

*Full Paper*

## **Perchlorate Selective PVC Membrane Electrode Based on Cobalt (II) Complex of p-Hydroxy Acetophenone Semicarbazone**

**Sulekh Chandra<sup>\*</sup>, Amrita Malik<sup>#</sup>, Praveen Kumar Tomar ,Avdesh Kumar and Sangeeta Sadwal**

*Department of Chemistry, Zakir Husain College (University of Delhi) J. L. Nehru Marg, New Delhi-110002, India*

\*Corresponding Author, Tel: +91-1122911267, Fax: +91-1123215906

E-Mail: [schandra-00@yahoo.com](mailto:schandra-00@yahoo.com) , [amritamalik30@yahoo.com](mailto:amritamalik30@yahoo.com)

*Received: 11 June 2011 / Accepted: 24 August 2011 / Published online: 30 August 2011*

---

**Abstract-** A new perchlorate selective poly(vinyl chloride) membrane electrode based on a cobalt(II) complex of p-Hydroxyacetophenonesemicarbazone as an ionophore was prepared. The electrode shows Nernstian slope of  $59.6 \pm 0.3$  mV/decade with improved linear range of  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M, with a comparatively lower detection limit  $5.4 \times 10^{-8}$  M between pH range of 2.0-10, giving a relatively fast response within  $\leq 8$  s and can be used for at least 13 weeks without any divergence in potential. The selectivity coefficient was calculated using matched potential method. The electrode can also be used in partially non-aqueous media having up to 20% (v/v) methanol, ethanol or acetone content with no significant change in the value of slope or working concentration range. It was successfully applied for the direct determination of perchlorate content in water and human urine samples.

**Keywords-** Ion Selective Electrodes, Perchlorate Ion, Co(II) p-HASC, Potentiometry

---

### **1. INTRODUCTION**

Perchlorate is considered as a new persistent inorganic contaminant because of its specific properties, such as high water solubility, mobility and stability [1]. Perchlorate salts are used in solid propellants for rockets, explosives, pyrotechnics, such as fireworks [2-4], gun

powder, air bag inflators, growth promoters and as thyreostatic drugs in cattle fattening [5]. Perchlorate salts are also found in food products [6,7], soil [8], milk [9], fertilizers [10], plants [11] and in human urine [12]. The toxicologic mechanisms through which perchlorate exerts its effects have been reviewed [13,14].

Therefore, to determine the perchlorate ion in various samples such as ground water, propellants, explosives and urine in the presence of other anions is a special importance [15]. Perchlorate ions have been determined directly or indirectly by a variety of classical and instrumental methods. These methods include volumetric titration [16], gravimetry [17], spectrophotometry [18], atomic absorption spectrometry (AAS) [19] and ion chromatography [20]. However, most of these methods are either time-consuming or require expensive instruments and also well-control experimental conditions and most importantly, suffer from various interferences of anionic or cationic species. Hence, major effects have been made to develop more convenient direct methods for the quick, easy and inexpensive assay of perchlorate ions in the different samples. Potentiometric detection based on ion-selective electrodes (ISEs) incorporating ion carriers, as a simple method, has several advantages, for example high speed, ease of preparation and procedures, simple instrumentation, short response time, no contamination, non-destructive, unaffected by colour or turbidity, wide dynamic range and 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 of perchlorate-selective electrodes. Most of these reported electrodes were polymeric liquid membranes based on ion exchangers, where the electro active species including perchlorate ion-association complexes with cations and different metal chelate [21], long chain quaternary ammonium ion [22] and organic dye [23], have been dissolved in various organic solvents. However, most of these electrodes are not sensitive and selective enough to permit selective measurement of low levels of perchlorate and also are susceptible to serious interferences from other common anions such as  $\text{OH}^-$ ,  $\text{NO}_3^-$ ,  $\text{SCN}^-$ ,  $\text{ClO}_3^-$  and  $\text{I}^-$ . Only recently, a few carrier-based perchlorate-selective electrodes with improved selectivity and sensitivity were reported [24-31]. Continuing efforts in this direction, we recently synthesized a perchlorate-selective PVC based electrode using a cobalt complex of p-Hydroxyacetophenonesemicarbazone, as a novel carrier for the potentiometric monitoring of perchlorate ion. The performance of proposed ion selective electrode in many respects such as linear range, detection limit, response time, and slope and life time is better than previously reported perchlorate selective electrodes in literature .

