



# Integrating photochemical vapor generation with photo-oxidation trapping for effective mercury removal from polluted water and its on-line monitoring



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## ABSTRACT

A new system was constructed and its performance evaluated for simultaneous mercury removal from water and on-line monitoring. The system consisted of a photochemical vapor generator (Photo-CVG, for mercury removal), a photo-oxidation trapping reactor (for collection of removed mercury) and a commercial atomic fluorescence spectrometer (AFS, for on-line monitoring). In the presence of organic acids, inorganic Hg(II) was converted by UV irradiation to mercury cold vapor in the Photo-CVG, which was then rapidly separated from the water sample in a gas-liquid separator (GLS) and transported to the photo-oxidation trapping reactor by air or argon for collection of the removed mercury and subsequent on-line monitoring by AFS for early-warning of mercury vapor leak to the environment. The factors affecting the efficiencies of cold vapor generation, transport, collection and on-line monitoring were carefully investigated. Under the optimized conditions, a limit of detection of  $0.003 \mu\text{g L}^{-1}$  was obtained for the proposed system by using only formic acid. Meanwhile, both the efficiencies of mercury removal and collection can be even close to 100% in the mercury concentration range of 2–100  $\mu\text{g L}^{-1}$ . The proposed system provided a safe, green, complete, simple and fast yet inexpensive method for low concentration mercury removal and on-line monitoring.

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## 1. Introduction

Due to its high level of toxicity, bioaccumulation and persistence, mercury has been regarded as one of the most toxic pollutants [1–3]. The United States Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) lists mercury and its compounds in the third place on the “Priority List of Hazardous Substances” and the European Water Framework Directive (2000/60/EG) classifies mercury as one of the thirty “precarious dangerous pollutants”. The World Health Organization (WHO) and the United States Environmental Protection Agency (EPA) suggest a maximum intake of mercury of  $1.6 \mu\text{g kg}^{-1}$  and  $0.1 \mu\text{g kg}^{-1}$  per week for human. For controlling and reducing mercury emission, many governments signed the Minamata Convention on Mercury in October of 2013, which brought a great pressure to major mercury emitters to reduce their mercury emission, including China and the United States [4]. Almost all of mercury species are toxic, with organic mercury compounds generally being more toxic than inorganic

species. Moreover, inorganic mercury ( $\text{Hg}^{2+}$ ) may be converted into more toxic compounds (such as methylmercury) under a certain environmental conditions such as light irradiation or biological activity [3]. The previous work [5] concluded that the most important sources of mercury pollution to aquatic system include atmospheric deposition, urban and industrial discharges, agricultural materials, and mining combustion. During the past several decades, a number of efforts have been derived to develop effective methods for the determination and removal of mercury in polluted water [6–10].

Among the methods used for the determination of mercury, cold vapor generation atomic absorption spectrometry/atomic fluorescence spectrometry/inductively coupled plasma optical emission spectrometry/inductively coupled plasma mass spectrometry (CVG-AAS/AFS/ICP-OES/ICP-MS) are the most frequently used methods because of the low memory effect, high sensitivity and anti-interferences capability owing to the advantages of CVG, including high sample introduction efficiency (nearly 100%), efficient matrix separation and analyte preconcentration [6,11,12]. However, the conventional CVG techniques using  $\text{SnCl}_2\text{-HCl}$  or sodium hydroborate ( $\text{NaBH}_4$ )-HCl usually use relatively toxic, unstable and expensive reagents. These reagents can be converted to secondary pollutants. Therefore, it is desired to develop a new CVG method to replace the conventional techniques. Recently, photochemical cold

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vapor generation (Photo-CVG) has been developed to eliminate the use of unstable or toxic reductants such as  $\text{SnCl}_2$  and  $\text{NaBH}_4$  [13–17]. Despite increasing interest in Photo-CVG over the past several years, this technique has been used for the determination of mercury but not for mercury removal.

Considering the adversely environmental and biological effect of mercury pollution in water, large amount of techniques have been developed to remove mercury from water, such as chemical precipitation [18], ion-exchange [19], adsorption [20], membrane filtration [21], and electrochemical treatment [22]. For example, Chang et al. [23] developed a new adsorbent mixing Au nanoparticles 13 nm in diameter with  $\text{Al}_2\text{O}_3$  particles 50–200  $\mu\text{m}$  in diameter for efficient removal of inorganic mercury, methylmercury, ethylmercury and phenylmercury. Wagner-Döbler et al. [24] described an enzymatic reduction method to remove inorganic mercury from wastewater by using mercury resistant bacteria. Although these methods are of high efficiency to remove mercury from aquatic system, they usually required a large excess of expensive adsorbents and chemicals. Moreover, a large amount of mercury-containing sludge is produced, which may be more danger to the environment and the human being. To overcome these drawbacks, photocatalytic reduction using a nano-catalyst or ultrasound-promoted reduction of inorganic mercury to mercury vapor ( $\text{Hg}^0$ ) for its removal has been reported [25, 26]. These methods not only used relatively expensive nanomaterials but also direct release  $\text{Hg}^0$  and possibly the nano-catalyst to the atmosphere and the environmental water. To the best of our knowledge, Photo-CVG without a nano-catalyst has not yet been used for low concentration mercury removal from mercury-polluted water.

