

The Coated-Wire Ion Selective Electrode (CWISE) of Chromate Using PVC-Membrane Based on Chitosan as A Carrier

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ABSTRACT

A coated-wire ion selective electrode (CWISE) based on chitosan as a carrier for detection of chromate, was developed. CWISE has easy measurement for field analysis, good selectivity and sensitivity. The CWISE's membrane consist of mixture an active material of chitosan, aliquat 336-chromate, polyvinylchloride (PVC) and dioctylphthalate (DOP) as plasticizer = 4:0.5:35:60.5 (% w/w) dissolved in tetrahydrofuran (THF) solvent (1:3 w/v). The electrode exhibited a good Nernstian slope of 29.77 ± 0.03 mV/decade and a linear concentration range from 10^{-6} to 10^{-1} M for chromate. The limit of detection was 1.862×10^{-6} M. It had response time of 20 – 40 sec, and could be used for 49 days. This chromate selective-electrode was found more selective towards the chromate ion than other anions, useable in pH range of 5.0 – 9.0 and temperature of 20 – 50 °C. It was applied as an electrode for direct determination of chromate in water samples and their result compared to standard spectrophotometric method.

Key words: Coated-wire ion selective electrode (CWISE), chromate ion, chitosan membrane, water samples

INTRODUCTION

Chromium is a metal that use in various industrial sectors such as electroplating, paints/pigments and leather tanning industries [1]. In waters, chromium can be found as Cr(III) in cationic form (Cr^{3+}) and Cr(VI) in anionic form as chromate (HCrO_4^- and CrO_4^{2-}) and dichromate ($\text{Cr}_2\text{O}_7^{2-}$). The Cr(VI) is more toxic, corrosive, carcinogenic, and has high solubility than Cr(III). The chromium species have bad risk for plants, animals and humans. The maximum concentration of Cr(VI) in waters based on the Government Regulation of Republic Indonesia Number 18 in 1999, are 0.05 ppm. The method for monitoring the chromium species presence in waters is needed.

There is a method which able for chromate analysis such as spectrophotometry. Although has a high accuracy, it is consume the time, need expensive instrumentation, an expert to operate, and cannot use in the field. Recently, ion-selective electrode has become one of the most important groups of chemical sensors [2, 3]. Ion selective electrode (ISE) is used as recognition elements (sensor). ISE offers several advantages, such as speed and ease of preparation and procedures, simple instrumentation, a relatively fast response, a wide dynamic range, reasonable selectivity and low cost [4–7]. Coated-wire ion selective electrode has possible for online analysis [8].

Recently, reported a number of the coated-wire ion selective electrode (CWISE) with highly selectivity and sensitivity for chromate using liquid membrane based on neutral carrier [9] and complexes [10 – 11] for determination of chromate ions. The electrode in this work is designed for the detection of chromate in water samples and suitable for laboratory and field analysis.

To generate an ideal ISE, the active material selection and proper membrane composition is needed, it will show a good Nernstian of potential response, low of detection limit, selective and has a long life [12]. These characters can be achieved from mikroporus, hydrophobic, and flexible membrane, in order to obtain optimum conductivity of membrane then it need metal soaking in the membrane [13]. The purpose of this study was to develop the potentiometric method using CWISE based on chitosan, as an alternative method to determination the presence of chromate in water. The ionophore concentration, additives, basic characteristics, influence of pH, temperature and interfering ions on the potentiometric response properties of the electrode were investigated.

EXPERIMENT

Aparatus

The potential were measured using a galvanic cell of the following type: Ag | AgCl | KCl (1M) || sample solution 10^{-8} – 10^{-1} M K_2CrO_4 | PVC–chitosan membrane | Pt electrode. All potentials were measured at 25 ± 0.5 °C using a digital pH/mV meter (model 955 Fisher Accuments). An UV-Visible spectrophotometer (model 1601 Shimadzu), and oven (Memmert). The activities of chromate ions were calculated according to the Debye–Hückle procedure [14]. The pH of sample solution was monitored by a digital pH meter (Hana).

