

Trace mercury in water were measured by dispersion-liquid microextraction combined with spectrophotometry

Ruijie Xiao^{1, 2}, Rui Qi¹, Guirong Cao¹

¹Institute of Disaster Prevention, Sanhe 065201, China;

²Hebei Key Laboratory of Earthquake Dynamics, Sanhe, 065201, China;

Abstract: An experimental method was developed for the determination of trace amounts of mercury by dispersion-liquid microextraction combined with spectrophotometry. Under a buffer medium of hydrochloric acid and sodium acetate at pH=4, mercury ions in the water were extracted by dispersion-liquid microextraction at the wavelength of 410nm, carbon tetrachloride was used as an extractant, methanol was used as a dispersant, dithizone-methanol solution was used as a chelating agent, the optimum conditions for extraction were obtained, Carbon tetrachloride 70uL, methanol 0.75mL, dithizone methanol solution 200uL. Under the optimal conditions, Lambert-Beer's law was satisfied at concentrations of 0.1-20µg/L, the detection limit is 64.2ng /L, The correlation coefficient of the standard curve was $R^2 = 0.9983$, the relative deviation was about 4.64%. Three water samples were measured, the recoveries were 96.8%-109.2%.

Keywords: dispersed liquid-liquid microextraction; Spectrophotometry; trace mercury

1. Introduction

With the development of various industries such as the combustion of fossil fuels[1], traditional smelting[2], papermaking[3], and chemical plastics, a large amount of wastewater containing heavy metals is being discharged, causing irreversible pollution to the water environment. Mercury is one of the heavy metals involved. In the twentieth century and beyond, China has experienced vigorous industrial growth, leading to an increasing exploration of mercury utilization and consequently a significant influx of mercury into the natural environment. Studies have shown that long-term exposure to mercury can cause cumulative toxicity[4-7], with the main health hazards of metallic and organic mercury including neurotoxicity, nephrotoxicity, immunotoxicity, reproductive toxicity, and embryonic developmental toxicity[8-10]. Therefore, the determination of mercury (Hg) in water can provide important evidence for water quality monitoring and assessment.

Mercury concentrations in water environments are generally at the level of milligrams per liter (mg/L) or even lower. Therefore, prior to analysis, it is necessary to perform separation and enrichment. Currently, common methods for separation and enrichment include membrane separation[11-12], cloud point extraction, and dispersive liquid-liquid microextraction (DLLME). DLLME is a novel liquid-phase microextraction technique first proposed by Rezaee in 2006. This method integrates sample introduction, extraction, and concentration, offering advantages such as simplicity, rapid operation, low cost, minimal environmental pollution, and high enrichment efficiency[13]. Sgarlata et al[14]. used a polymer aromatic hydrocarbon carrier membrane to separate Hg^{2+} from acidic aqueous solutions containing Cd^{2+} , Hg^{2+} , and Pb^{2+} . During the separation process, tetrabutylammonium chloride was utilized to enhance the strength of Hg^{2+} . Visser et al[15]. employed imidazolium-based hexafluorophosphate ionic liquid as an extracting agent to extract Cd(II) from water and achieved good extraction results in environmental water samples. In this study, dispersive liquid-liquid microextraction combined with spectrophotometry was used. Carbon tetrachloride was used as the extraction solvent, methanol as the dispersing agent, and dithizone as the chelating agent to establish a method for the determination of trace mercury in water.

2. Experimental part

2.1 Instruments and Reagents

The mercury standard solution ($1000\mu\text{g/L}$) was purchased from the National Nonferrous Metals and Electronic Materials Analysis and Testing Center. The lead reagent (with 80% content) was purchased from Tianjin Yongda Chemical Reagent Co., Ltd. Carbon tetrachloride, methanol, hydrochloric acid, and anhydrous sodium acetate are all of analytical grade. Deionized water was used as the experimental water source.

The 722-type visible spectrophotometer was purchased from Shanghai Hengping Scientific Instrument Co., Ltd. The centrifuge was purchased from Anhui Zhongke Zhongjia Scientific Instrument Co., Ltd. The pipette gun was obtained from DRAGONLAB. The BS-1E constant temperature shaking incubator was purchased from Jiangsu Jintan Yitong Electronic Co., Ltd. The pH meter was obtained from Xiayi County Jinbo Water Purification Technology Co., Ltd.

