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Microwave-enhanced cold vapor generation for speciation analysis of mercury by atomic fluorescence spectrometry

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ABSTRACT

A new and simple cold vapor generation technique utilizing microwave irradiation coupled with atomic fluorescence spectrometry is developed for the speciation analysis of mercury in biological and geological samples. In the presence of formic acid, inorganic mercury (Hg^{2+}) and total mercury (both Hg^{2+} and methylmercury (MeHg)) can be converted to mercury cold vapor (Hg^0) by microwave irradiation without and with H_2O_2, respectively. The cold vapor was subsequently released from the liquid phase and rapidly transported to an atomic fluorescence spectrometer for the mercury detection. Optimum conditions for vapor generation as well as interferences from concomitant ions were carefully investigated. The conventionally required evaporation of the remnants of acid or oxidants was avoided because no significant interferences from these substances were observed, and thus analyte loss and potential contamination were minimized. A limit of detection of $0.005\ ng\ mL^{-1}$ for total mercury or inorganic mercury was obtained. A precision of less than 3% (RSD) at $2\ \mu g\ L^{-1}$ of mercury species was typical. The accuracy of the method was validated by determination of mercury in geological and biological certified reference materials. The speciation analysis of Hg^{2+} and MeHg was achieved by controlling the conditions of microwave-enhanced cold vapor generation and validated *via* determination of Certified Reference Materials DORM-2, DORM-3 and a real river water sample.

1. Introduction

Mercury and its compounds attract more and more concern because of their highly toxic, bio-accumulative and non-degradable natures. For this reason, the US EPA has currently set the maximum permissible concentration of mercury in environmental water at $2\ ng\ mL^{-1}$ [1]. As a result, it is a great challenge to establish rapid, sensitive and accurate analytical methods for the determination of ultra-trace level of mercury. Cold vapor generation (CVG) coupled to atomic spectrometry (AS) is frequently used for routine analysis of mercury because of its unmatched sensitivity, elemental specificity, efficient matrix separation, and high sample introduction efficiency [2,3].

The conventional CVG for mercury is usually accomplished by using stannous chloride [4] or tetrahydroborate (THB) [5] as a reducing agent. Although these techniques are very efficient and accomplished in batch or continuous flow systems, there remain a number of serious impediments, including high blank arising from contamination from the THB and other reagents, the instability of THB solutions, interferences from transition and noble metals and production of various hazardous wastes. Therefore, significant efforts have been devoted to develop greener and interference-free CVG techniques to ameliorate or replace the conventional methods. Electrochemical CVG (EC-CVG) is one of the first successful methods utilizing electrons as a suitable alternative to $SnCl_2$ or THB for the reduction of Hg^{2+} but it requires careful selection of the cathode material [6]. Despite apparent advantages over the conventional approaches, EC-CVG has several shortcomings, including poor reproducibility and serious memory effects arising from reduced metals deposited onto the cathode surface. Sturgeon et al. and other groups [7–12] reported a promising new chemical vapor generation technique with which volatile species of hydride-forming elements, mercury, transition and noble metals could be generated through UV irradiation to their aqueous solutions in which low molecular weight organic acid had been added. This photochemical vapor generation (PVG) approach retains the principle advantages of conventional chemical vapor generation but further provides with simpler reaction, cost-effectiveness and greener analytical chemistry as well as expanding the range of application of CVG. It is note worthy that non-chromatographic speciation analysis of Hg^{2+}/MeHg was reported in previous studies based on different PVG conditions [12,13]. Recently, Bendicho [14] reported

