Atomic Spectroscopy

Article

Rapid Screening Analysis of Methylmercury in Fish Samples Using Stannous Chloride Reduction and Direct Sampling Electrothermal Vaporization Atomic Absorption Spectrometry

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Received: *10 August 2020,* ***Revised:*** *7 September 2020,* ***Accepted:*** *7 September 2020,* ***Available online:*** *11 September 2020.*

DOI: 10.46770/AS.2020.05.006

ABSTRACT: A rapid analysis of methylmercury (MetHg) in fish samples is reported by using stannous chloride reduction and direct sampling electrothermal vaporization atomic absorption spectrometry (ETV-AAS). After the simple reduction reaction using 10% $SnCl_2$ (w:v), Hg^{2+} was changed to volatile Hg^0 and vaporized from the analyte extraction solution. Then, the residual Hg species was determined with the direct sampling Hg analyzer without requiring chromatographic separation. Since the dominating organic Hg in fish tissues is mostly MetHg (methylmercury), the measured alkyl Hg residue can therefore be considered to be $MetHg^+$ for rapid screening. The LOD (detection limit) of the proposed method reached 0.6 μg/kg of MetHg with 0.4% - 6.3% RSD (relative standard deviation). No significant difference ($P > 0.05$) was found between the proposed method and the liquid chromatographic atomic fluorescence spectrometry (LC-AFS) method or certified values of reference materials, which proves the accuracy of the MetHg analysis in real marine and freshwater fish samples. The total testing time for one aliquot, including instrumental analysis (~3 min) and sample preparation, can be performed within 100 min. Considering the possible EtHg (ethylmercury) existence in most fish samples, it is suggested that this proposed method be used for future rapid screening analysis, which no doubt also offers considerable applicable potential for fast mercury speciation analysis to protect food safety.

INTRODUCTION

The effects of mercury (Hg) on the biological organisms are of great concern due to high toxicity, bioaccumulation, and persistence, once also causing the terrible Minamata disease in Japan.[1] Due to industrial contamination, geological activity and other sources, Hg contamination in foods can be considered a constant threat to public health.[2] There are different Hg species and their corresponding levels of toxicity require investigation. For instance, methylmercury ($MetHg^+$) is more toxic than inorganic mercury (iHg, namely Hg^{2+}) and ethylmercury ($EtHg^+$). To control MetHg, the FAO/WHO Codex Alimentarius Commission (CAC) has established the upper limit of 1 mg/kg MetHg for predatory fish and 0.5 mg/kg for non-predatory fish. Therefore, Hg speciation in fish samples should be closely monitored to ensure public health safety.

At present, most mercury speciation analysis in fish samples is performed using gas chromatography (GC)[3,4] or GC mass spectrometry (MS),[5] liquid chromatography (LC)[6-8] coupled with

atomic fluorescence spectrometry (AFS),[9,10] cold vapor atomic absorption spectrometry (CVAAS),[11] and inductively coupled plasma optical emission spectrometry (ICP-OES)[12] or inductively coupled plasma mass spectrometry (ICP-MS).[13] To ensure that the Hg species are not altered during sample preparation, some moderate sample pre-treatments[14] have always been utilized before chromatographic separation, including shaking and ultrasonic extraction using mild extractants, such as acid/alkali solutions with or without organic reagents. However, the sample preparation required for the chromatographic separation process involves extraction, separation, and purification, which are tedious and time-consuming. Even though conventional chromatographic spectrometry is a powerful technique for sensitive speciation analysis, the instrumentation is expensive, involves high operating costs, and thus is not available in smaller laboratories, especially in developing countries.

At present, the direct sampling Hg analyzer has become the most successful solid sampling analysis instrument.[15-17] It is mainly[15] composed of an electrothermal vaporizer (ETV), a catalytic pyrolysis furnace, an amalgam trap, and a detector. ETV fulfills direct introduction of the Hg species and matrices; catalytic pyrolysis fulfills decomposition of interfering organic components as well as atomization of Hg vaporized from sample; gold amalgamation via selectively trapping/releasing of Hg^0 vapor fulfills matrix separation and sensitivity enhancement. Due to the excellent analytical performance, the direct sampling Hg analyzer has been adopted as the standard method for Hg analysis in water and solid samples by the United States Environmental Protection Agency (USEPA).[18] It has been used to measure total Hg in fish, soil, oil, geological, and gas samples without acid digestion, and requires only 3-5 min for the total analytical process.[17,19-23] However, to the best of our knowledge, the direct sampling Hg analyzer was only used to detect total Hg rather than the Hg species, and was never coupled with a speciation separation technique.

