

PRE-COATED MERCURY FILM ON GLASSY-CARBON ELECTRODE FOR THE SIMULTANEOUS DETERMINATION OF Cu^{2+} , Zn^{2+} , Cd^{2+} , AND Pb^{2+} IN WATER

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ABSTRACT. A mercury film was pre-coated on glassy-carbon electrodes to improve the precision and detection limit of the electrodes in anodic stripping voltammetry. A mixed solution containing 0.1 mg/l Zn^{2+} , 0.01 mg/l Pb^{2+} , 0.01 mg/l Cd^{2+} , and 0.5 mg/l Cu^{2+} was used to investigate the simultaneous detection of these ions by the electrode. The influence of the base solution pH and the accumulation time on the electrochemical reactions of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were investigated, as well as the effect of the concentration of the film coating solution and the number of mercury coating step on the stripping signals of the four ions. Optimizing the parameters of the pre-coated mercury film improved the precision of the glassy-carbon electrode in evidence. When the base solution pH was 4.68, and the accumulation time was 300 s, the positions of the stripping peaks were optimal, and the peak signals were at a maximum. When the concentration of the film coating solution was 0.03 mol/l HgCl_2 , and the mercury coating step was repeated three times, the prepared electrode showed a moderately high elution peak with little noise. The optimized electrode demonstrated superior precision and detection limits in the simultaneous detection of Zn^{2+} , Cd^{2+} , Pb^{2+} , and Cu^{2+} , compared with the uncoated electrode. The calibration curves were highly linear with determination coefficients (R^2) of 0.9913 (Cu^{2+}), 0.9939 (Pb^{2+}), 0.9933 (Cd^{2+}), and 0.9962 (Zn^{2+}); the detection limits ($\mu\text{g/l}$) were 5 for Cu^{2+} , 1 for Pb^{2+} , 0.1 for Cd^{2+} , and 10 for Zn^{2+} , and the relative standard deviations obtained from five replicate experiments were 4.1% (Cu^{2+}), 2.1% (Pb^{2+}), 2.7% (Cd^{2+}), and 3.4% (Zn^{2+}). It is reasonable to suppose that the precision and detection limits of this mercury film electrode may meet the requirements for the simultaneous detection of multiple heavy metal ions in water in the natural environment.

Keywords: Glassy-Carbon Electrode, Mercury Film, Heavy Metal Ions, Anodic Stripping Voltammetry

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INTRODUCTION

Zn^{2+} , Cd^{2+} , Pb^{2+} , and Cu^{2+} are four heavy metal ions commonly found in natural water bodies, and anodic stripping voltammetry is the preferred method used for their detection. The problem is that the precision and detection limits of conventional glassy-carbon electrodes cannot meet the requirements needed for the simultaneous detection in practical applications. A typical case is the groundwater pollution incident of heavy metals in the Dabaoshan area of China in 2013. The detected concentrations of Cu^{2+} , Pb^{2+} , Zn^{2+} , and Cd^{2+} were 28.4, 4.4, 41.39 and 26.7 times the upper limits in the Chinese standard: Quality standard for groundwater (GB/T 14848-93). Such high concentrations of heavy metal ions may lead to severe soil contamination and damage to the health of residents via the food chain. Indeed, cancer mortality rates in Dabaoshan residents have increased to 84% of the total death rate [1]. Conventional detection methods such as high-performance liquid chromatography (HPLC) are limited by high-cost equipment and sophisticated procedures, and cannot achieve in-situ measurements of heavy metal ions in complicated water bodies [2-4]. The portability of the device and in-situ measurement capability allows anodic stripping voltammetry to achieve rapid detection of heavy metal ions in water, and so it can be employed in online monitoring and pre-alerts of heavy metal ions in complicated water bodies [5, 6]. As a core component for stripping analysis, glassy-carbon electrodes are limited by insufficient precision and detection limits for the simultaneous detection of different ions. The good chemical stability and high hydrogen over-potential of the glassy-carbon electrode means that improvements in the precision and detection limits can be achieved through a pre-plated mercury film, allowing the simultaneous detection of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} in water.