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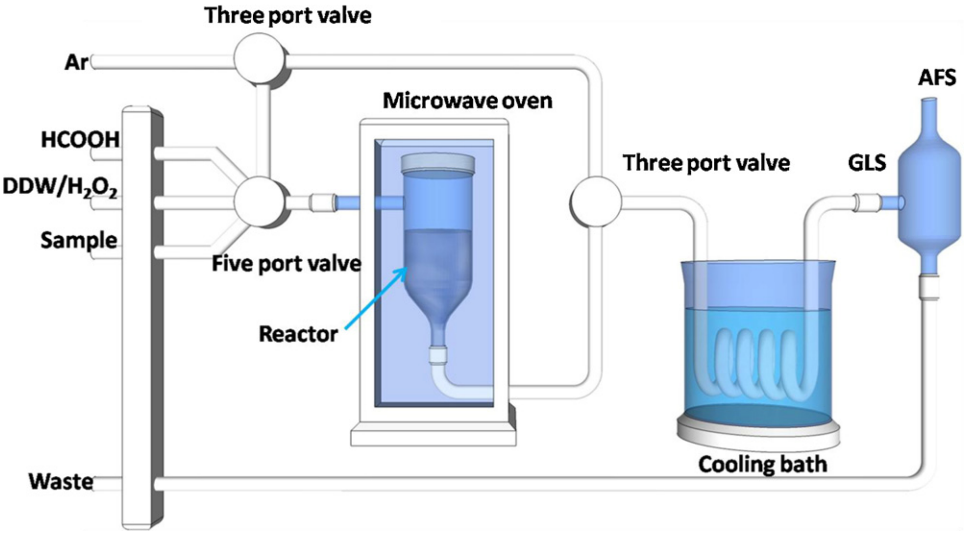

Fig. 1. Schematic diagram of the experimental setup.

a green sono-induced (SI) CVG technique wherein mercury vapor was produced following ultrasonication of inorganic mercury solutions. The CVG efficiency was found to be remarkably promoted when formic acid was added into the reaction medium. A solution cathode glow discharge (SCGD) and a dielectric barrier discharge (DBD) based CVG techniques were reported by Zhu et al. [15] and Wu et al. [16], respectively. The cold vapor formation was achieved even without reductant in these systems. The vapor generation efficiencies using these methods were improved by several folds in the presence of organic acids or alcohols.

Owing to its advantages of quick and even heating, microwave radiation was frequently utilized in analytical chemistry, including microwave digestion [17], microwave extraction [18], microwave-induced plasma [19], microwave-assisted sample combustion [20], and microwave-assisted thermal nebulization [21].

To our best knowledge, no reports about using microwave-assisted cold vapor generation for quantitative and speciation analysis of mercury have been found. Therefore, the purpose of this work was to characterize a new, simpler and more efficient CVG by shining microwave irradiation to sample solutions, and its application for quantification and speciation analysis of ultra-trace level of mercury in geological and biological certified reference materials by atomic fluorescence spectrometry (AFS). Optimum conditions for microwave enhanced cold vapor generation (MCVG) and interferences from concomitant ions were carefully investigated.

2. Experimental

2.1. Instrumentation

A microwave-assisted chemical reactor consisting of a home-made cylindrical quartz container (4.00 cm × 1.50 cm o.d. × 1.25 cm i.d.) placed in a commercial microwave oven (WP800 T, Galanz Microwave Oven Wiring Co., Fuoshan, China), was constructed. Since microwave distribution is spatially dependent, the quartz container must aim at the magnetron of microwave oven wherein microwave irradiation was produced, to ensure the irradiation to focus on the reaction solution. Two holes (2.0 mm i.d.) were made through the top of the microwave oven for inserting two polytetrafluoroethylene (PTFE) tubes (1.5 mm 0.d. ×1.0 mm i.d.) to connect the quartz container with a three-port and a five-port valve, respectively. The five-port valve was used to deliver sample, carrier solution, argon carrier gas and formic acid solution. The three-port valve was connected to the container, a quartz coil tube and another three-port valve used to control the direction of the argon carrier gas flow during MCVG. The coiled tube was immersed in an ice bath to ensure that no condensed liquid droplets were transported to the AFS atomizer during gas/liquid separation. Since the temperature of the effluent from the reactor was about 100 °C, the vapor pressure of water was increased causing an enhanced risk. The holes made on the body of microwave oven were sealed tightly with aluminum foil, which was served to protect the operator. An atomic fluorescence spectrometer (AFS-2202, Beijing Haiguang Instrument Co., Beijing, China) was used for detection of mercury cold vapor. A schematic of the instrumentation is presented in Fig. 1. The detection system was optimized independently, and the typical operating conditions for the determination of mercury were listed as follows: the height of the atomizer, 10 mm; the flow rate of carrier gas and shield gas, 300 and 1000 mL min^{-1}, respectively; the lamp current, 30 mA; and the negative voltage for the photomultiplier tube, −250 V.

