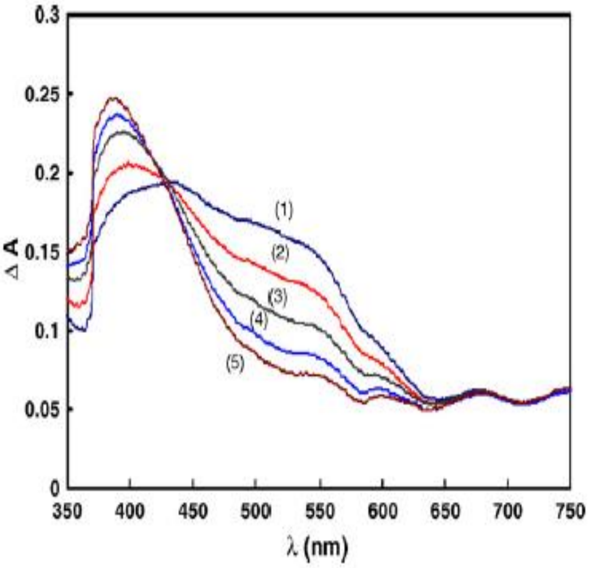


Fig 4. Effect of temperature on the rate of reaction. Conditions: pH 1.0; Pb(II), 1.0×10^{-5} M; bromopyrogallol red, 3.0×10^{-5} M; measuring time, 5.0 min from initiation of the reaction

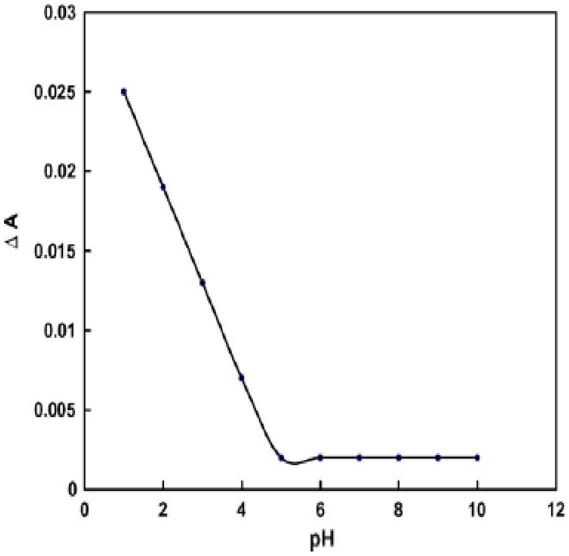


Fig 5. Effect of pH on the preconcentration recovery. Conditions: Pb(II), 5.0×10^{-6} M; flow rate, 0.1 ml min^{-1}; optimum conditions for determination of Pb(II)

Table 1. Interferences effect on the determination of 5.0 × 10−6 M, Pb(II)

Tolerance limit		Species
($W_{ion}/W_{Pb(II)}$)		
100		NH_4^+,Na^+ ,K^+,H_3BO_3 ,Hg^{2+},Ba^{2+},Cd^{2+} ,Co^{2+}
		,Ca^{2+},Pb^{2+},Sn^{2+},Sr^{2+},Tl^+
58		Al^{3+},Mg^{2+},Ni^{2+},Cu^{2+}
24		Fe^{2+},Fe^{3+}
15		Zn^{2+}
1		Sb^{3+},Ag^+

Table 2. Comparison of some methods for preconcentration and determination of thallium with proposed method

Reference	LDR (ng ml^{-1})	DL (ng ml^{-1})	Method
[51]	3.75–17.5	1	Solid–liquid extraction
[52] [40]	0.1–100 5–250	0.08 1	Potentiometric stripping
[53] [30] –	5–20 40–18000 2.1–2000	4 20 0.3	Liquid–liquid extraction Microcrystalline naphthalene Proposed method

Table 3

Determination of Pb(II) in the real samples after preconcentration				
Recovery %	ICP	Found (×10^{-8} M)	Added (×10^{-8} M)	Sample
–	-	–	–	
99.5	1.03± 0.05	1.07 ± 0.096	1.0	
98.3	4.95 ± 0.08	4.94 ± 0.079	5.0	Drinking water
98.3	8.02 ± 0.10	7.95 ± 0.089	8.0	
99.0	10.41 ± 0.03	10.33 ± 0.016	10.0	
–	–	–	–	
96.5	0.95 ± 0.08	0.96 ± 0.060	1.0	
97.3	4.85 ± 0.08	4.73 ± 0.075	5.0	River water
95.2	7.920 ± 0.07	7.62 ± 0.094	8.0	
98.7	9.95 ± 0.08	10.40 ± 0.076	10.0	

