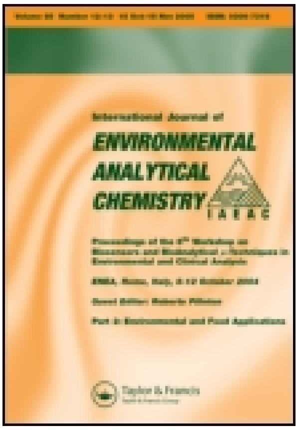

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# Chemically modified activated carbon with S-benzyldithiocarbazate as a new solid-phase extractant for preconcentration of mercury prior to ICP-AES determination

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# Chemically modified activated carbon with S-benzyldithiocarbazate as a new solid-phase extractant for preconcentration of mercury prior to ICP-AES determination

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A new sorbent S-benzyldithiocarbazate (SBDTC) modified activated carbon (AC-SBDTC) was prepared and studied for preconcentration for trace mercury(II) prior to inductively coupled plasma atom emission spectrometry (ICP-AES). The experimental conditions were optimised with respect to different experimental parameters using both batch and column procedures in detail. The optimum pH value for the separation of Hg(II) on the new sorbent was 3, while the adsorption equilibrium was achieved in less than 5 min. Complete elution of the adsorbed metal ions from the sorbent surface was carried out using 5 mL of $0.25\,\mathrm{mol\,L^{-1}}$ of HCl and 2% $CS(NH_2)_2$. Common coexisting ions did not interfere with the determination. The maximum static adsorption capacity of the sorbent under optimum conditions was found to be $0.55\,\mathrm{mmol\,g^{-1}}$. The detection limit of the present method was found to be $0.09\,\mathrm{ng\,mL^{-1}}$, and the relative standard deviation (RSD) was lower than 2.0%. The procedure was validated by analysing the certified reference river sediment material (GBW 08301, China), the results obtained were in good agreement with standard values. This sorbent was successfully employed in the separation and preconcentration of trace Hg(II) from the natural water samples yielding 80-fold concentration factor.

**Keywords:** S-benzyldithiocarbazate modified activated carbon (AC-SBDTC); solid-phase extraction; mercury; ICP-AES

## 1. Introduction

In recent years, the determination of mercury(II) has attracted great attention worldwide for its highly toxic effect on the environment, especially the aquatic system [1,2]. Mercury has been considered as a human health hazard because it may cause kidney toxicity, neurological damage, paralysis, chromosome breakage and birth defects [3]. Although there have been regulations to limit its level in water and sediments, it inevitably exists in the environment [4]. So, it is crucial to develop simple, rapid and efficient methods for monitoring mercury(II) for the reason that even low concentration of mercury in natural water supplies could have detrimental effects on wildlife and human beings.

A separation step is necessary due to the matrix interferences and the very low concentration of mercury in environmental samples [5–7]. The traditional liquid-liquid extraction method often requires large amounts of high purity organic solvent, some of

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which are harmful to health and cause environmental problems. Meanwhile, solid-phase extraction (SPE) has been widely used for environmental water sample pretreatment due to its higher enrichment factors, rapidity and environmental friendliness [8–10]. The principle of SPE is to enhance the selectivity and sensitivity of the methods by the transferring of the analyte from the aqueous phase to active sites of the adjacent solid phase. Accordingly, most sorbents for metal ions are prepared by immobilising regents onto the surface of a matrix, like silica gel [11–13], chelating material [14–16], activated carbon [17–19], and so on.

Among a large variety of sorbents, activated carbon has been most commonly used in various areas, notably in separation and preconcentration of heavy metal ions from aqueous system for its flexibility, simplicity, low cost and large surface area [20]. So far as we know, different kinds of organic ligands have been used to modify activated carbon through the non-oxidative surface treatment.

S-benzyldithiocarbazate (SBDTC) is a good metal complexing agent [21,22], but it has not been used to separate and preconcentrate metal ions up to now. In this work, the new extractant was prepared by immobilising SBDTC chemically on the surface of activated carbon, which has been oxidised in advance by nitric acid. The adsorption behaviour of analytes on the SBDTC modified activated carbon (AC-SBDTC) and the experimental conditions for the preconcentration process were investigated in detail. The result showed that mercury(II) can be selectively extracted by AC-SBDTC in acidic aqueous solutions in the presence of common coexisting metal ions. The new method was validated by the standard addition method, and the analytical precision and accuracy of the proposed method were satisfied.