The mercury film coating on the glassy carbon electrode consists of a myriad of tiny mercury droplets; dense and uniform mercury droplets are prerequisites for good electrode performance [7]. The working environment affects the extent of reactions on the electrode surface, and the coating parameters affect the mercury load on the electrode surface and the distribution of the mercury micro-drops. Recent studies to improve the precision and detection limit of glassy-carbon electrodes by mercury film pre-coating have focused on a single internal or external factor, such as coating potential, electrode rotation rate, etc. There have been few systematic studies of how the external working environment of the electrode and the internal coating parameters affect its electrochemical performance. These variables include: 1) the effects of base solution pH and electrode accumulation time on the stripping curves of the electrode. The base solution pH (denotes the working environment

of the mercury film coated electrode) and the accumulation time (a working parameter of the electrode) has a direct effect on the reaction rates of heavy metal ions on the mercury film. 2) The effects of coating solution concentration and the number of mercury coating steps on the stripping curves of the electrode. The coating solution concentration and the number of mercury film coating steps determine the mercury load on the electrode surface, and so affects the surface state and stability of the mercury film. 3) Electrochemical performance test. An electrochemical performance test can reflect the overall performance of the electrode and evaluate its practical applicability. Without intensive studies of base solution pH, electrode accumulation time, coating solution concentration, the number of mercury film coating steps and the electrochemical performance of the electrode, it is impossible to fully understand the effect of a pre-coated mercury film on the precision and detection limit of glassy-carbon electrodes.

In this study, stripping curves of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were obtained to reflect electrode performance. We investigated the effect of base solution pH and accumulation time on the electrochemical reactions of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} (at different concentrations) on the mercury film, as well as the effect of the coating solution concentration and number of coating step on the stripping signals of the different ions. Additionally, mercury film coated glassy-carbon electrodes were prepared under optimized parameters, and their electrochemical performance was tested.

RESULTS AND DISCUSSION

Effects of base solution pH and electrode accumulation time on the stripping curves of the electrode

Effects of base solution pH on the stripping curves of the electrode

The base solution pH affects the reaction rates of the target ions on the electrode surface, and thus affects the peak potential and the current of the stripping curves. The base solution used was a sodium acetate-acetic acid buffer containing 0.125 mol/l sodium acetate and 0.25 mol/l KCl, and its pH value ranged from 4.00 to 5.00 for gradient tests. The accumulation time was 350 s, and the concentration of the coating solution was 0.04 mol/L, with three coating steps.

Fig. 1 shows anodic stripping voltammetry curves of mercury film coated electrodes in base solutions with different pH values. The pH value of the base solution had no significant effect on the stripping current but did affect the stripping peak positions. The pH value of the base solution affected the collection of the data at the bottom of the stripping peaks in the scanning range,

thus affecting the detection accuracy. With a base solution pH of 4.00 (see Fig. 1a), the stripping peak potential was shifted to the right for all four ions tested, and the stripping peak of Cu^{2+} was out of the scanning range. With a base solution pH of 4.50 (see Fig. 1b), the stripping peak potential shifted slightly left, and the stripping peak of Cu^{2+} was within the scanning range, although its peak pattern was not complete and the data at the bottom of stripping peaks could not be collected. With a base solution pH of 4.68 (see Fig. 1c), the stripping peak potential was moderate, the stripping peak pattern was complete, and the data at the bottom of stripping peaks was fully collected for all four ions tested. Hence, the detection accuracy was improved. With a base solution pH of 5.00 (see Fig. 1d), the stripping peak potential shifted to the left, and the data at the bottom of the stripping peak of Zn^{2+} was not collected, which was attributed to the over-fast reaction of Zn^{2+} on the electrode surface.

