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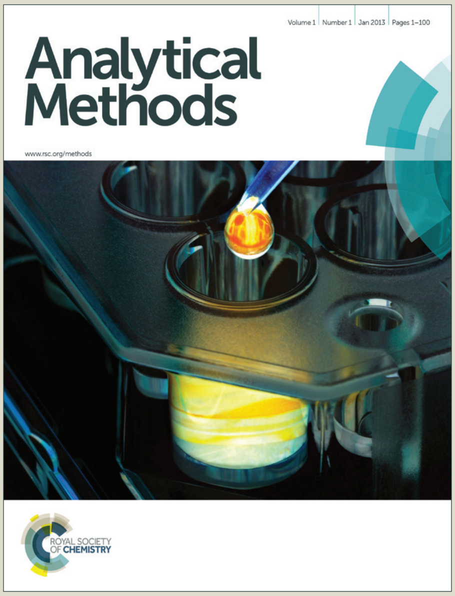

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Photochemical vapor generation and in situ preconcentration for determination of mercury by graphite furnace atomic absorption spectrometry

Chunlin He[a], Guanglei Cheng[b], Chengbin Zheng[a], Li Wu[b]* , Yong-Ill Lee[c], Xiandeng Hou[a,b]

[a]Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

[b]Analytical & Testing Centre, Sichuan University, Chengdu, Sichuan 610064, China. E-mail: wuli@scu.edu.cn

[c] Department of Chemistry, Changwon National University, Changwan 641773, Republic of Korea

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Abstract

A new and sensitive method is described for the on-line preconcentration and determination of ultra-trace mercury by coupling a trapping scheme based on coating gold nanorods onto the inner wall of the graphite furnace for mercury vapor from photochemical vapor generation (photo-CVG) and graphite furnace atomic absorption spectrometric (GF-AAS) detection. The optimal experimental conditions for the photo-CVG, trapping and atomization were carefully investigated, together with the interference from transition metals. The limit of detection of this method was found to be 0.02 μg L^{-1} and the precision was better than 5% at 0.1 μg L^{-1}. Mercury in four spiked water samples and two Certified Reference Materials were successfully determined by the proposed method.

Keywords: Photochemical vapor generation, In situ preconcentration, Gold nanorods, Mercury, Atomic absorption spectrometry

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Introduction

It is well known that mercury (Hg) contamination is a global problem which has attracted extensive attention worldwide[1, 2]. As a result, many sensitive and precise methods for mercury determination have been established[3-6], among which are cold vapor atomic absorption spectrometry (CV-AAS)[7, 8], inductively coupled plasma mass spectrometry (ICP-MS)[9-14], atomic fluorescence spectrometry (AFS)[15,16] and graphite furnace atomic absorption spectrometry (GF-AAS)[17-20].

Although the sample volume used in GF-AAS is tiny, high atomization temperature as well as alleviation of potential interferences in complex matrices are still necessary in conventional GF-AAS. What's more, it is difficult to directly determine Hg at the sub-ng g^{-1} level in real samples by GF-AAS. Thus, gas phase sample introduction appeared by turning the target elements into gaseous species. The advantage of gas phase sample introduction techniques[21, 22] lies in the separation and a possible preconcentration of the analyte and suppression of interferences. For mercury vapor generation, traditional reducing reagents used in aqueous solution including $SnCl_2$[13] and $NaBH_4$ or KBH_4.[23, 24]

Chemical vapor generation (CVG) using tetrahydroborate (THB, BH_4^-) remains the most popular and successful derivatization procedure enabling gaseous sample introduction into analytical atomic spectrometers that are routinely used for the determination of trace and ultrace amounts of elements such as As, Sb, Bi, Ge, Sn, Pb, Se, Te, Cd and Hg. But CVG using THB does have some disadvantages: (1) interference from transition metals which usually decreases sensitivity and

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reproducibility; and (2) its unstability in aqueous solution and potential contamination. So gas phase sample introduction methods with non-tetrahydroborate have been developed in an attempt to overcome these shortcomings[25-27], for example, photochemical vapor generation (photo-CVG)[26, 27] has appeared as a greener and more promising sample introduction technique for analytical atomic spectrometry.

