Indian Journal of Fundamental and Applied Life Sciences ISSN: 2231– 6345 (Online)
An Open Access, Online International Journal Available at www.cibtech.org/sp.ed/jls/2015/02/jls.htm
2015 Vol. 5 (S2), pp. 2967-2979/Moghimi and Moghani

Research Article

EXTRACTION OF COPPER WITH GRAPHENE OXIDE WITH COVALENTLY LINKED PORPHYRIN PRIOR TO DETERMINATION BY FLAME ATOMIC ABSORPTION SPECTROMETER

***Ali Moghimi[1] and Hossain Moghani[2]**
[1]*Department of Chemistry, Varamin (Pishva) Branch Islamic Azad University, Varamin, Iran*
[2]*Department of Chemistry, EslamShahr Branch Islamic Azad University, EslamShahr, Iran*
**Author for Correspondence*

ABSTRACT

A simple, highly sensitive, accurate and selective method for determination of trace amounts of Cu^{2+}in water samples.In this paper, a Graphene oxide with covalently linked porphyrin (GO–H_2P) based new sorbent was prepared. The modified Graphene oxide (GO–H_2P) was used for preconcentration of Cu(II) from aqueous solutions. The analytical variables were optimized by central composite design (CCD). Flame atomic absorption spectrometer was utilized for determination of Cu(II). The analytical features for sorption were found to be 5.2; 4.3 mL min^{-1} and 55.0 mL for pH, flow rate and sample volume, respectively. HNO_3 was used as eluent and maximum preconcentration factor was found to be 200.Elution parameters were also determined as 4 mL min^{-1}; 0.6 mol L^{-1} and 5.1 mL forflow rate, eluent concentration and eluent volume, respectively. Limit of detection and limit of quantification were found to be 49.6 and 163.7 ng L^{-1}, respectively. Validation of the developed method was performed using certified reference material (TMDA-53.3). The methodology was applied for determination of Cu(II) in natural water samples and satisfactory results were obtained.

Keywords: *Graphene Oxide with Covalently Linked Porphyrin (GO–H_2P), Preconcentration, Cadmium, Central Composite Design, Flame Atomic Absorption Spectrometer, Water*

INTRODUCTION

Graphenes are attracting renewed interests owing to recent advances in micromechanical exfoliation and epitaxial growth methods that make macroscopic 2D sheets of sp^2-carbon atoms available (Geim). A variety of simple yet elegant physics relating to its zero-gap semiconductor character has thus been demonstrated (Zhang). It would be very desirable to make these materials solution (or more accurately, dispersion) processable by coating or printing, which will open applications for large and/or flexible substrates. Graphite oxide (GO) is a possible candidate for this because it is a precursor to graphene through deoxidation either thermally or by chemical reduction (Lerf). Although GO itself has been studied for over a century (Brodie). Its structure and properties remain elusive, and progress has been made only recently to give materials with limited dispersability and electronic quality (Eaton). Copper at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems (Lerf).

The direct determination of trace metals especially toxic metal ions such as Cu(II), tin, arsenic, lead, antimony and selenium from various samples requires mostly an initial and efficient pre-concentration step (Leyden (a),; Takeshima,; Taylor,). This pre-concentration is required to meet the detection limits as well as to determine the lower concentration levels of the analyte of interest. This can be performed simply in many ways including liquid and solid phase extraction techniques (Nambiar,. Caroli,). The application of solid phase extraction technique for pre- concentration 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).

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), filter paper (Leyden), cellulose (Gennaro) and ion exchange resins (Grote). Silica gel, alumina, magnesia and zirconia are the major inorganic solid matrices used to immobilize the target organic modifiers on their surfaces

(Unger) 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). 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). 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 and Moghimi, 2013). 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 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). Selective solid phase extractors and pre-concentrators are mainly based on impregnation of the solid surface with certain donor atoms such as oxygen, nitrogen and sulfur containing compounds (Mahmoud, a; Mahmoud b; Tong; Dadler). 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 Cu(II)(Mahmoud, a; Mahmoud b) and pre-concentration of various cations (Leyden (b), 1976; Narin *et al.*, 2009; Moghimi, 2008; Thurman *et al.*, 2006; Moghimi *et al.*, 2007; Moghimi *et al.*, 2006; Moghimi, 2007; Moghimi, 2007; Moghimi, 2007) and 2- mercaptobenzothiazol-modified silica gel for on-line pre-concentration and separation of silver for atomic absorption spectrometric determinations (Qiaosheng *et al.*, 1998). Ammonium hexa-hydroazepin-1-dithiocarboxylate (HMDC)-loaded on silica gel as solid phase pre-concentration column for atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) was reported (Alexandrova). Mercapto-modified silica gel phase was used in pre-concentration of some trace metals from seawater (Moghimi *et al.*, 2010). Sorption of Cu (II) by some sulfur containing complexing agents loaded on various solid supports (Tajodini) was also reported. 2-Amino-1- cyclopentene-1-dithiocaboxylic acid (ACDA) for the extraction of silver (I), Cu (II) and palladium (II) (Moghimi *et al.*, 2009), 2-[2-triethoxysilyl-ethylthio] aniline for the selective extraction and separation of palladium from other interfering metal ions (Narin) as well as thiosemicarbazide for sorption of different metal ions (Campderros) and thioanilide loaded on silica gel for pre-concentration of palladium(II) from water (Narin) are also sulfur containing silica gel phases.

In the present work, Graphene oxide with covalently linked porphyrin (GO–H_2P) was employed for production of solid phase. The synthesized and characterized new sorbent (GO–H_2P) was utilized for preconcentration of Cu(II) from water samples. Determination of Cu(II) concentration was achieved by FAAS after preconcentration procedure. The experimental conditions were optimized by CCD.

