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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–CCl_4 (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_i) were recorded for quantification. Under the optimum conditions, the system provided a linear range of 2–50 $\mu g\,L^{-1}$, with a correlation coefficient of 0.9983 and a limit of detection (3σ) of 0.2 $\mu g\,L^{-1}$. 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 preconcentration 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 $HgCl_2$ (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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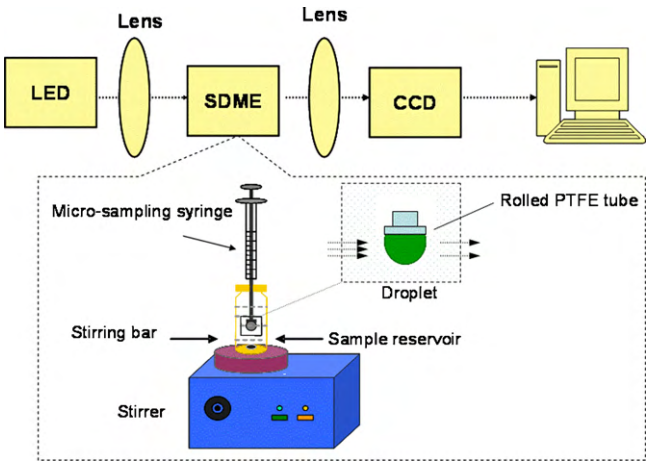

Fig. 1. Schematic diagram of the self-constructed miniaturized spectrophotometer.

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 μL 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 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–Lamber'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 μm 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 ($5–7.2 \times 10^{-8}$ g mL^{-1} of H_2O) and a high extraction constant (pK_{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 $NH_3 \cdot H_2O$ solution were used to adjust the pH of sample solutions. The complex reaction equation between Hg^{2+} and dithizone is $Hg^{2+} + 2H_2L \rightleftarrows Hg(HL)_2 + 2H^+$ (H_2L is dithizone).

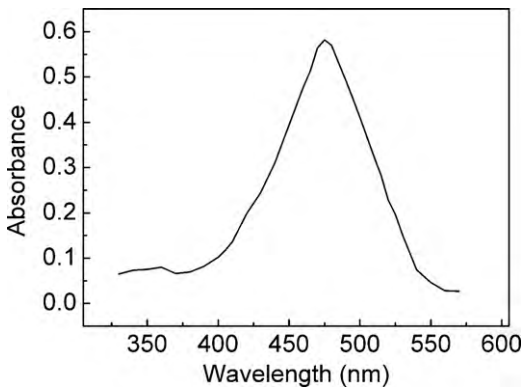

Fig. 2. Absorption spectra of Hg–dithizone complex.

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