

Analysis of Co(II) Concentration Using Cyclic Voltammetry Technique

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Abstract

Cobalt (Co), as one of the toxic and non-biodegradable heavy metals, has polluted most of the waters, which has an impact on human health and biotic components. Currently, the electrochemical method as a fast, accurate, and reliable technique for detecting heavy metals has been widely developed. Therefore, to obtain results with high accuracy, it is necessary to carry out the analysis under conditions suitable for the heavy metal to be analyzed. In this study, several parameters of Co metal content analysis, such as voltage range, scan rate, and pH were examined using the cyclic voltammetry technique. Metal content analysis using atomic absorption spectrometry was also carried out as a comparison. Based on the results of the analysis of Co metal in the waste solution, it shows that the measurement conditions for the analysis of Co(II) metal are each with a voltage range of 0.75 V to -1.5 V, a scan rate of 200 mV/s, and a pH of 7. The detection limit and quantization limit of Co(II) standard solution are 217.06 mg/L and 723.5 mg/L, respectively, with an RSD of 0.9% and a validity value of the correlation coefficient of 0.9992.

Keywords: cobalt, cyclic voltammetry, heavy metals

1. Introduction

Currently, water pollution caused by industry and community activities has resulted in waste containing heavy metals. Heavy metals in water are a serious problem because they are non-biodegradable, toxic, and can bioaccumulate in the food chain, threatening the survival of living things [1]. Some elements that are included in the heavy metal category are Co, As, Cr, Cd, Pb, Fe, Cu, Hg, Se, Sb, Mn, Zn, and Ni [2-4]. This study focuses on cobalt metal, one of several metals mentioned, because cobalt is commonly found in waters as a pollutant metal. Co-poisoning can also cause abnormalities in the heart and high blood pressure. Thus, this study will focus on Co as a metal pollutant. To determine the level of danger of a polluted stream, it must have a threshold value that is in accordance with applicable regulations. Therefore, an analytical method is needed to detect metals at low concentrations in water. Several methods commonly used in the determination of heavy metal levels are atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS), and electrochemical analysis. AAS has been widely used but has several

disadvantages, including requiring a different hollow cathode lamp for each metal element. When analyzing multiple metals in a sample, there's a challenge [5-6]. As one method for determining metal content, ICP-MS can measure more than one metal at the same time, but the process is expensive [7-8]. In addition, the analysis of metals such as Ca and Fe is a bit difficult using ICP-MS because of the interference spectra [9]. Compared to the two previous methods, electrochemical analysis methods such as voltammetry has many advantages and has been shown to have high sensitivity, a small detection limit with high accuracy on the g/L (ppb) scale, convenience of use, easy sample preparation, simple and quick analysis, and inexpensive [10-14]. In addition, with this method, it's possible to study the chemical species of the analyzed heavy metals [15]. However, to get results with high accuracy, measurement conditions that are in accordance with the heavy metal to be analyzed are needed [16]. Therefore, in this study, the conditions for measuring Co metal ion levels were tested using the cyclic voltammetry technique. Variations in the range of voltage, scan rate, and pH of the solution were studied to obtain the appropriate measurement conditions. Testing of metal ion

levels using AAS was also carried out as a comparison of the measurement results.

2. Materials and Method

In this study, the cyclic voltammetry method was controlled with the e-corder eDAQ 163 potentiostat, which was equipped with eChem v 2.1.0 software. The test uses a system of 3 electrodes with Pt wire each as a working electrode and a supporting electrode, as well as an Ag/AgCl (KCl 3M) as a reference electrode. The materials used are $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, concentrated HNO_3 , HCl , NaOH , KCl (all materials are pro-analysis and purchased from Merck), ethanol, water, aquabides, and chemical waste samples.

2.1 Testing the measurement conditions

A 10 mM Co(II) solution was used as a standard solution for testing the measurement conditions. Several parameters, such as voltage range, scan rate, and pH, were varied. Variations in the range of voltage, scan rate, and pH, respectively, are at voltages ranging from -0.75; -1.00; -1.25; and -1.50 V to 0.75 V; scan rates of 25, 50, 100, 200, and 250 mV/s; and pH 3, 4, 6, 7, and 8 were adjusted by the addition of HCl and NaOH . The manufacture of the calibration curve for Co metal to obtain the equation of the line and the coefficient of the relationship was carried out by measuring 10, 15, 20, 25, and 30 mM Co solutions, each of which was added 10 mL of 300 mg/L KCl solution. A determination of concentration using an atomic absorption spectrophotometer (AAS) as a comparison was also carried out.

