



Sensitive determination of mercury by a miniaturized spectrophotometer after in situ single-drop microextraction

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ABSTRACT

An in situ single-drop microextraction (SDME) method was developed for trace mercury determination by a miniaturized spectrophotometer, in which a simple and cheap light-emitting diode (LED) was employed as the light source, and a handheld charge coupled device (CCD) was served as the detector. A droplet of 0.006% dithizone–CCl₄ (m/v) was used as extraction phase and hanged on a rolled PTFE tube. LED light was adjusted carefully to pass through the centre of the droplet and the entrance slit of the CCD detector. The radiation intensities of 475 nm before and after SDME (I_0 and I_t) were recorded for quantification. Under the optimum conditions, the system provided a linear range of 2–50 $\mu\text{g L}^{-1}$, with a correlation coefficient of 0.9983 and a limit of detection (3σ) of 0.2 $\mu\text{g L}^{-1}$. The enrichment factor was about 69. The present method showed the merits of high sensitivity, simplicity, rapidity, low reagent consumption and field analysis potential. Finally, this method was successfully applied for the determination of the total mercury in spiked tap water sample, spiked river water sample and certified reference material (GBW (E) 080393, simulated water).

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1. Introduction

Mercury is a toxic, bio-accumulative and persistent pollutant that causes serious environmental and health problems [1,2]. These characteristics of mercury element have intrigued intense research efforts in developing sensitive, accurate, and simple analytical techniques to monitor mercury in biological and environmental samples [3,4]. Many analytical techniques have been applied for the determination mercury, including atomic absorption spectrometry (AAS) [5–8], atomic fluorescence spectrometry (AFS) [9–12], inductively coupled plasma optical emission spectrometry (ICP-OES) [13], inductively coupled plasma-mass spectrometry (ICP-MS) [14–16], electrochemical method [17], and ultraviolet–visible (UV–vis) spectrophotometry [18]. Thanks to its relatively inexpensive instrumentation and easy handling, UV–vis spectrophotometry is becoming one of the most common methods, which have even been used as national standard methods of China [19].

However, mercuric ions usually exist in the environment at trace levels with complicate matrix, thus extraction and pre-concentration procedures are often indispensable. Among the currently available extraction and preconcentration methods

[20–25], miniaturized preconcentration methods based on single-drop microextraction (SDME) have recently aroused a great interest, due to the favorable characteristics of simplicity, cheapness, rapidity, minimized organic reagents consumption [26–29]. Besides, a high enrichment factor can be easily obtained because of the microliters volume of the liquid drop [30–32].

In the present work, an in situ single-drop microextraction method was proposed for the spectrophotometric determination of mercury in real water samples. Because the SDME system was fixed during the whole analytical process, the risks of analyte loss and contamination were greatly reduced. To improve the compactness of our previous miniaturized spectrophotometer [33], a light-emitting diode (LED) was employed as a smaller and cheaper light source. A handheld charge coupled device (CCD) with high spectral resolution and sensitivity was applied as the detector of the miniaturized spectrophotometer. The optimization of experimental conditions, possible interferences, analytical figures and method validation, were investigated in detail.

2. Experimental

2.1. Reagents

The stock solution of Hg (1 g L^{-1}) was prepared by dissolving 0.1354 g HgCl₂ (Reagent grade, Chengdu Kelong, Chengdu, China) in proper amount of water with 2 mL 1% (v/v) HCl and kept in refriger-

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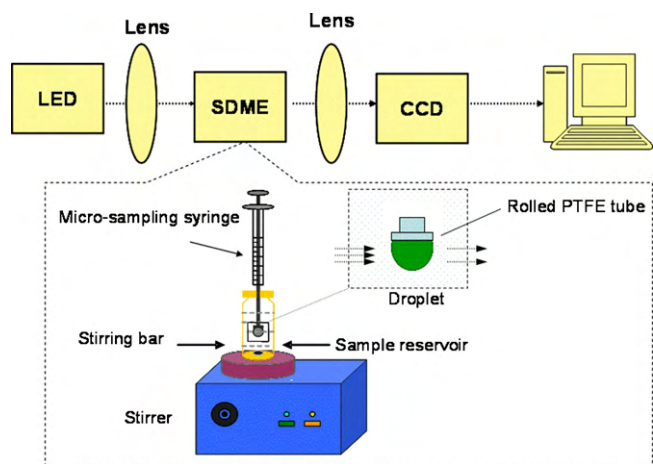


Fig. 1. Schematic diagram of the self-constructed miniaturized spectrophotometer.

ator at 4 °C. Working standard solutions were obtained by stepwise dilution of the stock standard solution.

