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Matrix-Assisted UV-Photochemical Vapor Generation for AFS Determination of Trace Mercury in Natural Water Samples: A Green Analytical Method

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ABSTRACT Direct matrix-assisted UV-photochemical/cold vapor generation for sample introduction was proposed for the determination of trace mercury in natural water by atomic fluorescence spectrometry. The optimal experimental conditions for the determination of mercury including sampling volume, UV irradiation time, carrier flow rate, pH, and the interference from coexisting metal ions were investigated in detail. Under the optimized experimental conditions, the limit of detection for total mercury was 0.03 ng mL^{-1} . The accuracy of the proposed method was validated by analyzing two certified reference water samples with satisfactory analytical results. This method is simple, fast, green, highly selective, ultrasensitive, and yet inexpensive.

KEYWORDS atomic fluorescence spectrometry, green analytical method, mercury, uv-photochemical vapor generation, water

INTRODUCTION

Mercury even at very low levels is toxic to living cells and has no beneficial biological functions.^[1] The U.S. Environmental Protection Agency (EPA) has set the maximum mercury allowable in natural waters down to 2 ng mL^{-1} ,^[2] and the Standard of the People's Republic of China (GB 5750–1985) has set it as low as 1 ng mL^{-1} . Therefore, ultrasensitive methods are needed for the determination of mercury in water samples. There are a variety of analytical techniques for the determination of trace mercury in natural water samples including inductively coupled plasma mass spectroscopy (ICP-MS),^[3] inductively coupled plasma optical emission spectroscopy (ICP-OES),^[4] atomic absorption spectrometry (AAS),^[5] and atomic fluorescence spectrometry (AFS),^[6] among which AFS is most frequently used for its high sensitivity, broad linear dynamic range and excellent selectivity.^[7]

Chemical vapor generation (CVG) has been widely used as an effective sample introduction method to atomic spectrometry in recent decades. In the conventional CVG for mercury, sodium (or potassium) tetrahydroborate (NaBH_4 or KBH_4) or stannous chloride (SnCl_2) is used to reduce Hg^{2+} to

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Hg^0 . Although the method is rapid and efficient, its disadvantages include interferences from transition metals, use of at least two reagents, and the instability of NaBH_4 solution, thus increasing the analytical cost and the possibility of analyte contamination or high blank level in ultratrace analysis.

Recently, several new methods have been reported for the CVG of mercury. One interesting approach is electrochemical cold vapor generation.^[8] However, it still suffers some problems similar to those of traditional CVG. UV photo-CVG has recently been introduced to analytical atomic spectrometry for sample introduction partially for its high tolerance of interference from transition metals.^[9–13] These methods can be used to determinate mercury, selenium, and other elements. For example, Wang et al.^[14] improved the UV photo-CVG method with nano- TiO_2 -formic acid in selenium speciation analysis; and Lopez-Rouco^[15] determined mercury in biotissues by AAS with ultrasound-assisted gas-liquid separation. These established methods are simple, sensitive, and selective, but chemical reagents are still needed.

Studies in environmental sciences and physical chemistry have shown that Hg^{2+} can be transformed into Hg^0 in distilled waters^[16,17] and natural water^[18,19,20] through dissolved organic carbon (DOC)-assisted photoreduction,^[21,22] DOC and dissolved oxygen-assisted reduction,^[23] and sunlight-induced reduction under the catalysis of Fe^{3+} ^[24] among others. Enlightened by these discoveries' and previous work on UV photo-CVG,^[25,26] we proposed a new matrix-assisted UV photo-CVG method for the AFS determination of trace mercury in natural water samples without any reagent that features simplicity, rapidness, green nature, and cost-effectiveness.

