Polymeric Membrane and Solid Contact Electrodes Based on Schiff Base Complexes of Co(III) for Potentiometric Determination of Perchlorate Ions

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New PVC based polymeric membrane electrodes (PME) and coated glassy carbon electrodes (CGCE) based on synthesized Schiff base complexes of Co(III): $[Co(Salen)(PBu_3)_2]ClO_4$, $[Co(Me_2Salen)(PBu_3)_2]ClO_4$, $[Co(Salen)(PBu_3)H_2O]ClO_4$; as anion carriers for potentiometric determination of ClO_4^- were studied. The PME and also CGCE electrodes prepared with $[Co(Me_2Salen)(PBu_3)_2]ClO_4$ showed excellent response characteristics to perchlorate ions. The electrodes exhibited Nernstian responses to ClO_4^- ions over a wide concentration range with low detection limits (1.0×10^{-6} mol L^{-1} for PME and 9.0×10^{-7} mol L^{-1} for CGCE). The electrodes possess fast response time, satisfactory reproducibility, appropriate lifetime and, most importantly, good selectivity toward ClO_4^- relative to a variety of other common inorganic anions. The potentiometric response of the electrodes is independent of the pH in the pH range 2.5-8.5. The proposed sensors were used in potentiometric determination of perchlorate ions in mineral water and urine samples. The interaction of the ionophore with perchlorate ions was shown by UV/Vis spectroscopy.

Key Words : Perchlorate selective electrode, PVC membrane electrode, Schiff base complex, Potentiometry, Sensors

Introduction

Perchlorate is regarded as an emerging persistent inorganic contaminant because of its specific properties such as high water solubility, mobility and considerable stability. Perchlorate have been used extensively as missile propellants, wet digestions, organic syntheses, electro-polishing of metals, animal feed additives, explosives, pyrotechnics and herbicides.[1] In addition, it has been found as a contaminant in certain fertilizers or Chilean saltpeter. The most common commercial compound is Ammonium Perchlorate, a kind of explosive solid rocket propellant (up to 70 wt.%) and an inflating reagent in automobile air bag inflation system. Moreover, perchlorate is a human health concern at high doses due to its ability to interfere with iodide uptake and the ability of the thyroid to regulate hormone production and metabolism.[2] Perchlorate salts have been used to treat patients with hyperactive thyroid glands (Graves' disease) and to carry out diagnostic tests.[3] Therefore, Perchlorate anions may be found at high concentration (more than 1000 ppm) in surface and ground waters due to disposal of perchlorate salts in different products.[3] Health risks at lower doses are still not well understood and studies are being conducted by the Environmental Protection Agency (EPA) in order to determine safe levels in drinking water. Thus, the determinations of perchlorate ions in different samples such as ground water, propellants, explosives and urine have been very important.

Several different methods have been used for the analysis of perchlorate ions in drinking water and environmental samples.[4-9] Ion chromatography has been primary means of these methods. However, most of these methods are either time-consuming or need expensive instruments and also well-control experimental conditions and, most importantly, suffer from various interferences of cationic or anionic species. Hence, major efforts have been made to develop more convenient direct methods for the quick, easy and inexpensive assay of perchlorate ions in different samples. One technique that holds excellent promise as a routine monitoring device is potentiometric measurement *via* an ion-selective electrode (ISE). Ion-selective polymeric membrane electrodes incorporating ion carriers with unique characteristics, such as ease of preparation, nondestructive, fast response, low cost, unaffected by color and turbidity, wide linear range, relatively low detection limit and especially reasonable selectivity, can be very suitable tools for determination of perchlorate ions in different samples.