## 2. Experimental

### 2.1 *Apparatus*

An IRIS Advantage ER/S inductively coupled plasma emission spectrometer (TJA, USA) was used for all metal ions determination. The instrumental parameters were those recommended by the manufacturer, and the wavelength selected was 194.2 nm. The pH values were adjusted with a pHS-10C digital pH meter (Xiaoshan Instrument Factory, China). Fourier transform infrared (FT-IR) spectra (4000–200 $cm^{-1}$) in KBr were recorded using Nicolet Nexus 670 FT-IR spectrometer (Nicolet, USA), and each spectrum was obtained after acquiring the same KBr background spectra. An YL-110 peristaltic pump (General Research Institute for Non-ferrous Metals, China) was used in the separation/preconcentration process. A self-made glass column (5 cm × 4 mm i.d.) was used in column SPE procedure.

### 2.2 *Chemicals and reagents*

Unless otherwise stated, reagents of analytical and spectral purity were used for all experiments and doubly distilled deionised water was used throughout. Activated carbon (AC), gas chromatographic grade, 100–200 mesh (Tianjin Guangfu Fine Chemical Research Institute, China) and S-benzyldithiocarbazate (SBDTC) (self-made) were used in this work. N,N-Dicyclohexylcarbodiimide (DCC) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Standard stock solution of Hg(II) (1 mg $mL^{-1}$) were prepared by dissolving a spectral pure grade chemicals chloride salts in double distilled water with the addition of hydrochloric acid and further diluted daily prior to use.

### 2.3 *Sample preparation*

Tap water samples taken from our research laboratory were analysed without pretreatment. River water was collected from Yellow River, Lanzhou, China. The water sample was filtered through a 0.45 µm membrane filter (Jinteng Instrument Factory, China), and acidified to a pH of about 1 with concentrated HCl prior to storage for use [23].

Sediment reference material GBW 08301 (river sediment, provided by the National Research Center for Certified Reference Materials, China), was treated according to previous procedure [24]. A 50 mg of the sample was accurately weighed into a 50 mL container and aqua regia (12 mL of concentrated hydrochloric acid and 4.0 mL of concentrated nitric acid) was added. The container was covered with a watch glass and was evaporated on a hot plate almost to dryness. Then 8.0 mL of aqua regia was added to the residue and the mixture was again evaporated to dryness. After cooling, resulting mixture was filtered through a 0.45 µm polytetrafluoroethylene (PTFE) millipore filter. The sample was diluted to 10 mL with double distilled water and preconcentrated using the new sorbent.

### 2.4 *Synthesis of new sorbent*

#### 2.4.1 *Preparation of S-benzyldithiocarbazate (SBDTC) [25]*

Potassium hydroxide (28.5 g) was completely dissolved in a 9 : 1 alcohol–water mixture (150 mL) and the mixture was cooled in ice. Hydrazine hydrate (25 g) was added to the solution, slowly with stirring. A solution of carbon disulphide (36.5 g) in alcohol (30 mL) was then added dropwise from a burette with constant stirring, over a period of 1 h. The temperature of the mixture was kept below 10°C during the addition. The resulting yellow oil was separated by means of a separatory funnel and dissolved in 2 : 3 alcohol–water mixture (120 mL), and then this solution was cooled in ice. Benzyl chloride (62.16 g) was added slowly with vigorous mechanical stirring; after the addition, the mixture was stirred for a further 10 min during which a white product separated. Ice-cooled water (100 mL) was then added and the stirring continued for another 10 min. The product was separated by filtration, washed with water and dried in air. The crude product was recrystallised from benzene (150 mL). Elemental analysis found 48.51% carbon, 5.00% nitrogen and 14.11% hydrogen, which can be calculated for $C_8H_{10}N_2S_2$.

#### 2.4.2 *Preparation of carboxylic derivative of activated carbon (AC-COOH) [26]*

Activated carbon powder was first purified with 10% (v/v) hydrochloric acid solution for 24 h so as to remove the metal ions and other impurities sorbed on it. Then 10 g of purified activated carbon was suspended in 300 mL of 5 mol $L^{-1}$ nitric acid solution under stirring and heating for 5 h at 60°C. The mixture was filtered and washed with deionised water to neutral and dried under vacuum at 80°C for 8 h. The product was carboxylic derivative of activated carbon (AC-COOH).

