Detection of Hg(II) in Coal Gangue with Anodic Stripping Voltammetry Method

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Abstract. Mercury is one of the common heavy metal elements in coal gangue, and it is very important to detect mercury in view of environment risk control. In this work, we develop a rapid and simple detecting method of mercury in coal gangue based on anodic stripping voltammetry. Through a large number of experiments, operational parameters of anodic stripping voltammetry detection for mercury have been optimized, including working electrode, reference electrode, auxiliary electrode, electrolyte, scanning mode, stirring rate, enrichment potential, accumulation time, rest time, scanning potential and scanning rate. Our study provides a quick and accurate detection method for Hg(II) in coal gangue.

1. Introduction
Coal gangue is an inevitable solid waste discharged during coal production, coal mining and washing. By 2015 about 3.7 billion tons of coal gangue has been reserved in China. Coal gangue in large quantities occupies a lot of land and causes much serious environmental impact on the mining area and its surroundings [1-3]. Mercury is one of the common heavy metal elements in coal gangue, which can enter the water through the rain and snow leaching, or flow directly into the vicinity of rivers or seep into the ground. Mercury has significant biological toxicity and can not be degraded by microorganism, which have various forms of mutual conversion and dispersion, it can be enriched and then enter the body through the food chain, causing chronic poisoning.

In order to solve environmental pollution and other risk of large quantities of solid waste, the scientists and the engineers pay much attention to the utilization of coal gangue to make products with high value, such as various building materials and products [4]. When presented in excess or under the wrong conditions, heavy metals can result in multiple toxic effects [5-6]. So it is very important to detect the heavy metals of the products in view of environment risk control.

People have developed many detection methods for determination of heavy metals, [7-9] including inductively coupled plasma mass spectrometry (ICPMS) [10], graphite furnace atomic absorption spectrometry,[11] and high-performance liquid chromatography with ICPMS.[12] However, these techniques are more suitable for laboratory conditions only and usually cost much testing time. Consequently it is difficult to be used for routine in-field monitoring of a large number of samples. Also mercury is a special element that has a strong volatility and is not as easy to test accurately. Therefore, it is needed to develop a rapid and simple determining method for Hg(II).
Voltammetric stripping techniques provide accurate measurements of low concentrations at the ppb levels for metal ions with rapid analysis times and low-cost instrumentation. In this work we present the electrochemical detection method of Hg(II) of coal gangue. Through a large number of experiments, operational parameters have been optimized. Our study provides a quick and accurate detection method for Hg(II) in coal gangue.

2. Experimental

2.1 Reagents and preparation of solution to be measured
All of the reagents were obtained from AkzoNobel Co., China and Alfa Aesar, China and were of analytical grade and hence used without further purification. Coal gangue samples were collected from one coal mine of Shanxi Province, China.

Before the anodic stripping voltammetric detection of Hg(II), it is necessary to dissolve the heavy metal elements into the water solution. Coal gangue is a kind of hard solid substance, and it is difficult to dissolve. The common methods to dissolve are wet digestion, dry ashing and microwave digestion. And wet digestion and microwave digestion are the most common methods.

Preparation of all the solutions was conducted by using de-ionized water. Most of the samples can be digested by wet method to achieve satisfactory digestion effect. The experimental conditions are as follows: the amount of coal gangue samples is 0.3~0.4 g, and the acids used for digestion are 5 mL HNO₃, 1 mL HF, 1 mL HClO₄ and 1 mL H₃PO₄.

3. Determination of measuring parameters
Currently reported electrodes that can effectively measure trace amounts of Hg(II) are gold electrodes and modified glassy carbon electrodes. The experimental parameters also differ depending on the conditions of the electrodes, the experimental equipment, and the experimental environment. In this work, the gold plate electrode was used as the working electrode, and the content of trace mercury was determined by an electrochemical workstation and an electrolytic cell. The concentration range of the measurement, the factors affecting the measurement accuracy, and the optimal conditions for the measurement were also sought.

