

Fabrication of a Highly Selective and Sensitive CrO_4^{2-} Sensor Based on a N,N' Bis(salicylidene)ethylenediaminocobalt(II) hydrate

Anuar Kassim¹, Majid Rezayi¹, Saeed AhmadZadeh¹, Tan Wee TEE¹, Noor Azah Yusof¹,
Lee Yook Heng²

¹Department of Chemistry Faculty of Sciences, Universiti Putra Malaysia 43400 Serdang, Selangor, Malaysia

²School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia,

43600 Bangi, Selangor D.E., Malaysia

Corresponding author: Majid Rezayi

Email: chem_Rezayi@yahoo.com

Abstract

In this work a membrane was prepared by use of N,N'Bis(salicylidene) ethylenediamino cobalt(II) hydrate ($\text{Co}(\text{SALEN})_2$) as an ion carrier, polyvinylchloride (PVC) as matrix, and 2-nitrophenyl octyl ether (2NPOE) as a plasticizer for an ion-selective electrode used in the measurement of CrO_4^{2-} anions in solution. The amounts of ($\text{Co}(\text{SALEN})_2$) and PVC were optimized in the preparation of the membrane. The response of the electrode was Nernstian within the concentration range 1.0×10^{-6} to 1.0×10^{-1} M. This sensor displays a drift in Nernstian response for this anion changes with the amount of ionophore and PVC. The effects of various parameters such as pH, different anion interferences, the amounts of ionophore and PVC and time on response of the coated ion-selective electrode were investigated. The response of the fabricated electrode at concentration range from 1.0×10^{-6} to 1.0×10^{-1} M is linear with a Nernstian slope of -28.33 mV.

Keywords : Ion-selective electrode; chromate (II) anion; N,N'Bis(salicylidene) ethylenediamino cobalt(II) hydrate

Introduction

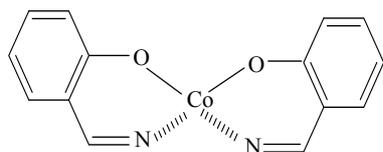
The two common oxidation states of chromium have been reported in the environment, Cr(III) and Cr(VI), are drastically different in physicochemical properties, chemical and biochemical reactivities. Cr(III) is considered to be a trace element essential for the proper functioning of living organisms [1-11] while Cr(VI) has toxic effects on biological systems. Occupational exposure to hexavalent Cr compounds leads to a diversity of clinical problems[12,13] and Cr(VI) compounds toxicity derives from its ability to diffuse through cell membranes and oxidize biological molecules [14].

One of the important toxic effects of Cr(VI) is carcinogenic nature of Cr(VI), which is related to the $\text{Cr(VI)} \leftrightarrow \text{Cr(III)}$ redox properties of this ion [15-18]. However, among different factors contributing to the mechanisms responsible for Cr(VI) reduction, the coordination geometry of its pre-redox forms seems to be underexplored. A detailed understanding of the coordination properties of this metal ion has still not been achieved because of the shortage of the respective bioinorganic models. For example, in the Cambridge Structural Database, there are only ca. 40 structures deposited containing the chromate complexes [19].

The Environmental Protection Agency (EPA) has adopted up to 0.01 ppm of total chromium as the maximum contaminant level in community water systems. In Brazil, the Health Ministry Administrative Rule no. MS 518, 03/25/2004 and the Environmental

National Agency (CONAMA) Resolution no. 357, 03/17/2005, adopted up to 0.05 ppm of total chromium as the maximum contaminant level in potable water and wastewaters, respectively. Sophisticated techniques as AAS, ICP etc are presently employed for chromium trace amount determination. However, these methods are disadvantageous in terms of cost and also unsuitability for routine analyses of a large number of samples[20-23]. Extensive efforts have been made to develop a good sensitive sensor for chromium.[24-27] However, most of the sensors already developed do not allow chromium estimation at lower concentrations (<1ppm). They exhibit poor selectivity in the presence of common anions, have a non-Nernstian response or a long response time.

