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A magnetic SPE method combined with CVG-AFS for the determination of $Hg^{2+}$ is established.

TOF
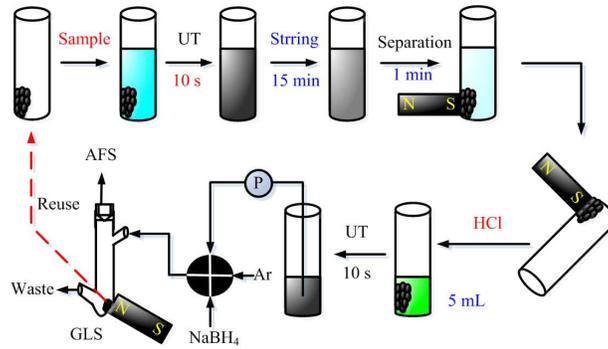
Sample
UT
10 s
Strring
15 min
Separation
1 min
N　S

AFS

Reuse

P

UT
10 s

HCl

N　S

5 mL

Waste

Ar

NaBH₄

GLS
N　S

# Magnetic solid-phase extraction combined with in situ slurry cold vapor generation atomic fluorescence spectrometry for preconcentration and determination of ultratrace mercury

Wang-bing Zhang *, Chu-xiao Sun, and Xin-an Yang

A simple and ultrasensitive magnetic solid-phase extraction method using gold nanoparticles modified $Fe_3O_4$ magnetic microsphere combined with in situ slurry cold vapor generation atomic
10 fluorescence spectrometry was developed for determination of trace $Hg^{2+}$. The main parameters affecting the extraction process such as time of sorption process, pH, amounts of gold nanoparticles and sorbent, enrichment factors, and reusability of sorbent were optimized. $Hg^{2+}$ could be adsorbed on sorbent in 2 mmol $L^{-1}$ HCOOH medium, even when the $Hg^{2+}$ concentration was as low as 0.02 μg $L^{-1}$. The complete extraction can be achieved within 15 min. Under the
15 premise of accurate detection, the enrichment factors were 10, 30 and 80 each for 2 mg, 5 mg, and 10 mg sorbent. The reusable performance of the sorbent was obviously affected by the amount of loaded gold nanoparticles. When the weight ratio of gold reaches 9.5 %, the modified magnetic nanoparitcles can be reused three times without causing a considerable loss in their adsorption efficiency. In addition, the potential interference was researched. Under the optimized conditions,
20 the detection limit of $Hg^{2+}$ was 1.5 ng $L^{-1}$, and relative standard deviation of 3.7% was obtained for determination of 0.05 μg $L^{-1}$ $Hg^{2+}$. The linear calibration range was 0.005-0.2 μg $L^{-1}$. The accuracy of the method was verified through analysis of certificated reference materials. The proposed method has been applied to the determination of Hg in environmental water samples.

## 1. Introduction

25 Mercury (Hg) is an element of both enviromental and health concern because of its high toxicity even at trace levels [1]. Hg has no beneficial biological function, and its presence in living organisms is associated with cancer, birth defects, and other undesirable outcomes [2-4]. World Health Organization (WHO)
30 has established a guideline value for Hg, which is 1 μg $L^{-1}$ in drinking water [5]. For routine detection, highly sensitive analytical detection techniques, such as atomic fluorescence spectrometry (AFS) [6-10], atomic absorption spectrometry (AAS) [11-13], and inductively coupled plasma mass spectrometry (ICP-
35 MS) [14-16], combined with chemical cold vapor generation (CCVG) [8, 9, 12, 13], electrolytic cold vapor generation (ECVG) [6, 7] and photochemical vapor generation (PCVG) [10, 17] are widely used. However, the concentrations of total dissolved Hg in natural waters varying from pg $L^{-1}$ level to 20 ng $L^{-1}$ [18], the
40 above mentioned analytical techniques are relatively insufficient for direct determination of Hg. Thus, an appropriate separation and preconcentration process before detection is required.