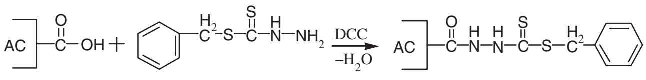

Figure 1. Synthetic route for activated carbon-bound S-benzyldithiocarbazate (AC-SBDTC).

### 2.4.3 *Preparation of activated carbon-bound S-benzyldithiocarbazate(AC-SBDTC)*

For the synthesis of activated carbon-bound S-benzyldithiocarbazate (AC-SBDTC), 4.0 g of SBDTC was dissolved in 30 mL of benzene, then 5.0 g of AC-COOH and 5.0 g N,N-dicyclohexylcarbodiimide (DCC) was added into it. The reaction mixture was stirred at room temperature for 48 h. The product (AC-SBDTC) was filtered off, washed with ethanol and dried under vacuum at 80°C for 8 h. The synthetic route of AC-SBDTC is illustrated in Figure 1.

## 2.5 *General procedures*

### 2.5.1 *Batch procedure*

A total of 20 mg of AC-SBDTC sorbent was suspended in 10 mL of a series of standards or sample solutions containing Hg(II), then the pH value was adjusted to the desired value with 0.1 mol $L^{-1}$ HCl or 0.1 mol $L^{-1}$ $NH_3 \cdot H_2O$. The mixture was then shaken vigorously for 30 min to facilitate adsorption of the metal ions onto the sorbent. After extraction, the suspend solution was centrifuged, and the supernatant was decanted. The concentrations of the metal ions in solution were directly determined by ICP-AES. The adsorbent was then eluted with HCl and $CS(NH_2)_2$ of optimum concentration and the desorbed metal ions were measured by ICP-AES.

### 2.5.2 *Column procedure*

A total 50 mg of AC-SBDTC was filled into a glass column (5 cm × 4 mm i.d.). The ends of the column were plugged with a small portion of glass wool to prevent loss of the sorbents during sample loading. After cleaning by passing through ethanol and pure water once more, the column was conditioned to the desired pH with 0.1 mol $L^{-1}$HCl or 0.1 mol $L^{-1}$ $NH_3 \cdot H_2O$. Each sample solution was passed through the column at a flow rate of 1.5 mL $min^{-1}$. Afterwards, the metal ions retained on the column were eluted with 0.25 mol $L^{-1}$ HCl + 2% $CS(NH_2)_2$ at a flow rate of 1.5 mL $min^{-1}$. The analytes in the elution were then determined by ICP-AES. An YL-110 peristaltic pump was used to regulate the flow rate throughout the column procedure.

## 3. Results and discussion

## 3.1 *Characterisation of the new sorbent*

To ascertain the presence of SBDTC in the functionalised activated carbon sorbents, FT-IR spectra in Figure 2 were obtained from carboxylic derivative of activated carbon (AC-COOH) and activated carbon-bound S-benzyldithiocarbazate (AC-SBDTC). Compared with the IR spectrum of AC-COOH, the new bands at 1044.71 and 1072.50 $cm^{-1}$ from the spectrum of AC-SBDTC is the characteristic of $\nu_{C\text{-}N}$, suggesting

