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ORIGINAL ARTICLE

# Graphene for separation and preconcentration of trace amounts of cobalt in water samples prior to flame atomic absorption spectrometry



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Cobalt

**Abstract** A new sensitive and simple method was developed for the preconcentration of trace amounts of cobalt (Co) 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 Co 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 Co. 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.

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## 1. Introduction

Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals. It is an essential micronutrient required for the growth of both plants and animals (Lemos et al., 2007). Cobalt can be beneficial for humans because it is part of

vitamin B<sub>12</sub> and since humans are unable to synthesize it, there is a need to ingest foods that contain it, such as fish, oysters, eggs, milk, and green vegetables (Underwood, 1977; Belitz and Grosch, 1987). The recommended dietary allowance (RDA) for vitamin B<sub>12</sub> for adults is 2.4  $\mu\text{g day}^{-1}$ , which contains 0.1  $\mu\text{g}$  of cobalt. Intake of less than this amount can lead to deficiency and to diseases such as pernicious anemia (Agency for Toxic Substances and Disease Registry [ATSDR], 2001). On the other hand, large amounts of cobalt can produce toxicological effects including vasodilation, flushing and cardiomyopathy in humans and animals (Chen and Teo, 2001). Therefore, the development of accurate and efficient determination methods for monitoring the level of cobalt

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concentration in the environmental samples is necessary and indispensable.

Several modern instrumental methods including spectrometry, atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), etc., have been used for determining traces of metal ions in various media (Dos Santos et al., 2005; Sreenivasa Rao et al., 2002; Dadfarnia and McLeod, 1994). However, due to low concentrations of metal ions in environmental samples and matrix interferences, the determination of metal ions in complex matrices is limited and requires preconcentration and/or separation of analytes to improve sensitivity and selectivity of analyses (Brown and Milton, 2005; Becker, 2005). Up to now, several methods have been designed for separation/pre-concentration of cobalt from various matrices, including liquid-liquid extraction (LLE) (Gupta and Khopkar, 1995), solid-phase extraction (SPE) (Yamini et al., 2004), coprecipitation (Divrikli and Elçi, 2002) and cloud point extraction (CPE) (Safavi et al., 2004), etc.

Among these techniques, solid-phase extraction (SPE) is a popular technique for achieving separation and preconcentration of metal ions in environmental samples (Safavi et al., 2006; Tuzen et al., 2008) has been developed and widely used because of its simplicity, rapidity, minimal cost, low consumption of reagents and the ability to combine with different detection techniques whether in on-line or off-line mode (Fritz, 1999). In the SPE procedure, the choice of the appropriate sorbent is a critical factor to obtain full recovery and a high-enrichment factor. Although numerous substances have been applied as solid-phase extraction sorbents, such as C18 silica (Jak et al., 2004), polymeric sorbents (Rao et al., 2004), and polyurethane foam (Lemos et al., 2007), their applicability is often limited only to a number of analytes. Thus, developing new SPE adsorbents is of high value.

Carbon materials are well known for their high adsorption capacity. They have been proven to possess great potential as adsorbents for removing many kinds of environmental pollutants: some examples are activated carbon (Ensafi and Shiraz, 2008), fullerenes (Vallant et al., 2007), carbon nanotubes (CNTs) (Shampur and Mostafavi, 2009), carbon nanohorn (Zhu et al., 2009), and carbon nanocones/disks (Jimenez-Soto et al., 2009).