## 2. EXPERIMENTAL

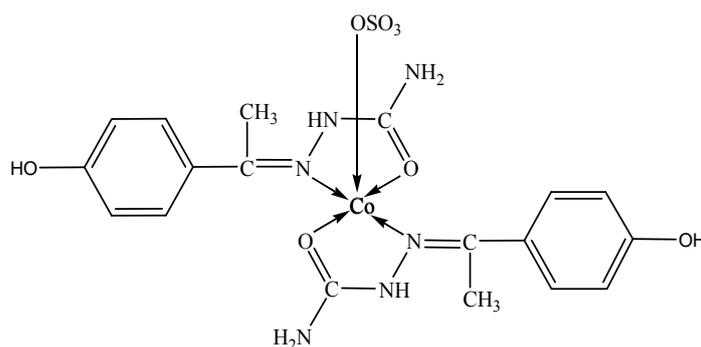
### 2.1. Reagents and apparatus

Reagent grade di-butyl phthalate (DBP), di-octyl phthalate (DOP), *O*-nitrophenyl octylether (*O*-NPOE), tri-*n*-butylphosphate (TBP) and cation additive hexadecyltrimethylammonium bromide (HTAB) were purchased from Merck. High molecular weight PVC powder, THF, and anionic salts were procured from Sigma-Aldrich. All the reagents were of highest pure grade and used without further purification. Standard solutions were freshly prepared in deionized water.

The complex used in the electrode preparation was synthesized in the laboratory and then characterized. Magnetic susceptibility was measured at room temperature on a Gouy balance using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  as a calibrant. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. The C, H, N were analyzed on a Carlo-Erba 1106 elemental analyzer. IR spectra (KBr) were recorded on a Perkin Elmer FTIR spectrum BX-II spectrophotometer. Electron impact mass spectrum was recorded on Joel-MS Route mass spectrometer.

### 2.2. Synthesis of ionophore

A hot ethanolic solution (20 mL) of the *p*-hydroxyacetophenonesemicarbazone as a ligand (0.002 mol) as reported earlier [32] and a hot ethanolic solution (20 mL) of the required metal salt [ $\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$ ] (0.0010 mol) were mixed together under constant stirring. This reaction mixture was refluxed at 80-85 °C for 6 h. On cooling, a green coloured complex separated out, which was filtered, washed with cold ethanol and dried over  $\text{P}_4\text{O}_{10}$  (Fig. 1). Yield 68%, m.p. 233°C; Mass (m/z)=540.9; Anal. calcd % for [ $\text{CoC}_{18}\text{H}_{22}\text{N}_6\text{O}_8\text{S}$ ]; C: 39.93, H:4.06, N:15.52; found C:39.88, H:4.01, N:15.49. IR spectrum of the ligand shows the bands in the region 1685 and 1582  $\text{cm}^{-1}$  may be assigned to the asymmetric or symmetric vibrations. On complex formation the position of these bands shifted toward lower side, which indicates that the coordination takes place through the nitrogen and oxygen atoms of [ $\nu$  (C=N)] and [ $\nu$  (C=O)] groups, respectively. Thus, it has been concluded that the ligand act as bidentate chelating agent [33] and infrared spectrum of the sulphate complex shows IR bands in the region of 1152, 1051 and 975  $\text{cm}^{-1}$  indicating unidentate [34] nature of sulphate group. At room temperature magnetic moment of the Co(II) sulphate complex lies in the range 1.98-2.04 B.M., this value is in tune with a high spin configuration. The low value of molar conductance (10-15  $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ ) carried out in DMF at the concentration of  $10^{-3}$  M, indicated the non-electrolytic nature of complex used as ionophore. The low value suggested the presence of anions inside the coordination sphere and bonded to the metal ion [35].



**Fig. 1.** Structure of Cobalt (II) complex of p-Hydroxyacetophenonesemicarbazone (I)

### 2.3. Electrode preparation

A perchlorate selective electrode was prepared by dissolving the mixture of fixed amount of ionophore, PVC powder, plasticizer and cation excluder in the w ratio of 4% ionophore (complex), 31% PVC, 63% o-NPOE and 2% HTAB in 5 mL of THF. The mixture was kept at room temperature the solvent is allowed to evaporate slowly so that a thin membrane is formed. The membrane was then cut and pasted to one end of Pyrex glass tube. The tube was then filled with internal filling and external solution of  $1.0 \times 10^{-1}$  M  $\text{KClO}_4$  for preconditioning for 24 h before use.

