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Complex of Co(III) as Receptor Molecule for Development of a New Perchlorate-Selective Polymeric Membrane Electrode

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A *bis*(dimethylgolyoximato)nitritopyridineCo(III), [Co(DMG) 2PyNO$_2$] incorporated in a plasticized poly (vinyl chloride) membrane was used to develop a perchlorate-selective electrode.The influence of membrane composition on the electrode response was studied. The electrode exhibits a nernstian response over the perchlorate concentration range 1.0×10^{-6} to 1×10^{-1} mol L^{-1} with a slope of 41.36 mV per decade of concentration, a detection limit of 7.8×10^{-7}, a wide working pH range (3-10) and fast response time (< 10 s). The proposed electrode was used for the determination of perchlorate in water, wastewater and human urine with satisfactory results.

Key Words: Ion-selective electrodes, Perchlorate determination, Human urine, Wastewater.

INTRODUCTION

In comparison with cation selective electrodes, only a small number of anion selective electrodes are known and their selectivity are often much worse than those of the cation selective electrodes. A classical membrane electrode for anions are based on quaternary ammonium and phosphonium salts and usually exhibits the Hofmeister[1]. Recently, much attention has been focused on new ion carriers possessing an anti-Hofmeister achieved in the case of membrane electrodes. In last few years, electrodes using PVC membranes incorporating complexes of metals with phthalocyanine, porphyrine and Schiff base derivatives have been reported for anions[2-12].

Perchlorate anions may be found at high concentration (more than 10000 ppm) in surface and ground waters around the world[13]. Such contamination is due to the perchlorate salts that are used in solid propellants and in a wide variety of industrial situations[14]. Perchlorate shows thyreostatic activity by inhibiting iodine uptake and may therefore hinder the ability of humans to produce hormones and regulate their metabolism. Perchlorate salts have been used to treat patients with hyperactive thyroid gland and to carry out diagnostics tests[15]. The determination of perchlorate ion has been carried out by these methods include volumetric titration, gravimetry, spectrophotometry, atomic absorption spectrometry and ion chromatography[16-20]. However, most of these methods are susceptible to interference from different cationic and anionic species and are either time-consuming or need sophisticated instruments.

Thus, the development of convenient direct methods for the assay of perchlorate ion in different samples is of urgent need and it is for this reason that extensive effort has been made to develop highly selective perchlorate electrodes.

Most of the reported perchlorate ion-selective electrodes were polymeric liquid membranes-based ion exchangers, where the electroactive species, including perchlorate ion-association complexes with cations and metal chelates[21-25], long chain quaternary ammonium ions[26-28] and organic dyes[29,30], have been dissolved in various organic solvents. In these liquid membranes, ion-pair formation between ClO_4^- and the cationic site may occur with some selectivity, but many of these electrodes are not sensitive and selective enough to permit selective measurement of low levels of perchlorate and are susceptible to interferences from other common anions such as OH^-, NO_3^-, SCN^- ions. Recently, a few carrier-based perchlorate-selective electrodes with improved selectivity and sensitivity were reported[31-35]. Thus, the development of more convenient perchlorate selective electrodes with modified sensitivity and selectivity for quick and accurate assay of perchlorate in different samples without prior separation steps is still of urgent need. In this paper, the construction and evaluation of a plasticized PVC membrane perchlorate-selective electrode based on a [Co-(dimethylgolyoximato)$_2$PyNO$_2$] has been described.

EXPERIMENTAL

Reagent grade tetrahydrofuran (THF) and polyvinyl chloride (PVC) of high molecular weight were selectophore products from Fluka. Dibutyl phthalate (DBP) and cetyltrimetyl ammonium bromide (CTMABr) were purchased from Merck and used as received. All other reagents used were for analytical reagent grade and doubly distilled water was used throughout. Thiocyante, dichromate, nitrate, nitrite, iodide, bromide, acetate, bromate, cyanide, carbonate, chloride, iodate, perchlorate solutions were prepared from sodium or potassium salts.

