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# IODIDE-, THIOCYANATE- and PERCHLORATE-SELECTIVE LIQUID MEMBRANE ELECTRODES BASED ON TRIS (2,2′,2″-SALICYLIDENE-IMINO)TRIETHYLAMINE-IRON (III)

**Nazife ASLAN[1,*], Adnan KENAR[1], Orhan ATAKOL[1], Esma KILIÇ[1]**

[1]*Department of Chemistry, Faculty of Science, Ankara University, ANKARA*

## ABSTRACT

New iodide-, thiocyanate- and perchlorate-selective liquid membrane electrodes based on the tris (2,2′,2″-salicylidene-imino)triethylamine-iron (III) complex has been reported. These electrodes exhibit linear Nernstian responses over the range $1.0 \times 10^{-1} - 1.0 \times 10^{-5}$ M for thiocyanate and perchlorate and $1.0 \times 10^{-1} - 1.0 \times 10^{-4}$ M for iodine, with slopes of 51.8 ± 1.4 mV per p[SCN], 55.9 ± 1.0 mV per p[$ClO_4$] and 55.2 ± 3.6 mV per p[I]. The effects of the pH and the liquid membrane composition were also investigated. The proposed electrodes have a fast response time and nearly micro molar detection limits. The lifetimes of the electrodes are at least one month. The potentiometric selectivity coefficients for some monovalent ions were evaluated by the mixed interference method. Applications of iodide and thiocyanate electrodes to potentiometric titration of these ions with silver nitrate are made.

**Keywords:** Iodide-, thiocyanate- and perchlorate-, Ion-selective electrode, Schiff base, Potentiometry.

***E-posta**: nazife.aslan@taek.gov.tr

## 1. INTRODUCTION

Anions play fundamental roles in a wide range of biological, medicinal and environmental processes. Therefore anion sensitive electrodes based on liquid ion-exchangers are a very important type of ion-selective electrode (ISE). A good many electrodes sensitive to various univalent anions and differing in design and composition of their ion-exchangers have been described up to the present day [1-4]. A common feature of this type of electrode is a homogenous phase, composed of a water-immiscible organic liquid containing a dissolved salt of the measured anion with a lipophilic cation. Theoretically, a liquid membrane ISE for any univalent anion can be prepared simply by soaking an arbitrary liquid membrane in a concentrated solution of the anion to be measured, whereby the liquid ion-exchanger is converted into the required form [5]. Schiff's base ligands are frequently used to complex anion binding metal ions. The Schiff's base complexes of $Ba^{2+}$, $Cu^{2+}$ or $Pb^{2+}$ were used as an ion-exchange sites in $ClO_4^-$ selective coated wire electrodes (CWEs) [6]. Sensors with the neutral complex of $Co^{2+}$ and a salophene are selective for $I^-$ over $ClO_4^-$ and $SCN^-$ ( $k^{pot}_{i,j} = -2.4$ and $-2.2$, respectively) [7].

The use of ion selective electrodes in environmental analysis offers several advantages over other methods of analysis. First, the cost of initial setup to make analysis is relatively low. The basic ISE setup includes a meter (capable of reading millivolts), a probe (selective for each analyte of interest), and various consumables used for pH or ionic strength adjustments. This is considerably less expensive than other methods, such as Atomic Absorption Spectrophotometry (AAS) or Ion Chromatography (IC). ISE determinations are not subject to interferences such as color in the sample. There are few matrix modifications needed to conduct these analyses. This makes them ideal for clinical use (blood gas analysis) and they have found practical application in the analysis of environmental samples, often where in-situ determinations are needed and not practical with other methods. Hence numerous electrodes have been developed for the analysis of samples containing many different ions.

Thiocyanate finds many industrial applications and, though not toxic as cyanide, it is harmful to aquatic life. Its determination at low levels in water and industrial effluents is therefore, important. Various ionophores for PVC or liquid membrane thiocyanate electrodes have been

reported in the literature. Among these, silver and gold tri-isobutylphosphine sulfide and 1,3-diphenylpropyl phosphine derivatives, mangan (II) Schiff base complexes [8-13].