During the last three decades, many efforts have been focused on the introduction perchlorate-selective electrodes. Most of these reported electrodes were polymeric liquid membranes based on ion exchangers, where the electroactive species including perchlorate ion-association complexes with cations and different metal chelates,[10-14] long chain quaternary ammonium ions[15-17] and organic dyes,[18,19] have been dissolved in various organic solvents. However, many of these electrodes are not sensitive and selective enough to permit selective measurement of low levels of perchlorate and also are susceptible to interferences from other common anions such as OH^-, NO_3^-, SCN^-, ClO_3^- and I^-. Thus, in the past decade, there has been a growing interest to search suitable ionophores to construct carrier-based perchlorate selective electrodes with improved selectivity and sensitivity.[20-26] These reported electrodes were based on coordinative ionophores that showed some extent selectivity and sensitivity. But, some of these electrodes still possess various limitations such as narrow concentration range, inadequate response time or poor reproducibility and selectivity and were usual polymeric membrane electrodes having an internal solution. Thus, it is still desirable to continue efforts to construct perchlorate-selective electrodes with wider concentration range and lower detection limit and, most importantly, solid contact perchlorate-selective electrodes for more stability and selectivity. The aim of this paper is developing new polymeric membrane (PME) and solid contact coated glassy carbon (CGCE) perchlorate ion-selective electrodes (ISEs) based on synthesized cobalt(III) complexes; $[Co(Salen)(PBu_3)_2]ClO_4$, $[Co(Me_2Salen)(PBu_3)_2]ClO_4$, $[Co(Salen)(PBu_3)H_2O]ClO_4$; (Fig. 1) as perchlorate ionophores for simple, selective and rapid determination of perchlorate ions in different samples.

Experimental

Reagents. Reagent grade *o*-nitrophenyl octyl ether (NPOE), diocthyl sebacate (DOS), dibuthyl sebacate (DBS), dimethyl sebacate (DMS) and dibuthyl phthalate (DBP) used as plasticizers, tetrahydrofuran (THF), hexadecyl trimethylammonium bromide (HTAB) and high relative molecular weight PVC (all from Merck) were used as received. Sodium and potassium salt of anions (all from Merck) were of highest purity available and used without any further purification except for vacuum drying. Doubly distilled water was used throughout for preparing all aqueous solutions. The pH adjustments were made with dilute hydrochloric acid or potassium hydroxide solution as required. The Schiff base complexes of cobalt(III) were synthesized and purified according to the previously reported procedures.[27,28]

Electrode preparation. The general procedure to prepare the PVC membranes was to dissolve varying amount of ionophore, additive HTAB and powdered high molecular weight PVC in 5 mL THF. To these, appropriate amount of plasticizers were added. Then, the mixture was shaken vigorously. The resulting solution was evaporated slowly at ambient temperature until an oily concentrated solution was obtained. A Pyrex tube (3 mm i.d. on top) was dipped into the solution for about 10 s, so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled up from the mixture and kept at room temperature for about 6 h. The tube was then filled with an internal filling solution (1.0×10^{-2} mol L^{-1} $NaClO_4$). The electrode was finally conditioned for 14 h by soaking in a 1.0×10^{-2} mol L^{-1} $NaClO_4$ solution. A silver/silver chloride was used as an internal reference electrode.

To prepare the coated glassy carbon electrodes (CGCE), a Metrohm glassy carbon electrode with a 3 mm diameter was used. The working surface of the electrode was polished with fine alumina slurries on a polish cloth, sonicated in distilled water and then dried in air. The polished glassy carbon electrode was dipped into the membrane solution mentioned above, and the solvent was evaporated slowly. A thin layer of membrane was formed on the glassy carbon surface, and the electrode was allowed to stabilize under ambient conditions overnight. The electrode was finally conditioned by soaking in a 1.0×10^{-2} mol L^{-1} $NaClO_4$ solution for about 24 h. An unmodified polished glassy carbon electrode was also tested for comparative purposes, and found that it did not show any potentiometric response to perchlorate ion solutions, after the conditioning period.

Emf measurements. All emf measurements with the polymeric membrane electrodes (PME) and coated glassy carbon electrodes (CGCE) were carried out with the following cell assembles:

Ag-AgCl/KCl (3 mol L^{-1})|internal solution, 1.0×10^{-2} mol L^{-1} $NaClO_4$|
PVC membrane|test solution|Ag-AgCl, KCl (satd) (PME)

Ag-AgCl (satd)|test solution|membrane|graphite surface (CGCE)

The emf observations were made relative to a double-junction silver/silver chloride electrode containing saturated solution of KCl (Metrohm) with the chamber filled with a potassium chloride solution. A silver/silver chloride electrode containing a 3 mol L^{-1} solution of KCl was used as the internal reference electrode.

