



Application of flow injection–green chemical vapor generation–atomic fluorescence spectrometry to ultrasensitive mercury speciation analysis of water and biological samples

Ruoxi Zhang ^{a,b}, Mengting Peng ^c, Chengbin Zheng ^c, Kailai Xu ^{c,*}, Xiandeng Hou ^{a,c,**}

^a Analytical & Testing Center, Sichuan University, Chengdu, Sichuan 610064, China

^b College of Earth Sciences, Chengdu University of Technology, Chengdu, Sichuan 610059, China

^c College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China

ARTICLE INFO

Article history:

Received 4 February 2016

Accepted 6 February 2016

Available online 12 February 2016

Keywords:

Mercury

Photochemical vapor generation

Ultrasonic vapor generation

Speciation analysis

Atomic fluorescence spectrometry

ABSTRACT

A simple, non-chromatographic and green method based on flow injection UV photochemical or ultrasonic vapor generation atomic fluorescence spectrometry (AFS) was developed for the determination and speciation analysis of mercury. Mercury cold vapor (Hg^0) was generated by using only formic acid and UV or ultrasonic irradiation, and was subsequently detected by AFS. Both mercury (Hg^{2+}) and methyl mercury (MeHg) can be converted to Hg^0 for the determination of total mercury with UV irradiation, while only Hg^{2+} can be reduced to Hg^0 with ultrasonic irradiation, thus determining only Hg^{2+} . Then, the concentration of MeHg can be calculated by subtracting the Hg^{2+} concentration from the total mercury concentration. The optimal conditions for the best cold vapor generation efficiencies are discussed in detail, together with interference from transition metals. This new speciation analysis not only provides high sensitivity for the determination of mercury species but further eliminates the use of toxic reducing reagents and avoids potential destruction of analyte species that occur in chromatographic separation. Moreover, a simpler and less toxic Hg^{2+} standard series can be used for the calibration of both Hg^{2+} and MeHg. The limit of detection is 0.005 or 0.01 $\mu\text{g L}^{-1}$ for total mercury with the UV or inorganic mercury with the ultrasonic irradiation, respectively. This method was successfully applied to ultrasensitive mercury speciation analysis of water and biological samples.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

It is well known that the toxicity, metabolism and bioavailability of mercury are strongly dependent on its chemical forms, and methylmercury (MeHg) is considered more toxic than other inorganic mercury species because of its accumulation and biomagnification in the food chain [1,2]. Thus, it is of great importance to develop rapid and sensitive analytical methods for speciation analysis of mercury in environmental and biological samples.

The most practical approach to speciation analysis of mercury is to hyphenate a sensitive atomic spectrometric detector to a powerful separation technique such as GC and HPLC [3–8]. Although these hyphenated techniques are powerful since they provide more species information, they could bring in several drawbacks including time-consuming, potential destruction of analyte species, higher instrumental and operational cost. Moreover, they usually require complicated sample preparation processes and complex interfaces. Therefore,

non-chromatographic approaches as alternatives of the hyphenation for selective discrimination of mercury species sometimes are welcomed because they are less time-consuming, more cost-effective and providing higher sensitivity and lower limit of detection. Therefore, various non-chromatographic methods have been developed for mercury speciation based on selective extraction, derivatization and atomization [9–14]. These non-chromatographic techniques are sensitive and efficient, but there are several disadvantages associated with these methods need to be resolved, such as the use of toxic (e.g., tin (II) chloride, SnCl_2) or unstable reducing reagent (tetrahydroborate, THB), complicated instrumentation and/or operation, and difficult automation. Therefore, it is still attractive to many analysts to realize green and simple speciation analysis of mercury without chromatographic separation.

