UV Irradiation Controlled Cold Vapor Generation Using SnCl_2 as Reductant for Mercury Speciation

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A simple and ultrasensitive method, which was based on cold vapor generation (CVG) coupled to atomic fluorescence spectrometry (AFS), was proposed for speciation analysis of inorganic mercury (Hg^{2+}) and methylmercury (MeHg) in water samples. In the presence of UV irradiation, all the mercury ($\text{MeHg} + \text{Hg}^{2+}$) in a sample solution can be reduced to Hg^0 by SnCl_2 ; without UV irradiation, only Hg^{2+} species can be determined. So the concentration of MeHg can be obtained from the difference of the total mercury and Hg^{2+} concentration; thus, speciation analysis of Hg^{2+} and MeHg was simply achieved without chromatographic separation. Under the optimized experimental conditions, the limits of detection were 0.01 ng mL^{-1} for both Hg^{2+} and MeHg. The sensitivity and limit of detection were not dependent on the mercury species, and a simple Hg^{2+} aqueous standard series can be used for the determination of both Hg^{2+} and MeHg.

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Introduction

Mercury is a highly dangerous toxic element because of its accumulative and persistent character in the environment. In recent years, more and more countries have implemented policies to control the mercury level in the environment. For example, the US Environmental Protection Agency (EPA) has set the upper limit of total mercury concentration in environmental water at $5 \text{ } \mu\text{g L}^{-1}$.¹ It is well known that the toxicity, biogeochemical behavior and transportation of mercury in the environment are heavily dependent on its chemical form. Methylmercury (MeHg) is the most commonly occurring organo-mercury compound in the environment and in biological materials, and it is the most toxic mercury species. MeHg is of particular concern because of its accumulation through the food chain.² As a consequence, not only total mercury but also MeHg should be determined for the evaluation of the toxicological and environmental impact of mercury.

In the last two decades, the development of species-selective analytical methodologies made possible the identification and quantification of Hg^{2+} and MeHg. The most common methods for mercury speciation are gas chromatography (GC) and high-performance liquid chromatography (HPLC) coupled with a mercury-specific detection system including atomic absorption spectrometry (AAS),^{3,4} atomic fluorescence spectrometry (AFS),⁵⁻⁹ atomic emission spectrometry (AES),¹⁰⁻¹² or inductively coupled plasma-mass spectrometry (ICP-MS).¹³⁻¹⁵ Although these detection methods are attractive for mercury speciation because of their high sensitivity and selectivity, the relatively high instrumental and/or running costs as well as relatively complicated instrumentation and operation are the drawbacks of these

hyphenated techniques for routine speciation analysis of mercury species. It should be pointed out, however, that the “species resolution” of such methods is much better with chromatographic separation, resulting in more species information.

Still, it is attractive to realize speciation analysis without chromatographic separation.¹⁶⁻¹⁸ It has been reported that UV irradiation can be used to reduce some heavy metal ions to their metal or lower oxidation state intermediates in many samples, but most often with TiO_2 or ZnO as a catalyst.¹⁹⁻²³ On the other hand, some metals in their organic states can also be converted to the inorganic state in aqueous solution with or without oxidation reagent, *i.e.*, Hg^{2+} , with UV irradiation, and then such metals can be determined by liquid chromatography and/or atomic spectrometry.²⁴⁻²⁷ But these techniques all need a separation or extra pretreatment procedure. In our previous work, with formic acid as a reductant, photo-induced chemical vapor generation was used for the determination of Hg^{2+} and MeHg by atomic fluorescence spectrometry, with the limit of detection of $0.003 \text{ } \mu\text{g L}^{-1}$ for total mercury with the UV or $0.2 \text{ } \mu\text{g L}^{-1}$ for Hg^{2+} with the Vis.²⁸ In this paper, we report that the traditional SnCl_2 system for mercury cold vapor generation can also be renewed by the same UV scheme to achieve the capability for mercury speciation analysis. Compared with the formic acid method, the sensitivity and the limit of detection of this work were not dependent on the species of mercury.