2.2 Measurement validation and application to waste sample

The value of the relative standard deviation determines the measurement parameters' accuracy. The formula for calculating the relative standard deviation are written in Equations (1) and (2).

$$SDR = \frac{s}{x} \times 100\% \quad (1)$$

$$S = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}} \quad (2)$$

The relative standard deviation was calculated with eight repetitions ($n = 8$). The test was carried out using a sample of a waste solution containing a metal mixture and the voltage range, scan rate, and pH were obtained while testing the conditions for measuring Co(II) levels in the solution.

3. Results and Discussion

3.1 Analysis of measurement conditions

Fig. 1 depicts how the voltage range affects the peak current produced. Based on the results, expanding the voltage range results in a significant increase in current.

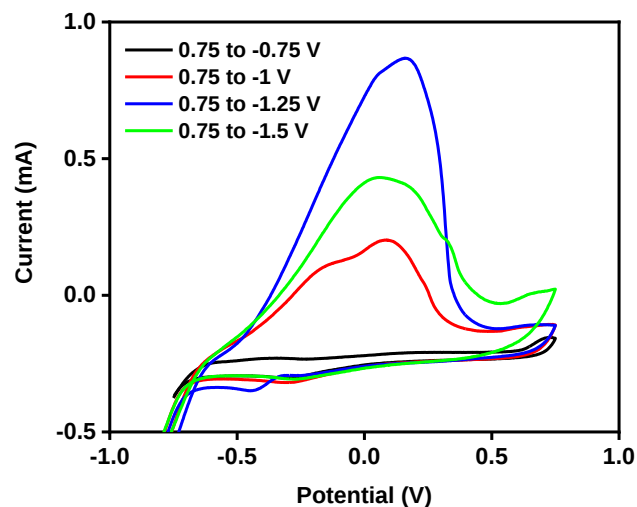


Figure 1. Cyclic voltammogram with different voltage ranges in 10 mM Co solution.

This is because a wider voltage range makes it easier to reduce metal ions in solution to metal. When compared to other voltage ranges, the voltage range from 0.75 V to -1.5 V produces the highest peak, with the greatest current generated. The amount of metal that interacts with the electrode surface and is oxidized during cycling increases at this voltage [17]. The resulting reaction is written in Equations (3).

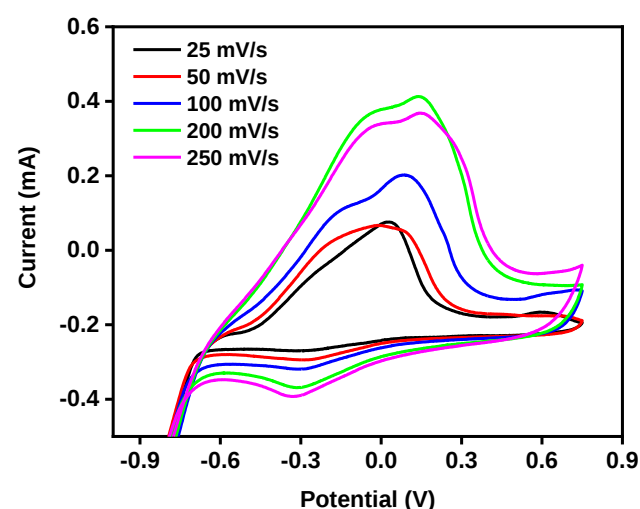
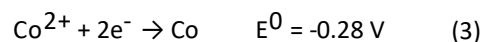


Figure 2. Cyclic voltammogram with different scan rates in 10 mM Co solution.

