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Development of the Potentiometric Method for Measurement of Cu

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Abstract

Potentiometry is one of method on measuring metals based on cell potential. Measurements using potentiometry are divided into comparative cells and concentration cells. Concentration cells is measurements of a cell's potential by using two solutions with different concentrations. The aim of this study was to develop a concentration cell potentiometric method equipped with applications so measurements is easier and faster. The added application able to calculate the results of experiments so that the calculation process becomes faster and easier. Validation results give the results of the R the value of 0.9990; LoD $7.6484x10^{-7}$, LoQ $6.2103x10^{-7}$, RSD 0.64%, and recovery 98.05%. This optimum measurement was carried out at 30 °C and pH 5. The results of Cu measurements in well water obtained the result of 0.9633 ppm. Measurements using the development of this method, get good validation results and can be used on measurements similar to those in the aquatic environment.

Keywords: Potentiometry, cell concentration, Copper (Cu), validation, aquatic environment

Abstrak (Indonesian)

Potensiometri adalah salah satu metode pengukuran logam berdasarkan potensi sel. Pengukuran menggunakan potensiometri dibagi menjadi sel pembanding dan sel konsentrasi. Sel konsentrasi adalah pengukuran potensial sel dengan menggunakan dua larutan yang sama dengan konsentrasi yang berbeda. Tujuan dari penelitian ini adalah untuk mengembangkan metode potensiometri sel konsentrasi dengan penambahan aplikasi sehingga pengukuran menjadi mudah dan cepat. Aplikasi yang ditambahkan adalah aplikasi yang dapat menghitung hasil eksperimen, sehingga proses perhitungan menjadi lebih cepat dan mudah. Hasil validasi memberikan hasil nilai R 0,9990; LoD $7,6484x10^{-7}$, LoQ $6,2103x10^{-7}$, RSD 0,64%, dan recovery 98,05%. Pengukuran ini optimum dilakukan pada suhu 30 °C dan pH 5. Hasil pengukuran Cu pada air sumur diperoleh hasil 0,9633 ppm. Pengukuran menggunakan pengembangan metode ini mendapatkan hasil validasi baik dan dapat digunakan pada pengukuran sejenis dengan pada lingkungan perairan.

Kata kunci: Potensiometri, sel konsentrasi, Tembaga (Cu), validasi, lingkungan perairan

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INTRODUCTION

One method that often used in measuring heavy metals in the environment is a potentiometer. The potentiometer is a chemical analysis by measuring the potential of electrochemical cells. Measurements can be made with concentration cells or comparison cells. Concentration cells consist of two half cells that have the same solution, but different concentrations (concentrated and runny). Both solutions are connected with salt bridges containing electrolyte solutions. Metal electrodes inserted into each solution were measured using a potential measuring device [1].

In concentration cells, Le Chatelier's principle applies where reduction increases with increasing metal concentration. So that reduction occurs in more concentrated solutions and oxidation occurs in dilute solutions [2]. A more concentrated solution functions as a cathode and a more aqueous solution functions as an anode so that there is an electron flow from the aqueous solution to the concentrated solution until equilibrium is achieved [3]. Furthermore, changes in electric current are measured using a voltmeter, then the measurement results were calculated using the Nerst equation

The method has advantages such as equipment is easy to use, inexpensive, adequate selectivity, low detection limit, good accuracy, and able to measure colored solutions [4]. In addition, the potentiometer can measure ion species such as Fe^{2+}, Fe^{3+}, Cu^{2+}, and others. Previous research on cell potentiometric concentrations included the determination of heavy metal Cu in leachate samples [5], determination of blood glucose [6], and manufacture of potentiometric hydrogen sensors [7].

The measurement results are potentially cell. This result is calculated using the Nerst equation. This calculation requires a relatively long time. By use the additional application, it can solve the problem. Additional applications can shorten the measurement time. Additional applications are embedded in the laptop. And then the application will be accessed via Android. This application contains standard measurement results, calibration curve graphs, and sample measurement results.

Method development must be validated to find out whether the method meets valid criteria. The validation parameters to be carried out are linearity, sensitivity, loD (a limit detection), loQ (a limit qualification), accuracy and precision. This study will approve the validation of cell methods with additional applications to find out validation criteria. In addition, this method can also be used in various conditions of pH and temperature for the best assessment of measurement results that can be produced.

MATERIALS AND METHODS

Materials

A set of glassware, Cu electrodes, multimeters, and a salt bridge is prepared. Then the material is prepared, namely 0.1M KCl, 0.1M $CuSO.5H_2O$, demineralized water, and agar powder.

Methods

The devices were made series by connecting two and a half cells supported by salt as shown on Figure 1. Figure 1 shows the concentration cell series for Cu. Two half-cell series containing concentrated and aqueous solutions connect to the salt bridge. Then the electrodes were inserted into each solution and connected to a multi-meter. The data that was read, then inputs into the application.