The stock chelating solution of dithizone (1 g L^{-1}) was prepared as follow [19]: firstly, 0.1 g dithizone (Reagent grade, Shanghai Chemical Reagents, Shanghai, China) was dissolved in 20 mL CCl_4 (Analytical-reagent grade, Chengdu Kelong, Chengdu, China); secondly, after filtration and extraction by 50 mL ammonia (1 + 100) for five times, water phase was collected together; finally, after neutralization with 6 mol L^{-1} HCl and extraction five times with 100 mL CCl_4 , organic phase was gathered into brown flask and preserved in refrigerator at 4 °C. Working standard solutions were obtained by appropriate dilution of the stock standard solution prior to use. All other chemicals used were of analytical-reagent grade if not specified. Double distilled water (DDW) was used throughout the experiment. To validate the accuracy of the proposed method, a standard reference material (GBW (E) 080393, simulated water) was purchased from National Center for Reference Material (Beijing, China).

2.2. Instrumentation

For SDME, a magnetic heating & stirring instrument (Model 78-1, Jiangshu Jintan Medically Instrumental Factory, China) and a $50 \mu\text{L}$ microsyringe (Ningbo Zhenhai Sanai Instrumental Factory, China) were employed. A self-made rolled polytetrafluoroethylene (PTFE) tube (about 5 mm length) was used to hang the droplet stably. The sample vials (8 mL) were provided by Guoxiang Glass-process Factory (Chengdu, China).

The self-constructed miniaturized spectrophotometer and single-drop microextraction system are shown in Fig. 1. The light of a LED (Shunda Electronic Co., Dongwan, China; 3 V, 5 mW) was focused through a fused silica lens ($f = 100 \text{ mm}$, diameter = 30 mm) to the droplet hanged on the rolled PTFE tube. After absorption, the residual radiation was focused through the other lens to the entrance slit of a CCD detector (CT100E, Crown Tech. Inc., USA). The experimental data were collected using the manufacturer's software suite (integral time 35 ms, average time 1 ms and interval time 35 ms) and subsequently processed with Microsoft Excel.

A commercial visible spectrophotometer (Vis 7200A, Techcomp, Shanghai, China) was used to examine the absorption spectra of Hg–dithizone complex.

2.3. Procedures

Before the in situ SDME, pH of the working solution was adjusted to 2.0 with 1% (v/v) HCl. As shown in Fig. 1, during the in situ SDME procedure, a droplet of 0.006% dithizone– CCl_4 (m/v) was hanged

on a rolled PTFE tube and served as extraction phase, while 6.0 mL sample was filled in the sample vial. Before detection, LED light was adjusted carefully to pass through the centre of the droplet and the entrance slit of the CCD detector. The radiation intensities of 475 nm before and after SDME (I_0 and I_i) were recorded. Absorbance can be calculated according to the Beer–Lambert's law ($A = -\log(I_i/I_0)$).

2.4. Sample collection

Tap water was collected from our laboratory. River water was taken at the depth of 50 cm of Funan river of Chengdu, China. All water samples were filtered with $0.45 \mu\text{m}$ micropore membrane before analysis. Organic mercury species were treated into mercury (II) according to the Ref. [19]. Briefly, 1000 mL water samples were decomposed with 4 mL 50 g/L potassium permanganate solution and 4 mL 50 g/L potassium persulfate solution in boiling water bath for 2 h, in order to convert all the mercury species to mercury (II). After that, 100 g/L hydroxylamine hydrochloride solution was added to reduce the residual oxidant.