The peak current height is also affected by the scan rate, as shown in Fig. 2. The cyclic voltammogram shows that increasing the scan rate from 25 to 200 mV/s causes the peak anode and cathode currents to increase, but decreases at 250 mV/s. The kinetics of electron transfer

originating from the metal ion redox reaction have an impact on this. If the electron transfer kinetics are slow, the magnitude of the peak potential separation will be larger and will increase as the scan rate increases [18]. As the scan rate increases, there is a potential shift toward the oxidation peak in a positive direction. This demonstrates that as the scan rate increases, a higher positive potential is required for the oxidation reaction to occur. This causes the electron transfer to be slow [19]. The resulting reaction are written in Equations (4) and (5).



In this study, the use of a scan rate of 200 mV/s in the analysis of the cobalt solution resulted in the highest peak current, so the next test will use a scan rate of 200 mV/s.

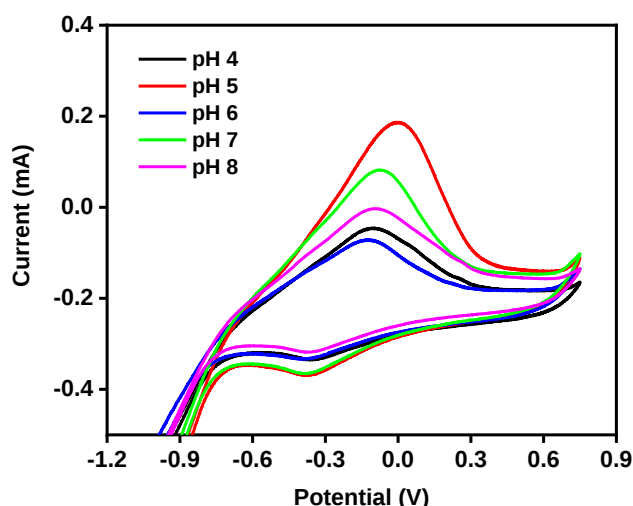


Figure 3. Cyclic voltammogram with different scan rates in 10 mM Co solution, scan rate 200 mV/s.

Fig. 3 shows how the pH of the solution affects the analysis of Co ion levels in the solution. Increasing the pH from 3 to 7 increases the peak current generated, but the current decreases again at pH 8. Among the pH differences used, pH 7 has the highest peak current compared to other pH values, which is 0.02 mA, which appears at the voltage 0.044 V. As a result, pH 7 was chosen as the pH measurement for the analysis of Co metal content in the water medium because at this pH, the cobalt is protonated, allowing the cobalt oxidation reaction to occur completely. Peak current, on the other hand, decreases as the pH rises above 7. Previous research has shown that pH 7 is the best pH for Co analysis [17,20]. The calibration curve is made using the measurement conditions obtained in the previous experiment, namely

using a voltage range of 0.75 V to -1.5 V, a scan rate of 200 mV/s, and pH 7. Based on the data shown in Fig. 4 and Table 1, the current increases and shifts along with the increase in Co concentration. This is due to the increasing concentration of Co ions. More Co metal will be observed on the electrode surface [17]. From the data in Table 1, the equation of the line shows the relationship between the standard concentration of Co and the oxidation peak or I_{pa} , namely $y = 0.097x - 1.186$. The resulting curve in the measurement of single metal ion Co shows a linear increase in current with a value of R^2 of 0.9992. This indicates that single metal ion Co can be detected properly. With a correlation coefficient value that is close to 1 or equal to 1, it can be said that this method can be used to analyze Co metals with good results [16].

3.2 Determination of calibration curves and their application to waste sample

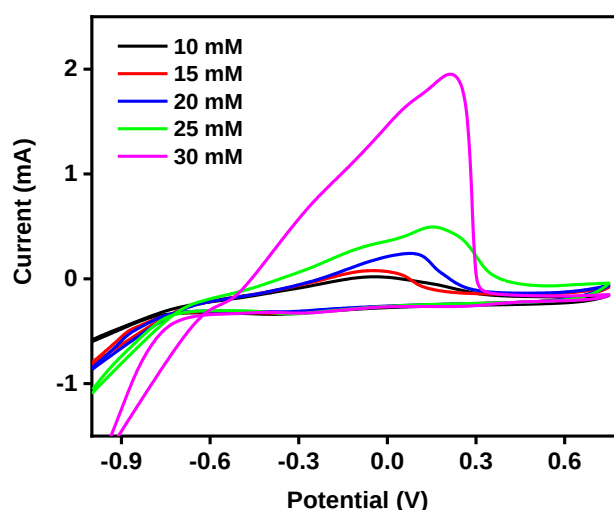


Figure 4. Cyclic voltammogram of concentration variations in metal Co with a potential of -1.5 V, scan rate 200 mV/s, and pH 7.

