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

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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

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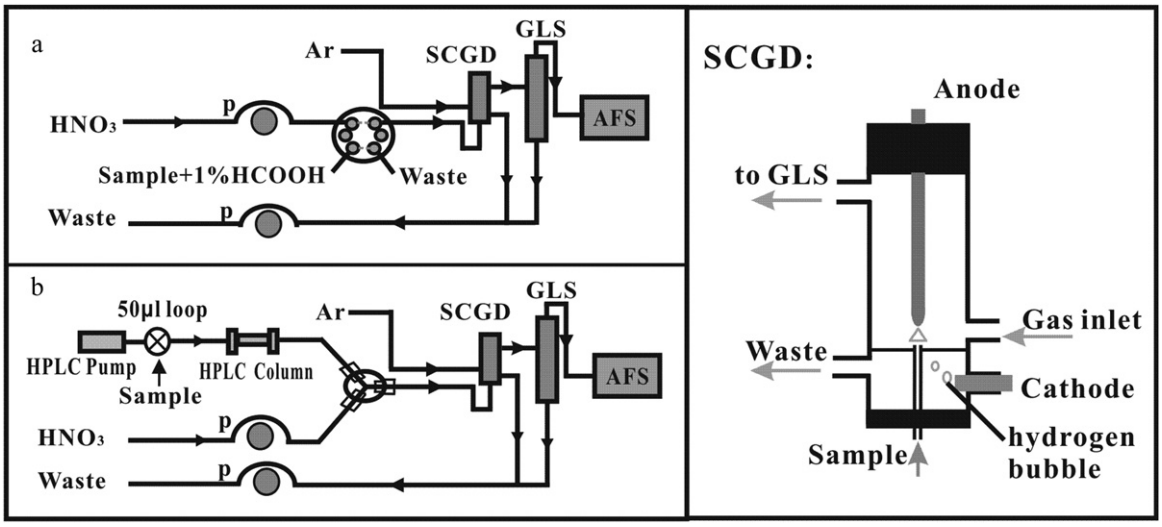

Fig. 1. Schematic illustration of FI-SCGD-AFS system (a) and HPLC–SCGD-AFS system (b) (P: peristaltic pump). The right shows the SCGD cell system, GLS refers to gas–liquid separator.

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.,

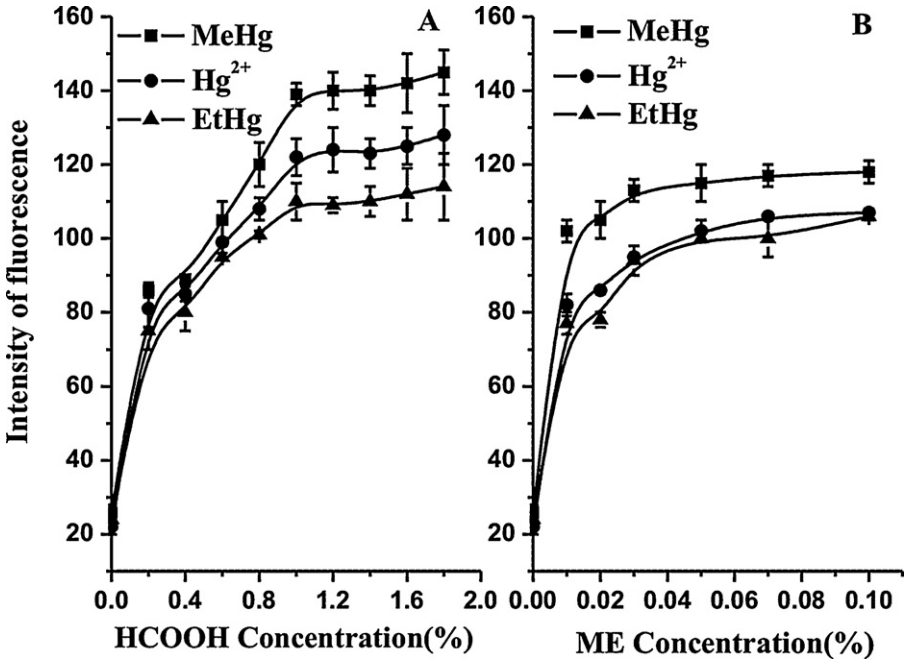

Fig. 2. Comparison of the effect of (A) formic acid (HCOOH) and (B) 2-mercaptoethanol (ME) on mercury fluorescence signal intensity. Each mercury species was present at 10 μg L^{-1}. Other conditions are given in Table 1. Error bars in the figure represent standard deviations of the results.