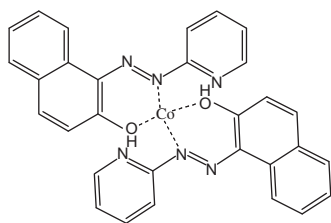
Graphene (G) is a new exciting carbon material being investigated today, not only out of academic curiosity but also with potential applications in mind (Rao et al., 2009). It is a two-dimensional material, composed of layers of carbon atoms forming six membered rings. Graphene is the mother of all graphitic forms including zerodimensional fullerenes, one-dimensional carbon nanotubes and three-dimensional graphite (Geim and Novoselov, 2007). Compared with other graphitic forms, graphene possesses extraordinary electronic, thermal, and mechanical properties such as ultrahigh specific surface area, good thermal conductivity, fast mobility of charge carriers, and high values of Young's modulus and fracture strength (Stoller et al., 2008; Lee et al., 2008; Balandin et al., 2008; Bolotin et al., 2008). To date, the unique planar structure of graphene provides tremendous potential applications in many fields. For example, graphene served as filler for the enhancement of mechanical and electrical properties in composite materials (Yang et al., 2009; Watcharotone et al., 2007).

Graphene-based materials were also used as sensors for the sensitive and selective detection of biomolecules (Lu et al., 2009; Chang et al., 2010; Shan et al., 2009), and graphene/polymer composite is a candidate for supercapacitors because of their high specific capacitance and good cycling stability (Zhang et al., 2010).

Exceptional properties make graphene a superior candidate as an adsorbent for SPE. Firstly, graphene has a large specific surface area (theoretical value 2630 m<sup>2</sup>/g [Stoller et al., 2008]), suggesting a high sorption capacity. Specifically, both sides of the planar sheets of graphene are available for molecule adsorption, whereas for CNTs and fullerenes, steric hindrance may exist when molecules access their inner walls. Secondly, graphene can be easily modified with functional groups, especially via graphene oxide which has many reactive groups (Park and Ruoff, 2009). Functionalization may further enhance the selectivity of SPE. Thirdly, CNTs usually contain trace amounts of metallic impurities that come from the metal catalysts used in their synthesis. These impurities may have negative effects on the applications of CNTs (Banks et al., 2006; Pumera and Miyahara, 2009). Graphene, on the other hand, can be synthesized from graphite without the use of metal catalysts, thus obtaining pure material. Fourthly, despite being chemically reduced, graphene sheets still have some hydrophilic groups such as hydroxyl and carboxyl groups. These hydrophilic groups can improve the water-wettability of graphene and enhance the retention and elution of polar compounds (Liu et al., 2011). These features make graphene very attractive as an adsorbent material.

Despite their potential advantages, less attention has been paid to the SPE applications of graphene. Dong et al. (Dong et al., 2010) and Tang et al. (Tang et al., 2010) recently reported the use of graphene as a matrix or probe for matrix-assisted or surface-enhanced laser desorption/ionization time-of-flight mass spectrometry. In these reports, graphene as adsorbent or extraction material was dispersed into the sample solution; centrifugation or filtration followed to separate or retrieve the tiny graphene from dispersion (Dong et al., 2010; Schniepp et al., 2006). However, the graphene sheets were difficult to isolate completely from the dispersions even by high-speed centrifugation because of the presence of miniscule sheets of graphene. Furthermore, the procedure is quite troublesome, tedious, and offers inefficient retrieval of graphene.

To ease the retrieval procedure, the SPE using graphene as the adsorbent in a column combined with flame atomic absorption spectrometry (FAAS) has been demonstrated by our research group (Wang et al., 2012). We extend its application 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; Shokoufi et al., 2007), was used to extract Co (structure of the Co-PAN complex is shown in Fig. 1). What is more, it possesses a benzene ring structure. Based on this, the Co-PAN is considered to have formed a strong  $\pi$ -stacking interaction with graphene when the sample solution passes through the column during which the Co-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



**Figure 1** Structural formulae of the Co-PAN complex.

of trace amounts of Co 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.

## 2. Methods

### 2.1. Apparatus

A Shimadzu (Kyoto, Japan) Model AA-6300C atomic absorption spectrometer equipped with deuterium background correction and a Co 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.