The complex was synthesized by method described previously and was identified by FT-IR and 1HNMR spectroscopy[36]:

Brown solid; yield 42/5 %, IR(KBr, ν_{max}, cm^{-1}): 3444, 3085, 2917, 1565, 1241, 1090, 508, 420; ^{1}H NMR (500 MHz, CDCl$_3$): 2.36 (S, 12H, dmgH), 7.30 (dd, 2H, J = 1086 Hz, J = 6.7, Py-H), 7.78 (t, 1H, J = 7.6 Hz, Py-H), 8.60 (d, 2H, J = 5.3 Hz, Py-H).

EMF measurements: Potentials were measured with a coring ion analyzer pH/mV meter relative to a double junction saturated calomel electrode (SCE) with the chamber filled with an ammonium nitrate solution at constant temperature (25 ± 0.1 ºC). A silver/silver chloride electrode containing a 3 M solution of KCl was as the internal reference electrode. The electrode cell assembly of the following type was used:

Ag-AgCl | KCl (3 M) | internal solution 1.0×10^{-3} M ClO_4^- | PVC membrane | tested solution | Hg-Hg$_2$Cl$_2$, KCl (saturated).

Preparation of membrane electrodes: Membranes containing different PVC/plasticizer ratios were studied and the optimum composition found was 30.0 wt % of powdered PVC, 62 wt % of plasticizer (DBP), 5 wt % of additive (CTMABr) and 3 wt % of the complex. These were mixed in 3 mL of THF and transferred into a glass dish of 5 cm diameter. The solution was left for the solvent to evaporate slowly and an oily mixture was obtained. A Pyrex tube (3 mm i.d.) was dipped into the mixture for *ca.* 30 s. Then the tube was pulled out and kept at room temperature for 12 h, so that a membrane for 0.3 thicknesses was formed at the end of the tube. The tube was then filled with an internal solution of 1.0 × 10^{-3} M perchlorate. The electrode was finally conditioned for 24 h by soaking in a 1.0 × 10^{-2} M perchlorate solution. A silver/silver chloride was used as an internal reference electrode.

RESULTS AND DISCUSSION

Preliminary poteniometric studies: In preliminary experiments, revealed that the plasticized PVC-based membrane electrodes containing [Co(dmgH)$_2$PyNO$_2$] as ionophore generates stable potential responses in solutions containing perchlorate, after conditioning for *ca.* 24 h in 1.0 × 10^{-2} M NaClO$_4$ solution. The membrane demonstrated a remarkable selectivity for perchlorate than other anions tested. The perferential response of the ionophore towards ClO_4^- is believed to be associated with the coordination of perchlorate with the metal center in this complex and it is the relative affinity of ClO_4^- as a suitable ligand for Co(III) that dictates the observed selectivity pattern of the electrodes.

The potential responses of the polymeric membrane electrode containing this complex of Co(III) as ionophore for a variety of anions are shown in Fig. 1.