Beijing, China) equipped with a mercury hollow cathode lamp (HCL) (253.7 nm, Beijing General Research Institute For Non-Ferrous Metals, China). The argon carrier gas was connected to the gas inlet of the SCGD. The effluent of GLS was directly connected to the atomizer of AFS using latex tubing (6 mm O.D. × 70 cm length). Coolant water circulating through the GLS was held at approximately 0.1 °C with a cooling water thermostat (SDC-6, Ningbo Scienz Bio-tech Co., Ltd., China) for the cooling of GLS.

2.2. Reagents, standards and mobile phases

All reagents used were at least of analytical agent grade and 18.2 MΩ cm resistivity Milli-Q water (90005-02, Labconco water pro ps, Canada) was used throughout this study. The following commercial products were used: nitric acid (Sinopharm Chemical Reagent Co., Ltd., China), formic acid (Tanjin Kaitong Chemical Reagent Co., Ltd., China), ammonium acetate (Tanjin Hongyan Chemical Reagent Co., Ltd., China), 2-mercaptothanol (Wuhan Goodti meBio-Technology Co., Ltd., China), HPLC-grade methanol (Tedia, USA), potassium hydroxide (Tianjin Reagent Chemicals Co., Ltd., China), dichloromethane (Tianjin Reagent Chemicals Co., Ltd., China), hydrochloric acid (Xinyang Chemical Reagent Co., Ltd., China), sodium thiosulfate (Beijing Asia-Pacific Chemical Co., Ltd., China).

The stock standard solution of inorganic mercury (GBW 08617), methyl-mercury (GBW 08675) and ethyl-mercury (GBW (E) 081524) were purchased from National Research Center for Standard Materials (Beijing, China). Stock solutions of inorganic mercury, methyl-mercury and ethyl-mercury were stored in pre-cleaned glass vials and kept at 4 °C. Working standard solutions for each individual mercury species were prepared daily by stepwise dilution of the stock solutions with Milli-Q water.

2.3. Samples

Certified reference material GBW 10029 (tuna fish, from National Research Center for Standard Materials, Beijing, China) was analyzed to demonstrate the accuracy of the present method. The fish tissue samples were taken from Beihai (Guangxi, China). The fish tissue was dried, cut into pieces and stored at 4 °C.

2.4. Sample preparation

The samples were prepared with referencing to literature [27]. Briefly, into a 50 mL glass centrifuge tube was added accurately weighed lyophilized and ground sample (~0.4 g) and 2 mL 25% (m/v) KOH (in methanol) and the tube was shaken overnight. Then, 6 mL of CH_2Cl_2 was added, and the solution was titrated by 1.5 mL concentrated HCl. The resulting solution was shaken for 15 min. After centrifuging at 3000 rpm for 15 min, the CH_2Cl_2 phase was accurately transferred into a 10 mL glass centrifuge tube and 1 mL of 10 mmol L^{-1} sodium thiosulfate was added. The mixture was shaken for 45 min. After centrifuging at 3500 rpm for 15 min, the water phase was taken as sample for the determination of organic mercury by HPLC–SCGD-AFS.

3. Results and discussion

The vapor generation is instantaneous and thus is easily coupled with flow injection. Therefore, a flow injection-atomic fluorescence spectrometry system based on SCGD was used to test the feasibility of vapor generation of MeHg and EtHg by SCGD in preliminary study. In addition to inorganic mercury (Hg^{2+}), MeHg and EtHg also can be directly transformed to elemental mercury by SCGD. Several experimental parameters of vapor generation were optimized through FI-SCGD-AFS system. At last, a simple interface of HPLC and AFS through SCGD was developed for the speciation of mercury species.

3.1. Effect of parameters on mercury vapor generation

The effect of concentration of formic acid, discharge current and argon flow rate were evaluated to achieve maximum sensitivity of fluorescence intensity of three mercury species. The peak height was used as the analytical parameter and three replicate injections for each data point were made.

