



Speciation of mercury by hydride generation ultraviolet atomization-atomic fluorescence spectrometry without chromatographic separation

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ABSTRACT

A novel ultraviolet (UV) atomization atomic fluorescence spectrometry (UV-AFS) without chromatographic separation was developed for quantitative speciation analysis of mercury (inorganic mercury (Hg^{2+}) and methylmercury (MeHg^+)) in food samples. In the proposed method, with 0.1% (m/v) KBH_4 used as a reductant, inorganic mercury was measured by using the non-ultraviolet radiation mode. However, under the ultraviolet atomization, the volatile MeHg^+ hydride (MeHgH) generated by KBH_4 can be transformed to elemental mercury vapor, and total Hg (MeHg and Hg^{2+}) was detected in this UV atomization mode. Under the optimized experimental conditions, the limits of detection (LODs) were found to be 0.015 and 0.081 mg L^{-1} , for Hg^{2+} and MeHg^+ . And the relative standard deviations (RSDs) ($n = 11$) were 2.4% and 0.4%, respectively. Spiked environmental water samples including seafood, fruits and vegetables were determined and satisfactory recoveries were obtained for MeHg^+ and Hg^{2+} detection.

1. Introduction

Mercury is one of the important environmental contaminant impacting on human and ecosystem health because of its accumulative and persistent character in the environment [1]. Currently, mercury pollution becomes a worldwide environmental problem [2,3]. The toxicity, bioavailability and mobility rely not only on their total concentration but also significantly on their chemical forms [4]. All mercury species are toxic, and organic mercury compounds generally were more toxic than inorganic species. Among them the Methylmercury (MeHg^+) is the most toxic species found in environmental and biological samples, due to their high biomagnification factor (up to 10^6) in the food chain and their high solubility [5,6]. Nowadays it is well known that mercury released into the environment can be transformed into the methylmercury form undergoes biogeochemical transformation processes by microorganisms and microalgae in aquatic environments [7]. Therefore, only monitoring the total mercury concentrations in the sample is not enough, it was necessary to select the proper method for speciation analysis, which provides more useful information to assess the toxicity and health risks of mercury [8,9]. Mercury speciation analysis commonly pays attention to methylated (MeHg^+) and Hg^{2+} species [10,11].

Atomic spectrometry [12], including atomic absorption

spectrometry (AAS) [13,14], atomic fluorescence spectrometry (AFS) [15,16] and inductively coupled plasma atomic emission spectrometry/mass spectrometry (ICP-AES/MS) [17–19], is most commonly used for Hg^{2+} detection. The most common approach for mercury speciation analysis is to hyphenate a powerful separation technique to a sensitive atomic spectrometric detector, for example, gas chromatographic (GC) [20–22], high performance liquid chromatographic (HPLC) [23,24], capillary electrophoresis (CE) [25,26] coupled to ICP-AES/MS, AAS, or AFS. Although these hyphenated techniques are powerful since they provide more species information because both species can be determined without obtaining the concentration of one of them by difference, they bring in several drawbacks like several problems originate from the difference in eluent flow rate or sample volume between the separation system and the detection system, and most hyphenated techniques using traditional nebulization for sample introduction have low sampling introduction efficiency, and cannot tolerate a high concentration matrix; and higher instrumental and operational cost of using hyphenated techniques can be a factor to consider in many cases [10,11,15]. Therefore, it is still attractive to many works to realize simple speciation analysis without chromatographic (non-chromatographic) separation [27–29]. Non-chromatographic methods based on varied chemical and physical behaviors of different Hg species open another avenue for mercury speciation analysis. Different atomization

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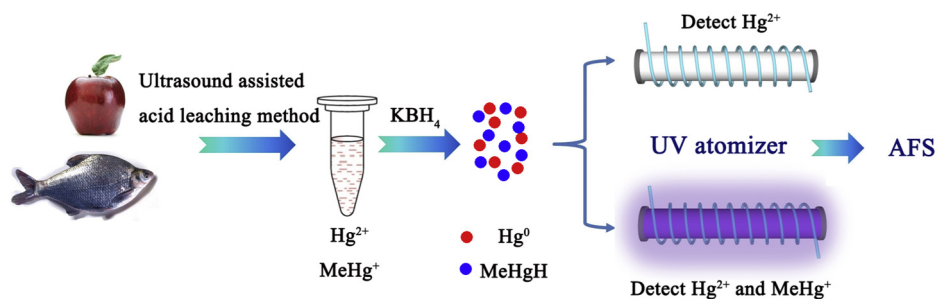


Fig. 1. Schematic diagram of the entire experimental procedure.

modes for the discrimination of inorganic and MeHg^+ by vapor generation-atomic spectrometry was also developed, including W-coil [30], DBD [31] and flame atomizer [32].