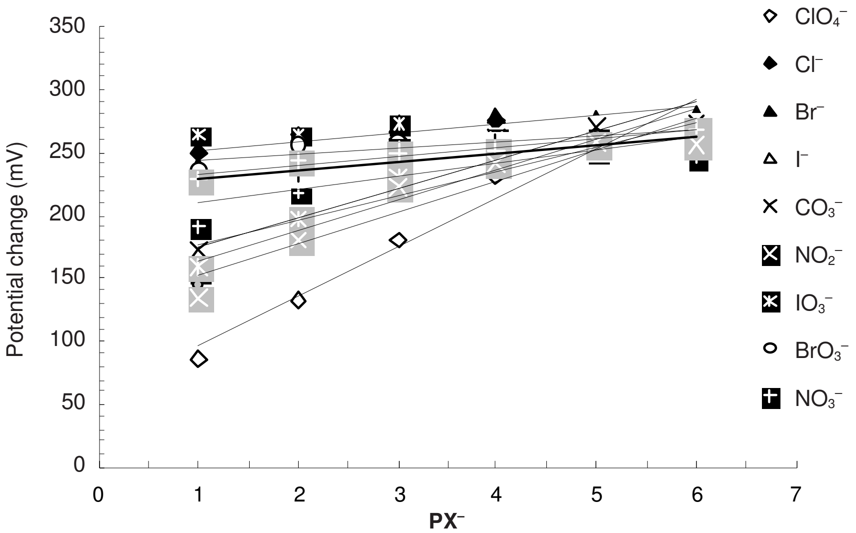

Fig. 1. Potential response of various anion selective electrode based on [Co(dmgH)$_2$PyNO$_2$]

Optimization of membrane components: It is well known that the sensitivity, selectivity and linearity of ion selective sensors not only depend on the nature of ionophores used but also significantly on the membrane composition and the properties of the plasticizers used[37-42].Thus, the effect of the membrane composition, the amount of the plasticizer on the potential response of the ClO_4^- sensor were investigated and the results are summarized in Table-1. As seen from Table-1, in the absence of ionophore, the electrode showed a negligible response slope (No. 1). Based on the results obtained on the optimization of the membrane composition, the membrane 2 with the optimized composition of DBP:PVC: $[Co(dmgH)_2PyNO_2]$: CTMABr per cent ratio of 62:30:3:5 was selected for the preparation the polymeric membrane electrode for perchlorate ion.

TABLE-1
COMPOSITION AND OPTIMIZATION OF MEMBRANES INGREDIENTS

No.	Composition in membranes (%)				Slope (mV/ decade)	Linear range (M)	R^2
	PVC	Plasticizer	Ionophore	CTAB			
1	30	65(DBP)	–	5	29.2	1.0×10^{-1}-1.0×10^{-6}	0.9305
2	30	62(DBP)	3	5	38.7	1.0×10^{-1}-1.0×10^{-6}	0.9156
3	30	62(DBP)	5	3	41.36	1.0×10^{-1}-1.0×10^{-6}	0.9507
4	30	57(DBP)	8	5	30.14	1.0×10^{-1}-1.0×10^{-6}	0.9406
5	30	67(DBP)	5	8	33.08	1.0×10^{-1}-1.0×10^{-6}	0.9229

Effect of internal reference solution: The influence of the concentration of the solution on the potential response of the ClO_4^- ion selective was studied. The $NaClO_4$ concentration was changed from 1.0×10^{-3} to 1.0×10^{-4} M and the potential response of the ClO_4^- ion selective was obtained. It was found that variation of the concentration of the internal solution did not cause any significant difference in the potential response, except for an expected change in the intercept of resulting Nernstian plot. A 1.0×10^{-3} M concentration of internal reference solution is quite appropriate for smooth functioning of the electrode system.

Effect of pH: The pH dependence of potential response of the proposed membrane sensors at two different concentrations of ClO_4^- ions in the pH rang 1-12 was tested and the results are shown in Fig. 2. The pH was varied by adding HCl or NaOH. The results indicated that the optimum pH was 3-9.5. At higher pH values the potential decreased due to the simultaneous response of the electrode to ClO_4^- and OH^- anions. On the other hand, at pH values lower than 3 the electrode potential decreased most probably due to the increase of the Cl^- ion concentration and simultaneous response of the electrode to perchlorate and chloride ions.

