

Perchlorate-selective polymeric membrane electrode based on bis(dibenzoylmethanato)cobalt(II) complex as a neutral carrier

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ABSTRACT

A synthesized bis(dibenzoylmethanato)Co(II) complex ($\text{Co}(\text{DBM})_2$), has been used as a ionophore for the preparation of a new perchlorate ion-selective electrode. The electrode exhibits a Nernstian response over the perchlorate concentration range of 8.0×10^{-7} – 1.0×10^{-1} M with a slope of 60.3 ± 0.5 mV per decade of concentration. The limit of detection as determined from the intersection of the extrapolated linear segments of the calibration plot is 5.6×10^{-7} M. The electrode shows good selectivity towards perchlorate with respect to many common anions. The response time of the sensor is very fast (≤ 5 s), and can be used for at least 2 months in the pH range of 2.0–9.0. The electrode was used to determine perchlorate in water and human urine. The interaction of the ionophore with perchlorate ions was demonstrated by UV–vis spectroscopy.

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1. Introduction

Perchlorate is regarded as a new emerging persistent inorganic contaminant because of its specific properties, such as high water solubility, mobility and considerable stability [1]. One of the major sources of this environmental contamination is the manufacture or improper storage or disposal of ammonium perchlorate which is used as a primary component of solid propellant for rockets, missiles, fireworks [2–4], or explosives in various military munitions and air bag inflators [5]. Perchlorate has also been found in food products [6–8], soil [9], milk [10], fertilizers [11], plants [12] and in human urine [13].

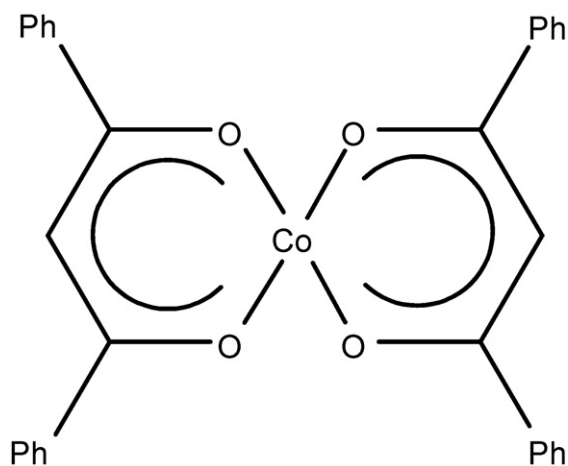
The perchlorate and iodide ion have a similar size, therefore can be taken up in place of it by the mammalian thyroid gland. In this way, perchlorate can be affected on the production of thyroid hormones. Moreover, other physiologic systems may be indirectly affected. It is due to the abnormalities in child development and the thyroid cancer. It poses the greatest threat in the drinking water of expectant mothers, children under 12 years and persons with mal-functioning thyroids. Perchlorate ions have also been applied as growth promoters and as thyrostatic drugs in cattle fattening [14]. Thyroid gland tumors were spotted in rodent animals after exposure to high dose of perchlorate [15]. The toxicologic mechanisms through which perchlorate exerts its effects have been reviewed in some reports [16–18].

According these findings, several organizations have been identified standard levels for perchlorate. The National Academy of Science's (NAS's), in the January 2005, was reported maximum permissible dose of $0.7 \mu\text{g}/\text{kg}/\text{day}$ for perchlorate concentration, which correlates to a drinking water equivalent level of $24.5 \mu\text{g}/\text{L}$ if drinking water is considered as the only source of perchlorate [19]. In February 2005, also the United States Environmental Protection Agency (US EPA) set the $24.5 \mu\text{g}/\text{L}$ as an official reference dose (RFD) for perchlorate in drinking water, which is consistent with the RFD recommended by NAS [20].

Therefore, determination of perchlorate ion in various samples such as ground water, propellants, explosives and urine in the presence of other anions is of special importance [21]. The determination of perchlorate ions has been carried out directly or indirectly by a variety of classical and instrumental methods, including volumetric titrations [22], gravimetry [23], spectrophotometry [24], atomic absorption spectrophotometry [25], and chromatography [14]. These methods also suffer from various interferences. Therefore, a simple, rapid, sensitive and selective method for the determination of perchlorate ion is required. One technique that holds excellent promise as a routine monitoring device is potentiometric measurement via an ion-selective electrode. It is well known that ISE is one of the few techniques that can measure both positive and negative ions depending on the nature of the ionophore. In fact a number of ion-selective electrodes for target cations and anions have been reported [26].

Potentiometric detection based on ion-selective electrodes (ISEs), as a simple method, has several advantages, such as speed, ease of preparation and procedures, simple instrumentation, fast

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Scheme 1. Molecular structure of bis(dibenzoylmethanato)cobalt(II) complex.

response, free of contamination, being nondestructive, unaffected by color or turbidity, wide dynamic range and reasonable selectivity. Over the last few years, the list of available electrodes has been grown substantially.