To obtain higher sensitivity and better limit of detection, one or more preconcentration and matrix separation steps are often necessary prior to instrumental detection. As a feasible and alternative approach, in-situ trapping of high volatility species in a pre-heated graphite furnace provides a good strategy for determination of very low levels of Hg by GF-AAS. It is well known that mercury vapor could form gold amalgamation[28] with different forms of gold such as gold filament and gold nanomaterials, as a result, the ultra-trace mercury could be trapped and preconcentrated in gold materials before its determination. Therefore, here we propose an on-line preconcentration and determination of ultra-trace mercury in water and biological samples based on coating gold nanorods onto the inner wall of a graphite furnace for preconcentration of mercury vapor from photo-CVG and subsequent detection by GF-AAS.

2 Experimental

2.1 Instrumentation and operation

A photochemical reactor, vapor generator was constructed as shown in Fig. 1. The reactor primarily consists of a coiled quartz tube (150 mm in length and 3.0 mm i.d.)

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and a low-pressure Hg vapor UV lamp (5 W, Shanghai Yaming Bulb Co., Shanghai, P. R. China). A GF-AAS (SpectrAA 220FS/220Z,Varian, USA) was used for the detection of mercury atomic absorbance, which was accomplished by use of a mercury hollow cathode lamp (analytical wavelength, 253.7 nm; spectral bandwidth setting, 0.5 nm; and lamp current, 4.0 mA) operated under the conditions summarized in Table 1. Peak area (integrated absorbance) was recorded for quantification.

The analyte solution was pumped to the quartz tube with 10% HCOOH carrier solution flushing the analyte to the photoreactor for UV irradiation. A peristaltic pump (Baoding Qili Pump, Ltd., Hebei, China) operated at 100 rpm, provided a solution flow rate of 7 mL min^{-1}. After UV irradiation, the reaction solution was flushed to a gas/liquid phase separator (GLS) which was, in turn, coupled via a 60 cm length of 1.1 mm i.d PTFE tubing to a 1.0 mm i.d quartz tip. The quartz tip was manually inserted into the graphite furnace during the analyte trapping process and retracted prior to atomization of the sample. A 200 mL min^{-1} flow of argon purge gas was introduced into the GLS to flush Hg^0 vapor to the graphite furnace.

2.2 Reagents and samples

All reagents are of analytical grade or better. All solutions were prepared using 18 MΩ cm^{-1} deionized water (DIW) produced in our laboratory (Chengdu Ultrapure Technology Co., Ltd., Chengdu, China). Varied concentrations of working solutions were prepared daily by diluting a 1000 mg L^{-1} stock solution of mercury (GBW08617) which was purchased from the National Research Center for Standard Materials of

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China with high purity formic acid purchased from Kelong Chemical Reagents (Chengdu, China). High-purity argon gas was obtained from Qiaoyuan Gas Company (Chengdu, China) and chemical modifier Pd for traditional GF-AAS was purchased from National Steel Materials Testing Center (Bejing, China).

The real water samples were collected from our laboratory, the river and the lake near our campus and Tiantai Mountain, Sichuan Province. The two human hair powder GBW09101b and GBW07601a from the National Research Center for Certified Reference Material (NRCCRMS) were also used to validate the accuracy of the proposed method.

2.3 Synthesis of gold nanorods and coating to graphite furnace

The synthesis of gold nanorods was the same as that described in the previous work [29] using a seeded growth protocol. Firstly, 0.2 mL $HAuCl_4$ solution (0.01 M) was added into 7.8 mL cetyltrimethylammonium bromide (CTAB, 0.1 M) to make the seed solution, then 0.48 mL (0.01 M) freshly prepared $NaBH_4$ was injected subsequently followed by rapid continuous inversion for few minutes, and kept at 30 ℃ water-bath for 2 h before use. Secondly, to grow gold nanorods, 1.6 mL $HAuCl_4$ (0.01 M) and 0.23 mL $AgNO_3$ (0.01 M) were mixed with 32 mL CTAB (0.1 M). The pH of the mixed solution was adjusted by 0.64 mL HCl (1.0 M) followed by the addition of 0.25 mL ascorbic acid (0.1 M). Then the seed solution (0.08 mL) was rapidly injected and mixed for 10 s. The reaction solution was left undisturbed 17 h in 30 ℃ water-bath. The UV-visible spectrum and a TEM image of the gold nanorods are presented in Fig.