A variety of approaches including solid-phase extraction (SPE)
45 [19-21], liquid-liquid extraction (LLE) [22], cloud point extraction (CPE) [23, 24] are being utilized for preconcentration of $Hg^{2+}$. Among these methods, SPE procedure is considered superior to others for its simplicity, low labor cost, low solvent consumption, safer working environment, and higher
50 enrichment efficiency [25, 26]. Now, the quest for new sorbents is

a key factor in improving analytical sensitivity and precision in SPE techniques. Some nanocomposites were explored for this purpose due to their high surface area-to-volume ratio and short diffusion route, which can result in high extraction
55 efficiency and rapid extraction dynamic [27, 28]. Among these nanoparticles, magnetic nanoparticels (MNPs) have attracted increasing attentions because of their unique functionality and separability [29]. In the past decades, some researchers focused on the development of preconcentration method for removing
60 heavy metals by using the magnetic sorbent in SPE [30-32]. Most of these sorbents were magnetic $Fe_3O_4$ core modified with different functional shells. For example, Hu's group [33] developed a new silica-coated $Fe_3O_4$ NPs for SPE of trace amounts of Cd, Cu, Hg, and Pb. Mehdinia *et al.* [34] reported a
65 rapid magnetic SPE system for derivatization of methylmercury by using $Fe_3O_4$/polyaniline NPs as sorbent. Zhai *et al.* [35] described a SPE method for preconcentration of mercury using 1, 5-diphenylcarbazide doped $Fe_3O_4$ NPs as extractant. Very recently, Hu *et al.* developed a novel ionic
70 liquid-based magnetic SPE system to preconcentrate and detect several heavy metal ions [36].

The aim of this work is to take advantage of quick adsorption of $Hg^{2+}$ on gold NPs-coated $Fe_3O_4$ (Au NPs-$Fe_3O_4$) sorbent, combined with in situ slurry cold vapor generation AFS for
75 high sensitivity determination of $Hg^{2+}$ in nature water samples. The main parameters affecting the extraction process such as time of sorption process, pH, amounts of Au NPs and sorbent, enrichment factors, and reusability of sorbent were researched and optimized. The influences of slurry vapor generation

parameters on the signal were also reported. This method had been applied for the determination of Hg in several water samples. To our knowledge, this is the first report of using Au NPs-Fe$_3$O$_4$ based sorbent for preconcentration, combined with in situ slurry CVG-AFS for determinaiton of Hg$^{2+}$.

## 2. Experimental section

### 2.1 Apparatus

A model AFS-230 double-channel non-dispersive atomic fluorescence spectrometer (Beijing Haiguang Instrument Co., Beijing, China) was employed throughout the experiments. High-intensity Hg hollow cathode lamps (General Research Institute for Nonferrous Metals, Beijing, China) were used as radiation sources, which had advantages over electrodeless discharge lamps in both stability and lifetime. A quartz tube (7 mm i.d.×14 mm length) was used as an atomizer into which the volatile species was swept by argon (Ar) flow. The flow rates of the carrier gas (Ar) and the shield gas (Ar) for the AFS instrument were 500 and 1000 mL min$^{-1}$, respectively; lamp current, 25 mA; and negative voltage for the photo-mulitiplier tube, -280 V. Two sequential gas-liquid separators, which depend on gravity to separate gas and liquid phases, were used for achieving better gas transfer efficiency.

Ultrasonic bath (UB) instrument (Shanghai Guante Ultrasonic Instrument Co., Shanghai, China) and an electric mixer model 101A (Jiangxi Instrument Co., Shanghai, China) were used for dispersing the sorbent in the solution.

### 2.2 Chemical reagents

All reagents were of highest available purity, and of at least analytical grade. High purity deionized water (DIW) was used throughout (Hangzhou Wahaha Group Co., Ltd. Hangzhou, China). The Hg$^{2+}$ standard solution was prepared by serial dilution of a 1000 mg L$^{-1}$ mercury stock solution (Dr. Ehrenstorfer GmbH-Bgm.-Schlosser-Str. bA-86199 Augsburg, Germany). A 0.25% NaBH$_4$ (m/v) − 0.16% (m/v) NaOH solution was prepared by dissolving NaOH and NaBH$_4$ (Sinopharm Chemical Reagent Co., Ltd) in high-purity deionized water. Argon of 99.99% purity was used as the carrier gas. HCOOH, HCl, HAc, NaOH were used to test the effects of the electrolytic solutions. Other reagents used to synthesize of sorbent including FeCl$_3$·6H$_2$O, HAuCl$_4$, NaAc, NaOH and NH$_2$OH·HCl (Sinopharm Chemical Reagent, Shanghai, China). The water reference materials GBW (E) 080392 obtained from China National Research Center for Certified Reference Materials were applied to evaluate the accuracy the present method.