Also chromium(VI) is present in effluent discharge from steelworks, electroplating, tanning and chemical industries. Its estimation in these effluents has become important due to its toxic nature. Therefore a direct, convenient method for chromium estimation is highly desirable. Ion-selective electrodes provide a convenient and rapid method of analysis. The development of a good sensitive sensor for chromium has long been a subject of concern to analytical chemists and several efforts have been made in this direction in the last two decades, selective inorganic ion exchangers are suitable materials for the preparation of membranes [28]. In this research, we used ($\text{Co}(\text{SALEN})_2$) (Structure I) as an ionophore in PVC matrix for designing an ion-selective electrode for CrO_4^{2-} anion.



Structure I : N,N'Bis(salicylidene) ethylenediamino cobalt(II) hydrate (Co(SALEN)₂)

Experimental

Apparatus

All potentiometric measurements were made at $25.0 \pm 0.1^\circ\text{C}$ using an Mettler Toledo ion meter (Seven Multi) and Mettler Toledo double junction silver/silver chloride reference electrode containing saturated potassium chloride solution. A silver/silver chloride electrode containing a 3 molL^{-1} solution of KCl was used as the internal reference electrode. The activities were calculated according to the Debye-Huckel procedure.

Reagents and materials

All chemicals were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Polyvinyl chloride (PVC) powder of high molecular weight, dioctylphthalate (DOP), dibutyl phthalate (DBP), 2-Nitrophenyl octyl ether (2NPOE), tetrahydrofuran (THF) of purity > 99%, and tridodecylmethylammonium chloride and tetradodecylammonium chloride were all obtained from Fluka Chemical Company and used as received. The sodium or potassium salts of the anions used (all from Merck, Aldrich, BDH or HmbG) were of the highest purity available, and used without any further purification except for vacuum drying over P_2O_5 . Doubly distilled de-ionized water was used throughout.

Membrane preparation and electrode construction

Membrane solutions were prepared by thoroughly dissolving 5.0 mg of the N,N'Bis(salicylidene) ethylenediamino cobalt(II) hydrate (Co(SALEN)₂), 62.0 mg of 2-nitrophenyl octyl ether (2NPOE), 30.0 mg of PVC and 3.0 mg of tetradodecylammonium chloride in 3 mL of fresh THF. The resulting solution was evaporated slowly until an oily mixture was obtained. A Pyrex tube (3 mm o.d) was dipped into the mixture for about 10s so that a nontransparent membrane of 0.3 mm thickness was formed. The tube was then pulled out from the mixture, and kept at room temperature for 24h. The tube was then filled with an internal solution ($1.0 \times 10^{-2} \text{ molL}^{-1} \text{ K}_2\text{CrO}_4$). The electrode was finally conditioned for about 24h by soaking in a $1.0 \times 10^{-2} \text{ molL}^{-1} \text{ K}_2\text{CrO}_4$ solution. A silver/silver-chloride electrode was used as the internal reference electrode (Diagram I).

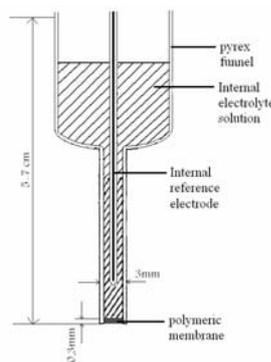
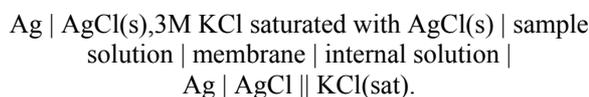


Diagram I : General assembly of the proposed ion-selective electrode.

Potential measurements

All measurements were made at $25 \pm 1^\circ\text{C}$ with a cell of the type:



The performance of each electrode was investigated by measuring its potential in K_2CrO_4 solutions prepared in the concentration range 1.0×10^{-1} to $1.0 \times 10^{-6} \text{M}$ by serial dilution of the 0.01M stock solution at a constant pH. The solutions were stirred and potential readings were recorded when they reached steady-state values. The data were plotted as observed potential versus the logarithm of the CrO_4^{2-} ion concentration.

