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ORIGINAL PAPER

Ultrasensitive determination of mercury in human saliva by atomic fluorescence spectrometry based on solidified floating organic drop microextraction

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Abstract We report on a new, rapid and simple method for the determination of ultra-trace quantities of mercury ion in human saliva. It is based on solidified floating organic drop microextraction and detection by cold vapor atomic fluorescence spectrometry (CV-AFS). Mercury ion was complexed with diethyldithiocarbamate, and the hydrophobic complex was then extracted into fine droplets of 1-undecanol. By cooling in an ice bath after extraction, the droplets in solution solidify to form a single ball floating on the surface of solution. The solidified microdrop containing the mercury complex was then transferred for determination by CV-AFS. The effects of pH value, concentration of chelating reagent, quantity of 1-undecanol, sample volume, equilibration temperature and time were investigated. Under the optimum conditions, the preconcentration of a 25-mL sample is accomplished with an enrichment factor of 182. The limit of detection (3σ) is 2.5 ng L^{-1}. The relative standard deviation for seven replicate determinations at 0.1 ng mL^{-1} level is 4.1%. The method was applied to the determination of mercury in saliva samples collected from four volunteers. Two volunteers having dental amalgam fillings had 0.4 ng mL^{-1} mercury in their saliva, whereas mercury was not detectable in the saliva of two volunteers who had no dental fillings.

Keywords Solidified floating organic drop microextraction · Mercury · Atomic fluorescence spectrometry · Saliva

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Introduction

Human saliva is one of very important body fluids which can be used as a biomarker for exposure to chemical pollutants [1–6]. Some toxic elements, ingested by human can be metabolized through saliva [2, 6]. Salivary mercury can potentially reflect the level of mercury inside the body or the exposure extent to mercury [3]. In addition to that, studies also reported that mercury could be released from dental amalgam fillings into mouth [3, 7]. The released mercury is regarded as one of the main sources of mercury exposure to humans who are not exposed due to their occupation nor eating seafood. Because of the toxicity and bioaccumulation nature of mercury [8, 9], it is very important to quantify the concentration of mercury in human saliva, which is very significant for further study on both toxicity of mercury and public health.

Normally, mercury can be determined by many well established methods and advanced instruments including atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICPMS), atomic fluorescence spectrometry (AFS) and atomic emission spectrometry (AES) [10–14]. The detection limits (DL) of these mentioned analytical instruments are very sensitive and can meet the requirements for detection of mercury in a wide range of concentrations. However, a preconcentration step of mercury has to be used before detection when its level is very low [10, 15–21]. So, it is significant and necessary to develop new methods for the enrichment of mercury in some special samples before analysis [22–25]. Normally, the level of mercury in human saliva is low and the reports about mercury analysis in human saliva were very scarce [26, 27]. Saliva is viscous since it contains proteins. It is not suitable to inject saliva samples directly into instruments for determination. The samples always need to be digested or diluted by acid before analysis. This pretreatment procedure results in a

further decrease in concentration of mercury in samples and makes it more difficult for detection definitely. Therefore, it is very important to develop new methods for ultrasensitive determination of mercury in human saliva.

Liquid phase microextraction (LPME) has been applied to the determination of pollutants at very low level in various samples in recent years [28–31]. The main advantage of LPME is the great reduction of solvent volume used during extraction compared with the conventional liquid-liquid extraction. High extraction efficiency and enrichment factor can be obtained because of large volume ration of donor to acceptor phase [28, 32, 33]. Li et al. [34] had developed a method for the determination of mercury in water samples that combines dispersive liquid-liquid microextraction (DLLME) with back-extraction (BE) and detection by capillary zone electrophoresis. Very high enrichment factor (625) was achieved. As one of new preconcentration methods, solidified floating organic drop microextraction (SFODME) has been developed in recent years [32, 35–39]. A very small volume of organic solvent with a melting point near room temperature is used during the extraction and the extraction procedure can be conducted by agitation [35]. After the transfer of analytes between these two phases, the hydrophobic analytes or complexes are extracted into the very fine drops in the aqueous solution. Under the proper stirring conditions, the fine drops in the solution can be re-converged into one drop and the drop is floated on the surface of aqueous solution. The solution is stirred for a designed period of time and then is put into ice bath. The liquid drop floating on the surface of the aqueous solution is changed into solid ball very fast [36–39]. The solid ball can easily be transferred into conical vial for dissolving and analysis. Because the very tiny volume of organic solvent is used in extraction, very high enrichment factor can be achieved [35–39].