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2.

The procedure to coat the gold nanorods to the graphite furnace was similar to the previous work[20]. About 40 μL gold nanorods solution was injected into the surface of the graphite furnace and then dried by administrating the graphite furnace temperature program as listed in Table 1.

2.4 Analytical procedure and sample preparation

The programme used for trapping and atomization of mercury is similar to that reported earlier by Zheng et al.[30] The process is briefly outlined below. Firstly, a solution of mercury standard or a prepared aqueous sample containing 10 % HCOOH was initially pumped into the quartz tube through the peristaltic pump. This process took 60 s, during this stage the quartz tip was inserted into the furnace. Secondly, the solution was irradiated with the UV source for 20 s. Thirdly, the valve was activated to pass 10% HCOOH carrier solution so as to flush the analyte solution through the quartz tube to the GLS. The volatile product was rapidly separated from the liquid by a flow of Ar and impacted onto the gold nanorods coated on the graphite furnace for trapping. The furnace was maintained at 50 ℃ for 60 s to trap Hg^0 and then the quartz tip was removed from the furnace prior to the atomization. Fourthly, the furnace temperature was raised to 800℃ for 2 s for atomization with Ar flow stopped. At last, the furnace was cleaned at 800℃ for additional 2 s. The graphite furnace temeprature program is summarized in Table 1.

Test sample volumes of 25.0 mL of water samples which containing 10 %

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HCOOH eventually were filtered through a 0.2 μm aqueous microfiltration membrane (Zhuoxin Instrument Co., Ltd., Beijing, China). An acid leaching method was used to extract mercury from GBW09101b and GBW07601a. An aliquot of 0.05 g GBW09101b or 0.07 g GBW07601a was accurately weighed into 10 mL plastic centrifuge tube, and then 5 mL of 5.0 mol L^{-1} HCl solution was added. The sealed centrifuge tube was sonicated for 60 min under the room temperature. After centrifugation at 6000 rpm for 20 min, the supernatants of the GBW09101b and the GBW07601a were quantitatively transferred to a precleaned 100 mL and 50 mL volumetric flask, respectively, the precipitate was dissolved in DIW again and the above steps were repeated, and the supernatants were transferred to the above flasks quantitatively in 10 % HCOOH finally. Then, the solutions were neutralized with 1.0 mol L^{-1} NaOH solution and diluted with DIW. Sample blanks were processed along with the samples.

3 Results and discussion

3.1 Optimazation of trapping and atomization temperature

The optimum operating conditions for GF-AAS in this work are summarized in Table 1. An aliquot of 7 mL of 2 μg L^{-1} Hg^{2+} solution containing 10 % HCOOH was used to investigate the effect of the temperature on the trapping efficiency using a carrier gas flow rate of 200 mL min^{-1}; with results shown in Fig. 3a. The trapping temperature significantly affects the trapping efficiency, with an optimum range of 45–100℃. Hg^0 trapping may occur at room temperature, because 45 ℃ is the lowest temperature

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controllable by the furnace temperature program, which is in accordance with the reported results[31]. The mercury atomic absorbance decreased rapidly in the temperature range of 100–200□, probably because of the partial desorption of analyte prior to the determination step at a higher trapping temperature. A temperature of 50□ was therefore selected for subsequent trapping experiments. In order to further conform the important role played by the gold nanorods in the proposed method, a bare graphite furnace without any gold nanomaterials was also used to compare the effect of trapping. As shown in Fig. 7, the sensitivity with gold nanorods preconcentration was improved at least 13-fold for a 7 mL sampling volume.

Zheng et al.[30] found that chemical modifiers (Pd or Ir permanent modifiers) did not noticeably enhance the performance of the system, and neither does this work. Therefore, we did not use any chemical modifiers during the experiments of photo-CVG for mercury atom trapping and GF-AAS detection.

The atomization temperature was optimized by fixing the trapping temperature at 50 □ and the carrier gas flow rate at 200 mL min^{-1}, with results shown in Fig. 3b. It can be seen that a plateau in the range of 750–850□ was obtained, so 800□ was used for the subsequent atomization experiments.