3. Results and discussion

3.1. Optimization of experimental conditions

3.1.1. Study on the absorption spectra of Hg–dithizone complex

In the preliminary experiment, we compared the absorbance signal by the use of dithizone, ammonium pyrrolidinedithiocarbamate (APDC) and diethyldithiocarbamic acid sodium salt (DDTC). Dithizone presented to be the most favorable complex due to the relatively high absorbance signal. Dithizone has a low solubility ($5\text{--}7.2 \times 10^{-8} \text{ g mL}^{-1}$ of H_2O) and a high extraction constant ($\text{p}K_{\text{ex}} = 26.85$ in CCl_4 at pH 1–1.5). Due to the high extraction capacity, dithizone was successfully applied for the extraction and determination of mercury [34,35]. In order to examine the maximal absorption spectra of Hg–dithizone complex, a commercial vis spectrophotometer was used to scan the absorption spectra of Hg–dithizone complex. As shown in Fig. 2, the maximum absorption wavelength of the complex is about 475 nm. Therefore, a commercial LED (390–600 nm) with maximum emission wave of 480 nm was employed in our experiment.

3.1.2. Effect of pH

The extraction efficiencies of different metal elements are varied in accordance to the pH of sample solution [36]. Hereby, ideally, the different metal elements can be extracted individually from the complicated sample matrix by simply controlling acidity. In our study, HCl and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution were used to adjust the pH of sample solutions. The complex reaction equation between Hg^{2+} and dithizone is $\text{Hg}^{2+} + 2\text{H}_2\text{L} \rightleftharpoons \text{Hg}(\text{HL})_2 + 2\text{H}^+$ (H_2L is dithizone).

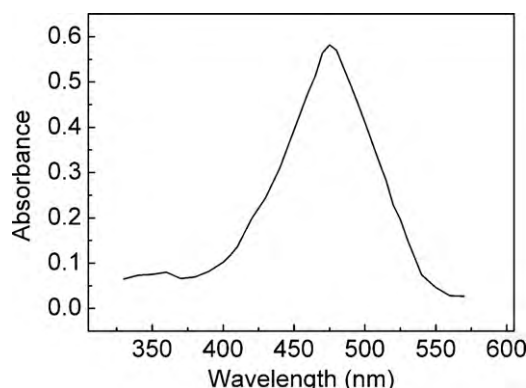


Fig. 2. Absorption spectra of Hg–dithizone complex.

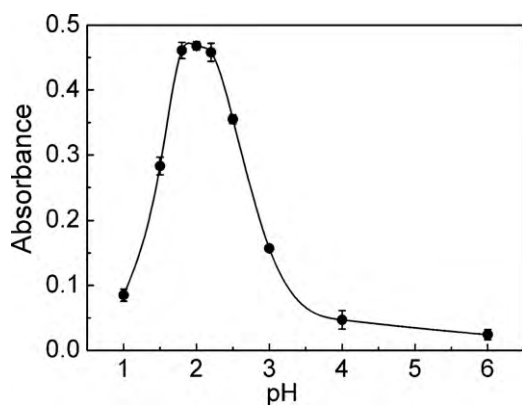


Fig. 3. Effect of pH of sample solution on the absorbance of Hg–dithizone complex. Other conditions: $[\text{Hg}^{2+}]$: $20 \mu\text{g L}^{-1}$; [dithizone]: 0.006% (m/v); volume of drop: $25 \mu\text{L}$; stirring rate: 480 r min^{-1} ; extraction time: 15 min.

Getting the knowledge from the complex reaction balance, low pH may lead to severe acid effect and the instability of $\text{Hg}(\text{HL})_2$, while high pH probably causes hydrolysis of Hg^{2+} and subsequently decomposition of $\text{Hg}(\text{HL})_2$, which finally decreases the absorbance signal. As shown in Fig. 3, relatively favorable extraction efficiencies of mercury ions were obtained in the studied pH value range of 1.8–2.2. The maximum absorbance was obtained at pH 2.0, due to the high complex formation constant between mercury and dithizone under such condition [36]. So pH of 2.0 was selected for further experiments.

