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Original article

A sensitive and compact mercury analyzer by integrating dielectric barrier discharge induced cold vapor generation and optical emission spectrometry

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ABSTRACT

An environmentally friendly, low power consuming, sensitive and compact mercury analyzer was developed for the determination of mercury in water samples by integrating a thin film dielectric barrier discharge induced cold vapor reactor and a dielectric barrier discharge optical emission spectrometer into a small polymethyl methacrylate plate (10.5 cm length × 8.0 cm width × 1.2 cm height). Mercury cold vapor was generated when standard or sample solutions with or without formic acid were introduced to the reactor to form thin film liquid and exposed to microplasma irradiation and subsequently separated from the liquid phase for transport to the microplasma and detection of its atomic emission. Limits of detection of 0.20 $\mu g\,L^{-1}$ and 2.6 $\mu g\,L^{-1}$ were obtained for the proposed system using or not using formic acid, respectively. Compared to the conventional microplasma optical emission spectrometry used for mercury analysis, this system not only retains the good limit of detection amenable to the determination of mercury in real samples, but also reduces power consumption, eliminates the generation of hydrogen and avoids the use of toxic or unstable reductant. Method validation was demonstrated by analysis of a certified reference material of water sample and three real water samples with good spike recoveries (88–102%).

1. Introduction

Mercury contamination poses serious threats to public health globally because of its long distance transportation, persistent toxic and bio-accumulative characteristics [1–3]. In October 2013, governments from 92 countries signed the United Nations Environment Programme (UNEP) Minamata Convention on mercury to prevent from increasing mercury emission from the anthropogenic activities [4]. In order to monitor mercury emission, a variety of methods have been developed for the determination of mercury including electrothermal atomic absorption spectrometry (ET-AAS) [5], cold vapor generation atomic absorption spectrometry/atomic fluorescence spectrometry (CVG-AAS/AFS) [6–8] and inductively coupled plasma optical emission spectrometry/mass spectrometry (ICP-OES/MS) [9,10]. Although these methods can meet the requirement of mercury routine analysis, the used instrumentations are large, expensive, gas and power consuming and not suitable for real-time field analysis of mercury. Significant efforts have been devoted to develop portable, inexpensive and accurate methods for field analysis of mercury, which include colorimetric or fluorescent sensor systems [11–14]. Although these approaches can partly overcome the mentioned drawbacks occurred in the atomic spectrometric techniques, most of them remain several limitations including serious interferences from similar metal ions, insufficient sensitivity (limit of detection, LOD > 100 $nmol\,L^{-1}$) and the need of carefully designed and expensive DNA probes.

Recently, some atomic spectrometers were successfully miniaturized and used for the determination of trace mercury in various samples [15–25]. Among these, miniaturized plasma OES are preferred because of their small size, elimination of light source, low power and gas consumption. These microplasmas include dielectric barrier discharge (DBD) [15–18], microstrip microwave-induced plasma (MIP) [19–21], direct current atmospheric

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pressure glow microdischarge (dc-μAPGD) [22], electrolyte cathode discharge (ELCAD) [23,24], and capacitively coupled plasma (CCP) [25]. Unfortunately, all the reported microplasmas are seriously influenced even extinguished by high concentration of condense water or hydrogen due to their low atomization/excitation capability. The analytical performance of microplasma OES would be significantly improved if analytes can be converted to “dry” state species without generating hydrogen prior to introduction to microplasma [26]. CVG is considered as the most mature technique to accomplish this purpose because it not only alleviates the spectral or matrix interferences arising from liquid phase but also provides an almost 100% sample introduction efficiency [14–20]. However, the conventional CVG techniques using $SnCl_2$-HCl or sodium hydroborate ($NaBH_4$)-HCl system either generate hydrogen or use relatively toxic, unstable and expensive reagents. Photochemical vapor generation (PVG) has been recently proved that can be used to transport mercury vapor to microplasma without using toxic chemicals and generating hydrogen and thus significantly improve analytical performance [27], whereas the power consumption (>20 W) and size of UV photoreactor are strangling its further evolution in microplasma OES. Therefore, it is still a great challenge to develop a simple, environmentally friendly and low power consuming CVG technique for microplasma OES. Recently, microplasma induced CVG was developed to determine Hg, I, Os, Cd and Zn, including solution cathode glow discharge (SCGD) induced CVG, liquid electrode glow discharge (LEGD) induced CVG and dielectric barrier discharge induced (DBDI) CVG [28–32]. Due to their low power consumption (<10 W) and small size of both cold vapor generator and detection system, we believe that microplasma induced CVG coupling to microplasma OES retains a great potential in the real time field analysis of mercury. To the best of our knowledge, however, there are no reports using microplasma induced CVG coupled with microplasma OES for elemental determination.

