Development of potensiometry method for Zn analysis

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Abstract. In this research, focus for analysis Zn ion using a concentration cell potentiometry method with a Hantexmultimeter. Concentration cells are electrochemical cell circuits where the same type of solution is used but different concentrations, the more concentrated solution being the more dilute cathode and solution to the anode. So that the flow of electrons from the dilutes solution to concentrated occurs until equilibrium is reached. The multimeter connected with computer to display data processing so the analysis be easier. This method has high accuracy 98.20% and precision 0.45%.This potentiometry method can be used as an alternative method of Zn analysis.

1. Introduction

Potentiometry is one instrument to measure cell potential by using a series of devices without using electricity or changing the composition of substances [1]. The series of tools used in the potentiometry method are electrochemical cells. Electrochemical cells are a set of devices consisting of two electrodes in two solutions. The two solutions connected by a salt bridge and measured by their potential with a voltmeter device [2]. Concentration cells are measurements of concentration cell potential using two similar but different concentrations of solution one of solution is more concentrated into a more dilute cathode and solution to anode so that electrons flow from dilute solutions to concentrated until equilibrium is reached [3].

Potentiometry methods can be used in the analysis of heavy metal ions in the environment. The advantages of equipment potentiometry methods are easy to assemble, relatively low-cost, adequate selectivity, low detection limit, high accuracy, low concentration range and can be used in colored solutions [4]. Potentiometry can measure more specific ions (such as Fe³⁺, Fe²⁺, Cu²⁺, Zn²⁺ ions, etc.) so that they can be used to measure the speciation of metal ions in the environment. Research has been done using potentiometry, among others the use of ion selective electrodes can determine the activity and concentration of different ions [5-7], determination of heavy metals mercury and determination of cadmium in river water [8,9].

Potensiometry using an analog voltmeter produces unstable data and long calculation times. This problem is the development of potentiometry methods using concentration cells with 365F hantex digital multimeters. In this study will develop potentiometry methods using multimeters and interfaces so that measurement data can be directly observed from a laptop. The development of this potentiometry method can be used in metal measurements. Beside that development of this methods must be validated to find out whether the method meets valid criteria.Validation parameters are linearity, sensitivity, LoD (Limit of Detection), LoQ (Limit of Qualification), accuracy and precision. Development of potentiometry methods using concentration cells will be tested for validation to determine the validation criteria.
2. Research Methods

2.1. Tools and Materials
The tools used in this study are a set of glassware, a set of potentiometric tools, sample bottles, 365F type Hantek multimeters, Zn electrodes. The ingredients used are potassium chloride (KCl), zinc sulfate (ZnSO₄), demineralized water.

2.2. Work Procedures

2.2.1. Cell Circuits
A salt bridge is prepared where the U pipe is filled with a solution of 0.5 M KCl and jelly, then the two ends of the pipe are clogged with cotton. Prepared 2 cups of 50 mL beaker glass, the first glass is placed 50 mL of Zn metal solution as standard with the known concentration and the second has 50 mL of comparative solution with a lower concentration. Then the two beaker are connected to a salt bridge and a Hantex multimeter. Zn electrodes are inserted into both beaker glass.

![Diagram of cell circuits with Hantex](image)

**Figure 1.** Cell series of concentration with Hantex

2.2.2. Validation of Potentiometric Methods

a. Linearity and Sensitivity Determination
The Zn standard solution which has been prepared with a concentration of 1.10⁻¹M, 1.10⁻²M, 1.10⁻³M, 1.10⁻⁴M, and 1.10⁻⁵M is measured by its potential with potentiometric methods. Calibration curve is made by connecting the graph between E (mV) and ln Zn concentration.

b. Determination of LoD and LoQ
LoD is determined by measuring the potential of Zn metal standard solution with a concentration of 1.10⁻¹M, 1.10⁻²M, 1.10⁻³M, 1.10⁻⁴M, and 1.10⁻⁵M. Then made a calibration curve from the results of the potentiometry obtained at various metal concentrations and calculated using the LoD = yB + 3 SB equation. For LoQ, it is determined by measuring potential blanks using existing cell circuits as many as 10 repetitions then the results are calculated using the LoQ = yB + 10 SB equation.