In the biological, medicinal and environmental processes Anions play fundamental roles in a wide range and because of their significance, the development of synthetic receptors and sensors for anions have been growing in importance over the past years [27–29]. Anions are larger than cations, so they require ionophores with a much larger binding site; anions have many different shapes; anions are more strongly hydrated than cations of the same size while their salvation by organic solvents is generally more difficult.

The traditional anion-selective membrane electrodes based on ion exchangers always display a Hofmeister selectivity sequence, as follows: perchlorate > thiocyanate > iodide \approx salicylate > nitrate > bromide > nitrite > chloride > sulfate, in which a membrane selectivity is controlled by the free energy of hydration of the ions involved, and recent studies have been more concerned on the electrodes using plasticized poly(vinyl chloride) (PVC) membranes incorporating different complexes as a carrier [30].

The perchlorate ion-selective electrode has an extensive history and has been under development for about 30 years. Several perchlorate-selective electrodes have been reported based on ion-association complexes between perchlorate anions and different organic compounds (long-chain quaternary ammonium ions, organic bases, organic dyes and metal chelates) [26,31–34]. All of these ion-selective electrodes suffer the lack selectivity and are composed of considerable interference effect from common contaminants such as OH^- , NO_3^- , MnO_4^- , IO_4^- , SCN^- and ClO_3^- ions. For most of these electrodes, a thorough study of their selectivity for a large number of inorganic and organic anions has not been carried out. However, in comparison, only a few recent reports on the carrier-based polymeric membrane perchlorate ion-selective electrodes are available [35–39].

This paper describes the construction and evaluation of a plasticized PVC membrane perchlorate-selective electrode based on $\text{Co}(\text{DBM})_2$ (Scheme 1) for simple, selective and rapid determination of perchlorate with high linear dynamic range. The response time of ion-selective electrodes especially in flow systems is very important, because the sampling rate and sensitivity for determination are dependent on the response time. The proposed electrode was used successfully for direct determination of perchlorate in the water and urine samples without need for prior separation steps.

2. Materials and methods

2.1. Reagent

For preparation of polymeric ion-selective membranes, poly(vinyl chloride) of high relative molecular weight was purchased from Fluka. Methyltriocetylammmonium chloride (MTOAC), tetrahydrofuran (THF), dibutyl phthalate (DBP), dioctyl phthalate (DOP), sulfuric acid, sodium hydroxide, and salts of all the anions, investigated as interferences, were all of analytical reagent grade from Merck and were used as received.

A 0.1 M stock solution of perchlorate was prepared by dissolving an appropriate, accurate amount of KClO_4 (Merck). A 1.0×10^{-7} – 1.0×10^{-1} M solution of perchlorate was prepared daily by sequential dilution of the appropriate stock solution with doubly distilled water. Sodium and potassium salts of anions (all from Merck) were of the highest purity available.

Adjustments of pH were made with dilute sulfuric acid or sodium hydroxide. Wastewater samples were filtered through filter paper.

The bis(dibenzoylmethanato)cobalt(II) complex was synthesized and purified by a previously reported method [40].

2.2. Construction and calibration of electrodes

The PVC based membranes were prepared by dissolving the appropriate amounts of PVC, $\text{Co}(\text{DBM})_2$, plasticizer (for example DBP), and an additive (MTOAC) with lipophilic cation in the minimum amount of THF. The optimum composition was 27.90% of powdered PVC, 66.20% of a plasticizer (DBP), 2.40% of an additive (MTOAC) and 3.50% of the corresponding ionophore ($\text{Co}(\text{DBM})_2$).

The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3 mm o.d.) was dipped into the mixture for about 10 s, so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for about 10 h. The tube was then filled with an internal filling solution (1.0×10^{-1} M KClO_4). The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} M KClO_4 solution. A SCE electrode (Standard Calomel Electrode) was used as the reference internal electrode.

2.3. Apparatus and emf measurements

A UV–vis spectrophotometer (Jasco, model V-540) with a 1.0 cm glass cuvette was used for the recording of absorption spectra. A perchlorate-selective PVC electrode and a saturated calomel electrode (SCE) were used as an indicator electrode and a reference electrode, respectively. The emf measurements were carried out at room temperature with a Schott pH meter Model GG-825 in the following cell.

2.3.1. S.C.E./test solution/ISE

The potential reading of each solution was recorded when it became stable, and then plotted as a logarithmic function of ClO_4^- anion concentration. The activities of anions were based on the activity-coefficient γ , data calculated from the modified form of Eq. (1) (Debye-Huckel Eq.), which is applicable to any ion:

$$\log \gamma = -0.511Z^2 \left[\frac{\mu^{1/2}}{(1 + 1.5\mu^{1/2}) - 0.2\mu} \right] \quad (1)$$

where μ is the ionic strength and Z is the valency. All measurements were carried out at 25 ± 0.1 °C.

