



Graphene for Preconcentration of Trace Amounts of Ni in Water and Paraffin-embedded Tissues from Liver Loggerhead Turtles Specimens Prior to Flame Atomic Absorption Spectrometry

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ABSTRACT

A new sensitive and simple method was developed for the preconcentration of trace amounts of Ni using 1-(2-pyridylazo)-2-naphthol (PAN) as chelating reagent prior to its determination by flame atomic absorption spectrometry. The proposed method is based on the utilization of a column packed with graphene as sorbent. Several effective parameters on the extraction and complex formation were selected and optimized. Under optimum conditions, the calibration graph was linear in the concentration range of 5.0–240.0 $\mu\text{g L}^{-1}$ with a detection limit of 0.36 $\mu\text{g L}^{-1}$. The relative standard deviation for ten replicate measurements of 20.0 and 100.0 $\mu\text{g L}^{-1}$ of Ni were 3.45 and 3.18%, respectively. Comparative studies showed that graphene is superior to other adsorbents including C18 silica, graphitic carbon, and single- and multi-walled carbon nanotubes for the extraction of Ni. In the present study, we report the application of preconcentration techniques still continues increasingly for trace metal determinations by flame atomic absorption spectrometry (FAAS) for quantification of Ni in Formalin-fixed paraffin-embedded (FFPE) tissues from Liver loggerhead turtles. The proposed method was successfully applied in the analysis of four real environmental water samples. Good spiked recoveries over the range of 95.8–102.6% were obtained.

Key word: Graphene; Solid-phase extraction; Preconcentration;

Flame atomic absorption spectrometry; Formalin-fixed paraffin-embedded (FFPE) ; tissues from Liver loggerhead turtles;Ni

INTRODUCTION

Ni at trace concentrations acts as both a micronutrient and a toxicant in marine and fresh water systems (Izatt *et al*,1991; Izatt *et al*,1985; Izatt *et al*,1995; Blake *et al*,1996; Arca *et al*,2001; Ghoulipour *et al*,2002; Hashemi *et al*,2001; Shcherbinina *et*

al,1990). This element is needed by plants at only very low levels and is toxic at higher levels. At these levels, Ni can bind to the cell membrane and hinder the transport process through the cell wall. Ni at nearly 40ng mL⁻¹ is required for normal metabolism of many living organisms (Gomes-Gomes 1995; Unger *et al*, 1979). On the other hand, Ni is an important

element in many industries. Thus, the development of new methods for selective separation, concentration and determination of it in sub-micro levels in different industrial, medicinal and environmental samples is of continuing interest. The determination of Ni is usually carried out by flame and graphite furnace atomic absorption spectrometry (AAS) (Boudreau *et al*, 1989) as well as spectrometric methods (Bruening *et al*, 1991; Mahmoud and Soliman, 1997 a).

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. Solid phase extraction determinations can be carried out on different efficient ways. One of the most appropriate performance features of SPE is achieved by using octadecyl silica membrane disks. SPE reduce the use of toxic solvent, disposal costs, and extraction time (Mahmoud *et al*, 1997 b, 45; Mahmoud *et al*, 1997b). 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 (Tong *et al*, 1990).

In our previous attempts, we modified SPE membrane disks with suitable compounds for selective determination of chromium (Dadler *et al*, 1987; Moghimi 2007) and lead (Mahmoud *et al*, 1990). Meanwhile, other investigators have successfully utilized these sorbents for quantitative extraction and monitoring trace amounts of lead (Leyden *et al*, 1976; Moghimi *et al*, 2009; Liu *et al*, 1992), copper (Liu *et al*, 1996; Mishenina *et al*, 1996; Wang *et al*, 1999), silver (Wang *et al*, 1997; Zhang *et al*, 1982), mercury (Zhou *et al*, 1983; Zargaran *et al*, 2008), cadmium (Tabarzadi *et al*, 2010), palladium (Shin *et al*, 2004), Ni (Moghimi *et al*, 2012) and UO_2 (Mahmoud *et al*, 1998; Moghimi *et al*, 2006, Pramod *et al* and Rafeeq *et al*).