2.2 Experimental method of DLLME of trace mercury

Take 5 mL of the prepared 5.0 mg/L mercury standard solution and transfer it to a 200 mL conical flask. Add hydrochloric acid-sodium acetate buffer solution to adjust the solution pH to 4. Mix well. Add 0.75 mL of methanol to the flask. Using a microsyringe, quickly inject $200\ \mu\text{L}$ of dithizone solution and $70\ \mu\text{L}$ of carbon tetrachloride. Place the flask in a shaking incubator and vigorously shake it for 6 minutes to obtain a homogeneous emulsion. Transfer the obtained emulsion to a centrifuge tube and place it in a centrifuge. Centrifuge at a speed of 4000 rpm for 4 minutes. Use a microsyringe to transfer the organic phase precipitate from the bottom to a semi-micro centrifuge tube. Dilute it to 5 mL with a methanol solution and mix well. Transfer the diluted solution to a 1 cm cuvette and use methanol as a blank control reagent. Measure the absorbance at a wavelength of 410 nm.

3. Experimental results and discussions

3.1 Absorption spectral curve

According to the designed experimental method, the absorbance of the solution was accurately measured within the range of 400-440 nm, and a schematic representation of the absorption spectrum was plotted, as shown in Figure 2-1. From the provided diagram, it can be observed that the mercury chelate exhibits its maximum absorption peak at 410 nm. The blank control reagent had no effect on the experimental measurements. Therefore, 410 nm was selected as the measurement wavelength.

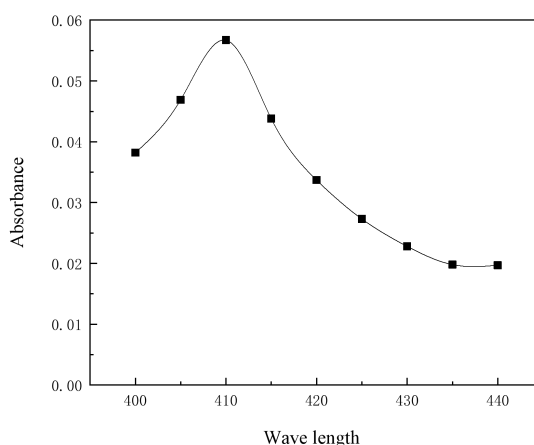


Figure 1 Absorption spectra of mercury-dithizone complexes

3.2 Amount of extractant

The amount of extractant used is one of the factors directly affecting the extraction efficiency. In general, increasing the volume of the extractant leads to an increase in the amount of the target analyte extracted, resulting in a higher recovery rate. However, it also leads to an increase in the volume of the extract, resulting in a decrease in its concentration. Therefore, under the premise of achieving a high extraction efficiency, it is preferable to use a smaller volume of the extractant.

After comparison, carbon tetrachloride was selected as the extractant. According to the designed experimental method, the effect of carbon tetrachloride volume on the absorbance was investigated within the range of 50-100 μ L. The obtained absorbance spectra are shown in Figure 2-2. From the graph, it can be observed that when the volume of carbon tetrachloride is 70 μ L, the absorbance reaches its peak and remains stable. Therefore, the experimental protocol selected a volume of 70 μ L for carbon tetrachloride.

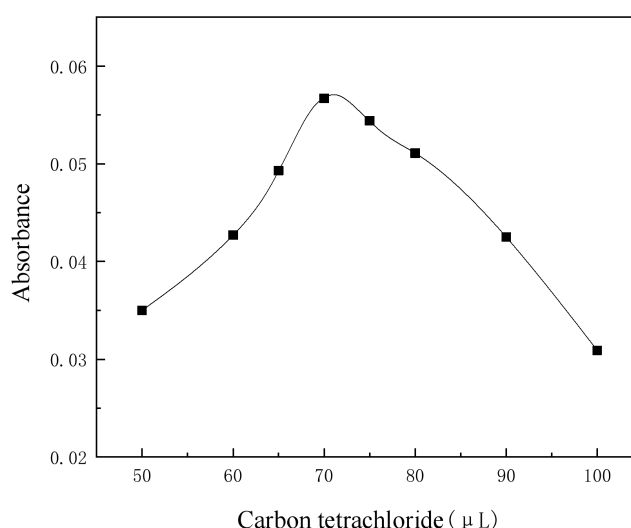


Figure 2 Absorption spectrum of carbon tetrachloride effect on absorbance

3.3 Amount of dispersant

The amount of dispersing agent used is a critical factor influencing the extraction efficiency. The magnitude of this factor primarily determines whether the dispersing agent can be uniformly dispersed in the aqueous phase, which in turn affects the formation of a stable and homogeneous emulsion, thus impacting the extraction efficiency.