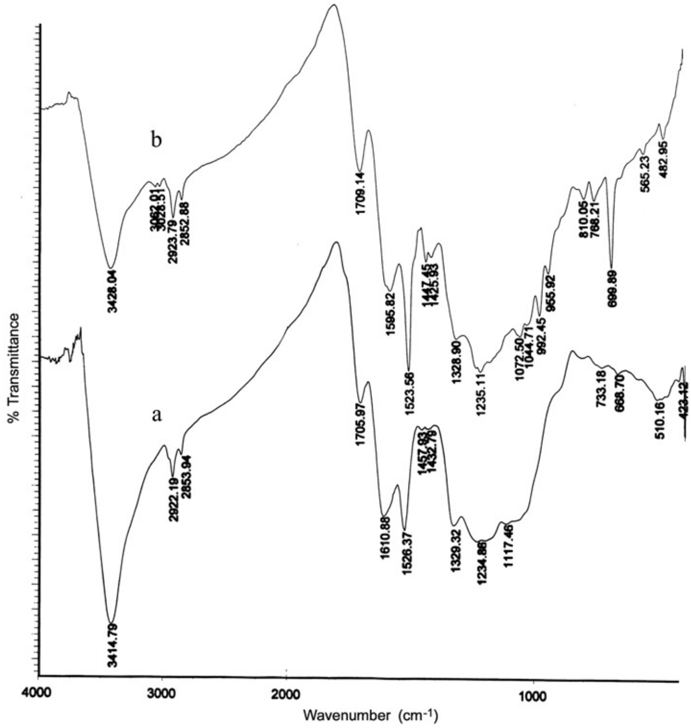

Figure 2. FT-IR spectra of carboxylic derivative of activated carbon (AC-COOH) (a) and activated carbon-bound S-benzyldithiocarbazate (AC-SBDTC) (b).

that S-benzyldithiocarbazate is covalently bonded to the activated carbon through amide bond formation [21,27]. The bands observed at 3248.04 and 992.45 $cm^{-1}$ may be assigned to the stretching vibration and deformation mode of N–H, respectively. The peak at 768.21 and 810.05 $cm^{-1}$ indicated the stretching vibration of C–S, and the one at 955.92 $cm^{-1}$ indicated C=S vibration in SBDTC. The weak band that appeared at 565.23 and 482.95 $cm^{-1}$ can be assigned to the mono-substitute characteristic vibration of the benzene ring [28]. All experimental results above demonstrate that SBDTC was modified on activated carbon successfully.

### 3.2 *Effect of solution pH*

The pH of the medium is one of the most important factors controlling the limit of extractability of Hg(II) ions. According to the batch procedure, the effect of pH on the adsorption of Hg(II) ions was tested by equilibrating 20 mg of sorbent with 10 mL of the solutions containing 1.0 $\mu g\,mL^{-1}$ of Hg(II) ions under different pH (1–6). The results were listed in Figure 3. As can be seen, quantitative extraction (>95%) of the analytes is found in range of pH 3–6. In order to ensure quantitative adsorption and avoid hydrolysing at higher pH values, pH 3 was selected as the enrichment acidity for subsequent work.

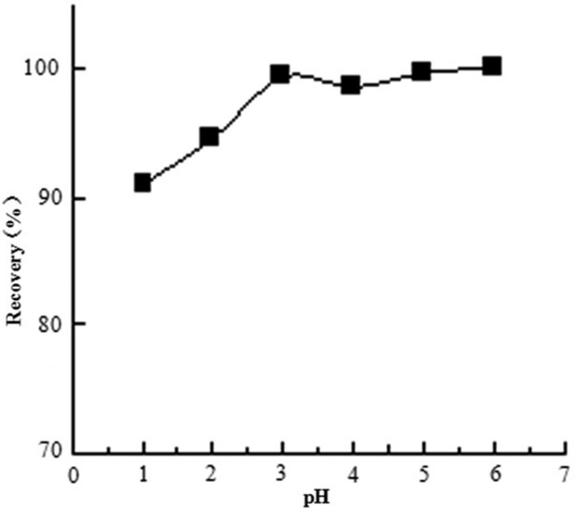

Figure 3. Effect of pH on analytes recovery of 10 mL of 1 µg mL$^{-1}$ Hg(II) after separation on 50 mg of AC-SBDTC; temperature: 25°C.

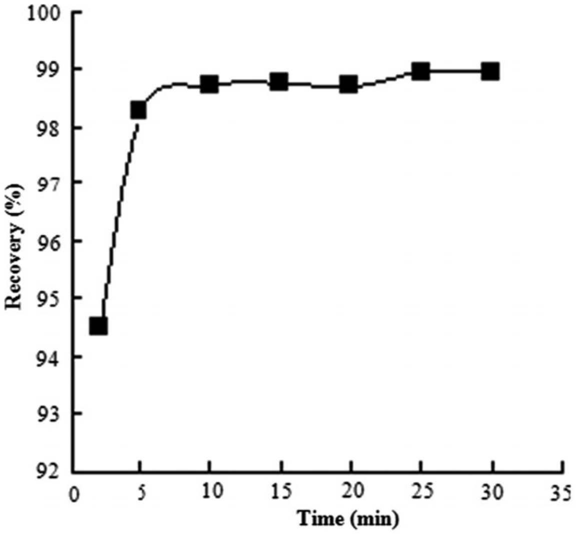

Figure 4. Effect of shaking time on analytes recovery of 10 mL of 1 µg mL$^{-1}$ Hg(II) after separation on AC-SBDTC at pH 3; AC-SBDTC: 20 mg; temperature: 25°C.