Experimental

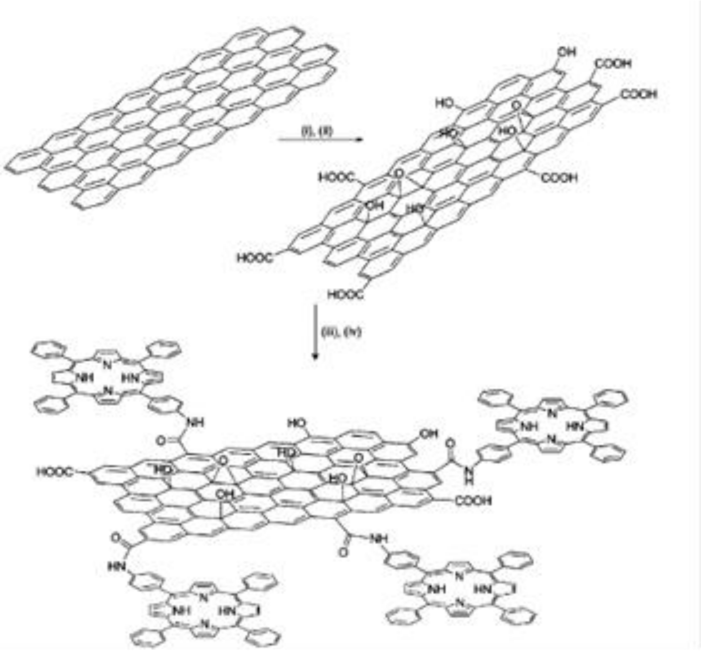
Reagents and Chemicals

The analytical grade deionized water was obtained by reverse osmosis system. All containers and glassware were kept overnight in 10% nitric acid and rinsed three times with water before use.1,000 mg L-1stock copper standard solution was prepared from $Cu(NO_3)_2.4H_2O$ (Merck) and diluted as required to the μg L^{-1} levels. In interference study, cations were added as nitrates and the anions were added as sodium salts. Feasibility of the suggested method was tested with Lake Ontario water certified reference material (TMDA-53.3, lot 0310).

Synthetic Procedures

Preparation of GO–H_2P

GO (15 mg) was stirred in 20 mL of oxalyl chloride at 80 °C for 24 h to activate the carboxylic units by forming the corresponding acyl chlorides. Then, the reaction mixture was evaporated to remove the excess oxalyl chloride and the brownish remaining solid (GO–COCl) was washed with anhydrous tetrahydrofuran (THF). After centrifugation, the resulting solid material was dried at room temperature under vacuum. For the covalent coupling between the free amino function of H_2P and the acyl chloride of GO, 15 mg of GO–COCl was treated under anaerobic, dry conditions with 7 mg of H_2P dissolved in 6 ml of dry THF at room temperature for 72 h. The hybrid material, namely GO–H_2P, was obtained as a brown-graysolidby filtration of the reaction mixture through 0.2 mm PTFE filter and the filtrate was sufficiently washed with methylene chloride (4× 20 ml) to remove non-reacted free H_2P and then with diethyl ether (2 × 20 mL) before being dried under vacuum.



Scheme 1: A schematic illustration for the preparation of GO with covalently linked H_2P. (i) H_2SO_4/HNO_3 (2: 1 v/v), (ii) $KClO_3$, 96 h, (iii) $(COCl)_2$,80 °C, 24 h, (iv) 5-(4-aminophenyl)-10,15,20-triphenyl-21,23*H*-porphyrin, THF, r.t., 72 h.

Apparatus

A Philips X Pert-Pro diffracrometer (Cu Kα λ=1.54060 A°, 30 mA, 40 kV), and Perkin Elmer Spectrum 65 FTIR-ATR spectrometer were used to confirm the synthesized GO–H_2P.Determination of Cu(II) in solutions were carried out by Perkin Elmer AAnalyst200FAASequipped with deuterium background correction. All measurements were performed inan air/acetylene flame. GFL 3005 orbital shaker having speed and time control was used forpreparation of the sorbent. During the solid phase extraction experiments, VelpScientificaSP311 peristaltic pump with Tygon tubes was used. A Thermo Orion 5 Star model pH meter, Heidolph MR 3001 K model magnetic stirrer, Sartorius TE214S electronic balance,Eppendorf Research micro pipettes were used for the present work. Funnel tipped glass tube(10x100 mm) equipped with stopcock was used as a column for the preconcentration experiments.

Preparation of Solid Phase

The commercially available Graphene oxide with covalently linked porphyrin (GO–H_2P) was activated by refluxing with 0.5 mol L^{-1} HNO_3 for 1 h to remove any adsorbed metal ions. Then it was filtered, washed with deionized water until the filtrate was neutral.

In order to synthesize physically bonded GO–H_2P, 10.0 g of Graphene oxide with covalently linked porphyrin (GO–H_2P) was added to 50.0 mL acetone containing 50 mg MSE and refluxed for 24 h. The product was filtered off and washed with deionized water and dried at room temperature.

General Enrichment Procedure

1.0 g of GO–H_2P was filled in the column and the effective factors on the preconcentration including pH, flow rate and selection of eluent type were investigated using the model solutions containing 5µg Cu(II). The determination of Cu(II) in eluates were achieved by FAAS. According to the precipitation of the metal hydroxides at alkaline environment, pH effect was evaluated within the range of 3-7. Experiments of flow rate for sorption and elution were performed at 3-20 mL min^{-1}. In order to choose a proper eluent for desorbing the Cu(II) from the sorbent surface, different mineral and organic acids were tested.The proposed analytical procedure for Cu(II) preconcentration was optimized using three level full factorial CCD. The optimization procedure was performed separately for sorption and elution. Three variables; pH, sample volume, flow rate and eluent volume, eluent concentration, flow rate were regarded as factors for sorption and for elution, respectively.