Salivary mercury can be used as biomarker for mercury exposure, but the level is very low. Sensitive quantification of trace mercury in it is very significant for toxicological study and risk assessment. However, to our best knowledge, both the preconcentration and the determination methods for mercury in human saliva are very lack. The objective of this paper is to establish a new, rapid, sensitive and precise method for the preconcentration and determination of mercury in human saliva by AFS after solidified floating organic drop microextraction.

Experimental

Instrumentation

The measurements of mercury were performed using a cold vapor atomic fluorescence spectrometer (CVAFS) (Suzhou Qingan Instruments Co., Suzhou, China, http://www.greencalm.com/). Mercury hollow cathode lamp was employed as radiation source. The 253.7 nm mercy wavelength was used in the subsequent determinations. Mercury cold vapor was produced using a chemical vapor generation cell [31]. Nitrogen (>99.99%) was used as both the carrier gas and the assistant gas at the flow rates of 300 mL min^{-1} and 500 mL min^{-1}, respectively. 0.4 mL of 10% (m/v) $SnCl_2$ was used as reducing reagent for mercury cold vapor generation. The voltage was set at 400 V after optimization for the good ratio between noise and signal. The pipettes and vessels were kept in 10% or 50% nitric acid for at least 24 h and subsequently washed three times with deionized water before use.

Reagents and solutions

All reagents used in this study were of analytical grade or better. The stock solution of Hg (1000 μg mL^{-1}) was obtained from National Institute of Metrology (Beijing, China, http://www.rmhot.com/). Working standard solutions were prepared daily by appropriate dilution of the stock solution with deionized water. 1.0 mol L^{-1} hydrochloric acid (HCl) and 1.0 mol L^{-1} sodium hydroxide (NaOH) were used to adjust the sample pH in the range of 1.0–12. The extraction solvent, 1-undecanol, was purchased from Beijing Chemical Reagent Co., China (http://www.crc-bj.com/). The solution of sodium diethyldithiocarbamate (DDTC) was prepared by dissolving appropriate amount of DDTC (Beijing Chemical Reagent Co., China, http://www.crc-bj.com/) in water. Nitric acid (HNO_3) solutions were prepared by dilution with deionized water from the concentrated acid. Ethanol was used to decrease the viscosity of organic phase. All solutions were prepared with deionized water (18.2 MΩ cm^{-1}) obtained from Easypure Barnstead Water Purification System (Thermo Scientific Co., USA, http://www.thermoscientific.com/).

Extraction procedure

A 25 mL of sample or standard solutions containing Hg^{2+} was placed in a 50 mL beaker with a stirrer bar. The pH of solutions was adjusted to 2.0 by 1.0 mol L^{-1} HCl. 100 μL of diethyldithiocarbamate (0.6%, m/v) was added into the solution. Then, the magnetic stirrer was turned on and the solution was stirred for 10 min at 500 rpm. After the solution was blended entirely, 60 μL of 1-undecanol was spiked into the stirring solution. Under the proper stirring conditions, the organic solvent droplet floated on the surface of the aqueous solution due to its lower density than that of water. During the stirring step mercury ions reacted with diethyldithiocarbamate (DDTC) to form Hg-DDTC complex and were extracted into 1-undecanol. After extraction was over, the beaker was placed in an ice bath in order to solidify the organic solvent. Because of low melting point (11 ◦C) of 1-undecanol the solidified drop was obtained rapidly. Then the solidified solvent was

immediately transferred to a 5 mL conical vial by a mini spatula and was diluted to 2.0 mL with ethanol. The whole sample was then poured into the reaction cell for elemental mercury generation and the concentration of mercury in the samples or standard solutions was determined by atomic fluorescence spectrometer.