### 2.3 Synthesis of materials

**2.3.1 Synthesis of Fe$_3$O$_4$** The Fe$_3$O$_4$ microspheres were synthesized based on the solvothermal method. [39] Briefly, FeCl$_3$·6H$_2$O (1.3 g) and NaAc (3.6 g) were added into ethylene glycol (40 mL) under vigorous stirring conditions. The homogeneous and yellow resultant solution was obtained and then it was placed into the Teflon lined autoclave with volume of 50 mL, reacted at 200 °C for 8 hours. The black product was collected with a magnet, and washed several times by ethanol, then dried at 80 °C for 12 hours under a vacuum.

**2.3.2 Synthesis of Au NPs-Fe$_3$O$_4$** 0.15 g Fe$_3$O$_4$ microspheres and 15 mL HAuCl$_4$ solution (0.1%, m/v) were added into a beaker (100 mL) stirred it to form homogeneous solution [40]. The pH value of the solution was adjusted to 7-8 with 0.1 mol L$^{-1}$ NaOH. Then, added a certain amount of NH$_2$OH.HCl (0.22 mol L$^{-1}$), and stirred the breaker at room temperature again. After 12 h, the solid product was collected through magnetic separation. Washed the product with DIW three times, and then dried it in vacuum at 260 °C for 4 hours to obtain magnetic red-brown powder of Au NPs-Fe$_3$O$_4$. Fig.1 showed the photography of Fe$_3$O$_4$, Au NPs-Fe$_3$O$_4$, and the magnetic properties of the product.
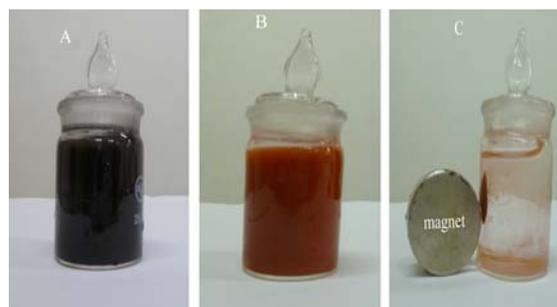


Fig.1 photographs of (A) and (B) for Fe$_3$O$_4$ and Au NPs-Fe$_3$O$_4$ solution after ultrasonic disperse, respectively; (C) for Au NPs-Fe$_3$O$_4$ solution after magnetic separation.

### 2.4 Sample preparation

GBW(E)080392 (National Resarch Genter for CRMs, Beijing, China) was diluted with DIW and 0.05 mol L$^{-1}$ HCOOH solution. The final concentration of HCOOH was 2 mmol L$^{-1}$ in the prepared solution. Several enviromental water samples: Yangtze River (Maanshan, China), Cihu River (Maanshan, China), and Huilin Lake (collected at the campus of Anhui University of Technology, Maanshan, China) were stored in polyethylene bottles at 4 °C in the refrigerator. The samples were filtered through 0.45 μm membrane filters to remove the suspended solid and added HCOOH (some smaples are spiked with 10 μg L$^{-1}$ Hg$^{2+}$ standard solution, in order to obtain solutions containing different Hg concentrations) before subject to the preconcentraiton process as detailed in the following sections.

### 2.5 Analytical procedures

The magnetic SPE and in situ slurry AFS determination of samples were described in Fig.2 and briefly, (1) 100 mL sample and 10 mg Au NPs-Fe$_3$O$_4$ were added into a 250 mL beaker with 10 s ultrasound treatment to form a homogeneous suspension; (2) this mixture was dispersed with the help of mechanical stirrer (400 rpm) for 15 min to promote the interaction between Hg$^{2+}$ and Au NPs-Fe$_3$O$_4$; (3) the sorbent was separated from the aqueous systems by applied magnetic field and then washed 3 times with DIW and (4), the sorbent was transferred to a tube and added 0.5 mol L$^{-1}$ HCl to 5.0 mL then dispersed this solution with ultrasound to form a homogeneous suspension for Hg$^{2+}$ detection. The method of additions was used for quantitative analysis. A complete cycle of the procedure lasted about 17 min.

