

## ANALYSIS OF ETHANOL USING COPPER AND NICKEL SHEET ELECTRODES BY CYCLIC VOLTAMMETRY

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### Abstract

Analysis of ethanol using copper and nickel sheet electrodes by cyclic voltammetry (CV) method has been carried out. The linear correlations between ethanol concentrations with current density were recorded for both electrodes. The results, of the study showed that the correlation coefficient using Cu electrode was  $r = 0.9957$  and limit of detection of 0.5% (v/v) comparatively, by Ni electrode the correlation coefficient of obtained  $r = 0.9956$  with the same limit of detection with Cu electrode. As a conclusion, it can be made that Cu electrode was a better electrode compared to Ni electrode for analyzing of ethanol using CV method, however it was observed that Cu electrode was easily oxidized by the formation of metal oxide on the electrode surface compared to Ni electrode.

### Abstrak

Satu kajian analisis etanol menggunakan elektrod kepingan kuprum dan nikel menggunakan kaedah voltammetri berkitar (CV) telah dijalankan. Hubungan linear antara kepekatan etanol dengan ketumpatan arus telah direkodkan untuk kedua-dua elektrod. Hasil kajian menunjukkan bahawa pekali korelasi daripada graf tentukan menggunakan elektrod Cu ialah  $r = 0.9957$  dengan had pengesanan 0.5% (v/v) berbanding dengan elektrod Ni dengan pekali korelasi ialah  $r = 0.9956$  dan had pengesanan sama dengan elektrod Cu. Kesimpulannya, elektrod Cu lebih baik berbanding elektrod Ni untuk analisis etanol menggunakan kaedah CV. Walau bagaimanapun, hasil kajian menunjukkan bahawa elektrod Cu lebih mudah mengalami proses pengoksidaan dalam larutan alkali dan membentuk sebatian logam oksida di permukaan elektrod berbanding elektrod Ni.

### Introduction

Alcohols in so many beverages require to be analyzed for the purpose of observation, health and commerce. The most used method for the determination of ethanol in beverages is based on the separation of compound by distillation for further measurement of a physical property such as the specific gravity. Instrumental methods such as liquid chromatography, gas chromatography, mass spectrometry, near and mid-spectroscopy, fluorimetry and colorimetry have also been described [1]. The enzymatic methods using alcohol oxidize or alcohol dehydrogenases have largely been used in the development of biosensors for ethanol determination of the alcohol content in beverages. However, all of them make use of expensive and sophisticated instrumentation or depend on strategies involving derivatisation of the analyte. Furthermore, in process control and routine analysis there is a need for methods that allow determination to be performed with some requirements such as speed, accuracy, high degree of automation and cost-effectiveness [2].

The cyclic voltammetry method was shown to be a good alternative compared to the most popular method, HPLC, because it is simpler, faster, less expensive, does not involve sample preparation techniques, and differences between the results obtained by the two methods are not statistically significant. The alternative method produces smaller amounts of residual solutions compared with HPLC. The total volume per analysis by the voltammetric method is 10 mL given that all standard solutions are prepared in the electrochemical cell, whereas large volumes of mobile phases are needed for HPLC analysis. When comparing both methods for routine analysis, the voltammetric method also has an advantage considering the waste management issue [3].

Cyclic stationary-electrode voltammetry, usually called as cyclic voltammetry (CV) is perhaps the most effective and versatile electroanalytical technique available for the mechanistic study redox systems [4]. It enables the electrode potential to be scanned rapidly in search of redox couples. Once located, a couple can then be characterized from the potentials of peaks on the cyclic voltammogram and from changes caused by variation of the scan rate. CV is often the first experiment performed in an electrochemical study [4]. Cyclic voltammetry can be used for quantitative analysis because cyclic voltammograms are convenient for the identification of short lived intermediates, and for the elucidation of the kinetics of electrode processes. For analytical purposes, one can measure the peak height, which is proportional to concentration, and use the peak potential as a qualitative indicator of the nature of the species [5].

