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Development of Chloride Electrode Coated Wire and Composite Systems for Determination Chloride Ion in Gunungkidul Spring Water

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Abstact: The purpose of this research was to find out effectiveness of chloride solid membrane electrode of coated wire system compared to solid membrane electrode of composite system, the Nernstian response and character's potential response (detection limit, selectivity and response time). The Chloride ISEs (Chloride Ion selective electrodes) in this research were the solid membrane chloride ISEs based AgCl. There were 2 types of chloride ISEs that develop, they were the chloride ISEs of coated wire and composite systems. Both types of electrodes were characterized. The selectivity was done by comparing Esel of the chloride standard solutions and Esel of the interference ions (Br^- and I^-). The measurement of chloride ions in water samples was done by using the coated wire chloride ISE, the composite chloride ISE and the Mohr method. The result of the two chloride ISE methods, we compared to that of standard method for chloride determination (Mohr) by using F-Test and Post Hoc Test (LSD and Duncan). Analysis by using F-Test and Post Hoc Test (LSD and Duncan) and Characterization results of both the methods showed that, coated wire chloride ISE was more effective compared to composite chloride ISE. Nernstian response at 59,83 mV/dekade, linier range measurement at 10^{-1}-10^{-5} M, limit detection 1.23×10^{-5} M, response time along 25 s and interfering ion of 10^{-4} M Br^-.

Key words: The chloride ISEs, coated wire electrode, composit electrode, Gunungkidul spring water.

1. Introduction

There have been some developed methods of measuring chloride ion concentration using ion selective electrodes. This method took attention of some scientists, because the method was very selective in responding to certain ions in the analyte. The basic concept of chloride ion electrode is a equilibrium between silver chloride salt in surface electrode and chloride ion in solution. The equilibrium will change when the chloride ion concentration in solution is changed. So, the diffusion of chloride ion can result in potential energy, which can be measured with potentiometer.

One kind of ISEs (ion selective electrodes) is membrane electrodes that respond analyte ions selectively [1]. The parameters of ion selective electrode method are characterised as detection limit, response time, selectivity, Nernstian factor and linear range response. In practice, detection limit on the order of 10^{-5}-10^{-6} M is measured for most of ion selective electrodes. Response time is the first instant at which the potential of the cell becomes equal to its steady-state value within 1 (mV) or has reached 90% of the final value [2]. The selectivity of an ISE (ion-selective electrode) depends on the stoichiometry of the complexes between its ionophore and the target and interfering ions [3]. Generally, an ISE follows the Nernstian factor equation 0.0591/n Volts/decade [4]. The linear range of the electrode for many electrodes, this range can extend from 1 Mol down to 10^{-6} or even 10^{-7} Mol. [5].

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Ion selective electrode based on the type of membrane electrode classified 5 types of glasses, solid membrane electrode, the electrode based on ion exchange and carrier neutral, gas electrode and the enzyme electrode. There are 3 kinds of solid membrane electrode: solid solution in the system, dense array system (composite) and plated metal systems. This type of system is similar to the type of metal-coated solid composition [6].

The solid membrane is one of the highly selective membrane in response to ions in the sample [7]. Ion selective electrode based on composite solid membrane (graphite, ionophores and solvents) has been developed they are for the determination of cesium ions, bromide, iron, and iodide [8-11].

This research used a solid membrane electrode Ag/AgCl coated wire and composite systems. The principle of this study is comparation of the two types of electrodes (ISE chloride coated wire and composite systems) with the standard method of chloride ions determination (Mohr method).

Comparison of the results of measurements was analyzed by F-test, a Post Hoc Test (LSD and Duncan). The purpose of this research was to find out effectiveness of chloride solid membrane electrode of coated wire system compared to solid membrane electrode of composite system, the Nernstian response and character's potential response (detection limit, selectivity and response time) and the results of comparative measurements of both ESI chloride.

