

## Application of Graphene as a Sorbent for the Preconcentration and Determination of Trace Amounts of Mercury in Water Samples by Hydride Generation Atomic Fluorescence Spectrometry

<sup>1</sup>Hai Yan Liu, <sup>1</sup>Xu Feng Meng, <sup>1</sup>Chao Li, <sup>2</sup>An Qiang Jia, <sup>1</sup>Jing Ci Li\* and <sup>1</sup>Jing Jun Ma\*\*

<sup>1</sup>Hebei Key Laboratory of Bioinorganic Chemistry, College of Sciences, Agricultural University of Hebei, Baoding 071001, China.

<sup>2</sup>College of urban and rural construction, Agricultural University of Hebei, Baoding 071001, China.

lijingci@hebau.edu.cn\*; mjjwjpmartin@sina.com\*\*

(Received on 23rd August 2013, accepted in revised form on 11th August 2014)

**Summary:** The potential of graphene as a solid-phase extraction adsorbent for the separation and preconcentration of mercury (Hg) was investigated. Hg<sup>2+</sup> was found to be quantitatively adsorbed onto graphene within pH 6.0-8.0, and then completely eluted with 4.0 mL of nitric acid/methanol (1:1, v/v) solution at a flow rate of 2.0 mL min<sup>-1</sup>. A new method using a microcolumn packed with graphene as a sorbent was developed for the preconcentration of trace amount of Hg<sup>2+</sup> prior to its determination by hydride generation atomic fluorescence spectrometry. Under the optimum experimental conditions, the detection limit of this method for Hg<sup>2+</sup> was 5.0 ng L<sup>-1</sup>, with an enrichment factor of 15.0, and the relative standard deviation was 3.5% at the 1.0 µg L<sup>-1</sup> Hg<sup>2+</sup> level. The method was then applied for the determination of trace amount of Hg<sup>2+</sup> in water samples with satisfactory results.

**Keywords:** Graphene; Solid phase extraction; Preconcentration; Hydride generation atomic fluorescence spectrometry; Mercury.

### Introduction

Carbon materials are known for their high adsorption capacity for environmental pollutants, some carbon materials, such as activated carbon [1], single-walled carbon nanotubes [2] and multi-walled carbon nanotubes [3] have already been used in solid-phase extraction (SPE). Graphene, which is considered as the basic building block of all graphitic forms (including carbon nanotubes, graphite, and fullerene C<sub>60</sub>), is a single-atom-thick, two-dimensional carbon material [4]. Compared with other graphitic forms, graphene shows many outstanding advantages, such as high surface area (2630 m<sup>2</sup>g<sup>-1</sup>), remarkable thermal and chemical stability, ultra-high mechanical strength, and low production cost [5, 6]. At present, graphene-based materials are applied in many fields, such as sensors and biosensors [7], energy storage [8], catalytic [9], and gas separation [10]. Moreover, the electron richness, hydrophobicity, nanosize, and  $\pi$ - $\pi$  electrostatic stacking property [11] of graphene enable it to function as an extraordinarily wonderful adsorbent or extraction material. Liu *et al.*, [12] developed an SPE technique using graphene as a novel adsorbent for the determination of eight chlorophenols in aqueous samples. They demonstrated that the preconcentration technique is an efficient, simple, and nonexpensive extraction procedure for high performance liquid

chromatography (HPLC) analysis. We then extended the application of the technique to inorganic analysis, and drew a consistent conclusion.

In the present work, the SPE using graphene as an adsorbent in a microcolumn combined with hydride generation atomic fluorescence spectrometry (HG-AFS) was demonstrated. The applicability of this approach was validated for the determination of Hg<sup>2+</sup> in water samples. Mercury is prevalent toxic heavy metals with significant environmental effects because of its persistent accumulation, high toxicity, wide use, and large distribution [13-17]. Therefore, sufficiently sensitive and reproducible analytical methods for the precise monitoring of this element at trace level must be developed.

### Experiment

A continuous flow AFS-3100 atomic fluorescence spectrometer (Haiguang Instrument Company, Beijing, China) was used for the analytical determinations. A pH3-3C digital pH meter equipped with a combined glass-calomel electrode (Dongxing Instrument Factory, Hangzhou, China) was used for pH adjustment. Empty SPE columns and SPE frits (Tegent Technology Ltd. Shanghai, China) were used for extraction.

---

\*To whom all correspondence should be addressed.