Results and discussion

In these experiments, Co(SALEN)₂ was used as an ion carrier to prepare CrO_4^{2-} selective membrane electrode in a PVC matrix. The potential response of the membrane electrodes to CrO_4^{2-} anion is shown in Fig 1. The electrode gives a linear response to chromate ions in the concentration range $1.0 \times 10^{-6} \text{M}$ - $1.0 \times 10^{-1} \text{M}$ with a Nernstian slope of 28.33 mV per decade of concentration and a correlation coefficient of 0.993 (Fig. 1). Repeated monitoring of the potential, at a fixed concentration, gives a standard deviation of 0.2 mV. This membrane, after being equilibrated for three days, exhibits a response time of 10s, and the potential remains constant for more than 15 min. It is seen that the membrane electrode responds to CrO_4^{2-} with Nernstian slope at a wide concentration range. Thus the membrane gives the best response to chromate anion.

The presence of cobalt atom in the macrocycle is expected to show strong complexation behaviour of the carrier for Chromate(II) ion. The ratio of ionophore (Table 1) to PVC and additive was varied in order to obtain a composition, which gives a membrane of best performance with regard to working concentration range, slope and response time. It was found that the membrane having 5 mg of ionophore and 30 mg PVC

gave the best results (Electrode A, B and C, Table 1). Therefore, the ionophore $\text{Co}(\text{SALEN})_2$ was selected as suitable sensor material for chromate anion in PVC matrix. Addition of an appropriate amount of plasticizers leads to optimum physical properties and

ensures high mobility of ions in the membrane. These solvent mediators strongly influence the working concentration range of the sensors. It is well known that plasticizers improve the electrochemical properties of the ion-selective electrodes.

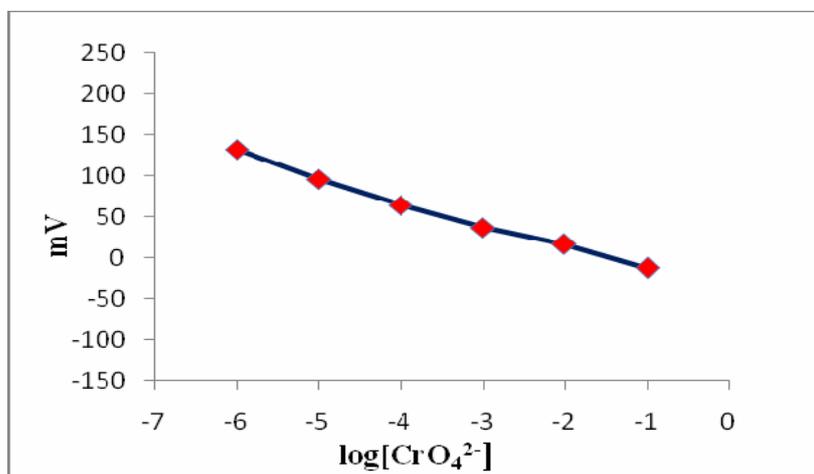


Figure 1 : The potential response of the membrane electrodes to CrO_4^{2-} anion

Table 1: Optimization of membrane ingredients for chromate(II) ion sensor

No.	Composition%				Slope	Linear range (M)	Detection limit	R^2
	PVC	Plasticizer,%	tetraDA	Co (salen) ₂				
A	30	DBP, 63	2	5	-27.63	10^{-6} to 0.01	1.94×10^{-6}	0.984
B	30	DOP, 62	3	5	-24.81	10^{-6} to 0.1	1.28×10^{-6}	0.988
C	30	2NPOE, 62	3	5	-28.33	10^{-6} to 0.1	1.52×10^{-6}	0.993
D	33	2NPOE, 62	nil	5	-22.44	10^{-6} to 0.1	1.09×10^{-6}	0.985
E	33	2NPOE, 62	5	nil	-15.80	10^{-6} to 0.01	6.89×10^{-6}	0.991

The effect of pH on the electrode potential (Fig. 2) shows that the useful working pH range where the potential remains constant is 7-10. The drift in potential at lower pH values appears to be due to the formation of dichromate and polychromate, which the electrode appears to respond.