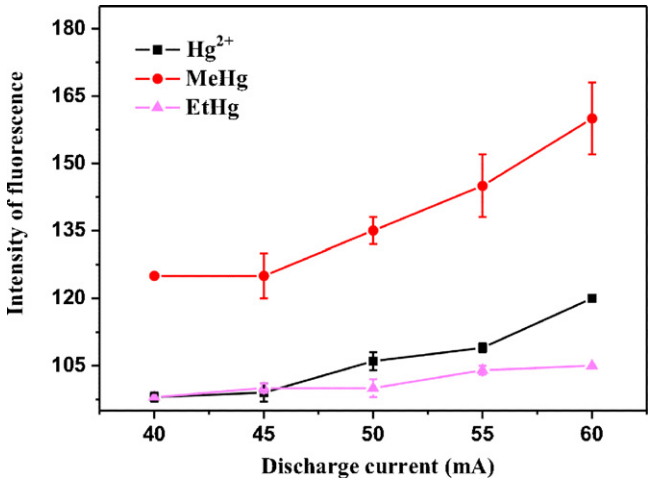

Fig. 3. Effects of discharge current on fluorescence signal intensity. Each mercury species was present at 10 μg L^{-1}. Other conditions are given in Table 1. Error bars in the figure represent standard deviations of the results.

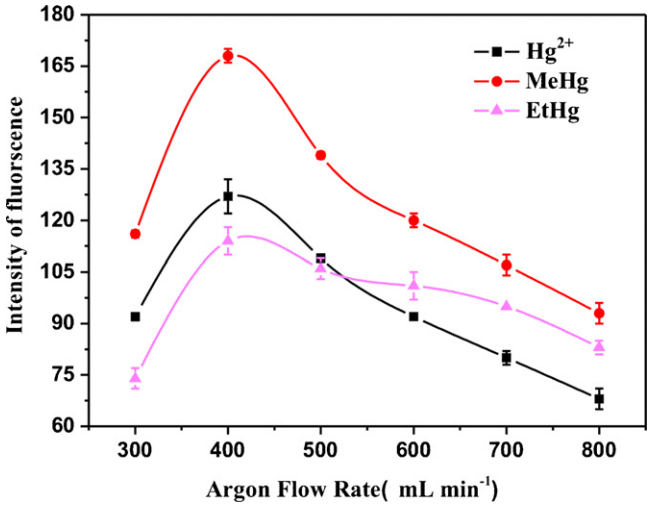

Fig. 4. Effects of argon carrier gas flow rate on fluorescence signal intensity. Each mercury species was present at 10 μg L^{-1}. Other conditions are given in Table 1. Error bars in the figure represent standard deviations of the results.

It was reported for both UV-CVG [20] and SCGD [25] that the sensitivity for Hg vapor generation can be enhanced by the presence of low-molecular weight organic substances. Therefore, the effect of concentration of formic acid (0–1.8%, v/v) added in mercury solutions mixed with carrier stream was investigated (Fig. 2A). Low fluorescence signals were observed for MeHg, EtHg and Hg^{2+} in the absence of formic acid in the solution, since SCGD can induce radical reactions in water to produce hydroxyl radical (•OH) and hydrogen radical (•H) which might result in the decomposition of organomercurials and reduction of Hg^{2+}. For three mercury species, the fluorescence signals were all increased sharply with the increase of formic acid concentration up to 1%, then leveled off. This probably is due to the organic compounds yield additional reducing reagents in the discharge [25]. In addition, higher concentration of formic acid caused the instability of the plasma due to more bubble production. Therefore, 1% of formic acid was chosen in the further studies.

The effect of discharge current on the Hg vapor generation was also investigated. The discharge can be operated at currents ranging from 40 to 60 mA. It is observed from Fig. 3 that all the fluorescence signals of MeHg, EtHg and Hg^{2+} increased with the increasing of discharge current. However, at very high currents, excessive heating of the anode took place and the discharge became unstable. Therefore, a discharge current of 55 mA was employed in the remaining parts of the study.