RESULTS AND DISCUSSION

The treatment of Graphene oxide with covalently linked porphyrin (GO–H_2P) can lead to the derivatization of both the edge carboxyl and surface hydroxyl functional groups via formation of amides (Karousis) or carbamate esters (Smith), respectively.

The formation of GO–H_2P was followed by ATR-IR spectroscopy. Initially, in the spectrum of GO, the carbonyl vibration appears at 1716 cm^{-1}, while there are fingerprints at 3616 cm^{-1} and 3490 cm^{-1} due to the presence of hydroxyl species at the basal plane of graphene. The covalent linkage of H_2P with the acyl chloride activated GO is evident from the presence of a band at 1630 cm^{-1}, which is characteristic for the carbonyl groups of the amide units (Cataldo).

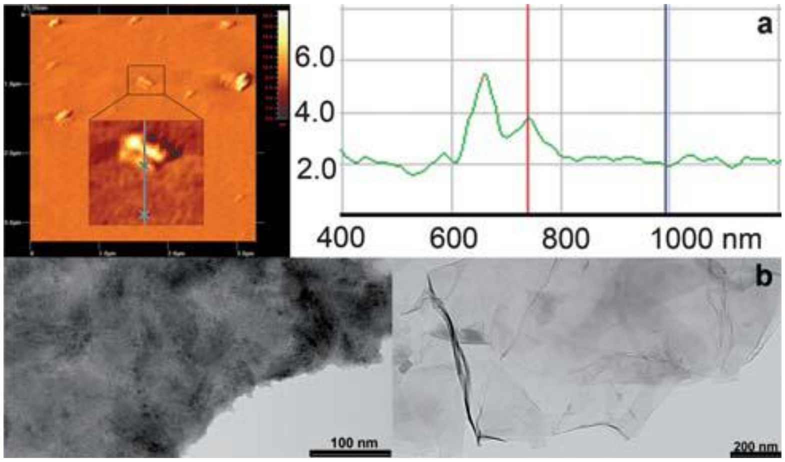


Figure 1: (a) Representative AFM image of GO–H_2P and profile analysis showing a height of 1.77 nm for the enlarged region. Section analysis of other regions of the image show height ranges of 1.5–3.5 nm. (b) TEM images of the intact graphite (left panel) and GO–H_2P hybrid material (right panel).

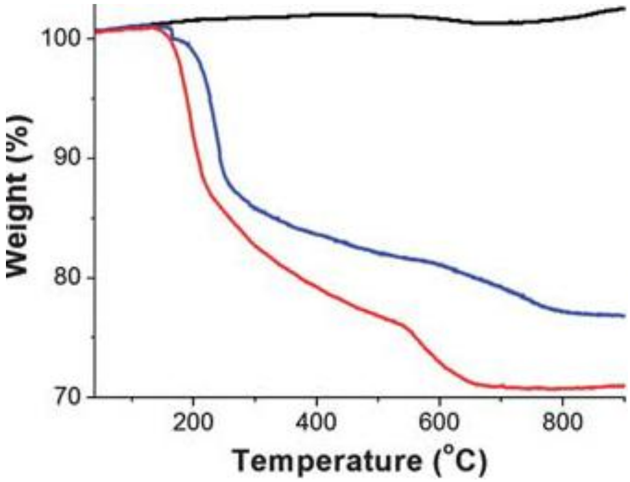


Figure 2: The TGA graphs of graphite (black), GO (blue) and GO–H_2P (red), obtained under an inert atmosphere

The amount of porphyrin attached onto the graphene sheet was evaluated by thermo gravimetric analysis. As compared with the TGA results of pure graphite, which is thermally stable up to 900 °C under nitrogen, and GO which decomposes above 600 °C, after having lost the oxygenated species at 240 °C (i.e. 14.7% weight loss), the 6% weight loss occurred in the temperature range 250–550 °C for the GO–H_2P material, is attributed to the decomposition of H_2P (Figure 2).

The GO–H_2P material forms a stable dispersion in DMF at a concentration not exceeding 1 mg mL^{-1}. The electronic absorption spectrum of GO–H_2P in DMF (Figure 3), shows (i)a broad signal monotonically decreasing from the UV to the visible region, which is attributed to GO and (ii) a characteristic band at 420 nm (Soret-band) corresponding to the covalently grafted H_2P units (the Q-bands at 516, 557, 589 and 648 nm wereflattened to the base line in the GO–H_2P material). Interestingly, the absorption of porphyrin in the GO–H_2P material is broadened, shortened and bathochromically shifted (ca. 2 nm) as compared to that of the free H_2P, a result that corroborates not only the linkage of porphyrin with the GO sheets but also electronic interactions between the two species (i.e. GO and H_2P) in the ground state. These results are in agreement with studies based on other hybrid systems consisting of porphyrins covalently grafted to carbon nanotubes and nanohorns (Karousis).