3.2 Optimization of generation conditions

3.2.1 Optimization of carrier gas flow rate

It is well known that the separation efficiency of gaseous hydrides from its liquid reaction medium is significantly dependent on the carrier gas flow rate.[32] Fixing the

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trapping temperature at 50 □, the effect on the absorbance signal with increase of carrier gas flow rate was evaluated in the range of 0-500 mL min^{-1}. As shown in Fig. 4a, the signal increased with the carrier gas flow rate up to 200 mL min^{-1} as a reault of efficient separation. However, the signal decreased when the carrier gas flow rate was higher than 200 mL min^{-1}. A higher carrier gas flow rate probably resulted in a lower trapping efficiency of the mecury vapor on the surface of the gold nanorods. Considering the efficient separation and trapping, an Ar flow rate of 200 mL min^{-1} was selected for subsequent experiments.

3.2.2 Optimization of concentration of formic acid

It has been reported that photo-CVG can be used to produce mercury vapor from Hg^{2+} solution with formic acid only[16]. So it is obvious that the concentration of formic acid has a great effect on the efficiency of the photo-CVG. As shown in Fig. 4b, a plateau of the absorbance signal appeared when the formic acid concentration was more than 10 % with the UV irradiation. No significant changes in the absorbance occurred at a higher concentration range of formic acid. In consideration of both the intensity and the stability of the signal, 10% formic acid was used for subsequent experiments of the photo-CVG.

3.2.3 Optimization of UV irradiation time

No signal can be detected without the UV irradiation. As shown in Fig. 4c, the absorbance signal was significantly affected by the irradiation time because the UV

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radiation determines the extent of radical formation and the efficiency of the reduction of mercury. When the irradiation time was longer than 5 s, the signal increased rapidly. A plateau of the absorbance intensity started when the irradiation time was more than 30 s. In order to save analytical time, 30 s irradiation time was chosen for later experiments.

3.3 Effect of concomitant ions

Transition metal ions are easily reduced to their metallic states or colloidal forms by conventional CVG or hydride generation. In this work, the interference effect of eight common concomitant ions, including hydride-forming elements as well as transition metal ions were investigated. As summarized in Table 2, no significant interference from these ions was detected, even at concentrations as high as 1000 μg L^{-1} for most of the concomitant ions in a solution containing 2 μg L^{-1} Hg^{2+}.

3.4 Analytical figures of merit

The calibration curves were obtained with and without preconcentration under the optimal experimental conditions. Linear correlation coefficients for calibration curves were better than 0.99 and the LOD, defined as the analyte concentration equivalent to 3-fold of standard deviation of 11 measurements of a blank solution, was 0.02 μg L^{-1} (based on a 7 mL sampling volume) for the proposed method. The precision, expressed as relative standard deviation (RSD) of 11 replicate measurements, was better than 5% even at a mercury concentration as low as 0.1 μg L^{-1}. As shown in Fig.

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5, compared with the photo-CVG-GF-AAS without preconcentration, the sensitivity with preconcentration was improved at least 13-fold for a 7 mL sampling volume. What's more, compared with the photo-CVG-GF-AAS using Au^{3+} as modifier, the sensitivity with preconcentration was also improved. The calibration curve established by conventional GF-AAS was also shown in Fig.5 with a temperature program shown in Table 3. It is evident that compared with the conventional GF-AAS, the sensitivity with preconcentration and without preconcentration were improved at least 400-fold and 30-fold, respectively, for a 7 mL sampling volume, when the sample injection volume is 10 μL and Pd as the chemical modifier was necessary during the measurements by conventional GF-AAS. Table 4 summarizes figures of merit characterizing the proposed method and compared its performance with those of published similar analytical methods.

3.5 Analysis of samples

Four real water samples were analyzed by use of the proposed method, with the analytical results summarized in Table 5. Because mercury in these samples was not detected, it was necessary to spike the water samples with Hg^{2+} standard solutions. The results show that adequate recoveries of Hg^{2+} were obtained. Two CRMs GBW09101b and GBW07601a were also analyzed to further validate the accuracy of the proposed method, with analytical results also listed in Table 5. No significant difference was found between the obtained and the certified values.