The standard solution of CuSO4.5H2O was made with concentrations of 10^{-1} M, 5.10^{-1} M, 10^{-2} M, 5.10^{-2}M, 10^{-3}M, 5.10^{-3}M, 10^{-4}M, 2.10^{-4}M, 2.10^{-4}M, 5.10^{-4}M, 10^{-5}M, 5.10^{-5}M and 10^{-6}M. Salt bridge is prepared to make 0.5M KCl and then add that 2g and boil and pour it into the pipe U.

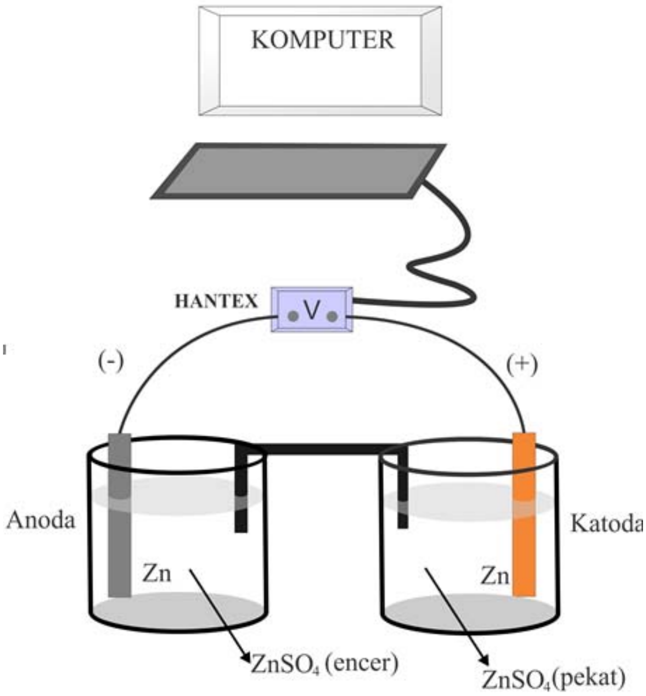

Figure 1. The circuit concentration cell

Data Analysis

Nerst Equation:

$$E= E°- \frac{RT}{nF} \times \ln \frac{[red]}{[oks]} \quad ....(1)$$

E = half cell potential
E° = standar electrode potential
n = mol
F = Faraday (96.500 Coulomb) [8]

LoD and LoQ Instrumen

$$LoD = y_B + 3\ SD \quad ....(2)$$

$$LoQ = y_B + 10\ SD \quad ....(3)$$

LoD and LoQ Method

$$LoD = \frac{3\ SD}{Slope} \quad ....(4)$$

$$LoD = \frac{3\ SD}{Slope} \quad ....(5)$$

Sd = Standard deviation [17]

Accuracy values are indicated by recovery values

$$\%\ Recovery = \frac{[sampel+spike]-[sampel]}{[spike]} x100\% \quad ....(6)$$

Precision is expressed by relative standar deviation (RSD)

$$\%RSD = \frac{SD}{\bar{x}} x\ 100\% \quad ....(7)$$

SD : standar deviation
RSD : relative standar deviation
x : concentration
$\bar{x}$: average consentration
n : samples [12]

RESULTS AND DISCUSSION

The development of analytical method must be tested for validation against standard known, therefore the Potentiometric methods with concentration cells must also be validated first. The validation parameters performed are linearity, LoD and LoQ, accuracy, and precision. Linearity is obtained by making a calibration curve on the standard. As a first step, a standard Cu measurement is performed to make a calibration curve. From the standard Cu measurements made, a calibration curve was obtained as shown in Figure 2.

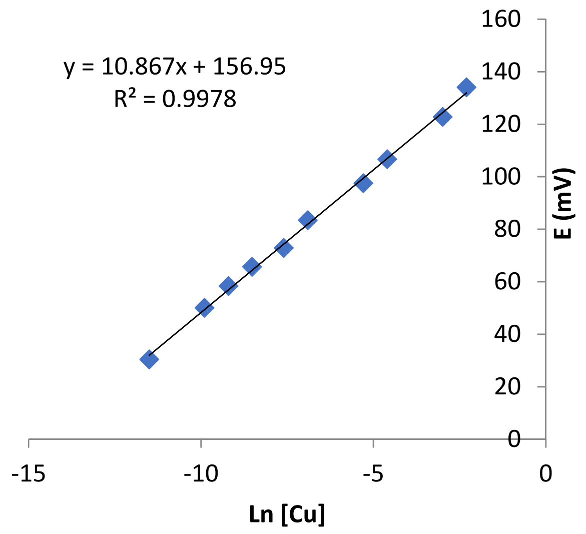

Figure 2. The standard of Cu Calibration Curve

Calibration curve was made with a standard concentration of 10^{-1}M, 5.10^{-1}M, 10^{-2}M, 5.10^{-2}M, 10^{-3}M, 5.10^{-3}, 10^{-4}M, 2.10^{-4}M, 5.10^{-4}M, 10^{-5}M, 5.10^{-5}M and the comparative solution 10^{-6}M. The curve is based on the Nerst equation so that the x axis is the cell potential and the y axis is Ln the concentration of Cu. The results obtained are slope (b) = 10.86 and intercepts (a) = 156.9 so that the regression line equation is obtained by = 10.86x + 156.9 with a coefficient of correlation (R) = 0.997. The correlation coefficient value obtained from the Cu standard curve match linearity requirements.