### 3.3 *Effect of shaking time*

The effect of shaking time on the percentage extraction of metal ions is considered to be of significant importance to determine the possible discrimination order in the behaviour of the newly synthesised adsorbent towards the different metal ions. In this work, different shaking time (range from 5 to 30 min) was studied for the percentage extraction of Hg(II) ions by the new adsorbent. Figure 4 shows the results of recoveries of Hg(II) vs. the

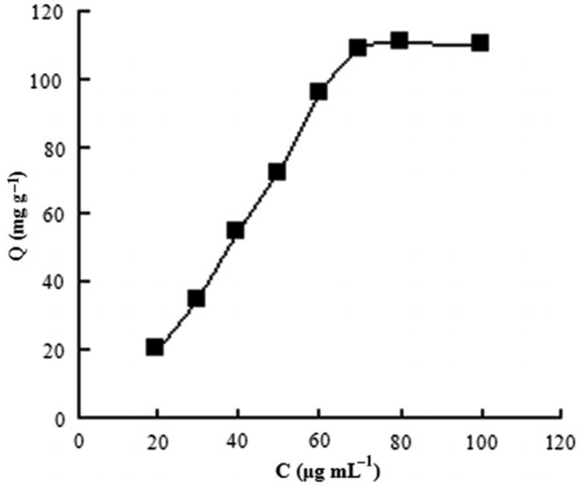

Figure 5. Effect of Hg(II) equilibrium concentration on the adsorption capacity of AC-SBDTC; pH: 3; AC-SBDTC 20 mg; sample volume 50 mL; temperature: 25°C.

shaking time in minutes. The result showed that the 95% uptake of Hg(II) was achieved within 5 min. It is clear that the present adsorbent had rapid adsorption kinetics, and is suitable for application in the solid-phase extraction of Hg(II).

### 3.4 *Static adsorption capacity of AC-SBDTC*

The adsorption capacity is an important factor because it determines how much adsorbent is required to quantitatively concentrate the analytes from a given solution. To measure the static adsorption capacity, 20 mg of the present sorbent was equilibrated with 50 mL of various concentrations of solutions at pH 3 (see Figure 5). The amount of ions adsorbed per unit mass of adsorption increased with the initial concentrations of the Hg(II) ions, till the plateau values (adsorption capacity values) were obtained. The maximum adsorption capacity of Hg(II) has been found to be 0.55 mmol g$^{-1}$, which is higher than 0.18 mmol g$^{-1}$(the capacity of activated carbon).

### 3.5 *Effect of elution condition on recovery*

The elution of Hg(II) was investigated by using various volumes and concentrations of HCl or HCl + $CS(NH_2)_2$ solutions as desorption reagent following the column procedure. The result showed that the reproducible results were not obtained by only using HCl as eluent, so the elution procedure was carried out by adding thiourea into the HCl solution. It was found that 0.25 mol L$^{-1}$ HCl + 2% $CS(NH_2)_2$ represented the best eluent for stripping off the adsorbed Hg(II), as shown in Table 1. This might be because thiourea and Hg(II) had a stronger coordinating ability than that of AC-SBDTC, so the coordination linkage of chelated Hg(II) was easily disrupted and subsequently the ions were released from the adsorbent into the desorption medium. The volume of HCl + 2% $CS(NH_2)_2$ solution was also studied, and 5 mL of 0.25 mol L$^{-1}$ HCl + 2% $CS(NH_2)_2$ was sufficient

Table 1. Effect of the elution condition for the recovery.

| HCl (mol $L^{-1}$)[a] | 0.10 | 0.25 | 0.50 | 1 | 2 | 4 |
|---|---|---|---|---|---|---|
| | Recovery (%) | | | | | |
| HCl | 1.18 | 1.95 | 3.46 | 5.83 | 24.07 | 56.38 |
| HCl + 2% $CS(NH_2)_2$ | 93.14 | 97.59 | 98.65 | 98.91 | 98.09 | 99.86 |
| Eluent volume (mL) | 2 | 3 | 4 | 5 | 6 | 7 |
| | Recovery (%) | | | | | |
| 0.25 mol $L^{-1}$ HCl + 2% $CS(NH_2)_2$ | 83.52 | 89.89 | 90.51 | 95.44 | 98.32 | 98.91 |

Note: [a]The eluent volume is 10 mL.

