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Development of Concentration Cell Potentiometric Method for Fe^{2+} and Fe^{3+} Speciation

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Abstract

The speciation of Fe^{2+} and Fe^{3+} iron ions using the concentration cell potentiometric method has been developed. The determination and speciation of metals that have been used include potentiometry using comparison electrodes, selective ion electrodes, and voltammetry. The concentration cell potentiometric method has the advantages of simple equipment, the use of common metal electrodes, high selectivity, and relatively low detection limits. The method validation results for Fe^{2+} and Fe^{3+} ion speciation was LOD: Fe^{2+} 0.22 mg/L and Fe^{3+} 0.29, LOQ: Fe^{2+} 0.92 mg/L and Fe^{3+} 0.01 mg/L; precision (1.17%; 1.2%) and accuracy (95.57%; 93.15%) based on CV Horwtz. This method has been well applied for Fe^{2+} and Fe^{3+} speciation in natural water samples. The concentrations of Fe^{2+} and Fe^{3+} species in Sekanak river water were (1.88 mg/L; 2.07 mg/L). Concentration of Fe^{2+} and Fe^{3+} species in well water samples (0.5 mg/L; 1.32 mg/L).

Keywords: Potentiometric method, Speciation of Fe, Validation

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Spesiasi ion besi Fe^{2+} dan Fe^{3+} menggunakan metode potensiometri sel konsentrasi telah dikembangkan. Penentuan dan spesiasi logam yang selama ini digunakan antara lain potensiometri menggunakan elektroda pembanding, elektroda ion selektif, dan voltametri. Metode potensiometri sel konsentrasi memiliki kelebihan antara lain rangkaian alat sederhana, penggunaan elektroda logam biasa, selektitivitas tinggi, dan limit deteksi yang reltif rendah. Hasil validasi metode untuk spesiasi ion Fe^{2+} dan Fe^{3+} berturut-turut LOD: Fe^{2+} 0,22 mg/L dan Fe^{3+} 0,29, LOQ: Fe^{2+} 0,92 mg/L dan Fe^{3+} 0,01 mg/L, presisi (1,17%; 1,2%) dan akurasi (95,57%; 93,15%) berdasarkan CV Horwtz. Metode ini telah diterapkan dengan baik untuk spesiasi Fe^{2+} dan Fe^{3+} pada sampel air natural. Konsentrasi spesies Fe^{2+} dan Fe^{3+} pada air sungai sekanak (1,88 mg/L; 2,07 mg/L). Konsentrasi spesies Fe^{2+} dan Fe^{3+} pada sampel air sumur (0,5 mg/L; 1,32 mg/L).

Kata Kunci: Metode potensiometri, Spesiasi Fe, Validasi

INTRODUCTION

Potentiometric method is a potential measurement analysis method that can be used to determine the concentration of metal ions in the sample. This method is an easy analysis method and has good accuracy and precision [1]. The potentiometric method can be done in two ways, namely with concentration cells and comparison cells. The potentiometric method with concentration cells uses two solutions that are the same but of different concentrations where the more concentrated solution serves as the cathode and the more dilute solution serves as the anode. In this study, the potentiometric method was carried out by means of concentration cells. This potentiometric analysis is an electrochemical analysis based on the relationship between the amount of analyte and the measured cell potential, as formulated by Nernst [2]. The

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potentiometric cell circuit includes a voltmeter that functions to measure the cell potential which will then be calculated using the Nernst equation.

This potentiometric tool can be used to analyze heavy metal levels. Analysis of heavy metal levels can be done by measuring total metal levels and metal ion levels, to measure metal ion levels by speciation. Speciation analysis is an analysis performed to identify and measure the amount of one or more individual chemical species in a sample [3]. The speciation analysis that can be used is the cell concentration potentiometric method, which is based on ion activity or sample concentration in different variations [4]. The measurement results obtained from the potentiometric method are potential values, which correlate with electrochemical materials. Electrochemical cells are a series of devices that involve electric current as a result of redox chemical reactions [5]. Electrochemical cells are divided into two namely Voltaic cells (Galvani cells) and electrolysis cells. Potential values obtained from measurements with the potentiometric method are converted to concentration values to determine the concentration of Fe metal ion speciation in water samples.

Potensiometry using an analog voltmeter produces unstable data and long calculation times [6], so it is necessary to develop a potentiometric tool that is able to work quickly and accurately using a digital multimeter. The purpose of this research is to validate the concentration cell potentiometric method on Fe^{2+} and Fe^{3+} speciation. Furthermore, applying the method to determine Fe^{2+} and Fe^{3+} species in Sekanak river water and well water.