Some researchers have used the cyclic voltammetry method for the purpose of analysis. Toledo has been the electroanalytical investigation of dopamine using cyclic voltammetry (CV) and the graphite-polyurethane composite electrode [6]. Artificial neural networks have been utilized in the electrochemical oxidation and determination of isoniazid (INH). It is desirable to have an unmodified electrode to oxidize INH at neutral pH with high efficiency. The requirement of electrode modification or electrochemical pretreatment steps should also be avoided in order to allow the frequent and repeated use of the electrode. The electrocatalytic oxidation of ionized INH by ferrocenyl methyl trimethyl ammonium at the platinum electrode in 0.10M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was studied by cyclic voltammetry (CV) [7].

An alternative analytical method, using a glassy carbon electrode, has previously been proposed and applied successfully to the quantification of molinate in phytopharmaceuticals. The working concentration range was about 10<sup>-4</sup> mol/L, for lower concentrations the voltammogram peak was not well defined and for higher concentrations strong adsorption on the electrode surface was observed, meaning that frequent cleaning of the electrode surface was necessary. This is an important drawback of voltammetry on solid electrodes. The electrochemical method developed was used to assess the decrease of molinate concentration in culture supernatant along a biodegradation process using mixed culture DC. On the basis of the electrochemical behavior of molinate at Hanging Mercury Dropping Electrode (HMDE), with potential detection of -0.320 V vs AgCl/Ag, an alternative method was developed for quantification of molinate in biological samples [3].

The purpose of this paper is to present and discuss results on the development of a new method for analysis of ethanol using cyclic voltammetry using Cu and Ni electrodes. The electrochemical behaviors and stability of both metals in alkaline solution also will be discussed.

## Experimental

### Solutions

All solutions were prepared by dissolving their analytical grade reagent (Merck) in deionised distilled water. KOH was used as the supporting electrolyte. Nitrogen was used to deaerate the solutions and to keep an inert atmosphere over the reaction solution during the oxidation process. Ethanol solutions were prepared by dilution of absolute ethanol (BDH laboratory supplies) with deionised distilled water. The calibration curve was made by using ethanol concentrations of 1, 2, 3, 4 and 5% (v/v).

### Preparation of nickel and copper electrodes

Cu and Ni metal sheets (99.98% purity, 0.5 mm thick, Aldrich Chemical Company) were used to prepare Cu and Ni electrodes. The metal sheet electrodes were prepared in square cut of 1 cm by length and wide respectively. The metal sheet electrodes were connected to silver wire with silver conducting paint prior to being covered with epoxy gum.

### Electrochemical behavior of the electrodes

Universal Pulse Dynamic EIS, Voltammetry, Voltalab potentiostat (Model PGZ 402) was used for electrochemical behavior measurements; data acquisition was accomplished using the Voltmaster 4 software. Cyclic voltammetry experiments were performed in a three electrode system using Ni or Cu metal sheet as a working electrode (anode), an Ag/AgCl (saturated KCl) or SCE as reference electrode and platinum wire as the counter electrode. All potentials given are with respect to the SCE reference electrode.

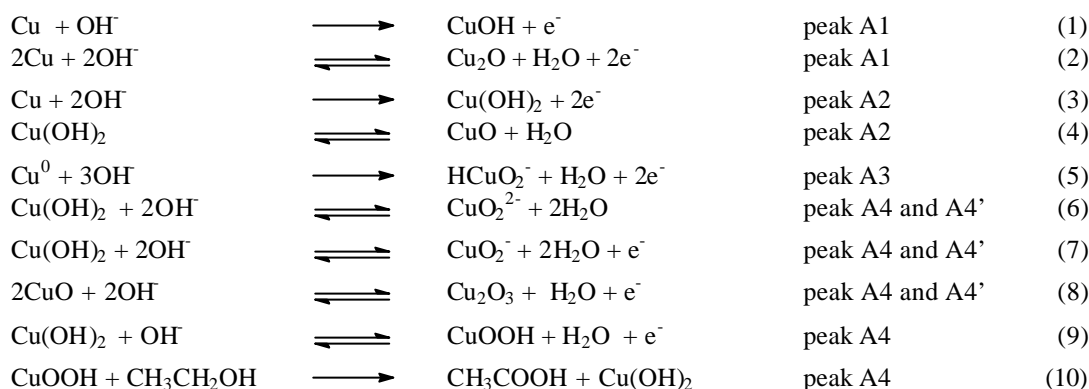
### Experimental procedure

The electrochemical process of ethanol was performed in a solution of KOH at room temperature. The electrochemical studies by cyclic voltammetry (CV) were performed in 25 mL capacity glass electrochemical cell.