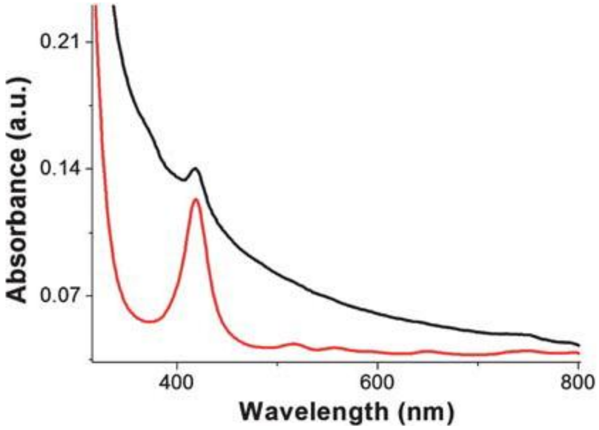


Figure 3: The UV-vis spectra of GO–H_2P (black) and free H_2P (red),obtained in DMF

Effect of pH

The pH of the sample solution plays important role in retention of metals on sorbent. The pH of the model solutions containing 5µg Cu(II) were adjusted to certain value using diluted HNO3 and NaOH. As shown in Figure 4, the recovery results were not dramatically affected by the change in pH between 4 and 7.According to this, pH=2.9 was chosen as centre value for the optimization procedure.

Desorption Reagent

0.5 mol L^{-1} of HNO_3, HCl, CH_3COOH, H_2SO_4 and $H2O_2$ were tested for desorption of Cu(II) from GO–H2P. The recovery percentages were varied between 5.7-87.9 % except HNO_3 elution experiments. It was observed that HNO3is the best as an eluent and the recovery percentage is 94.2±1.5 %.

Effect of Flow Rate on Sorption and Elution

The retention of a metal ion on the sorbent also depends on the flow rate of the sample solution. Thus, the both effect of flow rate of the sample and eluent on the sorption and desorption of copper ions were investigated between 3-20 mL min^{-1}. Quantitative results (> 95%) were obtained up to 10 and 8 mL min-1 for sorption and elution, respectively. In order to avoid an abrupt change in adsorption and increase the contact time of the sample solution with the sorbent,flow rate was selected as 4 mL min^{-1} for sorption and elution.

Optimization of Variables

Optimization of the preliminary studies was achieved by a three level full factorial CCD with20 runs. Table 1lists the maximum, minimum and center values of the variables for sorptionand elution. The metal concentration in solutions was determined with external standardcalibration method by FAAS. The experimental design matrix and the results for sorptionand elution are given in Table 2 and 3.Quadratic Eq. (1) and Eq. (2), which were obtained byusing data of response values, are given below for sorption and elution, respectively.

$$y = 0.512149 - 0.72568x_1 - 0.70171x_2 - 0.98307x_3 + 0.056576x_1^2 + 0.171216x_2^2 + 0.493081x_3^2 + 1.565725x_1x_2 + 1.556098x_1x_3 + 1.606563x_2x_3 \quad (1)$$

$$y = 0.683354 + 0.018073x_1 + 1.220284x_2 + 0.130563x_3 - 0.576576x_1^2 + 1.235323x_2^2 - 0.33237x_3^2 + 0.071216x_1x_2 - 0.06881x_1x_3 - 0.07098x_2x_3 \quad (2)$$

Table 1: Levels and the real values of factors utilized in CCD

Factors	*for sorption* *Levels*					*Factors*	*for elution* *Levels*				
	-α	-1	0	+1	+α		-α	-1	0	+1	+α
pH	3.3	4	5	6	6.7	Flow rate (mL min^{-1})	2.3	3	4	5	5.7
Flow rate (mL min^{-1})	2.3	3	4	5	5.7	Eluent Concentration (mol L^{-1})	0.08	0.25	0.50	0.75	0.92
Sample volume (mL)	8.0	25	50	75	92.0	Eluent Volume (mL)	3.3	4	5	6	6.7

Table 2: Experiments and recovery values for the sorption of Cu(II)

Run	X_1 pH	X_2 Flow rate (mL min^{-1})	X_3 Sample volume (mL)	Recovery, %	Response
1	4	3	25	99.91	11.636
2	6	3	25	104.58	0.218
3	4	5	25	112.41	0.081
4	6	5	25	82.40	0.057
5	4	3	75	113.56	0.074
6	6	5	75	13.10	0.012
7	4	5	75	113.47	0.074
8	6	5	75	99.30	1.420
9	5	4	50	100.62	1.623
10	3.3	4	50	81.40	0.054
11	6.7	4	50	72.30	0.036
12	5	2.3	50	96.00	0.250
13	5	5.7	50	81.91	0.055
14	5	4	8.0	99.56	2.272
15	5	4	92.0	99.30	0.316
16	5	4	50	104.58	0.087
17	5	4	50	112.41	0.277
18	5	4	50	113.62	0.076
19	5	4	50	105.37	0.250
20	5	4	50	100.97	1.054

Table 3: Experiments and recovery values for the elution of Cu(II)

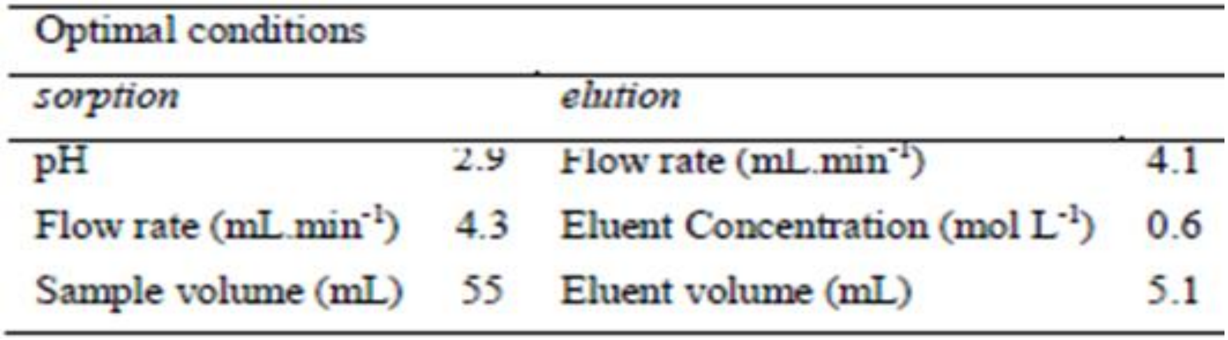
Run	X_1 Flow rate (mL min^{-1})	X_2 Eluent Concentration (mol L^{-1})	X_3 Eluent volume (mL)	Recovery, %	Response
1	3	0.25	4	100.56	1.786
2	5	0.25	4	95.60	0.227
3	3	0.75	4	105.68	0.176
4	5	0.75	4	96.88	0.320
5	3	0.25	6	107.40	0.135
6	5	0.25	6	108.36	0.120
7	3	0.75	6	104.28	0.234
8	5	0.75	6	100.80	1.250
9	4	0.5	5	99.60	2.500
10	2.3	0.5	5	98.80	0.833
11	5.7	0.5	5	95.90	0.244
12	4	0.08	5	105.50	0.182
13	4	0.92	5	102.30	0.435
14	4	0.5	3.3	54.78	0.022
15	4	0.5	5	108.35	0.120
16	4	0.5	5	95.60	0.227
17	4	0.5	5	96.90	0.323
18	4	0.5	5	102.50	0.400
19	4	0.5	5	100.80	1.250
20	4	0.5	5	96.90	0.833