The enrichment factor *EF*, was calculated by the ratio of the

sample volume and the detection volume after preconcentration. [25]

The recovery of proposed methode was determined according to the following equation:

$$5 \quad Recovery = \frac{I_{exp}}{I_{cal}} \times 100\%$$

Here, $I_{exp}$ means the signal intensity of initial solution with preconcentration. $I_{cal}$ means the signal intensity of solution after initial concentration of *EF*-fold increase.
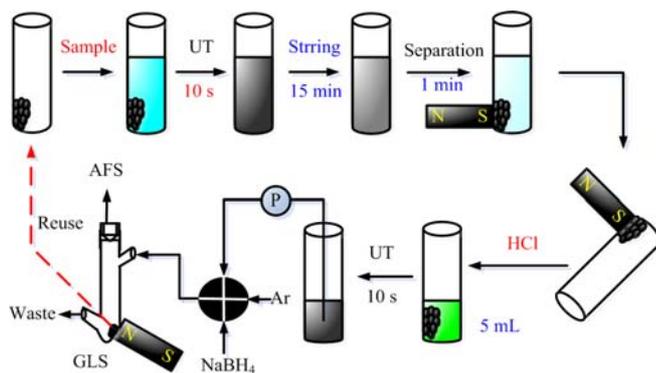


10 Fig.2 Steps of application of Au NPs-$Fe_3O_4$ as adsorbents for $Hg^{2+}$ analysis. UT for ultrasonic treatment; P for pump, and GLS for gas-liquid separator.

### 2.6 Characterization methods

Scan electron microcopy (SEM, Zeiss EVO LS-15) and high resolution transmission electron microscopy (HRTEM, JEM-
15 2100F, JEOL, Ltd, Japan) were applied to study the structure and morphology of as-synthesized Au NPs-$Fe_3O_4$. X-ray diffraction (XRD) patterns were obtained by using X'Pert Pro MPD diffractometer (PW3040/60, PAnalytical B.V, The Netherlands) with Cu K$\alpha$ radiation source. The loaded Au
20 element on the $Fe_3O_4$ was demonstrated by the analysis result of Energy Dispersive X-ray (EDS Zeiss EVO LS-15).
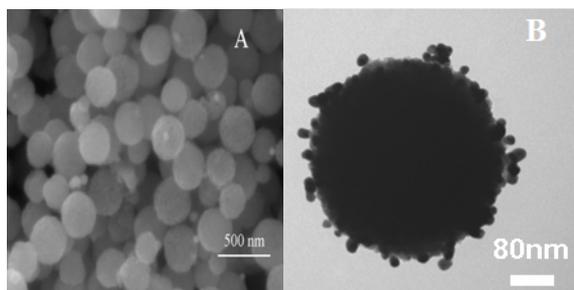


Fig.3 (A) SEM image of the $Fe_3O_4$; (B) TEM image of the Au NP-$Fe_3O_4$
25 sorbent.

## 3. Results and discussion

### 3.1 Characterization of the sorbent

It was observed from the SEM images (Fig. 3 A) that the $Fe_3O_4$ is of well spherical structure and high monodispersity in
30 size. The average diameters were about 200-300 nm. TEM

images (Fig. 3 B) indicated that the An NPs is deposited on the surface of $Fe_3O_4$. Fig. 4 A showed the XRD patterns before and after functionalization. The diffraction peaks at (220), (311), (100), (111) and (110) were indexed based on the $Fe_3O_4$
35 (JCPDF no. 65-3107). However, new peaks after the modification process occurred at (111), (100), and (332) that some $Fe_3O_4$ is oxidized into $Fe_2O_3$ during calcinations. EDS spectra in Fig. 4 B clearly showed the presence of a coating which contains Au.
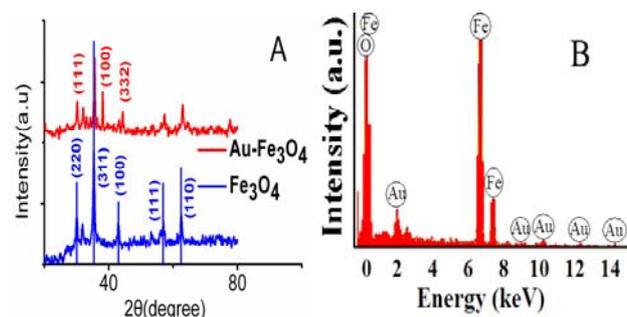


Fig.4-(A) XRD patterns of $Fe_3O_4$ and Au NP-$Fe_3O_4$, the blue curve represents the standard XRD pattern of $Fe_3O_4$; (B) EDS spectra of Au NP-$Fe_3O_4$.