2.4. Sensor selectivity

Potentiometric selectivity coefficients ($K_{\text{ClO}_4^-; \text{A}^-}^{\text{Pot}}$) were evaluated according to IUPAC guidelines using the separate solutions method (SSM) [41], in which the potential of a cell comprising the membrane electrode and a reference electrode is measured with two separate solutions, one containing the perchlorate ion A of the activity a_A (but no B) and the other containing the interfering ion B of the same activity $a_A = a_B$ (but no A). Here the measured potential values are expressed by E_A and E_B , respectively. Different interfering anions of a concentration of 1×10^{-3} M are utilized and the results are obtained using Eq. (2):

$$\log K_{\text{A},\text{B}}^{\text{Pot}} = \left[\frac{E_B - E_A}{S} \right] + \log a_A \left[\frac{1 - Z_A}{Z_A} \right] \quad (2)$$

where $K_{\text{A},\text{B}}^{\text{Pot}}$ is the potentiometric selectivity coefficient, S the slope of the calibration plot, a_A the activity of perchlorate, and Z_A and Z_B are the charges on ClO_4^- and the interfering anion, respectively.

3. Results and discussion

In this work, a cobalt(II) complex was examined as perchlorate-selective ionophores in polymeric membrane ISEs. In preliminary experiments, to investigate the suitability of the cobalt(II) complex, different membrane electrodes with this complex were prepared and potentiometric responses of these electrodes to different anions were measured. As seen in Fig. 1, except for ClO_4^- , all other anions tested showed weak responses due to lower interaction with the ionophore in the membrane. Therefore, membrane electrode based on Co(II) complex was found to be highly responsive to perchlorate ion relative to several other anions. Then for test the membrane, various performance characteristics, such as effect of membrane composition, selectivity, response time, sensitivity, lifetime, working range of the electrode at different concentrations of the anion and pH were investigated.

3.1. Preliminary potentiometric studies

It is well established that the selective interaction of an anion and a lipophilic ion carrier within the membrane

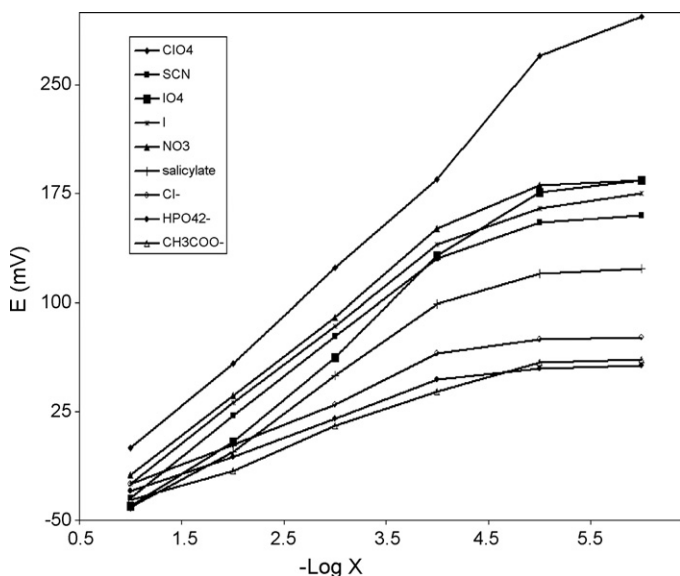


Fig. 1. Potential responses of various anion-selective electrodes based on cobalt(II) complex.

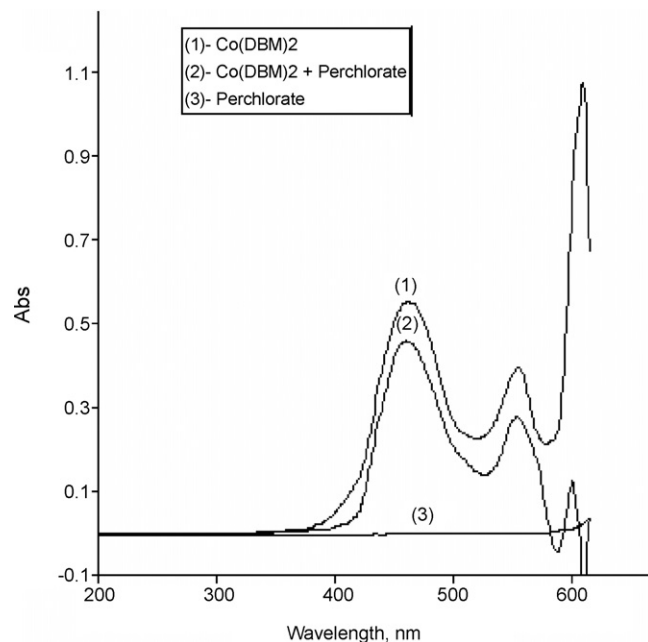


Fig. 2. UV-vis absorption spectra of 1.0×10^{-4} M Co(II) complex in acetonitrile in the (1) absence and (2) presence of 1.0×10^{-4} M ClO_4^- and (3) 1.0×10^{-4} M ClO_4^- without Co(II) complex.

