

## Anodic Stripping Voltammetry with Pencil Graphite Electrode for Determination of Chromium (III)

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**Abstract.** Chromium is required as micronutrient that has roles in insulin metabolism and blood glucose level regulation. Chromium (III) deficiency can cause hyperglycemia and glycosuria. However, a high amount of chromium in body can cause allergic reaction, organ damage, and even death because of its toxicity. Chromium is commonly used in steel industries. Simultaneously with the development of industry, the waste disposal that can endanger environment also increased. Therefore, a sensitive and specific analysis method for chromium detection is required. Stripping voltammetry is one of the voltammetric methods that is commonly used for heavy metal analysis due to the very low limit of detection (sub ppb). The present study was conducted to develop an analysis method for chromium (III) determination using pencil graphite electrode. Quantitative determination was performed for chromium (III) which measured at -0.8 to +1.0 V with deposition time for 60 s and 50 mV/s scan rate. Stripping voltammetric analysis of chromium (III) using pencil graphite electrode gave linear range at 12.5 to 75 ppm with limit of detection of 0.31 ppm.

### 1. Introduction

Chromium (III) is one of micronutrient that is required to maintain normal physiological function. However, when chromium exceeding the permitted limit, it can cause negative effect such as disturbing immune system and oxidative damage to the cellular components [1, 2]. This also confirmed by The Minister of Health of Republic Indonesia decree No. 907/MENKES/SK/VII/2002 which stated that the threshold value for chromium (III) in water is 0.05 ppm. Therefore a method for chromium (III) determination in trace amount need to be developed.

Some methods for chromium (III) determination has been widely developed. Some methods that are commonly used for chromium (III) determination include: inductively coupled plasma-atomic emission spectrometry (ICP-AES) [3], Inductively coupled plasma-mass spectrometry (ICP-MS) [4], flame atomic absorption spectrometry [5], spectrofluorometry [6] and visible spectrophotometry [1]. However, to determine both chromium species, i.e. chromium (III) and chromium (VI), these technique still require preconcentration or speciation stage. It is very important to differentiate between chromium (III) and chromium (VI), because chromium (VI) is easily reduced to chromium (III).

A sensitive and specific analysis method for detection of chromium metal and can differentiate between chromium (III) and chromium (VI) is required [7]. Voltammetric method is one of analysis method that can be applied for various sample. This method has some advantages, including simple preparation of sample and fast analysis [8]. Sample preparation usually only involve dissolution



without preconcentration and separation of major components, which eventually reduce error source with detection limit up to 0.1  $\mu\text{g/L}$  and relatively inexpensive instruments. Beside of that, voltammetric method enable investigation of chemical species of heavy metal that can be done with other methods. By finding out the chemical species, toxicity of a sample containing heavy metal can also be determined.

Stripping voltammetric for chromium determination is currently developing. This method has advantages compared to other analytical techniques in that it has very low detection limit [9]. Stripping analysis conducted in two steps, which are deposition of analyte onto the electrode surface (preconcentration) and stripping, which is the release of deposit [10].

The material of working electrode influences the performance of voltammetric method. Carbon based electrode utilization is currently growing in electroanalytical field because it has some advantages including wide electrical potential range, low background current, inexpensive, inert and suitable for wide variety of sensors [10]. Therefore, in the present study, we develop a stripping voltammetric method for chromium metal determination using pencil graphite as electrode.

## 2. Materials and methods

### 2.1. Determination of Chromium (III) Solvent

Chromium (III) solution was made from analytical grade chromium chloride ( $\text{CrCl}_3$ ) (Merck,  $\geq 98\%$ ) diluted in three solvents (double distilled water, 0.01 M hydrochloric acid and 0.33M acetate buffer pH 5.0). The solvents were trialed by measuring the current at potential range of -0.8 to +1.0 V with 90 s deposition time, 10 s cleaning time and 20 mV/s scan rate. Solution of 0.33 M acetate buffer pH 5.0 was used as supporting electrolyte. This supporting electrolyte was used throughout all experiments conducted in this study.