45 ### 3.2 Optimization of experimental conditions for preconcentration of Hg by magetic SPE

#### 3.2.1 Preconcentration time and adsorption capacity of sorbent
Generally, sufficient contact time is required to attain adsorption equilibrium for target compound on sorbent. It
50 could be found from Fig. 5 (A) that lower the $Hg^{2+}$ concentration was , longer the contact time needed. The contact time of 10 min with a stirring speed of 400 rpm was enough for complete adsorption of 0.1 μg $L^{-1}$ $Hg^{2+}$ from 50 mL solution. It would be reduced within 8 min for 0.4 μg $L^{-1}$ $Hg^{2+}$. Fig. 5 (B)
55 illustrated the how the measurement signal changed with different concentration of $Hg^{2+}$ solution when the preconcentration time was fixed at 20min. The good linear relationship (r=0.999) between the tested $Hg^{2+}$ concentration and the obtained signal intensity displayed potential
60 application of the proposed method in the field of analytical atomic spectroscopy.

We also tested the adsorption capacity of Au NPs-$Fe_3O_4$ for Hg via adding 10 mg sorbent to a series of 50 mL solution containing 0.2, 0.4, 1, 2 and 5 mg $L^{-1}$ $Hg^{2+}$, respectively. The
65 results showed that the saturated adsorptive capacity of Au NPs-$Fe_3O_4$ for $Hg^{2+}$ was 2.6 mg $g^{-1}$, which was enough for routine analysis of samples.

#### 3.2.2 Effect of Au NPs and reusability of sorbent
The experimental data indicated that the recovery after
70 preconcentration of $Hg^{2+}$ (0.05 μg $L^{-1}$, 200 mL) on bare $Fe_3O_4$ was only about 10% (Fig.6 A). Hence, $Hg^{2+}$ is difficult to be directly adsorbed on the $Fe_3O_4$ microspheres. Generally, gold amalgam was spontaneously formed by the reaction of Hg with Au [41]. In the present work, we employed Au NPs to adsorb
75 $Hg^{2+}$ in water. The result demonstrated that the recovery increased notably when the sorbent contained Au NPs. The adsorption amount of $Hg^{2+}$ on the sorbent increased with the enhancement of the gold loading and leveling off when 15 mL

0.1% (m/v) $HAuCl_4$ was added during the synthesis (the WAu arrived at 9.5% according to the EDS spectrum).
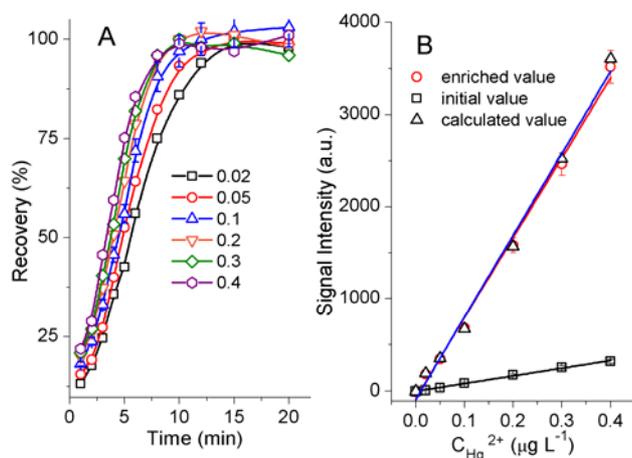


Fig.5  Effects of time of sorption process on the recovery of different concentration of $Hg^{2+}$ (sample volume 50 mL, 5 mg of adsorbent, 2 mmol $L^{-1}$ HCOOH as electrolyte)
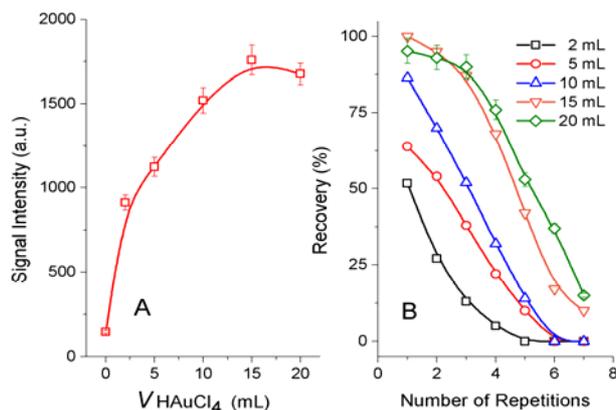


Fig. 6 (A) effect of $HAuCl_4$ on the adsorption of 0.05 μg $L^{-1}$ Hg, and (B) reusability of adsorbent *vs* the volume of $HAuCl_4$ during the synthesis. Sample volume 200 mL, 10 mg of adsorbent, 2 mmol $L^{-1}$ HCOOH as electrolyte, time of adsorption 15 min.