x_1, x_2 and x_3 represents the 1st, 2nd and 3rd factors. Derivatives of the equations in terms of x_1, x_2 and $x_3$were equalized to zero and solved using Microsoft$^{®}$Excel. The real values presented in Table 4 obtained from CCD and used as optimal conditions for further experiments.

Interference Effects

The preconcentration procedures of trace metal ions can be strongly affected by other ions. For this reason, the effects of matrix ions were investigated under optimal conditions. The results revealed that the GO–H_2P behaves as a neutral ionophore in the pH range 3.0 (Zelder) so that the copper 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 Cu(II) ions. The influence of the concentration of sodium acetate ion on copper recovery was investigated, and the results are shown in Table 4. As seen, the percent recovery of Cu^{2+} increasedwith 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 tolerance limit of coexisting ions was given in Table 5.The experiments indicated that, no further sample treatment or masking reagents are needed.

Table 4: Optimum preconcentration conditions for Cu(II) by GO–H_2P



Optimal conditions			
sorption		*elution*	
pH	2.9	Flow rate (mL.min^{-1})	4.1
Flow rate (mL.min^{-1})	4.3	Eluent Concentration (mol L^{-1})	0.6
Sample volume (mL)	55	Eluent volume (mL)	5.1

Effect of Sample Volume

The preconcentration studies were applied to solutions within the range of 25-1000 mL containing 5 µg amount of Cu(II) to explore the possibility of enriching at low concentrationwith high enrichment factor. The recovery value was obtained as 98.7 % at 1000 mL sample volume by analyzing 5 mL eluate and the highest preconcentration factor was found to be200.

Analytical Figures of Merit

The accuracy and precision (RSD, %)of the proposed solid phase extraction procedure under optimal conditions were investigated (*n*=10) as 102.0±0.2 % and 2, respectively. Limits ofdetection (LOD) and the limits of quantification (LOQ) were obtained by using a criterionsignal-to-noise ratio of 3 and 10, respectively. The results were calculated 49.6ng L^{-1}forLOD and 163.7ng L^{-1} for LOQ.

Validation and Application of the Improved Method

The developed procedure was validated by Cu (II) determination in certified reference material. The results are given in Table 6. A statistical evaluation was performed by Student'st test and *t* value was calculated as 2.95. Critical *t* value (4.30) is higher than the calculatedone at 95 % confidence level. This test showed no significant difference between Cu(II)concentration obtained from the presented method and the certified value.

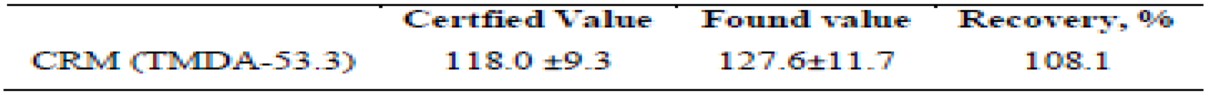
Table 5: Separation of copper from binary mixtures [a]

Diverse ion	Amounts taken(mg)	% Found	%Recovery of Cu^{2+} ion
Na^+	92.4	1.15(2.4)[b]	98.7(1.8)
K^+	92.5	1.32(2.3)	98.5(2.9)
Mg^{2+}	14.5	0.7(1.2)	98.9(1.8)
Ca^{2+}	26.3	2.25(3.0)	98.5(1.6)
Sr^{2+}	2.45	2.85(2.5)	98.4(2.0)
Ba^{2+}	2.66	3.16(2.1)	98.3(2.3)
Mn^{2+}	2.66	1.75(2.2)	97.3(2.8)
Co^{2+}	2.16	1.4(2.3)	99.1(2.9)
Ni^{2+}	1.65	2.0(2.4)	98.5(2.6)
Zn^{2+}	2.78	1.97(2.1)	98.4(2.2)
Cd^{2+}	2.55	1.92.0)	98.2(2.8)
Pb^{2+}	0.54	2.7(1.9)	97(2.7)
Hg^{2+}	0.44	2.81(2.1)	97.7(2.8)
Ag^+	2.63	3.45(2.9)	96.6(2.9)
Cr^{3+}	1.73	2.92(2.30	97.3(2.4)
UO^{2+}	2.84	2.8(2.1)	98.3(2.7)

[a] *Initial samples contained 10µg Cu^{2+} and different amounts of various ions in 100 mL water(0.1 M acetate ion).*

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

Table 6: Analysis of standard reference material



	Certfied Value	Found value	Recovery, %
CRM (TMDA-53.3)	118.0 ±9.3	127.6±11.7	108.1

Real Sample Analysis

To assess the applicability of the method to real samples, it was applied to the extraction and determination of copper from different water samples. Tap water(Tehran, taken after 10 min operation of the tap), rain water (Tehran, 20 January, 2015), Snow water (Varamin, 6 February, 2015) 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 copper ions can be quantitatively recovered from the water samples used. As is seen, the recovered copper ion reveals that the results are quite reliable and are in satisfactory agreement with those obtained by ICPAES (Tables 7).