3.1.3. Effect of dithizone concentration

The concentration of dithizone has a direct influence on the pre-concentration efficiency of Hg^{2+} . Dithizone concentration in the range of 0.001–0.010% (m/v) was examined carefully. As shown in Fig. 4, the absorbance signal was increased with the increase of dithizone concentration to 0.006%; higher dithizone concentration would lower down the signal intensity. At the same time, severe background absorption was observed after 0.006% dithizone. Generally, the enrichment factor of metal complex could be increased with increasing complex reagent concentration in SDME [29,35]. Therefore, on the one hand, lower dithizone concentrations will bring inefficient extraction of mercury ions. On the other hand, higher dithizone concentrations could lead to the mass increase of single droplet, which will cause instability of hanged droplet, partial deterioration of droplet, and finally absorbance signal loss. Hence, the concentration of dithizone of 0.006% (m/v) was selected for the further studies.

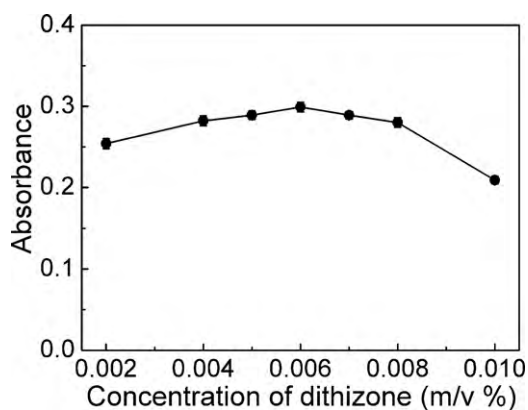


Fig. 4. Effect of dithizone concentration on the absorbance of Hg–dithizone complex. Other conditions: $[\text{Hg}^{2+}]$: $20 \mu\text{g L}^{-1}$; pH: 2.0; volume of drop: $25 \mu\text{L}$; stirring rate: 480 r min^{-1} ; extraction time: 15 min.

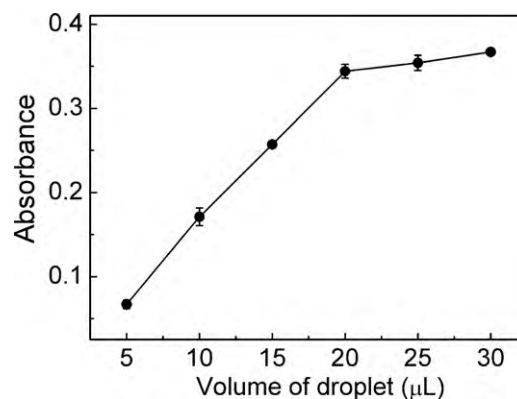


Fig. 5. Effect of droplet volume on the absorbance of Hg–dithizone complex. Other conditions: $[\text{Hg}^{2+}]$: $20 \mu\text{g L}^{-1}$; pH: 2.0; [dithizone]: 0.006% (m/v); stirring rate: 480 r min^{-1} ; extraction time: 15 min.

3.1.4. Effect of droplet volume

The droplet volume is an important condition in SDME. The effect of droplet volume on mercury signal was investigated in the range of 5–30 μL . The results illustrated in Fig. 5 show an enhancement of the analytical response by increasing the droplet volume. Obviously, surface area of the droplet is significantly increased when higher droplet volumes are used, resulting in higher mass transfer from the bulk aqueous solution to the organic droplet. However, when volumes larger than 25 μL were used, the droplet became unstable, and it was easily dislodged from the syringe needle tip. Therefore, a 25 μL droplet volume was chosen in this work.

3.1.5. Effect of extraction time

Generally, mass transfer is a time-dependent process and the maximum absorbance signal is attained when the system is at equilibrium. However, as long as extraction condition is reproducible, complete equilibrium needs not to attain to obtain accurate and precise analysis. The effect of extraction time has been studied by varying the exposure time of the droplet to the aqueous solution from 5 to 30 min. As illustrated in Fig. 6, the absorbance signal increased rapidly with the increase of the extraction time to 15 min, and then increased much slowly along the extraction time. In order to achieve a higher sample throughput, the extraction time of 15 min was selected for further studies.