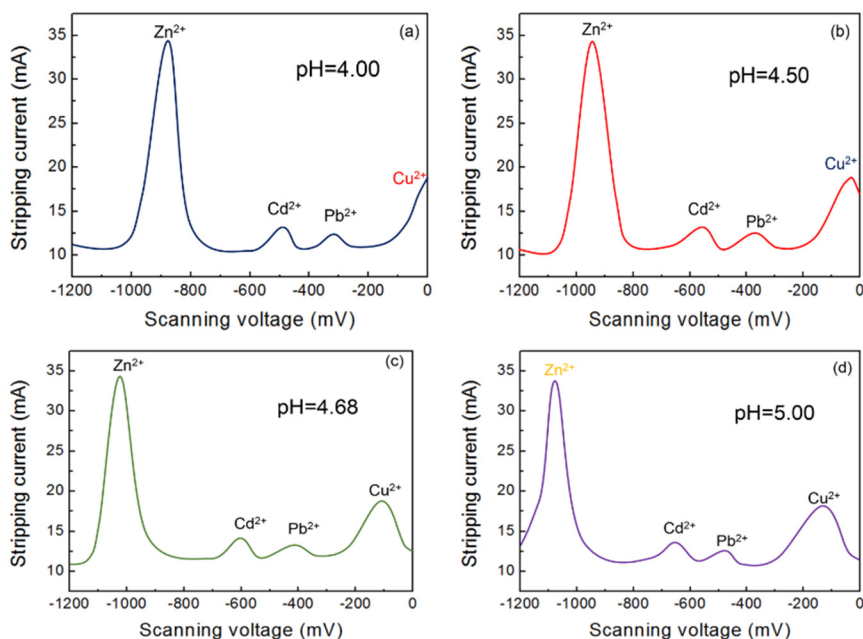


Figure 1. Stripping current curves of the electrode in different base solutions.

Contrary to the predictions of the Nernst equation, changes in the pH of the base solution affected the stripping peak position of the four ions. There were two possible reasons for this unexpected behavior. The first was competition between H^+ and the metal ions [8, 9]. Base solutions with different pH values have different concentrations of H^+ . When the concentration of H^+ was too high, the stripping process of heavy metal ions was inhibited

and resulted in a shift of the stripping peak position. The second was the formation of acetate [10]. The reversible ionization reaction of acetic acid occurs readily in solution, and the CH_3COO^- ion would like to combine with heavy metal ions. The concentration of CH_3COO^- decreased with decrease in pH. Consequently, the decrease in the concentration of acetate induces a shift in the position of the stripping peak. At a base solution pH of 4.68, the stripping peak potentials and currents are distinct, and the ion concentrations measured were closest to the standard solution. Hence, it was concluded that 4.68 was the optimum pH value of the base solution.

Effects of accumulation time on the stripping curves of the electrode

Target ions were enriched on the electrode, followed by reverse stripping. The accumulation time had a direct effect on the stripping peak current intensity. Scanning voltages were applied under the corresponding stripping potentials for Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} . The other three parameters selected were: a base solution pH = 4.68, a coating solution concentration of 0.04 mol/l, and three coating steps.

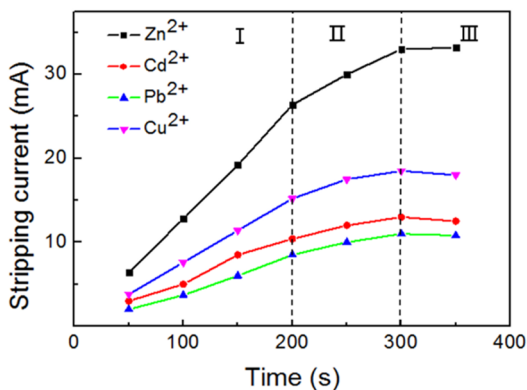


Figure 2. Effect of accumulation time on stripping currents for different ions.

Fig. 2 shows the effect of accumulation time on the stripping currents of the different ions. The effect of accumulation time on the stripping currents of the four ions can be divided into three stages. Stage I (50–200 s): the stripping peak currents of all ions increased rapidly with the accumulation time. This was attributed to the amalgam formed by the reduction of heavy metal ions on the mercury film. This was rapid as the concentrations of the heavy metal ions being reduced were low. Stage II (200–300 s): the enrichment of heavy metal ions on the mercury film was less rapid, resulting in lower rates of increase of the peak currents. Stage III (after 300 s):

amalgam on the mercury film approached saturation, and increases in accumulation time no longer led to increases in the current intensity of the stripping peak. Therefore, 300 s was the optimum accumulation time.