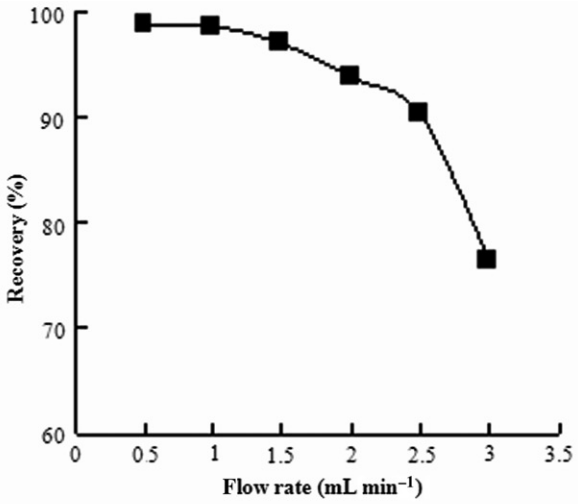

Figure 6. Effect of flow rate on analytes recovery of Hg(II). pH: 3; sample volume 50 mL; temperature: 25°C.

for complete elution for Hg(II). Therefore, 5 mL of 0.25 mol $L^{-1}$ HCl + 2% $CS(NH_2)_2$ was used as the eluent in further experiments. Meanwhile, it was found that the sorption capacity of the resin was practically constant after its repeated use more than 10 times.

### 3.6 *Effect of the flow rate*

The flow rate of sample solutions containing Hg(II) through the packed column is a very important parameter because the retention of elements on adsorbent depends upon the flow rate of the sample solutions. Its effect was investigated under the optimum conditions (pH, eluent, etc.) by the column method. The flow rates were adjusted in the range of 0.5 to 3.0 mL $min^{-1}$. As shown in Figure 6, the flow rate presented a strong influence on the sorption of Hg(II). Flow rates that were too small were not employed to avoid the longer extraction time. However, at flow rates greater than 1.5 mL $min^{-1}$, the recoveries of Hg(II) were less than 95% because Hg(II) ions could not be adsorbed sufficiently. To avoid the long time for extraction, the flow rate was maintained at 1.5 $mL\,min^{-1}$ throughout the column experiment.

### 3.7 *Maximum sample volume and enrichment factor*

To explore the possibility of adsorbing low concentrations of analytes from large volumes of solution, the effect of sample volume on the retention of metal ions was also investigated. For this purpose, 100–600 mL of sample solutions containing 1.0 µg Hg(II) were passed through the column with the optimum flow rate. The maximum sample volume can be up to 400 mL with the recovery >95%. A high enrichment factor of 80 was obtained since the final elution volume was 5 mL.

### 3.8 *Effect of coexisting ions*

The effect the other metal ions coexisting with Hg(II) was investigated. In these experiments, 1.0 $\mu g\,mL^{-1}$ of Hg(II) solutions containing the added interfering ions were analysed according to the static procedure. The tolerance limit was set as the amount of ions causing recoveries of the examined elements to be less than 95%. The results showed that up to 1000 $\mu g\,mL^{-1}$ of K(I) and Na(I), 500 $\mu g\,mL^{-1}$ of Ca(II), Mn(II), Co(II) and Mg(II), 20 $\mu g\,mL^{-1}$ of Zn(II), Ni(II), Fe(III), Al(III), and 5 $\mu g\,mL^{-1}$ of Cu(II), Pb(II), Cd(II) ions had no significant interferences in the preconcentration and determination of the analytes. At the same condition, the absorption experiments on the activated carbon were also carried out. The result showed that 1000 $\mu g\,mL^{-1}$ of K(I) and Na(I), 500 $\mu g\,mL^{-1}$ of Ca(II) and Mg(II), 20 $\mu g\,mL^{-1}$ of Zn(II), Ni(II), Fe(III), Al(III) and 5 $\mu g\,mL^{-1}$ of Cu(II), Pb(II), Cd(II), Co(II), Mn(II) ions did not interfere with the determination of Hg(II), which indicated the higher selectivity of AC-SBDTC.