### 2.2. Reagents and materials

Graphite powder (50 mesh), potassium permanganate ( $\text{KMnO}_4$ ), concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), and sodium nitrate ( $\text{NaNO}_3$ ) were purchased from Tianjin Tianda Chemical Reagent Company (Tianjin, China). A stock standard solution of Co at a concentration of  $1000 \mu\text{g mL}^{-1}$  was purchased from

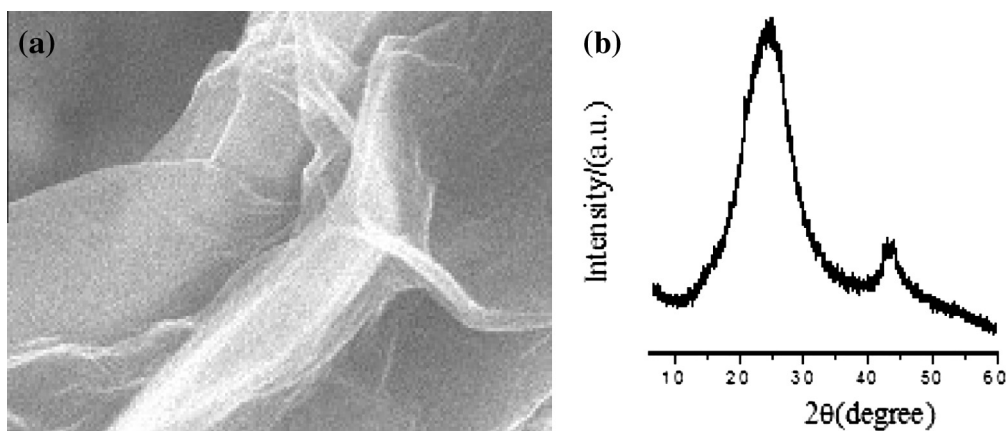
the National Institute of Standards (Beijing, China). Working standard solutions were prepared daily through serial dilutions of the stock solution with deionized water prior to analysis. The chelating agent,  $2.0 \text{ g L}^{-1}$  PAN solution, was prepared by dissolving the appropriate amount of 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, carbon purity  $>90\%$ , outer diameter  $<2 \text{ nm}$ , length  $5\text{--}15 \mu\text{m}$ ) and multi-walled CNTs (MWCNTs, carbon purity  $>98\%$ , outer diameter  $20\text{--}40 \text{ nm}$ , length  $5\text{--}15 \mu\text{m}$ ) were obtained from the Beijing Chemistry Reagent Company (Beijing, China).

Nitric acid ( $0.1 \text{ mol L}^{-1}$ ) was used to adjust the pH in the 2–3 range, and ammonium acetate buffers ( $0.2 \text{ mol L}^{-1}$ ) 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 ( $0.2 \text{ mol L}^{-1}$ ) was prepared by adding an appropriate amount of disodium hydrogen phosphate to sodium dihydrogen phosphate. Ammonium chloride buffer solutions ( $0.2 \text{ mol L}^{-1}$ ) 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.

### 2.3. 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  $\text{Cu K}\alpha$  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).



**Figure 2** SEM image and XRD pattern.

#### 2.4. 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<sup>-1</sup> acetate buffer solution.

#### 2.5. Recommended procedure

100.0 mL of the sample solution containing 100.0 µg L<sup>-1</sup> of Co was prepared. 2.5 mL of PAN (2.0 g L<sup>-1</sup>) 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<sup>-1</sup>. After the solution passed through it completely, the column was rinsed with 5.0 mL of deionised water, and the analytes retained on the column were eluted with 2.0 mL of 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> in methanol at a flow rate of 2.0 mL min<sup>-1</sup>. The analyte ions in the eluent were determined by FAAS. A blank was always taken through the whole procedure.

#### 2.6. 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<sub>2</sub>O<sub>2</sub> 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.