Application

Adequate amounts (0.2–0.5 g) of certified reference material (GBW10020, citrus leaf) were weighted into a PTFE container (30 mL) in triplicate. 10 mL of aqua regia was then added. The samples were decomposed in oven at 75 °C for 6 h. After digestion, the residue was diluted to 100 mL by deionized water. The pH was adjusted to 2.0 before analysis. Then the extraction procedure was applied for preconcentration of mercury in the solution.

The saliva samples were collected from four volunteers (one male, and three females). All of the volunteers were adults in the age of 25–58 years old. All of volunteers were forbidden from eating any seafood at least two weeks before saliva collection. The volunteers were informed about all details of our experiment and they all know the objective of our research. Two of volunteers were with dental amalgam fillings for about 10 years. The other two volunteers were without any dental problem. More than 6.0 mL of saliva samples were collected from each volunteer before breakfast. All of them were asked to rinse their mouth by deionized water before sample collection. 2.0 mL of the saliva samples were put into polytetrafluoroethylene (PTFE) container and digested by the mix of HNO_3 (4.0 mL) and H_2O_2 (1.0 mL) at 75 °C for 6 h in oven. After digestion, the residue was diluted to 25 mL by deionized water for preconcentration and determination.

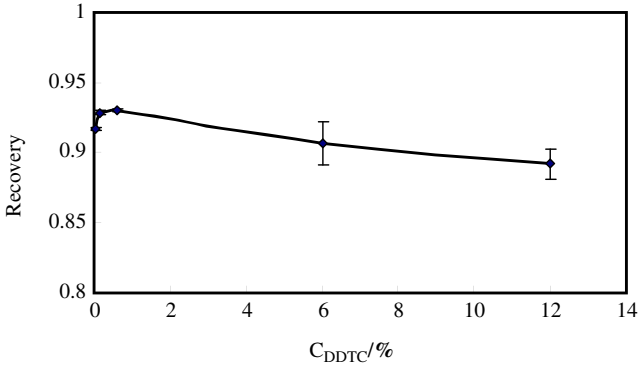

Fig. 2 Effect of concentration of DDTC on extraction of Hg^{2+}. (Conditions: 25 mL of 0.5 ng L^{-1} Hg^{2+} solution, pH 2.0, 100 μL of DDTC solution, 60 μL of 1-undecanol, extraction at 35 °C for 5 min, n=3, Y-axis value "1" means "100%")

Results and discussion

Effect of pH

Because pH plays an important role in metal-chelate formation and affects its chemical stability, the influence of pH on the extraction of mercury complex from solution into 1-undecanol was studied by varying the pH value within the range of 1.0–12.0. The other variables were kept constant. 1.0 mol L^{-1} hydrochloric acid (HCl) and 1.0 mol L^{-1}sodium hydroxide (NaOH) were used to adjust the pH of solutions. Figure 1 shows the influence of pH on the extraction efficiency of mercury by solidified floating organic drop microextraction. As can be seen in Fig. 1, the extraction recovery of mercury depended on the pH of solution. The recovery increased from pH 1.0 to pH 2.0 and remained constant in the range of 2.0–3.0. When pH was higher than 3.0, the recoveries decreased obviously. A pH values around 2.0 to 3.0 were found to be the optimum for the quantitative extraction of

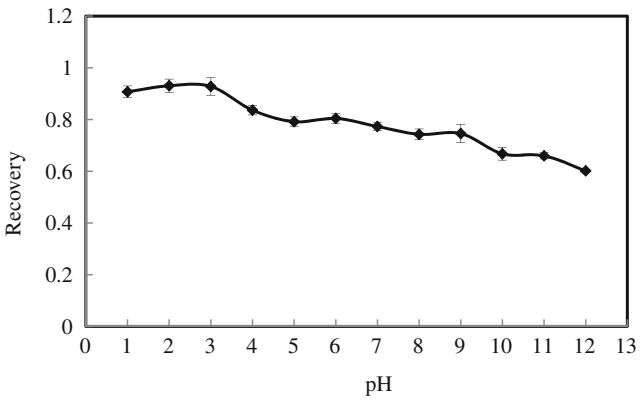

Fig. 1 Effect of pH on extraction of Hg^{2+}. (Conditions: 25 mL of 0.5 ng L^{-1} Hg^{2+} solution, 100 μL of 0.6% (m/v) DDTC solution, 60 μL 1-undecanol, extraction at 35 °C for 5 min, n=3, Y-axis value "1" means "100%")

