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Separation of Trace Amount Zn (II) Using Additional Carbonyl and Carboxyl Groups Functionalized-Nano Graphene

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Abstract: A novel and selective method for the fast determination of trace amounts of Zn(II)ions in water samples has been developed. The first additional carbonyl and carboxyl functionalized-nano graphene (SPFNano graphene). The presence of additional carbonyl and carboxyl groups located at the edge of the sheets makes GO sheets strongly hydrophilic, allowing them to readily swell and disperse in water. Based on these oxygen functionalities, different model structures of GO were used as absorbent for extraction of Zn (II) ions by solid phase extraction method. The complexes were eluted with HNO_3 (2M)10% $V.V^{-1}$ methanol in acetone and determined the analyte by flame atomic absorption spectrometry. The procedure is based on the selective formation of Zn (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^{TM} disks modified carbonyl and carboxyl functionalized-nano graphene oxide molecules covalently bonded together 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, SPFNano graphene, amount, stripping solvent, and sample flow rate were also investigated. Under the optimal experimental conditions, the break-through volume was found to about 1000mL providing a preconcentration factor of 500. The maximum capacity of the disks was found to be 456± 3 µg for Zn^{2+}.The limit of detection of the proposed method is 5ng per 1000mL.The method was applied to the extraction and recovery of Zn in different water samples.

Keywords: Zn(II), SPE, Octadecyl slica disks, FAAS, carbonyl and carboxyl functionalized-nano grapheme (SPFNano graphene).

INTRODUCTION

Zinc is considered as an essential micronutrient for humans, plants and animals. It plays an important role in several biochemical processes [1]. Zinc deficiency slows growth and development of the neonate. Zinc deficiency also leads to cognitive defects and impairs the immune system [2]. However, if it is in excess, it can also play an important role in the progression of several damages to human body, including disturbances in energy metabolism or increasing in oxidative stress [3]. Therefore, it is of great importance and significance for environment science and life science to separate and determine trace zinc in water samples. Although very sensitive analytical techniques, such as FAAS [4, 5, 19-20], ICP-MS [6] and ICP-AES [7] are used for the determination of trace zinc, it is impossible to directly determine the amount of zinc in water samples owing to the low concentration of zinc. In order to achieve accurate and reliable results, preconcentration step is necessary when the concentration of zinc is too low to be directly determined. Solid-phase extraction (SPE) is one of the most effective preconcentration methods because of simplicity, rapidity, high preconcentration factor and high recovery. The procedures for separation and preconcentration of zinc had been reported extensively [4–13]. Polyurethane foam loaded with 2-[2-(6- methyl-benzothiazolylazo)]-4-bromophenol [8] was used for separation of zinc in natural water samples. Silica gel functionalized with1, 5-bis(di-2-pyridyl)methylene thiocarbohydrazide [7], 1,8-dihydroxyanthraquinone [9] were used for the preconcentration of zinc in water samples. Ion flotation [10], Amberlite XAD-2 [11, 12], solvent extraction using LIX 84 I [13], poly(ethylene terephthalate), naphthalene [17,18] were also used for the separation of zinc in diverse samples.

However, using microcrystalline triphenylmethane loaded with malachite green as solid-phase extractant to separate and preconcentrate Zn (II) has not been reported in any literature. The aim of this work was to apply a thiazolylazo reagent, 5-[1(H)-Benzotriazole methylene]-8-quinolinol (BTMQ) in a CPE procedure for determination of Zinc in water samples. Some analogous