Effect of film coating parameters on the stripping curves of glassy-carbon electrodes

Effect of coating solution concentration

The coating solution concentration affects the mercury load on the electrode surface and thus affects the electrode stability. Glassy-carbon electrodes were coated in different HgCl_2 coating solutions (0.01–0.04 mol/l HgCl_2) for 70 s, and used for detection in different standard solutions (0.101 mg/l Zn^{2+} , 0.011 mg/l Cd^{2+} , 0.011 mg/l Pb^{2+} , and 0.056 mg/l Cu^{2+}). The other three parameters selected were a base solution pH = 4.68, an accumulation time of 300s, and three coating steps.

Fig. 3 shows the stripping curves of the four metal ions on the electrode prepared under different coating solution concentrations.

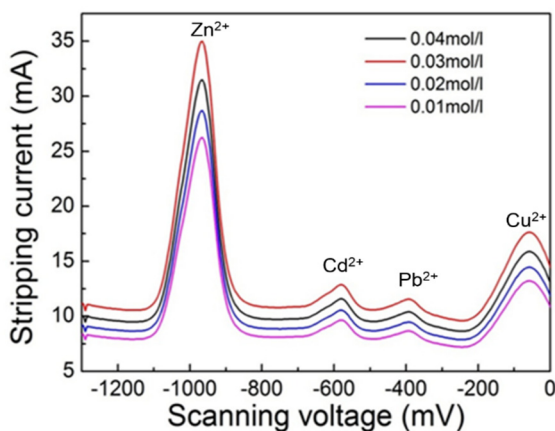


Figure 3. Stripping curves of different metal ions on electrodes prepared under different coating solution concentrations.

The stripping peak intensity increased and then decreased as the coating solution concentration increased, but the peak position remained constant. At a coating solution concentration of 0.01 mol/l, the stripping peak current intensities of all ions were smallest. At a coating solution concentration

of 0.02 mol/l, the stripping peak current intensities of all ions increased slightly. However, the intensities were still insufficient for adequate detection. At a coating solution concentration of 0.03 mol/l, the stripping peak current intensities of all ions were largest. At a coating solution concentration of 0.04 mol/l, the stripping peak current intensities of all ions decreased, and the accuracy also decreased. As the coating solution concentration increased, the mercury load on the electrode surface and the mercury micro-drop size increased, but the stability and detection accuracy of the mercury film increased and then decreased. As the coating solution concentration increased from 0.03 mol/l to 0.04 mol/l, the stripping peak value decreased. This can be attributed to the over-large size of mercury micro-drops, which degraded the stability of mercury film [11, 12]. In other words, peak values of all ions were maximized at a coating solution concentration of 0.03 mol/l, and little signal noise was observed, thus guaranteeing high stripping peak current intensity and good detection accuracy. Therefore, 0.03 mol/l was the optimum coating solution concentration.

Effects of coating step number

The coating step number was an important parameter that can reflect both the coating time and film formation cycle. When the mercury film was prepared with different coating numbers, the increase of the coating step number represents an extension of the coating time as well as the filming cycle. The coating time affects the size of the micro-mercury droplets, and the coating cycle affects the uniformity and compactness of the mercury film.

After the initial film formation, the micro-mercury droplets continued to form a film on the basis of the original film; the distribution of mercury micro-drops determines the amount of noise in the stripping curves. This study investigated stripping peak signals for glassy-carbon electrodes with one, two, and three coating steps for Cu^{2+} , Pb^{2+} , Zn^{2+} , and Cd^{2+} . The concentration of the coating solution was 0.03 mol/l, the pH of the base solution was 4.68, and the accumulation time was 300 s.

Fig.4 shows the stripping currents for electrodes prepared with different numbers of coating steps. Dual peak phenomena and large background waves were observed for the stripping potential of Zn^{2+} , and the stripping peak of Cd^{2+} was not observed. This can be attributed to the low density of mercury micro-drops on the electrode and poor electrode stability, leading to significant noise. With two coating steps, the density of mercury micro-drops increased, but the distribution was not uniform, resulting in excessive sensitivity of the electrode and significant noise. With three coating steps, peak values were reasonable, and the signal shapes were symmetric with little noise observed. Both the

density and distribution of mercury micro-drops on electrode were acceptable, resulting in good electrode stability and high detection precision. Therefore, the optimum number of coating steps was three.