Therefore, a novel, simple, non-chromatographic, low power, low temperature ($< 45\text{ }^\circ\text{C}$), and high efficiency atomization technique using ultraviolet (UV) radiation was proposed for the atomization of gaseous mercury hydrides for their speciation analysis by atomic fluorescence spectrometry (AFS). Hg^{2+} can be determined without UV radiation as elemental Hg vapor after hydride generation (HG) with low concentration of KBH_4 at the first time, while MeHg^+ can be transformed to methylmercury hydride (MeHgH) with low concentration of KBH_4 . Total mercury (MeHg^+ and Hg^{2+}) can be detected by AFS in the absence of UV atomizer at the second sample loading, because organic mercury hydrides can be converted to Hg^0 inside the low temperature UV atomizer. The methylmercury mercury concentration was calculated by subtracting the inorganic mercury concentration from the total mercury concentration. Based on the new atomization, a simple, fast, cost-effective, highly selective, ultrasensitive yet inexpensive method is established for the mercury speciation analysis.

2. Experimental section

2.1. Instrumentation

All measurements were performed with a double-channel non-dispersive atomic fluorescence spectrometer, model AF-2200 (Beijing Beifen Ruili Analytical Instrument (Group) Co., Ltd., Beijing, China). The detection was performed on the atomic fluorescence spectrometer with a high-intensity mercury hollow cathode lamp (General research institute for non-ferrous metals, Beijing, China) and two sequential gas liquid separators (GLS). Argon with a purity of 99.999% (Chengdu Tai Yu gas Co., Ltd., Chengdu, China) was used as carrier gas to transport the analytes to AFS and shield gas for the atomizer. The UV atomizer was a low-pressure Hg vapor UV lamp (15 W, Philips Co., Holland) wrapped with a quartz tube (15.0 mm i.d., Guoxiang Glass Factory, Chengdu, China). Three kinds of materials, quartz tube, polytetrafluoroethylene (PTFE) tube and silicone tube were tested in the experiment. The UV atomizer was placed inside a black box, which served to protect skin and eyes of operators from UV radiation.

2.2. Reagents and standards

All reagents used in this work were of analytical-reagent or higher grade and used without further purification. Water used in all experiments was purified by a water purification system (Ulupure, Chengdu, China) with a resistivity of $18.2\text{ M}\Omega\text{ cm}$. KBH_4 , KOH , H_2O_2 and high purity acid HCl , HNO_3 was obtained from Kelong Chemical Reagents (Chengdu, China). Standard solutions of heavy metals, the 1000 mg L^{-1} inorganic mercury, Pb(II) , Cd(III) , Zn(II) , Se(IV) , As(III) , Cr(III) , Na(I) , Fe(III) stock solution and 100 mg L^{-1} Te(VI) stock solution (National Research Center for Standard Materials of China) were used in the interference study. A certified reference material (GBW08675) from the

national research center for standard materials of china was used to further validate the accuracy of the proposed method. A 65 mg L^{-1} methylmercury chloride (MeHg^+) stock solutions (Beijing Tanmo quality Testing Technology Co., Ltd., Beijing, China) were used in the experiments. Working standard solutions of different concentrations were prepared by stepwise diluting the stock standard solution with water when it is necessary. All solutions were stored at $4\text{ }^\circ\text{C}$ in refrigerator.

2.3. Sample preparation and analysis procedure

Sample preparation is a key step for the accurate determination of mercury in different sample matrices. For mercury speciation analysis, microwave/sonication assisted acid leaching or alkaline dissolution methods are more favorable and have experienced sustaining increase in recent years because of their simple devices and high extraction efficiencies [33]. Ultrasound assisted acid leaching method was selected for the subsequent experiments.

7 fresh seafood samples, 5 fruit and vegetable samples were obtained from a local fish market. The sonication-assisted acid leaching procedure was used to liberate Hg^{2+} and MeHg^+ from the seafood samples. Briefly, 0.2 g of sample was accurately weighed into a 10 mL plastic centrifuge tube, and 10 mL of 5% (v/v) HCl solution was added. The centrifuge tube was put in a water bath for 30 min sonication at room temperature. After centrifugation at 4000 rpm for 10 min. The supernatant was quantitatively transferred to a new 10 mL plastic centrifuge tube. The residue was extracted with another 5 mL 5% (v/v) HCl under the same conditions and then centrifuged. The two portions of supernatant solutions were combined and filtered through a $0.22\text{ }\mu\text{m}$ filter prior to analysis.

A schematic diagram of the entire experimental procedure is shown in Fig. 1. In the proposed procedure, standard solution or sample was mixed with HCl and KBH_4 , and the generated mercury hydrides and elemental mercury cold vapor were separated in the GLS and flushed by the argon gas flow to the UV atomizer for atomization and AFS detection. The fluorescence intensity measured by the atomic fluorescence spectrometry (AFS) is mercury signal without the irradiation of the UV lamp; whereas the fluorescence intensity measured by the atomic fluorescence spectrometry (AFS) is the signal of mercury and methylmercury under the conditions of the ultraviolet lamp irradiation. The optimized experimental parameters of the AFS instrument are listed in Table 1.

3. Results and discussion

3.1. Method development

In order to verify the feasibility of the high efficiency atomization technique using ultraviolet (UV) radiation method, the experiment compares the atomic fluorescence intensity of mercury and methylmercury in the presence and absence of UV lamp radiation, respectively. The results shown in Fig. 2, we found that UV irradiation has

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