To ease the retrieval procedure, the SPE using graphene as the absorbent in a column combined with flame atomic absorption spectrometry (FAAS) has been demonstrated by our research group (Wang *et al*, 2012). We extend its applica-

tion to other inorganic analyses. 1-(2-Pyridylazo)-2-naphthol (PAN), a chelating agent which forms stable complexes with a number of metals and has found numerous applications in trace element separation and pre-concentration methods (Narin and Soylak., 2003; Shokouhi *et al*, 2007), was used to extract Co (structure of the Ni-PAN complex is shown in Fig. 1). What is more, it possesses a benzene ring structure. Based on this, the Ni-PAN is considered to have formed a strong π -stacking interaction with graphene when the sample solution passes through the column during which the Ni-chelate is retained. The factors influencing the efficiency of SPE and FAAS determination were systematically studied. The proposed method has been applied for the determination the National Institute of Standards (Beijing, China). Working standard solutions were prepared daily through serial dilutions of the stock solution with deionized water prior to analysis.

The chelating agent, 2.0 g L⁻¹ PAN solution, was prepared by dissolving the appropriate amount of PAN (Shanghai Chemistry Reagent Company, Shanghai, China) in absolute ethanol. Stock solution of diverse elements was prepared from high purity compounds. Single-walled CNTs (SWCNTs, car- Figure 1 of trace amounts of Ni in water samples with satisfactory results. It reveals great potential of graphene as an excellent sorbent material in analytical processes for metal ions once again.

METHODS

Apparatus

A Shimadzu (Kyoto, Japan) Model AA-6300C atomic absorption spectrometer equipped with deuterium background correction and a Ni hollow-cathode lamp as the radiation source were used for absorbance measurements at a wavelength of 240.7 nm. All measurements were carried out in an air/acetylene flame. The instrumental parameters were adjusted according to the manufacturer's recommendations. A pH3-3C digital pH meter equipped with a combined glass-calomel electrode (Hangzhou Dongxing Instrument Factory, Hangzhou, China) was used for pH adjustment. The SPE experiments were performed on an Agilent vacuum manifold processing station with a Gast vacuum pump (Tegent Technology Ltd. Shanghai, China). The empty SPE columns (3.0 mL) and SPE frits were purchased from Agilent.

Reagents and materials

Graphite powder (50 mesh), potassium permanganate (KMnO_4), concentrated sulfuric acid (H_2SO_4), and sodium nitrate (NaNO_3) were purchased from Tianjin Tianda Chemical Reagent Company (Tianjin, China). A stock standard solution of Ni at a concentration of $1000 \mu\text{g mL}^{-1}$ was purchased from high purity (>90%, outer diameter <2 nm, length 5-15 μm) and multi-walled CNTs (MWCNTs, carbon purity >98%, outer diameter 20-40 nm, length 5-15 μm) were obtained from the Beijing Chemistry Reagent Company (Beijing, China).

Nitric acid (0.1 mol L^{-1}) was used to adjust the pH in the 2–3 range, and ammonium acetate buffers (0.2 mol L^{-1}) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions resulting in solutions with a pH range of 4.0–5.0. For a pH range of 6.0–8.0, a phosphate buffer solution (0.2 mol L^{-1}) was prepared by adding an appropriate amount of disodium hydrogen phosphate to sodium dihydrogen phosphate. Ammonium chloride buffer solutions (0.2 mol L^{-1}) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions, resulting in solutions with a pH range of 9.0–10.0.

All reagents used were of analytical reagent grade. Deionized water was used in the preparation of all solutions. All glassware and columns were kept in 10% nitric acid for at least 24 h and subsequently washed four times with deionized water before application.

Synthesis and characterization of graphene

Graphene nanoparticles were synthesized according to our previously reported study (Wang *et al.*, 2012). The size and morphology of G was observed by scanning electron microscopy (SEM) using an S-3000N microscope and X-ray diffraction (XRD) measurement was carried out using a Rigaku D/max-rB diffractometer with Cu K α radiation. In Fig. 2a, the SEM image shows the graphene agglomerate, consisting of almost transparent carbon nanosheets with thin wrinkled and silk-like structures. XRD patterns in Fig. 2b reveal that the graphene nanosheets' peak at $2\theta = 26.2^\circ$, which is the characteristic peak of graphene (Rao *et al.*, 2009).