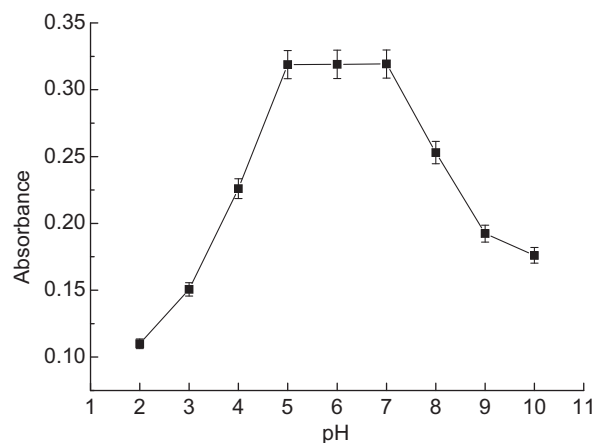
### 3. Results and discussion

#### 3.1. 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 Co 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.

#### 3.2. 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 Co 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<sup>-1</sup> PAN solution was chosen to account for other extractable species that might potentially interfere with the assaying of Co.



**Figure 3** Effect of pH on the absorbance of Co obtained from SPE-FAAS. Extraction conditions: water sample volume, 100.0 mL; PAN volume, 2.5 mL; eluent type, 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> in methanol; eluent volume, 2.0 mL; concentration of Co, 100.0 µg L<sup>-1</sup>; flow rates of sample and eluent solution, 2.0 mL min<sup>-1</sup>.

#### 3.3. 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 microcolumn, 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 Co on graphene was examined in the range of 0.5–5.0 mL min<sup>-1</sup>. 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<sup>-1</sup>, respectively. A 2.0 mL min<sup>-1</sup> flow rate of the sample and eluent solutions was chosen in subsequent experiments.

#### 3.4. 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 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 Co in different volumes (25.0–1000.0 mL) and the recommended procedure was followed. It was observed that Co 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 final eluent volume (2.0 mL). In the present study the possible preconcentration factor was 200.

#### 3.5. 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 Co was found to be 20.6 mg g<sup>-1</sup>.

**Table 1** Effect of type and concentration of eluting agent on recovery of Co.

Eluent	Recovery <sup>a</sup> (%)
1.0 mol L <sup>-1</sup> NaOH	65.4 ± 2.2
2.0 mol L <sup>-1</sup> NaOH	71.3 ± 2.6
1.0 mol L <sup>-1</sup> HCl	68.6 ± 2.3
2.0 mol L <sup>-1</sup> HCl	73.6 ± 2.4
3.0 mol L <sup>-1</sup> HCl	78.5 ± 2.5
1.0 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	67.5 ± 2.4
2.0 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	63.4 ± 2.1
3.0 mol L <sup>-1</sup> H <sub>2</sub> SO <sub>4</sub>	52.2 ± 2.0
0.5 mol L <sup>-1</sup> HNO <sub>3</sub>	70.0 ± 2.2
1.0 mol L <sup>-1</sup> HNO <sub>3</sub>	76.2 ± 2.3
2.0 mol L <sup>-1</sup> HNO <sub>3</sub>	80.5 ± 2.5
1.0 mol L <sup>-1</sup> CH <sub>3</sub> COOH	66.9 ± 2.3
2.0 mol L <sup>-1</sup> CH <sub>3</sub> COOH	75.5 ± 2.8
0.5 mol L <sup>-1</sup> HNO <sub>3</sub> in methanol	89.3 ± 3.0
1.0 mol L <sup>-1</sup> HNO <sub>3</sub> in methanol	92.7 ± 3.0
2.0 mol L <sup>-1</sup> HNO <sub>3</sub> in methanol	95.8 ± 3.2

<sup>a</sup> Average of five determinations ± standard deviation.