Response characteristics of the perchlorate-selective electrode: Ion-selective electrode characterization performed with a mathematical and computational program is very useful for the determination of detection limits and selectivity constants, among others[43,44]. In accordance with this, the slope, detection limit and selectivity

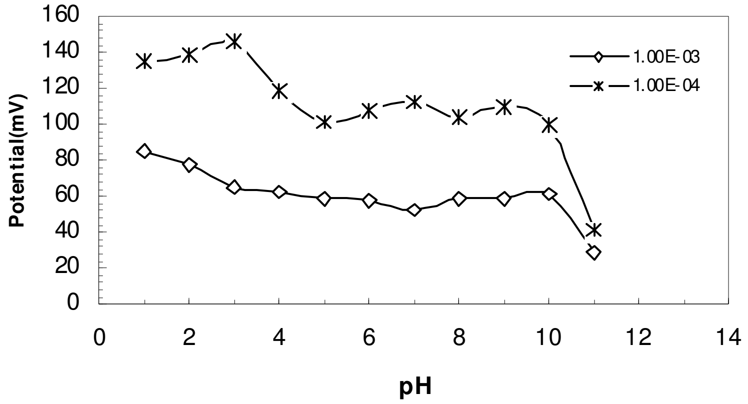

Fig. 2. Influence of pH test on the potential response of the perchlorate selective electrode at different ClO_4^- concentrations: 1.0×10^{-3} and 1.0×10^{-4} M

coefficients of the perchlorate electrode were determined by fitting calibration data to the Nikolskii-Eisenman equation or to the formalism of Bakker *et al.*[45] for mixed-ion solutions of primary and interfering ions of different charge. The slope and detection limit of the electrode were evaluated from repeatedly carrying out calibration graphs between 1.0×10^{-1} and 1.0×10^{-6} M. The calibration parameters thus obtained are included in Table-2. As can be seen a near-Nerstian response, low detection limit and good calibrator reproducibility were obtained. The response time was obtained from the dynamic response curves corresponding to perchlorate concentration steps to obtain a 10 times more concentrated solution. The values obtained for different perchlorate concentrations are included in Table-2 and show a very rapid response even for low concentration. The experimental results showed that the lifetime of the electrode was more than 3 months. During this time the detection limit and slope of the electrodes remained almost constant.

TABLE-2
RESPONSE CHARACTERISTICS OF THE PERCHOLRATE-SELECTIVE ELECTRODE

Slope (mV/decade)	41.36
Linear range (mol/L)	1×10^{-1} to 1×10^{-6}
Response time (s)	<10
Working pH range	3-10
Life time (months)	>3

Selectivity: The selectivity behaviour is obviously one of the most important characteristics of an ion selective electrode that is relative electrode response in solution primary anion (A) over other anions present in solution (B), which is usually expressed terms of poteniometric selectivity coefficient ($K_{A,B}^{pot}$). The potentiometric selectivity coefficient was determined by the fixed interference method (FIM)[44] at 1.0×10^{-1} M concentration of the interfering species. The results are summarized in Table-3. From the data given in the Table-2, it is revealed that the proposed perchlorate sensor is highly selective. In the Table-3, the analytical performance and selectivity coefficient of the proposed electrode based on the cobalt complex was also compared with the corresponding values previously reported for the electrodes based on different metal ion complexes as ClO_4^- ion carriers. As seen, the proposed perchlorate electrode showed somewhat similar, in most of the cases or superior in some case, response characteristics and selectivity behaviour to the perchlorate sensors prepared previously.

TABLE-3
POTENTIOMETRIC SELECTIVITY COEFFICIENTS

Ion	log K ClO_4^-, j				
Br^-	-1.00	-4.0	-	-4.3	-3.0
IO_3^-	-1.97	-	-	-	-
I^-	-1.52	-2.0	-	-3.3	-1.5
SCN^-	-1.31	-1.4	-2.3	-2.1	-2.0
CN^-	-1.54	-	-	-	-
NO_2^-	-2.77	-4.4	-3.1	-3.4	-3.3
CH_3COO^-	-1.90	-5.2	-4.8	-4.5	-2.8
CO_3^{2-}	-2.00	-	-6.9	-	-
BrO_3^-	-1.51	-	-	-	-
NO_3^-	-1.61	-	-	-4.1	-3.8
$Cr_2O_7^{2-}$	-2.78	-	-	-	-
Cl^-	-1.90	-5.0	-2.0	-4.6	-3.7
Reference	This work	31	35	32	46