is essential for the development of anion-selective membranes [35–37,42–45]. In the case of organometallic compounds [46] and metalloporphyrin derivatives [31,35,43,44], the anion selectivity is mainly governed by a specific interaction between the central metals and the anions rather than the lipophilicity of the anions or a simple opposite charge interaction with anions [47]. The preferential response of the ionophore used towards ClO_4^- is believed to be associated with the coordination of perchlorate to the metal center in the complex bis(dibenzoylmethanato)cobalt(II), and it is the relative affinity of the ClO_4^- as a suitable ligand for Co(II) that dictates the observed selectivity pattern of the electrodes.

The UV-vis spectrum presented in Fig. 2, indicates that there is a specific interaction between the Co(II) complex and the perchlorate ions. The results show that the absorption bands of a solution of 1.0×10^{-4} M Co(II) complex in acetonitrile, having two maxima at wavelengths of 460 and 555 nm, have changed absorbance in the presence of an equimolar amount of perchlorate ions. It has been well established that when a ligand with donating atoms of hard character such as oxygen atom is coordinated to a metal ion, some hard character is imparted to the metal ion and the probability of the interaction between the metal center and other hard atoms is increased. Since four oxygen atoms are coordinated to the Cobalt atom in $\text{Co}(\text{DBM})_2$, the Co(II) becomes relatively hard, and capable of interacting with ClO_4^- anion. Another factor that can contribute to the hardness of the metal center in the $\text{Co}(\text{DBM})_2$ complex is the π -back bonding, which renders Cobalt atom harder in character and capable interaction with ClO_4^- ion.

The intensity of an absorption bond is proportional to the transition probability integral which in turn is related to the symmetry of the ground state and excited state wave functions. When ClO_4^- is coordinated, the approximate symmetry of $\text{Co}(\text{DBM})_2$ is changed from D_{4h} to C_{4v} . This change seems to have a diminishing effect on the intensity of the transition, presumably due to the mismatch of the new symmetries of the ground state and excited state wave functions.

Table 1
Composition and optimization of membranes ingredients

No.	PVC (%)	Plasticizer (%)	Ionophore (%)	MTOAC (%)	Slope (mV decade ⁻¹)	Linear range (M)	R ²
1	27.68	DOP, 66.35	2.15	3.82	-56.3	1.0 × 10 ⁻¹ –5.0 × 10 ⁻⁶	0.9887
2	32.59	DOP, 62.93	2.61	1.87	-49.7	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁵	0.9931
3	33.45	DOP, 59.55	3.80	3.20	-58.3	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁵	0.9932
4	28.36	DOP, 62.47	5.62	3.55	-61.5	1.0 × 10 ⁻¹ –5.0 × 10 ⁻⁶	0.9964
5	33.57	DOP, 55.03	6.35	5.05	-56.5	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁶	0.9976
6	31.96	DBP, 63.03	1.90	3.01	-63.9	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁶	0.9925
7	30.05	DBP, 64.88	2.09	2.99	-63.1	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁶	0.9933
8	29.92	DBP, 65.01	2.98	2.09	-61.8	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁶	0.9942
9	27.90	DBP, 66.20	3.50	2.40	-60.3	1.0 × 10 ⁻¹ –8.0 × 10 ⁻⁷	0.9943
10	30.07	DBP, 61.53	5.20	3.20	-54.3	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁶	0.9984
11	33	DBP, 62	5	-	-26.5	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁵	0.9714
12	30	DBP, 65	-	5	-11.3	1.0 × 10 ⁻¹ –1.0 × 10 ⁻⁵	0.9453

The selectivity is governed by the selective chemical recognition of the elements and not through the electrostatic interactions with the membrane. It is well known that high selectivity in ion sensors can be achieved by using chemical recognition principles in their construction [48].

3.2. Influence of membrane composition

Polymeric ISE membranes consist of polymer matrix, membrane solvents (plasticizers) and active components such as ionophores and ionic additives. In general the selectivity, working concentration range and stability of an ion-selective sensor depends not only on the nature of an ionophore, but also are strongly influenced by the nature and amount of solvent mediator, the plasticizer/PVC ratio and, especially, the nature of additives used [49].