### 2.4. Emf measurements

Potentiometric study of the electrode was carried out by the following cell assembly:  $\text{Hg-Hg}_2\text{Cl}_2$ , KCl (saturated) | internal solution  $1.0 \times 10^{-1}$  M  $\text{KClO}_4$  | PVC membrane | test solution |  $\text{Hg}_2\text{Cl}_2$ -Hg, KCl (saturated).

Potential differences between the ion selective electrodes and the double junction calomel electrodes were measured with Systronics type 335 digital pH, mV meter at room temperature. Several membranes incorporating CoL as carrier was made to study the behavior of best optimized membrane and the one which generated the best Potentiometric response was further studied in detail for selectivity, pH range and the determination of perchlorate ion in the water samples.

### 2.5. Procedure for the determination of perchlorate in water and urine samples

Water and urine samples of different perchlorate concentrations were prepared by adding known amounts of perchlorate to blank water and urine. The pH of an appropriate volume of perchlorate sample was adjusted at 7.0 by the addition of an appropriate amount of HCl or NaOH and the solution was diluted to 50 mL with distilled water. The perchlorate-selective and reference electrodes were immersed and the perchlorate concentration was determined by

direct potentiometry by using the standard addition technique. A blank value for the corresponding blank water sample or urine was also obtained to correct the above results.

### 3. RESULT AND DISCUSSION

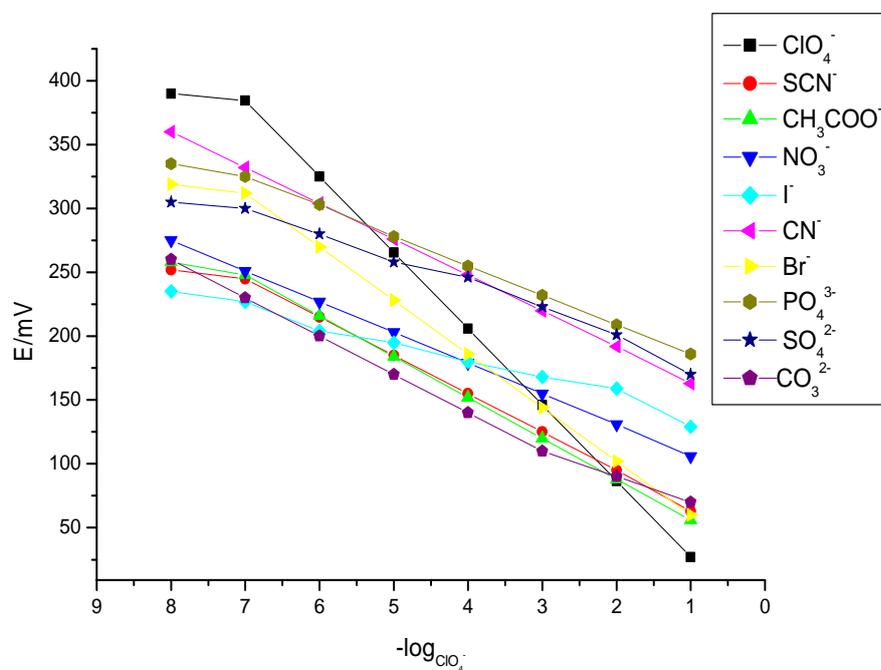
Many tetragonally-coordinated M(II) complexes with square planar structure, where M(II)=Co, Ni and Cu have been used as an ionophore in a PVC based membrane to prepare electrodes with significant potentiometric selectivity toward anions. Since the central metals are capable of increasing their coordination 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 oxygen, nitrogen atoms and the high sensitivity of the electrode toward this anion can be rationalized.