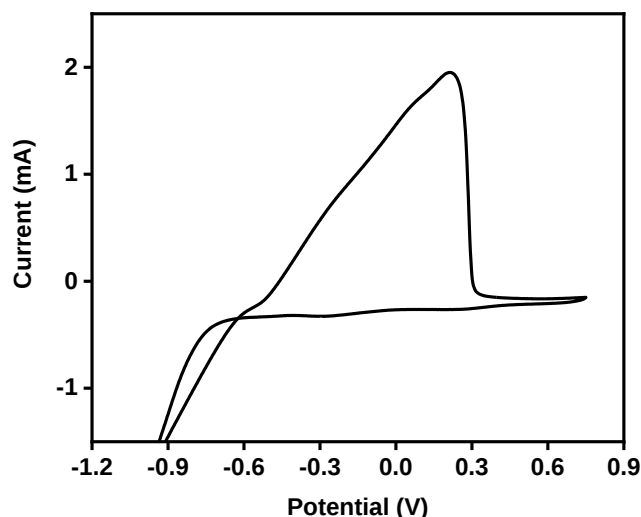
Table 1. Relation between current and concentration.

Concentration (mM)	Current (mA)
10	-0.21
15	0.28
20	0.74
25	1.21
30	1.75

Tests of Co levels carried out using AAS are shown in Table 2. The measurement of single metal ion Co^{2+} using AAS also showed a linear increase in current with an R^2 value of 0.9988. Based on the R^2 value obtained, it shows that the single metal ion of cobalt can be detected properly using AAS.

Table 2. Cobalt standard series absorbance results.

Concentration (mg/L)	Absorbance
0.2	0.0075
0.4	0.0127
1.2	0.3373
1.6	0.0512

**Figure 5.** Voltammogram of waste sample.

A chemical waste solution containing an unknown concentration of a mixed residual solution was tested. The appearance of a significant peak at 0.1 V is the detected metal cobalt, according to the data in Fig. 5. Because there is a linear relationship between concentration (C) and current, the obtained straight-line equation can be used to calculate sample concentration (mA). Based on the science data from the waste sample, the concentration of Co in the sample was calculated by plugging the current value into the standard curve equation $y = 0.097x - 1.186$. According to these calculations, the average Co concentration in the sample was 648.4 mg/L. Furthermore, the Co levels obtained were compared to levels measured using the AAS method. Co-metal content can be measured using the AAS instrument at a wavelength of 580 nm and a Co-metal cathode lamp. Because there is a linear relationship between concentration (C) and absorbance, the obtained straight-line equation can be used to calculate sample concentration (A). The results of testing the metal content of Co on the sample are based on calculations, and the concentration of Co in the sample is 510.70 mg/L, as shown in Table 3. As shown in Table 2, measurements of relative standard deviation in a solution of Co 15 mM were also carried out. The average current value for Co metal is 0.000286 mA, with an relative standard deviation (RSD) value of 0.9%. This value indicates a good level of precision because it has an RSD value of <5% [21]. Furthermore, the

detection limit of the standard Co(II) solution obtained was 2.30 mM or equivalent to 648.4 mg/L and the quantization limit was 2.57 mM or equivalent to 723.5 mg/L.

Table 3. Measurement results of Co levels in samples using AAS.

Sample name	Concentration	Absorbance
Chemical waste	510.70 mg/L	0.0326

4. Conclusion

The voltage range, scan rate, and pH of the solution were investigated using cyclic voltammetry for Co-ions detection. During cycling, the voltage range influences the interaction of Co-ions with the electrode surface and causes them to oxidize. The scan rate influences the kinetics of electron transfers resulting from Co-ion redox reactions. If the electron transfer kinetics are slow, the magnitude of the peak potential separation will increase as the scan rate increases. Protonation and oxidation reactions are affected by the pH solution, resulting in a high peak current. As a result, the Co-ion detection parameters are 0.75 V to -1.5 V potential, 200 mV/s scan rate, and pH 7.

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