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Compounds of BTMQ such as 2-(6-methyl-2-benzothiazolylazo)-5- diethyl aminophenol (MBTAE) [22–24] and 2-(2-thiazolylazo)- 5-diethylaminophenol (TADAP) [25–27] have been applied as a precolumn derivatizing reagent in high-performance liquid chromatography (HPLC). Another analogue, 2-(6-bromo-2-benzothiazolylazo)-5-diethyl aminophenol, was synthesized and applied to the spectrophotometric determination of nickel [28] and zirconium [29]. According our knowledge, the use of BTMQ in analytical procedures has not been reported before. For instance, Yan’s group utilized L-cysteine to modify multiwalled carbon nanotubes (MWCNTs) resulting in a novel extractant for preconcentration of Cd (II) [33]. Unlike pristine MWCNTs, the sorption of Cd (II) onto the modified MWCNTs is not influenced by ionic strength in a wide range. Similar strategy also has been used by Chang and his coworkers to exploit ethylenediamine-grafted MWCNTs extractant [34]. The new extractant shows higher adsorption capacities for SPE of Cr (III), Fe(III) and Pb(II).

In the present report, we wish to describe a proper concentrative method for assessment of trace levels of Zn in different water samples. To the best of our knowledge, octadecyl silica membrane disks modified by (SPFNano graphene,) have not been used for Zn isolation and preconcentration, previously of this work was the development of a rapid, efficient and highly sensitive method for selective extraction and concentration of ultra trace amounts of Zn^{2+} ions from aqueous media using octadecyl silica membrane disks modified by carbonyl and carboxyl functionalized-nano graphene and grapheme oxide molecules covalently bonded (SPFNano graphene) and FAAS determination.

EXPERIMENTAL

Reagents

All acids were of the highest purity available from Merck and were used as received. Methanol and Chlorofom were of HPLC grade from Merck. Analytical grade nitrate salts of litium, sodium, potassium, magnesium, calcium, strontium, barium, zinc, cadmium, lead, nickel, cobalt (II), and Zn(II) were of the highest purity. Ultra pure organic solvents were obtained from E. Merck, Darmstat, Germany, and High Purity double distilled deionized water was used throughout the experiments.

The stock standard solution of Zn^{2+} was prepared by dissolving 0.1000g of the Zn powder in 10mL concentrated nitric acid and diluted to 1000mL with water in a calibrated flask. Working solutions were prepared by appropriate dilution of the stock solution.

The synthesis of the SPFNano graphene, is illustrated in Fig. 1.

Synthesis of SPFNano graphene

The presence of additional carbonyl and carboxyl groups located at the edge of the sheets makes GO sheets strongly hydrophilic, allowing them to readily swell and disperse in water [55,56]. Based on these oxygen functionalities, different model structures of GO (Fig. 1) have been proposed in the literature [53, 54, 57].

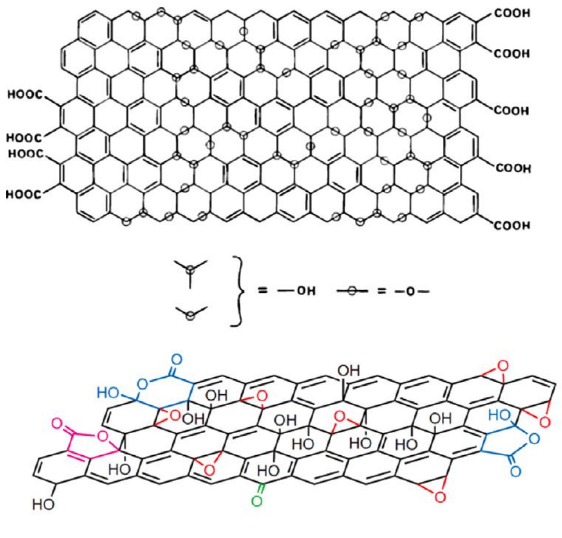

Fig. 1. Variations of the Lerf–Klinowski model indicating ambiguity regarding the presence (top, adapted from Ref. [53]) or absence (bottom, adapted from Ref. [54]) of carboxylic acids on the periphery of the basal plane of GO graphitic platelets. (Reproduced with permission from [54].)

Apparatus

Determination of Zn^{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).