Table 7: Recovery of copper added to 1000mL of different water samples (contaning 0.1Macetate at pH= 5.0)

Sample	Cu^{2+} added (μg)	Cu^{2+}determined(ng.mL^{-1})	ICP-AES
Tap water	0.0	1.74(1.4)[a]	ND
	10.0	11.98(3.2)	11.7
Snow water	0.0	4.45(2.4)	ND
	10.0	14.97(2.0)	14.7
Rain water	0.0	2.65(2.3)	ND
	10.0	12.75(2.4)	12.3
Sea Water	0.0	12.64(2.3)	12.5
	10.0	22.93(2.0)	23.1

[a] *Values in parentheses are %RSDs based on five individual replicate analysis*

[b] *Not detected.*

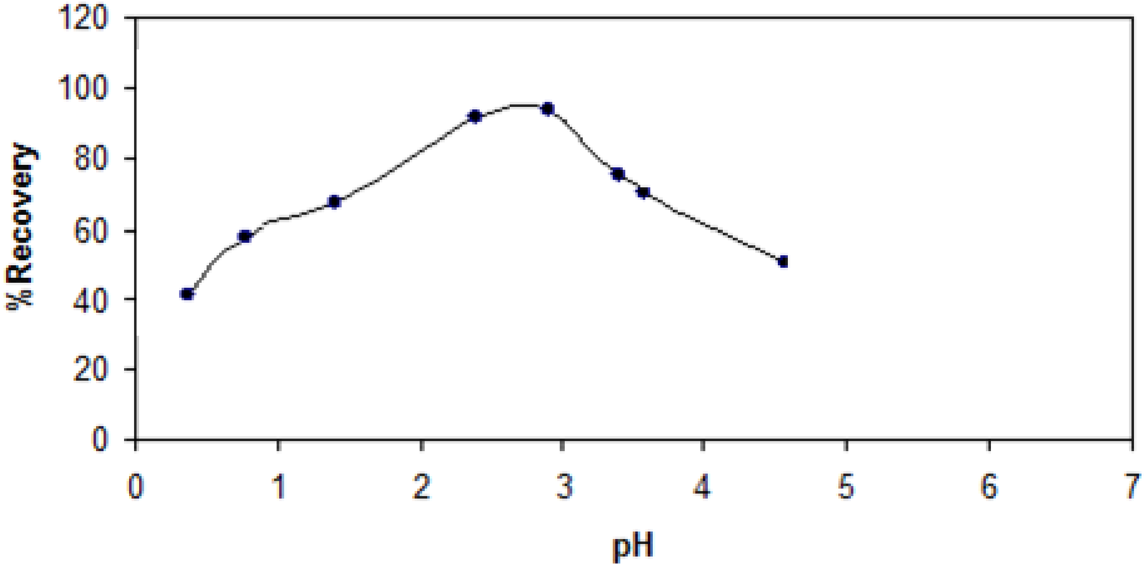


Figure 4: Influence of sample pH and dissolving solvent of GO–H_2P on the percentage recovery of Cu(II)

Table 8: Comparison with other solid phase adsorbents

References	Eluent	Preconcentration factor	Method	Chelating agent/solid phase adsorbent
Pawliszyn	7 mol L^{-1}HCl	200	FAAS	Dithizone/microcrystalline naphthalene
Akama	0.1 mol L^{-1} HNO3	50	Atomic absorption spec-trophotometry	β-Naphthol/polyurethane foam
Alfassi	10 mol L^{-1} HCl	200	FAAS	Dithizone/silica gel
Hagen	Tetraphenyl-borate	80	Anodic stripping voltammetry	HgI_4^{2-}-Aliquat-336/naphthalene
Moghimi 2013	H_2SO_4 –H_2O_2 mixture	40	ICP-AES	DuoliteGT-73 resin
Huang	Water	5	FAAS	Dithioacetal/SiO_2
Krueger	1 mol L^{-1}HBr	50	FAAS	Hexathia18 crown-6 tetraone/Empore disk
Shamsipur	1 mol L^{-1}HBr	100	FAAS	1,5-Diphenylcarbazone/SDS coated alumina
Cuculic	HNO_3	–	ICP-AES	1,5-Bis(2-pyridyl)-3-sulfophenylmethylene) thiocarbonohydrazide/Dowex anion exchange resin
Gupta	6 mol L^{-1}HCl	50	FAAS	4-(2-Pyridyl azo) resorcinol/nano-sized SiO2
Choi	2 mol L^{-1} HNO_3 in acetone	300	FAAS	2-Mercaptobenzoxazole/chromosorb
Present work	HNO_3	200	FAAS	Graphene oxide with covalently linked porphyrin (GO–H_2P)