Experimental

Reagents and standard solutions

All reagents were of at least analytical grade. Doubly distilled water (DDW) was used throughout the whole work. Potassium tetrahydroborate (AR, Chengdu Kelong Chemical Reagent Factory, Chengdu, China) (0.01% w/v) stabilized with 0.5% (w/v) NaOH was freshly prepared by dissolving 0.01 g KBH_4

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and 0.5 g NaOH in DDW, and diluted to 100 mL with DDW. SnCl_2 (AR, Chengdu Kelong Chemical Reagent Factory, China) solution (6.0% w/v) was prepared by dissolving 6.0 g SnCl_2 in 1 mL hydrochloric acid and diluted to 100 mL with DDW. Mercury stock standard solution of 1000 mg L^{-1} was purchased from the National Research Center for Certified Reference Materials (NRCCRM, China). The methylmercury stock standard solution of 1000 mg Hg L^{-1} was prepared by dissolving the appropriate amount of the methylmercury chloride solid (Alfa Aesar, Karlsruhe, Germany) in methanol. The standard solutions were prepared daily by step dilution of stock standard solutions and used for the related experiments. The interference metal ion solutions were prepared by dilution of the corresponding stock standard solution of 1000 mg L^{-1} .

Apparatus

The instrumentation was described in detail in our previous work, and is briefly summarized here.^{28,29} A cold vapor generator was constructed, as shown in Fig. 1. The reactor mainly consists of a coiled quartz pipe (3 mm i.d. and 250 mm in length) and a quartz container (15 mm i.d. and 250 mm in length). The quartz container, wrapped by the coiled quartz pipe, was used to hold a high-pressure Hg vapor UV lamp (125 W) inside to protect the lamp from the cooling water. The generated mercury cold vapor was detected by an atomic fluorescence spectrometer (AFS-2202, Beijing Haiguang Instrument Co., Beijing, China). The optimal instrumental conditions were: Hg hollow cathode lamp current, 30 mA; the voltage of photomultiplier tube, -250 V; argon gas flow rate, 500 mL min^{-1} ; and the observation height, 12 mm. Due to the monoatomic nature of cold mercury vapor, the atomic fluorescence of mercury was detected without any further atomization. Through a three-way valve, the argon (99.99%) flow was switched to skip the reactor in the process of cold vapor generation, but to pass through the reactor to carry the mercury vapor to the AFS after the reaction. The sample introduction device was a manufacturer-designed, computer-programmable, intermittent sampling system, mainly consisting of a peristaltic pump, as shown in Fig. 1.

Procedure

For the programmable operation procedure, the mercury sample and the SnCl_2 solution were sucked for 20 s into the reactor in step 1. The sampling volume was 2.4 mL. In step 2, the mixture of the sample solution and 6.0% SnCl_2 solution were irradiated by the UV lamp for 5 s, with argon flow bypassing the reactor. Meanwhile, the sample channel was shifted from the sample solution to carrier solution when the pump stopped. In step 3, the argon flow, together with the carrier solution, was passed through the reactor to flush the mixture to the gas-liquid separator shown in Fig. 1a, and then mercury vapor was introduced into the AFS for the measurements of atomic fluorescence. At the same time, the SnCl_2 solution was pumped into the reactor, too. The AFS signal was recorded in this step, and the peak area was selected for quantification. Step 4 was 6 s for making ready for the next measurement. Figure 2 illustrates a typical signal profile obtained from a solution containing 5 ng mL^{-1} MeHg.

Results and Discussion

Selection of the reductant

Using KBH_4 to produce mercury cold vapor for CVG-AFS is now a common method for the determination of trace mercury

Fig. 1 The schematic diagram of the UV-CVG-AFS instrumentation. GLS: gas/liquid separator. (a) UV irradiation of the mixture; (b) UV irradiation of the sample prior to the CVG for the study of mechanism.