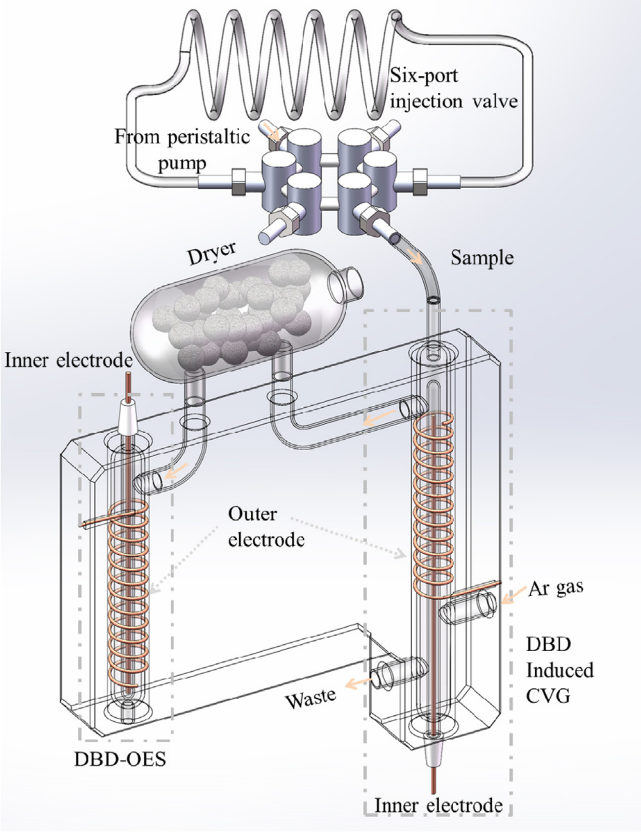

Fig. 1. Schematic of the experimental set-up.

Therefore, the purpose of the present work was to utilize flow injection thin film (TF) DBDI-CVG to couple with a DBD-OES for the detection of mercury in water samples. Mercury cold vapor (Hg^0) generated from the TF-DBDI-CVG system can be efficiently and rapidly separated from liquid phase and transported to the DBD microplasma for further atomization/excitation without introducing moisture and hydrogen. Thus the analytical performance particularly LOD could be significantly improved to 0.2 $\mu g\,L^{-1}$, which much lower than the maximum allowable concentration by World Health Organization (5 $\mu g\,L^{-1}$). It is worth to note that the DBDI-CVG and the DBD-OES can simultaneously work by sharing one single power supply. Therefore, the instrumental setup could be further miniaturized and the power consumption was reduced to about 10 W, which make the proposed system retain great potential for the real time field analysis of mercury.

2. Experimental

2.1. Instrumentation

The full instrumental setup is shown in Fig. 1 and mainly consists of a flow injection TF-DBDI-CVG system, a cylindrical dryer filled with $CaCl_2$ and a DBD-OES. The flow injection TF-DBDI-CVG system comprises a peristaltic pump (BT100-02, Baoding Qili Precision Pump Co., Ltd.), a six-port injection valve (Genuine Rheodyne Co., USA) equipped with a 3.0 mL sampling loop and a TF-DBDI-CVG reactor. The reactor integrates both cold vapor generation and gas liquid separation functions and is constructed according to the previous work [32]. Briefly, a copper wire (1.7 mm in diameter) housed in a small quartz tube (2.0 mm i.d. × 4.0 mm o.d. × 60 mm in length) is used as inner electrode and inserted into a big quartz tube (6.0 mm i.d. × 8.0 mm o.d. × 75 mm in length). The big quartz tube is tightly and evenly wrapped with copper wire (0.4 mm in diameter), which is used as outer electrode. Sample solution is introduced to the reactor, yielding a thin liquid film on the outer surface of the small quartz tube. The thin liquid film not only increases the plasma-liquid interaction area but also facilitates rapid escape of mercury vapor from the liquid phase. The DBD-OES is similar to that reported in previous work [33] and consists of a DBD excitation source and a commercial hand-held charge coupled device (CCD) spectrometer (Maya 2000 Pro, Ocean Optics Inc., Dunedin, FL, USA) with 0.4 nm of spectral resolution and a detectable spectral range from 200 to 600 nm. The DBD excitation source consists of a quartz tube (4.0 mm i.d. × 6.0 mm o.d. × 60 mm in length) and two copper wire electrodes, which one (1.7 mm in diameter) inserted into a quartz tube (2.0 mm i.d. × 4.0 mm o.d. × 45 mm in length) is used as inner electrode and the other (0.4 mm in diameter) tightly wrapped around the outer side of the tube is used as outer electrode, respectively. In order to miniaturize and immobilize the instrumentation, the DBDI-CVG reactor and DBD-OES were finally integrated on a small polymethyl methacrylate (PMMA) plate (10.5 cm length × 8.0 cm width × 1.2 cm height). The photograph of the DBDI-CVG-DBD-OES is showed in Fig. 2. A compact ac neon sign electron transformer power supply (NGB408BL, Electronic Equipment Factory of Jinshi, Guangzhou, China; 14 cm length × 6 cm width × 5 cm height, with a rated output of 8 kV, 30 kHz, and 24 W at 220 V, 60 Hz input) was used to supply power to both the DBDI-CVG reactor and DBD excitation source for generating and sustaining their plasma. The optical emission of mercury from the DBD excitation source is focused onto an optical fiber, and finally recorded with the CCD spectrometer.

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