Thus to optimize potentiometric performance of perchlorate-selective electrode various PVC membrane based on Co(DBM)₂ were prepared and investigated. The effect of different composition on the electrode responses in terms of slope, detection limit and linear range are investigated and reported in Table 1.

As membrane solvent, the plasticizers can greatly affect the responses of the ion-selective electrodes. It has been reported that different plasticizers can switch the selectivity of the membrane and change the response range dramatically [26]. Further improvement in the performance has been attempted by the addition of appropriate amounts of plasticizers to the membranes. The plasticizers to be used in membranes should exhibit high lipophilicity, high molecular weight, low tendency for exudation from the polymer matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the membrane and adequate dielectric constant [50,51]. Therefore, the effect of plasticizer type on the response characteristics of the perchlorate-selective sensors was investigated using two plasticizers with different polarities, including DOP, DBP. It is obvious from Table 1 that among two different plasticizers used, DBP gives better response. It should be noted that the nature of plasticizer influences both the dielectric constant of the membrane and the mobility of ionophore and its complex with ClO₄⁻ [26].

The optimization of permselectivity of membrane sensors is known to be dependent on the incorporation of additional membrane compounds. In fact, it has been demonstrated that the presence of lipophilic charged additives improves the potentiometric behavior of ISEs not only by reducing the ohmic resistance [52] and improving the response behavior and selectivity [53] but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode. Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface [53]. Therefore, the effects of ionic additive concentrations in the membrane were investigated at several carrier/additive weight ratios. As is evident from the data in

Table 1, the presence of 2.4% MTOAC as a suitable lipophilic additive in provided electrode will improve the sensitivity of the PVC membrane considerably with Nernstian potential responses (No. 9).

The best results in terms of stability and selectivity against perchlorate were observed when the membrane was prepared with 3.50 wt% of ionophore, 27.90 wt% PVC, 66.20 wt% of DBP as a plasticizer and 2.40 wt% of MTOAC as an additive (No. 9).

3.3. Effect of internal reference solution

In accord with generally adopted ion sensor response formalism, the influence of the concentration of internal standard solution (KClO₄) on the potential response of the polymeric membrane electrode for ClO₄⁻ ion based on Co(BDM)₂ was studied. The concentration was varied from 1.0 × 10⁻¹ to 1.0 × 10⁻⁴ M and the potential response of the electrode was obtained (Fig. 3). The results showed that the concentration of the internal solution does not result in any significant difference between the potential electrode response of slope while parameters like measuring range and detection limit changed to considerable extent, except for an expected change in the intercept of the resulting Nernstian plots. In fact, the main factor in making the potential slope and response to remain constant is the appropriate membrane thickness and the decrease in the trans-membrane flux [54]. Thus, the KClO₄ concentration of 1.0 × 10⁻³ M, that was quite appropriate for smooth functioning of the electrode system, was selected for the internal standard solution.

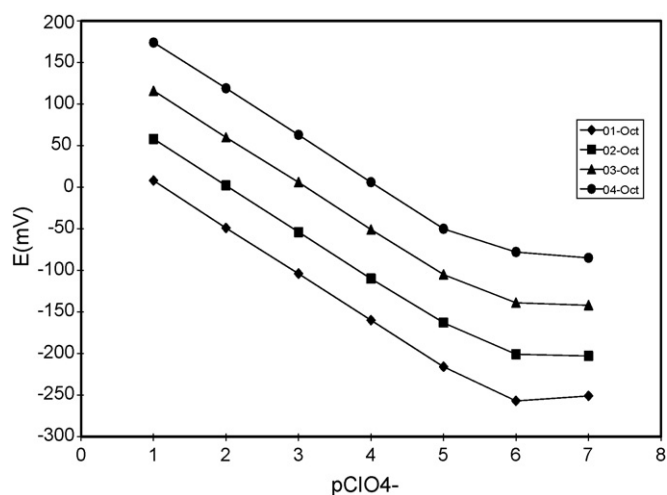


Fig. 3. Effect of concentration of internal reference solution on the electrode response at various external perchlorate concentrations in the range of 1.0 × 10⁻¹ M–1.0 × 10⁻⁴ M.

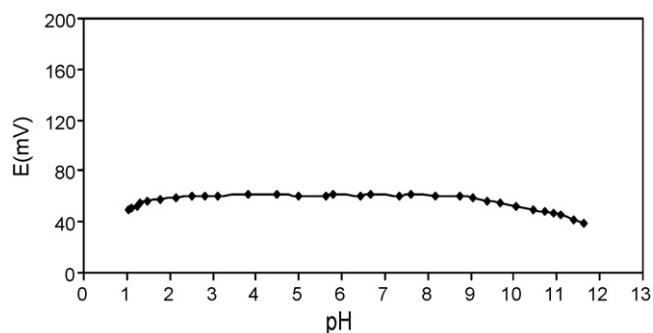


Fig. 4. Influence of pH on the potential response of the perchlorate-selective electrode to 1.0×10^{-3} M ClO_4^- .