#### 3.1. Influence of membrane composition

The selection of a suitable carrier is the most important phenomena in recognition mechanism of the analyte ion, but some other aspects such as use of membrane additive, plasticizers [36,37] and polymer matrix must not be ignored. The sensitivity, linearity and selectivity for a given ionophore depend significantly on the membrane composition, nature and the amount of additives used with respect to the taken ionophore [38]. In fact it has been demonstrated that the presence of lipophilic positively charged additives improves the potentiometric behavior of certain selective electrodes not only by reducing the ohmic resistance [39,40] and improving the response behavior and selectivity [41,42] but also, in cases where the extraction capability of the ionophore is poor, by enhancing the sensitivity of the membrane electrode [43]. Perchlorate selective electrode worked well as plasticizer/PVC ratio nearly 2:1 (w/w) corresponding to the maximum sensitivity of the electrode [44]. The ionophore/additive ratio of 4:1 was most optimized for the response characteristics of the electrode; this ratio corresponds to the changes in selectivity values and Nernstian response of the electrode [45]. Best membrane response was recorded for S. No. 3 in the Table 1 which comprises of PVC 31%, *O*-NPOE 63%, ionophore 4% and HTAB 2% (w) which gave the reasonable response characteristics.

**Table 1.** Optimization and different composition of membranes (w%)

S.No.	PVC	Plasticizer	Ionophore	Excluder HTAB	Slope (mV/decade)	Response Time (s)
1	32	59 (DBP)	1	8	42.5±0.6	20
2	30	61 (DOP)	4	5	44.5±0.4	13
3	31	63 ( <i>o</i> -NPOE)	4	2	59.6±0.3	≤8
4	33	60 ( <i>o</i> -NPOE)	3	4	56.4±0.6	14
5	32	61 (TBP)	4	3	41.5±0.5	18

**Fig. 2.** Potentiometric response of various ion selective electrodes based on Co(II) p-HASC

### 3.2. Response characteristics

After the calibration of the electrodes, the electrode generated the stable potential response for perchlorate ion. The role of internal filling solution concentrations was studied on the potential response of the electrode [25], which is correlated to the detection limit of the proposed perchlorate electrode. The plot in Fig. 3 indicates that the best response was obtained for the perchlorate ion. The calibration curve slope was found to be (59.5±0.3) mV/decade in the linear range of  $1 \times 10^{-7}$  to  $1 \times 10^{-1}$  M  $\text{ClO}_4^-$  ion concentration. The limit of

detection, as determined from the intersection of the two extrapolated segments of the calibration graphs, was  $5.4 \times 10^{-8}$  M. This concentration range and detection limit was found to be compatible with other perchlorate electrodes. The overall optimized membrane potentiometric response characteristics have been summarized in Table 2 and the results shows that the proposed electrode has a near-Nernstian response, low detection limit .

The selectivity of the resulting electrode is characterized by the lipophilicity of the analyte ion relative to the interfering ion, and the relative strength of the complex formed in the membrane. In the case of organometallic compounds 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 [46].

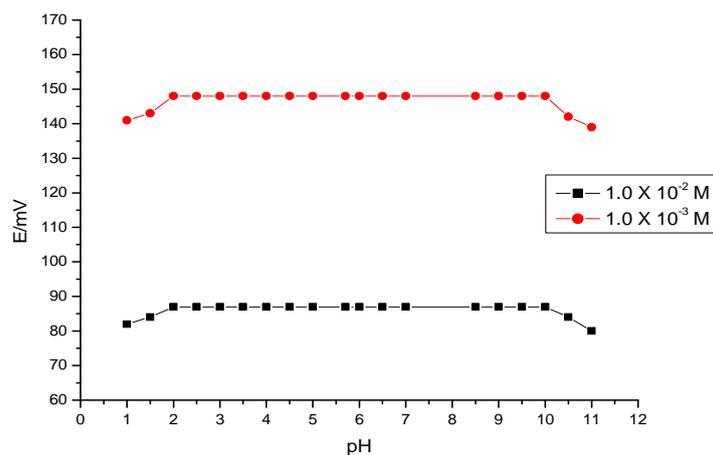
**Table 2.** Characteristics of optimized nickel (II)-selective membrane electrode.