### 2.2. Electrodeposition of Chromium (III)

To the voltammetric cell containing 3 mL of supporting electrolyte, 3 mL of 50 ppm chromium (III) was inserted followed by measurement of current generated using Metrohm<sup>®</sup>  $\mu\text{Autolab}$  potentiostat at scanning range from -1.5 to +1.0 V with 90 s deposition time, 10 s cleaning time and scan 20 mV/s rate. The reference electrode, counter electrode and working electrode used in the present study were Ag/AgCl, platinum and pencil graphite, respectively. The working geometric area was 0.314  $\text{cm}^2$ . The detection of chromium (III) was performed in 0.33 M acetate buffer pH 5.0. All potentials given in this work are with respect to the Ag/AgCl sat. reference electrode.

### 2.3. Measurement with Cyclic Voltammetry

To the voltammetric cell containing 3 mL of supporting electrolyte, 3 mL of 50 ppm chromium (III) was inserted, followed by measurement of current generated using Metrohm<sup>®</sup>  $\mu\text{Autolab}$  potentiostat at scanning range from -1.000 to +1.000 V with 90 s deposition time, 10 s cleaning time and 50 mV/s scan rate.

### 2.4. Determination of Optimum Deposition Time and Scan Rate

To the voltammetric cell containing 3 mL of supporting electrolyte, 3 mL of 50 ppm chromium (III) was inserted followed by measurement of current generated using Metrohm<sup>®</sup>  $\mu\text{Autolab}$  potentiostat at scanning range from -1.5 to +1.0 V with 10 s cleaning time and 20 mV/s scan rate. The deposition time was varied at 30, 60, 90, 120 and 180 s at fixed scan rate of 20 mV/s. While for determination of optimum scan rate, the deposition time was fixed at 60 s and the scan rate was varied at 10, 20, 50, and 100 mV/s.

### 2.5. Determination of Linear Concentration Range

Solutions containing 1 to 500 ppm chromium (III) were measured using Metrohm<sup>®</sup>  $\mu\text{Autolab}$  potentiostat at scanning range from -1.5 to +1.0 V with 10 s cleaning time, optimum deposition time and optimum scan rate.

### 2.6. Calibration Curve

Solutions of chromium (III) with concentration of 12.5, 25, 50, 62.5 and 75 ppm was measured using Metrohm<sup>®</sup>  $\mu$ Autolab potentiostat at scanning range from -1.5 to +1.0 V with 10 s cleaning time, at optimum deposition time and optimum scan rate.

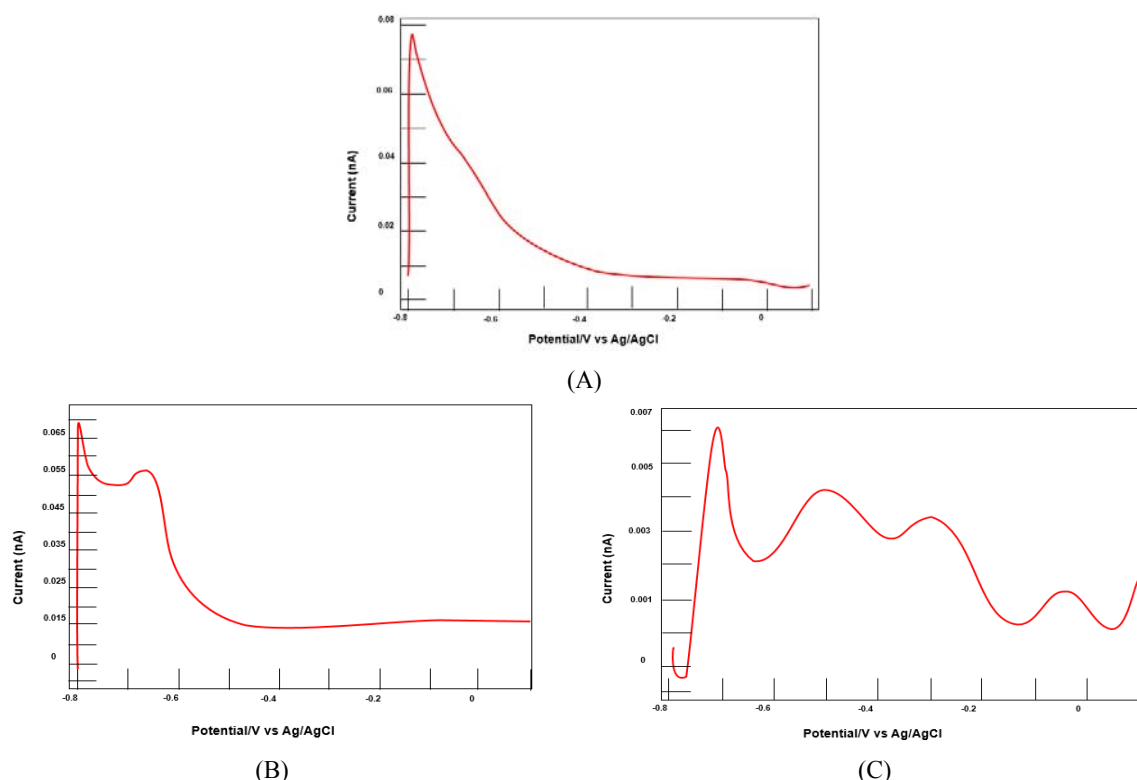
### 2.7. Determination of Measurement Precision