MATERIALS AND METHODS

Materials

A set of Glassware, multimeter, laptop, analytical balance, U-pipe for salt bridge, Iron Metal (Fe) electrode, KCl, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, demineralized water, agar, well water, and river water.

Methods

The tools used in this research are glassware, Hantek 365F multimeter, Windows 10 computer, PHP (Hypertext Preprocessor) and C programming language. The materials used are Pb metal electrode, KCl salt bridge, demineralized water, Pb acetate standard solution 10^{-6} M, and sample water.

The concentration cell potentiometry device is assembled by connecting two half cells through two glass beakers and connected by a voltmeter as shown in **Figure** 1.

The picture above shows a potentiometric circuit of a concentration cell type voltaic cell. In this circuit, the solutions at the anode and cathode are the same but of different concentrations. The solutions at the anode and cathode are connected by a salt bridge. The electrodes inserted into each glass beaker are connected by a cable that is directly connected to the multimeter. The multimeter that has been connected to a computer/laptop will display the potential (mV) and be inputted into an IoT-based web page that will process the data into concentration automatically. Standard solutions were made with concentrations as shown in the **Table** 1.

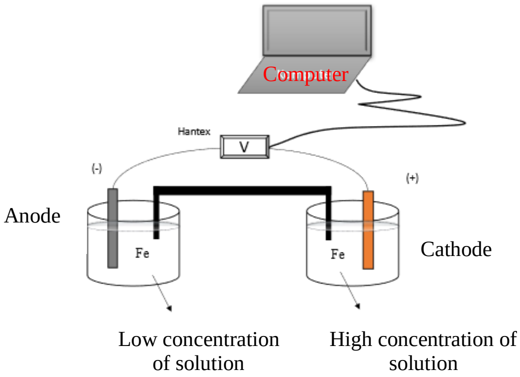


Figure 1. Potentiometric Device

Table 1. Concentrations of Standard Solution

Number	Concentration (M)
1	1×10^{-1}
2	5×10^{-2}
3	1×10^{-2}
4	5×10^{-3}
5	1×10^{-3}
6	5×10^{-4}
7	2×10^{-4}
8	1×10^{-4}
9	5×10^{-5}
10	1×10^{-5}

The salt bridge is made from KCl and agar powder that is brought to a boil and poured into a U-pipe.

Analysis of Data

- Nernst Formula

$$E = E^{o}{}_{sel} - \frac{RT}{nF} \text{ x } \ln \frac{C_{red}}{C_{oks}} \qquad (1)$$

- Accuracy

$$\%RSD = \frac{[sampel+spike]-[sampel]}{[spike]} \; x \; 100\% \qquad (2)$$

- Precision

$$CV\ (\%) = 2^{1\ -\ 0,5\ \log C} \qquad (3)$$

- Linearity

  $y = ax + b$ (4)

- LoD and LoQ Instrument

  $LoD = yB + 3SD$ (5)

  $LoQ = yB + 10SD$ (6)

- LoD and LoQ Method

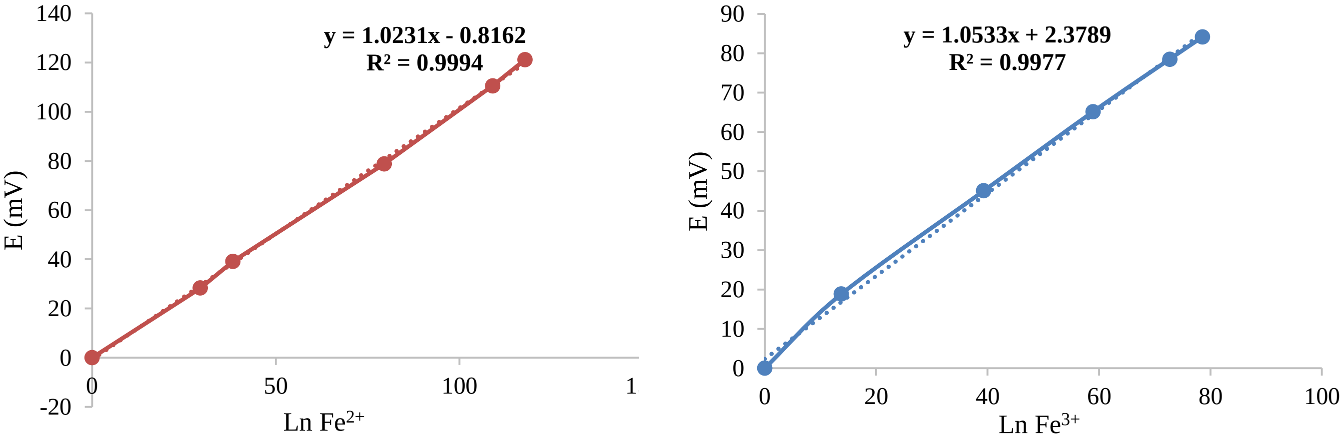
  $LoD = \frac{3SD}{slope}$ (7)