Column preparation

Graphene (30.0 mg) was placed in a 3.0 mL SPE column using an upper frit and a lower frit to avoid adsorbent loss. Prior to extraction, the column was preconditioned with 10.0 mL methanol and 10.0 mL deionized water, respectively. The column was then conditioned to the desired pH with 5.0 mL of 0.2 mol L^{-1} acetate buffer solution.

Recommended procedure

100.0 mL of the sample solution containing $100.0 \mu\text{g L}^{-1}$ of Ni was prepared. 2.5 mL of PAN (2.0 g L^{-1}) solution was added and the pH value was adjusted to 5.0 with acetate buffer solution. The resulting sample solution was passed through the column at a flow rate of 2.0 mL min^{-1} . After the solution passed through it completely, the column was rinsed with 5.0 mL of deionized water, and the analytes retained on the column were

Sampling

Tap, sea, and river water samples used for the development of the method were collected in polytetrafluoroethylene (PTFE) containers from the Hebei Province. Before the analysis, the organic content of the water samples was oxidized in the presence of 1% H_2O_2 and then concentrated nitric acid was added. These water samples were then filtered using a 0.45 μm pore size membrane filter to remove suspended particulate matter and stored in a refrigerator in the dark before analysis.

Analysis of sample paraffin-embedded tissues from liver loggerhead turtles

Specimens

Selected areas from fresh frozen tissues from liver loggerhead turtles specimens were sliced in three pieces (numbered as 1, 2 and 3) of approximately $10 \text{ mm} \times 5 \text{ mm} \times 2 \text{ mm}$ each. Sets of pieces of set 1 (controls), were placed into a vacuum chamber at 50°C overnight to dry (until a constant weight was obtained) and the sets 2 and 3 were subjected to the standard 10% buffered formalin fixation and paraffin embedding histological process using a tissue processor (Tissue-Tek VIP, Sakura Finetek USA Inc., Torrance, CA). After the paraffin embedding process, tissues were subsequently excised from the blocks with a titanium knife and deparaffinized in xylene at 55°C for 1 h in the tissue processor (the set 2), or with hexane at 20°C .

°C for 1 week with frequent changes of the solvent in handling-based procedure (the set 3). Xylene was of a grade routinely used for the FFPE process and hexane was of "Optima" grade (Fisher Scientific). Upon deparaffinization, the tissue samples were dried in a vacuum chamber until constant weight was obtained. Each dried sample (of the sets 1-3) was divided into three portions (5-10 mg each) to be further analyzed as triplicates.

RESULTS AND DISCUSSION

Effect of pH

Sample pH had a critical effect on the adsorption of target compounds by affecting the existing form of target compounds, the charge species and density on the sorbents surface (Jiao *et al.*, 2012). A series of experiments was performed by adjusting the pH from 2.0 to 10.0 with nitric acid, ammonium acetate, phosphate and ammonium chloride. The results illustrated in Fig. 3 reveals that the absorbance is nearly constant in the pH range of 5.0–7.0. The progressive decrease in the extraction of Ni at low pH is due to the competition of the hydrogen ion with the analyte for the reaction with PAN. Accordingly, pH 5.0 was selected for subsequent work and real sample analysis.

Influence of the amount of PAN

The effect of the amount of PAN on the absorption was studied using various volumes of the reagent ranging from 0.5 mL to 3.5 mL. The signal of Ni was increased with the increase of PAN volume up to 2.0 mL, and then kept constant. Hence, 2.5 mL of 2.0 g L⁻¹ PAN solution was chosen to account for other extractable species that might potentially interfere with the assaying of Ni. Sample and eluent solution, 2.0 mL min⁻¹

Effect of flow rates of sample and eluent solution

The efficiency of metal preconcentration essentially depends on the flow rate of the sample solution to pass through the micro-column, whereas the flow of eluent solutions affects the recoveries. The time taken is also a considerable factor. Therefore, the effect of the flow rate of the sample and eluent solutions on the recoveries of Ni on graphene was examined in the range of 0.5–5.0 mL min⁻¹. The flow rate of the sample and eluent

solutions had no obvious influence on the quantitative recoveries of analytes at the range of 0.5-4.0 and 0.5–2.0 mL min⁻¹, respectively. A 2.0 mL min⁻¹ flow rate of the sample and eluent solutions was chosen in subsequent experiments.