### 3.9 *Analytical precision and detection limits*

Under the selected conditions, 11 portions of 10 $\mu g\,L^{-1}$ Hg(II) standard solutions (100 mL) were treated and analysed simultaneously following the column procedure. The relative standard deviation (RSD) of the method was 1.9%, which indicated that the method showed good precision for the analysis of Hg(II) in solution samples. In accordance with the definition of IUPAC [29], the detection limit of the method was calculated based on three times of the standard deviation of 11 runs of the blank solution. The detection limit ($3\sigma$) of the proposed method was 0.09 $ng\,mL^{-1}$.

### 3.10 *Comparison with other methods*

The analytical characteristics of separation and determination of Hg(II) by solid-phase extraction with AC-SBDTC as an extractor were compared with those of the other reported methods, and the result is given in Table 2. As seen from the data, the proposed method had a relatively high adsorption capacity compared to other methods reported. The LOD and enrichment factor of this method are also comparable. The simple preparation and rapid adsorption kinetics are also obvious advantages compared with other methods.

Table 2. Comparative results of various methods for determination of Hg(II) by SPE.

| Reagent(s) used | Capacity (mmol g$^{-1}$) | LOD[a] (ng ml$^{-1}$) | Enrichment factor | Reference |
|---|---|---|---|---|
| Silica gel/xylenol orange | 0.02 | | 333 | 2 |
| YPA$_4$ chelating resin | 0.19 | 0.20 | 100 | 5 |
| Hg(II)-imprinted hybrid sorbent | 0.20 | 0.06 | | 7 |
| Nanometer SiO$_2$/PAR | 0.28 | 0.43 | 50 | 8 |
| Polyaniline | 0.05 | 0.05 | 120 | 9 |
| Silica gel-loaded/dithizone | 0.12–0.20 | | 200 | 12 |
| XAD-2/2-aminoacetylthiophenol | 0.24 | 0.23 | 300 | 15 |
| Activated carbon/ethylenediamine | 0.30 | 0.09 | | 25 |
| Activated carbon/SBDTC | 0.55 | 0.09 | 80 | This work |

Note: [a]LOD: limit of detection.

Table 3. Analytical results for the determination Hg(II) in natural water samples.

| Samples | Concentration (μg g$^{-1}$) | | | | Recovery (%) |
|---|---|---|---|---|---|
| | Certified | Found | Added | Sum | |
| GBW 08301 | 0.22 ± 0.02 | 0.21 ± 0.04[a] | | | 95.5 |
| Tap water | | Unfound | 0.50 | 0.51 ± 0.02 | 102.0 |
| | | | 1.00 | 0.98 ± 0.06 | 98.0 |
| Yellow River water | | 0.89 ± 0.03 | 0.50 | 1.37 ± 0.05 | 96.0 |
| | | | 1.00 | 1.89 ± 0.08 | 100.0 |

Note: [a]X ± s ($n = 5$), X: average value for five determinations, s: standard deviation.

### 3.11 *Analysis of real samples*

The proposed method was then applied for the determination of Hg(II) in tap water, Yellow River water and GBW 08301 samples by ICP-AES. Meanwhile, the standard addition method was used, and the results for the recovery of Hg(II) are presented in Table 3. The result showed that, the recoveries of analytes were in range of 95.5–102.0%, demonstrating that the interference species in the matrix were eliminated after the solid-extraction procedure. Therefore, it indicated the suitability of the present adsorption for preconcentration of Hg(II) from water samples.

## 4. Conclusion

A novel chemically modified activated carbon containing SBDTC has been successfully synthesised and applied to solid-phase extraction and preconcentration of Hg(II). The new sorbent exhibited good characteristics, such as simple preparation, good selectivity and easy elution. In comparison to some known methods, the significant characteristics are the higher absorption capacity and shorter equilibrating. The determination of Hg(II) in the certified reference material showed good accuracy. The proposed procedure can be successfully applied for the determination of Hg(II) in water samples without any effect from the interfering ions.

## References

[1] E.M. Soliman and S.A. Ahmed, Int. J. Environ. Anal. Chem. **89**, 389 (2009).