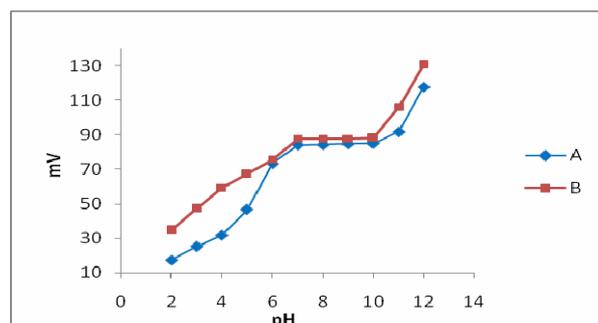


Figure 2: Variation of membrane potential with pH of $[\text{CrO}_4^{2-}]$: (A) 1.0×10^{-2} M, (B) 1.0×10^{-3} M.

Furthermore the effect of internal solution on response of the electrode was investigated where the results obtained for four measurements from 10^{-4} M to 10^{-1} M were obtained. The best concentration of internal solution was found to be 10^{-2} M potassium chromate (Electrode B), where the highest response of almost Nernstian behavior was obtained (Table 2 and Fig.3).

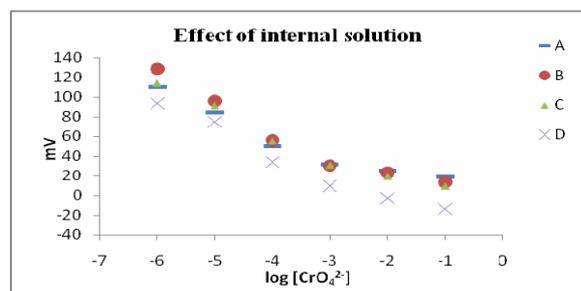


Fig. 3: The effect of concentrations of potassium chromate as an internal solution (A) 1.0×10^{-1} M, (B) 1.0×10^{-2} M, (C) 1.0×10^{-3} M, (D) 1.0×10^{-4} M,

Table 2: Effect of internal solution on the response of the chromate(II) ion sensor

Electrode	Slope	Linear range (M)
A	27.73	10^{-6} to 0.01
B	28.33	10^{-6} to 0.01
C	28.01	10^{-6} to 0.01
D	27.34	10^{-6} to 0.01

The dynamic responses of the proposed chromate electrode for step changes in concentration of CrO_4^{2-} ion, from low to high concentrations are shown in Fig. 4. The time for the electrode to reach 90% of the steady response was <15 s.

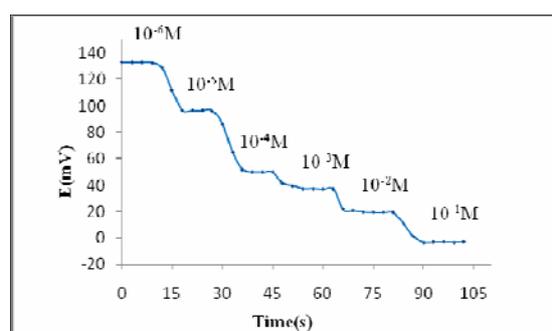


Figure 4: The dynamic response time of the potentiometric chromate(II) ion sensor for different concentrations of chromate solutions.

The response of the sensor for other doubly charge anions is summarised in Fig. 5. All anions produced responses with slopes and detection limit values that were poorer than the the CrO_4^{2-} response. The anion response is in the order of: $\text{CrO}_4^{2-} > \text{CO}_3^{2-} > \text{C}_2\text{O}_4^{2-} > \text{SO}_4^{2-}$.

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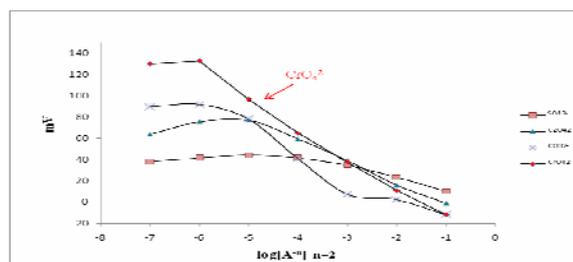


Figure 5: The response of CrO_4^{2-} ion-selective sensor based on ionophore $\text{Co}(\text{salen})_2$ to other doubly charge anions

The response of the sensor for other single charge anions and halides is shown in Figs. 6 and 7. All anions produced responses with slopes and detection limit values poorer than the response towards CrO_4^{2-} . The anion response order of the sensor is $\text{CrO}_4^{2-} > \text{BrO}_3^- > \text{OH}^- > \text{Cl}^- > \text{Br}^- > \text{SCN}^- > \text{CH}_3\text{COO}^-$.