One of standard concentration from chromium (III) standard solution was measured at optimum condition three times and the precision of the measurement was determined.

## 3. Results and discussion

### 3.1. Determination of Chromium (III) solvent

Three solvents were trialed in the present study, i.e. 0.01 M hydrochloric acid, acetate buffer pH 5.0 and double distilled water. The measurement was conducted at potential range of -0.8 to +1.0 V with 90 s deposition time, 10 s cleaning time and 20 mV/s scan rate with anodic stripping voltammetry method. The result of the measurement of the solvents is presented on Figure 1. This trial was conducted to investigate the correction factor of solvent background to avoid the presence of undesired current peaks which come from the solvent background.

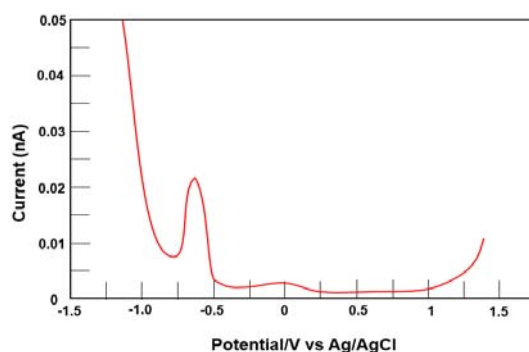


**Figure 1.** Stripping voltammogram of (A) 0.01 M hydrochloric acid; (B) acetate buffer pH 5.0; and (C) double distilled water. Condition of measurement: scan rate: 20 mV/s, deposition potential: -1.260 V vs Ag/AgCl, deposition time 90 s.

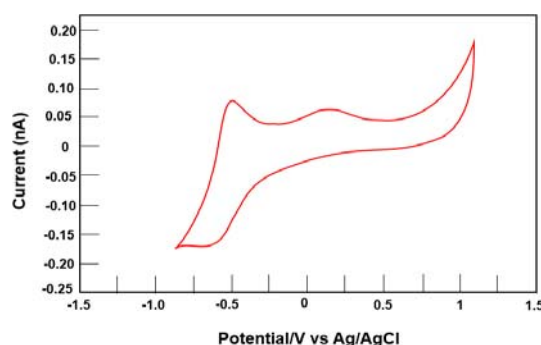
From Figure. 1 it can be observed that no peak detected for 0.01 M hydrochloric acid at potential range -0.8 to +1.0 V. While for acetate buffer pH 5.0 and double distilled water some peaks were observed. Therefore hydrochloric acid was chosen as chromium (III) solvent in the present study. It can be concluded that chromium (III) solution can be made by dissolving chromium (III) chloride in 0.01 M hydrochloric acid pH 2.0 as solvent.