3.1. Effect of electrode pre-treatment
Electrode pretreatment is a very important step in this experiment. The polishing and cleaning of the auxiliary electrode can initially remove the oxide layer on the electrode surface and make it smoother. However, an auxiliary electrode is required for activation if it is to further process the electrode so that it can operate normally. In addition to the removal of the oxide film, the activation can remove organic and inorganic substances on the surface of the electrode. When using an electrode that has not been subjected to the activation treatment, the background may be unstable due to the different electrical characteristics of the impurities on the surface of the electrode, causing problems such as reverse current. Using the activated electrode for experiments will have a very stable background, resulting in a better experimental curve. The contrast between the two is shown in Fig. 1. Therefore, the activation step needs to be performed at each experiment.
3.2. The effect of bottom fluid

This experiment requires the base fluid to have good conductivity. Since deionized water is not electrically conductive, it is necessary to add an appropriate amount of electrolyte solution. The added electrolyte should have the following characteristics:

1) It is difficult to participate in the electrochemical reaction;
2) The ionic strength and the diffusion coefficient are kept constant;
3) The concentration is suitable;
4) The reaction is not involved in the solution.

This experiment compared the same acidity of HNO₃ and HCl bottom liquid, and compared mercury stripping voltammetric curves at different concentrations of Cl⁻ at the same acidity. It was found that it was difficult to measure the peak mercury discharge current in HNO₃, but the voltammogram was very obviously be detected in HCl, as shown in Fig. 2.

![Dissolution curves of mercury in 1mol/L nitric acid (line a) and 1mol/L hydrochloric acid (line b).](image)

We can conclude that in the acidic solution chloride ions have a crucial influence on the determination of the mercury ion elution peak. The sensitization effect of chloride ion on the elution peak of mercury is due to the fact that when the mercury is dissolved, its bivalent ion and chloride ion combine to form insoluble Hg₂Cl₂, so that the reaction equilibrium proceeds in favour of the formation of mercury ions, accelerating the dissolution reaction. When the chloride concentration is low, the peak current increases significantly with increase of chloride concentration, as shown in Fig. 3.
When the chloride ion concentration is high, since the amount of dissolved mercury ions is constant, when it reaches saturation, it will not continue to increase, but the position of its dissolution peak will move forward with the increase of chloride ion concentration, such as See Fig. 4. According to the experimental results, we can see that the chloride ion can saturate the peak current at a very low concentration, while the excessively high chloride ion concentration will only affect the position of the elution peak, and will not affect the current intensity. So the choice for the concentration of chloride ions only needs to be kept at a concentration, which is not too low or too high.

3.3. Influence of enrichment potential
The enrichment potential has a great influence on the experiment. If the selection of the enrichment potential is too small, mercury ions may not be efficiently enriched, resulting in very small peak currents when eluted and thus unable to be further analyzed. If the selection of the enrichment potential is too large, mercury ions can be effectively enriched, but at the same time, too many other ions will be enriched to interfere with the experiment. At the same time, too large enrichment potential will electrolyze the gas to generate bubbles on the surface of the working electrode, thereby hindering the enrichment process. Therefore, when the enrichment potential is too large, the elution voltammogram will be very unstable, and the elution peak current may even decrease. The experimental results are shown in Fig. 5. In this work, based on the experimental results, -0.4 V was selected as the enrichment potential.
3.4. Effect of accumulation time
The longer the enrichment time, the greater the amount of metal ions will enrich on the electrode and the greater the current will generate when eluted. However, when the enrichment time is long enough, after the metal ions to be measured have been completely enriched on the electrode, the increase of the enrichment time will not continue to affect the peak current. Therefore, in a certain range, the elution peak current is positively correlated with the enrichment time, but when the time is too long, the curve will tend to be flat and eventually become a straight line, that is, when the enrichment time is large to a certain extent, the peak current will no longer change with the enrichment time. This conclusion can be seen in Fig. 6 and Fig. 7.

![Graph](image1.png)

Fig.5. The relationship between the dissolution peak and the enrichment potential.

![Graph](image2.png)

Fig.6. The dissolution curves of mercury at different concentration times. (a: 30s; b: 60s; c:120s; d:180s; e: 240s; f: 300s; g: 360s; h: 480s)

![Graph](image3.png)

Fig.7. The relationship between the dissolution peak of mercury and the time of enrichment.
The dissolution peak is not more obvious with the prolongation of enrichment time, because the peak current is proportional to the concentration of metal ions rather than the amount of enrichment. Even if the metal ions are not completely enriched, analysis can be performed as long as the experimental conditions and the enrichment time are guaranteed at the same concentration. If you choose to fully enrich the mercury element, you will need a longer experiment time and waste time and cost. Therefore, when selecting the enrichment time, it is only necessary to ensure that the elution peak is obvious. The general choice is 120–300 s.