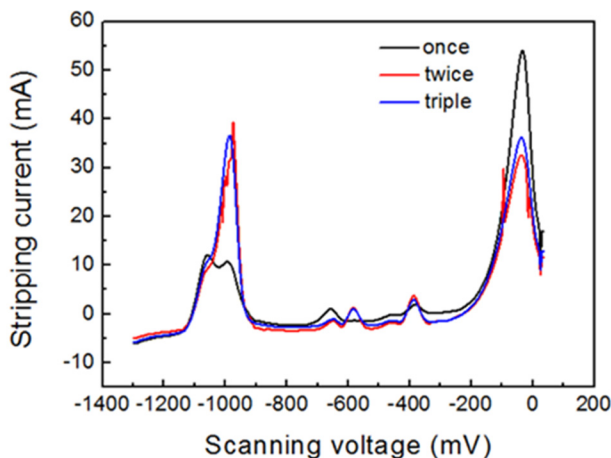


Figure 4. Stripping currents by electrodes prepared with different coating cycles.

Electrochemical performance test

The electrochemical performance of mercury film coated electrodes prepared under the optimized parameters discussed above was evaluated. In addition to overall performance, calibration curves, detection limits, and reproducibility were investigated.

Calibration curve

Standard solutions with a concentration gradient of 0.02 mg/l were prepared and measured. Taking Zn^{2+} as an example, a calibration curve was drawn based on the linear relationship between the Zn^{2+} concentration and the peak current. Fig. 5 shows linear correlation of Zn^{2+} concentration (0.03–0.15 mg/l) vs. peak current. The calibration curve obtained was $y = 78.2142x + 14.4464$, and the determination coefficient (R^2) was 0.9913. Similarly, R^2 for Cd^{2+} , Pb^{2+} , and Cu^{2+} were 0.9939, 0.9933, and 0.9962, respectively.

The calibration curve is a guarantee of the detection accuracy of the electrode. The closer the determination coefficient is to 1, the better the electrode performance. Joanna Smajdor *et al.* [13] proposed a renewable glassy-carbon electrode, and the R^2 reported was 0.99. The R^2 values of all electrodes prepared in this study were > 0.99 , indicating high detection accuracy.

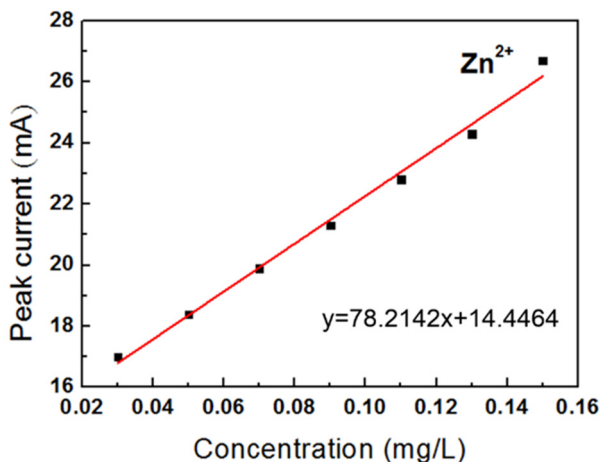


Figure 5. The calibration curve of Zn^{2+} .

Detection limit

The lower detection limit of the electrode was determined by the ratio of the response signal to the noise (signal-to-noise ratio), and the critical level defined as a signal-to-noise ratio = 3. A suitable amount of pure sub-boiling distilled water was used as a blank solution for a control experiment, and the mercury film electrode prepared under the optimal parameters was used to scan the blank solution. The standard deviation of the scan for ten equipotential differences in the scanning curve was used as the electrode noise. Fig. 6 shows the scanning results of a blank solution at 100 mV intervals. The stripping currents were within 9–12.5 mA, the range was concentrated, and the electrode noise was small. The detection limits ($D = 3N/S$, D for detection limit, N for noise and S for sensitivity) calculated were 5 $\mu\text{g/l}$, 10 $\mu\text{g/l}$, 1 $\mu\text{g/l}$, and 0.1 $\mu\text{g/l}$ for Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} , respectively.