The reusing ability of the sorbent in several successive adsorption processes was tested. The obtained results in Fig.6 (B) documented that the reusable performance of sorbent was strongly affected by the amount of loaded gold. Larger gold mass resulted in better reusable performance. When $W_{Au}$ (weight ratio) reached the value of 9.5 %, the modified MNPs can be reused three times without considerable loss in their adsorption efficiency.

**3.2.3 Sorbent amount and enrichment factor** In order to know the suitable mass of functional sorbent for adsorbing $Hg^{2+}$, different amounts of sorbent varying from 2 to 10 mg were tested. From Fig. 7, we can find that the extraction efficiency peaked at 100% by only adding 2 mg sorbent in 50 mL of 0.05 μg $L^{-1}$ $Hg^{2+}$ solution. When sample volume increased to 150 mL, at least 5 mg of sorbent was needed to ensure high adsorption efficiency (> 90%). Continued to increase the sample volume to 400 mL, 10 mg of sorbent can meet the demand of adsorption. Under the same conditions, the recoveries of $Hg^{2+}$ are 62% and 25% each for 5 mg and 2 mg

sorbent, respectively. Since the $Hg^{2+}$ concentration in real sample is very low, increasing the sample volume might be a good choice to enhance the detection accuracy. Therefore, 10 mg sorbent was used during the adsorption experiments.
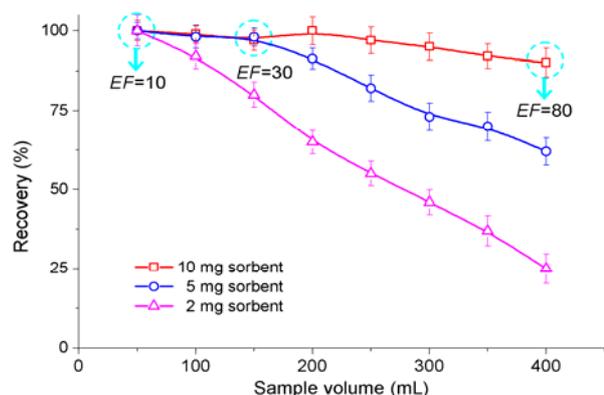


Fig. 7 Effect of adsorbent amount and sample volume on the recovery of 0.05 μg $L^{-1}$ Hg (2 mmol HCOOH as electrolyte, time of adsorption 15 min.).

Enrichment factor (EF) is one of the key factors for evaluating the performance of preconcentration method. On the one hand, the EF was corresponded with the sample volume and detection volume according to the definition. This relationship was studied by fixing sample volume and sorbent mass in 100 mL and 10 mg, respectively, and setting the detection volume after preconcentration to 1, 2, 4, 5 and 10 mL, respectively. The data indicated that the signal intensity of $Hg^{2+}$ increased with decreasing detection volume. During the determination process of samples, however, we found that the transfer line was easily clogged at a low detection volume (< 4 mL) because the slurry solution of sorbent is too viscous, which cause the magnetic material gathered into a relatively large aggregates. Hence, we selected 5 mL detection volume after preconcentration for analysis. On the other hand, the EF was also corresponded with the sorbent mass. From Fig.7 we can see that the EF are 10 for 2 mg sorbent, 30 for 5 mg sorbent and 80 for 10 mg sorbent respectively under the premise of accurate detection (recovery > 90%).

**3.2.4 Effect of pH** The effect of the sample pH on the adsorption of $Hg^{2+}$ on Au NPs-$Fe_3O_4$ sorbent was discussed at pH ranging from 1.0 to 12.0. The pH of samples is adjusted by NaOH and HCl. The results documented that the adsorption efficiency of $Hg^{2+}$ remained constant  in a wide pH ranging from 2.0 to 8.0, which was close to the pH of the waste water and natural water. Next, we chose some $Hg^{2+}$ samples containing different electrolytes in the above pH range and tested the effect of electrolytes on the adsorption properties. The recovery of $Hg^{2+}$ in HCOOH medium was higher than that in HCl and PBS medium, indicating that the organic acid medium could be  more conducive to the adsorption of $Hg^{2+}$ on the sorbent. Effects of HCOOH concentration on the recovery of Hg were examined. The recovery was decreased when the HCOOH concentration was over 3.0 mmol $L^{-1}$, thus, 2.0 mmol $L^{-1}$ HCOOH was selected as medium for all subsequent experiments.