SPFNano graphene, (40 mg) were packed into an SPE ENVI-18 DISK^{TM} disks. Solid phase extractions were carried out by glassy membrane disks, ENVI-18DISK^{TM} 47mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 A˚ 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 was performed with glassy membrane disks, ENVI-18 DISK^{TM} 47mm diameter ×0.6 mm thickness containing octadecyl silica bonded phase (30 µm particles, 70 A˚ pore size) from Supelco. The disks were used in conjunctions with a standard Millipore 47mm filtration apparatus connected to water aspirator.[46]

Sample Treatment: The water samples were filtered through 45µm nylon filters. Sampling vessels were polyethylene bottles soaked in 1 mol.L^{-1} HNO_3 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 Zn (II).Then, 5mL of methanol was added to a 90mL portion of each before analysis. The surface of the ENVI-18 DISK^{TM} disks was modified with SPFNano graphene, and therefore could retain Zn^{2+} ions properly. Instead, 10 mg of SPFNano graphene, an appropriate volume of an organic solvent (5mL) miscible with water. The most suitable solvent under the experimental conditions was acetone.

Disk cleaning and conditioning: A disk was placed in the apparatus and was washed with 10mL 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 10mL of methanol, immediately followed by 10mL of water, without letting the surface of the disk dry. This step pre-wets the disk surface prior to extraction. Improper performance of this step causes slow flow – rate and poor analytic 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 (100mL 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 dry (about 5 minute).

Analytic elution: In order to elute the analytic selectively, exactly 5 mL of acidified solvents 0.1M 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 concentrations of Zn (II) in the elution were then determined by FAAS using an external calibration graph.

RESULTS AND DISCUSSION

Evaluation of the role of the SPFNano graphene,

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

Choice of eluent

In order to select the most appropriate eluent for the quantitative stripping of the retained Zn (II) on the disks, 5mL of various non organic (each containing 10% V.V^{-1} methanol) and different organic solvents were tested. The results tabulated in Table3. As can be seen, the best eluting solvents were found to be 5mL of HNO_3 (2M)10% V.V^{-1} methanol, resulting in quantitative elution of Zn(II) from the disk. It should be emphasized that presence of HNO_3 (2M)10% V.V^{-1} methanol in any kind of employed solvents helps to better the contact of eluent with hydrophobic surface of the disk.

Table 3.Effect of different eluting solvents on Percentage recovery of Zn(II) adsorbed on the disk [a]

	% Recovery		
Stripping solution	2ml	5ml	10ml
Nitric acid(2M)10% V.V^{-1} mthanol	82.3(2.5)[b]	92.5(2.6)	97.5(2.0)
Acidified methanol [c]	33.5(2.4)	83.2(2.2)	83.5(2.7)
Ammoniacal methanol[d]	23.4 (2.3)	87.5(2.6)	86.3(2.8)
Nitric acid(1M)10% V.V^{-1} mthanol	82.5(1.7)	99.61.5)	98.8(2.7)
Acetonitril	36.6(2.8)	46.6(5.5)	69.0(2.6)
Formic acid(1M)10% V.V^{-1} mthanol	45.6(1.2)	68.3(2.0)	77.5(2.5)
Hydrochloric acid(1M)10% V.V-1 mthanol	52.7(1.9)	92.5(2.6)	91.2(2.6)
Hydrochloric acid(1M)10% V.V^{-1} mthanol	51.6(2.5)	66.0 (2.5)	97.3(1.9)
Methanol	52.8(1.9)	85.5(2.3)	85.4(2.0)
Ethanol	64.0(2.5)	85.4(2.1)	87.9(1.9)

[a] Initial samples contained 10 µg of each Zn in 100 mL water.
[b] Values in parentheses are RSDs based on five individual replicate analysis.
[c] Acidified solvents obtained by addition of 0.1*M* HCl.
Ammoniacal solvents obtained by addition of 0.1*M* NH_3

Table 2. The effect of presence of SPFNano graphene, on extraction perce of Zn(II)[a].