Properties of the electrode	Values
Type of electrode	Plasticized PVC membrane electrodes
Optimum composition w%	4:2:63:31[I: HTAB: O-NPOE:PVC]
Conditioning time and concentration	24 h, $1.0 \times 10^{-1}$ M
Linear working range	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$ M
Slope	$59.6 \pm 0.3$ mV/decade
pH	2.0-10
Detection limit	$5.4 \times 10^{-8}$ M
Lifetime	13 weeks
Response time	$\leq 8$ s
Storage	Buffer pH 5.5 with $\text{KClO}_4$

### 3.3. Effect of pH and non-aqueous medium

The pH dependence of the potential response of the proposed membrane electrode at two different concentration solutions, one of  $1.0 \times 10^{-2}$  and the other  $1.0 \times 10^{-3}$  M of  $\text{ClO}_4^-$  ions in the pH range of 1.0-11 was tested and the results are shown in Fig. 5. As can be seen, the electrode potential was independent of pH in the range 2.0-10. The deviation of the potential at low pH may be due to the increase of  $\text{Cl}^-$  ion and at higher pH values, drop in potential values due to the interference of hydroxide ions.

The effect of non-aqueous medium has also investigated by using electrode No. 3 in methanol-water, ethanol-water and acetone-water mixtures. The electrode worked satisfactorily up to 20% (v/v) of non-aqueous content. Hence, the electrode assembly can be used in a non-aqueous medium when its concentration is not more than 20% (Table 3).



**Fig. 3.** Effect of pH on the potentiometric response of perchlorate selective electrode

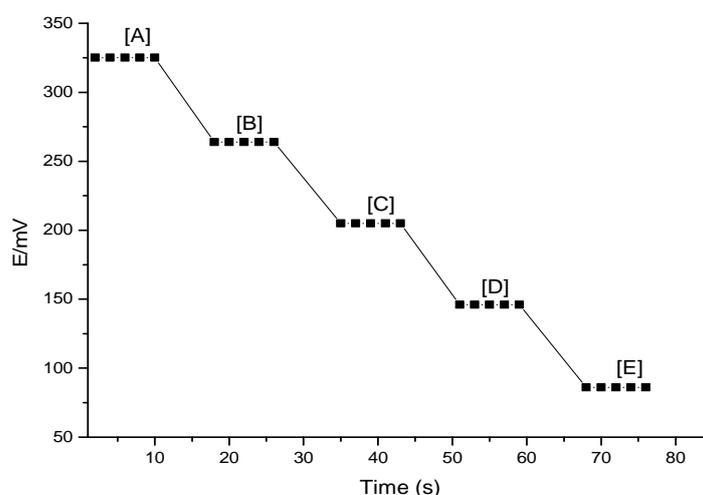
**Table 3.** Effect of partially non-aqueous medium on the working of perchlorate selective electrode.

Non-aqueous content (%, v/v)	Slope (mV/decade of activity)	Working concentration Range (M)
0	59.6	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
Methanol		
10	59.6	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
15	59.5	$5.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
20	59.5	$1.0 \times 10^{-7}$ to $10 \times 10^{-7}$
Ethanol		
10	59.6	$1.0 \times 10^{-7}$ to $10 \times 10^{-1}$
15	59.5	$5.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
20	59.4	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
Acetone		
10	59.6	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$
15	59.4	$1.3 \times 10^{-7}$ to $1.0 \times 10^{-1}$
20	59.3	$1.0 \times 10^{-7}$ to $1.0 \times 10^{-1}$

### 3.4. Dynamic response time and life time of electrode

It is an important factor for any ion-selective electrode. According to IUPAC recommendation, the response time of the electrode is defined as the time between the additions of analyte to the sample solution and the time when a limiting potential has been reached. In this study the practical response time of the proposed electrode was recorded by changing the concentration from the lower ( $1.0 \times 10^{-6}$  M) to the higher ( $1.0 \times 10^{-2}$  M).

The actual potential vs. time trace is shown in Fig. 4. As can be seen, in whole the concentration range, the electrode reaches the equilibrium response in a very short time  $\leq 8$  s. Lifetime studies were based on monitoring the change in electrode's slope and linear response range with time. Among all the membranes prepared in this study, the lifetime of the electrode having o-NPOE plasticizer was maximum and found to be 13 weeks. During this period, the electrodes were used over extended period of time (one hour per day). The performances with respect to slope and detection limit were measured and results are summarized in Table 4. After 13 weeks a slight gradual decreases in the slopes (from  $59.6 \pm 0.3$  to  $51.2 \pm 0.6$  mV/decade) was observed. However, it is important to emphasize that the membranes were stored in a  $1.0 \times 10^{-1}$  M  $\text{KClO}_4$  solution when not in use.