2.2. Reagents and samples

All solutions were prepared using doubly distilled water (DDW). The standard solutions of mercury and methylmercury were prepared daily by dilution of stock standard solutions of mercury (1000 mg L^{-1}) and methylmercury (100 mg L^{-1}), respectively. Formic acid, acetic acid and propionic acid solutions were directly diluted from corresponding organic acid (Kelong Chemical Reagents Factory, Chengdu, China) with DDW. High-purity HCl, HNO_3, H_2SO_4, NaCl, $NaNO_3$, Na_2SO_4 and $Na_2S_2O_8$ were also purchased from Kelong Chemical Reagents Factory. High purity Ar (99.99%) was obtained from Qiaoyuan Gas Co. (Chengdu, China). Several certified reference samples from the National Research Center for Certified Reference Materials (Beijing, China) and the Institute of Geophysical and Geochemical Exploration (Langfang, China) were used to validate the accuracy of the proposed method. The performance of speciation analysis by the proposed methodology was validated *via* determination of two biological Certified Reference Materials (DORM-2 Dogfish Muscle and DORM-3, Fish protein) from the National Research Council Canada (NRCC) and a river water sample collected from a river near campus.

2.3. Sample preparation and analytical procedure

According to the method described by Scriver et al. [22], approximately 200 mg and 250 mg subsamples of DORM-2 and DORM-3 were weighed and put into 50 mL precleaned Teflon vessels, respectively, with 10 mL of formic acid added. The flasks were wrapped with black adhesive tape and then put in a water bath sonication at 50 °C for 5 h. After centrifugation at 4000 rpm for 10 min, the supernatant was transferred to a precleaned volumetric flask and diluted with DDW. Sample blanks were processed along with the samples. The river water was obtained from the shore by sampling aliquots into pre-cleaned quartz bottles and directly transporting them to the laboratory for immediate study.

The entire analytical procedure is computer-programmable, and its information can be found in details in our previous works [9,12]. Briefly, about 2.0 mL sample together with a formic acid solution were delivered to the microwave chemical reactor for a typical irradiation time of 60 s or 20 s to generate the cold vapor. H_2O_2 was simultaneously pumped into the reactor during this step when total mercury was to be determined. It should be noted that the Ar carrier gas flow bypassed the reactor during this time. Subsequently, the sample channel was shifted from sample solution to carrier solution (DDW). The argon flow (300 mL min^{-1}), together with the carrier solution (at a flow rate of 6.0 mL min^{-1}), passed through the reactor to flush the mixture to the ice bath, and then further swept this mixture to the gas-liquid separator (GLS) wherein the vapor was rapidly separated from the liquid and delivered into the AFS spectrometer for detection.