2. Experiments

2.1 Material

Some chemicalin (AgCl, KCl, KI, KBr, HCl and paraffin) for the research is purchasing from E-Merck and Sigma. Graphite powder is from Research Center, Department of Forestry, Jakarta.

2.2 Instrumentation

Instruments used in the research were one set of potentiometer (Orion 710), one set of electrolysis tool, pH meter, and some glassware.

2.3 Procedure

2.3.1 Electrode Preparation

Coated wire chloride ISE was based on coating of AgCl salt on wire silver (Ag) using the electrolysis process. While composite system chloride ISE is based on a mixture membrane of 60% AgCl powder, 20% graphite and 20% solid paraffin and then coated on surface of silver wire electrode [12].

2.3.2 Potential Measurement

Potential cell of system that contain chloride ion was measured by potentiometer. The cell configuration used for potentiometric measurement was the type of:

Ag/AgCl/KCl (sat):3MKCl∷sample solution ‖ membrane ‖ Ag

EMF measurements were carried out with a silver/silver ORION (chloride electrode) coupled with an ORION pH/Ion-meter 710A. The concentrations of chloride ion in the sample solutions were varied from 10^{-1} to 10^{-8} M in stirred solutions. The EMF values were recorded when the reading on ion-meter became stable.

2.3.3 Electrode Characterization

Chloride ISEs were characterized by the calibration curve to determine the detection limit, linear range measurement and Nernstian factor. Response time and the selectivity of interference ions (Br^- and I^-) were also measured [13].

2.4 Analysis Methods

The concentration of chloride ions in the sample solution was measured by the working electrode (coated wire and composite chloride ISE) and a reference electrode Ag/AgCl. The measurement results were compared to the results of the measurement Mohr method by using F-test, Post Hoc Test (LSD and Duncan) with SPSS 16 for windows.

3. Results and Discussion

3.1 Potential Cell and Linier Range Response

The potential response as function of chloride concentration was measured by potentiometric method. As the Nernst equation, potential response was equivalent to the ion analyt concentration. The relation between potential cell and concentration of chloride ion were depicted in graph E_{sel} vs log [Cl⁻] (Figs. 1 and 2).

Fig. 1 shows that, the linear curve coated wire chloride ISE occurred at a concentration of 10^{-1} M-10^{-5} M. While Fig. 2 shows that, the linear curve composite chloride ISE occured at concentrations of 10^{-1} M-10^{-4} M. Two electrodes resulted in similar graph, so, they have similar function.

3.2 Nernstian Factor

Graphic of Nernstian E_{sel} vs log [Cl⁻] for coated wire and composite chloride ISE are showed at Figs. 3 and 4.

Fig. 3 shows that, a Nernstian response of coated wire chloride ISE is 59.83 mV/decade. This slope follows the formula 0.0591/n, so that, the ISE has Nernstian respon. Fig. 4 shows slope of the composite chloride ISE is 51.14 mV/decade. This slope is in the sub-Nernstian because under 0.0550/n.
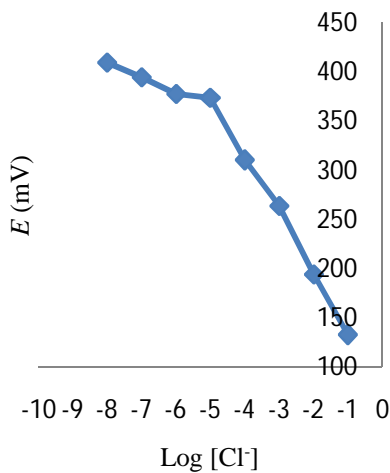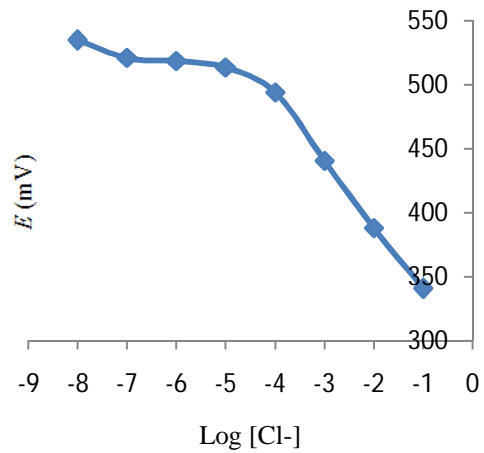

Fig. 2   Graph of E_{sel} vs log [Cl⁻] with composite chloride ISE.