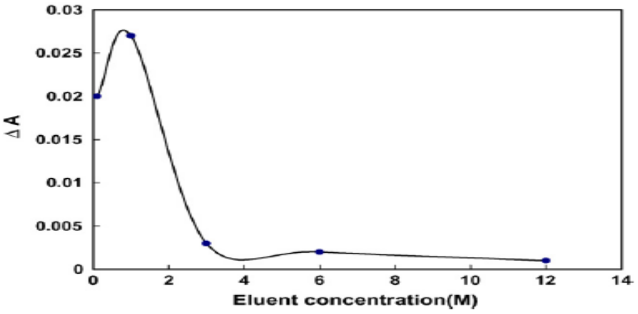


Fig 6. Effect of HCl concentration for elution. Conditions: Pb(II), 5.0×10^{-6} M; pH 1.0; HCl, 1.0 ml; optimum conditions for determination of Pb(II)

Retention capacity of the adsorbent

The retention capacity of organic-solution-processable functionalized-nano graphene (SPFGraphene) adsorben was determined by a batch method. The 20 ml solution of Pb(II) 1.0×10^{-4}M in pH 5.0 was transferred in to a separating funnel and 3 g adsorbent was added. The separating funnel was shaken vigorously for 30 min. Concentration of Pb in the filtrate was determined according to calibration curve data and then adsorbed amount of Pb was calculated. The retention capacity (mg adsorbed Pb/ g adsorbent)was obtained to be 0.1672 mg $g^{-1}$of adsorbent or2.01 mg $g^{-1}$of ligand.

Calibration graph, reproducibility and detection limit

Aseries of standard solutions of Pb(II) were treated under the above mentioned optimized experimental conditions. Pb concentration can be determined in the range of 4.2×10^{-9} to 2.3×10^{-5}M with linear equation; $\Delta A = 0.00078\times C + 0.0056$ and regression coefficient of $r^2 = 0.9988$ (ΔA is absorbance signal after preconcentration and C is molar concentration of Pb×106). The experimental limit of detection is 1.42×10^{-9}M (S/N =3). The relative standard deviation (R.S.D.%) for 10 replicate measurements of 5.0×10^{-9}, 1.0×10^{-8}, 1.0×10^{-7}, 3.0×10^{-6} and 1.0×10^{-5}M of Pb(II) were 3.04, 2.95, 2.11, 3.12 and 1.90%, respectively.

Influence of foreign ions

The influence of contaminant species presented in various samples on the determination of 5.0×10^{-6} M, Pb(II)was investigated. The tolerance limit was defined as the concentration of added ions, causing a relative error less than 3% (Table 1). Some metal cations can be adsorbed on microcrystalline naphthalene at different pH values. This proposed adsorbent is not only able to remove anions of the Pb(II) solution but also can decrease the interference of some cations. Some of important ions that can be found in the real samples with Pb(II) such as Sn^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Ca^{2+}, Pb^{2+} and Tl^{1+} do not have any interference on the determination of Pb(II). Al and Fe can be troublesome in the determination procedure but with preconcentration their interference decreases. The reported method is selective and simple and it has excellent capacity factor. Among other mentioned methods in Table 2 stripping volt ammetry has a good sensitivity but it needs expensive apparatus and needs the operator to be skillful.

Conventional solvent extractions are not sensitive enough and they consume a large amount of solvent. Also most of extracting solvents are toxic and volatile.

On the basis of the results obtained from the Pb(II) standards, the recommended preconcentration method has been successfully applied prior to spectrophtomeric determination of low values of Pb in the tap water(Tehran, taken after 10 min operation of the tap),rain water(Tehran, 22 January, 2007)samples. The analysiswas performed by using the standard addition technique. The results are summarized in Table 3. Good recoveries in all samples were obtained. This method was reliable through comparing with eachother[32-36].

Conclusion

Solid–liquid extraction with microcrystalline naphthalene is an effective separation and preconcentration technique for trace elements. The method has the advantages of being simple, inexpensive and selective This proposed preconcentration method has a high enrichment factor (100) which develops possibility of determining concentration levels as lowas sub micro amounts of Pb with eliminating the interference of some diverse ions. The selected determination procedure (after preconcentration) is convenient, sensitive and fairly selective.

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