3.5. Effect of stirring rate
During the enrichment process, the solution needs to be stirred to increase the enrichment efficiency. To maintain a large current in the enrichment process, it is necessary to create a convection effect by stirring so that ions can be transferred to the surface of the electrode rather than relying solely on slow diffusion. Stirring in the stripping voltammetry experiment is essential, and the peak current increases with the stirring rate, as shown in Fig. 8.

![Fig.8. The dissolution curves of mercury at different stirring rates](image)

However, when the stirring rate is so large that a vortex is formed in the solution, due to excessive mechanical action of the auxiliary electrode surface and excessive bubbles in the solution, it will adversely affect the experiment and lead to a decrease in the peak current, as shown in Fig. 9. Therefore, the choice of the stirring rate needs to be controlled so that it cannot be too low and not so high as to produce a significant vortex in the solution.

![Fig.9. Stripping voltammetry of mercury with excessive stirring rate (a) and proper stirring rate (b)](image)

3.6. Influence of rest time
After the enrichment process is completed, it is necessary to stop the stirring to make the solution system standstill for a while so that the enriched metal is uniformly diffused on the surface of the electrode, so that a good elution voltammetry curve can be obtained. The experimental results show
that the longer the rest time, the better the diffusion of metal ions, the peak current will increase, and finally tend to a stable value, as shown in Fig. 10 and Fig. 11. According to the plot of the peak current and the rest time, considering the experimental efficiency at the same time, 30s is selected as the rest time.

![Stripping voltammogram of mercury at different stationary time](image1)

**Fig.10.** Stripping voltammogram of mercury at different stationary time (0-120s)

![The relation diagram of the peak current of the stationary time and the dissolution of mercury](image2)

**Fig.11.** The relation diagram of the peak current of the stationary time and the dissolution of mercury

### 3.7 Effect of scan rate

In general, the peak current intensity increases as the scan rate increases. If the electrode reaction is controlled by the diffusion process, the peak current intensity in a certain range is proportional to the square root of the scan rate. In this experiment, the results showed that the electrode reaction actually controlled the diffusion process, and the fitting curve was as shown in Fig. 12. The fitting result was: \( y=-0.9861x-1.0981, \) \( R^2=0.9977. \) Therefore, increasing the scan rate appropriately can increase the peak current and increase the sensitivity. However, the scan rate should not be too large, because too large a scan rate will increase the capacitive current but will affect the sensitivity, but also lead to less data points to make the curve less accurate.
3.8 Interference experiment

The experimental results show that 100-fold manganese, zinc, chromium, cadmium, arsenic, and other ions have no effect on the determination of the mercury ion elution peak current, as shown in Fig. 13. The 10-fold increase in copper ions has a significant effect on the elution peak of mercury ions, as shown in Fig. 14.

Fig.12. Relationship between square root of scanning rate and current of dissolution peak

Fig.13. Stripping voltammograms of mercury with adding 100 times manganese, zinc, chromium, cadmium and arsenic interference ion (line b) and without interference (line a)
Fig.14. Stripping voltammograms of mercury with adding 10 times copper interference ion (line b) and without interference (line a)

4. Conclusion
From the experimental results mentioned above, the optimized operational parameters have been obtained as Table 1.

Table 1. The optimized operational parameters for anodic stripping voltammetric detection of Hg(II) of Coal Gangue

| Measuring condition | Value or details |
|---------------------|------------------|
| working electrode   | gold plate electrode |
| reference electrode | saturated calomel electrode |
| auxiliary electrode | platinum wire electrode |
| electrolyte         | 1mol/L HCl |
| scanning mode       | differential pulse anodic stripping method |
| stirring rate       | 400 r/min |
| enrichment potential| -0.4V |
| accumulation time   | 480s |
| rest time           | 30s |
| scanning potential  | -0.4–0.8V |
| scanning rate       | 4 mV/s |

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