Graphene with an average external diameter of 40 nm was obtained from the XFNANO Materials Tech Co., Ltd.(Nanjing, China). Graphene (30.0 mg) was placed in a 5.0 mL SPE column using an upper frit and a lower frit to avoid adsorbent loss. Prior to extraction, the column was sequentially preconditioned with 10.0 mL of methanol and 10.0 mL of deionized water. The column was then conditioned to the desired pH with 10.0 mL of 0.2 mol L<sup>-1</sup> phosphate buffer solution. All reagents used were of analytical reagent grade. Deionized water was used to prepare all solutions. All glassware and empty columns were submerged in 10% nitric acid for at least 24 h and subsequently washed four times with deionized water before application.

Exactly 60.0 mL of sample solution containing 1.0 µg L<sup>-1</sup> of Hg<sup>2+</sup> was prepared. PAN solution (0.5 mL, 2.0 g L<sup>-1</sup>) was added, and the pH was adjusted to 7.0 with phosphate 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 completely passed, the column was rinsed with 5.0 mL of water, and the analytes retained on the column were eluted with 4.0 mL of nitric acid/methanol (1:1, v/v) at a flow rate of 2.0 mL min<sup>-1</sup>. The analyte ions in the eluent were introduced into the AFS using the flow injection system. In all determinations, the blanks, standards, and samples were subjected to the same experimental procedure.

## Results and Discussion

In the SPE procedure, preliminary experiments showed that recovery was relatively low. PAN, a chelating agent that produces stable complexes with a number of metals and has numerous applications in trace element separation and preconcentration methods [18, 19], is used to extract Hg<sup>2+</sup>. PAN also possesses a benzene ring structure. On the basis, Hg-PAN is considered to form a strong  $\pi$ -stacking interaction with graphene when the sample solution passes through column, during which the Hg-chelate is retained. Sample pH influences the chelating reaction and further affects the enrichment of Hg<sup>2+</sup>. 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. As shown in Fig. 1, quantitative recoveries (>95%) were obtained for Hg<sup>2+</sup> ions within pH 6.0–8.0. All subsequent studies were carried out at pH 7.0 by using phosphate buffer solution.

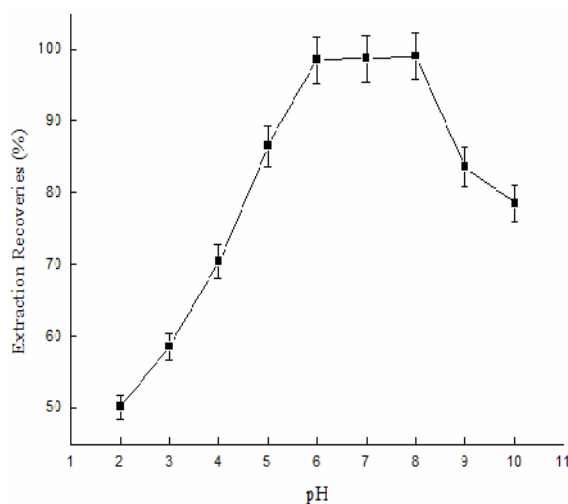


Fig. 1: Effect of pH on the extraction recovery of Hg obtained from SPE-HG-AFS. Experimental conditions: water sample volume, 60.0 mL; PAN volume, 0.5 mL; eluent type, nitric acid/methanol (1:1, v/v); eluent volume, 4.0 mL; concentration of Hg, 1.0 µg L<sup>-1</sup>; flow rates of sample and eluent solution, 2.0 mL min<sup>-1</sup>.

The effect of sample flow rate on the recoveries of Hg<sup>2+</sup> on graphene was examined within the range of 0.5-2.0 mL min<sup>-1</sup>. Results showed that the flow rate had almost no impact on the enrichment of Hg<sup>2+</sup> ion; thus, the maximum flow rate was adopted for achieving better extraction. The sample volume was also investigated within the range of 25.0-500.0 mL. Results demonstrated that the quantitative recovery (>95%) of Hg<sup>2+</sup> was obtained when the sample volume was <200.0 mL. Considering the enrichment factor and analysis time, 60.0 mL was ultimately chosen for routine analysis.

About 1.0 mol L<sup>-1</sup> HNO<sub>3</sub>, 1.0 mol L<sup>-1</sup> HCl, nitric acid/methanol (1:1, v/v), and methanol were investigated for the elution of Hg<sup>2+</sup> from the graphene SPE column. Results indicated that nitric acid/methanol (1:1, v/v) was the best eluent and was thus used in subsequent experiments. To obtain the optimum enrichment factor of Hg<sup>2+</sup> and meet the required injection volume for HG-AFS, the eluent volume was optimized within 2.0-8.0 mL. Data showed that 3.0 mL effectively eluted Hg<sup>2+</sup>. To maintain a reasonable elution capacity, 4.0 mL was selected for further experiments.