Conclusion

In the present study, a new sorbent is prepared by using Graphene oxide with covalently linked porphyrin (GO–H_2P) and for preconcentration of Cu(II) from natural water samples. The modified Graphene oxide with covalently linked porphyrin (GO–H_2P) was prepared easily and sorbed Cu(II) rapidly. The preconcentration parameters pH, flow rate and sample volume for sorption procedure was obtained by CCD as 5.2, 4.3 mL min-1, 55.0 mL, respectively. Elution parameters, flow rate, eluent concentration and eluent volume were also obtained as 4.1 mL min^{-1}, 0.6 mol L^{-1} and 5.1 mL, respectively. Enrichment factor was found to be 200 when 1000 mL of water sample(included 5μg) passed through the GO–H2P column. The interference effects of some ions were also investigated according to the improved method. The tolerance limits were between750-10,000 times greater as can be seen in Table 5. The mean recovery values for spiked water samples were satisfactory and confirmed the validity of the method. Additionally, mean %RSD value was 2 and showed that the precision of the method is quite good. Preconcentration factor, LOD, RSD, eluent type and concentration and detection technique of present work was compared with literature data in Table 8. In most cases, suggested method for Cu preconcentration with GO–H_2P is comparable to, or better than, some of the previously reported Graphene oxide with covalently linked porphyrin (GO–H_2P) based modified adsorbents. Finally, the proposed method can be suggested as simple, sensitive, accurate and repeatable method for determination of Cu(II) after preconcentration. This new enrichment procedure can also be applied to some other metal ions.

ACKNOWLEDGEMENTS

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

REFERENCES

Akama Y, Ito M and Tanaka S (2000). Selective separation of cadmium from cobalt, copper, Cr (III) and zinc by water-based two-phase system of tetrabutylammonium bromide. *Talanta* **52** 645-651.

Alexandrova A and 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.

Alfassi ZB and Wai CM (1990). *Preconcentration Techniques for Trace Elements* (CRC Press. B. Ca, Raton Ann Arbor London) 113-116.

Arpadjan S, Vuchkova L and Kostadinova E (1997). Study of the adsorption behavior of heavy metal ions on nanometer-size titanium dioxide with ICP-AES. *Analyst* **122** 243-250.

Boll I, Kramer R, Brunner J and Mokhir A (2005). Oligonucleotide-Templated Reactions for Sensing Nucleic Acids. *Journal of the American Chemical Society* **27** 7849-7855.

Boudreau SP and Cooper WT (1989). Analysis of thermally and chemically modified silica gels by heterogeneous gas-solid chromatography and infrared spectroscopy. *Analytical Chemistry* **61** 41-47.

Brodie BC (1859). Graphite, Graphene, and Their Polymer Nanocomposites. *Transaction of Royal Society of London* **149** 249.

Bruening ML, Mitchell DM, Bradshaw JS, Izatt RM and Bruening RL (1991). Removal of cesium from alkaline waste solution: Part II – Column ion exchange study. *Analytical Chemistry* **63** 21-27.

Brunner J, Mokhir A and Kramer R (2003). Copper(II)-Quenched Oligonucleotide Probes for Fluorescent DNA Sensing. *Journal of the American Chemical Society* **125** 12410-12415.

Campderros ME, Acosta A and 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 and Horvath Z (1991). Selective pre-concentration and solid phase extraction of chromium(III) from natural water by silica gel-loaded dithizone phases. *Analytica Chimica Acta* **248** 241-247.

Cataldo F (2003). Structural analogies and differences between graphite oxide and C_{60} and C_{70} polymeric oxides (fullerene ozopolymers). *Fullerenes Nanotubes and Carbon Nanostructures* **11**(1) 1–13.

Choi YS and 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. *Bulletin of the Korean Chemical Society* **24** 222-228.

Cuculic V, Mlakar M and Branica M (1997). Synergetic adsorption of copper(I1) mixed ligand complexes onto the SEP-PAK Cl8 column. *Analytica Chimica Acta* **339** 181-189.

Dadler V, Lindoy LF, Sallin D and Schlaepfer CW (1987). Selective pre-concentration and solid phase extraction of chromium(III) from natural water by silica gel-loaded dithizone phases. *Australian Journal of Chemistry* **40** 1557-1563.

Eaton AD, Clesceri LS and Greenberg AE (1995). *Standard Methods for the Examination of Water and Waste Water, 19th* edition (American Public Health Association, Washington, DC).

Geim AK and Novoselov KS (2007). The rise of graphene. *Nature Materials* **6** 183-191.

Gennaro MC, Baiocchi C, Campi E, Mentasti E and Aruga R (1983). Undesirable and harmful metals in wines—Determination and removal). *Analytica Chimica Acta* **151** 339-344.

Grote M and Kettrup A (1985). Liquid-liquid extraction of noble metals by formazans: Analytical Applications of Silver Extraction by ortho-Substituted Formazans. *Analytica Chimica Acta* **175** 239-244.

Gupta R, Singh D and Kaur H (2013). New records of some Heteropteran bugs from North India. *Bionotes* **15**(3) 80-81.

Hagen DF, Markell CG and Schmitt GA (1990). Enhanced biosensor performance for on-site field analysis of explosives in water using solid-phase extraction membranes. *Analytica Chimica Acta* **236** 157-163.

Huang X, Chang X, He Q, Cui Y, Zhai Y and Jiang N (2008). Tris(2-aminoethyl) amine functionalized silica gel for solid-phase extraction and preconcentration of Cr(III), Cd(II) and Pb(II) from waters. *Journal of Hazardous Materials* **157** 154.

Karousis N, Sandanayaka ASD, Hasobe T, Economopoulos SP, Sarantopouloua E and Tagmatarchis N (2011). Graphene oxide with covalently linked porphyrin antennae: Synthesis, characterization and photophysical properties. *Journal of Materials Chemistry* **21** 109.

Krueger CJ and 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. *Analytical Chemistry* **67** 3363-3369.

Kvitek RJ, Evans JF and Carr PW (1982). Denaturation of purple membranes at the air/water interface studied by SEM). *Analytica Chimica Acta* **144** 93-98.