Reagents

Chitosan (DD of 65%), a high molecular weight of polyvinylchloride (PVC), dioctylphthalate (DOP) were used as received from Sigma Aldrich. Potassium chromate, sodium hydroxide, acetic acid (3 %), tetrahydrofuran (THF), phosphoric acid (85%), alcohol (96%), ultra pure grade nitric acid and sulphate acid, difenylcarbazine, acetone, natrium acetic, natrium phosphate, natrium chloride were products from Merck. Aliquat 336-chromate was prepared by extracting appropriate amount of aliquat 336-Cl in potassium chromate solution 1 M. A platinum wire (99,9% ; Ø 0.5 mm) is products from Aldrich and RG-58 coaxial cable as connector CWISE to mV potentiometer. All solutions were prepared using distilled water. Wastewater samples were filtered with filter paper. A stock solution of chromate was prepared by dissolving appropriate amount of potassium chromate in 100 mL of water. The working solutions were prepared by successive dilutions with water and buffered at pH 5.0 using the phosphate buffer solution.

Preparation of Membrane Electrode

The membrane electrode was prepared by mixing thoroughly chitosan, aliquat 336-chromate, PVC, and DOP as plasticizer. The mixture had to be vigorously stirred immediately for 3 h after the addition on THF solvent (1:3 %v/w) for an easy dissolution of PVC. To prevent dust and air streams from spoiling the mixture, was placed a filter paper on the top of glass ring. The solution was allowed stay overnight at room temperature.

Construction and Potential Measurement

About 1 cm in length and 0.5 mm in diameter of platinum wire sealed into the end of glass tube and soldered onto shielded RG-58 coaxial cable. Then the coated wire dipped into this solution 10 times and evaporated in minutes. A membrane formed on the platinum wire surface and allowed to stand overnight in the oven at 50°C. Prior to use the electrode was initially conditioned by soaking it in a 1 M of potassium chromate. The first conditioning time was approximately 24 h, then 10 – 60 min for successive used.

The utility, composition of polymer membrane, basic characteristic, sensitivity and selectivity of chromate coated-wire electrode were investigated. An Ag/AgCl electrode was used as an internal reference electrode. The measurement of electrode potential was made under constant conditions by taking 25 mL of solutions for each measurement in a cell thermostated at 25±0.5 °C. The performance of electrode was investigated by measuring its potential in the working potassium chromate solutions of 10⁻⁸ – 10⁻¹ M. The electrode immersed to a constant depth in solution and stirred at constant rate of magnetic stirring bar. The potential readings recorded when it became stable. The data were plotted as observed potential vs. the logarithm of the chromate concentration. After the measurement, electrode was rinsed by water.

The application of chromate determination in water sample using the UV-Visible spectrophotometry and potentiometry method. Both of them were tested for their accuracy and precision.

RESULT AND DISCUSSION

Influence of Membrane Composition

Several membrane compositions were investigated by varying the ratio of chitosan, PVC, and DOP as plasticizer. The optimization of membrane composition (Table 1) showed the amount of chitosan as ionophore, the PVC/plasticizer ratio and addition of aliquat 336-chromate significantly influence the electrode sensitivity. The amount of ionophore, PVC, DOP, aliquat 336-chromate and parameter of solubility (Δd_m) were factors could influence the potential response of chromate electrode. The addition of ionophore less or more than 4% generated the potential response of chromate coated-wire electrode. Most of it probably due to some inhomogenities in membranes [15].