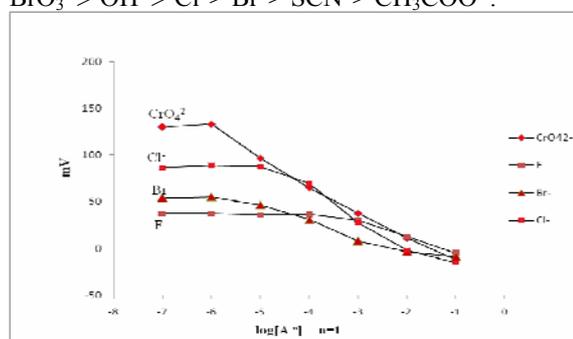


Figure 6: The response of the CrO_4^{2-} ion-selective sensor based on ionophore $\text{Co}(\text{salen})_2$ towards halide anions

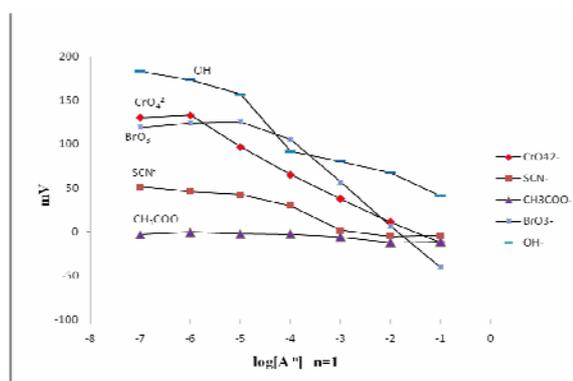


Figure 7: The response of the CrO_4^{2-} ion-selective sensor based on ionophore $\text{Co}(\text{salen})_2$ for other single charge anions

Conclusion

The chromate sensor investigated here exhibits good response and selectivity towards CrO_4^{2-} ion. It exhibits near Nernstian slope (-28.33mV per decade), wide linearity (1.0×10^{-1} to 1.0×10^{-6} mol l^{-1}) and good potentiometric selectivity for CrO_4^{2-} ion over many anions.