### 3.2. Characteristics of Chromium (III) Solution with Acetate Buffer pH 5.0 as Supporting Electrolyte

Before performing further measurement, electrodeposition experiment was conducted to identify general characteristics of chromium (III) solution with acetate buffer pH 5.0 as supporting electrolyte using anodic stripping voltammetry and cyclic voltammetry measured at potential range of -1.5 to +1.5 V using pencil graphite electrode. The result is presented on Figure 2 and Figure 3.



**Figure 2.** Voltammogram of typical peak of chromium (III) solution using stripping voltammetry. Condition of experiment: concentration of Cr(III) = 50 ppm, scan rate = 20 mV/s, deposition potential 1.260 V vs Ag/AgCl, deposition time= 90 s.

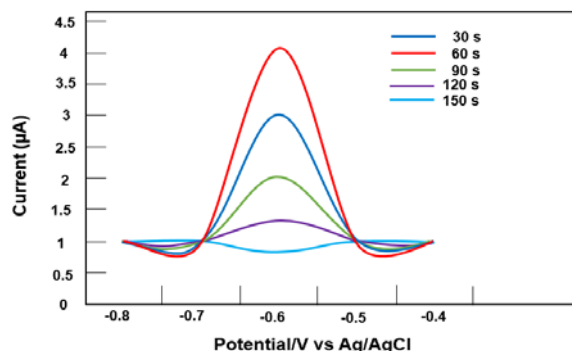


**Figure 3.** Voltammogram of chromium (III) solution using cyclic voltammetry. Experiment condition: concentration of Cr(III) = 50 ppm, scan rate = 20 mV/s, deposition potential 1.260 V vs Ag/AgCl, deposition time= 90 s.

Fig. 2 shows that the peak current was detected at potential value of -0.634 V. This result was supported by cyclic voltammetry result as presented on Fig. 3, which showed cyclic voltammogram at potential of -0.6 V. Measurement of cyclic voltammetry was conducted to gain additional qualitative information regarding electrochemical reaction of chromium (III). From this results it can be proposed that typical peak of chromium (III) that can be measured using pencil graphite electrode is at -0.634 V peak.

### 3.3. Determination of Optimum Deposition Time

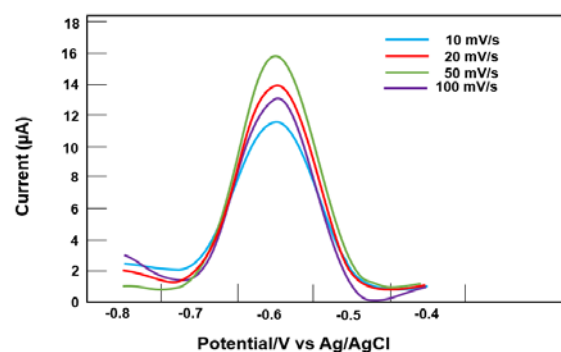
The effect of deposition time can be observed by comparing voltammogram results of chromium (III) solution measurement with varied deposition time. The results are presented on Fig. 4. Optimum deposition time for determination of chromium (III) using pencil graphite electrode is 60 s, as indicated by the highest peak of current detected.



**Figure 4.** Voltammogram of 50 ppm chromium (III) solution with various deposition time for determination of optimum deposition time.

### 3.4. Determination of Optimum Scan Rate Condition

On stripping stage, the height and width of peak current can be affected by scan rate. Therefore in the present study, the optimum scan rate was determined. The effect of scan rate was determined by comparing voltammogram of chromium (III) solution with 60 s deposition time and varied scan rate. The results of the experiment is presented on Fig. 5. The results indicate that scan rate affect the height of current peak of chromium (III). The best scan rate was observed at 50 mV/s, because it gave high curve with relatively narrow peak.



**Figure 5.** Voltammogram of 50 ppm chromium (III) solution with various scan rate for determination of optimum scan rate. Experiment condition: deposition time = 90 s, deposition potential = -1.260 V.

