Rapid Detection of As(III) in Coal Gangue with Anodic Stripping Voltammetry Method

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Abstract. It is important to detect arsenic content in the process of comprehensive utilization of coal gangue in view of environment risk control. In this work, we proposed a rapid detection method of As(III) in coal gangue with anodic stripping voltammetry, and optimized the operating parameters by a large number of experiments. The result shows that the anodic stripping voltammetry can accurately analyse As(III) in coal gangue in real time. Anodic stripping voltammetry method is suitable for small and medium-sized enterprises because of its short detection time and low cost of equipment.

1. Introduction
Coal gangue is one of the largest industrial solid wastes in China, which occupies a large area of land and has high environmental risks [1]. Resource utilization is an effective way for these industrial wastes to solve these problems. At present, the utilization rate of the industrial solid waste in China is increasing, but the quality of resource-based products and heavy metal residues are becoming increasingly prominent [2]. If the product quality and environmental risk could not be strictly controlled, the large-scale utilization of industrial solid waste will bring a series of safety and environmental problems, which will limit its prospects for resource utilization [3].

Coal gangue is rich in heavy metal elements. Heavy metals have obvious biological toxicity and strong migration ability [4]. They can enter the atmosphere through weathering or water through leaching [5]. Arsenic is a harmful trace element to human beings [6]. Acute arsenism can lead to death, while chronic arsenism can lead to loss of appetite, gastrointestinal diseases and skin keratosis [7]. Therefore, in order to avoid secondary pollution caused by arsenic, it is necessary to detect arsenic content in the process of comprehensive utilization of coal gangue.

However, the relationship between traditional detection technology and large industrial solid waste recycling technology is not perfect, and there is a lack of expertise for rapid detection of As(III) in coal gangue [8]. In this work, we proposed an electrochemical method for the determination of As(III) in coal gangue, and optimized the operation parameters through a large number of experiments. The
result shows that the anodic stripping voltammetry can accurately analyse As(III) in coal gangue in real time.

2. Experimental

2.1. Reagent
The reagents in this study came from China Alfa Aesar Company and China Akzo Nobel Company. They were analytical reagents and could be used without further purification. Coal gangue samples were collected from a coal mine in Shanxi Province.

2.2. Solution
Ultra-pure water was used to prepare all the solutions. Most of the samples could be digested by wet method to achieve satisfactory digestive effect. The experimental conditions were as follows: the amount of gangue sample was 0.3 ~ 0.4 g, and the digestive acid was 5 mL nitric acid, 1 mL hydrogen fluoride, 1 mL hydrochloric acid and 1 mL phosphoric acid.

The gold electrode was polished to mirror shape and cleaned by ultrasonic in nitric acid, absolute ethanol and distilled water [9]. The treated gold electrode on the electrode containing 0.1 M potassium chloride solution with cyclic voltammetry scan, scan potential was set to -0.2 ~ 0.6 V, when the redox peak potential difference was less than 100 mV, indicating that the electrode had been processed clean.

3. Results and Discussion
At present, gold electrode and modified glassy carbon electrode are effective electrodes for the determination of trace As(III) [10]. Gold electrode is more convenient in use, so it is more suitable for rapid detection of arsenic in coal gangue [11]. In this work, gold electrode was used as working electrode to determine trace arsenic content by electrochemical workstation and electrolytic cell.

3.1. Selection of Scanning Method
Anodic stripping voltammetry has many scanning methods, including differential pulse anodic stripping voltammetry (DPV), square wave voltammetry (SWV), linear sweep voltammetry (LSV) and normal pulse voltammetry (NPV) [12]. In this experiment, the four scanning methods mentioned above were compared and the best scanning method for the determination of arsenic was explored. The basic experimental conditions were as follows: the concentration of As(III) was 50 mg/L, scanning range was -0.2~0.3 V, enrichment potential was -0.9 V, the enrichment time was 120 s, the rest time was 60 s. The parameters of DPV were as follows: the potential increment was 4 mV, the amplitude was 25 mV, the pulse width was 0.05 s, the sampling width was 0.02 s, pulse period was 0.5 s. The parameters of SWV were as follows: potential increment was 4 mV, the frequency was 15 Hz, and the pulse amplitude was 25 mV. The parameters of LSV were as follows: scanning speed was 100 mV/s, the sampling interval was 1 mV. The parameters of NPV were as follows: potential increment was 4 mV, the pulse width was 0.05 s, the sampling width was 0.02 s, pulse period was 0.2 s. The experimental results are shown in Figure 1. By comparing the peak shapes and heights SWV can be determined to be the best scanning method.
3.2. The effect of electrolytes

The type and concentration of electrolyte have great influence on the morphology and electrodeposition of As(III) [13]. When arsenic is detected by anodic stripping voltammetry, the commonly used electrolytes are hydrochloric acid, sulphuric acid, nitric acid, phosphate buffer and phosphoric acid. According to previous studies, the signal of HCl proved the Gaussian distribution shape and showed good recurrence in anodic stripping voltammetry experiments [14]. As the result, HCl is considered to be an ideal electrolyte in our work. In order to study the influence of the concentrations of HCl on the peak discharge current of As(III), the concentrations of HCl of 0.1 mol/L, 0.2 mol/L, 0.3 mol/L, 0.5 mol/L, 1 mol/L, 2 mol/L and 3 mol/L were conducted respectively for comparison, and the results were shown in Figure 2. The other experimental conditions were as follows: the concentration of As(III) was 50 mg/L, sweep range was -0.2~0.4 V, enrichment potential was -0.8 V, accumulation time was 120 s. As can be seen from Figure 2, the peak discharge current increases with the increase of HCl concentration. However, when the concentration of HCl reaches 1 mol/L, the peak discharge current of arsenic (III) is basically stable, so the optimal concentration of HCl in this experiment is 1 mol/L.
3.3. The effect of the enrichment potentials