Analytical applications: The proposed percholrate-selective electrode was satisfactorily applied to the determination of perchlorate in mineral water, tap water, waste water and human urine. The analyses were performed by direct potentiometry using the standard addition technique. In the absence of samples containing perchlorate, known amounts of perchlorate were added. The results obtained are summarized in Table-4. As is obvious, the recovery is quantitative at various perchlorate concentrations tested.

TABLE-4
DETERMINATION OF PERCHLORATE ION IN MINERAL WATER, TAP WATER, WASTEWATER AND HUMAN URINE

Sample	Perchlorate (μg mL^{-1})		
	Added	Found	Recovery (%)
Mineral water	10	9.95	99.50
	100	99.90	
	500	99.90	
Tap water	10	9.99	99.96
	100	99.98	
	500	99.98	
Wastewater	10	9.90	99.00
	100	99.93	
	500	99.78	
Human urine	10	9.97	99.73
	100	99.95	
	500	99.85	

REFERENCES

1. F. Hofmeister and Zur Lehre Von der Wirkung der Salze, *Arch. Exp. Pathol. Pharmacol. (Leipzig)*, **24**, 247 (1888).
2. P. Buhlmann, E. Pretsch and E. Bakker, *Chem. Rev.*, **98**, 1593 (1998).
3. S. Ozawa, H. Miyagi, Y. Shibata, N. Oki, T. Kunitake and W.E. Keller, *Anal. Chem.*, **68**, 4149 (1996).
4. A. Mitsana-Papazoglu, E.P. Diamandis and T.P. Hajiioannou, *Anal. Chim. Acta*, **159**, 393 (1984).
5. H. Hisamoto, D. Siswanta, H. Nishihara and K. Suzuki, *Anal. Chim. Acta*, **304**, 171 (1995).
6. E. Malinowska, J. Niedaolka and M.E. Meyerhoff, *Anal. Chim. Acta*, **432**, 67 (2001).
7. E.D. Steinle, S. Amemiya, P. Buhlmann and M.E. Meyerhoff, *Anal. Chem.*, **72**, 5766 (2000).
8. M. Shamsipur, S. Sadeghi, H.H. Naeimi and H. Sharghi, *Pol. J. Chem.*, **74**, 231 (2000).
9. A. Malon. A. Radu, W. Qin, A. Ceresa, M. Maj-Zurawska, E.Bakker and E. Pretsch, *Anal. Chem.*, **75**, 3865 (2003).
10. S. Amemiya, P. Buhlmann, Y. Umezawa, R.C. Jagessar and D.H. Burns, *Anal. Chem.*, **71**, 1049 (1999).
11. W. Wraoblewski, J. Przygorzewska, G. Roskicki and Z. Brzozka, *Chem. Anal. (Warsaw)*, **47**, 335 (2002).
12. V. J. Wotring, D.M. Johnson and L.G. Bachas, *Anal. Chem.*, **62**, 1506 (1990).
13. B.E. Logan, *Biorem. J.*, **2**, 69 (1998).
14. J.I. Kroschwitz and M. Howe-Grant, The Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, New York, Vol. 18, edn. 4, p. 167 (1996).
15. G.A. Goodman, L.S. Goodman, T.W. Rall and F. Murad, The Pharmacological Basis of Therapeutics, Panamericana, Madride, edn. 7, p. 1489 (1989).
16. R.J. Baczuk and W.T. Bolleter, *Anal. Chem.*, **39**, 93 (1967).
17. A.I. Vogel, Text Book of Quantitative Inorganic Analysis, Longman, London, edn. 4, p. 498 (1978).