### 3.5. Determination of Linear Concentration Range

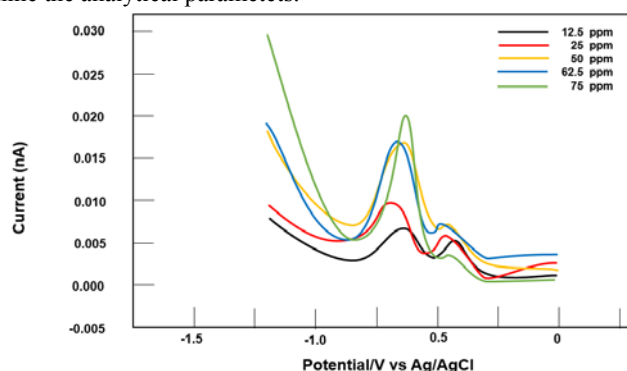
Determination of chromium (III) within 1 to 500 ppm concentration range was performed at potential range of -1.5 to +1.0 V with 60 s deposition time, 10 s cleaning time and 50 mV/s scan rate. The results of measurement is presented on Table 1.

**Table 1.** Determination of chromium (III) in acetate buffer pH 5 with concentration ranging from 1 to 500 ppm.

Concentration (ppm)	Peak Current (µa)
1.0	1.0056
12.5	3.1153
25.0	5.3865
50.0	9.1768
62.5	11.2880
75.0	14.7840
100.0	8.2300

125.0	2.1639
150.0	11.5919
200.0	8.1233
250.0	9.0375
500.0	11.2880

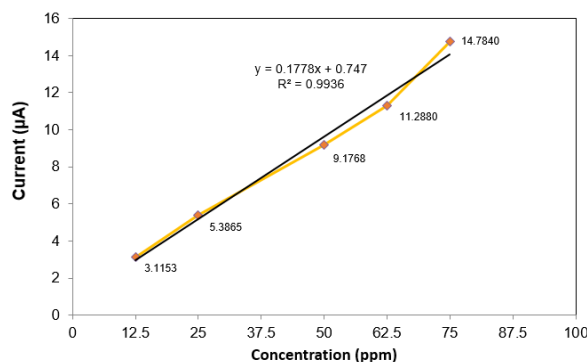
Linear concentration range for chromium (III) determination using pencil graphite electrode was investigated to determine the linear range between height of current peak and concentration of chromium (III). The results of measurement at linear concentration range is presented on Fig. 6, while the data of current peak height against chromium (III) concentration is presented on Table 2. When all data points were used to make calibration curve, the regression coefficient value (R) was very low (0.3860) indicating that it was not linear. We tried to make linear regression using part of the data points. We obtained a good linear regression with five data points, ranging from 12.5 to 75 ppm ( $R = 0.9936$ ). Therefore, we choose the concentration range of chromium (III) from 12.5 to 75 ppm to determine the analytical parameters.



**Figure 6.** Typical peak response of chromium (iii) voltammogram. Experiment condition: solvent= 0.01 m hydrochloric acid, chromium (iii) concentration = 12.5, 25, 50, 62.5 and 75 ppm was performed sequentially with 60 s deposition time, 50 mv/s scan rate and deposition potential at -1.260 v.

**TABLE 2.** Results of measurement of chromium (III) at linear range

Concentration (ppm)	Peak current ( $\mu\text{A}$ )			Average of peak current ( $\mu\text{A}$ )
	1	2	3	
12.5	2.0744	3.5727	3.6988	3.1153
25.0	5.3566	6.3093	4.4936	5.3865
50.0	9.0228	9.8727	8.6350	9.1768
62.5	11.3660	12.5140	9.9840	11.2880
75.0	16.0400	13.5280	-	14.7840



**Figure 7.** Calibration curve of chromium (iii) with 0.01 m hydrochloric acid as solvent, 60 s deposition time, -1.260 v deposition potential, and 50 mv/s scan rate.

Fig. 7 showed the range of concentration that gave linear correlation against peak current height of chromium (III). The range of linear concentration at 12.5 to 75 ppm gave correlation coefficient of 0.9936, which indicate good relationship with correlation equation of  $y = 0.1778x + 0.7470$ .

#### 4. Conclusions

Pencil graphite electrode can be used as a working electrode for determination of chromium (III) with optimum condition achieved at 60 s deposition time and 50 mV/s scan rate. Linear range of chromium (III) measurement with the proposed condition was 12.5 to 75 ppm with 0.31 ppm limit of detection.

#### 5. References

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