In the process of Hg vapor generation, stannous chloride was frequently employed as the reducing agent to react with Hg^{2+} to form the volatile Hg^0 species for chemical vapor generation (CVG) AAS or AFS measurement under typical conditions. During this reaction, Sn^{2+} only reduces Hg^{2+} rather than alkyl mercury including $MetHg^+$ and $EtHg^+$; so, alkyl mercury remains in the reaction system after that. Though this principle is reported for alkyl mercury analysis,[24] it has not been applied to direct sampling Hg analyzer. For this, we decided to match $MetHg^+$ analysis with the direct sampling Hg analyzer, in which the residual Hg species after the Hg^{2+}-Sn^{2+} reaction should almost all be alkyl mercury. Moreover, $MetHg^+$ accounts for 70%–95% of Hg content in fish, while the $EtHg^+$ percentage is very low.[25] Thus, for the purpose of rapid screening of fish samples, the residual Hg can be considered to be $MetHg^+$. This subtraction strategy has been adopted to determine $MetHg^+$ coupled to cold vapor atomic absorption spectrometry (CVAAS) using liquid sampling systems, where $MetHg^+$ = total Hg – Hg^{2+}.[26] However, this method still requires two measurements including acid digestion for total Hg analysis. If the direct sampling Hg analyzer can be applied to measure the residual Hg species mentioned above, the $MetHg^+$ content can be obtained directly and quickly. As a result, the analytical efficiency and speed would be significantly improved.

In this work, we utilized stannous chloride to reduce Hg^{2+} to volatile Hg^0 and vaporize it from the analyte extraction solution. Then, the residual Hg species can be measured by direct sampling Hg analyzer based on ETV-gold amalgamation-AAS, regardless of chromatographic separation, and can then be considered the $MetHg^+$ presence in fish samples. After optimization, the proposed method resulted in 0.6 μg/kg detection limit (LOD) and < 10% relative standard deviation (RSD). The analytical performance is comparable to liquid chromatography-atomic fluorescence spectrometry (LC-AFS). This proposed analytical method, no doubt, has considerably applicable potential for fast mercury speciation analysis in small size laboratories without LC-AFS.

EXPERIMENTAL

Instrumentation. The direct sampling Hg analyzer (Model 5E-HGT2321, Changsha Kaiyuan Hongsheng Technology Co., Ltd, Changsha, P. R. China) consists of thermal quartz tube as ETV, catalytic pyrolysis furnace, gold amalgamation, and AAS detector. The detector is equipped with a 253.7 nm Hg-boosted hollow cathode lamp (HCL) and long/short light paths for measuring low/high Hg concentrations, respectively. The operating parameters are listed in Table 1. O_2 (99.999%, *v/v*) was employed as the carrier gas as well as the combustion-supporting gas for dehydrating and ashing sample.

Materials and Reagents. All chemicals were of superior analytical reagent grade and purchased from Sinopharm Chemical Reagent (Beijing, P.R. China), unless otherwise stated. Standard

Table 1. Programs of Direct Sampling Hg Analyzer

ETV Program		Temperature (°C)	Hold time (s)	O_2 flow rate (mL/min)
Drying		260	5	220
Ashing/vaporization		850	80	
Catalytic pyrolysis furnace		600	/	
	Absorption tank clean	120	15	
Detection	**Heating amalgam**	800	12	
	Detection furnace	200	50	

Fig. 1 The analytical schematic diagram for MetHg in fish sample by the proposed method.