in various samples. Because of its strong reducibility, however, KBH_4 can also reduce MeHg even without UV irradiation, furthermore Hg^{2+} and MeHg could not be differentiated; thus it is difficult to use this method in speciation analysis without chromatographic separation. Segade³⁰ reported that MeHg cannot be reduced to Hg^0 when the concentration of KBH_4 is as low as 0.0001% (w/v); thus 0.0001% KBH_4 solution as the reducing reagent was tested in this work. However, our experimental results revealed that about 10% MeHg was reduced without UV irradiation even when the concentration of KBH_4 was that low. This may originate from some differences in the design of the two reactors. Traditionally, SnCl_2 is used for the determination of mercury by cold vapor atomic absorption spectrometry. Occasionally, SnCl_2 has also been used as a reductant for speciation analysis of mercury, but additional pretreatments such as microwave digestion³¹ or UV irradiation³² with or without oxidation reagent before reducing MeHg to Hg^0 is necessary. It was found in this work that SnCl_2 cannot reduce MeHg to Hg^0 , except under UV irradiation. Without UV irradiation, only Hg^{2+} species can be reduced by SnCl_2 . This means that the concentration of MeHg can be indirectly obtained from the difference of the concentration of total mercury (with UV) and the concentration of inorganic Hg^{2+} (without UV).

Optimization of the irradiation time

In this UV-CVG system, the maximum fluorescence signals

Fig. 2 Typical AFS signal profile of the proposed method for MeHg using SnCl_2 as reductant, with a standard solution of $5 \mu\text{g L}^{-1}$ MeHg.

of Hg^{2+} and MeHg appeared sharply even the irradiation time was as short as 5 s, as shown in Figs. 2 and 3. It was also found that the irradiation time (varied from 5 to 40 s) would not significantly affect the determination in terms of signal-to-background ratio or the precision of the measurements. But both Hg^{2+} and MeHg atomic fluorescence signals decreased as the irradiation time increased, when the irradiation time was >10 s. The reason for this signal fall is that more Hg^0 deposited on the internal surface of the quartz reactor (black observed after long time use) as the irradiation time became longer than 10 s. The black deposit was dissolved and determined by atomic absorption to verify the mercury deposition. Figure 3 also shows that the sensitivity for the two species appears significantly different when the irradiation time is more than 10 s. In consideration of fluorescence intensity, stability, and similar sensitivity for Hg^{2+} and MeHg, 5 s was chosen for use in latter experiments for both Hg^{2+} and MeHg. If the irradiation time is too short, MeHg could not be completely reduced; and if the irradiation time is too long, mercury vapor could be lost before it is determined.

Optimization of the concentration of SnCl_2

The study of how the concentration of SnCl_2 affects the intensity of atomic fluorescence showed that, when the concentration of SnCl_2 changed from 1 to 10% (w/v), the results were satisfactory in terms of signal-to-background ratio or the precision of the measurements (Fig. 4). It is worthwhile to note that, unlike traditional CVG-AAS, stable maximum signal can be obtained under very low concentration of SnCl_2 , even below 1%. With the low concentration of SnCl_2 in this CVG system, there are many advantages: minimal reagent blank, a cleaner method, and low analytical cost. Meanwhile, the sensitivities of Hg^{2+} and MeHg are similar within the SnCl_2 concentration range from 1 to 10%. The similar sensitivity resulted in the following advantages: the relatively less toxic and cheaper Hg^{2+} standard series can be used to calibrate both Hg^{2+} and MeHg, eliminating the use of more toxic and expensive MeHg standard series. In consideration of signal intensity, stability, and sufficient reductant for the CVG, 6% SnCl_2 was used for the determination of Hg^{2+} and MeHg in this work.

Optimization of the concentration of hydrochloric acid in SnCl_2 solution

To prevent hydrolysis, we dissolved SnCl_2 in hydrochloric acid first, and then diluted the solution with DDW. Therefore, the effect of the HCl concentration in SnCl_2 solution on the

Fig. 3 Effect of irradiation time on the intensity of atomic fluorescence for mercury, with a standard solution of $5 \mu\text{g L}^{-1}$ MeHg or Hg^{2+} . Error bars: one standard deviation.