### Results and discussion

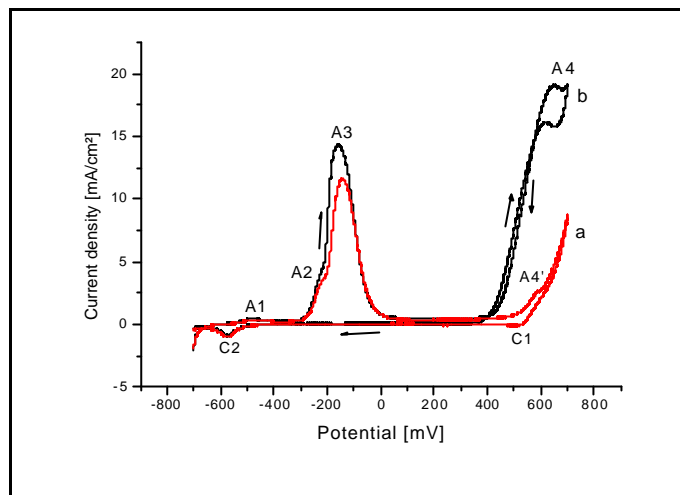
#### The cyclic voltammetry of copper and nickel electrodes

Figure 1(a) shows the cyclic voltammogram of 0.8 M KOH with the sweep potential from potential -700 up to +700 mV, and then return from +700 mV up to -700 mV. Figure 1 (b) shows the cyclic voltammogram of 0.25 M ethanol in 0.8 M KOH. The A1, A2, A3 and A4 peaks represent the anodic peaks. These peaks related to the oxidation of Cu (0) to Cu (I), Cu (I) to Cu (II) and Cu (II) to Cu (III). The oxidation reaction that occurred at A1, A2, A3 and A4 peaks (Figure 1) were represent as follows:



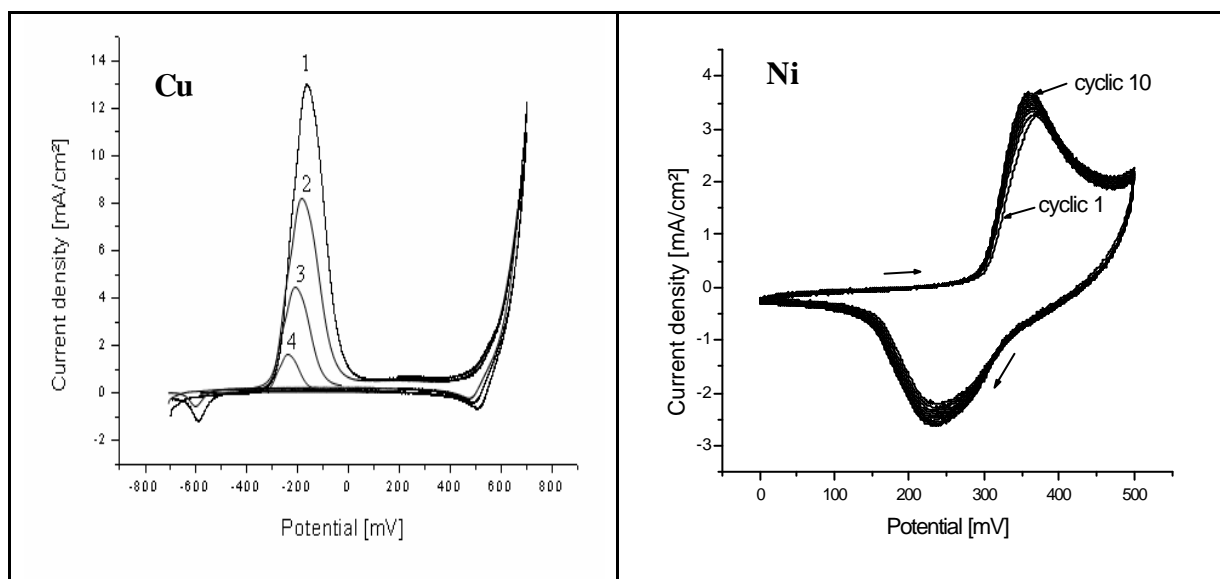
The A4 peak at Figure 1 shows the oxidization peak of ethanol, when added ethanol (Figure1 (a)) increasing current density at A4 peak was observed. The C1 peak in shows the reduction process of Cu (III) to Cu (II) whiles the C2 peak shown the reduction of Cu (II) to Cu (I). The C3 peak represents the reduction process of Cu (I) to Cu (0) [8-10].