c. Accuracy
Accuracy measurement using potential spikes. Standard solutions Zn with concentrations of 1.10⁻¹M, 1.10⁻²M, and 1.10⁻⁴M each were taken 10mL and then put into a 100mL measuring flask and 90 mL of well water samples were added to the boundary markers. Then the potential solution was measured using a series of cells and calculated using the equation.

\[
\% \text{ Recovery} = \frac{[\text{sample} + \text{spike}]}{[\text{spike}]} \times 100\%
\]
d. Precision

Precise measurement is done by measuring the potential of the Zn 10^{-4} M standard solution with a series of cells 10 times repetition at the same time and condition. Then the calculation is done using the equation

$$SD = \sqrt{\frac{\sum(x-x)^2}{n-1}}$$

and

$$\%RSD = \frac{SD}{\bar{x}} \times 100\%.$$  \hspace{1cm} (2)

2.2.3. Measurement of metal Zn using potentiometry

Prepared as much as 50 mL of bore well water was put into a 100mL beaker. Prepared a comparison solution of metal Zn with a concentration of 10^{-6} M as much as 50 mL was put into a 100 mL beaker. Then it is measured by a series of cells that have been prepared to determine the concentration of metals contained in the wellbore water. Calculation results obtained from the nerst equation.

3. Results and Discussion

Figure 1 shows the calibration curves created in the 10^{-1} M to 10^{-5} M concentration range with a comparison concentration of 10^{-6}. The results obtained show the value of $R^2 = 0.9974$ and the regression equation $y = 20.191x + 248.59$

![Figure 2. Calibration curve of Zn standard solution](image)

The calculation results for LoD and LoQ instruments obtained LoD results of 4,681.10^{-7} ppm while for LoQ obtained a value of 3,464.10^{-7} ppm. The calculation results for the LoD result method obtained are 4,596.10^{-7} ppm and LoQ is 3,304.10^{-7} ppm. The accuracy value obtained is 98.20% for the concentration of 1.10^{-5} M. The value of accuracy is the suitability of the results of the analysis and the real value [10]. Recovery value is acceptable if the accuracy value is between 80-120% [11]. This indicates that this method has accuracy according to the provisions.

Precision is the proximity of measurement values that are carried out repeatedly for the same object. Precision functions to see the accuracy of a method. The precision value obtained for cell potentiometry method of concentration with Hantex is 0.45%. This result is obtained from the Relative Standard Deviation value (RSD). Judging from the precision value this method has good accuracy because it has an RSD below 2%.
Figure 3. Effect of temperature on cell potential

Figure 3 shows the effect of temperature on cell potential, where the cell potential is optimal at 30°C. Low temperatures will cause small solubility so that the resulting cell potential is not stable. High temperatures cause kinetic energy and ion movement to increase, resulting in higher cell potential [12].

Figure 4. Effect of pH on cell potential

The optimum pH for Zn measurements using potentiometric cells using Hantex concentration is 5. At pH below 5 there is an excess of H\(^+\) ions and affects the ion transfer rate. Ion H\(^+\) will interfere with the process of transfer of charge to the cathode and anode because positive ions in hydrogen will take part in capturing negative ions, thus disrupting the measurement process. At pH above 5 there is an excess of OH\(^-\) ions and metal precipitation occurs to Zn(OH)\(_2\), this interferes with the measurement process. The results of measurements of well water samples obtained results 4.815.10\(^{-5}\) M or 3.129.10\(^{-6}\) ppm.

4. Conclusion
The concentration cell potentiometry method with the Hantexmultimeter used in this study provides good results for Zn metal measurements. The best conditions for measurement are 30°C and pH 5. This method works to find Zn metal in water.

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