Results and Discussion

Preliminary potentiometric studies. Previous studies revealed that the Schiff base-metal ion complexes containing central metal ions such as Cr(II), Mn(II), Fe(III), and Ce(III) exhibit anion selectivity deviating from Hofmeister series.[29-33] Thus, we were interested to investigate the possibility of the use of our synthesized Schiff base complexes (Fig. 1) as an anion carrier in liquid membrane electrodes. Therefore, in preliminary experiments different membrane electrodes with these complexes were prepared and potentiometric responses of these electrodes to different anions were obtained. The electrode based on $[Co(Me_2Salen)(PBu_3)_2]ClO_4$ Schiff base complex (L3) showed excellent potential responses to ClO_4^- than the other complexes L1 and L2. The potential responses of the PVC membrane electrode containing L3 to different anions, after conditioning in the potassium salt solution of each anion, in the concentration range 5.0×10^{-7}-2.5×10^{-1} mol L^{-1} are shown in Figure 2. As seen, except for ClO_4^-, all other anions tested showed weak responses due to lower interaction with the ionophore in the membrane. We therefore studied in detail the properties of a perchlorate-selective electrode based on complex L3.

The potential responses of the PVC membrane electrodes containing different Schiff base complexes as a carrier to

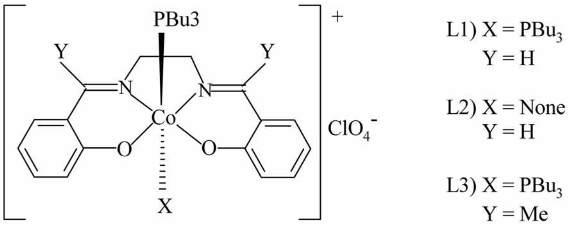

Figure 1. Structure of cobalt(III) Schiff base complexes.

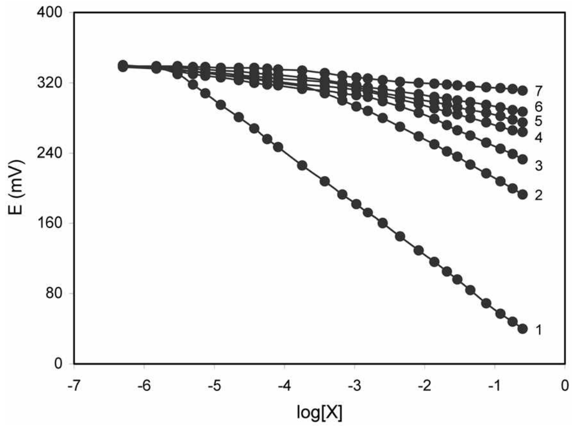

Figure 2. Potential responses of various anion selective electrodes based on cobalt complex L3: (1) ClO_4^-; (2) SCN^-; (3) I^-; (4) NO_2^-; (5) Br^-; (6) NO_3^-; (7) SO_4^{2-}.

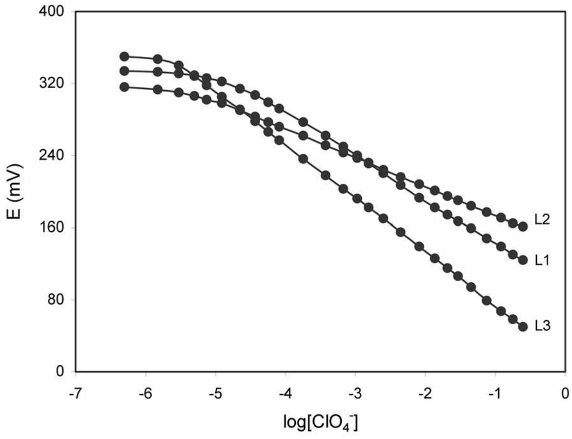

Figure 3. Potential response of various cobalt(III) complexes (L1-L3) to perchlorate ions.

perchlorate ions are shown in Figure 3. As can be seen from Figure 3, under similar experimental conditions, the efficiency of complex L3 as a ClO_4^- ion carrier in the membrane is more than the other two complexes L1 and L2 most probably due to the existence of PBu_3 and Me group in the coordination ligand around cobalt central ion. This can show the effect of organic ligand structure of metal ion complexes on the response of carrier-based anion selective electrodes.