At about 0.65 V the formation of a soluble Cu (III) species was took place. By adding 2% (v/v) of ethanol (Figure 1), an irreversible process was seen in the region corresponding to the electrochemical formation of Cu (III) species. Clearly, copper exhibits an unusual electrochemical behavior with regard to the oxidation of ethanol at low potentials [11]. Therefore the formation of Cu (III) species at  $E > 0.6$  V may have a similar role in the electrocatalytic process. The cyclic voltammogram at Figure 1 shows that the maximum oxidation current of ethanol took place at 650 mV. Cu metal is easily oxidized to form oxide compounds in the alkaline medium, which would formed oxide coating on the surface of the electrode,  $\text{Cu}_2\text{O}$ ,  $\text{CuO}$ , and  $\text{Cu}(\text{OH})_2$ , besides the other species depending on the potential, pH of the solution, the mass-transport conditions, ageing and surface restructuring processes [1].



**Figure 1:** Cyclic voltammograms for Cu solid electrode in (a) 1.0 M KOH and (b) 1.0 M KOH + 1% (v/v) ethanol Anodic sweep from  $-700$  mV to  $+700$  mV (vs. SCE). Scan rate  $10 \text{ mVs}^{-1}$

Figure 2 indicates that Cu electrode was relatively unstable compared to Ni electrode in alkaline solution especially at higher concentration, but Cu electrode has a good reactivity in alkaline solution. Reactivity and stability of electrode were very important in the electrochemical oxidation process. Therefore for the purpose of electroanalytical technique, the electrode used should be free from the deposition of oxide or oxyhydroxide compounds on its surface.



**Figure 2:** Cyclic voltammograms of Cu and Ni solid electrodes in 1.0 M KOH. Anodic sweep from  $-700$  mV to  $+700$  mV vs. SCE (for Cu) and 0 to 500 mV vs. SCE (for Ni). Scan rate  $15 \text{ mVs}^{-1}$  and 4 cycles for Cu and  $10 \text{ mVs}^{-1}$  and 10 cycles for Ni

The effect of ethanol concentration may cause the increase of current density and shift ethanol oxidation potential peak (A4 peaks in Figure 3) up to more positive potential. The effects of ethanol concentration do not increase the peak height (current density) for the A2 and A3 peaks. The linear relationship between the analytical signal (current density) and the ethanol concentration were observed at anodic potential 700-750 mV (A4 peaks Figure 3).