3.4. Influence of pH

The pH of the sample solution is an important factor, often influencing the response of ion-selective electrodes. Thus, the effect of sample solution pH on the perchlorate response characteristics of optimized membrane composition described above was studied by adding diluted solutions of H_2SO_4 or NaOH and adjusting the pH by a pH-meter in the range of 1.0–12.0 (Fig. 4).

The results showed that the electrode potential was independent of the pH of the solution in the range of 2.0–9.0. Drastic potential changes are observed at higher and lower pH values. This is most probably due to the simultaneous response of the electrode to perchlorate and sulfate ions at $\text{pH} < 2.0$, and at higher $\text{pH} > 9.0$, the potential drop may be due to interference of hydroxide ions. The hydroxide ion will compete with perchlorate ion for the cationic site in the membrane. On the other hand, since the Co(II) complex is susceptible to hydrolysis at $\text{pH} < 2.0$ or $\text{pH} > 9.0$, it is safe to perform the measurements in the pH range of 2.0–9.0.

The working pH range, over which the electrode can be used, covers the pH of most natural and industrial waters.

3.5. Calibration curve and response characteristics of the electrode

The potentiometric response of the membrane electrode to different concentrations of ClO_4^- was examined over the concentration range 1.0×10^{-7} – 1.0×10^{-1} M using the optimized membrane composition and conditions described above. For this purpose, appropriate aliquots of a stock solution of perchlorate were introduced to the cell, and the corresponding potentials were determined. The potential readings were plotted against $-\log$ of the perchlorate concentration. The electrodes based on Co(BDM)_2 exhibited linear responses to the concentration of ClO_4^- ions in the range of 8.0×10^{-7} – 1.0×10^{-1} M. The respective slopes of calibration graphs were 60.3 ± 0.5 mV per decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graphs, was 5.6×10^{-7} M. This concentration range and detection limit was found to be compatible with other perchlorate electrodes. The characteristic properties of the optimized membrane are summarized in Table 2. The results show

Table 2
Response characteristics of the perchlorate-selective electrode

Slope (mV decade ⁻¹)	60.3 ± 0.5
Linear range (M)	1.0×10^{-1} – 8.0×10^{-7}
Detection limit (M)	5.6×10^{-7}
Response time (s) 1×10^{-1} – 1.0×10^{-6} M	≤ 5
Working pH range	2.0–9.0
Life time (months)	2<

Table 3
Life time of optimized ClO_4^- ISE

Linear range (M)	Slope (mV decade ⁻¹)	Time (day)
8.0×10^{-7} – 1.0×10^{-1}	-60.3 ± 0.5	1
8.0×10^{-7} – 1.0×10^{-1}	-60.3 ± 0.5	5
8.0×10^{-7} – 1.0×10^{-1}	-60.3 ± 0.5	10
8.0×10^{-7} – 1.0×10^{-1}	-60.3 ± 0.5	15
8.0×10^{-7} – 1.0×10^{-1}	-60.3 ± 0.5	20
8.0×10^{-7} – 1.0×10^{-1}	-60.3 ± 0.5	35
8.0×10^{-7} – 1.0×10^{-1}	-60.1 ± 0.5	50
1.0×10^{-6} – 1.0×10^{-1}	-60.1 ± 0.5	60
5.0×10^{-6} – 1.0×10^{-1}	-59.9 ± 0.5	75
5.0×10^{-6} – 1.0×10^{-1}	-59.9 ± 0.5	80

that the proposed electrode has a near-Nernstian response, low detection limit and good calibration reproducibility.

The response time was obtained from the dynamic response curves corresponding to perchlorate concentration steps to obtain a 10 times more concentrated solution. The average response 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 ≤ 5 s over the entire concentration range and the potentials stayed constant after this time.

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. It was observed that there was no significant change in the slope of the curve on successive days. The electrode was tested over a period of 2 months to investigate its stability. During this period, the electrode was in a perchlorate solution (1.0×10^{-3} M) and used everyday. The perchlorate-selective electrode worked over a period of at least 2 months and no appreciable change in the calibration characteristics or response time was observed. During this time, the detection limit and slope of the electrodes remained almost constant. After 2 months, very slight gradual decrease in slopes was observed. It should be noted that, during these 2 months, the electrode was almost in daily use, and then it was washed with water, kept in solution if dried, and kept aside for testing in the next days.

The properties such as slope, working range, and response time of the electrode were found to be reproducible (Table 3).