The purpose of this work is therefore to accomplish the integration of mercury removal from water, collection of removed mercury and on-line monitoring into a single system by using only Photo-CVG without any catalyst. The proposed technique uses only formic acid and then retains the advantages of the conventional CVG, eliminates the use of expensive, unstable and toxic reductant and the generation of sludge. It is worthwhile to note that generated mercury vapor was on-line trapped in a quartz tube by photo-oxidation, thus avoiding a secondary pollution of mercury. Any mercury leak from the system was on-line monitored by use of AFS.

## 2. Experimental

### 2.1. Instrumentation

A schematic of the whole experimental system is shown in Fig. 1. The system comprises a peristaltic pump (BT100-02, Baoding Qili Precision Pump Co., Ltd., China), a photochemical vapor generator, a homemade gas liquid separator (GLS), a photo-oxidation reactor and a commercial atomic fluorescence spectrometer (AFS-2202, Beijing Haiguang Instrument Co., Beijing, China). The spectrometer fitted with a quartz atomizer

**Table 1**  
Instrumental operating parameters for AFS.

Parameter	Value
PMT voltage	– 300 V
HCL main current	80 mA
HCL assistant current	40 mA
Carrier gas flow rate	500 mL min <sup>-1</sup>
Shield gas flow rate	800 mL min <sup>-1</sup>
Observation height	10 mm
Quantification mode	Peak area

and a coded high intensity mercury hollow cathode lamp (HCL) was used for determination or monitoring of atomic mercury vapor from the system. The optimized operating conditions are summarized in Table 1. The photochemical vapor generator consists of a polytetrafluoroethylene (PTFE) tube (18 cm × 1.0 mm i.d. × 1.2 mm o.d.) wrapped around a low pressure mercury vapor UV lamp (253.7 nm, 15 W, Philip, Holland). The photo-oxidation reactor used for trapping the removed mercury vapor was similar to the photochemical vapor generator, but quartz tubes (25 cm × 1.5 mm i.d. × 2.0 mm o.d.) with different length were used as an alternative to the PTFE tube. Both the photochemical vapor generator and the photo-oxidation reactor were wrapped with aluminum foils, which served to increase efficiency by reflecting UV radiation from the lamp back onto the reaction zone.

### 2.2. Standard solutions

All solutions were prepared by using high purity 18.2 M $\Omega$  cm deionized water (DIW) produced from a water purification system (Chengdu Ultrapure Technology Co., Ltd., China). 1000 mg L<sup>-1</sup> stock standard solution of mercury (GBW08617) was obtained from the National Research Centre for Certified Reference Materials, China. Calibration solutions were prepared daily by dilution of the stock standard solution with DIW and formic acid (88%, Kelong Chemical Factory, China). The wastewater samples were prepared by adding the stock standard solution to real river water. High purity argon (99.99%) was purchased from Qiaoyuan Gas Co. (Chengdu, China). The river water was collected from the Funan River of Chengdu City.

### 2.3. Procedure

The standard, sample or wastewater solutions containing formic acid were pumped through the photochemical vapor generator to expose to the UV irradiation and the mercury vapor ( $\text{Hg}^0$ ) was generated immediately in the generator. After UV irradiation, the solution was flushed into the GLS wherein an argon flow was introduced to separate  $\text{Hg}^0$  from liquid phase. Mercury cold vapor was directly transported into the AFS for the detection of mercury atomic fluorescence signal or swept

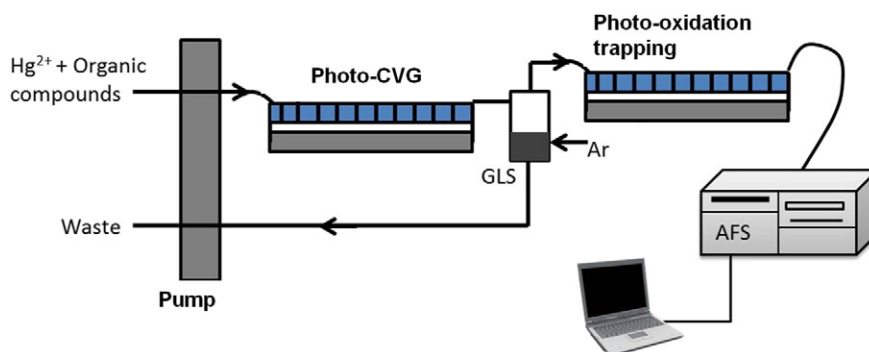


Fig. 1. Schematic of the experimental set-up.

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