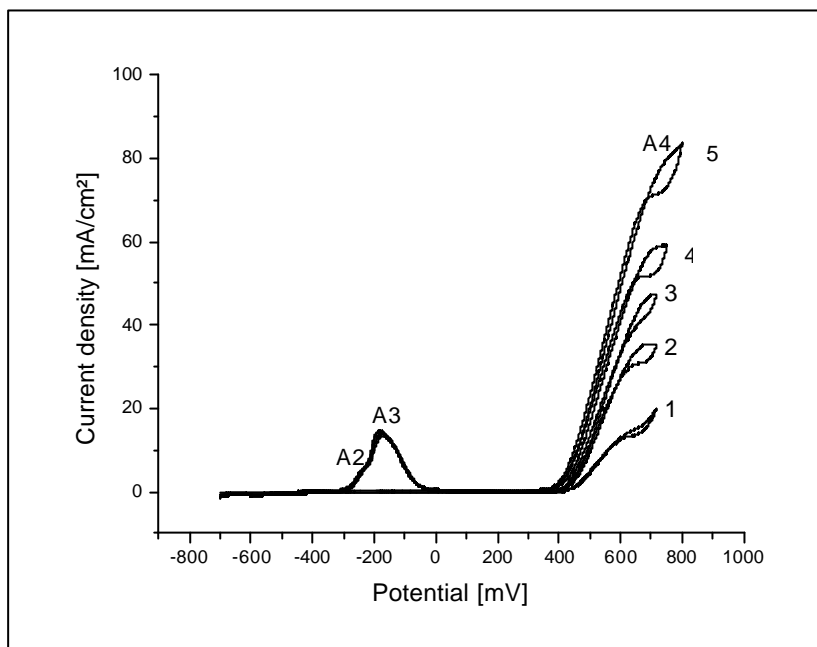
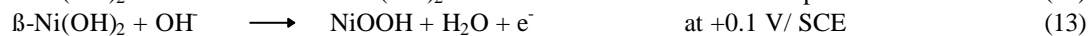
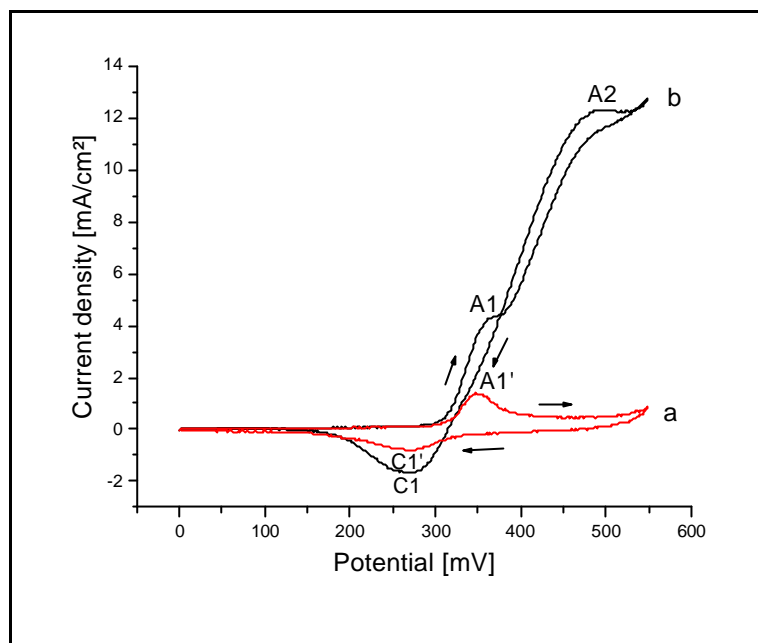


Figure 3: Cyclic voltammograms for Cu solid electrode in (1) 1% (2) 2% (3) 3% (4) 4% and (5) 5% (v/v) ethanol + 1.0 M KOH. Anodic sweep from  $-700$  mV to  $+700$  mV (vs. SCE). Scan rate  $10 \text{ mVs}^{-1}$

The oxidation peak for the oxidation of Ni (II) to Ni (III), which is due to the changes from  $\text{Ni(OH)}_2$  to  $\text{NiOOH}$ , was represented by A1 peak (anodic peak) in Figure 4 (a and b). Oxidation of Ni (0) to Ni (II) which occurred at more negative potential or hydroxide region was not shown in this cyclic voltammogram. Based on the cyclic voltammetry, the reaction mechanism for the oxidation processes occurred on the Ni based electrode surface were as follows:





**Figure 4:** Cyclic voltammograms for Ni solid electrode in (a) 1.0 M KOH and (b) 4% (v/v) ethanol + 1.0 M KOH. Anodic sweep from 0 mV to +550 mV (vs. SCE). Scan rate 10 mVs<sup>-1</sup>

Oxidation of Ni (0) or Ni metal to Ni (II) in the form of  $\alpha\text{Ni}(\text{OH})_2$  was always occurred in the negative potential (-0.8 V up to -1.5 V) as already suggested by many researches [12-18]. While at potential -0.8 V up to +0.3 V, represent the changing process of  $\alpha\text{Ni}(\text{OH})_2$  to  $\beta\text{Ni}(\text{OH})_2$ , where a  $\text{Ni}(\text{OH})_2$  was easily change to  $\beta\text{Ni}(\text{OH})_2$ . A1 peak represents the oxidation process of  $\beta\text{Ni}(\text{OH})_2$  to NiOOH.