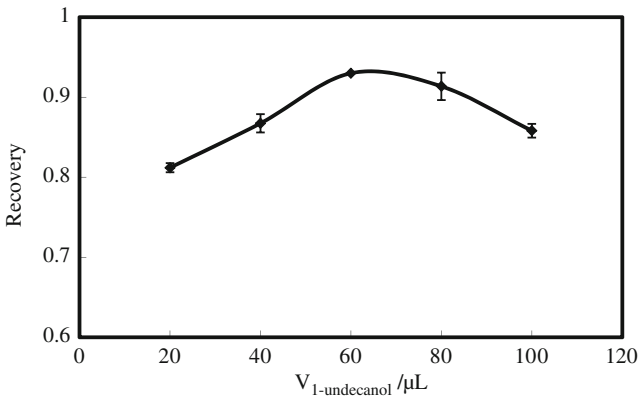

Fig. 3 Effect of 1-undecanol volume on extraction of Hg^{2+}. (Conditions: 25 mL of 0.5 ng L^{-1} Hg^{2+} solution, pH 2.0, 100 μL of 0.6% (m/v) DDTC solution, extraction at 35 °C for 5 min, n=3, Y-axis value "1" means "100%")

Table 1 Analytical characteristics of the method

Element conditions	Concentration range(ng mL^{-1})	Regression equation	R^2	LOD (ng mL^{-1})[a]	RSD(%)
Hg^{2+} without preconcentration[b]	5.0–100.0	A=1.65 C+1.32	0.9991	2.0	1.9
Hg^{2+} with preconcentration[c]	0.025–10.0	A=300.91 C+3.74	0.9931	0.0025	4.1

[a] LOD means limit of detection (3σ)

[b] The injection volume of Hg^{2+} standard solution was 60 μL

[c] Solution volume was 25 mL

mercury complex in solution. Hence, pH 2.0 was chosen as the optimum for subsequent experiments.

Effect of diethyldithiocarbamate concentration

In general, the concentration of the chelating reagent has a remarkable influence on the extraction efficiency. In order to select the optimal concentration of diethyldithiocarbamate (DDTC), the effect of the chelating reagent's concentration on the extraction efficiency was investigated with the other experimental parameters remaining constant. To minimize the possible volume changes caused by solution addition, 100 μL of DDTC with different concentrations was added. The concentrations varied in the range of 0.03%–12% (m/v). The results in Fig. 2 revealed that the extraction recovery increased with an increase in DDTC concentration from 0.03% up to 0.6%. The results also indicated that the presence of too excess amount of the chelating reagent resulted in a decrease in extraction efficiency. Therefore, 0.6% (m/v) diethyldithiocarbamate solution was chosen for further study.

Effect of extraction solvent volume

The organic solvent volume used in the extraction procedure determines enrichment performance. In order to evaluate the effect of organic solvent volume on the extraction efficiency, different volumes of 1-undecanol in the range of 20–100 μL were subjected to the extraction procedure. The results were shown in Fig. 3. By increasing the volume of 1-undecanol from 20 μL to 60 μL the recovery and extraction efficiency were enhanced. When the volume of 1-undecanol was larger than 60 μL, the recovery decreased. Therefore, 60 μL of 1-undecanol was chosen for subsequent experiments in order to achieve higher enrichment factor.

Other experimental conditions including extraction temperature and time, sample volume, ion strength and potential effect caused by interfering ions were also investigated and discussed in our paper. The details were shown in the electronic supplementary material (ESM). After optimization, the extraction was conducted at 35 °C with 5 min of extraction time (Figure S1 and S2, Electronic Supplementary Material, ESM). The results also indicated that the extraction efficiency and recovery were quantitative between 20 mL to 400 mL of sample volume. The tolerable ion strength was below 2% (m/v) of NaCl and the potential interfering ions did not cause obvious effect on the extraction efficiency and recovery (Table S1, ESM).