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4 Conclusions

A simple, sensitive and reliable analytical method based on photo-CVG for mercury atom trapping and GF-AAS detection has been proposed for determination of ultratrace mercury in water samples. In-atomizer atom trapping of mercury on the inner wall of graphite furnace coated with gold nanorods was used for the preconcentration of the mercury vapor. The proposed method has the following advantages: (1) it is rapid, sensitive and simple for the determination of ultratrace mercury; (2) it is a greener method compared to other mercury cold vapor generation schemes, since both the HCOOH and its by-products are relatively environmentally friendly; and (3) interferences from common transition metals were effectively eliminated. Ongoing work is to explore applications of this preconcentration methodology for determination of other photo-CVG- or hydride-forming elements by varying the nanomaterials coated on the inner wall of the graphite furnace.

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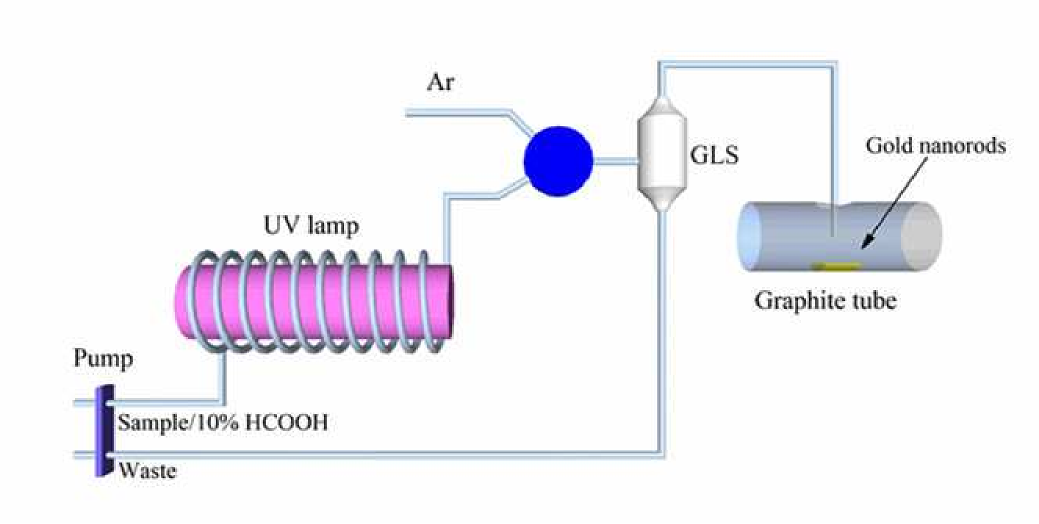

Fig. 1 Schematic diagram of the photo-CVG-GF-AAS. GLS: gas liquid separator.