Breakthrough volume

The measurement of breakthrough volume is important in solid phase extraction because breakthrough volume represents the sample volume that can be preconcentrated without the loss of

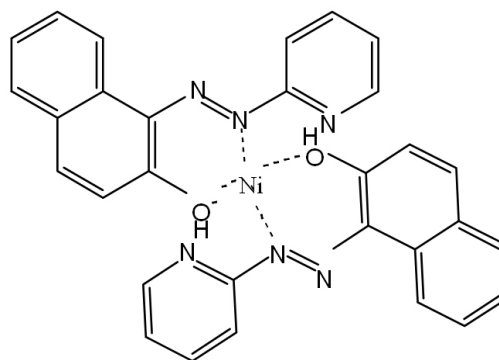


Fig. 1: Structural formulae of the Ni-PAN complex

Table 1: Effect of type and concentration of eluting agent on recovery of Ni

Eluent	Recovery (%)
1.0 mol L ⁻¹ NaOH	63.4 ± 2.2
2.0 mol L ⁻¹ NaOH	71.3 ± 2.6
1.0 mol L ⁻¹ HCl	68.6 ± 2.3
2.0 mol L ⁻¹ HCl	73.6 ± 2.4
3.0 mol L ⁻¹ HCl	78.3 ± 2.3
1.0 mol L ⁻¹ H ₂ SO ₄	65.3 ± 2.4
2.0 mol L ⁻¹ H ₂ SO ₄	63.4 ± 2.1
3.0 mol L ⁻¹ H ₂ SO ₄	32.2 ± 2.0
0.5 mol L ⁻¹ HNO ₃	70.0 ± 2.2
1.0 mol L ⁻¹ HNO ₃	76.2 ± 2.3
2.0 mol L ⁻¹ HNO ₃	80.3 ± 2.3
1.0 mol L ⁻¹ CH ₃ COOH	66.9 ± 2.3
2.0 mol L ⁻¹ CH ₃ COOH	53.3 ± 2.8
0.5 mol L ⁻¹ HNO ₃ in methanol	89.3 ± 3.0
1.0 mol L ⁻¹ HNO ₃ in methanol	92.7 ± 3.0
2.0 mol L ⁻¹ HNO ₃ in methanol	93.8 ± 3.2

a Average of five determinations ± standard deviation

analyte during elution of the sample (Mester and Sturgeon, 2003). The breakthrough volume of the sample solution was tested by dissolving 10.0 µg of Ni in different volumes (25.0–1000.0 mL) and the recommended procedure was followed. It was observed that Ni was quantitatively recovered when the sample volume was less than 400.0 mL. When the sample volume exceeded 400.0 mL, the recovery was decreased. The preconcentration factor for preconcentration and extraction is calculated by the ratio of the highest sample volume for analyte (400.0 mL) and the lowest eluent volume (2.0 mL). In the present study the possible preconcentration factor was 200.

Adsorption capacity

In order to evaluate the adsorptive capacity of graphene, a batch method was used. 100.0 mL of

solution containing 1.0 mg of metal ion at pH 5.0 was added to 30.0 mg sorbent. The mixture was filtered, after shaking for 10 min. 10.0 mL of the supernatant solution was determined by FAAS. The capacity of the sorbent for Ni was found to be 20.6 mg g⁻¹.