3. Results and discussion

3.1. Proposed mechanism

Although CVG techniques have been widely used for elemental or speciation analysis, possible mechanisms remain largely in the “discussion stage” because of its complicated reaction nature [2]. For PVG, SI-CVG and SCGD-CVG, formic acid or other low weight molecular organic acids are speculated to be decomposed and produce reducing radicals such as $H^{\bullet}$ and/or $CO^{\bullet}$. These radicals are favorable for reduction of mercury or production of volatile species of some elements. Previous work [23,24] reported that decomposition of formic acid is reversible, and can be easily realized in a hot water medium via two reaction pathways including decarbonylation and decarboxylation:

$$CO + H_2O \leftrightarrow HCOOH \leftrightarrow CO_2 + H_2 \qquad (1)$$

Moreover, a water-catalyzed reaction can remarkably decrease the potential barrier for the reaction path, and has been studied theoretically by several groups [25,26]. These produced hydrogen and carbon monoxide can be used as effective reductant in organic chemistry and environment chemistry. Recently, reduction of nitrate in water was obtained by using formic acid as a reductant [27]. Therefore, we speculate that these reduced gases from formic acid may reduce Hg^{2+} to Hg^0 in this system. Once Hg^0 is generated, it is rapidly liberated from liquid phase and swept to the AFS by carrier gas, i.e.,

(2)$CO/H_2 + Hg^{2+} \rightarrow Hg^0$

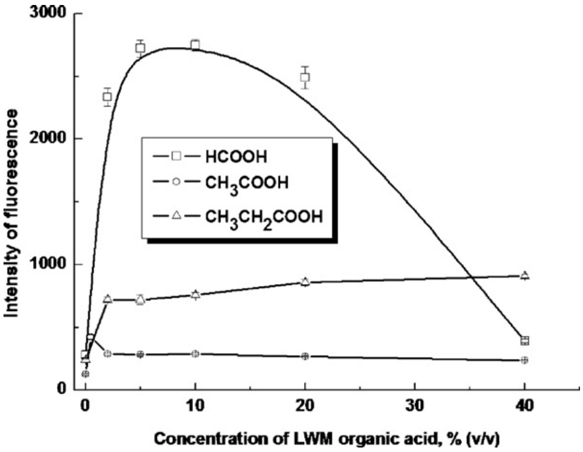

Fig. 2. Effect of LWM organic acids on the response from 5 μg L^{-1} Hg^{2+}. Experimental conditions: irradiation time, 60 s; and irradiation power, 700 W.

In contrast to the conventional heating techniques, microwave heating is more rapid because electromagnetic waves directly act on polar molecules of the medium, rapidly heating the solution from inside rather than relying on the heat transfer from an external source. Therefore, homogenous heating can be achieved in a very short time. Microwave energy has been applied to accelerate the reduction of double bonds and hydrogenolysis of several function groups using formate or formic acid as the hydrogen donor [28]. Microwave was thus chosen as a heating technique to accelerate the decomposition of formic acid and then improve the yield of mercury vapor in this system. An oil bath heated to 220 °C by an electric furnace was used as an alternative to a microwave oven to gain insight into the role played by microwave radiation in the proposed methodology. The results showed that the final product provided by the electric furnace was similar to that arising from use of the microwave system, but the reaction time (100 s) was longer and the CVG efficiency was lower. Moreover, Sturgeon also found that the ultrasound-assisted vapor generation efficiency of mercury was increased with increasing temperature of the reaction [29]. Therefore, microwave herein work most probably mainly as a powerful, rapid and easy means of controlling the thermal source for CVG.

