Journal of Chromatography A, 1218 (2011) 4462–4467

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Solution cathode glow discharge induced vapor generation of mercury and its application to mercury speciation by high performance liquid chromatography–atomic fluorescence spectrometry

Qian He, Zhenli Zhu*, Shenghong Hu, Lanlan Jin

State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China

ARTICLE INFO

Article history:
Received 7 September 2010
Received in revised form 22 March 2011
Accepted 11 May 2011
Available online 18 May 2011

Keywords:
Solution cathode glow discharge
Vapor generation
Mercury speciation

ABSTRACT

A novel solution cathode glow discharge (SCGD) induced vapor generation was developed as interface to on-line couple high-performance liquid chromatography (HPLC) with atomic fluorescence spectrometry (AFS) for the speciation of inorganic mercury (Hg^{2+}), methyl-mercury (MeHg) and ethyl-mercury (EtHg). The decomposition of organic mercury species and the reduction of Hg^{2+} could be completed in one step with this proposed SCGD induced vapor generation system. The vapor generation is extremely rapid and therefore is easy to couple with flow injection (FI) and HPLC. Compared with the conventional HPLC–CV-AFS hyphenated systems, the proposed HPLC–SCGD-AFS system is very simple in operation and eliminates auxiliary redox reagents. Parameters influencing mercury determination were optimized, such as concentration of formic acid, discharge current and argon flow rate. The method detection limits for HPLC–SCGD-AFS system were 0.67 $\mu g\,L^{-1}$ for Hg^{2+}, 0.55 $\mu g\,L^{-1}$ for MeHg and 1.19 $\mu g\,L^{-1}$ for EtHg, respectively. The developed method was validated by determination of certified reference material (GBW 10029, tuna fish) and was further applied for the determination of mercury in biological samples.

1. Introduction

Mercury is a well recognized global pollutant and one of the most toxic elements in environment, easily passing through biological membranes, such as skin, respiratory, and gastrointestinal tissues [1]. Mercury has been introduced into the environment as three major forms, elemental Hg^0, inorganic Hg^{2+} and organic Hg. The inorganic mercury (Hg^{2+}) and methyl-mercury (MeHg) are the two major species generally found in various biological samples [2]. As the bioavailability and toxicity of mercury is greatly affected by its chemical speciation, it is important to develop a simple method to simultaneously determine mercury species in biological samples with high sensitivity and good accuracy.

Both hyphenated techniques and non-chromatographic speciation analysis methods [3–5] have been proposed for mercury speciation. The hyphenated techniques of chromatographic system are widely employed since it can provide the most complete information on the species distribution and even structure. It is achieved by coupling the chromatographic system such as gas chromatography (GC) [6], high performance liquid chromatography (HPLC) [7–10], ion chromatography [11,12] and capillary electrophoresis (CE) [13] with a highly sensitive element detector, including AAS, AFS, ICP-MS and ICP-AES. AFS is an ideal detection technique for speciation studies concerning hydride forming elements (mainly As, Se and Sb) and Hg [14]. In recent years, HPLC–CV-AFS is used extensively to mercury speciation ascribed to its high sensitivity and low cost.

In previous HPLC–CV-AFS hyphenated system, organic mercury species were usually digested with post-column on-line oxidation, such as bromine [15], potassium dichromate [16] and potassium persulfate [17,18]. Although the chemical oxidation can be achieved at ambient temperature, long reaction time for efficient conversion is necessary and both oxidative and reductive reagents like KBH_4 are needed. Meantime, some studies [19] used post-column ultraviolet light to convert organic mercury species to Hg^{2+}, followed by reduction to Hg^0 to produce fluorescence signals in AFS. Although the UV irradiation system facilitates the decomposition of organic mercury species, their integration into an online system complicates the system design and the reductive reagents are still needed. Later studies found that under UV irradiation, the decomposition of organic mercury species and the reduction of Hg^{2+} could be completed in one step with formic acid [20] or formic acid and sodium formate mixture as a hole scavenger on nano TiO_2 [21], which simplified the flow system and eliminated the possibility of contamination originating from additional chemicals. Interestingly, Yin et al. [22] had developed a new method using photo-induced chemical vapor generation (CVG) with formic acid in mobile phase as reaction reagent as interface to on-line couple HPLC with AFS for

* Corresponding author. Tel.: +86 27 67883455.
E-mail address: zhuzl03@gmail.com (Z. Zhu).