It is well-known that in the case of ionophores based on different metal ion complexes, in addition to the electrostatic interaction between the central metal ion and analyte anion, there is a coordination action between both species involved.[29-33] Thus, the selectivity sequence is dominated by both electrostatic and coordination forces and it is expected that both the nature of the central metal ion and the coordination ligand properties play important roles in determining the selectivity of the ionophore towards a specific anion. Thus, UV/Vis was used as a suitable tool to show interaction between the cobalt complex (L3) and perchlorate anions. As illustrated in Figure 4, in acetonitrile, the complex (1.0×10^{-4} mol L^{-1}) showed an absorption peak at 417.4 nm. The addition of an equimolar amount of sodium perchlorate to this solution resulted in a simultaneous distinct decrease in absorption band with an intensive wavelength shift to 389.2 nm and also the appearance of a new band with absorption maximum at 618.4 nm. The substantial decrease in the absorbance of ionophore complex with appearance of a new peak and change of the color of the solution, after contact of the carrier solution with ClO_4^- ions, revealed the specific interaction between the ionophore in the membrane and perchlorate ions.[34-36] Moreover, to show the extent of selectivity of the ionophore to the perchlorate ions, the influences of other anions on the spectrum of the cobalt ionophore complex were also investigated, and almost no detectable spectral changes were observed.

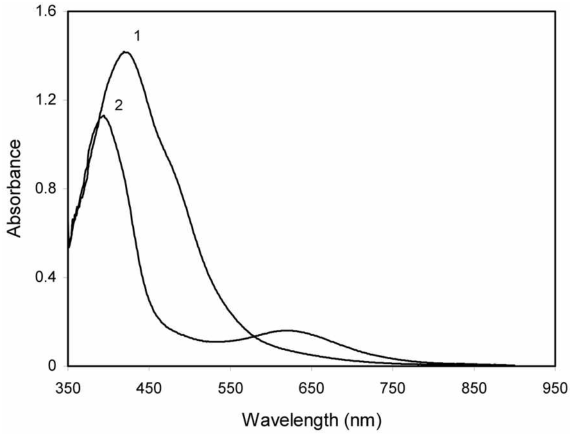

Figure 4. UV/Vis absorption spectra of 1.0×10^{-4} mol L^{-1} solution of L3 in the (1) absence and (2) the presence of 1.0×10^{-4} mol L^{-1} of $NaClO_4$ in dry acetonitrile.

Optimization of membrane components. The sensitivity, selectivity and linearity of ion selective sensors not only depend on the nature of the ionophores used but also significantly on the membrane composition and the properties of the plasticizers and additives used.[37-41] Thus, the effect of the membrane composition, the nature and of the plasticizer and the amount of additive on the potential response of the ClO_4^- sensor were investigated and the results are summarized in Table 1. As seen from Table 1, the key ingredient in the membrane is ionophore L3. In fact, in the absence of ionophore, the resulting membrane revealed a very limited response due to the lipophilic characteristic of perchlorate anions. Since the nature of the plasticizer influences both the dielectric constant of the membrane phase and the mobility of the ionophore molecules, it was expected that the kind of plasticizer plays an important role in determining the ion selective electrode characteristics.[38-42] Among six plasticizers examined, NPOE resulted in the best sensitivity and linear range. Moreover, 3.2% of the ionophore and a plasticizer/PVC ratio of 2 (No. 2) were chosen as the optimum amount in the PVC membrane. A further addition of ionophore (3.5%) however resulted in some decreased response of the electrode most probably due to some inhomogeneities of the membrane.[43]

It has been clearly shown that in liquid membrane electrodes based on neutral carriers, the presence of lipophilic

Table 1. Optimization of membrane ingredients

No.	Composition (%)				Slope (mV/decade)	linear range (mol L^{-1})
	PVC	Plasticizer	L3	HTAB		
1	32.0	NPOE, 65.0	3.0	0.0	54.4	1.2×10^{-5} - 4.5×10^{-2}
2	32.0	NPOE, 64.8	3.2	0.0	56.5	7.5×10^{-6} - 7.6×10^{-2}
3	32.0	NPOE, 64.5	3.5	0.0	55.2	1.2×10^{-5} - 1.2×10^{-1}
4	32.0	NPOE, 64.6	3.2	0.2	57.1	4.9×10^{-6} - 1.8×10^{-1}
5	32.0	NPOE, 64.4	3.2	0.4	59.3	3.0×10^{-6} - 2.5×10^{-1}
6	32.0	BA, 64.4	3.2	0.4	41.2	5.7×10^{-5} - 4.5×10^{-2}
7	32.0	DOS, 64.4	2.6	0.4	44.1	3.7×10^{-5} - 7.6×10^{-2}
8	32.0	DBS, 64.4	2.6	0.4	36.4	8.2×10^{-5} - 4.5×10^{-2}
9	32.0	DBP, 64.4	2.6	0.4	39.6	8.2×10^{-5} - 7.5×10^{-2}
10	32.0	DMS, 64.4	2.6	0.4	32.7	1.8×10^{-4} - 2.9×10^{-2}