Fig. 3   Graphic of Nernstian E_{sel} vs log [Cl⁻] for coated wire chloride ISE.

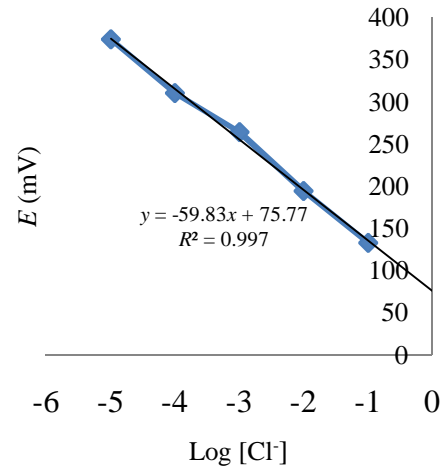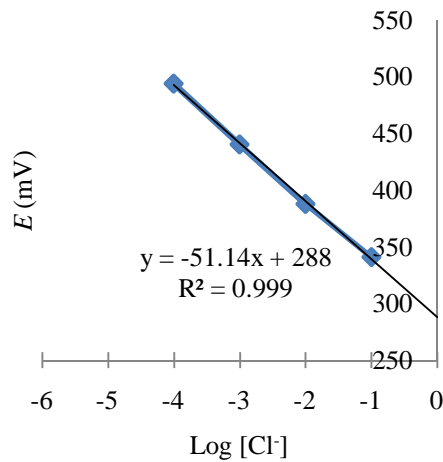**Fig. 1   Graph of E_{sel} vs log [Cl⁻] with coated wire chloride ISE.**

Fig. 4   Graph of Nernstian E_{sel} vs log [Cl⁻] for composite chloride ISE.

3.3 Detection Limit

Determination of the detection limit is obtained from the extrapolation of the graph E_{sel} vs. log [Cl$^-$]. Horizontal regression equation y_A and regression Nernstian equation y_B, with $y_A = y_B$, the detection limits was obtained. Lower detection limit of coated wire chloride ISE was at a concentration of 1.23×10^{-5} M and composite chloride ISE was at a concentration of 5.13×10^{-5} M.

3.4 Response Time

Coated wire chloride ISE has a response time of 25 s. Composite chloride ISE has a response time of 38 s.

3.5 Interference Ions Selectivity

Interference Ions selectivity was calculated by using Nikolsky-Eisenman equation on a separate solution system:

$$\log K_{A,B}^{pot} = \frac{(E_B - E_A)}{2{,}303\, RT/Z_A F} + \left(1 - \frac{Z_A}{Z_B}\right) \log a_A \quad (1)$$

The results of the calculation of I$^-$ and Br$^-$ selectivity coefficients of coated wire chloride ISE were shown at Tables 1 and 2 for composite chloride ISE.

3.6 Determination of Cl$^-$ Ions Concentration in Gunungkidul Ground Water by Chloride ISE

Concentrations of the samples were calculated using the regression equation Nernstian, where y is E_{sel} of sample and x is the log concentration of the sample. The results of the calculation with the measurement of coated wire chloride ISE are presented in Table 3 and composites chloride ISE in Table 4.

Table 1 I$^-$ and Br$^-$ selectivity coefficients of coated wire chloride ISE.

C (M)	$K_{A,B}^{pot}$ I$^-$	$K_{A,B}^{pot}$ Br$^-$
10^{-1}	1.09×10^{-6}	3.05×10^{-3}
10^{-2}	1.03×10^{-6}	3.19×10^{-3}
10^{-3}	1.75×10^{-6}	6.72×10^{-3}
10^{-4}	2.09×10^{-3}	0.36×10^{-3}
10^{-5}	2.33×10^{-3}	3.09×10^{-3}

Tabel 2 I$^-$ and Br$^-$ selectivity coefficients of composite chloride ISE.