The lower detection limit of an electrode determines its application range. Arancibia, V *et al.* [14] proposed a Nafion-mercury coated glassy-carbon electrode for the detection of Cd^{2+} . The detection limit reported for Cd^{2+} was 0.8 $\mu\text{g/l}$ at pH = 3.5 and an accumulation time of 100 s. This method was similar to that proposed in our study, but the detection limit in our study was similar. In another study, a complex polymer modified glassy-carbon electrode was used to detect Pb^{2+} in soft water by stripping voltammetry [15]. The detection limit for Pb^{2+} measured at an accumulation time of 45 min, and a base solution pH of 4.5 was 1.2 $\mu\text{g/l}$. In our study, a lower detection limit for Pb^{2+} was achieved (0.1 $\mu\text{g/l}$) with a much shorter accumulation time of 300 s, indicating significant improvements in detection efficiency.

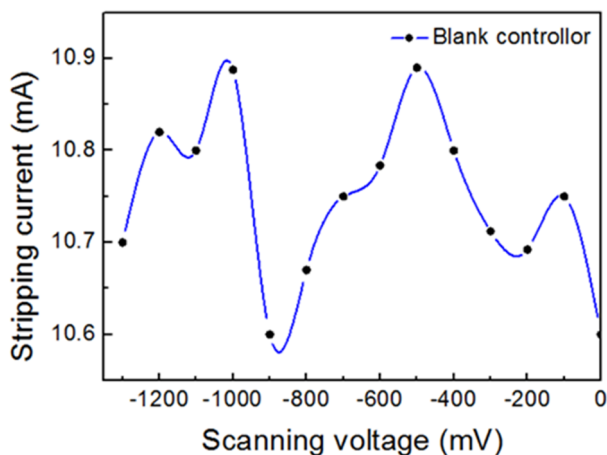


Figure 6. Scanning results of a blank solution.

Reproducibility

The mercury load on the mercury film coated electrode decreased as the number of detection cycles increased. The stability of the electrode was evaluated by multiple repeatability tests. Table 1 summarizes the test results using a mixed solution containing 0.1 mg/l Zn^{2+} , 0.01 mg/l Pb^{2+} , 0.01 mg/l Cd^{2+} , and 0.5 mg/l Cu^{2+} , and also gives the concentration confidence intervals at the 95% confidence level. The step potential was 4 mV. As shown in Table 1, the RSDs for the detection of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} were 3.4%, 2.7%, 2.1% and 4.1%, respectively. The mean concentrations measured were (mg/l) 15.15 -- 15.17 for Zn^{2+} , 1.01 -- 1.04 for Cd^{2+} , 1.45 -- 1.48 for Pb^{2+} and 6.65 -- 6.66 for Cu^{2+} , respectively.

Table 1. Repeatability test results and confidence interval with 95% confidence level of the mixed solution containing 0.1 mg/l Zn^{2+} , 0.01 mg/l Pb^{2+} , 0.01 mg/l Cd^{2+} , and 0.5 mg/l Cu^{2+} .

	1	2	3	4	5	RSD (%)	Mean concentration (mg/l)
Zn^{2+}	14.72	14.96	14.85	15.26	15.99	3.4	(15.15, 15.17)
Cd^{2+}	0.99	0.98	1.04	1.03	1.03	2.7	(1.01, 1.04)
Pb^{2+}	1.44	1.43	1.44	1.48	1.50	2.1	(1.45, 1.48)
Cu^{2+}	6.77	6.77	6.19	6.70	6.87	4.1	(6.63, 6.66)

Currently, great efforts are being made to improve the repeatability of detection by electrodes. A typical example is Jesid Lara *et al.* [16]. They used a polymer-modified glassy-carbon electrode and simultaneously measured Pb^{2+} and Cd^{2+} in a 9.0 $\mu\text{g/l}$ mixed solution. At a base solution pH of 4, an RSD of 2.0% for cadmium and 2.5% for lead were obtained from seven replicate experiments. By comparison, our electrode was prepared by a more convenient preparation method and had similar repeatability.