Argon is usually employed as both carrier gas and auxiliary gas in AFS. The role of the argon carrier gas of SCGD is bringing volatile mercury species, produced in the SCGD, into the atomizer. Experiments were undertaken to optimize the carrier gas flow rate from 300 to 800 mL min^{-1}. As can be seen in Fig. 4, the maximum signals for MeHg, EtHg and Hg^{2+} were all obtained at a flow rate of 400 mL min^{-1}. If carrier gas is excessive, the concentrations of element mercury in atomizer will be diluted and its residence time would be shorten, which resulted in low sensitivity. However, lower argon flow rate cannot bring volatile mercury into atomizer efficiently thus decreased the sensitivity [24]. Accordingly, a carrier gas flow rate of 400 mL min^{-1} was chosen for the remaining studies.

3.2. The vapor generation efficiencies for three mercury species

The vapor generation efficiencies for each of the mercury species were estimated from a comparison of the fluorescence intensity of 10 μg L^{-1} mercury standard solutions and waste solutions after the standards submitted to SCGD by FI-SCGD-AFS system. Signals for MeHg, Hg^{2+} and EtHg wastes were about 9.2% (±0.20%), 9.6% (±0.05%) and 11.4% (±0.10%) of the feed values, respectively, resulting in the vapor generation efficiencies of about 90.8% (±0.20%), 90.4% (±0.05%) and 88.6% (±0.10%) for MeHg, Hg^{2+} and EtHg, respectively.

3.3. Speciation of mercury by HPLC–SCGD-AFS

Since the decomposition of organic mercury species and the reduction of Hg^{2+} is instantaneous and could be completed in one step with this proposed SCGD induced vapor generation system, it was easy to couple it with HPLC for the speciation of mercury. The HPLC effluent was mixed with carrier stream and entered into the SCGD cell. The products of SCGD were swept by an argon stream through a gas–liquid separator (GLS) and the effluent of GLS was directly connected to the atomizer of AFS using latex tubing for determination.

To separate the three species of mercury, a mobile phase consisting of Milli-Q water, 0.06 mol L^{-1} NH_4Ac (pH 6.8) and 2-mercaptoethanol was employed. 2-Mercaptoethanol was used as an ion-pair reagent in the mobile phase for HPLC separation of mercury species [8]. The effect of 2-mercaptoethanol concentration on separation was studied in the range from 0.01 to 0.12% (v/v) and the result is shown in Fig. 5. It is observed that the three mercury species can be completely baseline separated except the concentration of 2-mercaptoethnol at 0.12%. Moreover, increasing the 2-mercaptoethnol concentration significantly decreased retention times of the three mercury species. Therefore, the concentration of 2-mercaptoethnol was set as 0.10% in the mobile phase for the later studies. Meantime, the effect of formic acid added in samples mixed with the carrier stream on the sensitivity of mercury was also investigated, but no evident enhancement for the signal of mercury was found. It indicated that the organic substances (2-mercaptoethanol) in the mobile phase could also increase the vapor generation efficiency of mercury as well as formic acid.

In order to identify whether this phenomena was induced by 2-mercaptoethanol, a flow injection coupled with atomic fluorescence spectrometry based on SCGD (FI-SCGD-AFS) system was employed. The effect of 2-mercaptoethanol (ME) on the efficiency of mercury vapor generation was evaluated by varying the concentration of ME from 0 to 0.1% (v/v) (Fig. 2B). Similar to formic acid, it was found that 2-mercaptoethanol is effective in enhancing the mercury fluorescence signal. The fluorescence signals of the three