Eluent type and its volume

In order to choose the best solvent for desorption of the adsorbed analytes on graphene, many reagent solutions were investigated. The results were given in Table 1. As can be seen, the recoveries of Ni were not so satisfactory when HCl, HNO₃, H₂SO₄, CH₃COOH and NaOH were used as eluents solely. Good quantitative recovery for analyte ions could be obtained with 2.0 mol L⁻¹ HNO₃ in methanol. The effect of eluent volume on the recovery of Ni was also studied by using 2.0 mol L⁻¹ HNO₃ in methanol; it was found that quantitative

Table 2: Effect of interfering ions on the recovery of 100.0 µg L⁻¹ Ni in water samples using SPE-FAAS

Interferent	Concentration (µg L ⁻¹)	Added as	Interferent /Ni ²⁺ ratio	Recovery (%)
Na ⁺	150,000,000	NaNO ₃	1,500,000	95.4
K ⁺	150,000,000	KNO ₃	1,500,000	93.6
Ba ²⁺	10,000	BaCl ₂	100	93.5
Al ³⁺	10,000	Al(NO ₃) ₃ ·9H ₂ O	100	95.6
Cr ³⁺	10,000	Cr(NO ₃) ₃ ·9H ₂ O	100	95.2
Mn ²⁺	10,000	MnSO ₄ ·H ₂ O	100	93.3
Ca ²⁺	10,000	CaCl ₂	100	95.3
Mg ²⁺	10,000	Mg(NO ₃) ₂	100	98.2
Cu ²⁺	6000	Cu(NO ₃) ₂ ·3H ₂ O	60	96.0
Ag ⁺	6000	AgNO ₃	60	93.2
Fe ³⁺	3000	FeCl ₃	30	96.3
Ni ²⁺	3000	Ni(NO ₃) ₂ ·6H ₂ O	30	95.0
Pb ²⁺	3000	Pb(NO ₃) ₂	30	93.5
Cd ²⁺	4000	Cd(NO ₃) ₂	40	93.4
Zn ²⁺	4000	ZnCl ₂	40	96.3
NO ₃ ⁻	130,000,000	KNO ₃	1,300,000	98.3
Cl ⁻	50,000,000	NaCl	500,000	96.3
F ⁻	10,000,000	NaF	100,000	93.4
CH ₃ COO ⁻	1,000,000	CH ₃ COONa	10,000	95.2
PO ₄ ⁻	100,000	Na ₃ PO ₄ ·12H ₂ O	1000	93.2
HCO ₃ ⁻	100,000	KHCO ₃	1000	93.8
CO ₃ ⁻	30,000	Na ₂ CO ₃	300	96.2
SO ₄ ²⁻	10,000	Na ₂ SO ₄	100	96.4
HPO ₄ ²⁻	10,000	Na ₂ HPO ₄ ·12H ₂ O	100	

recoveries could be obtained with 2.0–4.0 mL of 2.0 mol L⁻¹ HNO₃ in methanol. Therefore, the volume of 2.0 mL of 2.0 mol L⁻¹ HNO₃ in methanol was used in the following experiments.

Column reuse

To investigate the stability and the potential regeneration of the sorbent, several extraction and elution operation cycles were carried out following the column procedure. It was found that the column can be reused after being regenerated with 10.0 mL methanol and 10.0 mL double distilled water, and it is stable up to at least 50 adsorption–elution cycles without a significant decrease in the recovery of Ni. This is of great importance especially when the sorbent does the job with satisfactory analytical performance after using several cycles in solid-phase extraction.

Effects of coexisting ions

The effects of common coexisting ions on the adsorption of Ni on graphene were investigated. In these experiments, 100.0 mL solutions containing 100.0 µg L⁻¹ of Ni and various amounts of interfering ions were treated according to the recommended procedure. The tolerance limit is defined as the ion concentration causing a relative error smaller than ±5% related to the preconcentration and

determination of analytes. The results, summarized in Table 2, show that the presence of major cations and anions in natural water has no significant influence

on the adsorption of Ni ion under the selected conditions.