C ion (M)	$K_{A,B}^{pot}$ I$^-$	$K_{A,B}^{pot}$ I$^-$
10^{-1}	3.21×10^{-3}	0.19
10^{-2}	1.53×10^{-3}	0.16
10^{-3}	4.63×10^{-4}	0.13
10^{-4}	6.10×10^{-4}	0.67

Table 3 [Cl$^-$] in sample with coated wire chloride ISE.

Spring water	C_{Cl^-} (M)	C_{Cl^-} (ppm)
Jebul	6.03×10^{-4}	21.41
Mudal	6.80×10^{-4}	24.14
Beji	5.35×10^{-4}	18.99

Table 4 [Cl$^-$] in sample with composite chloride ISE.

Spring water	C_{Cl^-} (M)	C_{Cl^-} (ppm)
Jebul	5.25×10^{-4}	18.64
Mudal	4.17×10^{-4}	14.80
Beji	2.75×10^{-4}	9.76

3.7 Measurement of Chloride Ions Contents with Mohr Method

Contents of chloride ions were calculated by Eq. (2):

$$[\text{Cl}^-] \ (\text{mg/L}) = \frac{(A-B) \times N \times 35.450}{V} \quad (2)$$

The results of research were shown at Table 5.

3.8 Comparation of Method

Third measurement results were compared using F-test (Table 6) and LSD (Table 7).

Statistical value of F calculation > F table, that F calculation = 21,596 and F Table ($F_{(2, 6, 0.05)}$) = 5.14, then H_0 is rejected, thus, further test Post Hoc Test (should be done LSD test) (Table 7). F test showed that were deferences among the methods. LSD analysis results showed the method 1 did not differ significantly from method 3, while the second method differs significantly from method 3.

Table 5 Date of Mohr Titration Results.

Spring water	AgNO$_3$ (V)	Content of Cl$^-$ (ppm)
Jebul	8.03	22.49
Mudal	8.17	23.19
Beji	6.90	16.84
Blanko	3.53	-

Table 6 F-test analysis.

ANOVA (ppm_Cl)	Sum of squares	Df	Mean square	F	Sig.
Between groups	111.719	2	55.860	21.596	.002
Within groups	15.519	6	2.587		
Total	127.238	8			

[*]The mean difference is significant at the 0.05 level.

Tabel 7 Results of LSD analysis.

Multiple comparisons							
Dependent variable (ppm_Cl)						Confidence interval 95%	
	Metode (I)	Metode (J)	Mean difference (I-J)	Std. error	Sig.	Lower bound	Upper bound
LSD	1	2	6.387[*]	1.31	0.003	3.17	9.599
		3	-1.833	1.31	0.212	-5.04	1.379
	2	1	-6.387[*]	1.31	0.003	-9.59	-3.174
		3	-8.220[*]	1.31	0.001	-11.4	-5.007
	3	1	1.833	1.31	0.212	-1.38	5.047
		2	8.220[*]	1.31	0.001	5.01	11.433

Description: Method 1 (coated wire chloride ISE method), Method 2 (chloride composite ISE method) and Method 3 (Mohr method).

4. Conclusions

Nernstian response, detection limit and response time for coated wire chloride ISE were 59.83 mV/decade in the measurement range of 10^{-1}-10^{-5} M, 1.23×10^{-5} M and 25 s, the interference just caused Br^- ion 10^{-4} M. while for composite chloride ISE was 51.14 mV/decade in the measurement range 10^{-1}-10^{-4} M, 5.13×10^{-5} M and 38 s, interference caused by Br^- ion. Analysis of F-test, Post Hoc Test (LSD and Duncan) showed that, coated wire chloride ISE better than composites chloride ISE.

Acknowledgements

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