additives are necessary to introduce permselectivity, so that without such additives many electrodes fail to respond properly.[39,44] As seen, in the absence of additive, the proposed electrode with the optimum amount of ligand (No. 2) doesn't show Nernstian response characteristics. It has shown that the presence of lipophilic positively charged additives such as HTAB improves the potentiometric behavior of anion selective electrodes not only by improving the response behavior but also by enhancing the sensitivity of the membrane electrode.[39] Thus, the presence of a lipophilic cationic ion exchanger in the membrane composition was tested. The presence of 0.4% HTAB (No. 5) provided electrodes with Nernstian behavior in wider concentration range potential response.

Effect of internal reference solution. The influence of the concentration of the internal solution on the potential response of the ClO_4^- ion selective PME was studied. The $NaClO_4$ concentration was changed from 1.0×10^{-1} to 1.0×10^{-4} mol L^{-1} 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 the resulting Nernstian plot. A 1.0×10^{-2} mol L^{-1} concentration of the internal reference solution was chosen because of the better correlation coefficient of the calibration plot ($R^2 = 0.998$).

Response characteristics of the perchlorate-selective electrodes. Before use, the liquid membrane electrode must be conditioned by soaking in the anion solution in order to ensure the equilibrium at the membrane-water interface. Optimum conditioning time for the PME and CGCE in a 1.0×10^{-2} mol L^{-1} sodium perchlorate solution was found to be 14 and 24 h, respectively. The conditioned electrodes then generated stable potentials when placed in contact with ClO_4^- solutions. The average time required for the membrane sensors to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of a series of perchlorate ion solutions, each having 10-fold difference in concentration, was less than 7 s over the entire concentration range and the potentials stayed constant after this time. The standard deviation of the potential responses over a period of 4 h in 1.0×10^{-3} mol L^{-1} of ClO_4^- ions was 0.9 mV ($n = 24$) which shows good stability of potential responses of the proposed electrodes. Moreover, the potential reading for the electrode dipped alternatively into stirred solutions of 1.0×10^{-3} and 1.0×10^{-4} mol L^{-1} of ClO_4^- represented a standard deviation of 0.7 mV ($n = 6$).

The lifetime of an ion-selective electrode is usually defined as the time interval between the conditioning of the membrane and the moment when at least one of its response characteristics changes. The relative lifetime of the proposed perchlorate electrodes was studied by periodically recalibrating in a standard ClO_4^- solution and calculating the response slope over the range of 5.0×10^{-7} to 5.6×10^{-1} mol L^{-1} $NaClO_4$ solutions. Before each measurement, the electrodes were conditioned in a 1.0×10^{-2} mol L^{-1} sodium perchlorate. The experimental results showed that the lifetime of the ClO_4^--selective electrodes were about two month. During this time the detection limit and slope of the electrodes remained almost constant.

The emf response of the proposed ClO_4^- selective electrodes based on Schiff base complex L3 (prepared under optimal membrane ingredients) at varying concentrations of perchlorate ions (Fig. 5) indicated a linear range from 3.0×10^{-6} to 2.5×10^{-1} mol L^{-1} for PME and from 1.5×10^{-6} to 1.8×10^{-1} mol L^{-1} for CGCE. The slopes of calibration curves were 59.3 ± 0.4 mV/decade ($n = 6$) for PME and 58.4 ± 0.3 mV/decade ($n = 6$) of ClO_4^- ion concentration for

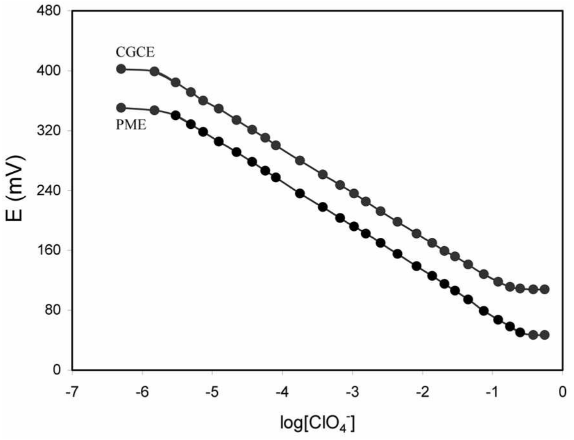

Figure 5. Calibration graphs for the PME and CGCE.