stock solutions of Hg (1000 mg/L) were purchased from the National Research Center for Certified Reference Materials (NRCCRM) (Beijing, P. R. China). Working standard solutions were obtained by stepwise dilution with purified water obtained from the Milli-Q integral water purification system (Millipore Corporation, USA). Certified reference material (CRM) of fish tissue sample (QC457B-2, MetHg: 507±28 μg/kg) (China SFAPA Testing Technology Company Limited of Dalian, Dalian, P. R. China) was used for method development and verification. The real fish samples were purchased at local supermarkets. These fish samples were descaled and skinned, the muscle tissue separated, and then mashed into fine paste. The mashed fish samples were pre-frozen at -80 °C for 12 h (Model HYC-940, Haier Co., Ltd. Qingdao, P. R. China) and further freeze-dried for 48 h in a freeze-dryer (Virtis Genesis 25L, SP Scientific, USA). Finally, these freeze-dried samples were ground and sieved through a 60 mesh sieve.

Sample preparation and analytical procedures. The sample preparation was modified from the Chinese national standard method of GB 5009.17[27] and the analytical procedures were performed as shown in Fig. 1. The detailed steps were as follows: (1) The fish samples (0.5 g) were weighed into a centrifugation tube. (2) 10 mL HCl (5 mol/L) was added to the tube, then mixed for 1 h in an ultrasonic water bath at ambient temperature to assist the extraction. (3) The analyte mixture was centrifuged at 8000 r/min for 15 min, then 1 mL of the supernatant was transferred to another centrifugation tube. (4) 1 mL of 10% $SnCl_2$ (*w:v*) solution was added with 1 mL supernatant to react with Hg^{2+} for 15 min using ultrasonic water bathing at ambient temperature. The stannous chloride reaction was performed in a sealed glass box connected to a miniature vacuum pump, in which a small chamber, filled with active carbon, was fixed in the gas line between the glass box and the vacuum pump. The active carbon was replaced periodically. (5) A certain amount of the residual solution was introduced into the direct sampling Hg analyzer for Hg measurement, and for fast screening analysis since it is considered to be present as MetHg. According to the sample mass and reagent volume, the dilution factor was found to be 40-fold.

Table 2. The Optimal Parameters for LC-AFS

Instruments	Parameters	Values
LC	Reversed-phase C18 column	Agela MP-C18 (150 mm × 4.6 mm i.d., 5 μm)
	Mobile phase	5% acetonitrile + 60 mM ammonium acetate + 10 mM cysteine
	Flow rate (mL/min)	1.0
	Injection volume (μL)	100
HG	Reducing agent	2% KBH_4 / 0.5% KOH (m/v)
	Acid	7% HCl (v/v)
	Oxidizing agent	1% $K_2S_2O_8$ / 0.5% KOH (m/v)
	UV irradiation	19 W
AFS	Hollow cathode lamp (HCL)	Hg
	PMT voltage (mV)	270 - 300
	HCL current (mA)	30
	Carrier gas (mL/min)	300
	Shield gas (mL/min)	600
	Pump speed (r/min)	35
	Atomization	Ar/H_2 diffusion flame

LC-AFS analysis. The LC-AFS instrument (SA-20, Beijing Titan Instrumental Co., Ltd., Beijing, P.R. China), equipped with a Hg hollow cathode lamp (Beijing Research Institute of Nonferrous Metals, Beijing, P. R. China) and a LC column (MP-C18, 250 mm × 4.6 mm i.d., 5 μm, Tianjin Bonna-Agela Technique Co., Ltd., Tianjin, P. R. China), was employed to measure the Hg species in the fish samples for validation of the proposed method according to the Chinese national standard method of GB 5009.17. After injecting the analyte solution, the effluent from the LC column was subjected to HG, where all separated Hg species were changed to Hg^{2+} by $K_2S_2O_8$ under UV irradiation, then reduced to Hg^0 by KBH_4 in HCl medium. Subsequently, the generated volatile Hg^0 species passed to the AFS by carrier gas for measurement. The instrumental parameters of LC-HG-AFS are shown in Table 2. Ar gas (99.999%, *v:v*), containing 10% H_2 (99.999%, *v:v*), was employed to fulfill the atomization of Hg in AFS.