Table 1. Optimization of Membrane Composition

No	Membrane Composition (%)				(Δd_m) (cal/cm ³) ^{1/2}	Slope (mV/decade)
	Chitosan	Aliquat 336-CrO ₄ ²⁻	PVC	DOP		
1	8	0,5	30	61,5	1,374	21,73
2	7	0,5	30	62,5	1,285	29,60
3	7	-	30	63	1,410	24,00
4	7	0,5	35	57,5	1,259	39,88
5	6	0,5	30	63,5	1,196	26,90
6	4	-	35	61	1,175	27,20
7	4	0,5	35	60,5	0,992	29,77

A little amount of chitosan addition decreased ion process transport from analytes to the membrane, but in contrary it caused the membrane swell and hidrofobless. When the membrane was swelling, the mobility of chains polymer were increased and facilitated the solvent penetration. The chromate ions were bounded in membrane phase, diffused to leave the membrane and provide opportunities for water molecules or others to fill the free volume of polymer, it influenced potential response of chromate electrode. The value of solubility indicator (Δd_m) was influence a number of Nernst factor. The homogenous and hydrophobic membrane increased spread the active group of $-NH_3^+$ from available chitosan on the surface membrane, so the ions transport from analyte to membrane occurs optimally.

The Nersnt factor can be influenced by amount of PVC. The appropriate amount of PVC caused the mechanical character of membrane were more powerful and more hydrophobic. However, if PVC has excessive amounts, the structure of chitosan in the membrane could be rigid and resulted a small of potential response. The addition of DOP as plasticizer can be overcome it. DOP were able to homogenize PVC and make the flexible membrane and rigidless. Flexible membrane character increase movement of the active material and analyte in the membrane, ISE response as increase as the membrane conductivity [5].

The optimized composition of the membrane was 4% chitosan, 35% PVC, 60.5% DOP, 0.5% additive. The potential response of the membrane was greatly improved in the presence of aliquat 336–chromate as additive.

Table 2. Characteristics of Chromate Coated-Wire Electrode

No.	ISEs Characteristics	Values
1	Nernst factor	29.77±0.03 (mV/decade)
2	Linier concentration range	$1 \times 10^{-6} - 1 \times 10^{-1}$ M / 0.1162-11620 ppm
3	Detection limit	1.862×10^{-6} M / 0.216 ppm
4	Soaking time in K_2CrO_4 1 M solution	20 min
5	Response time	20 – 40 sec
8	Life time	49 days
9	Working pH range	5.0 – 9.0
10	Temperature stability	20 – 50 °C
11	Selectivity order	$CrO_4^{2-} > CH_3COO^- > H_2PO_4^- > Cl^-$

Response Characteristics of the Electrode

Ion selective electrode characterization performed with a mathematical and computational program is usefull for the determination of detection limits and selectivity value. The detection limit and selectivity coefficient of the chromate electrode were determined by making calibration data to the Nernst and Nicolski–Eisenman equation for mixed–ion solution of primary and interfering ion.

The characteristics of the chromate coated-wire electrode were summarized in Table 2. It showed a Nernstian slope, low detection limit, fast response time, and the ability of reproducible production.

The Response Time

The response time of the electrode was measured after successive immersion the electrode in a chromate solution series from from 10^{-6} to 10^{-1} M. At higher concentration of

solution, the response time run faster than at lower concentration. At higher concentration which is has more chromate ions, the time equilibrium is easy to reached. At concentration of 10^{-6} – 10^{-1} M, the result of response time is less than 40 minutes. This result shows the chromate electrode has a good characteristic.

Influence of Soaking Membrane

In this research the membrane was soaked in a high concentration of solution, it made the membrane satisfied with the analyte, it caused the conductivity of membrane increase so that generate a better reproducibility and lifetime [13]. The membrane of electrode was soaked by potassium chromate solution of 1 M.

The curve (Figure 1) showed of the optimize soaking time was in 20 min. At this time, the necessity of water in membrane for dissosiation process was fulfilled. This process generated the ion exchange between chromate ion at interface of membrane, with the chromate ion in solution.