Analytical performance

Under the optimized conditions, the calibration curve was obtained by preconcentrating a series of the solutions according to procedure under experiment. The curve was linear from 5.0 to 240.0 µg L⁻¹ for Ni. The calibration equation is $A = 3.16 \cdot 10^{-3}C + 0.0042$ with a correlation coefficient of 0.9992, where A is the atomic absorbance of Ni, obtained by peak height, in the eluent at 240.5 nm and C is its concentration in the sample solution (µg L⁻¹). The limits of detection and quantification defined as 3SB/m and 10SB/m (where SB is standard deviation of the blank and m is the slope of the calibration graph) were 0.36 and 1.20 µg L⁻¹, respectively. The relative standard deviation (RSD) for ten replicate measurements of 20.0 and 100.0 µg L⁻¹ of Ni were 3.45% and 3.18%, respectively.

Analytical application

The proposed method was used for the determination of Ni in several water samples. The

Table 3: Analytical results of Ni determination (dissolved fraction) in certified reference materials and spiked natural water samples with the SPE-FAAS method (n = 3)

Sample	Ni ²⁺ added (µg)	Ni ²⁺ determined (ng.mL ⁻¹)	ICP-AES
GSBZ 50,030-94 (µg L ⁻¹)	0.0	28.53 (2.0)	28.20(2.0)
Tap water(Tehran, 20January, 2014)	0.010.0	1.74(2.0) ^a 11.95(2.6)	ND ^b 11.6
Snow water(Tehran , 5 February ,2014)	0.010.0	4.84(2.1)14.96(2.4)	ND14.6
Rain water (Tehran, 20 January, 2013)	0.010.0	2.65(2.3)12.46(2.3)	ND12.3
Sea Water Tehran , 16 February ,2013)	0.010.0	12.65(2.4)22.96(2.0)	12.423.1
Development of a methodology for the determination of Ni ²⁺ in FFPE tissue	0.0	N.D	N.D ^b
	10.0	^b 9.95(2.2)	10.05(2.5)

^a Values in parentheses are %RSDs based on five individual replicate analysis ^b Not detected.

Table 4 : Comparison of the performance of graphene with several other adsorbents (C18 silica, graphitic carbon, SWCNTs, and MWCNTs) for the SPE of Ni

Sorbent materials	Graphene	C18 silica	Graphitic carbon	MWCNTs	SWCNTs
Recoveries (%)	96.2	53.6	48.3	78.3	82.5

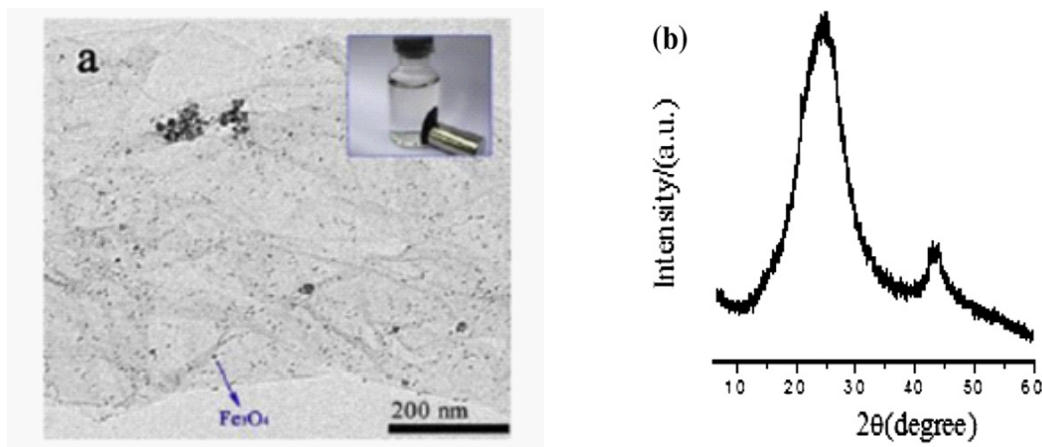


Fig. 2: SEM image and XRD pattern

results, along with the recovery for the spiked samples, are given in Table 3. The recoveries for the addition of different concentrations of Ni to water samples were in the range of 95.8–97.6%. To verify the accuracy of the proposed procedure, the method was used to determine the content of Ni in the National Standard Reference Material for Environment Water (GSBZ 50030-94) after the appropriate dilution and development of a methodology for the determination of Ni²⁺ in FFPE tissue. The results for this test are presented in Table 3. A good agreement between the determined values and the certified values was obtained.