### 3.3 Determination conditions

Conventional SPE usually needs an elution program in order to ensure the subsequent analysis performance. This step can make the method time-consuming. In this paper, HCl solution was directly added to the tube which contains the sorbent, and then dispersed the solution with ultrasound to form a homogeneous suspension for $Hg^{2+}$ detection. The signal intensities of Hg increased significantly when HCl concentration varying from 0.1 to 0.5 mol $L^{-1}$, and then decrease with the further increasing of HCl concentration. The highest signal appeared at the concentration of 0.5 mol $L^{-1}$.

The dependence of signal intensity on $NaBH_4$ concentration for 5 mL slurry sloution was recorded. It was also appeared that the signal intensity of Hg increases proportionally with the $NaBH4$ concentration until it was up to 0.25% (m/v), and decreased thereafter. Thus, 0.25% $NaBH_4$ was used as the optimized concentration.

The $NaBH_4$ should be perpared in basic meidum in order to stabilize this reagent. The concentration of NaOH was in the range of 0.06-0.24% (m/v). The signal increased with the increasing of sodium hydroxide concentration. When the concentration reached 0.16 %, the signal varied slightly. Thus, 0.16% (m/v) NaOH was used.

The Ar flow rate was also optimized by varying from 300 to 900 mL $min^{-1}$. The signal intensity of Hg increases remarkably with the increasing of Ar flow rate until it reached 500 mL $min^{-1}$, after which the signal decreased. Therefore, the Ar flow rate of 500 mL $min^{-1}$ was chosen.

### 3.4 Effect of interference

The effects of common co-existing ions on the adsorption of $Hg^{2+}$ on Au NPs-$Fe_3O_4$ were taken into account. The effect was expressed as the recovery in the presence of interfering ions relative to the interference-free response. The results were summarized in Table 1. We can find that large amounts of alkali and alkaline earth metal ions have no obvious influence on the adsorption of mercury. The interferences caused by $Fe^{3+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Cd^{2+}$ and $Pb^{2+}$ on the adsorption of 0.1 µg $L^{-1}$ $Hg^{2+}$ were also studied. It can be clearly seen that among the common ions, $Co^{2+}$, $Cu^{2+}$ and $Ni^{2+}$ caused the most serious interferences. The presence of 0.1 mg $L^{-1}$ $Co^{2+}$ in sample solution produced 16% signal suppression, while 0.5 mg $L^{-1}$ led to 57% signal suppression. The presence of 0.1 mg $L^{-1}$ $Cu^{2+}$ in sample solution resulted in 24% suppression of signal; 0.5 mg $L^{-1}$ $Cu^{2+}$ led to 61% signal suppression. The presence of 0.5 mg $L^{-1}$ $Ni^{2+}$ in sample solution, however, resulted in 43% signal increase. The the tolerable concentrations of $Co^{2+}$,$Cu^{2+}$,$Ni^{2+}$ are 0.05 mg $L^{-1}$, 0.05 mg $L^{-1}$ and 0.1 mg $L^{-1}$ respectively.

### 3.5 Analytical performance

Under the optimized conditions, the analytical performance of the proposed method with Au NPs-$F_3O_4$ as asorbent for slurry CVG of mercury detected by AFS was evaluated. The data documented that the linear range was strongly dependent on the sampling volume. With a 50 mL sampling volume, the linear ranged from 0.02 µg $L^{-1}$ to 0.8 µg $L^{-1}$ (Fig. 4 (B)). When the sampling volume went up to 200 mL, the linear range was down to 0.005-0.2 µg $L^{-1}$. The limit of detection (LOD) of Hg in aqueous solution using the definition $3s/m$ ($s$ is the standard deviation and $m$ is the slope of the calibration graph), was 1.5 ng $L^{-1}$ for 200 mL sampling volume. The relative standard deviation (R.S.D.) for 11 replicate determinations of 0.05 µg $L^{-1}$ was 3.7%. Table 2 summarized analytical figures of merit achieved using this method and compared performance with that of several other preconcentration methods.