Fig. 4 Effect of SnCl_2 concentration on the signal intensity, with a standard solution of $5 \mu\text{g L}^{-1}$ Hg^{2+} or MeHg. Error bars: one standard deviation.

atomic fluorescence intensity should be studied. If the HCl concentration was higher than 1%, the signal decreased rapidly as its concentration increased in the determination of MeHg; when the HCl concentration was lower than 1%, the SnCl_2 hydrolysis would occur. The Hg^{2+} signal was HCl concentration-independent, as shown in Fig. 5. So it is important to control the concentration of hydrochloric acid in order to obtain the comparable intensity between inorganic mercury and MeHg. In this work, 1% HCl concentration was used for further experiments.

Calibration curves of Hg^{2+} and MeHg and limits of detection

Under the optimal experimental conditions and instrumental parameters, calibration curves composed of at least five points, with ranges from 1 to $10 \mu\text{g L}^{-1}$ for Hg^{2+} and MeHg, respectively, with or without UV irradiation, were daily constructed for the measurements. Calibration curves with at least 0.99 or better linear correlation coefficients can be routinely obtained. In the presence of UV radiation, the sensitivity for Hg^{2+} was the same as that for MeHg. Figure 6 illustrates typical calibration curves obtained for Hg^{2+} and MeHg, respectively. Therefore, in the presence of UV, MeHg can be decomposed and the total mercury can be reduced and thus determined with SnCl_2 . However, without UV, only Hg^{2+} species can be determined. Then the concentration of MeHg can be obtained from the difference of the total mercury

Table 1 Analytical figures of merit of this work compared with those obtained by other methods

	UV-CVG-SnCl ₂ -AFS	UV-CVG-HCOOH-AFS (Ref. 28)	HPLC-ICP-MS (Ref. 15)	HPLC-CVG-AAS (Ref. 4)	HPLC-CVG-ICP-MS (Ref. 13)	HPLC-CVG-AFS (Ref. 26)
Sensitivity/mL ng ⁻¹ , X(Y) ^b	544 (541)	614 (37.5)		0.33 (0.34) ^a		
LOD/ng mL ⁻¹ , X(Y) ^b	0.01 (0.01)	0.003 (0.2)	5 (7)	1.3 (1.1)	0.05 (0.06)	8 (11)
RSD, %	0.8	3.6 (4.4)	≤ 5 (≤ 9)	4.3 (5.5)	≤ 2	7.3 (4.2)
	(5 ng mL ⁻¹)	(5 ng mL ⁻¹)		(50 ng mL ⁻¹)		(50 ng mL ⁻¹)

a. The unit is L µg⁻¹. b. X and Y is for MeHg and Hg²⁺, respectively.

Fig. 5 Effect of the HCl concentration on the signal, with a standard solution of 5 µg L⁻¹ MeHg and Hg²⁺. Error bars: one standard deviation.

Fig. 6 Calibration curves of Hg²⁺ and MeHg overlapped very well, showing no sensitivity difference for the two species.

concentration and the Hg²⁺ concentration. The LOD was defined as the analyte concentration calculated by using three-fold standard deviation of 11 measurements of a blank solution, divided by the slope of the calibration curve. The LODs for Hg²⁺ and MeHg were both found to be 0.01 µg L⁻¹. The analytical figures of merit also compared favorably with those by some other methods, as shown in Table 1.

Generation efficiency

Guo and Sturgeon³³ reported that the generation efficiency of a new CVG system could be estimated by the ratio of the resultant atomic spectrometric signal to that from conventional CVG of mercury using NaBH₄ as a reductant. With 6% SnCl₂ solution and 5 µg L⁻¹ Hg²⁺ or MeHg, therefore, the Hg⁰ vapor generation efficiency was estimated according to Sturgeon's method. The efficiency of Hg²⁺ to Hg⁰ vapor of this work was estimated to be near 100%, with or without UV irradiation. With UV irradiation, MeHg can also be almost 100% converted to Hg⁰ vapor, so the total mercury can be quantified under UV irradiation. However, no signal for MeHg was detected in the SnCl₂ CVG system without UV irradiation, and this means that the conversion efficiency of MeHg to Hg⁰ vapor is minimal without UV. In further experiments shown in Fig. 1b, *i.e.*, with UV irradiation on MeHg only and prior to its mixing with SnCl₂, the conversion efficiency of MeHg to Hg⁰ vapor was less than 25% even with irradiation time as long as 120 s. In order to convert all MeHg to Hg²⁺ before reduction to Hg⁰, one must mix MeHg with an oxidant before UV irradiation, or one must elevate the reaction temperature. It is still unclear why MeHg can be almost completely converted to Hg⁰ just as Hg²⁺ when the MeHg-SnCl₂ mixture is exposed to UV light. The photochemical reaction can be complicated and awaits further studies.