The first step of the anodic stripping voltammetry is the electrolytic enrichment process [15]. Electrolytic enrichment process is the enrichment of the measured substance on the electrode by electrolysis. In order to improve the enrichment effect, we can accelerate the test substance delivered to the electrode surface by stirring the solution, and the enrichment effect is also affected by the electrode potential, electrolysis time and stirring speed and other factors. In order to study the effect of enrichment potential on peak discharge current of As(III), the enrichment potentials of -0.4 V, -0.5 V, -0.6 V, -0.7 V, -0.8 V, -0.9 V, -1.0 V, -1.1 V, -1.2 V and -1.3 V were compared, respectively. The results are shown in Figure 3. Based on the Figure 3, the peak discharge current is basically stable with increasing accumulation potential. However, the peak discharge current drops sharply after the enrichment potential reaches -0.8 V. Considering that under ultra-low enrichment potential, the refractory ions will be dissolved, which will affect the detection of arsenic. Therefore, the optimal enrichment potential is determined as -0.8 V.
3.4. The effect of the enrichment time

Many studies had shown that the enrichment effect was closely related to the enrichment time, too short or too long enrichment time will inhibit the enrichment effect [16]. In order to study the influence of enrichment time on the peak discharge current of As(III), different enrichment time of 30 s, 60 s, 90 s, 120 s, 150 s and 180 s were conducted respectively for comparison, and the results were shown in Figure 4. It can be seen that the peak discharge current increases with the increase of enrichment time. However, the peak discharge current of As(III) dramatically decreased when enrichment time reached 120 s. Therefore, the optimal enrichment time of the experiment is 120 s.

![Figure 4](image)

Figure 4. The effect of different enrichment time on peak current.

3.5. The impact of the 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 [17]. In order to study the influence of the rest time on the peak discharge current of As(III), the rest time of 30 s, 60 s, 90 s, 120 s and 150 s were conducted respectively for comparison, the results were shown in Figure 5. As can be seen from Figure 5, the peak discharge current increases with the increase of the rest time. However, when the rest time reaches 90 s, the peak discharge current of As(III) is basically stable, so the best rest time of the experiment is 90 s.

![Figure 5](image)

Figure 5. Effect of different resting time on peak current.
3.6. Linear range
Within the linear range, the maximum peak current of arsenic is linearly correlated with the concentration of arsenic, and within this range, the precision and accuracy can meet the requirements [18]. In order to study the linear range of arsenic, the concentrations of arsenic in the range of 1~100 ug/L were compared, and the results were shown in Figure 6. Based on the Figure 6, when the concentration of As(III) ranges from 1 to 60 ug/L, the element concentration and peak current show good linearity, and \( R^2 = 0.983 \).

![Figure 6. Peak current of As(III) at gold electrode with different concentrations.](image)

4. Conclusion
According to the above experimental results, the optimized operation parameters are shown in Table 1.

| Measuring condition         | Value or details |
|-----------------------------|------------------|
| scan method                 | SWV              |
| concentration of HCL        | 1 mol/L          |
| enrichment potentials       | -0.8 V           |
| rest time                   | 120 s            |
| static time                 | 90 s             |
| linear range                | 1~60 μg/L        |

In order to verify the accuracy and feasibility of this method, we analyzed the concentration of As(III) in the standard substance of coal fly ash and the standard substance of soil and sediment with the above operation parameters. The test results are shown in Table 2.
Table 2. The detection results of As(III) in standard substances.

| Sample                              | Detected value (mg/kg) | Reference Value (mg/kg) |
|-------------------------------------|------------------------|-------------------------|
| GBW 08401 standard substance of coal fly ash | 14.91±1.52             | 11.4±0.6                |
| GBW 07435 standard substance of soil and sediment | 20.70±2.39             | 14.5±0.8                |

Samples of coal gangue and fly ash were collected from Guizhou Province and Shanxi Province of China. As(III) was tested by this method and compared with the results of ICP-OES, which are as shown in Table 3.

Table 3. The detection results of As(III) in typical coal gangue and fly ash of China with the method of this work and ICP-OES in standard substances.

| Sample                              | Detected value (mg/kg) | ICP-OES Value (mg/kg) |
|-------------------------------------|------------------------|-----------------------|
| coal gangue in Guizhou Province     | 46.89±5.83             | 47.46                 |
| fly ash in Guizhou Province         | 28.62±3.47             | 27.93                 |
| coal gangue in Shanxi Province      | 30.99±10.66            | 26.41                 |
| fly ash in Shanxi Province          | N.D.                   | N.D.                  |

From the above test results, we can conclude that the method given in this work is accurate enough for rapid detection of As(III) in coal gangue. Anodic stripping voltammetry method is suitable for small and medium-sized enterprises because of its short detection time and low cost of equipment.

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