**Table 1** Effect of coexisting ions on determination of mercury (0.1µg $L^{-1}$)

| Species | Concentration (mg $L^{-1}$) | Concentration ratio [M]/[Hg] | Recovery (%) |
|---|---|---|---|
| KCl | 100 | 1000000 | 101 |
| $Na_2CO_3$ | 100 | 1000000 | 93 |
| $NaHCO_3$ | 100 | 1000000 | 92 |
| $Ca(NO_3)_2$ | 100 | 1000000 | 98 |
| $MgCl_2$ | 100 | 1000000 | 94 |
| $Zn(NO_3)_2$ | 20 | 200000 | 101 |
| $NaAsO_2$ | 10 | 100000 | 97 |
| $KH_2PO_4$ | 100 | 1000000 | 101 |
| $KHPO_4$ | 100 | 1000000 | 97 |
| $FeCl_3$ | 20 | 200000 | 105 |
| $FeCl_2$ | 20 | 200000 | 102 |
| $Mn(NO_3)_2$ | 5 | 50000 | 95 |
| $PbCl_2$ | 0.5 | 5000 | 101 |
| $CdCl_2$ | 0.1 | 1000 | 96 |
| | 0.5 | 5000 | 92 |
| $CoCl_2$ | 0.1 | 1000 | 84 |
| | 0.5 | 5000 | 43 |
| $CuSO_4$ | 0.1 | 1000 | 76 |
| | 0.5 | 5000 | 41 |
| $Ni(NO_3)_2$ | 0.1 | 1000 | 112 |
| | 0.5 | 5000 | 143 |

### 3.6 Real samples

The accuracy of the proposed method was verified by analysis of a certified reference material (GBW (E) 080392). Because of the significant interferences arising from the presence of some metal ions including $Cu^{2+}$ and $Ni^{2+}$, the method of additions was used to reduce this influence. The results showed a good agreement between certified value (0.01 mg $L^{-1}$) and determined concentrations of Hg (9.88 µg $L^{-1}$). The analytical procedure had been applied to the determination of $Hg^{2+}$ in different types of water samples, *i.e.*, river water and lake water. The reliability of the proposed method was tested with recovery experiments by adding $Hg^{2+}$ standard solutions into the sample solutions before the preconcentration process. The analytical results were listed in Table 3, and the recoveries were satisfactory. The relative standard deviation for 5 replicate determinations of Hg in nature water samples was 6.2%.

**Table 2** Comparison of performance with other methodologies

| Method | SV [c] (mL) | LOD (ng L$^{-1}$) | RSD (%) | Ref. |
|---|---|---|---|---|
| SPE-ICPMS | 100 | 0.49 | 4.8 | 21 |
| LLE-CVG-AAS | 20 | 2.30 | 2.8 | 22 |
| CPE-CVG-ICPMS | 10 | 5.00 | - | 23 |
| CPE-SD [a] | 500 | 1.65 (mg L$^{-1}$) | 1.8 | 24 |
| MSPE-ICPMS [b] | 250 | 0.10 | 8.3 | 33 |
| MSPE-GCMS | 50 | 100 | 4.1 | 34 |
| MSPE-CVG-AAS | 200 | 160 | 2.2 | 35 |
| MSPE-CVG-AFS | 200 | 1.50 | 3.7 | This work |

[a, b, c] mean spectrophotometric determination, magnetic SPE and sample volume, respectively.

**Table 3** Determinations of Hg in different type water samples

| Samples | Value [a] (μg L$^{-1}$) | Value [b] (μg L$^{-1}$) | Added (μg L$^{-1}$) | Found (μg L$^{-1}$) | Recovery (%) |
|---|---|---|---|---|---|
| Yangtze river | 0.107 ± 0.006 | N.D. [c] | 0.050 | 0.155 | 96.0 |
| | | | 0.100 | 0.215 | 108.0 |
| | | | 0.200 | 0.292 | 92.5 |
| Hulin lake | 0.232 ± 0.012 | 0.288± 0.097 | 0.200 | 0.421 | 94.5 |
| | | | 0.300 | 0.537 | 101.7 |
| | | | 0.400 | 0.630 | 99.5 |
| Cihu river | 0.064 ± 0.008 | N.D. | 0.050 | 0.113 | 98.0 |
| | | | 0.100 | 0.157 | 93.0 |
| | | | 0.150 | 0.227 | 108.7 |

[a], [b] determination by the CVG-AFS with and without magnetic SPE (n=5; mean ± S.D.).

[c]: N.D. not detected.

## 4. Conclusions

A novel and sensitive magnetic SPE has been firstly developed for the preconcentration and determination of mercury in several water samples. Au NPs-Fe$_3$O$_4$ magnetic sorbent with magnetically responsive cores and functional shells offers several advantages including fast adsorption, high capacity, maximum separability and reusability. In comparison with traditional SPE, this method avoids using elution program. The proposed method allows mercury determination at trace levels in river and lake water samples with high accuracy and reproducibility. Currently, this method is mainly a batch process, though we hope the automating extraction process using flow injection or sequential injection system could be made to fully explore the advantages of magnetic nanoparticales sorbent in further studies.

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## Notes and references

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