18. J.A. Weiss and J.B. Stanbury, *Anal. Chem.*, **44**, 619 (1972).
19. M. Gallego and M. Valcarcel, *Anal. Chim. Acta*, **169**, 161 (1985).
20. P. Batjoens, H.F. De Brabander and L. T'Kindt, *Anal. Chim. Acta*, **275**, 335 (1993).
21. N. Ishibashi and H. Kohara, *Anal. Lett.*, **4**, 785 (1971).
22. T.J. Rohm and G.G. Guilbault, *Anal. Chem.*, **46**, 590 (1974).
23. A.C. Wilson and K.H. Pool, *Talanta*, **23**, 387 (1976).
24. S.S.M. Hassan and M.M. Elsaied, *Talanta*, **33**, 679 (1986).
25. A.K. Jain, M. Jahan and V. Tyagi, *Analyst*, **112**, 1355 (1987).
26. C.J. Coetzee and H. Freiser, *Anal. Chem.*, **40**, 2071 (1968).
27. C.J. Coetzee and H. Freiser, *Anal. Chem.*, **41**, 1128 (1969).
28. S. Back, *Anal. Chem.*, **44**, 1696 (1972).
29. A.G. Fogg, A.S. Pathan and D.T. Burns, *Analyst*, **73**, 220 (1974).
30. M. Kataoka and T. Kambara, *J. Electronal. Chem.*, **73**, 279 (1976).
31. C. Sanchez-Pedreno, J.A. Ortuno and J. Hernandez, *Anal. Chim. Acta*, **415**, 159 (2000).
32. M.R. Ganjali, M. Yousefi, T. Poursaberi, L. Naji, M. Salavati-Niasari and M. Shamsipur, *Electroanalysis*, **15**, 1476 (2003).
33. M. Shamsipur, M. Soleymanpour, M. Akhond, H. Sharghi and A.R. Hasaninejad, *Sens. Actuators B*, **89**, 9 (2003).
34. J. Lizondo-Sabater, M.-J. Segui, J.M. Lioris, R. Martinez, T. Pardo, F. Sancenon and J. Soto, *Sens. Actuators B*, **101**, 20 (2004).
35. M.A. Zanjanchi, M. Arvand, M. Akbari, K. Tabatabaeian and G. Zaraei, *Sens. Actuators B*, **113**, 304 (2006).
36. H.A.O. Hill and K.G. Morallee, *J. Chem. Soc. (A)*, 554 (1969).
37. A. Malon, A. Radu, W. Qin, A. Ceresa, M. Maj-Zurawska, E. Bakker and E. Pretsch, *Anal. Chem.*, **75**, 3865 (2003).

38. T. Rosatzin, E. Bakker, W. Simon and K. Suzuki, *Anal. Chim. Acta*, **280**, 197 (1993).
39. E. Bakker, P. Buhlmann and E. Pretch, *Chem. Rev.*, **97**, 3083 (1997).
40. A. Solyemanpour, M. Shamsipur, M. Akhond, H. Sharghi and A.R. Massah, *Talanta*, **58**, 237 (2002).
41. A. Solyemanpour, M. Shamsipur, M. Akhond and H. Sharghi, *Electroanalysis*, **16**, 282 (2004).
42. M. Shamsipur, A. Solyemanpour, M. Akhond, H. Sharghi and M.H. Savari, *Electroanalysis*, **17**, 776 (2005).
43. J. Janata, M. Josowicz, P. Vansek and D.M. DeVaney, *Anal. Chem.*, **70**, 179 (1998).
44. P. Kane and D. Diamond, *Talanta*, **44**, 1847 (1997).
45. E. Bakker, R.K. Mervura, E. Pretsch and M.E. Mererhoff, *Anal. Chem.*, **66**, 3021 (1994).
46. A. Solymanpour, E. Hamidi Asl and S.M. Nabavizaheh, *Sens. Actuators B*, **120**, 447 (2007).

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