[2] J. Fan, C. Wu, Y. Wei, C. Peng, and P. Peng, J. Hazard. Mater. **145**, 323 (2007).

[3] S.E. Manahan, *Environmental Chemistry*, 6th ed. (Lewis Publishers, Ann Arbor, 1994), p. 185.

[4] Y.H. Jin, A.B. Clark, J.C.S. Robbert, H. Al-Refai, J.A. Taylor, T.A. Kunkel, M.A. Resnick, and D.A. Gordenin, Nat. Genet. **34**, 326 (2003).

[5] H.M. Jiang, B. Hu, Z.C. Jiang, and Y.C. Qin, Talanta **70**, 7 (2006).

[6] H. Faghihian, A. Hajishabani, S. Dadfarnia, and H. Zamani, Int. J. Environ. Anal. Chem. **89**, 223 (2009).

[7] G.H. Wu, Z.Q. Wang, J. Wang, and C.Y. He, Anal. Chim. Acta **582**, 304 (2007).

[8] Y.H. Zhai, X.J. Chang, Y.M. Cui, N. Lian, S.J. Lai, H. Zheng, and Q. He, Microchim Acta **154**, 253 (2006).

[9] M.V. Balarama Krishna, D. Karunasagar, S.V. Rao, and J. Arunachalam, Talanta **68**, 329 (2005).

[10] Q. He, X.J. Chang, H. Zheng, N. Jiang, Z. Hu, and X.Y. Wang, Int. J. Environ. Anal. Chem. **88**, 373 (2008).

[11] Y.M. Cui, X.J. Chang, X.B. Zhu, and X.J. Zou, Int. J. Environ. Anal. Chem. **88**, 857 (2008).

[12] E.M. Mohamed, M.O. Maher, and E.A. Mohamed, Anal. Chim. Acta **415**, 33 (2000).

[13] L.J. Zhang, X.J. Chang, Y.H. Zhai, Q. He, X.P. Huang, Z. Hu, and N. Jiang, Anal. Chim. Acta **629**, 84 (2008).

[14] G.P.C. Rao, M.M. Rao, S.S. Veni, K. Seshaiah, A. Ramesh, and K.S. Murthy, Int. J. Environ. Anal. Chem. **86**, 443 (2006).

[15] M. Soylak, S. Saracoglu, L. Elci, and M. Dogan, Int. J. Environ. Anal. Chem. **82**, 225 (2002).

[16] Y. Guo, B. Din, Y. Liu, X. Chang, S. Meng, and J. Liu, Talanta **62**, 207 (2004).

[17] I. Narin, M. Soylak, L. Elci, and M. Dogan, Talanta **52**, 1041 (2000).

[18] A. Ucer, A. Uyanik, and S.F. Aygun, Sep. Purif. Technol. **47**, 113 (2006).

[19] M. Ghaedi, F. Ahmadi, and M. Soylak, J. Hazard. Mater. **147**, 226 (2007).

[20] R. Qadeer and J. Hanif, J. Chem. Soc. Pak. **15**, 227 (1993).

[21] M. Tofazzal, H. Tarafder, A. Asmadi, Siti M.S. Talib, A.M. Ali, and K.A. Crouse, Transition Met. Chem. **26**, 170 (2001).

[22] M. Das and S.E. Livingstone, Inorg. Chim. Acta **19**, 5 (1976).

[23] Y.M. Cui, X.J. Chang, Y.H. Zhai, X.B. Zhu, H. Zheng, and N. Lian, Microchem. J. **83**, 35 (2006).

[24] T.M. Florence, Talanta **29**, 345 (1982).

[25] Har Lal Singh and A.K. Varshney, Appl. Organomet. Chem. **15**, 762 (2001).

[26] Z.H. Li, X.J. Chang, X.J. Zou, X.B. Zhu, R. Nie, Z. Hu, and L.J. Li, Anal. Chim. Acta **632**, 272 (2009).

[27] H.T. Tang, *Organic Compound Spectra Determination* (Publishing House of Beijing University, Beijing, 1992), p. 124.

[28] Q.N. Dong, *IR Spectrum Method* (Publishing House of the Chemical Industry, Beijing, 1979), p. 104.

[29] G.L. Long and J.D. Winefordner, Anal. Chem. **52**, 2242 (1980).