Determination of Mercury at a Dithizone-Modified Glassy Carbon Electrode by Anodic Stripping Voltammetry

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(Received August 6, 2001; Accepted November 2, 2001)

Mercury is one of the most abundant heavy metals in the environment, and its toxic effects have been recognized for a long time. Due to its dangerous and harmful properties for the health of human being, the determination of mercury is very important for environmental protection. The typical methods for determining mercury are atomic absorption spectrophotometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and mass spectrophotometry (MS). Although these methods have good sensitivity, they require expensive instruments, well-controlled experimental conditions, and profound sample-making.

Because of its advantages of easy fabrication, excellent sensitivity, fast response, good selectivity and low cost, chemically modified electrodes (CMEs) have drawn much attention in every field of analytical chemistry. CMEs have been widely used in analytical chemistry, especially in electroanalytical chemistry, and have been successfully used to determine trace levels of heavy metal.¹⁻⁵ Until now, various CMEs for determining mercury have been reported. Gao and his coworkers⁶ determined mercury using a ferrocenylpolythia crown ether-Nafion modifeid GCE. Navrátilová *et al.*⁷ reported a humic acid-modified carbon paste electrode (CPE) for the determination of mercury. Cai *et al.*^{8,9} have determined mercury using a liquid anion exchanger (Amberlite LA2) modified CPE and 2-mercapto-4(3H)-quinazolinone modified CPE, respectively. To our knowledge, the determination of mercury using a dithizone-modified glassy carbon electrode has not been reported.

Dithizone contains azo and hydrosulfide groups, which are good electron donors. Dithizone is widely used in extraction spectrophotometry because it can form stable complexes with many metal ions under proper conditions. From this perspective, we fabricate a dithizone-modified glassy carbon electrode to improve the sensitivity of determining mercury. As expected, 1×10^{-7} mol/L Hg^{2+} had no voltammetric response at a bare glassy carbon electrode (GCE) after being accumulated at -0.80 V for 5 min. However, the peak current of 1×10^{-7} mol/L Hg^{2+} at a dithizone-modified GCE was greatly enhanced under the same conditions.

In this work, dithizone-modified GCE was investigated to determine trace levels of mercury. Dithizone-modified GCE has the following advantages: easy fabrication, low detection limit, fast response and good selectivity. Using this dithizone-modified GCE, trace levels of mercury in seawater samples were determined and the average recovery was 100.96%.

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Experimental

Reagents and solutions

Every standard solution of 1.00 mg/mL dithizone (Shanghai Reagent Corporation, China) was prepared by dissolving it into chloroform. Stock solutions of Hg^{2+} were prepared from $\text{Hg}(\text{NO}_3)_2$ into deionized water. Other chemicals used were of analytical reagent. All reagents were used as received.

Apparatus

All measurements were carried out on an MF-1A multifunction voltammetric analyzer (Jiangsu Electroanalysis Instruments Corporation, China) and voltammograms were recorded with a 3086 x-y recorder (Yokogawa, Japan). A three-electrode system, including a dithizone-modified glassy carbon electrode as a working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE), was employed. All potentials were reported *versus* SCE.

Preparation of a dithizone-modified electrode

Prior to coating, a glassy carbon electrode (with effective area 7.00 mm^2) was first dipped into 1:1 HNO_3 and ethanol for 1 min, respectively; and then polished on microcloth pads. After that, the electrode was ultrasonicated in deionized water for about 30 s.

Dithizone films were prepared by adding $10.00 \mu\text{L}$ of 1.00 mg/mL dithizone onto a pretreated GCE with a microsyringe. The solvent was then allowed to evaporate at room temperature. Before the measurement, the electrode was rinsed with deionized water to remove any weakly adsorbed reagents.

Determination of Hg^{2+}

A certain volume of a Hg^{2+} standard solution was added into 0.1 mol/L KI (pH 2.00) and accumulated at -0.80 V for 5 min while stirring the solution. The solution was then kept quiet for 30 s and voltammograms were recorded from -0.80 V to 0.00 V. The peak heights were measured at -0.21 V. For repeated determinations on the same electrode, the potential was held at 0.20 V for 60 s to remove any previous deposits.

Results and Discussion

Anodic stripping behavior of mercury

From Fig. 1, it can be seen that the 1×10^{-7} mol/L Hg^{2+} in 0.1 mol/L KI (pH 2.00) had no voltammetric response at a bare

Fig. 1 Stripping voltammograms of 5×10^{-7} mol/L Hg^{2+} on (a) bare GCE, and (b) dithizone-modified GCE. The accumulation potential was -0.80 V; the accumulation time, 5 min; the amount of dithizone, $10.00 \mu\text{L}$; and the scan rate, 200 mV/s .

Fig. 2 Effect of 1.00 mg/mL dithizone on the peak current of 5×10^{-7} mol/L Hg^{2+} . All other conditions as in Fig. 1.

GCE after being accumulated at -0.80 V for 5 min (curve a). However, under the same conditions, a peak current of 1×10^{-7} mol/L Hg^{2+} at the dithizone-modified GCE increased greatly (curve b). This suggests that a dithizone-modified GCE can improve the sensitivity of determining trace levels of mercury. The oxidation peak potential of mercury is -0.21 V.