C1 (cathodic peak) in Figure 4(a and b) represents two forms of crystallographic from oxyhydroxide  $\alpha$  and  $\beta$  [12]. Nickel oxyhydroxide (NiOOH) is capable to oxidize a number of functional groups, for example primary alcohols may be oxidized to carboxylic acids. Nickel has been reported to be a good electrode for the oxidation of various organic compounds [12]. A redox couple of nickel, i.e., nickel hydroxide ( $\text{Ni}(\text{OH})_2$ ) and nickel oxyhydroxide (NiOOH) were shown to be involved in the oxidation of alcohol at nickel electrode in alkaline media. Nickel oxyhydroxide (NiOOH) involved in the reaction that will oxidized ethanol to acetaldehyde and further oxidized to acetic acid. Most of acetaldehyde was oxidized to acetic acid because its oxidation rate is faster than ethanol. The reaction of organic compounds with the nickel oxides of higher valences is usually the rate of determination step.

Nickel is known to have an oxidation state of Ni (0), Ni (II), Ni (III) and Ni (IV). With ethanol in the reaction mixture, at +300 mV and below, the oxidation of ethanol is sustained by the involvement of adsorbed hydroxyl group (from KOH) on the electrode surface, while at higher potentials region (+300 mV to +500 mV) the electrooxidation process is attributed to the formation of NiOOH species (Figure 4b). However, without ethanol, the adsorption of hydroxyl group (from KOH) and the formation of NiOOH on the electrode surface occurred at higher potential (Figure 4a). Adsorption of ethanol on the electrode surface will occurred immediately after the formation of NiOOH completed. Both C1 and C1' peaks are the cathodic peaks which represent the  $\beta\text{NiOOH}$  and  $\alpha\text{NiOOH}$ , respectively.

Figure 4a shows the cyclic voltammogram using the nickel electrode in KOH (without ethanol). When 0.25 M ethanol was added (Figure 4b), a new peak was observed (A2), which represents the electrochemical oxidation of ethanol peak ( $E_p$  anodic). Cyclic voltammogram of the electrochemical oxidation of ethanol was found to be a irreversible process. The cyclic voltammogram obtained in Figure 2 shows that Ni electrode is very stabile in alkaline solution.

Figure 5 shows the effect of ethanol concentration to current density. Figure 5 shows the peak current density increased with increasing of ethanol concentration. While the A1 peak was not affected by the ethanol concentration. Figure 5 shows that linear correlations between the analytical signal (current density) and the ethanol concentration at potential  $\pm 475$  mV.

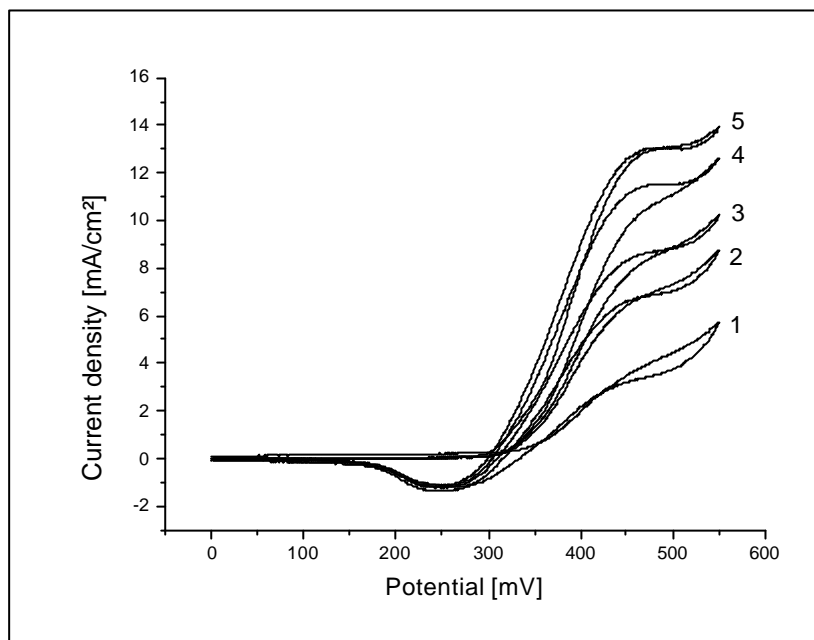


Figure 5: Cyclic voltammograms for Ni solid electrode in: (1) 1% (2) 2% (3) 3% (4) 4% and (5) 5% (v/v) ethanol + 1.0 M KOH. Sweep scan from 0 mV to 550 mV (vs.SCE). Scan rate  $10 \text{ mVs}^{-1}$