**Fig 4.** Dynamic response of proposed electrode for step changes in the concentration of  $\text{ClO}_4^-$  (M): [A]  $1.0 \times 10^{-6}$ , [B]  $1.0 \times 10^{-5}$ , [C]  $1.0 \times 10^{-4}$ , [D]  $1.0 \times 10^{-3}$ , [E]  $1.0 \times 10^{-2}$

### 3.5. Selectivity

Selectivity behavior is one of the most important characteristic properties of an ion selective electrode. Potentiometric selectivity coefficient ( $K_{A,B}^{\text{pot}}$ ) values for the proposed electrode were determined by IUPAC recommended matched potential method (MPM) [43]. According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion ( $A=1.0 \times 10^{-2}$  M perchlorate ions) and the interfering ion ( $B=1.0 \times 10^{-1}$  M) that

gives the same potential change in a reference solution ( $1.0 \times 10^{-2}$  M of perchlorate ions). Thus, first the change in potential is measured upon changing the primary ion activity is measured, and then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient ( $K_{A,B}^{\text{pot}}$ ) is determined as:

$$K_{A,B}^{\text{pot}} = \Delta A / a_B$$

Where  $\Delta A = a'_A - a_A$ ,  $a_A$  is the initial primary ion activity and  $a'_A$  is the activity of A, in the presence of the interfering ion,  $a_B$ . The resulting potentiometric selectivity coefficients are given in Table 4. Table 4 derives the conclusion that the selectivity coefficients for common anions are in the range of  $1.6 \times 10^{-2}$  -  $4.6 \times 10^{-3}$  M. The obtained selectivity coefficients results revealed that these anions did not disturb the function of the proposed perchlorate-selective membrane electrode.

**Table 4.** Selectivity coefficient  $K_{A,B}^{\text{pot}}$  values of perchlorate-selective electrode by MPM

Interfering ion (B)	Selectivity coefficients	Interfering ion (B)	Selectivity coefficients
$\text{CO}_3^{2-}$	$3.7 \times 10^{-2}$	$\text{SO}_4^{2-}$	$2.6 \times 10^{-2}$
$\text{NO}_3^-$	$2.8 \times 10^{-3}$	$\text{NO}_2^-$	$3.1 \times 10^{-3}$
$\text{CH}_3\text{COO}^-$	$4.6 \times 10^{-3}$	$\text{I}^-$	$4.4 \times 10^{-2}$
$\text{PO}_4^{3-}$	$3.3 \times 10^{-3}$	$\text{Br}^-$	$4.0 \times 10^{-2}$
$\text{SCN}^-$	$2.2 \times 10^{-4}$	$\text{HCO}_3^-$	$2.3 \times 10^{-2}$
salicylate	$1.6 \times 10^{-2}$	$\text{Cr}_2\text{O}_7^{2-}$	$3.7 \times 10^{-4}$

### 3.6. Comparison of the proposed electrode with previously reported electrodes

Proposed electrode compared with previously best reported perchlorate selective electrodes [24,25,27,28,31]. The results show that the proposed electrode mainly has fast response, better linear dynamic range and detection limit as reported earlier. As is obvious from Table 5, in most cases, the slope, linear range, detection limit, pH range, response time and selectivity coefficients of the proposed electrode are superior to those of other electrodes reported earlier.

**Table 5.** Comparison of response characteristic of perchlorate selective electrodes with previous reported electrodes

S. No	Linear range (M)	Slope (mV/decade)	Detection limit (M)	Response time (s)	pH range	References
1	$5.0 \times 10^{-5}$ - $1.0 \times 10^{-1}$	55	$1.3 \times 10^{-5}$	3	3-12	Seghui et al., 2002
2	$8.0 \times 10^{-6}$ - $1.6 \times 10^{-1}$	57.8	$5.0 \times 10^{-6}$	<10	4-10	Shamsipur et al., 2003
3	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	56.8	$8.3 \times 10^{-7}$	<15	3-10	Zanjanchi et al., 2006
4	$1.0 \times 10^{-1}$ - $5.0 \times 10^{-7}$	59.3	$2.0 \times 10^{-7}$	<10	3-11	Ganjali et al., 2007
5	$1.0 \times 10^{-1}$ - $5.0 \times 10^{-6}$	57.3	$2.5 \times 10^{-6}$	10	1.4-6.05	Mahajan et al., 2010
6	$1.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$	59.6	$5.4 \times 10^{-8}$	$\leq 8$	2-10	Proposed work