3.1.6. Effect of stirring rate

Agitation of the sample solution plays an important role for enhancing extraction efficiency and reducing extraction time. A better mass transfer between the sample solution and the extrac-

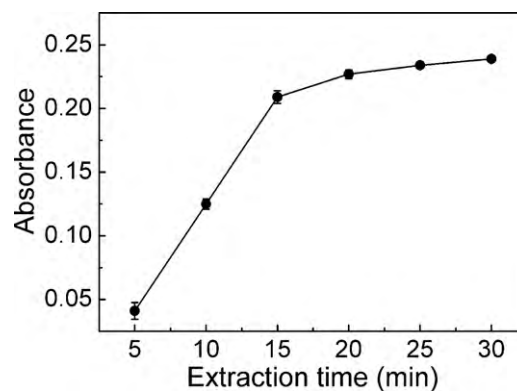


Fig. 6. Effect of extraction time on the absorbance of Hg–dithizone complex. Other conditions: $[\text{Hg}^{2+}]$: $10 \mu\text{g L}^{-1}$; pH: 2.0; [dithizone]: 0.006% (m/v); volume of drop: $25 \mu\text{L}$; stirring rate: 480 r min^{-1} .

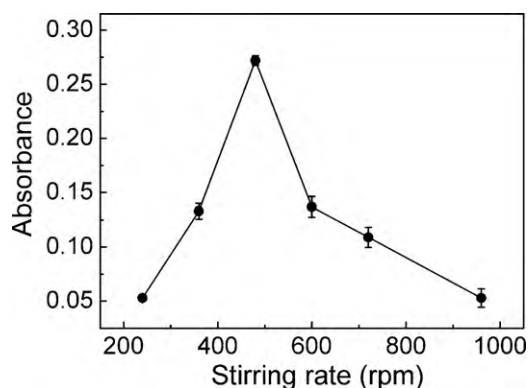


Fig. 7. Effect of stirring rate on the absorbance of Hg–dithizone complex. Other conditions: $[\text{Hg}^{2+}]$: $20 \mu\text{g L}^{-1}$; [dithizone]: 0.006% (m/v); pH: 2.0; volume of drop: 25 μL ; extraction time: 15 min.

Table 1
Effect of interferences from foreign ions on the recovery of $10 \mu\text{g L}^{-1} \text{Hg}^{2+}$.

Foreign ion added	Interference/Hg(II) ratio	Recovery (%)
K^+	500	101 ± 2
Na^+	500	100 ± 3
Ca^{2+}	500	99 ± 2
Mg^{2+}	500	99 ± 3
Fe^{2+}	200	100 ± 2
Zn^{2+}	200	101 ± 3
Mn^{2+}	200	98 ± 3
Pb^{2+}	200	106 ± 3
Cd^{2+}	200	108 ± 2
Co^{2+}	200	100 ± 3
Sn^{2+}	150	99 ± 2
Ti^{3+}	120	101 ± 4
Ag^+	60	99 ± 2
Cu^{2+}	1.2	102 ± 4
Cu^{2+} ^a	120	99 ± 3

^a After adding 100 μL 0.4% (m/v) salicylaldehyde to eliminate interference from Cu^{2+} .

tion droplet could be obtained at fast stirring speed, arising from the reduction of thickness of static solution layer around the hanged drop [30,35]. Although efficiently improving the enrichment factors and reducing the extraction time for SDME, higher stirring rate than 480 rpm would result in the deterioration and even smash of the droplet, which finally decreased absorbance signal intensity (Fig. 7) and enlarged standard deviation. Finally, 480 rpm was selected for further experiments.

3.2. Interferences

In order to apply the proposed method to the real water samples, the interference from some potential co-existing ions was examined. The results are listed in Table 1. The tolerated ratios of foreign substances to $10 \mu\text{g L}^{-1} \text{Hg}^{2+}$ were above 100 for Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Zn^{2+} , Mn^{2+} , Pb^{2+} , Cd^{2+} , Co^{2+} , Sn^{2+} , Ti^{3+} ; 60 for Ag^+ ; while only 1.2 for Cu^{2+} . The big interference probably caused

Table 2
Comparison of the methods for mercury determination.