RESULTS AND DISCUSSION

Stannous chloride reaction conditions. Stannous chloride is frequently employed to react with Hg^{2+} to form the volatile Hg^0 species and then remain alkyl mercury, such as $MetHg^+$ and $EtHg^+$, in the residual solution. This is the basic principle of MetHg analysis in this work. Thus, the effect of $SnCl_2$ on the Hg species possibly existing in the fish samples was investigated. Here, 1 mL of single elemental solution of Hg^{2+}, $MetHg^+$, and $EtHg^+$ and their mixture were employed to react with 1 mL 10% $SnCl_2$ (*w:v*) solution, respectively. The 3% Hg^{2+} recovery obtained (as listed in Table 3) shows that more than 97% was removed from the analyte solution; while MetHg and EtHg remained at more than 96% and 94%, respectively. In addition, the recovery of mixture of Hg^{2+} (10 μg/L) + MetHg (10 μg/L) + EtHg (6 μg/L) was 98% after $SnCl_2$ reaction. It proved that the Hg^{2+}-Sn^{2+} reaction using 1 mL 10% $SnCl_2$ (*w:v*) solution fulfilled the alkyl Hg residual without significant Hg^{2+} interference in the standard solution medium.

Table 3. Effect of $SnCl_2$ on Hg Species after Hg^{2+}-Sn^{2+} Reaction (n=3)

Sample [a]	Added (μg/L)	Residue Measured (μg/L)	RSD (%)	Recovery [b] (%)
Hg^{2+}	10	0.15	12	3.0±0.4
MetHg	10	4.8	4	96±4
EtHg	6	2.83	1	94±1
Mixed	10 (Hg^{2+}) 10 (MetHg) 6 (EtHg)	7.8	6	98±6

[a] For Hg^{2+}, $MetHg^+$, or $EtHg^+$, 1 mL of single elemental solution was mixed with 1 mL 10% $SnCl_2$ (*w:v*) solution. So, the dilution factor is 2.
[b] The recovery is calculated as follows: (Residue measured × 2)/added × 100%. For Hg^{2+}, the added is 10 μg/L; for MetHg, the added is 10 μg/L; for EtHg, the added is 6 μg/L; for mixed, the added is 16 μg/L (MetHg + EtHg).

Fig. 2 The tolerance of $SnCl_2$ for Hg^{2+} concentration in real sample analysis. The Y axis shows the residual Hg (alkyl mercury) in solution after 40-fold dilution during the extraction process. So, the certified Hg residual concentration should be 12.7 ± 0.7 μg/L considering MetHg: 507±28 μg/kg.

The tolerance of $SnCl_2$ in real samples. However, the tolerance of $SnCl_2$ for Hg^{2+} is limited by the Hg^{2+} presence in real samples. Therefore, a CRM sample of fish tissue (QC457B-2) was prepared according to the sample preparation method mentioned above, where different Hg^{2+} concentrations were spiked into the extracted analyte solution ready for measurement. As shown in Fig. 2, the measured Hg presence is in accordance with the certified value of MetHg in the CRM before 200 μg/L Hg^{2+} spiking, indicating no obvious Hg^{2+} interference. With an increase in Hg^{2+} concentration in the range of > 200 μg/L, the amount of measured Hg obviously increased. This was possibly due to excessive Hg^{2+} which cannot be completely reduced with 1 mL 10% $SnCl_2$ (*w:v*) solution. Of course, if needed, one can increase the concentration of $SnCl_2$ to enhance the reduction reaction. In practice and considering a 40-fold dilution obtained during sample preparation, it is impossible that 8 mg/kg (approximately 200 μg/L × 40) Hg^{2+} would exist in real fish samples. As a result, 1 mL 10% $SnCl_2$ (*w:v*) solution was used for MetHg analysis in real fish samples.

Determination of Hg^{2+} species in real fish samples. The subtraction method adopted to detect $MetHg^+$ was coupled to the CVAAS, where $MetHg^+$ = total Hg – Hg^{2+}.[28,29] However, the proposed method enables the direct analysis of MetHg after Hg^{2+}-Sn^{2+} reaction. Based on reverse thinking, the Hg^{2+} present in the fish samples can be obtained via the calculation Hg^{2+} = total Hg – $MetHg^+$. Thus, total Hg must first be measured by the direct sampling Hg analyzer. It is another advantage that direct sampling Hg analyzer is capable to measure total Hg in real fish sample without digestion process.