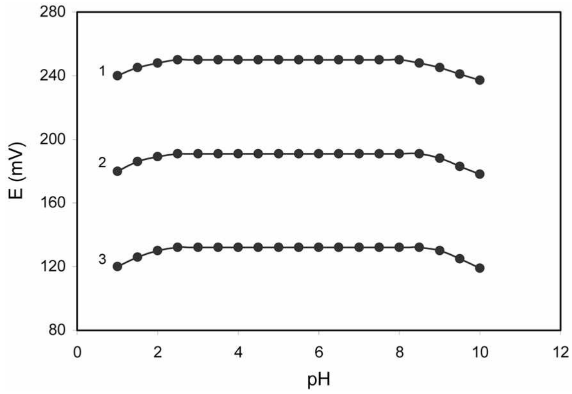

Figure 6. Effect of pH of the test solution on the potential response of the perchlorate-selective electrode (PME) at three different ClO_4^- concentrations: (1) 1.0×10^{-4} mol L^{-1}; (2) 1.0×10^{-3} mol L^{-1}; (3) 1.0×10^{-2} mol L^{-1}.

CGCE at 25 °C. The limit of detection, as determined from the intersection of two extrapolated segments of the calibration graph, was 1.5×10^{-6} and 9.0×10^{-7} mol L^{-1} for the PME and CGCE, respectively.

Effect of pH. The pH dependence of the potential response of the proposed membrane sensors at three different concentrations of ClO_4^- ions in the pH range of 1-10 was tested and the results are shown in Figure 6. As seen, the electrode potential was independent of pH in the range 2.5-8.5. The observed potential drift at lower pH values is most probably due to the increase of the Cl^- ion concentration and simultaneous response of the electrode to perchlorate and chloride ions. While at higher pH values the drift could be due to the interference of OH^- and the simultaneous response of the electrode to ClO_4^- and OH^- anions.

Effect of non-aqueous media on the electrode response. In some cases the samples may contain non-aqueous content to dissolve the ingredients of sample properly. Thus, it's appreciable the electrode can work well in such media. Therefore, the performance of the proposed sensors was investigated in partially non-aqueous media using methanol, ethanol and acetone mixtures with water. The calibration plot of the electrode was obtained in the different mixture (v/v) of methanol-water, ethanol-water and acetone-water. From the data obtained (Table 2), it was concluded that the membrane electrodes worked satisfactorily in mixtures up to 30% (v/v) non-aqueous content. In these mixtures the working concentration range and slope didn't change reasonably, only a little decrease was observed. Therefore, the electrodes can be applied in solution having up to 30% non-aqueous content. However, above 30% non-aqueous content, the slope and working concentration range were reduced, and the potentials showed drift probably due to leaching of the membrane ingredients and so caused a significant interference in electrode functioning.

Table 2. Effect of partially non-aqueous media on the response of ClO_4^--selective polymeric membrane electrode (PME)

Non-aqueous content (% v/v)	Slope (mV/decade)	linear range (mol L^{-1})
0	59.3	3.0×10^{-6} - 2.5×10^{-1}
Methanol		
10	59.1	5.0×10^{-6} - 2.5×10^{-1}
20	59.0	5.0×10^{-6} - 2.5×10^{-1}
30	58.3	7.5×10^{-6} - 1.8×10^{-1}
Ethanol		
10	58.9	7.5×10^{-6} - 2.5×10^{-1}
20	58.6	1.2×10^{-5} - 2.5×10^{-1}
30	57.8	2.2×10^{-5} - 1.2×10^{-1}
Acetone		
10	58.8	5.0×10^{-6} - 2.5×10^{-1}
20	57.9	1.2×10^{-5} - 1.8×10^{-1}
30	57.0	7.0×10^{-5} - 7.5×10^{-2}