Table-1: Analytical results of Hg<sup>2+</sup> determination (dissolved fraction) in certified reference materials and spiked natural water samples with the SPE-HG-AFS method (n=3).

Sample	Certified Concentration ( $\mu\text{g L}^{-1}$ )	Added ( $\mu\text{g L}^{-1}$ )	Found <sup>a</sup> ( $\mu\text{g L}^{-1}$ )	Recovery (%)
GSBZ50016-90	1.120±0.120	–	1.071±0.042	95.6
	2.240±0.240	–	2.191±0.085	97.8
Tap water <sup>b</sup>		0.0	<LOD	–
		1.0	0.952±0.050	95.2
		2.0	1.936±0.082	96.8
		0.0	0.780±0.048	–
Nandaihe Sea water <sup>c</sup>		1.0	1.752±0.081	97.2
		2.0	2.752±0.102	98.6
		0.0	<LOD	–
		1.0	0.950±0.054	95.0
Daqing River water <sup>d</sup>		2.0	1.928±0.090	96.4
		0.0	<LOD	–
		1.0	0.951±0.048	95.1
		2.0	1.930±0.087	96.5

LOD: limit of detection.

<sup>a</sup> Mean of three experiments±standard deviation.

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

<sup>c</sup> From Qinhuangdao, China.

<sup>d</sup> From Baoding, China.

In this work, the effects of some representative potential interference were tested to evaluate the possible interference. The tolerance limit was taken as the concentration of the interfering ions causing a variation in the fluorescence intensity of Hg<sup>2+</sup> in the sample to within ±5%. Under the optimal experimental conditions, large amounts of alkali and alkaline metal ions (e.g., Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) and anionic species (e.g., Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>3</sub><sup>2-</sup>) did not interfere with the determination. Regarding other potentially interfering ions as commonly interferent transition elements, 1000  $\mu\text{g L}^{-1}$  of Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup>, as well as 500  $\mu\text{g L}^{-1}$  Mn<sup>2+</sup>, Pb<sup>2+</sup>, and 100  $\mu\text{g L}^{-1}$  of Cd<sup>2+</sup>, had no influence. Interference from high-concentration of Fe<sup>3+</sup> was eliminated by adding EDTA at a concentration of 5% (m/v).

The analytical characteristics of the SPE-HG-AFS method for the determination of Hg<sup>2+</sup> were evaluated. The calibration graph showed good linearity within 0.02-5.0  $\mu\text{g L}^{-1}$ , and the regression equation was  $I=766.36C_{\text{Hg}}+17.64$  ( $C$  is in  $\mu\text{g L}^{-1}$ ) with  $R^2=0.9992$ . Based on three times the background noise, the limit of detection (LOD) was 5.0 ng L<sup>-1</sup> for Hg<sup>2+</sup>. The relative standard deviation (RSD) for 11 replicate measurements of 1.0  $\mu\text{g L}^{-1}$  of Hg was 3.5%. The enhancement factor calculated was 15.0.

To determine the reliability of this methodology, it was applied to the determination of Hg<sup>2+</sup> in several water samples such tap, sea, and river water collected in PTFE containers from Hebei province. The samples were filtered through a 0.45  $\mu\text{m}$  pore size membrane filter to remove suspended particulate matter and stored in a refrigerator in

darkness. The results are shown in Table-1. The recoveries of different concentrations of Hg<sup>2+</sup> added to water samples were ranged within 95.0–98.6%. To verify the accuracy of the proposed procedure, the method was then used to determine the content of Hg<sup>2+</sup> in National Standard Reference Material for Environment Water (GSBZ50016-90) after appropriate dilution. These results are presented in Table 1. The determined values well agreed with the certified values.

## Conclusion

The proposed method revealed the great potential of graphene as an advantageous sorbent material for SPE. Using Hg as model analyte, the graphene-packed SPE columns showed reliable and attractive analytical performance for the analysis of environmental water samples. Some advantages of graphene as SPE adsorbent were demonstrated, such as high sorption capacity, good reusability, and fine reproducibility.

## Acknowledgements

This project was sponsored by Hebei province science and technology support project (No. 13228124); the Youth Foundation of the Department of Education of Hebei Province (No. QN20131014); and the Science Foundation of the Agricultural University of Hebei (No. LG201305).