To investigate the feasibility of Hg^{2+} calculation, a real fish sample was employed to determine the total Hg and MetHg concentrations with different Hg^{2+} spikes. As shown in Table 4, the dominating Hg species in this real fish sample is MetHg, accounting for 61%-79%, which is consistent with other studies.[25,30] In addition, the Hg^{2+} spike recoveries are at different levels ranging from 99%-104%, proving favorable accuracy for inorganic Hg analysis by the proposed method. However, Hg^{2+} is not the main target species of this work but can be applied when needed.

Table 4. Recovery Analysis of Hg Species in Fish Samples (n=3)

Sample	Measured MetHg (μg/kg)	Add Hg^{2+} (μg/kg)	Total Hg (μg/kg)	Calculated Hg^{2+} (μg/kg)[a]	Recovery (%)
Sea bass	22.8±2.6	0	28.7±1.1	5.9	—
		50	80.6±2.9	51.9	104±4
		200	227.4±8.5	198.7	99.4±3.7
Fish CRM (QC457B-2)	491±8	0	808±26	317	—

Table 5. Comparison of This Proposed Method with Others Reported Previously

Methods	Sample	LOD	Analysis time (min)	Recovery (%)	Ref.
GC-ICP-MS	Fish	0.3 μg/kg	200	87-117	2
HS-SPME-GC-PD-OES	Hair	Hg^{2+}: 0.35 μg/kg MetHg: 1 μg/kg	220	85-93	4
LC-ICP-MS	Blood	Hg^{2+}: 0.02 ng/g MetHg: 0.04 ng/g	17 (instrumental analysis)	80-95	6
MSPE-HPLC-ICP-MS	Fish/water	Hg^{2+}: 0.74 ng/kg MetHg: 0.67 ng/kg	795	81-118	8
LC-PVG-AFS	Fish/hair	MetHg: 1.06 μg/kg	55	93-105	9
HPLC-CV-AFS	Fish	Hg^{2+}: 0.6 μg/kg MetHg: 0.56 μg/kg	600	98-103	10
FI-DBD-AAS	Fish	Hg^{2+}: 0.35 ng/g MetHg: 0.54 ng/g	41	95-106	11
CV-AFS	Mushroom	Hg^{2+}: 0.6 ng/g Total Hg: 3.2 ng/g	—	94-104	29
HPLC-ICP-MS	Fish/water	Hg^{2+}: 15 ng/kg MetHg: 17 ng/kg	300	93-114	31
ETV-amalgamation-AAS	Fish	MetHg method LOD: 0.6 μg/kg Absolute LOD: 3 pg	The whole time: 100; Instrumental analysis: < 5	85-106	This work

Analytical performances. Under the optimized conditions, the analytical figures of merit were evaluated. The linearity of the calibration curve was investigated by measuring a series of standard solutions ranging from 0 – 20 ng in long light path and 20 – 500 ng in short light path, and with linear regression coefficients (R^2) of 0.999 and 1, respectively. The absolute LOD and limit of quantification (LOQ) for MetHg was 3 pg and 10 pg, respectively, calculated by taking 3 or 10 times the standard deviation of the blank solution divided by the slope of the calibration from 11 repeated measurements. So, the method's LOD and LOQ was 0.6 μg/kg and 2 μg/kg using 0.2 mL sample size (maximum loading for sampling boat of direct sampling Hg analyzer), respectively, and considering a 40-fold dilution. Actually, the proposed analytical sensitivity is comparable to LC-AFS, proving a promising application for fast screening analysis of MetHg in fish samples. The RSDs for MetHg in real samples (salmon, cod, *Trachinotus ovatus*, and flatfish) were in the range of 0.4%-6.3%, indicating good analytical precision. In addition, the recoveries for marine (*Larimichthys crocea*, spiked with 120, 240, and 480 μg/kg MetHg) and freshwater (mandarin fish, spiked with 20, 40, and 80 μg/kg MetHg) fish samples ranged from 85% to 106%, demonstrating favorable analytical accuracy.