MATERIALS AND METHODS

Instrumentation

A photochemical reactor was constructed as shown in Fig. 1. The reactor primarily consisted of a quartz tube (250 mm in length and 15.0 mm i.d.) and a low-pressure Hg vapor UV lamp (15 W, Philips Co., Holland). An atomic fluorescence spectrometer (AFS-2202, Beijing Haiguang Instrument Co., Beijing, P. R. China) was used for the detection of the mercury atomic fluorescence. The optimal instrumental conditions for this work are listed here: Hg hollow cathode lamp current is 30 mA; photomultiplier tube voltage is

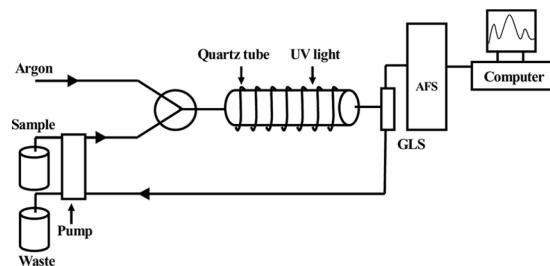


FIGURE 1 Schematic diagram of the UV photo-CVG-AFS instrumentation. GLS = gas–liquid separator. AFS = atomic fluorescence spectrometer.

–260 V; observation height is 8 mm; reading time is 20 s; delayed time is 1 s; carrier gas argon flow rate is 600 mL min^{-1} ; and irradiation time is 3.6 s (National Research Center for Standard Materials, Beijing, China).

Reagents

All reagents are of analytical grade or better. Working solutions of mercury are prepared by serial dilutions of a mercury standard stock solution of 1000 $\mu\text{g mL}^{-1}$ with subboiled double-distilled water (DDW) prior to use. Water samples collected from the Lotus Pond on Sichuan University campus and Funan River of Chengdu were filtered prior to analysis. Certified reference water samples (GBW080393 and GBW080392) were purchased from the National Research Center for Certified Reference Materials (NRCCRM, Beijing, China).

Working Procedure

The whole programmable operation procedure consisted of four steps. Step 1 was of 6 s duration for preparing for sampling procedure. In Step 2, the mercury standard or sample solution was sucked for 35 s via the peristaltic pump into the reactor with a sampling volume of 6.8 mL. In Step 3, the peristaltic pump stopped for 1 s, and the sample solution was irradiated by the UV for 3.6 s. Meanwhile, the sampling channel was shifted from the sample solution to the carrier solution (DDW). In Step 4, the argon flow, together with the carrier solution (DDW), was passed through the reactor to propel the solution to the gas–liquid separator (GLS) (Fig. 1) to separate and introduce mercury vapor into the AFS for measurement. This step took 26 s, during which the mercury AFS signal was recorded in peak area mode. The whole procedure took about 68 s. To clean up

the quartz tube, 5% nitric acid solution was used after each run for 10 s, and then followed by DDW for 10 s.

RESULTS AND DISCUSSION

Effect of Irradiation Time

The received dose of UV radiation determines the extent of radical formation and the efficiency of the reduction of mercury. As an important parameter, the effect of the irradiation time of the sample in the flow-through reactor was investigated from 3.6 to 35 s, as shown in Fig. 2. Increasing the irradiation time resulted in proportional decrease in the signal intensity, most probably due to the competitive process between the UV photo-CVG and its reverse reaction.^[25] To make sure that Hg^{2+} is effectively converted to Hg^0 to achieve relative high sensitivity, the irradiation time should be short, and 3.6 s was selected for use.

Effect of Carrier Gas Flow Rate

The relationship between atomic fluorescence intensity of mercury and the argon gas flow rate in the range of 400–800 mL min^{-1} was investigated. The maximum signal intensity was achieved when the argon flow rate was 600 mL min^{-1} . Low argon flow rate would lead to incomplete vaporization or loss of Hg during transport, while high argon flow rate would result in dilution of the mercury vapor.^[25]

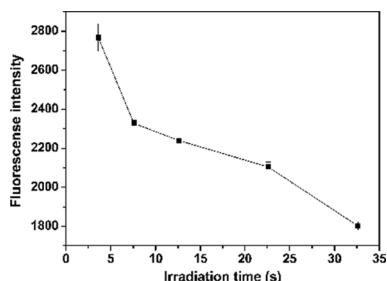


FIGURE 2 Effect of irradiation time on the AFS signal of 5 ng mL^{-1} Hg^{2+} .