In this study, methanol was chosen as the dispersing agent. According to the designed experimental method, the effect of different volumes of methanol (ranging from 0.6 mL to 0.9 mL with intervals of 0.05 mL) on the absorbance was investigated, and the absorbance spectra were plotted (see Figure 2-3). From the graph, it can be observed that as the volume of methanol increases, the absorbance also increases. The maximum absorbance is achieved at a methanol volume of 0.75 mL. However, if the volume of methanol continues to increase, the absorbance decreases significantly. The main reason for this phenomenon is that when the volume of methanol is too small, the extraction solution cannot be effectively and uniformly dispersed in the water, resulting in a lower extraction efficiency. On the other hand, when the volume of methanol is too large, the solubility of the detected components in water increases, making them less prone to enrichment by the extractant and thus reducing the extraction efficiency. Therefore, the optimal volume of methanol chosen for this experiment is 0.75 mL.

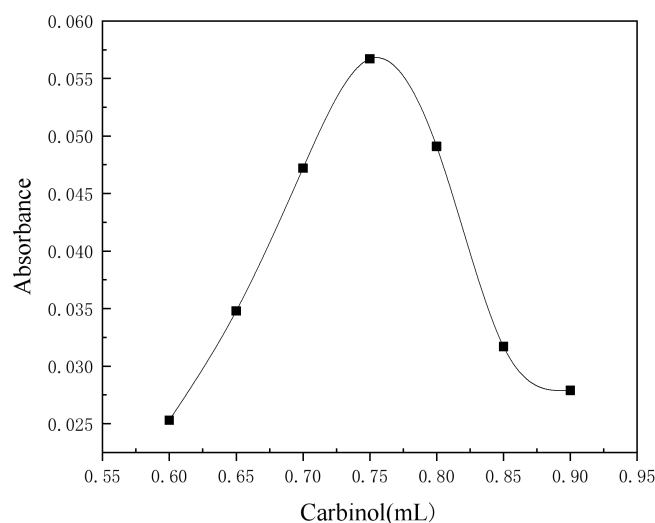


Figure 3 Absorption spectrum of the effect of methanol dosage on absorbance

3.4 Dosage of dithizone

The main function of the chelating agent is to form stable hydrophobic complexes with metal ions, facilitating the extraction of metal ions into the organic phase. In this study, a chelating agent called dithizone with a concentration of 0.1 mol/L was selected. According to the designed experimental method, the effect of different volumes of dithizone (ranging from 170 μ L to 230 μ L with intervals of 10 μ L) on the absorbance was investigated, and the absorbance spectra were plotted (see Figure 2-4). From the graph, it can be observed that when the volume of dithizone reaches 200 μ L, the absorbance reaches its peak and tends to stabilize. Therefore, for this experiment, a volume of 200 μ L of 0.1 mol/L dithizone solution was chosen as the optimal concentration.

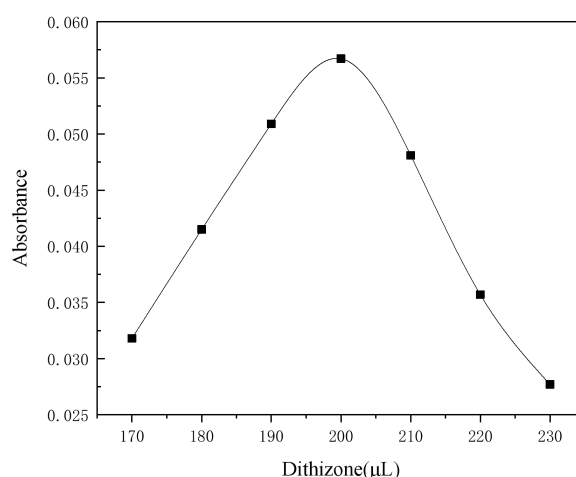


Figure 4 Absorption spectrum of the effect of dithizone reagent dosage on absorbance

3.5 Effect of pH value and buffer solution dosage

The pH value of the solution can affect the formation of hydrophobic complexes and, consequently, the efficiency of extraction. According to the designed experimental method, the absorbance at pH values ranging from 2 to 6 was investigated, and the absorbance spectra were

plotted (see Figure 2-5). From the graph, it can be observed that the absorbance reaches its maximum value at pH 4. Therefore, the experimental environment for this study was chosen to be pH 4.