Recovery degree represents the degree of ion loss during the detection process, and it reflects the accuracy of the electrode. The recovery degree was not applicable in our study due to the absence of impurity ions in the solution system [17, 18].

CONCLUSIONS

Improvement of the precision and detection limit of glassy-carbon electrodes by mercury film coating is critical for water body monitoring and pre-alerts for the natural environment. In this work, a systematic investigation was conducted of the working environment, and the coating parameters for a mercury film coated electrode. The electrochemical performance of the optimized electrode was evaluated in the simultaneous detection of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} .

1. The pre-coated mercury film parameters were optimized. At a base solution pH of 4.68 and an accumulation time = 300 s, stripping peaks for all ions exhibited complete peak shapes and maximum peak values. At a coating solution concentration of 0.03 mol/l and after three coating steps, the prepared electrode exhibited advisable stripping peak intensities for all ions with a low signal-to-noise ratio.

2. The mercury film coated electrode prepared and operating under optimized parameters demonstrated admirable electrochemical performance. R^2 values of the four ions were all greater than 0.99, and the highest value was 0.9962. The detection limits were all lower than 10 $\mu\text{g/l}$, and was as low as 0.1 $\mu\text{g/l}$ for Pb^{2+} , with RSD values in the range 2.1% to 4.1%.

As a core component of a rapid detector, such precision and detection limits may enable the mercury film coated electrode to be applicable in simultaneously detecting multiple heavy metal ions in complicated water bodies.

EXPERIMENTAL SECTION

Equipment and reagents

Film coating and testing used an electrochemical analyzer (Safeda Technologies, China). The working electrode was a glassy-carbon electrode (diameter = 3 mm), the reference electrode was Ag/AgCl (3M KCl), and the auxiliary electrode was Pt. The base solution pH was measured with a pH meter (Mettler Toledo, China) and an electronic balance used for weighing was purchased from Jingtian electronic equipment, Shanghai, China.

All reagents used were Guaranteed Reagent (GR) grade. The coating solution used was a HgCl_2 solution, and the standard solution was a mixed solution of Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} . These solutions were prepared by adding sub-boiled distilled water into a 1000 mg/l standard solution for atomic absorption. The base solution was a sodium acetate-acetic acid buffer prepared from sodium acetate, potassium chloride, and acetic acid (purchased from Shanghai Pharmaceuticals Holding Co., Ltd). The pH of the solution was set by adjusting the amount of acetic acid added.

Preparation of mercury film coated glassy-carbon electrode

The mercury film coated glassy-carbon electrode was prepared using an electrochemical analyzer. In pre-treatment, the electrode was polished using buckskin until no scratches were observed, rinsed with deionized water, and wiped with filter paper. Then, the electrode was manually polished for 60 s, using a polishing medium of Al_2O_3 powder (particle size of 30 μm) mixed with deionized water, and rinsed. The film was removed after each testing cycle to minimize errors.

At the coating stage, 5 ml of pure water and 5 ml of film coating solution (HgCl_2) were injected into the detector cell of the electrochemical analyzer, a backward voltage was applied on the working electrode for 60 s and then left untouched for 10 s with no voltage applied. The concentration (mol/l) of HgCl_2 solution used was 0.1, 0.2, 0.3 and 0.4. The number of coating steps ranged from 1 to 3.

Detection of heavy metal ions

The heavy metal ions in a mixed solution containing Cu^{2+} , Zn^{2+} , Cd^{2+} , and Pb^{2+} were detected using the mercury film coated glassy-carbon electrode prepared under optimized parameters. The stripping frequency and the working voltage of the electrochemical analyzer were set at 2 ms and -1.3 V,

respectively, and the step potential was 4mV. 1 ml of standard solution, 5 ml of electrolyte, a 1 ml test sample, 5 ml of pure water, and 5 ml of film coating solution were added together and mixed.

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