In Table 5, this proposed method is compared to previously reported literature. The instrumental LOD of Hg using the direct sampling Hg analyzer was comparable to CV-AFS or CV-AAS, but inferior to ICP-MS analysis. However, in spite of the dilution factor from the sample preparation, the established method LOD (0.6 μg/kg) is competent to the fast detection of MetHg in fish samples. If necessary, some preconcentration approaches, such as MSPE, SPME, *etc.* (Table 5), can be utilized to pre-concentrate analyte to enhance the detection capacity of MetHg.

The proposed method's analytical time including sample preparation and instrumental analysis time was < 100 min, of which the sample preparation of extraction, purification and reaction process accounts for > 90 min. Thus, 100 min is less than used with most of methods listed in Table 5. It is more important that the practical analysis time using the direct sampling Hg analyzer requires only ~3 min, which is obviously shorter than that by the LC methods. So, several dozen samples can be processed in one batch by the proposed method, leading to a significant time savings for real sample analysis in comparison to the LC methods.

Method validation and real sample analysis. To validate the feasibility of the proposed method, several real fish samples were used. The presence of alkyl Hg was determined in all samples by the established method (n = 3) as well as the LC-AFS method in accordance with the Chinese national standard method of GB 5009.17. As shown in Table 6, the relative deviations between the proposed method and the LC-AFS standard method or certified values are from 0.8% to 3.0% in real marine and freshwater fish samples. In addition, there is no significant difference ($P > 0.05$) between the proposed method and the LC-AFS method. Their results show favorable consistency of MetHg analysis with the certified or standard method values. The whole analytical time, including sample preparation can be accomplished within 100 min, verifying fast analysis of alkyl Hg including MetHg in real fish samples. In addition, the results in Table 6 show that the MetHg levels in freshwater fish are obviously lower than in marine fish samples, which is in agreement with other previous reports.[25,30] It can, therefore, be stated that the proposed method is a fast screening method for MetHg presence in fish samples. When also MetHg and EtHg speciation analysis is required, LC atomic spectrometry can be further utilized.

Table 6. Determination of MetHg Species in Real Fish Samples (n=3)

Sample	The proposed method (μg/kg)	LC-AFS or certified (μg/kg)	Relative deviation (%)	P value [a]	Recovery [b] (%)
Fish CRM (QC457B-2)	491±8	507±28	0.8	0.457	97
Trachinotus Ovatus (Marine)	135±6	136±1	1.0	0.676	99
Larimichthys crocea (Marine)	268±5	275±5	1.8	0.319	97
Snapper (freshwater)	36.3±1.0	35.3±2.0	3.0	0.488	103
Mandarin fish (freshwater)	35.5±1.1	36.7±1.9	2.4	0.531	97

CONCLUSIONS

The direct sampling Hg analyzer was utilized in this report for the fast measurement of MetHg in fish samples by employing stannous chloride reduction. After the simple reduction reaction, Hg^{2+} was changed to volatile Hg^0 and vaporized from the analyte extraction solution. Based on the results, the residual Hg species can be quickly determined by direct sampling Hg analyzer regardless of chromatographic separation. Because the dominating organic Hg in fish tissue is mostly MetHg, therefore, for fast screening analysis the measured alkyl Hg residue can be used as a measure for the MetHg presence. The proposed method achieved 0.6 μg/kg LOD with good precision. The analytical sensitivity is comparable to results by LC-AFS or LC-CVAAS and furthermore, sample preparation and testing can be accomplished within 100 min. On the other hand, the Hg^{2+} presence in the fish samples can be calculated by subtracting the total Hg and alkyl Hg values. This proposed method no doubt has considerable potential for fast screening Hg speciation. Considering the detrimental effect on humans from MetHg in fish, this proposed method should be used for rapid screening analysis to protect food safety.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This investigation was funded within the Central Public-interest Scientific Institution Basal Research Fund (No. Y2019XK05/1610072018003), Agricultural Science and Technology Innovation Program of CAAS (No. CAAS-ZDRW202011), and National Key Research and Development Program of China (No. 2016YFF0103306). As well, sincerest thanks to the support of the Agricultural Science and Technology Innovation Program presided over by Yongzhong Qian.

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