Interference of coexisting ions

In this work, the effects of eleven coexisting ions on the determination of Hg²⁺ and MeHg were investigated. It was found that the tolerable amounts of coexisting ions for Hg²⁺ are larger than those for MeHg, so Table 2 only reports the results with MeHg. Large amounts of Cu²⁺ and Fe³⁺ can cause interference with the determination of MeHg but not of Hg²⁺. The maximum tolerable concentration of interfering ions for MeHg are summarized in Table 2. With higher SnCl₂ concentration, the tolerable amounts of Al³⁺ and Zn²⁺ can be increased. These tolerable concentration levels show that this method is applicable to the analysis of some types of environmental waters and drinking water for mercury and MeHg.

Potential application in speciation analysis

To evaluate the usefulness of the proposed method for the speciation analysis of Hg²⁺ and MeHg, we collected water samples after the tap opened at full flow for 10 min. In one trial we added 2 µg L⁻¹ MeHg and in the other we added 2 µg L⁻¹ MeHg and 3 µg L⁻¹ Hg²⁺, and then we analyzed by the proposed method; our analytical results are listed in Table 3. Without UV irradiation, the recovery of MeHg of 1.5% is neglectable, while that of Hg²⁺ is 101%; with UV irradiation, the recoveries for both MeHg and Hg²⁺ are satisfactory. Meanwhile, the accuracy of the proposed method was further validated by analysis of a certified reference water sample, GBW(E)080393 (with certified inorganic mercury concentration: 100 µg L⁻¹), with a relative error ranging from 2% to 4% by the proposed method with UV or without UV irradiation.

Conclusions

To conclude, a new method was proposed for speciation

Table 2 The effect of some coexisting ions on the recovery of MeHg (5 $\mu\text{g L}^{-1}$, 6% SnCl_2)

Coexisting ions, M^{2+}	$[\text{M}^{2+}]/\mu\text{g L}^{-1}$	$[\text{M}^{2+}]/[\text{Hg}^{2+}]$	Recovery, %
As(III)	500	100	92
As(V)	1000	200	88
Co^{2+}	1000	200	95
Cu^{2+}	1000	200	87
Fe^{3+}	500	100	96
Ni^{3+}	10000	2000	137
Pb^{2+}	10000	2000	86
Al^{3+}	100	20	76
$\text{Al}^{3+ \text{ a}}$	1000	200	101
Ca^{2+}	10000	2000	99
Mg^{2+}	10000	2000	96
Zn^{2+}	10	2	105
$\text{Zn}^{2+ \text{ a}}$	100	20	81

a. With higher SnCl_2 concentration, 20%.

analysis of Hg^{2+} and MeHg, based on the UV-controlled CVG with AFS detection. The new method proved to be one of the most sensitive methods for the determination of Hg^{2+} and MeHg yet also very simple. Both the reaction and the instrumentation are simple, and it is a fast, accurate and cost-effective method for water sample analyses for trace Hg^{2+} and MeHg without any complicated separation procedures.

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Table 3 The recovery of added MeHg and/or Hg^{2+} standard from a tap water sample

	Mercury added/ $\mu\text{g L}^{-1}$	Found $A \pm 3SD$ (n)/ $\mu\text{g L}^{-1}$	Rec., %
Without UV irradiation	0	1.19 ± 0.01	
	2(MeHg)	1.22 ± 0.04	1.5
	3(Hg^{2+}) + 2(MeHg)	4.23 ± 0.19	101(Hg^{2+})
UV irradiation	0	1.84 ± 0.03	
	2(MeHg)	3.66 ± 0.08	91
	3(Hg^{2+}) + 2(MeHg)	6.88 ± 0.25	101

a. Data = average $\pm 3 \times$ standard deviation (3 measurements).

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