SPFNano graphene,	pH	Extraction percent of Zn(II)
Absence	2-6	0.07(6.7)[b]
Presence	2-6	98.8(2.7) to 65(2.9)

[a] Initial samples contained 10μg of Zn(II) in 100mL of water.
[b] Values in parentheses are RSD_S based on five individual replicate analyses.

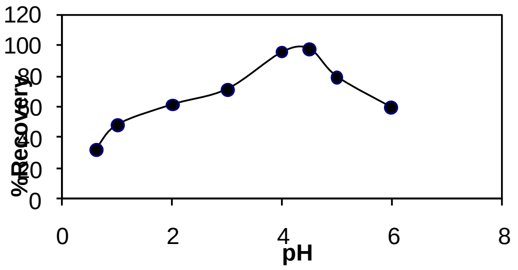

Fig. 2. Influence of sample pH on the percentage recovery of Zn(II).

The effect of the pH

The pH of the sample solutions were adjusted to different values between 2-9 by addition of hydrochloric acid or a suitable buffer such as sodium acceate-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 Zn (II).Then, percentage recovery at various pH values was determined (Fig .2). According to the results shown in Fig.2 up to pH 3.8-4.0, 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 SPFNano graphene, occurs and there is a weak tendency for retention between Zn (II) and SPFNano graphene, whereas at higher values (pH>5), Zn (II) reacts with hydroxide ions to produce $Zn(OH)_2$. Therefore, sodium acceate-acetic acid buffer with pH=4.5 was used for the preconcentration step. Other solvents used for dissolving SPFNano graphene, were methanol and ethanol. The influences of these solvents on the recoveries as a function of pH are compared and shown in Fig. 2.

Mean while, other organic solvents were not tested because of their restricted solubility and formation of two phases with aqueous solutions and incompatibility with flame higher pH values (>7) were not tested because of the possibility of the hydrolysis of octadecyl silica in the disks [47, 48]. Zn (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 (< 4.0), nitrogen atoms of the SPFNano graphene, 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 Zn^{2+} ions by the modified disks, different counter anions were tested Table 4, it is immediately obvious that the nature of the counter anion strongly influences the retention of Zn ions by the disk. The results revealed that the SPFNano graphene behaves in pH range 3.8-4.0 [28, 27]. So that the Zn 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 Zn (II) ions. The influence of the concentration of sodium acetate ion on Zn recovery was investigated, and the results are shown in Table 4. As seen, the percent recovery of Zn^{2+} 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 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 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 10-100 mL.min^{-1}, the retention of Zn (II) was not considerably affected by the sample solutions flow-rates and leads to reproducible and satisfactory results (Fig. 3). Thus, the flow-rate was maintained at 89mL.min^{-1} throughout the experiment.

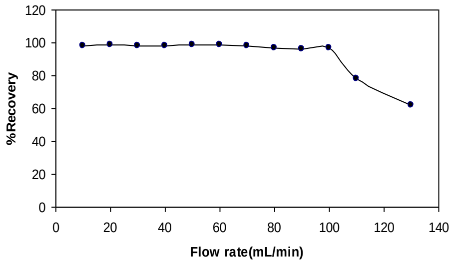

Fig. 3. The effect of the flow-rate on extraction percent of Zn(II).

Quantity of the SPFNano graphene, the optimum amount of SPFNano graphene, for the quantitative extraction of Zn (II).was also investigated by adding various amounts of it to solution (between 2-20 mg). The results are listed in Table 5. The experimental results revealed that the extraction of Zn (II).was quantitative using a sample solution containing more than 10 mg SPFNano graphene, . Hence, subsequent extractions were performed with 15mg of SPFNano graphene, .

Table 5. Influence of the SPFNano graphene, amount on the recovery of Zn(II) ions [a].