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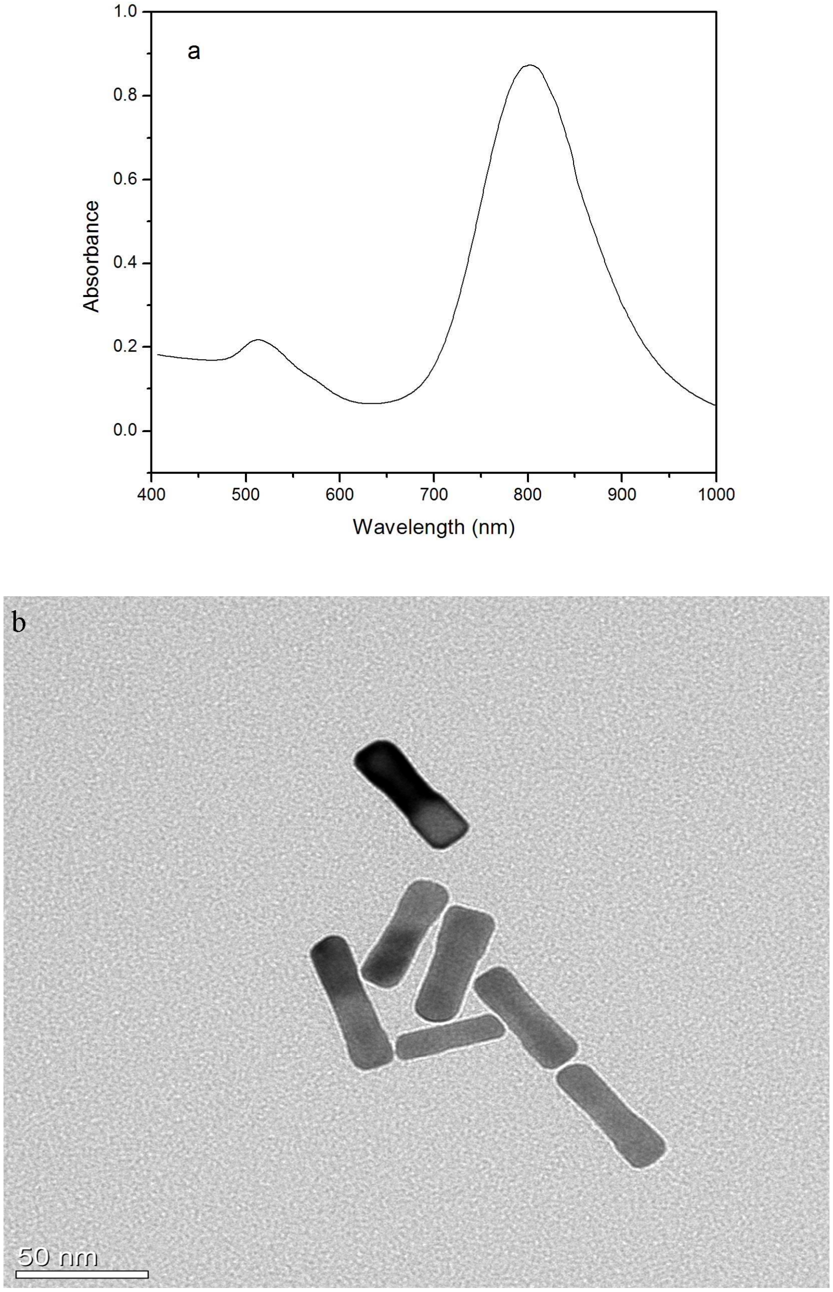

Fig.2 (a) UV-visible spectrum of gold nanorods; and (b) a TEM image of the prepared gold nanorods.