0021-9673/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2011.05.034

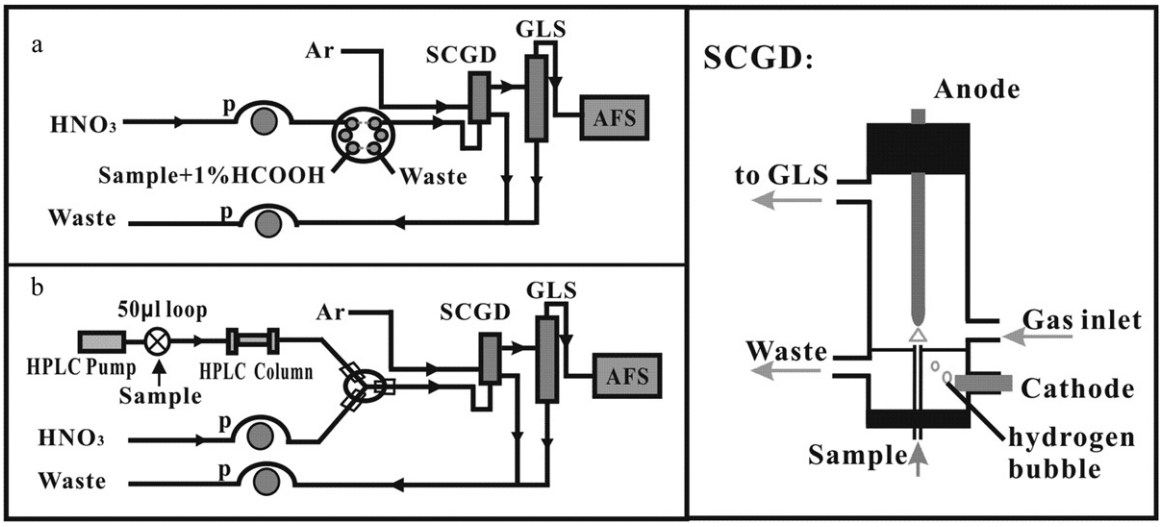

Fig. 1. Schematic illustration of FI-SCGD-AFS system (a) and HPLC–SCGD-AFS system (b) (P: peristaltic pump). The right shows the SCGD cell system, GLS refers to gas–liquid separator.

the speciation of mercury. Similar approaches were proposed later such as acetic acid and 2-mercaptoethanol used as photochemical reagent in the mobile phase [23] and the organic mercury compounds could be on-line converted to elemental Hg in the presence of L-cysteine, HCl and KBH_4 [24], without post-column interface, strong oxidants and organic solvents.

Recently, solution cathode glow discharge provides a new alternative vapor generation method of mercury [25] and iodine [26] with rapid vapor generation speed and elimination of redox regents. SCGD uses an electrolyte solution as the cathode in a dc glow discharge, with a metal counter electrode positioned in the atmosphere above the solution. It is characterized by in situ generation of highly reactive species, such as the hydroxyl radical (•OH) and hydrogen radical (•H) in water, thereby eliminating the need for externally supplied sources of any redox regents. In our previous study, a cold vapor generation technique for Hg analysis was proposed based on SCGD [25]. Without need for chemical reducing agent, dissolved mercury (Hg^{2+}) were readily converted to volatile mercury vapor. However, the feasibility of vapor generation of methyl-mercury and ethyl-mercury by SCGD has never been tested and therefore the speciation of mercury species (inorganic mercury, methyl-mercury and ethyl-mercury) has never been done through SCGD coupled with HPLC–AFS.

In the present work, the SCGD induced vapor generation of methyl-mercury and ethyl-mercury as well as inorganic mercury was investigated by AFS. In addition, it was designed as an interface to couple HPLC with AFS for mercury speciation. The decomposition of organic mercury species and the reduction of Hg^{2+} could be completed in one step with SCGD induced vapor generation system without any redox reagents. Parameters influencing mercury separation and determination were optimized and analytical figures of merit were determined.

2. Experimental

2.1. Instrumentation

The schematic experiment setup of the FI-SCGD-AFS and HPLC–SCGD-AFS system is presented in Fig. 1. The SCGD design has been described in detail elsewhere [25]. For FI-SCGD-AFS system, a model FIA-3110 flow injection system (Beijing Titan Instrumentals Co., Ltd., Beijing, China) equipped with two peristaltic pumps and a standard rotary injection valve (eight ports on the rotor and eight ports on the stator) was connected to SCGD cell. After the sample loop (300 μL) was filled with sample mixed with 1% formic acid, the injection valve was switched to the injection position to introduce sample into the carrier stream (pH 1.3 HNO_3) manually. The carrier stream was supplied to the SCGD cell through a peristaltic pump (BT 100-1L, Baoding Langer Constant Flow Pump Co., Ltd., China). For HPLC–SCGD-AFS system, sample was injected by a Rheodyne model 7725i injection valve with a 50 μL sample loop (Rheodyne, Cotati, CA, USA) and the mobile phase was delivered by a LC-10AT VP (Shimadzu, Japan) pump. The HPLC separation was achieved by using a ZORBAX SB-C18 column (2.1 mm × 50 mm × 5 μm, Agilent, USA). The HPLC effluent was mixed with carrier stream and entered into the SCGD cell. The operational parameters of FI-SCGD-AFS and HPLC–SCGD-AFS systems are shown in Table 1.

Table 1
FI-SCGD-AFS and HPLC–SCGD-AFS operating conditions for mercury determination and separation.

Parameter	Optimized value
Flow injection	
Injection volume	300 μL
HPLC	
Column	ZORBAX SB-C18, 2.1 mm × 50 mm × 5 μm
Mobile phase	0.06 mol L^{-1} ammonium acetate, 0.1% 2-mercaptothanol, pH 6.8
Flow rate of mobile phase	0.4 mL min^{-1}
Injection volume	50 μL
SCGD vapor generation	
Discharge current	55 mA
Argon flow rate	400 mL min^{-1}
Concentration of HNO_3	pH 1.3
Flow rate of HNO_3	1.5 mL min^{-1}
AFS	
Lamp	Mercury hollow cathode lamp, 253.7 nm
PMT voltage	−280 V
Flow rate of auxiliary gas	600 mL min^{-1}
Lamp current	40 mA
Atomizer temperature	Room temperature
Atomizer height	8.0 mm

When mercury containing standards were introduced into the SCGD plasma, volatile mercury species were produced. The products were swept by an argon carrier gas through a gas–liquid separator (GLS), and then detected by model AFS-9130 atomic fluorescence spectrometer (Beijing Titan Instrumentals Co., Ltd.,