Lerf A, He H, Forster M and Klinowski J (1998). Structure of Graphite Oxide Revisited**.** *The Journal of Physical Chemistry B* **102** 4477.

Leyden DE and Luttrell GH (1975). Automated separation and preconcentration of copper(II) from natural waters using a column treatment. *Analytical Chemistry* **47** 1612-1616.

Leyden DE, Luttrell GH, Nonidez WK and Werho DB (1976). Adsorption of Co(II) and Cu(II) on silica gel surface modified with pyridinium ion from acetone and ethanol solutions. *Analytical Chemistry* **48** 67-72.(b)

Leyden DE, Luttrell GH, Sloan AE and DeAngelis NJ (1976). Automated separation and preconcentration of copper(II) from natural waters using a column treatment. *Analytica Chimica Acta* **84** 97-102.(a)

Mahmoud ME (1997). 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. (a)

Mahmoud ME (1997). Silica-immobilized formylsalicylic acid as a selective phase for the extraction of iron(III). *Talanta* **44** 15-21.(b)

Moghimi A (2007). Preconcentration and Determination of Trace Amounts of Heavy Metals in Water Samples Using Membrane Disk and Flame Atomic Absorption Spectrometry. *Chinese Journal of Chemistry* **25**(10) 640-645.

Moghimi A (2008). Preconcentration of Copper(II) Using Mesoporous Organo-Silicas and Determination by Flame Atomic Absorption Spectrometry. *Chinese Journal of Chemistry* **52**(2) 155-163.

Moghimi A (2013). Separation of lead(II) paraffin-embedded tissues from liver loggerhead turtles specimens by organic-solutionprocessable functionalized-nano graphene prior to determination by flame atomic absorption spectrometry (FAAS). *African Journal of Pure and Applied Chemistry* **7**(2) 79-90.

Moghimi A and Tajodini N (2010). Preconcentration of Copper(II) in Water Samples Using Polyurethane Foam/2-(6'-Ethyl-2'-benzothiazolylazo) chromotropic Acid. *Asian Journal of Chemistry* **22**(5) 3325-3334.

Moghimi A, Ghiasi R, Abedin AR and Ghammamy S (2009). Solid phase extraction of Cd(II) using mesoporous organosilicas and determination by FAAS. *African Journal of Pure and Applied Chemistry* **3**(3) 051-059.

Moghimi A, Tehrani MS and Waqif Husain S (2006). Preconcentration and Determination of Copper(II) Using Octadecyl Silica Membrane Disks Modified by 1,5-Diphenylcarhazide and Flame Atomic Absorption Spectrometry. *Material Science Research India* **3**(1a) 27-32.

Nambiar DC, Patil NN and Shinde VM (1998). Liquid-liquid extraction of chromium(III) with triphenylphosphinesulphide: Application to medicinal and environmental samples. *Fresenius' Journal of Analytical Chemistry* **360** 205-212.

Narin I, Soylak M, Elic L and Dogan M (2000). An Evaluation of Loading Rate of Dust, Pb, Cd, and Ni and Metals Mass Concentration in the Settled Surface Dust in Domestic Houses and Factors Affecting Them. *Talanta* **52** 1041-1047.

Nayebi P and Moghimi A (2006). Perconcentration and Determination of copper(II) by 1-(2-Pyridyl Azo)2-Naphtol(PAN) modified Octadecyl Silica. *Oriental Journal of Chemistry* **22**(3) 507-512.

Ohta K, Tanahasi H, Suzuki T and Kaneco S (2001). Preconcentration of trace copper with yeast for river water analysis. *Talanta* **53** 715-722.

Pawliszyn J (1997). *Solid-Phase Microextraction, Theory and Practice* (Wiley-VCH, New York).

Shamsipur M, Ghiasvand AR and Sharghi H (2001). Selective preconcentration of ultra tracecopper(II) using octadecyl silica membrane disks modified by a recently synthesized glyoxime derivative. *International Journal of Environmental Analytical Chemistry* **82** 23-29.

Shamsipur M, Ghiasvand AR and Yamini Y (1999). Synthesis of a New α-Dioxime Derivative and Its Application for Selective Homogeneous Liquid-Liquid Extraction of Cu(II) into a Microdroplet Followed by Direct GFAAS Determination. *Analytical Chemistry* **71** 4892-4897.

Tajodini N and Moghimi A (2010). Preconcentration and Determination of Ultra Trace Cobalt(II) in Water Samples Using Co(II)-Imprinted Diazoaminobenzene- Vinylpyridine Copolymers. *Asian Journal of Chemistry* **22**(5) 3335-3344.

Takeshima M, Yokoyama T, Imamoto M and Asaba H (1969). Technetium labeling of bi, tri and tetradentate ligands derived from 2-aminocyclopentene-1-dithiocarboxylic acid: Characterization and biodistribution of their oxo and nitrido 99mtechnetium complexes. *Journal of Organic Chemistry* **34** 730-735.

Taylor KZ, Waddell DS and Reiner EJ (1995). Application of Multiwalled Carbon Nanotubes as a Solid-Phase Extraction Sorbent for Chlorobenzenes. *Analytical Chemistry* **67** 1186-1192.

Thurman EM and Mills MS (1998). *Solid-Phase Extraction, Principles and Practice* (Wiley, New York).

Tong A, Akama Y and Tanaka S (1990). Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay. *Analytica Chimica Acta* **230** 179-185.

Unger K (1979). *Porous Silica* (Elsevier, Amsterdam).

Zelder FH, Brunner J and Kramer R (2005). Chemical control of biomolecular interaction modules. *Chemical Communication* 902-911.

Zhang Y, Tan YW, Stormer HL and Kim P (2005). Experimental observation of the quantum Hall effect and Berry's phase in grapheme. *Nature* **438** 201.