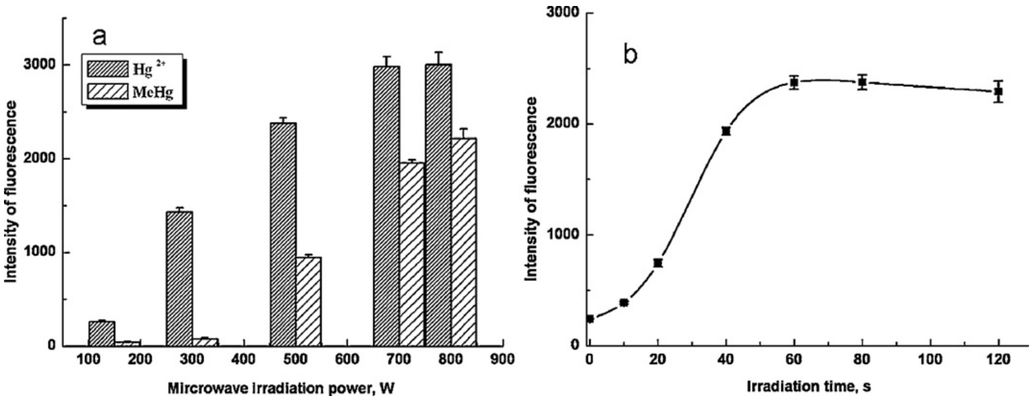

Fig. 3. (a) Effect of microwave power on response from 5 μg L^{-1} Hg^{2+} or MeHg. Experimental conditions: 60 s irradiation time; and 10% formic acid. (b) Effect of irradiation time on response from 5 μg L^{-1} Hg^{2+}. Experimental conditions: 700 W microwave power; and 10% (v/v) formic acid.

3.2. Effect of organic acids

The effects of organic acids including formic, acetic and propionic, on MCVG efficiency were investigated, and the results were summarized in Fig. 2. The results indicate that MCVG of mercury is strongly dependent on the kind and the concentration of organic acid present, with the most efficient medium being formic acid. In the absence of formic acid, no detectable signals were obtained. Response from mercury increases significantly in the range 0–5% (v/v) formic acid followed by a slight decrease beyond 15% (v/v). A large amount of gas arising from its decomposition may dilute the mercury vapor in the transport gas and result in this signal decrease, with a formic acid concentration >15% (v/v). Thus, 10% (v/v) formic acid was selected for subsequent experiments. Although acetic acid and propionic acid can also be used to generate mercury vapor, the efficiency is much lower than that from formic acid.

3.3. Effect of microwave power and irradiation time

The effect of microwave power on response was investigated using 5 μg L^{-1} solutions of mercury species under optimized experimental conditions and 120 s of irradiation time. The results are summarized in Fig. 3a. The signal from either Hg^{2+} or MeHg increases over the range 100–700 W microwave power. No obvious signals from MeHg were detected when microwave power was less than 300 W. Although a signal plateau from Hg^{2+} is achieved beyond 700 W, the signal from MeHg is still increased with increasing microwave power, and is much lower than that from Hg^{2+}, even at the maximum power (800 W). Under optimized experimental conditions and 700 W microwave power, 5 μg L^{-1} Hg^{2+} solution containing 10% (v/v) formic acid was used to investigate the effect of irradiation time, as shown in Fig. 3b. Response increases over the range of 0–60 s, reaching a plateau over which a stable maximum signal was achieved. Therefore, A 60-s irradiation time was selected for subsequent experiments.

3.4. Effect of inorganic acids

Inorganic acids, such as HCl, H_2SO_4 and HNO_3, were previously reported suppressing the efficiencies of PVG [12], SI-CVG [14] and SCGD-CVG [15]. Therefore, the effects of inorganic acids on the response were investigated in this work. A signal decrease by 50% was found in 1 M HCl medium. For HNO_3 and H_2SO_4, there were no noticeable effects on the response, even at concentrations as high as 5 M and 1 M, respectively. This is particularly beneficial as HNO_3 is often required in many digestion procedures and it would otherwise need to be removed prior to analysis. Substituting NaCl, $NaNO_3$ or Na_2SO_4 for their corresponding acids, a similar trend was observed. Combined with earlier reports [12,14,15] strong complexes arising from the reaction between Hg^{2+} and Cl^- probably resulted in this signal decrease.