Limit of detection (LoD) is the lowest concentration of analyte from a sample that can be detected [8]. The quantification limit (LoQ) is the lowest concentration of analyte that can be determined [9]. LoD and LoQ are distinguished by the detection limits of instruments and methods. For instruments obtained LoD 6.1817×10^{-7} mol/L and LoQ 7.6142×10^{-7} Mol/L. For the method obtained LoD results 2.547 Mol /L and LoQ 34.516 Mol/L. This result is better than previous research. Validation of the development of cell potentiometric methods concentration in leachate measurements carried out previously LoD 1.217×10^{-6} and LoQ 1.560×10^{-6} [5].

The precision test was carried out with repeatability parameters to determine the measurement results [8]. Repeatability is a type of accuracy of measurements made repeatedly on the same conditions, methods, materials, operators and laboratories in a short time [9]. Good precision values must meet the relative standard deviation value (RSD) $\leq$ 2% [11]. The RSD value of this method is 0.3% so that it meets the requirements of good accuracy.

The value of accuracy is the suitability of the results of analysis and true value [10]. Accuracy values are indicated by recovery values. Accuracy values can be accepted if the recovery value is between 80 - 120% [12]. The method used to determine accreditation is the spike method. From the measurement and calculation, the recovery value of 98% means that this method meets the requirements.

Additional applications used in this study are web-based applications. Web-based applications are one type of application that can be accessed via the internet and intranet. This web application uses browser technology for access and portable networks [13]. This application runs on localhost with the help of XAMPP in Windows. XAMPP is a software for developing websites with PHP programming and can be used as a local server for making MySQL databases [14]. PHP is a programming language to create a web so that it is dynamic [15]. Apache is the producer of web pages according to what the user wants. MySQL stands for Structured Query Language is an application for managing databases [16]. XAMPP used is XAMPP for Windows version 7.3.1 with PHP version 7.3.1.

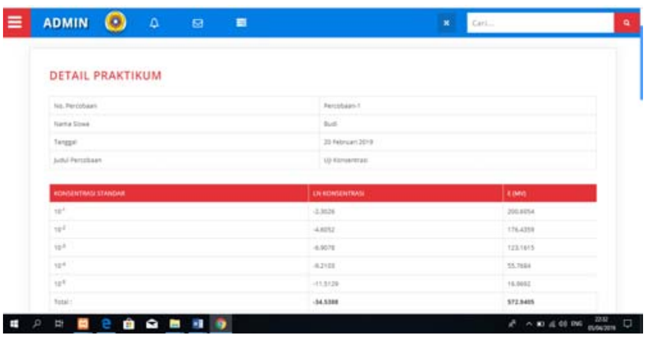

Figure 3. Input data from experimental results on the application

Figure 3 shows the standard Cu measurement data that was entry in the application. With this application the standard measurement data was produced to produce a standard calibration curve. After obtaining a calibration curve to the next step is to enter the sample measurement data. Then the concentration of Cu in the sample used will be read. Sample measurement display can be seen in figure 4.

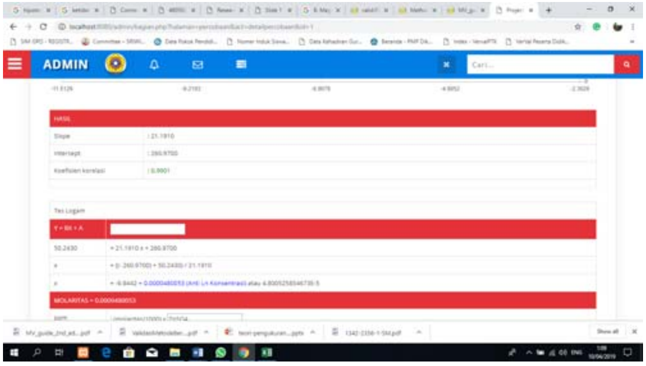

Figure 4. Results of sample measurements in the application

The picture above shows the results of the sample concentration. The sample concentration was calculated based on linear regression equations.

CONCLUTION

Development of a potentiometer method with concentration cells provides good validation test criteria. The application used in this measurement can shorten the measurement time. Measurement of Cu metal in liquid samples is easier.

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