### 3.6. 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 Co were not so satisfactory when HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH and NaOH were used as eluents solely. Good quantitative recovery for analyte ions could be obtained with 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> in methanol. The effect of eluent volume on the recovery of Co was also studied by using 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> in methanol; it was found that quantitative recoveries could be obtained with 2.0–4.0 mL of 2.0 mol L<sup>-1</sup>

HNO<sub>3</sub> in methanol. Therefore, the volume of 2.0 mL of 2.0 mol L<sup>-1</sup> HNO<sub>3</sub> in methanol was used in the following experiments.

### 3.7. 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 Co. This is of great importance especially when the sorbent does the job with satisfactory analytical performance after using several circles in solid-phase extraction.

### 3.8. Effects of coexisting ions

The effects of common coexisting ions on the adsorption of Co on graphene were investigated. In these experiments, 100.0 mL solutions containing 100.0 µg L<sup>-1</sup> of Co 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 Co ion under the selected conditions.

### 3.9. 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

**Table 2** Effect of interfering ions on the recovery of 100.0 µg L<sup>-1</sup> Co in water samples using SPE-FAAS.

Interferent	Concentration (µg L <sup>-1</sup> )	Added as	Interferent/Co <sup>2+</sup> ratio	Recovery (%)
Na <sup>+</sup>	150,000,000	NaNO <sub>3</sub>	1,500,000	97.4
K <sup>+</sup>	150,000,000	KNO <sub>3</sub>	1,500,000	95.6
Ba <sup>2+</sup>	10,000	BaCl <sub>2</sub>	100	95.7
Al <sup>3+</sup>	10,000	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	100	97.6
Cr <sup>3+</sup>	10,000	Cr(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O	100	97.2
Mn <sup>2+</sup>	10,000	MnSO <sub>4</sub> ·H <sub>2</sub> O	100	95.3
Ca <sup>2+</sup>	10,000	CaCl <sub>2</sub>	100	97.5
Mg <sup>2+</sup>	10,000	Mg(NO <sub>3</sub> ) <sub>2</sub>	100	98.2
Cu <sup>2+</sup>	6000	Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	60	96.0
Ag <sup>+</sup>	6000	AgNO <sub>3</sub>	60	95.2
Fe <sup>3+</sup>	5000	FeCl <sub>3</sub>	50	96.3
Ni <sup>2+</sup>	5000	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	50	97.0
Pb <sup>2+</sup>	5000	Pb(NO <sub>3</sub> ) <sub>2</sub>	50	95.7
Cd <sup>2+</sup>	4000	Cd(NO <sub>3</sub> ) <sub>2</sub>	40	95.4
Zn <sup>2+</sup>	4000	ZnCl <sub>2</sub>	40	96.5
NO <sub>3</sub> <sup>-</sup>	150,000,000	KNO <sub>3</sub>	1,500,000	98.5
Cl <sup>-</sup>	50,000,000	NaCl	500,000	96.3
F <sup>-</sup>	10,000,000	NaF	100,000	95.4
CH <sub>3</sub> COO <sup>-</sup>	1,000,000	CH <sub>3</sub> COONa	10,000	97.2
PO <sub>4</sub> <sup>3-</sup>	100,000	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O	1000	95.2
HCO <sub>3</sub> <sup>-</sup>	100,000	KHCO <sub>3</sub>	1000	95.8
CO <sub>3</sub> <sup>2-</sup>	50,000	Na <sub>2</sub> CO <sub>3</sub>	500	96.2
SO <sub>4</sub> <sup>2-</sup>	10,000	Na <sub>2</sub> SO <sub>4</sub>	100	96.4
HPO <sub>4</sub> <sup>2-</sup>	10,000	Na <sub>2</sub> HPO <sub>4</sub> ·12H <sub>2</sub> O	100	95.7

**Table 3** Analytical results of Co determination (dissolved fraction) in certified reference materials and spiked natural water samples with the SPE-FAAS method ( $n = 5$ ).