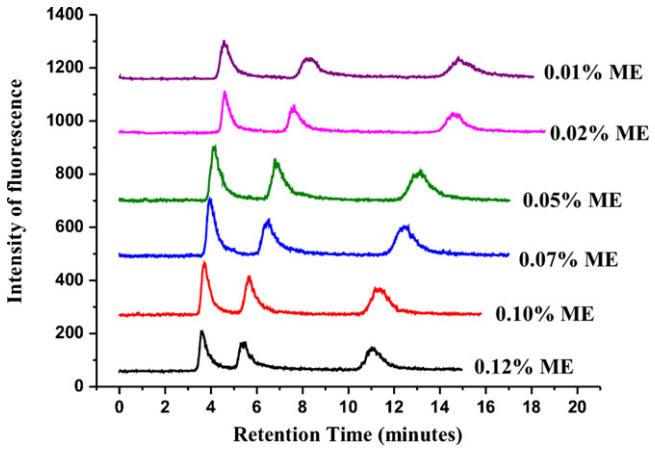

Fig. 5. Effects of 2-mercaptoethanol (ME) concentration on separation performance of mercury species in the mobile phase containing 0.06 mol L^{-1} NH_4Ac at pH 6.8. Concentration of mercury species: 100 μg L^{-1}. All spectra have the same intensity scale and have been shifted vertically for clarity.

studied mercury species all raised sharply when the concentrations of ME were increased from 0 to 0.03%, but then reached a relatively steady level for further increase in ME concentrations up to 0.1%. Moreover, the fluorescence signals of all the three mercury species when generated in the presence of 0.03% 2-mercaptoethanol were comparable (about 80%) to those generated with 1.0% formic acid. Since 2-mercaptoethanol was already present in the mobile phase at a concentration of 0.1%, which is sufficient to enhance the efficiency of mercury vapor generation to an extent similar to 1.0% formic acid, addition of formic acid is not needed for mercury speciation in the present developed method.

Under the optimum conditions of separation and determination, the three mercury species were fully resolved with a mobile phase of 0.06 mol L^{-1} NH_4Ac and 0.1% 2-mercaptoethanol at pH 6.8 and the separation completed within 13 min.

3.4. Analytical figures of merit

The figures of merit for three mercury species by HPLC–SCGD-AFS system were investigated under the optimized conditions (Table 2). Calibration curves based on peak height were linear for three species in the concentration range studied (5–200 μg L^{-1} for HPLC–SCGD-AFS system). Higher concentrations of mercury were not investigated because of possible contamination of the system.

The detection limits (LOD) for HPLC–SCGD-AFS system were calculated based on a 3σ criterion, where σ is the estimate of the standard deviation of eleven repetitive measurements of nitric acid blank. The LOD for Hg^{2+}, MeHg and EtHg were found to be 0.67 μg L^{-1}, 0.55 μg L^{-1} and 1.19 μg L^{-1}, respectively. The detection limits of the present method are comparable to that with other photochemical vapor generation techniques (Table 3). In addition, the relative standard deviation ($n = 3$) with a 50 μg L^{-1} standard was 5.9% for Hg^{2+}, 2.7% for MeHg and 5.4% for EtHg, respectively. The recoveries were 97.7%, 101.5% and 100.1% for MeHg, Hg^{2+} and EtHg by spiking 50 μg L^{-1} mercury species into tap water, respectively. The reason for the differences in sensitivities of three mercury species is not clear now. It indicated that the efficiency of vapor generation may depend on the chemical form of mercury in the sample. Similar results were also reported in conventional chemical vapor generation [28] and photochemical vapor generation system. For example, the sensitivity of methylmercury is much higher than that of Hg^{2+} in photochemical vapor generation [29].

Table 2
Analytical performance of the developed HPLC–SCGD-AFS system.

Compound	MeHg	Hg^{2+}	EtHg
Linearity equation	$Y^a = 1.90$ (± 0.10)$X^b + 4.1$ (± 5.5)	$Y = 1.57$ (± 0.07)$X + 2.9$ (± 7.3)	$Y = 0.88$ (± 0.06)$X + 8.5$ (± 6.0)
Correlation coefficient	0.9974	0.9969	0.9934
LOD (μg L^{-1})	0.55	0.67	1.19
RSD (%)	2.7[c]	5.9	5.4
Retention time ± SD (min)	3.81 ± 0.11	5.94 ± 0.30	11.68 ± 0.27
Recovery (%)	97.7[d]	101.5	100.1

[a] Peak height.
[b] Concentration (μg L^{-1}).
[c] Standard concentration, 50 μg L^{-1}, $n = 3$.
[d] Recovery for spiking with 50 μg L^{-1} of each individual mercury species, $n = 3$.

Table 3
Comparison of the developed HPLC–SCGD-AFS system with other photochemical vapor generation techniques in terms of limits of detection (LOD) for mercury species.