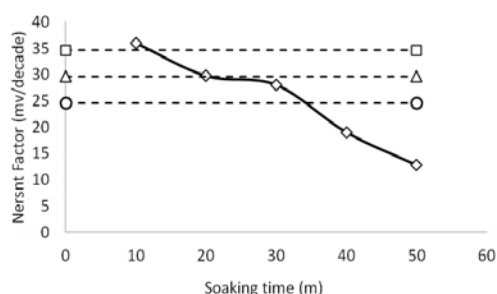


Figure 1. The Influence of Soaking Time to The Nersnt Factor, \diamond – The soaking effect, \square – The upper of Nernst factor, Δ – The teoritical of Nersnt value, \circ – The under of Nernst factor.

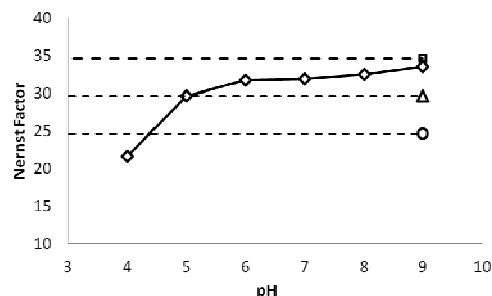


Figure 2. The Nernst factor in various pH, \square – The upper limit of allowed Nersnt factor, \diamond –The effect of pH to the Nernst factor, Δ – The teoritical value of Nernst factor, \circ – The under limit of Nernst factor

The Life Time

The electrode was tested and had stability over one months. The soaking of electrode in solution for extended periods, resulted a slight gradual decrease of the slope. It was caused by absropsi of water in the membrane for each measurement, and resulted leaching of the chitosan from the membrane [10]. To overcome it, before measurement of potential response, the membrane of electrode evaporated for 12 h in the oven. This process could decrease amount of water which absorbed in the membrane, so that the mecanical and hidrophobicity of membrane could increase.

Influence of pH

The pH dependence of electrode potential was examined at 4.0 – 9.0. The effect of pH for 10^{-6} – 10^{-1} M of chromate was illustrated in Figure 2. The active group of chitosan and chromate species changed appropriate the pH of solution. In a high of pH, the OH^- ion maybe competed with the chromate ion. It supposed the chromate ion and OH^- ion coordinated competitively with the membrane. At the pH below of 5.0, the dichromate ions start to

formed and free chromate ions start to decreased [16], it were effected the potential responses of chromate electrode. Figure 1 showed the potentials remain constant from pH of 5.0 – 9.0. It means the electrode was suitable for chromate determination in a wide pH range from 5.0 to 9.0.

Influence of Temperature

The chromate selective electrode had a good performance at temperature of 20 – 50 °C. It was showed from Nernst factor which had closest to teoritical of Nernst factor. At the temperature of 25 – 35 °C, the electrode was in the optimum condition, it was showed by Nersnt value of 28.07; 28.97 and 28.31 mV/decade. The increasing of the temperature genarated a good performance of chromate electrode because of the chromate ion-exchange was increase. It made the activities of chromate ion in membrane reached to the equilibrium. The more chromate ion between the membrane surface and chromate ion in analyte solution, the bigger potential response of the electrode.

Table 3. The Value of Selectivity Coefficient

p[CrO ₄ ²⁻]	Ion Activities		K _{CrO₄²⁻, Cl⁻} ^{pot}	K _{CrO₄²⁻, H₂PO₄⁻} ^{pot}	K _{CrO₄²⁻, CH₃COO⁻} ^{pot}
	CrO ₄ ²⁻	X (10 ⁻³ M)			
6	8,85 x 10 ⁻⁷	8,85 x 10 ⁻⁴	-1 x 10 ⁻⁴	-9,93 x 10 ⁻⁴	-9,97 x 10 ⁻⁴
5	8,85 x 10 ⁻⁶	8,85 x 10 ⁻⁴	-1 x 10 ⁻³	-9,89 x 10 ⁻³	-10 x 10 ⁻³
4	8,83 x 10 ⁻⁵	8,83 x 10 ⁻⁴	-0,098	-0,098	-0,1
3	8,65 x 10 ⁻⁴	8,65 x 10 ⁻⁴	-1,00	-0,979	-1,00
2	7,71 x 10 ⁻³	7,71 x 10 ⁻⁴	-10,00	-9,67	-9,79
1	5,37 x 10 ⁻²	5,37 x 10 ⁻⁴	-98,69	-98,69	-98,69