Method	Relative LODs ($\mu\text{g L}^{-1}$)	Absolute LODs (ng)	Sample volume (mL)	Applicable for field analysis	Ref.
SDME miniaturized spectrophotometer	0.2	1.2	6	Yes	This work
Carbon nanotube based sensor	640	640	1	Yes	[37]
Stripping voltammeter	170	850	5	Yes	[17]
SPE flow injection spectrophotometer	0.9	54	6	No	[18]
Membrane preconcentration CV-AAS	0.0038	5.7	1500	No	[8]
Photo-induced CVG-AFS	0.003	0.0072	2.4	No	[9]
Glow discharge CV-ICP-OES	0.7	105	15	No	[13]
CPE-HPLC-ICP-MS	0.004	0.1	25	No	[16]

Table 3
Analytical results for Hg(II) in spiked water samples.

Sample	Detected ($\mu\text{g L}^{-1}$)	Spiked ($\mu\text{g L}^{-1}$)	Found ^a ($\mu\text{g L}^{-1}$)	Recovery %
Tap water	ND ^b	10.0	10.0 ± 0.6	100
	ND ^b	8.0	7.8 ± 0.4	98
	ND ^b	5.0	4.9 ± 0.3	98
River water	ND ^b	10.0	10.6 ± 0.2	106
	ND ^b	5.0	4.9 ± 0.2	98

^a Value = mean \pm S.D. (n = 3).

^b Not detectable.

by the effective chelating between dithizone and Cu^{2+} under acid condition of pH 2, while the other extraneous elements are hardly chelated with dithizone under such condition [36]. Meanwhile, the strong absorbance of Cu–dithizone in 475 nm was also observed, which could finally interfere mercury determination. Therefore, additional masking reagents, such as salicylaldehyde, are needed to eliminate its interference in real water samples containing high Cu^{2+} matrix. After adding 100 μL 0.4% (m/v) salicylaldehyde, the interference resistance ratio was enhanced to 120.

3.3. Analytical figures of merit

The calibration graph was linear in the range of $2\text{--}50 \mu\text{g L}^{-1}$ for Hg (II) with a correlation coefficient of 0.9983. The limit of detection, defined as $C_L = 3S_B/m$ (where C_L , S_B and m are the limit of detection, standard deviation of the 11 measurements blank and slope of the calibration, respectively), was $0.2 \mu\text{g L}^{-1}$. RSD of 4.9% was obtained by five replicated measurements of $20 \mu\text{g L}^{-1} \text{Hg}$ (II). The enrichment factor defined as the slope ratio of calibration curve after and before extraction was about 69. The LOD of the proposed method is compared with some recent literature values involving portable and not portable instruments (Table 2). As can be seen from Table 2, the LOD of this method is more favorable than those obtained by other portable instruments. Although atomic spectrometric methods generally receive better LODs, it should be noted that they are much more expensive and not applicable for field analysis.

3.4. Determination of mercury in real water samples

The proposed method was employed to determine total mercury in spiked tap water and spiked river water. 100 μL 0.4% (m/v) salicylaldehyde was added into river water samples to mask Cu^{2+} . The analytical results are given in Table 3. The recoveries of mercury in spiked water samples were in the range of 92–108%. To further verify the accuracy, the proposed method was applied to determine Hg (II) in certified reference material (GBW (E) 080393, simulated water). The analytical result, $0.104 \pm 0.002 \text{mg L}^{-1}$ (2% RSD, n = 3), was in good agreement with the certified value of $0.100 \pm 0.004 \text{mg L}^{-1}$.

4. Conclusions

A sensitive method for mercury determination was proposed by using in situ SDME and a self-constructed miniaturized spectrophotometer. Besides a high enrichment factor, the merits of this method include low cost, low organic reagent consumption and easy operation. The proposed method has been successfully applied for the determination of trace mercury in water samples and also showed the potential for the analysis of other metals. The miniaturized system opened a promising avenue for sensitive field analysis.

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