Acknowledgements

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References

- 1 D. Burrows, (1983), Chromium: Metabolism and Toxicity, CRC Press, Boca Raton, FL.
- 2 V. Bianchi, A. Zantedeschi, A. Montaldi, and J. Majone, (1984), *Genetic approaches in the study of chromium toxicity*, Toxicol. Lett. **8**, 279.
- 3 S. De Flora and K.E. Wetterhahn, (1989), *Lower rim alkylammonium-substituted calix[4]arenes as "proton-switchable" extractants for chromate and dichromate anions*, Life Chem. Rep. **7**, 169.
- 4 D.M. Stearns, L.J. Kennedy, K.D. Courtney, P.H. Giangrande, L.S. Phieffer, and K.E. Wetterhahn, (199), *Apoptosis of Lymphocytes in the Presence of Cr(V) Complexes: Role in Cr(VI)-Induced Toxicity* Biochemistry, **34**, 910.
- 5 P.R. Wittbrodt and C.D. Palmer: Environ, (1995), *Catalysis of Manganese(II) on Chromium(VI) Reduction by Citrate*, Sci. Technol. **29**, 255.
- 6 Anderson, R. A., 1989, Nutritional chemistry of chromium, Sci. Total Environ., **86**, 75.
- 7 Nieboer, E.; Jusys, A. A., 1988, In Chromium in Natural and Human Environments; Nriagu, J.O., Nieboer, E., eds., Wiley Interscience: New York, 81-104.
- 8 Mertz, W.; J. Nutr, (1993), *Chromium in Human Nutrition: A Review*, 123, 626.
- 9 Anderson R. A., (1995), In Handbook of Metal-Ligand Interactions in Biological Fluids, Bioinorganic Medicine, Berthon, G., ed., Dekker, New York, 1, 261.
- 10 Vincent, J.B., (2000), *Bis(ethylenediamine- κ 2N,N')(2-oxido-5-sulfonatobenzoato- κ 2O1,O2)chromium(III) dehydrate*, Acc. Chem. Res., **33**, 503.
- 11 Anderson, R. A., (1998), *The nutritional biochemistry of Chromium(III)*, Nutr. Rev., **56**, 266.
- 12 Gad, C. S., (1989), *Determination of Cr^{3+} , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$ in environmental matrixes by high-performance liquid chromatography with diode-array detection (HPLC-DAD)*, Sci. Total Environ, **86**, 149.
- 13 Lee, K. P., Ulrico, C.E., Geil R. G., Ttochimowicz, H. J., (1989), *Silsequioxane 3-n-Propylpyridinium chloride: a new polymer for the potentiometric analysis of Cr(VI) in electroplating and leather industry wastes* Sci. Total Environ., **86**, 83.
- 14 Shaffer, R.E., Cross, J.O., Rose-Pehrsson S.L., Elam, W.T., (2001), *Speciation of chromium in simulated soil samples using X-ray absorption spectroscopy and multivariate calibration*, Anal. Chim. Acta **442**, 295.
- 15 Connett PH, Wetterhahn KE Struct Bond, (1983), *Metabolism of a carcinogen chromate by cellular constituent*, **54**, 93.
- 16 Bianchi A, Bowman-James K, Garcia-Espana E (eds), 1997, *Supramolecular chemistry of anions*. Wiley-VCh, NY, Chichester, Weinheim, 148.
- 17 Codd R, Dillon CT, Levina A, Lay PA, (2001), *Studies on the genotoxicity of chromium: from the test tube to the cell*, Coord Chem Rev **216–217**, 537.
- 18 Wilkinson G, Gillard RD, McClaverty JA, 1987, *Comprehensive coordination chemistry*, 1st edn. Pergamon, Oxford, New York.
- 19 Allen FH, (2002), *The Cambridge Structural Database: a quarter of a million crystal structures and rising*, Acta Crystallogr B **58**, 380.
- 20 Jain, A. K., Gupta, V. K., Singh, L. P., Srivastava P., Raison, J. R., (2005), *Anion recognition through novel C-thiophenecalix[4]resorcinarene: PVC based sensor for chromate ions*, Talanta, **65**, 716.
- 21 Davidson, C. M., Thomas, R.P., McVey, S.E., Perala, R., Littlejohn D., Ure, A.M., Anal., (1994), *Some sources of variability in application of the three-stage sequential extraction procedure recommended by BCR to industrially-contaminated soil*, Chim. Acta, **291**, 277.
- 22 Menon, S., Yilmaz, M., J. Mol. Struct, (2001), *Polymer Supported Calix[4]Arene Derivatives for the Extraction of Metals and Dichromate Anions*, **595**, 101.
- 23 Miret, A., Ruffo, J., Sastre, A. M., Cortina, J. L., (1996), In Chemical Industry and Environment II, Piccinini, N., Delorenzo, R. eds., Politecnico di Torino, Torino, Ch. 1.
- 24 Wang, K., Yu, R., (1986), *Chemiluminescence flow system for the monitoring of chromium(VI) in water*, Fenxi Huaxue, **14**, 599.
- 25 Feng, D., Chen, C., (1983), *Silsequioxane 3-n-Propylpyridinium chloride: a new polymer for the potentiometric analysis of Cr(VI) in electroplating and leather industry wastes*, Huaxue Xuebao, **41**, 371.
- 26 Hasan, S.S.M., Abbas, M.N., Moustafa, G.A.E., (1996), *Hydrogen chromate PVC matrix membrane sensor for potentiometric determination of chromium(III) and chromium(VI) ions*, Talanta, **43**, 797.
- 27 Jain, A. K., Gupta, V.K., Singh, L.P., Srivastava P., Raison, J. R., (2005), *Anion recognition through novel C-thiophenecalix[4]resorcinarene: PVC based sensor for chromate ions*, Talanta, **65**, 716.
- 28 Alfaya, A.A.S., Gushikem, Y., J., (1999), *Antimony (V) Oxide Adsorbed on a Silica-Zirconia Mixed Oxide Obtained by the Sol-Gel Processing Method: Preparation and Acid Properties*, Colloid Interf. Sci., **209**, 428.