Potentiometric selectivity coefficients. The selectivity behavior is the most important characteristics of an ion selective electrode as it determine the applicability of any sensor at the presence of foreign ions in the samples. Selectivity interprets relative electrode response for the primary ion (A) over other ions present in solution (B), which is usually expressed in terms of potentiometric selectivity coefficient ($K_{A,B}^{pot}$). The potentiometric selectivity coefficients were determined by the matched potential method (MPM).[45] This is a recommended procedure which has advantage of removing limitations imposed by Nicolsky-Eisenman equation while calculating selectivity coefficient by other usual methods. These limitations usually include non-Nernstian behavior of interfering ions and also inequality of charges of primary and interfering ions.[46] In this method the selectivity coefficient was determined by measuring the change in potential upon increasing in primary ion activity from an initial value of a_A to a'_A and a_B represents the activity of interfering ion added to the reference solution of primary ion of activity a_A which also brings about same potential change. The match potential method selectivity is then determined as $K_{A,B}^{MPM} = a'_A - a_A/a_B$. The activity coefficients of proposed ClO_4^--selective electrodes were

Table 3. Potential selectivity coefficients of various interfering anions

Interfering anion	log ($K_{A,B}^{pot}$)	
	PME	CGCE
Br^-	−3.9	−4.2
NO_3^-	−3.6	−4.0
SO_4^{2-}	−4.1	−4.4
Cl^-	−3.8	−4.1
I^-	−1.8	−2.2
SCN^-	−1.7	−2.0
F^-	−3.6	−4.1
ClO_3^-	−2.9	−3.2
$C_2O_4^{2-}$	−3.0	−3.3
OAc^-	−3.3	−3.6
NO_2^-	−2.9	−3.4
HCO_3^-	−3.1	−3.5

Table 4. Determination of perchlorate ions in mineral water and human urine

Sample	Perchlorate (μg mL^{-1})		
	Added	Found	Recovery%
Mineral water	10.0	9.7 ± 0.4	96.0
	100.0	98.2 ± 0.6	98.2
	1000.0	1025 ± 1.2	102.5
Human urine	10	10.1 ± 0.5	101.0
	100	97.9 ± 0.6	97.1
	1000	1029 ± 2.0	102.9

taken in a 1.0 × 10^{-4} mol L^{-1} $NaClO_4$ reference solution. The resulting selectivity coefficients obtained for PME and CGCE are listed in Table 3. From the data given in Table 3, it is revealed that the proposed perchlorate electrodes have good selectivity toward perchlorate ions with respect to anions such as chloride, bromide and nitrate. So, the disturbance produced by these anions is negligible in the determination process of perchlorate ions in the presence of foreign anions. Moreover, a comparison between the selectivity coefficients for the PME and, especially CGCE, with those previously reported for other ionophore based perchlorate ion-selective electrodes[20-26] revealed that the proposed electrodes show somewhat similar, in most cases or even superior, in some cases, selectivity behavior to the PVC membrane sensors prepared previously. However, the proposed electrodes based on the cobalt Schiff base complex are superior in terms of concentration range, detection limit and response time. Moreover, it should be noted that lack of internal solution and more mechanical stability are the most advantages of proposed solid contact CGCE over usual perchlorate selective liquid membrane electrodes reported previously.[47]

Analytical applications. Quantitative measurements of perchlorate ions in water and also urine were found to be important because of health effect of perchlorate ion in human being.[48] The high perchlorate selectivity of the proposed electrodes makes it potentially useful for monitoring the concentration of perchlorate ions in different samples. Thus, to assess the practical application of proposed perchlorate-selective electrode, it was used for the determination of perchlorate ions in mineral water (Damavand mineral water, marketed in Iran) and urine sample. Different amounts of ClO_4^- ions were spiked into mineral water and also urine sample, and then the ClO_4^- contents of the samples were measured. The results of the analysis of the samples are given in Table 4. As is obvious, the recoveries obtained by the proposed perchlorate-selective electrode are quantitative at the various perchlorate concentrations tested.

Conclusions

This work revealed that the proposed liquid membrane perchlorate-selective electrodes PME and CGCE based on cobalt Schiff base complex, L3, could be used as useful analytical tools and interesting alternatives for the determination of perchlorate ions in different samples. The electrodes showed good sensitivity, low detection limit, appropriate selectivity and stability and applicability over a wide pH range. The electrodes characteristics such as linear range, detection limit, life and response time and specially selectivity are comparable to the previously reported PVC membrane perchlorate-selective electrodes. Major advantage of the proposed electrodes concerns their applicability of direct measurement of perchlorate ions in different samples such as mineral water and urine without prior separation steps.

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