  $LoQ = \frac{10\ SD}{slope}$ (8)

Where:
E = cell potential
E° = standard electrode potential
n = mol
C = concentration (mol/L)
F = Faraday constant (96,500 C)
K = Temperature (K)
RSD = relative standard deviation
SD = standard deviation
R = 8.314 J / mol
n = sample ions

RESULTS AND DISCUSSION

This study was tested to validate against known standards. The validation parameters in this study are linearity, LoD and LoQ, accuracy, and precision. Linearity assessment is done by linear regression which combines regression model, outlier rejection, and assumption evaluation with significance test [7]. Linearity in this study was obtained by determining the calibration curve in the standard solution so that the equation y=ax+b was obtained. From the measurement of Fe with Fe^{2+} and Fe^{3+} speciation in the standard solution that has been carried out, a calibration curve is obtained as shown in **Figure** 2 (a) and (b).



(a) (b)

Figure 2. Calibration curve of (a) Fe^{2+} standard solution and (b) Fe^{3+} standard solution

In the $FeSO_4{\cdot}7H_2O$ standard solution to measure the Fe^{2+} speciation potential, the calibration curve above was obtained, with the results of slope (b) = 1.0231, and intercept (a) = -0.8162 so that the regression equation y = 1.0231x - 0.8162 and correlation coefficient (R) = 0.9994 which meets the linearity requirement.

In the $FeCl_3{\cdot}6H_2O$ standard solution to measure the Fe^{3+} speciation potential, the calibration curve above was obtained, with the results of slope (b) = 1.0533, and intercept (a) = 2.3789 so that the regression equation y = 1.0533x + 2.3789 and correlation coefficient (R) = 0.9977 which meets the linearity requirements.

The next parameters are LoD and LoQ. Limit of detection (LoD) is a parameter for the smallest limit test that a tool or instrument has to measure a certain amount of analyte [8]. Limit of quantification (LoQ) is the lowest concentration of analyte that can be determined [9]. LoD and LoQ were analyzed by method and instrument formulas. By method in $FeSO_4{\cdot}7H_2O$ standard solution, the LoD value of 0.22 mg/L and LoQ of 0.92 mg/L were obtained. While in the instrument, the LoD value is 0.29 mg/L and LoQ is 0.77 mg/L. In $FeCl_3{\cdot}6H_2O$ solution, LoD and LoQ values of 0.008 mg/L and 0.01 mg/L were obtained (method). Instrumentally obtained by 0.009 mg/L and 0.02 mg/L. Based on the Fe quality standard in the lowest water is 0.3 mg/L [10]. This shows that this potentiometric tool can measure metals below the quality standard. Next is precision which shows how close the difference in value is when repeating measurements [11]. This precision parameter was obtained at 1.17% in $FeCl_3{\cdot}6H_2O$ solution and 1.2% in

$FeSO_4 \cdot 7H_2O$. Based on the criteria if less than 2% then the precision is good [12]. Accuracy can be defined as the degree of closeness between the predicted value and the actual value [13]. To determine the accuracy can be by calculating the percentage of recovery [14]. The accuracy value is acceptable if the recovery result is between 80-120% [15]. From the measurement and calculation results, the percentage recovery on $FeSO_4 \cdot 7H_2O$ is 95.57 and 93.15% on $FeCl_3 \cdot 6H_2O$ which shows the data is accepted

After the validation results show good criteria according to the established standards. Furthermore, Fe^{2+} and Fe^{3+} measurements were carried out on water samples. The samples in this study were Sekanak river water and well water. **Table** 2 below is the measurement results of Fe^{2+} and Fe^{3+} metal ion levels obtained.

Table 2. Measurement results of Fe^{2+} and Fe^{3+} levels in the sample

Number	Sample	Concentration of sample (mg/L)	
		Fe^{2+}	Fe^{3+}
1	Sekanak river water	1.88	2.07
2	Well water	0.5	1.32

Quality standards according to Government Regulation of the Republic of Indonesia Number 22 of 2021 concerning the Implementation of Environmental Protection and Management National Water Quality Standards can be a reference to draw conclusions from the measurement of metal levels in waters. According to the applicable regulations, the quality standard for Fe metal in river water is 0.3 mg/L and in well water is 1 mg/L [8].

CONCLUSION

The development of potentiometric method for Fe^{2+} and Fe^{3+} speciation measurement showed good validation test according to the criteria based on the parameters and can be used to determine Fe^{2+} and Fe^{3+} species in Sekanak river water and well water.

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