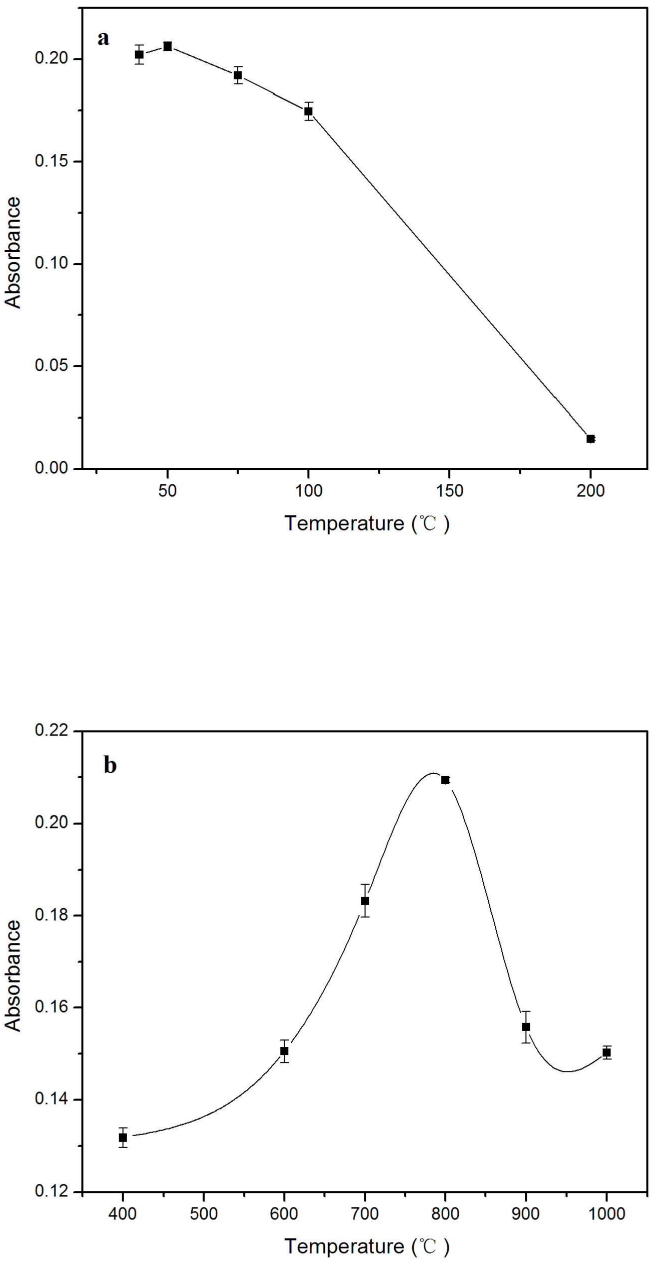

Fig. 3 Effect of (a) trapping and (b) atomization temperature on mercury atomic absorbance from a 7 mL sampling volume of a solution of 2 μg L^{-1} Hg^{2+}.

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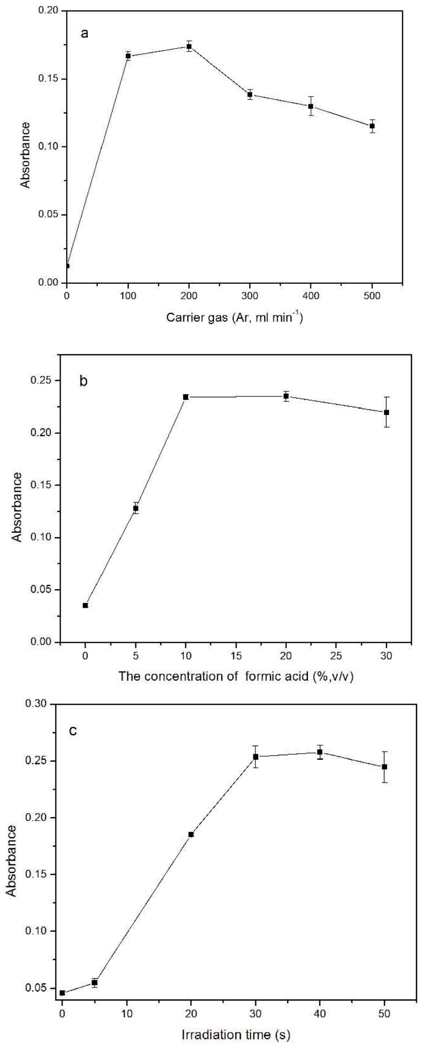

Fig. 4 Effect of (a) carrier gas flow rate, (b) concentration of formic acid and (c) UV irradiation time on mercury atomic absorbance, with 2 μg L^{-1} Hg^{2+} solution.

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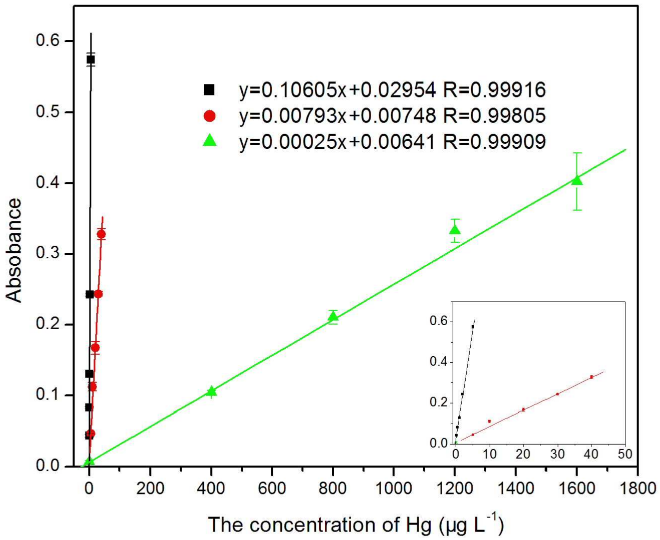

Fig. 5 Calibration curves for Hg. Red, photo-CVG-GF-AAS without preconcentration; black, photo-CVG-GF-AAS with preconcentration; green, traditional GF-AAS (with a sampling volume of 10 μL and 2 μL of Pd chemical modifier). The inset shows the details of the black and red curves.