The Selectivity of Electrode

Selectivity is the most important characteristic of the ISE membrane, describing its specificity towards the primary ion in the presence of interfering ions. For polymer membranes, interference by other sample ions is mainly dictated by their competitive extraction into the membrane phase [11]. The selectivity coefficient for different ions were determined as described by the fixed interference method (FIM) [10]. The selectivity of electrode to chromate ion was showed in Table 3. The concentration of interfering anions was made at 10⁻³ M.

The K^{pot} values (Table 3) showed the ions of Cl⁻, H₂PO₄⁻, and CH₃COO⁻ were not affecting the performance of electrode at lower (10⁻⁶ M) or higher (10⁻¹ M) of chromate concentration than interfering ions. In a high concentration of chromate, the electrode is more selective to the chromate ion, and in the contrary. If the concentration of chromate has same value with the interfering ion (10⁻³ M) and the K^{pot} values less than 1, it means the electrode more selective to the chromate ion than interfering ion. The interfering effect of the ion was in the following order: CrO₄²⁻ > CH₃COO⁻ > H₂PO₄⁻ > Cl⁻.

Application

The chromate coated-wire electrode was applied to determination chromate ion in water samples. The analysis was performed by direct potentiometry, and the result compared with UV-Visible spectrophotometry analysis. The result are summarized in Table 4.

Table 4. Determination of chromate in synthetic and water samples by UV-Vis and CWISE

Sample (ppm)	UV-Vis (ppm)	Accuracy (%)	Precision (%)	CWISE (ppm) ^a	Accuracy (%)	Precision (%)
Synthetic	5.33	93,2	97,1	6.1	99,68	99,85
Water	1.083	87	93,13	2.174	94,3	97,53

^a Mean value \pm standard deviation (n = 7)

As seen from Table 4, the amount of chromate ion in the solution can be accurately determined with the coated-wire electrode. The accuracy of spectrophotometric method and potentiometric method were calculated from relative mistake (%). The accuracy of ISE showed a good result and precision was calculated from standard of deviation. To determine whether the UV-Vis spectrophotometric as a standard method can be replaced by potentiometric method using chromate-CWISE in water samples, the result in Table 4 show their correlation tested using the regression equation. The x-axis is the UV-Vis spectrophotometry as standard method and the y-axis is the potentiometric method. The result of calculation obtained by the regression equation for water samples :

$$\text{Potentiometric method} = 1.99 + 0.91 \text{ standard method} \quad (1)$$

The sensitivity of chromate CWISE was showed by slope value (b) = 0.91; point of intersection, intercept (a) = 1.99. The calculation of standard deviation (S) obtained $S_{y/x} =$; $S_a = 2.16$ and $S_b = 0.12$. The t-test resulted the appropriate t value for DF (n - 2) at 95% limit of confidence were obtained 4.30. The value of crossover point accuracy (a) = $a \pm t.S_a = 1.99 \pm 1.33$; and slope (b) = $b \pm t.S_b = 0.91 \pm 0.07$. The result in Table 4 and its calculation showed the electrode could be used in the environmental monitoring of chromate ion.

CONCLUSION

Based on results discussed in this paper, chitosan as a carrier and aliquat 336-chromate as an additive can be regarded for construction of a PVC membrane coated-wire ISE for chromate ion. The proposed sensor has been shown to have good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range) and is easy to prepare and use. This electrode can be used for determination of chromate in water samples.

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