## References

1. W. Xie, C. Han, Y. Qian, H. Y. Ding, X. M. Chen and J. Y. Xi, Determination of

- neonicotinoid pesticides residues in agricultural samples by solid-phase extraction combined with liquid chromatography–tandem mass spectrometry, *J. Chromatogr. A*, **1218**, 4426 (2011).
2. S. Mohanapriya and V. Lakshminarayanan, Simultaneous purification and spectrophotometric determination of nickel present in as-prepared single-walled carbon nanotubes (SWCNT), *Talanta*, **71**, 493 (2007).
  3. Y. Q. Cai, G. B. Jiang, J. F. Liu and Q. X. Zhou, Multiwalled carbon nanotubes as a solid-phase extraction adsorbent for the determination of bisphenol A, 4-n-Nonylphenol, and 4-tert-Octylphenol, *Anal. Chem.*, **75**, 2517 (2003).
  4. C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam and A. Govindaraj, Graphene: the new two-dimensional nanomaterial, *Angew. Chem. Int. Edit.*, **48**, 7752 (2009).
  5. H. Q. Chen, M. B. Muller, K. J. Gilmore, G. G. Wallace and D. Li, Mechanically strong, electrically conductive, and biocompatible graphene paper, *Adv. Mater.*, **20**, 3557 (2008).
  6. J. A. Matthew, C. T. Vincent and B. K. Richard, Honeycomb carbon: a review of graphene, *Chem. Rev.*, **110**, 132 (2010).
  7. C. H. Lu, H. H. Yang, C. L. Zhu, X. Chen and G. N. Chen, A graphene platform for sensing biomolecules, *Angew. Chem. Int. Edit.*, **48**, 4785 (2009).
  8. G. X. Wang, B. Wang, X. L. Wang, J. Park, S. X. Dou, H. Ahn and K. Kim, Sn/graphene nanocomposite with 3D architecture for enhanced reversible lithium storage in lithium ion batteries, *J. Mater. Chem.*, **19**, 8378 (2009).
  9. G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth and R. Mulhaupt, Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives as highly active catalysts for the suzuki–miyaura coupling reaction, *J. Am. Chem. Soc.*, **131**, 8262 (2009).
  10. D. Jiang, V. R. Cooper and S. Dai, Porous graphene as the ultimate membrane for gas separation, *Nano Lett.*, **9**, 4019 (2009).
  11. Q. Su, S. P. Pang, V. Alijani, C. Li, X. L. Feng and K. Mullen, Composites of graphene with large aromatic molecules, *Adv. Mater.*, **21**, 3191 (2009).
  12. Q. Liu, J. B. Shi, L. X. Zeng, T. Wang, Y. Q. Cai and G. B. Jiang, Evaluation of graphene as an advantageous adsorbent for solid-phase extraction with chlorophenols as model analytes, *J. Chromatogr. A*, **1218**, 197 (2011).
  13. S. Rapsomanikis and P. J. Craig, Speciation of mercury and methylmercury compounds in aqueous samples by chromatography-atomic absorption spectrometry after ethylation with sodium tetraethylborate, *Anal. Chim. Acta*, **248**, 563 (1991).
  14. A. Collasiol, D. Pozebon and S. M. Maia, Ultrasound assisted mercury extraction from soil and sediment, *Anal. Chim. Acta*, **518**, 157 (2004).
  15. M. Tuzen and M. Soylak, Mercury contamination in mushroom samples from Tokat, Turkey, *B. Environ. Contam. Tox.*, **74**, 968 (2005).
  16. M. Tuzen, I. Karaman, D. Citak and M. Soylak, Mercury(II) and methyl mercury determinations in water and fish samples by using solid phase extraction and cold vapour atomic absorption spectrometry combination, *Food Chem. Toxicol.*, **47**, 1648 (2009).
  17. M. Tuzen, O. D. Uluozlu, I. Karaman and M. Soylak, Mercury(II) and methyl mercury speciation on *Streptococcus pyogenes* loaded Dowex Optipore SD-2, *J. Hazard. Mater.*, **169**, 345 (2009).
  18. X. S. Zhu, X. H. Zhu and B. S. Wang, Determination of trace cadmium in water samples by graphite furnace atomic absorption spectrometry after cloud point extraction, *Microchim. Acta*, **154**, 95 (2006).
  19. N. Shokoufi, F. Shemirani and Y. Assadi, Fiber optic-linear array detection spectrophotometry in combination with dispersive liquid–liquid microextraction for simultaneous preconcentration and determination of palladium and cobalt, *Anal. Chim. Acta*, **597**, 349 (2007).