#### 4. ANALYTICAL APPLICATIONS

The proposed perchlorate-selective electrode was found to work under laboratory conditions. It was successfully applied for the direct determination of perchlorate content in drinking water samples and human urine. To each of one of these samples we have added a  $\text{KClO}_4^-$  solution with concentration in the range of (15, 25, 50 and 20, 40) ppm as a standard. 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 ions by drinking water and human urine

Sample	Added (ppm)	Found (ppm)	Recovery %
Drinking water	15	14.82	98.8
	25	24.55	98.2
	50	49.76	99.5
Human urine	20	19.82	99.1
	40	39.78	99.4

#### 5. CONCLUSIONS

A Co(II) complex of p-Hydroxyacetophenonesemicarbazone performed well as a neutral carrier in developing a new perchlorate selective membrane electrode. The electrode showed better selectivity and Potentiometric behaviour as compared to previously reported electrodes. The electrode display a near Nernstian slope  $59.6 \pm 0.3$  mV/decade in the wide linear range of  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M with a lower detection limit  $5.4 \times 10^{-8}$  M and the optimum response time of  $\leq 8$  s. Durability and lifetime of the electrode was reported to be

better than previous work. The present electrode permits direct measurement of perchlorate in water and urine samples without prior separation steps.

### **Acknowledgements**

The authors acknowledge the DRDO, Delhi for financial supporting this work and R. P. Singh for his helpful suggestions.

### **REFERENCES**

- [1] S. Sridhar, T. W. Collette, and A.W. Garrison, *Environ Sci. Technol.* 33 (1999) 3469.
- [2] E. T. Urbansky, *J. Biochem.* 2 (1998) 81.
- [3] E. T. Urbansky, and M. R. Schock, *J. Environ. Manage.* 56 (1999) 79 .
- [4] M. L. Magnuson, E. T. Urbansky, and C. A. Kelty, *Anal. Chem.* 72 (2000) 25.
- [5] P. Batjoens, H. F. De Brabander, and L. T. Kindt, *Anal. Chem. Acta* 275 (1993) 335.
- [6] A. J. Krynsky, R. A. Niemann, and D. A. Nortrup, *Anal. Chem.* 76 (2004) 5518 .
- [7] C. A. Sanchez, K. S. Crump, R. I. Krieger, N. R. Khandaker, and J. P. Gibbs, *Environm. Sci. Technol.* 39 (2005) 9391.
- [8] P. Winkler, M. Minter, and J. Wiley, *Anal. Chem.* 76 (2004) 469.
- [9] A. B. Kirk, E. E. Smith, K. Tian, T. A. Anderson, and P. K. Dasgupta, *Environm. Sci. Technol.* 37 (2003) 4979.
- [10] S. Susarla, T. W. Collette, A. W. Garrison, and S. C. Mc Cutcheon, *Environm. Sci. Technol.* 33 (1999) 3469.
- [11] J. J. Ellington, N. L. Wolfe, A. W. Garrison, J. J. Ivans, J. K. Avants, and Q. Teng, *Environm. Sci. Thnol.* 35 (2001) 3213 .
- [12] L. Valentin-Blasini, J. P. Mauldin, D. Maple, and B. C. Blunt, *Anal. Chem.* 77 (2005) 2475 .
- [13] J. Wolff, *Pharmacol. Rew.* 50 (1998) 89 .
- [14] Z. Li, L. F. Xiao, D. Byrd, G. M. Deyhle, D. E. Sesser, M. R. Skeels, and S. H. Lamm, *J. Occup. Environ. Med.* 42 (2000) 200 .
- [15] J. I. Kroschwiz, M. Howe-Grant, R. E. Kirk, and D. F. Othmer, *Encyclo. Chem. Tech.* Wiley, New York 18 (1996) 167 .
- [16] R. J. Baczuk, and W. T. Bolleter, *Anal. Chem.* 39 (1967) 93.
- [17] A. I. Vogel, *Text Book of Quantitative Inorganic Analysis*, fourth ed., Longman, London (1978) 498.
- [18] J. A. Weiss, and J. B. Stanbury, *Anal. Chem.* 44 (1972) 619.
- [19] M. Gallego, and M. Valcarcel, *Anal. Chim. Acta* 169 (1985) 161.
- [20] P. Batjoens, H. F. De Brabander, and L. T. Kindt, *Anal. Chim. Acta* 275 (1993) 335.