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Table 1 Graphite furnace program

Programme	Step	Temperature □	Hold time s	Ar Gas L min^{-1}
Loading	1	40	60.0	3.0
Trapping	2	50	80.0	stop
Atomization	3	800	2.0	stop
Cleaning	4	800	2.0	3.0

Table 2 Effect of concomitant ions on the recovery of mecury[a]

M^{n+}	$[M^{n+}]$/ μg L^{-1}	Recovery/ %
Ni^{2+}	1000	93
Cu^{2+}	1000	96
Co^{2+}	1000	105
Fe^{3+}	1000	80
Mg^{2+}	1000	101
Zn^{2+}	1000	83
Ca^{2+}	1000	101
As(III)	500/100	115/104

a Average recovery based on three measurements. The typical precision of the determination was <4% RSD for a 2 μg L^{-1} solution of mecury in 10 % HCOOH.

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Table 3 The temperature program of mercury measurement by conventional GF-AAS

Step	Temperature □	Hold time s	Ar Gas L min^{-1}
1	85	5.0	3.0
2	95	40.0	3.0
3	120	10.0	3.0
4	400	5.0	3.0
5	400	1.0	3.0
6	400	2.0	0.0
7	1800	0.8	0.0
8	1800	2.0	0.0
9	2000	2.0	3.0
10	2000	2.0	3.0

Table 4 Analytical figures of merit in comparison with those by other methods

Methods	Preconcen-tration	Sampling volume, mL	LOD, μg L^{-1}	RSD ([a]), %	Ref.
Photo-CVG-AAS	Yes	15	0.1	7-8(3)	19
Photo-CVG -Pd modified GF-in situ trapping-AAS	Yes	50	0.06	20(-)	33
Flow Injection -CV-AAS	No	-	0.5	6(5)	34
Ionic liquid-CV-AAS	Yes	1000	0.01	1.2(5)	35
gold amalgamation -AAS	Yes	500 [b]	0.12[c]	3.6	36
On-line microwave Flow Injection -CV-AAS	Yes	10	0.01	1.0	37
CVG-GNP coated QTA IAT-AAS	Yes	5	0.01	4.0(0.5)	20
Photo-CVG- gold nanorods-GF-AAS	Yes	7	0.02	5.0(0.1)	This work

[a] Concentration of Hg (II), μg L^{-1}. [b] mg. [c] ng g^{-1}.

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Table 5 Determination of mercury in samples by this method

Sample	Certified (mg kg^{-1})	Hg added (μg L^{-1})	Found^{a} (μg L^{-1})	Recovery (%)
Tap water	-	0	ND	-
	-	0.5	0.48 ± 0.02	96
	-	1	0.99 ± 0.04	99
Lake water	-	0	ND	-
	-	0.5	0.52 ± 0.02	104
	-	1	1.00 ± 0.05	100
Funan River water	-	0	ND	-
	-	0.5	0.48 ±0 .03	96
	-	1	1.02 ± 0.01	102
Tiantai Mountain water	-	0	ND	-
	-	0.5	0.47 ± 0.04	94
	-	1	0.99 ± 0.04	99
GBW09101b^{b}	1.06±0.28	-	1.05±0.15	-
GBW07601a^{b}	0.36±0.08	-	0.34±0.02	-

a. Mean and standard deviation of results (n = 3). ND = not detected. b. mg kg^{-1}.

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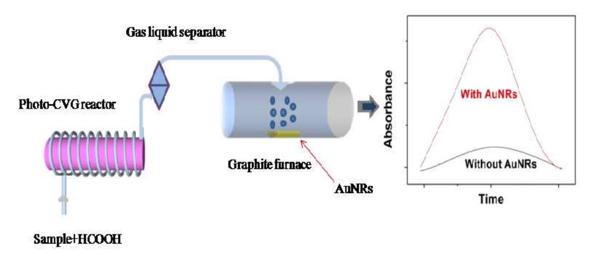

Mercury vapor from photo-chemical vapor generation (CVG) was enriched in gold nanorods (AuNRs) for enhancing sensitivity by GF-AAS.

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