Sample	Certified	Added	Found <sup>a</sup>	Recovery of Co (%)
GSBZ 50,030-94 ( $\mu\text{g L}^{-1}$ )	14.38 $\pm$ 1.0	–	13.67 $\pm$ 0.60	95.1
	28.75 $\pm$ 2.0	–	27.89 $\pm$ 1.02	97.0
Tap water <sup>b</sup> ( $\mu\text{g L}^{-1}$ )		0.0	5.65 $\pm$ 0.25	–
		10.0	15.23 $\pm$ 0.60	95.8
		15.0	20.13 $\pm$ 0.72	96.5
Sea water <sup>c</sup> ( $\mu\text{g L}^{-1}$ )		0.0	30.58 $\pm$ 1.03	–
		30.0	60.52 $\pm$ 2.05	99.8
		50.0	81.88 $\pm$ 2.56	102.6
		0.0	18.85 $\pm$ 0.70	–
River water <sup>d</sup> ( $\mu\text{g L}^{-1}$ )		20.0	38.51 $\pm$ 1.32	98.3
		25.0	43.60 $\pm$ 1.45	99.0
		0.0	16.74 $\pm$ 0.68	–
River water <sup>e</sup> ( $\mu\text{g L}^{-1}$ )		20.0	36.30 $\pm$ 1.25	97.8
		25.0	41.37 $\pm$ 1.38	98.5
		0.0	–	–

<sup>a</sup> Mean of five experiments  $\pm$  standard deviation.

<sup>b</sup> From drinking water system of Baoding, China.

<sup>c</sup> Beidaihe sea water, Qinhuangdao, China.

<sup>d</sup> Yongding river water, Baoding, China.

<sup>e</sup> Juma river water, Baoding, China.

5.0 to 240.0  $\mu\text{g L}^{-1}$  for Co. The calibration equation is  $A = 3.16 \times 10^{-3}C + 0.0042$  with a correlation coefficient of 0.9992, where  $A$  is the atomic absorbance of Co, obtained by peak height, in the eluent at 240.7 nm and  $C$  is its concentration in the sample solution ( $\mu\text{g L}^{-1}$ ). The limits of detection and quantification defined as  $3S_B/m$  and  $10S_B/m$  (where  $S_B$  is standard deviation of the blank and  $m$  is the slope of the calibration graph) were 0.36 and 1.20  $\mu\text{g L}^{-1}$ , respectively. The relative standard deviation (RSD) for ten replicate measurements of 20.0 and 100.0  $\mu\text{g L}^{-1}$  of Co were 3.45% and 3.18%, respectively.

### 3.10. Analytical application

The proposed method was used for the determination of Co in several water samples. The results, along with the recovery for the spiked samples, are given in Table 3. The recoveries for the addition of different concentrations of Co to water samples were in the range of 95.8–102.6%. To verify the accuracy of the proposed procedure, the method was used to determine the content of Co in the National Standard Reference Material for Environment Water (GSBZ 50030-94) after the appropriate dilution. The results for this test are presented in Table 3. A good agreement between the determined values and the certified values was obtained.

### 3.11. 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  $\mu\text{g L}^{-1}$  of Co. 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 Co 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. Cobalt 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 Co 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 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,

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

Sorbent materials	Graphene	C18 silica	Graphitic carbon	MWCNTs	SWCNTs
Recoveries (%)	96.2	55.6	48.5	78.3	82.7

but still inferior to graphene. No Co was present in the flow-throughs and washing solutions for MWCNTs and SWCNTs, indicating that CNTs also have good sorption capacities for Co. 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 HNO<sub>3</sub> as eluent solvent, the recovery of Co on SWCNT column can reach 92.3%. Nevertheless, increasing the volume of the eluent solvent will reduce the preconcentration 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.

#### 4. Conclusions

In conclusion, the proposed method reveals the great potential of graphene as an advantageous sorbent material in SPE. Using Co 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 fine reproducibility. Although the obtained results of this research were related to the Co determination, the system could be a considerable potential guide for the preconcentration and determination of other metals.

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