Comparison with other sorbent materials

In this work, we report a comparison between graphene with several commonly used reserved-phase sorbent materials including C18 silica, graphitic carbon, and CNTs. For this purpose, the same amount (30.0 mg) of different adsorbents was packed in 3.0 mL SPE columns. The columns were loaded with 100.0 mL of sample solutions containing 100.0 µg L⁻¹ of Ni. All the work is done under the optimized conditions of graphene selected above. The C18 silica was evacuated from a Supelclean LC-18 SPE tube (Shanghai Chuding Instrument Company, Shanghai, China). The Ni in the flow-through, washing solution, and eluate were all determined.

As shown in Table 4, the graphene-packed column yields the highest recoveries (96.2%) among the studied adsorbents. This result definitely justifies the worth of graphene as an SPE adsorbent. Ni

could be detected in the flow-through and washing solution after loading on a C18 column, indicating that 30.0 mg C18 silica is insufficient for the retention of chelates. To obtain acceptable results with C18, more adsorbent should be packed in the column to enhance the adsorption capacity. For instance, with a C18 column packed with 300.0 mg C18 silica, the recoveries of Ni can reach 93.5%. However, increasing the adsorbent amount will add to the cost of analysis and is unfavorable for instrument miniaturization. Graphitic carbon performed even more poorly than C18. It was proposed that graphitic carbon did not give the expected extraction efficiency because of its large size and blank volume and less active sites for adsorption (Zhou *et al.*, 2006). So it is noted that adsorption capacity of the adsorbents

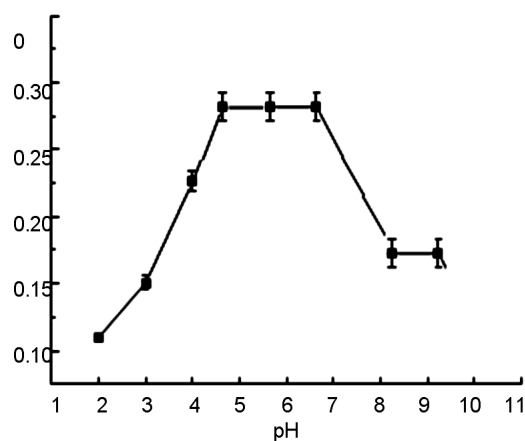


Fig. 3: Effect of pH on the absorbance of Ni obtained from SPE- FAAS. Extraction conditions: water sample volume, 100.0 mL; PAN

was generally in the following order: Graphene >C18 silica >Graphitic carbon. For MWCNTs, the recovery was approximately 78.3%, which is evidently inferior to that of graphene. Recoveries for columns using SWCNTs were higher than MWCNTs, but still inferior to graphene. No Ni was present in the flow-throughs and washing solutions for MWCNTs and SWCNTs, indicating that CNTs also have good sorption capacities for Ni. Thus, the lower recoveries on CNTs should be ascribed to extremely stable adsorption and incomplete elution. Increasing the volume of the eluent solvent can improve the recovery, e.g., with 5.0 mL HNO₃ as eluent solvent, the recovery of Ni on SWCNT column can reach 92.3%. Nevertheless, increasing the volume of the eluent solvent will reduce the pre-concentration factor.

The advantage of graphene over C18 and graphitic carbon mainly lies in its higher sorption capacity. In addition, compared with CNTs, achieving complete elution with graphene is more facile. The above experimental results indicated that graphene is a very promising adsorbent material.

CONCLUSIONS

In conclusion, the proposed method reveals the great potential of graphene as an advantageous sorbent material in SPE. Using Ni as model analyte, the graphene-packed SPE columns showed reliable and attractive analytical performance in the analysis of environmental water samples. Higher recoveries were achieved with graphene than with other adsorbents including C18 silica, graphitic carbon, and CNTs, owing to the large surface area and unique chemical structure of graphene. Some other advantages of graphene as an SPE adsorbent have also been demonstrated, such as high sorption capacity, good reusability, and high reproducibility. Although the obtained results of this research were related to the Ni determination, the system could be a considerable potential guide for the preconcentration and determination of other metals.

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