Effects of supporting electrolytes and pH values

The voltammetric response of Hg^{2+} in various supporting electrolytes, such as KCl, KI, KNO_3 , NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 , NaAc (each 0.1 mol/L) and 0.01 mol/L HCl, was investigated. Finally, it was found that the peak current of 5×10^{-7} mol/L Hg^{2+} was the highest in 0.1 mol/L KI among these supporting electrolytes. In 0.1 mol/L KI, the effects of different pH values (adjusted with dilute HNO_3 and NaOH) on a peak current of 5×10^{-7} mol/L Hg^{2+} were examined. It was found that the peak current gradually increases from pH 7.00 to 2.00. In pH 1.00, the peak current conversely decreased. Hence, 0.1 mol/L KI (pH 2.00) was selected as the electrolyte in this work.

Effect of amount of dithizone

The influence of the amount of dithizone on the peak current is shown in Fig. 2. With increasing the amount of dithizone, the number of reactive sites of the complexing reaction steadily increased. Therefore, the peak current increased at the beginning. But when the amount of dithizone exceeded $10.00 \mu\text{L}$, the films became thicker and blocked the electron transfer from the mercury to the electrode; consequently, the peak

Fig. 3 Effect of the accumulation potential on the peak current of 5×10^{-7} mol/L Hg^{2+} . All other conditions as in Fig. 1.

Fig. 4 Effect of the accumulation time on the peak current of 5×10^{-7} mol/L Hg^{2+} . All other conditions as in Fig. 1.

current decreased. Thus, in our experiment, the amount of 1.00 mg/mL dithizone was $10.00 \mu\text{L}$.

Effect of the accumulation potential and time

The accumulation potential, a very important factor in anodic stripping voltammetry (ASV), can greatly influence the sensitivity of the determination. Plots of the peak current versus the accumulation potential are shown in Fig. 3. It was found that the peak current becomes higher with the accumulation potential shifting towards negative values. At a more negative potential, Hg^{2+} was reduced more completely. Hence, the peak current increased. When the accumulation potential was in the range from -0.70 V to -1.00 V, the peak current changed slowly. Finally, -0.80 V was chosen as the accumulation potential in our measurement.

The influence of the accumulation time is shown in Fig. 4. The peak current increases with extending the accumulation time. Under the same experimental conditions, a longer accumulation time would lead Hg^{2+} to be reduced more completely and cause the peak current to increase. However, when the accumulation time was longer than 5 min, the peak current changed slowly. Thus, the accumulation time was 5 min in our experiment.

Scan rate

The relationship between the peak current and scan rate was examined. It was observed that the peak current of Hg^{2+} is

Table 1 Influence of other metal ions on the peak current of 5×10^{-7} mol/L Hg^{2+}

Interferent	Concentration/mol L ⁻¹	Signal change, %
Cd^{2+}	5×10^{-5}	-1.02
Pb^{2+}	5×10^{-5}	-2.12
Ca^{2+}	5×10^{-3}	-1.24
Mg^{2+}	5×10^{-3}	-1.32
Zn^{2+}	5×10^{-3}	-0.98
Co^{2+}	5×10^{-4}	-1.46
Ni^{2+}	5×10^{-4}	-1.76
Mn^{2+}	5×10^{-4}	-1.30
Cu^{2+}	5×10^{-4}	-4.24
Fe^{3+}	5×10^{-4}	-2.68

proportional to the scan rate from 20 mV/s to 300 mV/s, suggesting that the electrochemical process is controlled by adsorption rather than by diffusion.

Response to Hg^{2+}

The relationship between the peak current and the concentration was also investigated. The peak current was linear with the concentration of mercury in the range from 2.5×10^{-9} mol/L to 7.5×10^{-7} mol/L. The detection limit (signal-to-noise = 3) was 5×10^{-10} mol/L after being accumulated at -0.80 V for 5 min. The coefficient of variation, determined on one single electrode at a concentration of 5×10^{-7} mol/L Hg^{2+} , was calculated to be 2.9% ($n = 8$).

Interference

Several other metal ions were examined under the conditions optimized for an Hg^{2+} determination. The results are shown in Table 1. It was found that the interference of these metal ions on the peak current, 5×10^{-7} mol/L Hg^{2+} , was not serious, suggesting that the dithizone-modified GCE has good selectivity for Hg^{2+} determination.

Determination of Hg^{2+} in seawater samples

Dithizone-modified GCEs have been used to determine trace levels of Hg^{2+} in seawater samples. The experimental parameters were the same as described above. The concentrations of Hg^{2+} were determined using the method of standard additions. The results are summarized in Table 2.

Conclusions

In short, dithizone-modified GCE can greatly improve the sensitivity of determining Hg^{2+} in ASV compared with a bare

Table 2 Determination of Hg^{2+} in seawater samples using dithizone-modified GCEs

Sample	Added/mol L ⁻¹	Expected/mol L ⁻¹	Found/mol L ⁻¹	Recovery, %
A	0.00		4.46×10^{-9}	
	5×10^{-9}	9.46×10^{-9}	9.82×10^{-9}	103.81
B	0.00		5.26×10^{-8}	
	5×10^{-8}	1.026×10^{-7}	1.01×10^{-7}	98.44
C	0.00		3.33×10^{-8}	
	5×10^{-8}	8.33×10^{-8}	8.28×10^{-8}	99.40
D	0.00		0.00	
	2.5×10^{-7}	2.5×10^{-7}	2.48×10^{-7}	99.20
E	0.00		2.06×10^{-9}	
	2×10^{-9}	4.06×10^{-9}	4.22×10^{-9}	103.94

GCE. On a dithizone-modified electrode, Hg^{2+} was first preconcentrated *via* forming a complex with dithizone under proper conditions, and then reduced on the surface of the electrode. Finally, reduced mercury was anodically stripped during a potential sweep from -0.80 V to 0.00 V. The reactions at the electrode may be written as follows:

(1) Preconcentration process

(2) stripping process

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