3.5. Effect of oxidizing substances

It is well known that determination of total mercury is not sufficient for evaluating its toxicity, which is strongly dependent on its chemical form in samples. Although hyphenated techniques are powerful and practical because they can provide more species information, hyphenation introduces several disadvantages, such as destruction of speciation and increase of expense [30]. Non-chromatographic techniques for speciation analysis can overcome these drawbacks to a certain extent [31,32]. Therefore, another principle purpose of this study was to establish a non-chromatographic technique for speciation analysis of mercury by optimizing the microwave power. However, the CVG efficiency of MeHg was much lower than that of Hg^{2+} using only microwave irradiation. It is fortunate that the CVG efficiency of MeHg increased significantly with increasing concentration of H_2O_2 throughout the range 0–1.0% min, followed by the same efficiency as that obtained from Hg^{2+} beyond 1% (v/v). Most notably, the optimum irradiation time was significantly reduced to 20 s in the presence of 1% (v/v) H_2O_2, and the effect of irradiation time on the response from solutions of Hg^{2+} and MeHg containing 1% H_2O_2 was summarized in Fig. 4. Although the role played by H_2O_2 is yet unclear, decomposition of H_2O_2 likely produces OH radicals, which is favorable to attack formic acid and MeHg, and enhanced the efficiencies of decomposition of formic acid and MeHg compared to the case when a pure solution of formic acid alone is used. This advantage provides a new, simple and non-chromatographic method for speciation analysis of mercury: only Hg^{2+} can be determined under the reaction conditions of 300 W microwave power and 60 s irradiation time; whereas in the presence of 1% (v/v) H_2O_2, total mercury can be determined with 700 W microwave power and 20 s irradiation time. Therefore, in the case of samples (such as natural environmental water and fish samples) containing mainly MeHg and Hg^{2+}, the concentration of MeHg can be evaluated by subtracting the Hg^{2+} concentration from total mercury.

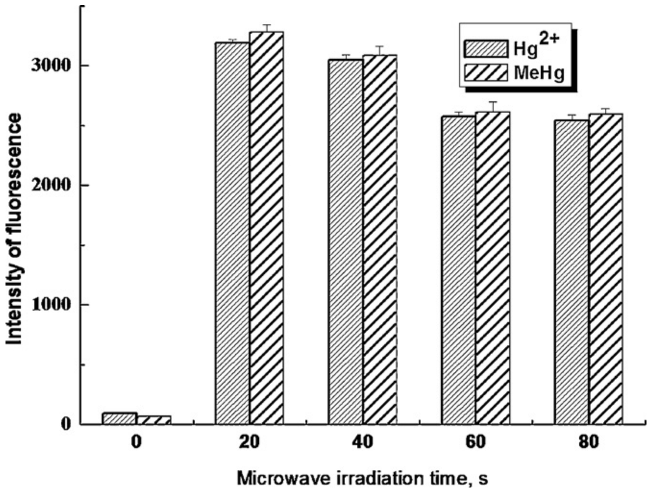

Fig. 4. Effect of irradiation time on response from 5 μg L^{-1} Hg^{2+} or MeHg. Experimental conditions: 1% (v/v) H_2O_2; 10% formic acid; and 700 W microwave power.

Table 1
Effect of concomitant ions on the recovery of mercury.[a]

Test species	$[M^{n+}]$ μg L^{-1}	$[M^{n+}]/[Hg^{2+}]$	Recovery %
As^{3+}	50,000	10,000	106
Bi^{2+}	5000	1000	85
Ca^{2+}	50,000	10,000	96
Co^{2+}	50,000	10,000	103
Cr^{6+}	50,000	10,000	114
Cu^{2+}	5000	1000	84
Fe^{3+}	50,000	10,000	115
Ge^{2+}	5000	1000	75
Mg^{2+}	50,000	10,000	98
Ni^{2+}	50,000	10,000	97
Sb^{2+}	5000	1000	85
Se^{4+}	5000	1000	100
Sn^{2+}	5000	1000	65
Te^{4+}	500	100	89
Cl^-	5000	1000	94
NO^{3-}	50,000	10,000	99
$SO_4{}^{2-}$	5000	1000	86

[a] Experimental conditions: 5 μg L^{-1} Hg^{2+}; 10% HCOOH; 700 W microwave power; 60 s irradiation time.