Cold vapor generation (CVG) coupled with atomic spectrometry is considered as the most promising technique for highly sensitive determination or speciation analysis of mercury owing to its high efficiency of sample introduction and effective matrix separation [15–19]. Reduction of Hg^{2+} to Hg^0 and further liberation from a sample solution is commonly realized by using SnCl_2 or THB in the presence of an inorganic acid such as HCl [12,14]. Although these methods are very efficient, there still remain a number of serious impediments to further evolution

* Corresponding author.

** Correspondence to: X.D. Hou, Analytical & Testing Center, Sichuan University, Chengdu, Sichuan, 610064, China.

E-mail addresses: xukailai@scu.edu.cn (K. Xu), houxid@scu.edu.cn (X. Hou).

of these CVG methods besides use of relatively toxic and relatively expensive reagents, including high blank arising from reducing agents and inorganic acids, inconsistent response from different mercury species and so on. Fortunately, a promising greener and cheaper CVG technique, namely photochemical vapor generation (PVG) has been introduced for generation of volatile species of a number of elements, including mercury and other elements [5,11,20–29]. Moreover, more and more efficient and green techniques have been used to generate mercury vapor and demonstrated for successful determination of trace level mercury in recent years, such as sono-induced (SI) CVG [30,31], solution cathode glow discharge-(SCGD) induced CVG [32], dielectric barrier discharge (DBD)-induced CVG [33] and microwave-induced CVG (MI-CVG) [34]. These methods not only retain the principle advantages of conventional CVG but also provide simpler reactions, higher anti-interference capacity, elimination of generation of H_2 (better compatibility with low power plasma sources) [26] and greener analytical chemistry as well as potentially lower blanks and improved limits of detection.

It was proved that selective CVG of mercury species at different conditions was a promising technique for non-chromatographic speciation analysis of mercury. With formic acid or $SnCl_2$, Hou et al. [11,12] have successfully developed non-chromatographic AFS methods for the speciation analysis of Hg^{2+} and MeHg simply by turning a UV lamp on or off. However, these non-chromatographic techniques still need to be greener or more sensitive.

Our work [11] reported that both Hg^{2+} and MeHg can be converted to Hg^0 by using the UV PVG technique, while only Hg^{2+} can be reduced to mercury vapor in the presence of formic acid with high-intensity ultrasonication [30,31]. Therefore, the purpose of this work was to implement a new, greener, more sensitive non-chromatographic method that integrated flow injection SI-CVG and UV PVG for determination and speciation analysis of mercury in environmental and biological samples by AFS.

2. Experimental

2.1. Reagents and materials

All chemicals used in this work were of at least analytical grade. All solutions were prepared using 18.2 M Ω -cm deionized water (DIW) produced by a water purification system (Chengdu Ultrapure Technology Co., China). 1000 mg L⁻¹ stock standard solutions of MeHg (GBW08675) and Hg^{2+} (containing 3% HNO_3 , GBW08617) were purchased from National Research Center for Standard Materials (NRCMS, Beijing, China). Standard solutions were prepared daily by dilution of the stock solutions with high-purity formic acid (88%, Kelong Chemical Factory, China). Argon was of high purity (99.99%) and purchased from Qiaoyuan Gas Company (99.99%, Sichuan, China).

The proposed method was used for the determination of inorganic and total mercury in river water and tap water samples. Certified Reference Materials from NRCMS (GBW10029) and NRC Canada (DORM-4 and TORT-3) were used for further validation of the accuracy of the proposed method.

2.2. Instrumentation

A commercial hydride generation non-dispersive atomic fluorescence spectrometer (AFS-2202E, Beijing Haiguang Instrumental Co., Beijing, China) equipped with a four-channel peristaltic pump, a quartz gas-liquid separator (GLS), a quartz atomizer and a coded high-intensity mercury hollow cathode lamp was used for AFS measurements.