- [21] S. S. M. Hassan, and M. M. Elsaied, *Talanta* 33 (1986) 679.
- [22] C. J. Coetzee, and H. Freiser, *Anal. Chem.* 41 (1969) 1128.
- [23] A. G. Fogg, A. S. Pathan, and D. T. Burns, *Analyst* 73 (1974) 220.
- [24] M. J. Segui, J. Lizondo-Sabater, R. Martinez-Manez, F. Sancenon, and J. Sato, *Analyst* 127 (2002) 387.
- [25] M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi, and A. R. Hasaninejad, *Sens Actuators B* 89 (2003) 9.
- [26] J. Lizondo-Sabater, M. J. Segui, J. M. Lioris, R. Martinez-Manez, T. Pardo, and F. Sancenon, *J. Soto, Sens. Actuators B* 101 (2004) 20.
- [27] M. A. Zanjanchi, M. Arvand, M. Akbari, K. Tabatabaeian, and G. Zaraei, *Sens. Actuators B* 113 (2006) 304.
- [28] M. R. Ganjali, P. Norouzi, F. Faridbod, M. Yousefi, L. Naji, and M. Salavati-Nisari, *Sens. Actuators B* 120 (2007) 494.
- [29] A. Soleymanpour, B. Garaili, and S. M. Nabavizadeh, *Monatsh Chem.* 139 (2008) 1439.
- [30] B. Rezaei, S. Meghdadi, and S. Bagherpour, *J. Hazardous Materials* 161 (2009) 641 .
- [31] R. K. Mahajan, D. Nandani, and R. K. Puri, *Anal. Lett.* 43 (2010) 2114 .
- [32] J. Liu, W. Yi, Y. Wan, L. Ma, and H. Song *Bioorg. Med. Chem.* 16 (2008) 1096.
- [33] S. Chandra, *Sangeetika*, V. P. Tyagi, S. Raizada, *Synth. React. Inorg. Met-Org. Chem.* 33 (2003) 147 .
- [34] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination compounds*, third ed., Wiley Interscience, New York (1978).
- [35] S. Chandra, and U. Kumar, *Spectrochim. Acta A* 61 (2005) 219.
- [36] A. M. De Los, A. Perez, L. P. Marin, J. C. Quintana, and M. Yazdani-Pedram, *Sens. Actuators B* 89 (2003) 262.
- [37] S. Sadeghi, F. Faithi, A. A. Esmaeili, and S. Naeimi, *Sens. Actuators B* 114 (2006) 928.
- [38] E. Bakker, P. Buhlmann, and E. Pretsch, *Chem. Rev.* 97 (1997) 3083.
- [39] U. Schaller, E. Bakker, U. E. Spichiger, and E. Pretsch, *Anal. Chem.* 66 (1994) 391.
- [40] D. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, and E. Pungor, *Anal. Chim. Acta* 171 (1985) 119.
- [41] R. Eugster, P. M. Gehring, W. E. Morf, U. Spichiger, and W. Simon, *Anal. Chem.* 63 (1990) 285.
- [42] T. Rosatzin, E. Bakker, K. Suzuki, and W. Simon, *Anal. Chim. Acta* 280 (1993) 197.
- [43] Y. Umezawa, K. Umezawa, and H. Sato, *Pure Appl. Chem.* 67 (1995) 507.
- [44] M. Mazloum, A. A. Ensafi, M. Salavati, and S. Mirhoseimi, *Anal. Chim. Acta* 462 (2002) 25.
- [45] M. Huser, P. M. Gehrig, W. E. Morf, W. Simon, C. Lindner, J. Jeney, K. Toth, and E. Pungor, *Anal. Chem.* 63 (1991) 1380.

- [46] J. I. Kroschwiz, M. Howe-Grant, R. E. Kirk, and D. F. Othmer (fourth ed.), *Encyc. Chem. Tech.*, Wiley, New York 18 (1996) 167.