#### Calibration curve for ethanol using Cu and Ni electrodes

Figure 6 shows the calibration curve for the concentration of ethanol with current density for both Cu and Ni electrodes. From the calibration curve obtained using both Cu and Ni electrodes, the correlation coefficient ( $r$ ) recorded were 0.9957 and 0.9956, respectively. For the purpose of analysis, the slope and limit of detection were also determined, where the sensitivity of the technique is correctly defined as the slope of the calibration curve [19]. The slope for the calibration curve using both Cu and Ni electrodes were 15.165 and 2.1727, respectively (Table 1). From this single parameter, it could be concluded that Cu electrode was more sensitive compared to Ni electrode for the analysis of ethanol using CV method. Limit of detection for both electrodes were approximately about 0.5% (v/v).

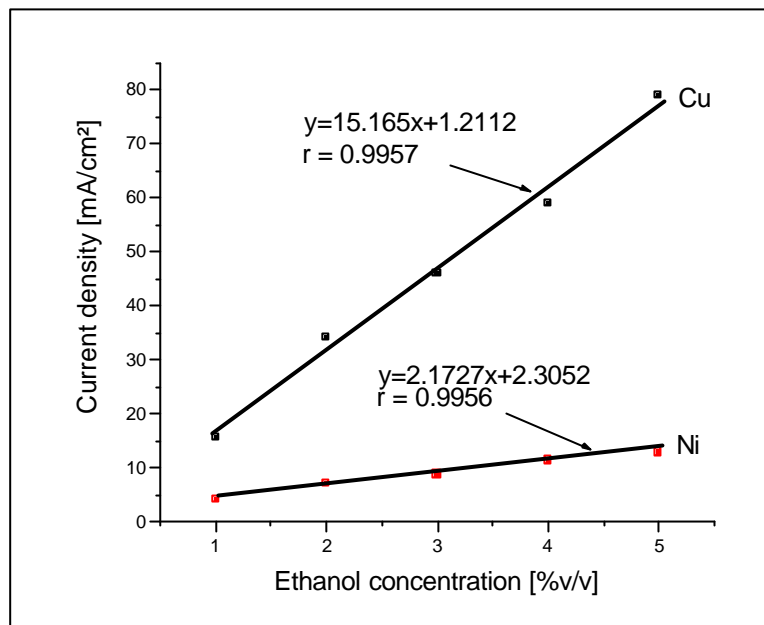


Figure 6. Calibration curve plot for the data in Figure 3 and 5 using Cu and Ni electrodes

Table 1. Analytical parameters of ethanol using cyclic voltammetry method

Parameters	Cu electrode	Ni electrode
Peak potential ( $E_p$ anodic)	0.7-0.8 V	0.450-0.475 V
Equation regression linear	$y = 15.165x + 1.2112$	$y = 2.1727x + 2.3052$
Slope	15.165	2.1727
Intercept	1.2112	2.3052
Correlation coefficient (r)	0.9957	0.9956
Coefficient of determination ( $R^2$ )	0.9915	0.9913
Limit of detection	0.5% (v/v)	0.5% (v/v)

### Conclusions

Cu and Ni electrodes were found to be a good working electrode (anode) for the analysis of ethanol using CV method. Based on the calibration curve obtained (current density vs. concentration), Cu electrode was found to be more sensitive compared to the Ni electrode, however, Cu electrode was unstable in alkaline solution by the formation of oxide compounds on the electrode surface. Thus, it must be clean for every determination, while the same treatment was not required for Ni electrode. This method was found to be suitable for the determination of ethanol in beverages sample.

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