SPFNano graphene, amount (mg)	Recovery(%) of Zn(II)
2	32.20(2.5)[b]
5	45.40(2.0)
8	83.20(2.8)
10	95.7(2.8)
15	98.5(2.9)
20	98.6(2.8)

[a] Initial samples contained 10 µg of each Zn in 100 mL water.

[b] Values in parentheses are RSDs based on five individual replicate analysis.

Table 4. Percent recovery of Zn from the modified membrane disk in the presence of 0.01 M of different counter anions [a].

counter anion	%Recovery
Cl^-	14.8
Br^-	25.9
ClO_4^-	34.0
SCN^-	45.8
Picrate	70.9
Acetate	96.0

[a] Initial samples contained 10µg of Zn(II) in 100mL of water.

Disk efficiency

Undoubtedly, one of the major parameters affecting in 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^{TM} 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 10replicates. These observations are represented in Fig. 4

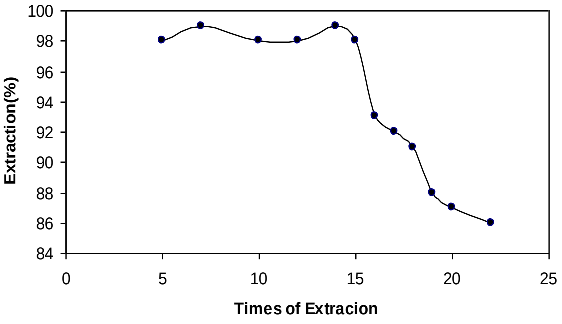

Fig. 4. Influence of eluent(5mL of methanol)type on disk efficiency.

Analytical Performance

When solutions of 10µg Zn in 10, 50, 100, 600, 1000, 2000, 2500 and 3000mL solutions under optimal experimental conditions were passed through the disks, the Zn (II) was quantitatively retained in all cases. Thus, the breakthrough volume for the method must be greater than 2500mL, providing a concentration factor of >500. The limit of detection (LOD) of the method for the determination of Zn (II) was studied under the optimal experimental conditions. The LOD based on 3σ of the blank (5mL of methanol) is 5 ng per 1000mL.

The capacity of modified disks(5mg SPFNano graphene,) was determined by passing 50mL portions of sample solutions containing 8mg of Zn and 0.1M sodium acceate-acetic acid buffer with pH 3.8-4.0, 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 456±3µg of Zn^{2+} on the disk.

In order to investigate the selective separation and determination of Zn^{2+} ions from its binary mixtures with various metal ions, an aliquot of aqueous solutions (50mL) containing 10µg Zn^{2+} and mg amounts of other cations was taken and the recommended procedure was followed. The results are summarized in Table 6. The results show that the Zn (II) ions in binary mixtures are retained almost completely by the modified disk, even in the presence of up to about 100mg of various ions. Meanwhile, retention of other cations by the disk is very low and they can be separated effectively from the Zn^{2+} ion. Its is interesting to note that, in other experiments, we found that in the presence of high enough concentrations $NH_2OH.HCl$ as a suitable reducing agent (> 0.5M) [48].

Analysis of water samples

To assess the applicability of the method to real samples, it was applied to the extraction and determination of Zn from different water samples. Tap water (Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20January, 2012), Snow water (Tehran , 16 February ,2012) and Sea water (taken from Caspian sea, near the Mahmoud-Abad shore) samples were analyzed (Table 7). As can be seen from Table 4 the added Zn ions can be quantitatively recovered from the water samples used. As is seen, the recovered Zn ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES.

CONCLUSION

Results presented in this work demonstrate well the tremendous possibilities offered by the solid phase extraction of trace amounts of Zn (II) in water samples using Octadecyl Silica membrane disks modified by (SPFNano graphene) and its determination by FAAS. The method developed was simple, reliable, and precise for determining Zn in water. Also, the proposed method was free of interference compared to conventional procedures to determine Zn [49-52]. The method can be successfully applied to the separation and determination of Zn in binary mixtures.

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