Analytical performance

The analytical characteristics of the developed method were evaluated by processing standard solutions under the optimized experimental conditions. The enhancement factor was calculated as the ratio between the slopes of a calibration curve submitted to the extraction procedure and a calibration curve without preconcentration (Table 1). A 182.4-fold enrichment factor was achieved by applying 25 mL of solution. A limit of detection (LOD) defined as the concentration of mercury produced the signal intensity as three times the standard deviation of the blank signal (3σ) was found as 0.0025 ng mL^{-1}. The relative standard deviation (RSD) resulted from the analysis of seven replicates at 0.1 ng mL^{-1} of Hg^{2+} (25 mL) was 4.1%. The calibration graph was dynamically linear in the range of 0.025 ng mL^{-1} to 10.0 ng mL^{-1} with a correlation coefficient of 0.9931. The presented method was quite sensitive and adequate to determine the ultra trace mercury in human saliva samples.

In order to validate this established method, the extraction procedure was applied to the certified reference material (GBW10020, citrus leaf). The certified value and found

Table 2 Determination of mercury in human saliva samples from four volunteers. (Volunteers 1 and 2 had dental amalgam fillings, and volunteers 3 and 4 had no dental fillings. The results (ng·mL^{-1}) are from triplicate analyses)

Sample	Measured[a]	Spiked	Found[a]	Recovery[b] (%)
Saliva 1	0.43±0.03	2.50	2.64±0.04	88.4
Saliva 2	0.40±0.03	1.00	1.27±0.05	87.0
Saliva 3	ND[c]	0.50	0.41±0.02	82.0
Saliva 4	ND	1.00	0.87±0.05	87.0

[a] Mean ± standard deviation

[b] 100×[(found-measured)/spiked]

[c] Not detectable

value by the presented method were 150±20 ng g^{-1} and 143±17 ng g^{-1}, respectively. The recovery was 95.4%. The good agreement between the obtained result and the certified value indicated that the established method was reliable and capable for real sample analysis.

Determination of Hg^{2+} in human saliva

To further validate the capability of our method for ultrasensitive determination of mercury in some special samples, the established analytical method was applied to the determination of mercury in human saliva. The concentrations of Hg^{2+} in the two human saliva samples from the volunteers who were with dental amalgam fillings were 0.43 and 0.40 ng mL^{-1}. However, there was no detectable Hg^{2+} in the saliva samples from the other two volunteers without fillings. Although the concentrations of mercury in saliva were very low, the results indicated the possibility of released mercury from dental amalgam fillings. The results of sample analysis were shown in Table 2. To further verify the accuracy of the method, the standard solutions of Hg^{2+} were also added into the studied human saliva samples before extraction and the recoveries were calculated. The results in Table 2 demonstrated that the method was reliable and sensitive enough for human saliva sample analysis.

Comparison with other methods

Determination of mercury in saliva samples by solidified floating organic drop microextraction in this paper was compared with the other reported methods for Hg^{2+} preconcentration (Table S2, ESM). The preconcentration method developed in our experiment showed a comparatively low detection limit and high enrichment factor.

Conclusions

Our study demonstrates that combination of solidified floating organic drop microextraction with atomic fluorescence spectrometry can be used as a very powerful tool for the determination of ultra trace mercury in human saliva. By using diethyldithiocarbamate as chelating reagent, the complex can be extracted into 1-undecanol which is very feasible to be applied as extract solvent for solidified floating organic drop microextraction. Effective separation and high enrichment factor (182.4) for mercury preconcentration can be achieved by the developed microextraction procedure.
The main advantages of the established method are simplicity, sensitive and low cost with the minimum use of toxic organic solvent. The preconcentration method yielded a detection limit of Hg^{2+} at level as low as 0.0025 ng mL^{-1} with good accuracy and good reproducibility. The developed method was proved to be sensitive and effective enough for human saliva sample analysis. The results of this study also demonstrated that mercury could be released into human saliva. It is very interesting and significant to quantify the concentration of mercury in human saliva. The established method will be very useful and helpful for further study of mercury metabolism in human body.

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