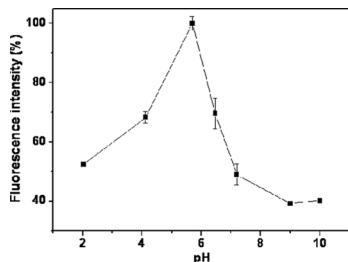


FIGURE 3 Effect of pH on the AFS signal of 5 ng mL^{-1} Hg^{2+} .

Considering both the intensity and stability of the signal, a carrier gas flow rate of 600 mL min^{-1} was chosen for further experiments.

Effect of Sample pH

In the proposed method, pH plays an important role affecting the generation efficiency of mercury vapor. Therefore, the effect of sample pH on the response was studied (Fig. 3): the fluorescence intensity of mercury increased with increasing pH from 2.0 to 5.7, and reached its maximum at pH 5.7; and higher pH decreased the signal as found in Viera's work.^[26] Therefore, pH = 5.7 was chosen for use in this work.

Interference

Conventional CVG systems suffer serious interference from many coexisting transition metal ions, especially Co^{2+} , Cu^{2+} , Fe^{3+} , and Ni^{2+} . The reason is that their metallic states or colloidal forms of transition metals reduced by KBH_4 or NaBH_4 could scavenge or decompose the volatile analytes before phase separation.^[11] In this work, the effect of potential interference of Co^{2+} , Cu^{2+} , Fe^{3+} , and Ni^{2+} on the determination of mercury was therefore investigated. It was found that no significant interference existed from as high as 100 mg L^{-1} for Co^{2+} , 0.1 mg L^{-1} for Cu^{2+} , and 50 mg L^{-1} for Fe^{3+} and Ni^{2+} in the samples containing 5 ng mL^{-1} Hg^{2+} , as shown in Table 1.

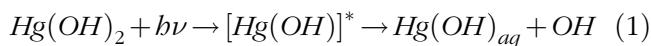
Discussion of Photochemical Reduction of Mercury

Several possible mechanisms have been proposed for the process of reduction of Hg^{2+} to Hg^0 under UV irradiation. Without organic compounds, the direct photochemical reduction of mercury is probably due to many Hg species, such as its complexes with OH^- , HS^- or Cl^- , which can absorb radiation in the

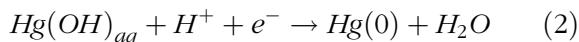
TABLE 1 Influence of Coexisting Metal Ions on the Determination of 5 ng mL^{-1} Hg^{2+} by the Proposed Method

Interference ions	Concentration (mg L^{-1})	Recovery (mean $\pm \sigma$, $n = 3$) (%)
Co (II)	100	94 \pm 4
Ni (II)	50	91 \pm 2
Cu (II)	0.1	107 \pm 2
Fe (III)	50	97 \pm 3

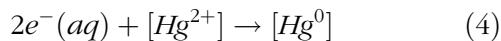
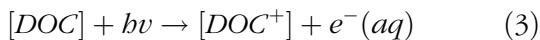
highly energetic UV range (270–400 nm) of the solar spectrum.^[27] The absorbed photons initiate a series of electron transfer reactions, resulting in the reduction of Hg (II) and the formation of free ligand radicals. The photolytic reduction of dissolved Hg(OH)₂ can be schematized here:^[23]



Hg(OH)_{aq} is unstable in natural water and is likely quickly reduced to elemental mercury through Reaction (2):



However, the complexity of natural water leads to the diversified mechanisms of its photochemical reaction. Cooper^[21] and Zepp^[22] suggested that the DOC in natural water can contribute to the photochemical reduction of mercury via absorbing solar radiation to emit aqueous electrons, which are then available to reduce Hg (II) through reactions (3) and (4). The general reactions might occur as follows:



Apart from aqueous electron theory, a mechanism of photosensitization (PS) is also proposed to elucidate the process of photochemical reduction of Hg (II). In the PS mechanism, the energy is transferred from photosensitizers in the water to molecular oxygen, resulting in the formation of singlet oxygen at first, and subsequently the singlet oxygen, with its fully spin-paired electrons, can attack and oxidize organic molecules effectively; in the process Hg species can be liberated and then reduced by sequential photochemical reactions.^[23]

The metal ion in natural water may further promote the photochemical reduction process, because the complex of Fe(III)-organic acid coordination compounds [Fe(III)-OACC] can be photochemically degraded into organic free radicals,^[24] which are able to reduce Hg(II) to Hg⁰:

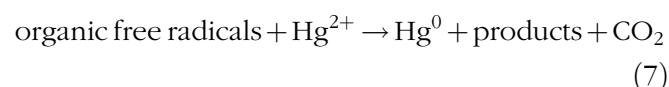
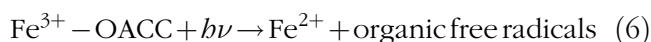


TABLE 2 Analytical Figures of Merit of the Proposed Method

Variable	Value
Sensitivity (mL ng ⁻¹)	326
LOD (ng mL ⁻¹)	0.03
Linear correlation coefficient (R)	0.9993
Precision (<i>n</i> = 5, 10 ng mL ⁻¹)	3.4%
Linear range (ng mL ⁻¹)	0.25–15.0

Although the proposed mechanisms about photochemical reaction for mercury are diversified, the vital role the matrix of a water sample plays in the photochemical reduction is undoubtedly important. The trace organic matrix and water itself make the matrix-assisted UV photo-CVG for trace mercury in natural waters possible, achieving a reagent-free analytical method.

Analytical Figures of Merit

The analytical figures of merit for the proposed procedure are summarized in Table 2. Sensitivity is defined as the slope of the calibration curve. The LOD based on three times the standard deviation of 11 measurements of a blank solution was found to be 0.03 ng mL⁻¹, with the upper linear dynamic range of 15.0 ng mL⁻¹. The linear correlation coefficient was better than 0.999, and the precision for 10 ng mL⁻¹ Hg was found to be 3.4% (*n* = 5).

Analytical Application

To evaluate the accuracy of the proposed analytical method, two certified water samples were analyzed for mercury by standard addition method, and the analytical results are listed in Table 3. A *t*-test shows that the analytical results by the proposed method have no significant difference from the certified values at the confidence level of 95%. Besides, two natural water samples were analyzed by the same method, with the results listed in Table 4. The results show that this method can be used to determine trace Hg²⁺ in natural water samples.

TABLE 3 Analytical Results for Mercury in Certified Reference Samples by the Proposed Method

Sample	Certified value ^a (ng mL ⁻¹)	Found value ^a (ng mL ⁻¹)
GBW080393	100.0 ± 4.0	106.0 ± 3.0
GBW080392	10.0 ± 0.5	12.2 ± 1.2

^aAverage ± standard deviation (*n* = 3).

TABLE 4 Analytical Results for Mercury in Real Water Samples by the Proposed Method

Sample	Added (ng mL ⁻¹)	Detected ^a (ng mL ⁻¹)
Lotus Pond	0	nd
	0.25	0.21 ± 0.04
	0.50	0.40 ± 0.02
Funan River	0	nd
	0.25	0.35 ± 0.04
	0.50	0.60 ± 0.10

^aAverage ± standard deviation (n = 3).

nd = not detected.

CONCLUSIONS

The matrix-assisted UV photo-CVG-AFS method has been successfully developed for the determination of trace mercury in natural water. This method has several advantages: (1) it is simple, fast, and cost-effective; (2) it is sensitive and accurate enough for the determination of trace mercury water samples; and (3) it is a green analytical method without use of any chemical reagent.

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