Species	Detection method	LOD (μg L^{-1})	Reference
MeHg/Hg^{2+}/EtHg	HPLC–SCGD-AFS	0.55/0.67/1.19	This work
MeHg/EtHg/PhHg	HPLC–UV-CVG-AFS	0.81/0.20/0.87	[20]
MeHg/Hg^{2+}/EtHg	HPLC–UV-CVG-AFS	0.22/0.53/0.18	[23]
MeHg/Hg^{2+}/EtHg	HPLC–UV-CVG-AFS	0.03/0.08/0.03	[22]

Table 4
Results of mercury species contents in GBW 10029 and dry fish tissue samples.

Sample	Certified value (ng g^{-1})	Determined values (ng g^{-1})		
	MeHg	MeHg	EtHg	Hg^{2+}
GBW 10029	840[a] ± 30[b]	853 ± 35	–	–
Shrimp tissue	–	482 ± 32	263 ± 28	–
Cuttlefish tissue	–	193 ± 3	–	–

[a] $n = 3$.
[b] Standard deviation.

3.5. Method application for the speciation of mercury

The accuracy of the method was evaluated by analyzing MeHg content in certified reference material GBW 10029 (tuna fish). Only the MeHg was detected in the tuna fish sample. Inorganic mercury was not measured because the certified value is below the LOD of the present method. The results are summarized in Table 4, which shows good agreement between the determined

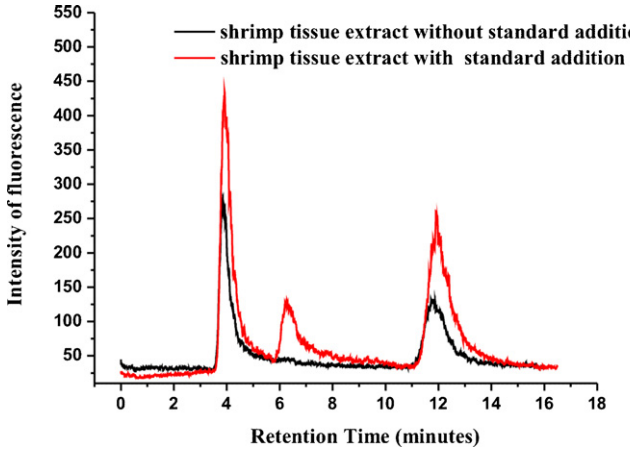

Fig. 6. Chromatogram of shrimp tissue extract sample spiked with or without 100 μg L^{-1} each Hg species. Operation conditions are given in Table 1.

value and the certified value. The proposed method was also applied to the speciation of mercury in dry fish tissue samples. Fig. 6 shows the chromatograms obtained from shrimp tissue extract with and without standard addition of 100 $\mu g\,L^{-1}$ of mercury standards. Both MeHg and EtHg were detected in the shrimp tissue sample. Our previous study [25] had reported the negative effect of chloride ion on mercury vapor generation. And the organic substances like formic acid and 2-mercaptoethanol used in this experiment enhance the efficiency of mercury vapor generation. Taking these potential interferences in biologic tissues into consideration, the method of standard addition was used to determine the mercury concentration in CRM and the dry fish tissue samples.

4. Conclusions

A novel method for the speciation of Hg^{2+}, MeHg and EtHg with HPLC–AFS has been developed based on solution cathode glow discharge induced vapor generation. The organic mercury species were decomposed and reduced to elemental Hg in one step through SCGD induced advanced redox processes. It eliminates the need for chemical redox reagents. The vapor generation of three mercury species can be readily accomplished in a plain HNO_3 medium. The vapor generation is instantaneous and therefore easily coupled with flow injection and HPLC. The presence of either formic acid or 2-mercaptoethanol could greatly enhance Hg vapor generation efficiency. The 2-mercaptoethanol in the mobile phase is enough for this purpose, thus no formic acid was used in HPLC–SCGD-AFS system. Under optimized conditions, separation of Hg^{2+}, MeHg and EtHg could be achieved on a C18 reverse phase column within 13 min. The developed method was validated by determination of certified reference material GBW 10029 and was further applied in determination of biological samples.

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