Table 2
The calibration parameters and LODs under different conditions by MCVG/AFS.

Method	Sensitivity (μg L^{-1})	*R*	RSD, % (*C*, μg L^{-1})	LOD (μg L^{-1})	Reference
Oil bath 180 °C	236	0.9991	8.2 (2)	0.1	This method
300 W	266	0.9998	3.0 (2)	0.05	
700 W	463	0.9995	2.5 (2)	0.008	
700 W + 1% (v/v) H_2O_2	469	0.9998	2.2 (2)	0.005	
$SnCl_2$	541	0.9985	0.8 (5)	0.01	[33]
$NaBH_4$ + HCl	100	0.9999	3.7 (NF)	0.03	[34]
Photochemical CVG	614	0.9995	3.6 (5)	0.003	[12]
Sono-induced (SI) CVG[a]	0.196	0.9992	4.4 (NF)	0.3	[14]
SCGD based CVG[b]		0.9997	1.2 (20)	0.7	[15]
DBD based CVG[b]	1840	0.9995	2.1 (10)	0.090	[16]

C, concentration; NF, not found.

[a] Detected by atomic absorption spectrometry.

[b] Detected by inductively coupled plasma optical emission spectrometry.

Table 3
Determination of Hg in certified reference materials by the proposed method.

Sample	Description	Determined[a] (μg L^{-1} or μg kg^{-1})	Certified (μg L^{-1} or μg kg^{-1})
GBW(E) 080392	Water	10.0 ± 0.5	9.7 ± 0.52
GBW 09101	Human hair	2160 ± 210	2090 ± 172
GSS-1	Soil	32 ± 4.0	29 ± 4.0
GSS-3	Soil	60 ± 4.0	62 ± 5.0
GSS-4	Soil	590 ± 50	603 ± 26
GSS-5	Soil	290 ± 30	296 ± 28

[a] Mean and standard deviation of results (*n* = 3).

3.6. Interferences

The major drawback of conventional CVG is the aforementioned interference caused by transition and noble metals, especially Fe, Co, Ni, and Cu, because these ions are very easily reduced to the metallic state or colloidal forms by THB and they scavenge or decompose the volatile analyte in the liquid phase. In this study, the effects of 17 concomitant ions on this chemical vapor generation of mercury were investigated. As summarized in Table 1, no obvious interferences from Fe^{3+}, Co^{2+}, Ni^{2+} or Cu^{2+} were detected, even at concentrations as high as 50 mg L^{-1} for Fe^{3+}, Co^{2+} and Ni^{2+}. It is possible that these metal ions could not be reduced to their metallic states or colloidal forms in this system, which can adsorb mercury vapor or form amalgam with Hg^0, and then seriously suppress the response. It is still unknown why there are no negative effects from common oxidation substances such as Cr^{6+}, H_2O_2, $NO_3{}^-$, and $S_2O_8{}^{2-}$, even at high concentrations. The significant interference arising from most hydride-form elements or alkaline earth elements was not found, either. However, Sn^{2+} caused a serious interference, most probably because Hg^{2+} is reduced to Hg^0 by $SnCl_2$ and liberated from aqueous phase prior to the MCVG.