In Table 4, the response characteristics of the proposed electrode are compared with those of several recently reported selective electrodes for ClO_4^- ions [37–39,55–62]. The results show that the proposed electrode mainly has fast response and in compare of other fast response electrode [39,60,62] have the better linear dynamic range and detection limit. Many tetragonally-coordinated M(II) complexes with square planar structure, where $\text{M(II)} = \text{Co}$, Ni , Cu , have been used as neutral carriers into a PVC membrane to prepare electrodes with significant potentiometric selectivity toward anions such as iodide and nitrate. Since the central metals are capable of increasing their coordination number to five or six by interacting with polar solvent molecules or anions, direct interaction between the central metals and the analyte anions is possible in spite of the fact that these complexes are neutral. In addition, the electron density on the central metal varies by the extent of electron donation from the donor atoms of the equatorial ligands. Consequently, the interaction of the Co complex with perchlorate having hard oxygen atoms and the high sensitivity of the electrode toward this anion can be rationalized. As is obvious from Table 4, in most cases, the slope, linear range, detection limit, and selectivity coefficients of the proposed electrode are superior to those of other electrodes reported in literature.

Table 4
Comparison of some characteristics of the proposed electrode with previous ClO_4^- ISEs

Ref.	Response time (s)	Slope (mV decade ⁻¹)	Working pH range	Linear range (M)	DL (M)	Interfering ion with $K^{\text{Pot}} \geq 1.0 \times 10^{-2}$
Proposed electrode [37]	≤ 5 ≤ 14	60.3 57	2.0–9.0 2–12	8.0×10^{-7} – 1.0×10^{-1} 5.0×10^{-6} – 1.0×10^{-2}	5.6×10^{-7} 1.1×10^{-6}	IO_4^- , SCN^- , I^- , NO_3^- , CO_3^{2-} , SO_4^{2-} , SO_3^{2-} , BrO_3^- , I^- , Br^- , ClO_3^- , Cl^- , HCO_3^- , NO_3^-
[38]	≤ 10	59.5	4–12	4.0×10^{-7} – 1.0×10^{-1}	2×10^{-7}	MnO_4^-
[39]	≤ 10 <5	59.1 60.0	4–12 1.2–12.5	7.0×10^{-7} – 1.0×10^{-1} 1.0×10^{-6} – 1.0×10^{-1}	4×10^{-7} 6.6×10^{-7}	MnO_4^- $\text{C}_2\text{O}_4^{2-}$, HCO_3^- , SO_4^{2-} , SO_3^{2-} , BrO_3^{2-} , NO_2^- , F^- , Cl^- , $\text{Cr}_2\text{O}_7^{2-}$
[55]	<10	57.8	4.0–10.0	8.0×10^{-6} – 1.6×10^{-1}	5.0×10^{-6}	Cl^- , SCN^- , Br^- , SO_4^{2-} , NO_3^- , NO_2^- , F^- , CN^-
[56]	<15	56.8	3–10	1.0×10^{-6} – 1.0×10^{-1}	8.3×10^{-7}	CO_3^{2-} , SO_4^{2-} , NO_2^- , $\text{C}_2\text{O}_4^{2-}$, Cl^- , SCN^-
[57]	≤ 10	60.6	3.5–12	1.0×10^{-6} –1.0	8.0×10^{-7}	SCN^- , Br^- , CN^- , ClO_3^- , CO_3^{2-} , NO_3^- , I^- , $\text{C}_2\text{O}_4^{2-}$, CrO_4^{2-}
[58]	<10	–	3.5–11	5.0×10^{-7} – 1.0×10^{-1}	2.0 – 5.0×10^{-7}	SCN^- , Br^- , CN^- , ClO_3^- , CO_3^{2-} , NO_3^- , $\text{C}_2\text{O}_4^{2-}$, CrO_4^{2-} , I^-
[59]	<10	48.3	2–10	1.0×10^{-5} – 1.0×10^{-2}	5.6×10^{-6}	SO_4^{2-} , SO_3^{2-} , Cl^- , F^- , HCO_3^- , Br^- , NO_3^- , ClO_3^-
[60]	3	51.3–55.7	2–10.5	5.2×10^{-6} – 1.0×10^{-1}	9.3×10^{-6}	SO_4^{2-} , Cl^- , HCO_3^- , Br^- , NO_3^- , CH_3COO^- , $\text{C}_2\text{O}_4^{2-}$, HPO_4^{2-}
[61]	<8	59.9	2.5–9.5	5.0×10^{-7} – 4.0×10^{-1}	4.0×10^{-7}	I^-
[62]	3	55	3–12	5.0×10^{-5} – 1.0×10^{-1}	1.3×10^{-5}	CH_3COO^- , Cl^- , NO_3^- , CO_3^{2-} , BrO_3^{2-} , PO_4^{3-}

3.6. Selectivity of the electrode

The most important characteristics of any ion-sensitive sensor are its response to the primary ion in the presence of other ions in solution, which is expressed in terms of the potentiometric selectivity coefficient. Potentiometric selectivity coefficients ($K_{\text{ClO}_4^-; \text{A}^-}^{\text{Pot}}$) describing the preference of the membrane for an interfering ion A⁻ relative to ClO_4^- . The experimental selectivity coefficients depend on the activity and the method of their determination. Different methods of selectivity determination have been found in the literature. In the present study, the selectivity coefficients were determined using the separate solutions method, according to IUPAC recommendations [41], using 1.0×10^{-3} M solutions of ClO_4^- and interfering ions.