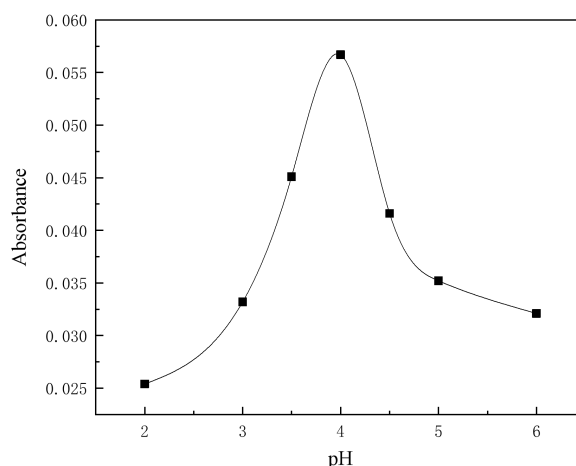


Figure 5 Absorption spectra of the effect of pH environment on absorbance

3.6 Effect of coexisting ions

According to the experimental method, the potential interference of ions that may be present in actual samples on mercury ion determination was studied. The determination was performed on a standard solution of $10 \mu\text{g/L Hg}^{2+}$, and the coexisting substances were considered non-interfering when the relative error did not exceed $\pm 5\%$. The following coexisting substances did not interfere with the determination: 00 times the concentration of Li^+ , Na^+ , K^+ ; 300 times the concentration of Ca^{2+} , Mg^{2+} , Pb^{2+} , Sn^{2+} , Mn^{2+} ; 50 times the concentration of Fe^{3+} , Ag^+ , Ba^{2+} ; 20 times the concentration of Zn^{2+} , Ni^{2+} , Cd^{2+} . Therefore, the system exhibits high selectivity for the detection of mercury ions.

3.7 Working curve, detection limit and extraction rate

A series of standard solutions of mercury ions with different concentrations were prepared, and their absorbance was measured at 410nm, as shown in Figure 2-6. The linear regression equation indicates a good linear relationship between the concentration of mercury ions and the absorbance in the range of $0.1 \mu\text{g/L}$ to $20 \mu\text{g/L}$. The linear regression equation is expressed as $A = 0.01757 + 0.0039C (\mu\text{g/L})$, with a correlation coefficient (R^2) of 0.9983. The detection limit of the method was determined to be 64.2 ng/L based on eight parallel measurements of the standard blank solution. The relative standard deviation (RSD) of the measurement results was 4.64%. Using a standard solution of $10 \mu\text{g/L}$ mercury ions, an absorbance of 0.058 was obtained. Subsequently, adding 5 mL of $10 \mu\text{g/L}$ mercury ion solution and measuring the absorbance yielded 0.061. This process was repeated, and the absorbance finally stabilized at 0.062. Calculations showed that the extraction efficiency was 93.44%.

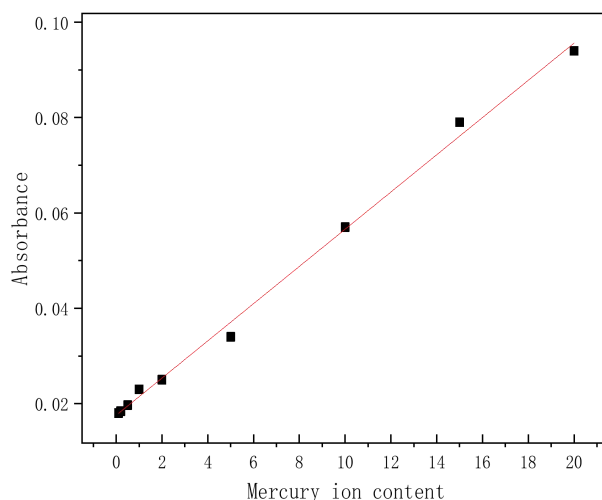


Figure 6 Linear fitting curve of mercury ion concentration and absorbance

3.8 Determination of trace mercury in water samples by dispersive liquid-liquid microextraction

According to the on-site experimental research method, analysis and determination of mercury ions were conducted in the tap water of North Campus, tap water in Yanjiao, and seawater from the Golden Coast area. The samples were measured in parallel five times, and the spiked recovery rates of the water samples ranged from 96.8% to 109.2%. The results are shown in Table 2-1.

Table 1 Measurement results and spiked recoveries of experimental water samples

Water sample	Before adding / ($\mu\text{g/L}$)	Additive quantity / ($\mu\text{g/L}$)	After adding scalar/ ($\mu\text{g/L}$)	Added scalar recovery /%
North school	0.34	0.1	0.438	98
tap water		0.25	0.613	109.2
Yanjiao tap	0.16	0.1	0.263	103
water		0.25	0.402	96.8
Gold Coast	2.34	0.1	2.437	97
waters		0.25	2.597	102.8

4. Conclusion

The combination of dispersive liquid-liquid microextraction technique and spectrophotometry has been employed for the extraction of trace mercury in water samples. The method exhibits a detection limit of 64.2 ng/L and a relative standard deviation (RSD) of 4.38%. The spiked recovery rates for environmental water samples range from 96.8% to 109.2%, indicating that the method is characterized by its simplicity of operation, relatively high sensitivity, low organic solvent usage, and environmental friendliness. It holds significant application value in the determination of trace mercury in practical water samples.

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