A flow-through photoreactor for the UV PVG of both Hg^{2+} and MeHg consisted of a coiled quartz tube (50 cm \times 3.0 mm i.d. \times 4.0 mm o.d.) wrapped around a low-pressure mercury vapor UV lamp (254 nm, 15 W, Philips Co., Holland). Selective SI-CVG of Hg^{2+} can be

obtained using a flow-through sonoreactor consisting of another coil quartz tube (50 cm \times 3.0 mm i.d. \times 4.0 mm o.d.) put in the water bath of an ultrasonication cleaner (AS3120A, Nanjing Science Instrument Co., China). Ultrasonic power could be fixed at any desired amplitude level using a power setting in the range of 0–120 W. Using flow injection, the analyte solution was pumped through a six-port injection valve to a 2.0 mL polytetrafluoroethylene (PTFE) sample loop with high-purity deionized water (DIW) carrier solution selectively flushing the analyte to the photoreactor or the sonoreactor via a three-way valve for UV irradiation or ultrasonication irradiation. A schematic of the instrumentation is presented in Fig. 1. After UV or ultrasonication irradiation, the reaction solution was flushed to the GLS wherein a 500 mL min⁻¹ flow of argon purge gas was introduced to transport the mercury vapor separated from liquid phase to the quartz atomizer for AFS measurement.

2.3. Procedure

For the programmable operation procedure, solutions of the mercury standards or samples containing formic acid at different concentrations were initially sucked for 20 s into a 2.0 mL sample loop through a six-port valve in step 1. In step 2, the six-port valve and the three-way valve were activated to pass DIW carrier solution at a flow rate of 5.5 mL min⁻¹ so as to flush the analyte solution through the photoreactor or the sonoreactor for UV or ultrasonication irradiation for 40 s. In step 3, the irradiated solution was swept into the GLS at a flow rate of 7.0 mL min⁻¹ wherein the argon flow was passed through to separate mercury vapor from the liquid phase and further transported it into the AFS for the measurements of mercury atomic fluorescence, and this step took 20 s during which the AFS signal was recorded. The signal peak area was used for quantification. Finally, 6 s of duration time was used to prepare for the next measurement in step 4. The whole procedure took about 1.5 min.

3. Results and discussion

3.1. Optimization of instrumental parameters

Optimization of the parameters of AFS, including shield gas flow rate, carrier gas flow rate, Hg hollow cathode lamp (HCL) current and photomultiplier tube (PMT) voltage as well as observation height, was performed by monitoring the AFS signal with 2 mL 5 ng L⁻¹ solutions of Hg^{2+} sampled to the PVG or the SI-CVG, as summarized in Table 1. Finally, 900 mL min⁻¹, 30 mA, -250 V and 10 mm were selected for shield gas flow rate, HCL current, PMT voltage and observation height, respectively.

The carrier gas flow rate through the GLS significantly affected the AFS response as it influenced analyte concentration in the carrier gas, analyte transport efficiency, as well as analyte residence time in the quartz atomizer. A plateau was obtained in the range of 400–600 mL min⁻¹, which likely reflects a simple balance between serious dilution of analyte at higher argon flow rates and low transport efficiencies of mercury cold vapor from the liquid phase at lower flow rates.

3.2. Effect of ultrasonic power on SI-CVG

The effect of ultrasonic power on the SI-CVG of mercury or methylmercury has been previously investigated by Bendicho's group [30]. However, it is still necessary to validate this parameter because no information concerning the SI-CVG of mercury using flow-through sonoreactor is available. A 2 mL solution of 5 ng mL⁻¹ Hg^{2+} or MeHg was used to investigate the effect of the ultrasonic power on the AFS signal, with results shown in Fig. 2. AFS response from Hg^{2+} increased significantly with the increasing ultrasonic power throughout the range of 0–80 W followed by a plateau at higher power. However, no AFS signal could be detected even at the maximum power (120 W)

Download English Version:

<https://daneshyari.com/en/article/1227500>

Download Persian Version:

<https://daneshyari.com/article/1227500>

[Daneshyari.com](https://daneshyari.com)