Preparation of copper amalgam (CuHg) as working electrode for analysis of selenium

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Abstract. Selenium is an essential trace element for human. Beside the range of concentration, the beneficial and toxic effects of selenium are also depending on which chemical form it takes. In nature or environment and some organisms, selenium is present both in organic and inorganic forms where some studies revealed that inorganic species especially selenite are more toxic than the organics matter. Various methods are used to analyse selenium, but it is usually to determine the total selenium, not designed for field applications, requires several preparation steps prior to actual determination, and needs a lot of chemicals. These problems can be solved by voltammetry methods by using dropping or film mercury as a working electrode. The nature of poisonous mercury becomes a limitation in the use of this working electrode. A copper amalgam (CuHg) as working electrodes was successfully prepared for the analysis of selenium. CuHg working electrode was made in a simple way, namely by deposition of copper (Cu) on the surface of Cu wire with potential and at certain time, then dipped into a solution of saturated mercury salt to form the amalgam. Cyclic voltammetry was used to investigate the electrochemical properties of selenium with 0.1 M HCl as a supporting electrolyte. Cyclic voltammetry technique was conducted on the working potential range of -300 mV (E\textsubscript{i}) to -800 mV (E\textsubscript{f}). Profiles of cyclic voltammogram were influenced by the scan rate applied. In addition, SEM images showed that the adsorption of selenium occurred on the surface of CuHg working electrode.

1. Introduction
Selenium (Se) is an essential trace element for biological system, but it will be as a toxic if it presents excessively. The toxic effects of selenium is strongly depending on its chemical form. In general, inorganic selenium compounds are more toxic than the organic ones [1]. The most common forms of selenium in water are selenite (Se(IV), SeO\textsubscript{3}\textsuperscript{2-}) and selenate (Se(VI), SeO\textsubscript{4}\textsuperscript{2-}). The formation of selenate from selenite is slow, and both forms exist together in solution [2]. Selenite is approximately 10-fold more toxic than selenate [3].

Atomic absorption spectrometry with hydride generation is one of the powerful methods for selenium determination due to its low detection limit. The method is inconvenient and normally not available in several laboratories in Indonesia because it is expensive, not easy for actual measurements, require previous preparation steps, and needs a lot of chemicals.
Electrometric is widely diffused as alternative methods due to the capability for concentration evaluation quantitatively up to the trace levels as well as the instrumentation is relatively cheap. Cyclic voltammetry, one of electrometric methods, is carried out for the initial electro analytical studies for any compound. This method is carried out to characterize the electrochemical processes of the compounds before investigated in depth using other techniques [4]. Analysis of selenium using copper amalgam as working electrode has been investigating previously [5-8]. This paper reports the cyclic voltammetry study of selenite ion using copper amalgam (CuHg) as working electrode.

2. Experiment
2.1. Apparatus
All measurements were performed using an eDAQ potentiostat model EA163 with an e-corder unit connected to a PC, in combination with a three-electrode cell incorporating platinum wire (Nilaco, Japan) as the auxiliary electrode, Ag/AgCl electrode (3 M KCl) as reference, and copper amalgam (CuHg) as working electrode.

2.2. Chemicals and reagents
All chemicals used were of analytical grade. Cu wire was obtained from PT. Freeport Indonesia. Copper sulfate pentahydrate, hydrochloric acid 37%, and mercury nitrate were purchased from E.Merck. Sodium selenite pentahydrate 99% was purchased from Sigma Aldrich, Japan. Ultra-pure water (resistivity 18.2 MΩ cm) was prepared using Milli-Q water systems, Millipore-waters USA at Research Centre for Chemistry, Indonesian Institutes of Sciences.

3. Procedures
3.1. Copper amalgam (CuHg) preparation
Copper amalgam CuHg as working electrode was made by deposition of Cu from CuSO₄ 0.1 M at potential deposition 15 V for 35 s onto Cu wire with diameter 0.4 cm, then immersed in saturated mercury salt. Copper amalgam (CuHg) electrode was sequentially cleaned with ultra-pure water and acetone. It was then dried at room temperature.

3.2. Standard solution preparation
Sodium selenite pentahydrate of ± 0.05 g was diluted with 100 mL of 0.1 M HCl in volumetric flask for selenite standard solution. More dilute standard solution was prepared by weighing and dilution with 0.1 M HCl. These standard solutions were prepared prior to its use.

3.3. Cyclic voltammetry of selenite ion
Cyclic Voltammetry (CV) of selenite ion was studied using 0.1 M HCl media as supporting electrolyte refer to previous literatures [9-11]. The copper amalgam (CuHg) and Ag/AgCl were used as the working and reference electrode, respectively. The general procedure used to obtain cyclic voltammograms was as follows: An amount of 5 mL selenite ion solution 1 mM was placed in a voltammographic cell and scanned from -300 to -800 mV with potential accumulation -450 mV and accumulation time 600 s.

4. Result and discussion
At the copper amalgam (CuHg) electrode, electrodeposition of selenite ion 1 mM was characterized by cathodic and anodic peak potential at ca -700 mV and -600 mV (vs Ag/AgCl), respectively. The cyclic voltammogram is shown in Figure 1A. When the concentration of selenite ion was 50-fold lower than 1 mM, anodic peak could not be found (Figure 1B) which indicates that the selenite ion reduction was not totally reversible but quasi-reversible.
To confirm that the observed peaks were related to the reduction of selenite ion, CV was carried out with different selenite ion concentration. Figure 2 shows that cathodic peak at ca. −700 mV (vs Ag/AgCl) was referred to the reduction peak of selenite ion since Ipc increased with increasing of selenite ion concentration.

The effect of increasing scan rate (from 10 to 200 mV/s) to potential and current peak of reduction selenite ion were observed under the same experiment conditions. As the scan rate of CV was increased, the reduction peak Ipc increased and shifted more negative. Figure 3 shows the CV of selenite ion in 0.1 M HCl recorded at different scan rate. This result indicates that there was a linear relationship between the scan rate (ν) and the peak current with correlation coefficient $r^2 = 0.95745$ as shown in Figure 4A. The linear regression equation is given by: $Ipc (\mu A) = -0.4667\nu - 3.8205$ and $Ipa (\mu A) = 0.1076\nu + 2.2495$. On the other hand, a linear relationship between the square root of the scan rate ($\sqrt{\nu}$) and the peak current with correlation coefficient $r^2 = 0.97039$ as shown in Figure 4B was also observed. The linear regression equation is given by: $Ipc (\mu A) = -9.1337\sqrt{\nu} + 36.7444$ and $Ipa (\mu A) = 2.3001\sqrt{\nu} - 9.4288$. This implies that the mechanism was controlled by a mixture of both adsorption and diffusion.
Figure 3. Cyclic voltammogram of selenite ion 20 µM in 0.1 M HCl recorded at different scan rate.

Figure 4. (A) Plot of the cathodic and anodic peak current of selenite ion 20µM in 0.1 M HCl as a function of scan rate. (B) Plot of the cathodic and anodic peak current of selenite ion 20µM in 0.1 M HCl as a function of the square root of the scan rate.

5. Conclusion
The characteristic electrochemical processes of the selenite ion in 0.1 M HCl on the copper amalgam (CuHg) electrode have been investigated. The reduction process is a quasi-reversible reaction with a characteristic cathodic and anodic peak at ca -700 mV and ca -600 mV (vs Ag/AgCl), respectively. The limiting current is controlled by diffusion and adsorption process.
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