The potentiometric selectivity coefficients of the proposed electrode are summarized in Table 5. It is seen that the electrode has a good selectivity for perchlorate ions over a number of other inorganic and organic anions. Additionally, if we take into account the selectivity coefficients, the prepared electrode $\text{Co}(\text{BDM})_2$ -DBP shows a quite selective response to perchlorate. Thus for instance, in this electrode, the logarithm of the selectivity coefficients is lower than -2.0 for most of the tested anions (except for thiocyanate, periodate, iodide and nitrate), indicating that these anions would not interfere to any significant extent in the determination of perchlorate.

Table 5
Potentiometric selectivity coefficients of various interfering anions

Interfering anion	$\log K_{\text{ClO}_4^-; j}$	Interfering anion	$\log K_{\text{ClO}_4^-; j}$
SCN^-	-0.73	SO_4^{2-}	-2.74
I^-	-1.35	CO_3^{2-}	-2.54
IO_4^-	-0.69	BrO_3^-	-2.23
ClO_3^-	-2.12	Salicylate	-2.34
$\text{C}_2\text{O}_4^{2-}$	-2.97	NO_2^-	-2.46
NO_3^-	-1.7	Br^-	-2.13
CN^-	-2.25	F^-	-2.62
Cl^-	-3.12	$\text{Cr}_2\text{O}_7^{2-}$	-2.06
HCO_3^-	-3.65	SO_3^{2-}	-2.19
IO_3^-	-2.31	HPO_4^{2-}	-3.51
CH_3COO^-	-4.61	H_2PO_4^-	-3.82

The selectivity coefficients were obtained for the proposed electrode show a selectivity sequence of anion in the following order: $\text{ClO}_4^- > \text{SCN}^- > \text{IO}_4^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{CN}^- > \text{IO}_3^- > \text{Salicylate} > \text{NO}_2^- > \text{Cl}^- > \text{CH}_3\text{COO}^-$.

The selectivity sequences follows the Hofmeister Series ($\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{HCO}_3^- > \text{CH}_3\text{COO}^- > \text{SO}_4^{2-} > \text{HPO}_4^{2-}$) although some slight deviations might be interpreted because of some preferential coordination of this ionophore with certain anions.

4. Applications of the method

The high perchlorate selectivity of the electrode based on $\text{Co}(\text{DBM})_2$ as a neutral carrier makes it potentially useful for monitoring the concentrations of perchlorate in real samples. To assess the applicability of the membrane electrode for real samples an attempt was made to determine ClO_4^- in several water samples using the standard addition method. The proposed electrode was applied to the recovery of perchlorate ion from river and tap water and human urine samples with satisfactory results. The results are summarized in Table 6. Good recoveries were obtained in all samples. The results indicate that the proposed electrode can be successfully applied to the determination of perchlorate at concentrations normally present in different matrices.

Table 6
Determination of perchlorate in spiked samples

Samples	Added perchlorate ($\mu\text{g L}^{-1}$)	Found perchlorate ($\mu\text{g L}^{-1}$)	Recovery (%)
Drinking water	1.39	1.41 ± 0.03	102%
	2.77	2.75 ± 0.17	99.3%
	4.16	3.96 ± 0.19	95.3%
	6.92	7.14 ± 0.24	103.1%
River water	13.85	13.48 ± 0.64	97.3%
	27.70	26.46 ± 0.85	95.5%
	41.55	42.59 ± 0.89	102.5%
Human urine	69.25	68.07 ± 1.21	98.3%
	27.70	27.01 ± 0.95	97.5%
	41.56	42.89 ± 1.13	103.2%
	55.40	54.60 ± 1.24	97.5%
	69.25	68.19 ± 1.35	98.5%

5. Conclusions

A cobalt(II) complex performed well as a neutral carrier in developing a new perchlorate-selective electrode. The electrode characteristics such as linear range, detection limit, life and response time and especially selectivity are comparable to the previously reported PVC membrane perchlorate-selective electrodes. Another major advantage of the proposed electrode concerns its facile applications. The present electrode permits direct measurement of perchlorate in real samples without prior separation steps, thus considerably simplifying the determination procedure compared with other analytical methods. With regard to the sensitivity, the electrode was similar to most of the sensitive perchlorate electrode reported.

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