3.7. Figures of merits

Table 2 summarizes figures of merits achieved using the proposed method for sample introduction in comparison to those of several other analytical methods. Under the experimental conditions of 700 W microwave power, 20 s irradiation time, 10% (v/v) formic acid and 1% (v/v) H_2O_2, typical calibration curves obtained for Hg^{2+} and MeHg can be characterized by the following calibration functions: $I_{Hg^{2+}} = 468.69C_{Hg^{2+}} - 42.28$ and $I_{MeHg} = 478.15C_{MeHg} + 39.01$ for Hg^{2+} and MeHg, respectively. Linear coefficients are better than 0.99 in both cases and there is no significant difference in the efficiency of generation for these two species. The linear range can be extended up to 20 μg L^{-1} and is limited by optical saturation of the detector. The limit of detection (LOD) was calculated from three times the standard deviation of 11 measurements of a blank solution divided by the slope of the calibration curve to yield LODs of 0.005 μg L^{-1} for both Hg^{2+} and MeHg. This is comparable to other similar methods, as summarized in Table 2. Precision of replicate measurement, expressed as a relative standard deviation (RSD, *n* = 11), is better than 3% at a concentration of 2 μg L^{-1}. The accuracy of the proposed method was validated by analysis of certified reference geological and biological materials, with analytical results summarized in Table 3. No significant differences are evident between the obtained and certified values.

3.8. Potential application for speciation analysis

DORM-2 and DORM-3 were analyzed to validate the possibility of mercury speciation analysis by the proposed method. Direct vapor generation of mercury species from the digests of these

Table 4
Evaluation of the possibility of the proposed methodology for mercury speciation analysis.

Sample	Added (μg L^{-1})		Detected[a] (μg L^{-1})			Certified (μg L^{-1})		
	Hg^{2+}	MgHg	Hg^{2+}	Total Hg	MeHg	Hg^{2+}	Total Hg	MeHg
DORM-2	–	–	0.17 ± 0.02[b]	4.75 ± 0.18[b]	4.58 ± 0.16[b]	–	4.64 ± 0.62[b]	4.47 ± 0.32[b]
DORM-3	–	–	ND	0.335 ± 0.040[b]	0.335 ± 0.040[b]	–	0.382 ± 0.060[b]	0.355 ± 0.056[b]
Real water samples	5	0	4.62 ± 0.30	4.66 ± 0.25	0	–	–	–
	0	5	0.15 ± 0.08	4.83 ± 0.32	4.68 ± 0.26	–	–	–

ND, not detectable.

[a] Mean and standard deviation of results (*n* = 3).

[b] mg kg^{-1}.

samples could not be successful because of the high residual fish muscle or protein. After centrifugation, the supernatant of the digests from DORM-2 and DORM-3 were diluted 20-fold and 5-fold using DDW and formic acid prior to vapor generation, respectively. The analytical results are summarized in Table 4. For DORM-2, no significant difference is evident between the obtained and certified value. The obtained result from DORM-3 is slightly lower than the certified one because only 5 folds dilution was made and high organic compounds still remained in the solution. Higher degree of dilution can not be feasible due to the low content of mercury. A real water sample was used to further evaluate the application of this method for speciation analysis. It was necessary to spike the water with standard calibration solutions due to the low level of mercury species present. Good recoveries of both added mercury species were obtained, as shown in Table 4. These results show that Hg^{2+} concentration can be selectively determined based on 300 W microwave power and 60 s irradiation time, and total mercury can be determined with 700 W microwave power, 20 s irradiation time in the presence of 1% (v/v) H_2O_2. Thus, the concentration of MeHg can be calculated by difference from the total mercury concentration in some samples.

4. Conclusion

Highly efficient CVG of mercury was achieved in the presence of formic acid using microwave heating of the aqueous analyte solution. This novel analytical methodology provides an extremely sensitive, simple, selective and cost-effective technology for this determination as well as permits speciation analysis based on different vapor generation conditions. The proposed microwave-enhanced CVG system is a viable alternative to conventional CVG for determination and speciation analysis of trace level mercury in real samples without prior chromatographic separation. There are no negative effects from common oxidation substances such as H_2O_2 and HNO_3 usually used for sample digestion. Ongoing work in our laboratory is exploring the combination of this methodology with on-line microwave digestion for direct analysis of mercury in solid samples. This combination will remarkably reduce analyte loss and potential contamination, improve sample throughput and simplify procedures for sample analysis (on-line sample preparation). This will hopefully further broaden the application area of non-THB CVG [35].

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