Perchlorate is present in various compounds commonly used as propellants. The determination of perchlorate, which is important for the assessment of the purity of propellants, becomes difficult in the presence of various other ions. For this purpose several perchlorate selective electrodes [14-19], both the solid and liquid membrane types, have been constructed during the last years and their analytical applications for the determination of perchlorate in solid propellants [18] and in presence of other ions have been investigated [19].

Due to the importance of iodide in many biological systems, varieties of ionophores have been used in the preparation of iodide ion-selective electrodes. These iodide ion-carriers include Schiff base complexes of Co (II) [20], porphyrins [21], silver (I)-thiourea complexes [22], (nickel (II)-tetraazaannulene macrocyclic complex [23] and transition metal chelates of bis furfural-semi-o-tolidine [24].

As a continuation of our previous work [25] we report on the preparation and assessment of the thiocyanate-, iodide- and perchlorate- selective liquid membrane electrodes based on the Schiff base Fe (III) complex (tris (2,2′,2′′-salicylideneimino)triethylamine-iron (III)) Figure1. The response time and the life time of the electrode and its selectivity against some anions were investigated. Finally, we studied whether this electrode could be potentiometrically employed in argentometric titrations.

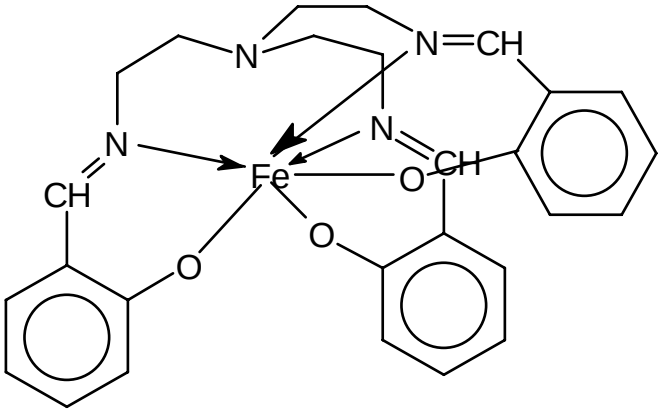


**Figure 1.** Structure of tris-(2,2′,2′′salisiliden-imino)triethyl)amine-iron(III) (Trensal-Fe(III)).

## 2. EXPERIMENTAL

Potential measurements were carried out with an ORION 720 A Model pH-ion meter. The reported potential values are given against a saturated calomel electrode (SCE). Measurements were made with the electrodes immersed to a depth of 1.5 cm in a sample solution being stirred by a magnetic stirrer. All of the experimental work was carried out at 25 ± 1°C, and the pH values were determined using a combined glass pH electrode.

All of the chemicals were of reagent grade and used without further purification. All of the solutions were prepared using deionized water. A 0.1 M stock solution of iodine- was purchased from ORION (94-53-06) and the stock solutions of thiocyanate and perchlorate were prepared by using sodium thiocyanate and sodium perchlorates purchased from Merck and were standardized. Solutions of $10^{-1}$ to $10^{-6}$ M were freshly diluted from 0.1 M stock solution of these ions. Nitrobenzene (Merck) was purified according to Ref. [26].

After tris(2,2′,2″-salicylidene-imino)triethylamine (0.125 mmol) was dissolved in acetonitrile (50 mL), a solution of $FeCl_3$ (0.125 mmol) in ethanol (25 mL) was added. The resulting solution was mixed and refluxed for 48 h by heating. The precipitated crystals (trensal-Fe(III) complex) were filtered off and dried at 110 – 120 °C in an oven [27].

After trensal-Fe (III) complex (4 mg) was dissolved in nitrobenzene (1.0 mL), the resulting solution was mixed with a solution prepared by the dissolution of 40 mg Fe $(NO_3)_3$ in 1.0 mL water. This mixture was shaken for 20 min. The nitrobenzene phase was separated from the water phase. The separated nitrobenzene phase was washed with water several times. After the washing procedure, any water that might have remained in the medium was removed by the addition of anhydrous sodium sulphate. This nitrobenzene phase was then used to prepare an ion-selective liquid membrane.

The electrode was prepared by a procedure similar to that of [28]. A graphite rod (0.7 cm in diameter and 0.5 cm in length) was mounted into the lower end of glass tubing (approx. 10 cm long and internal diameter of 0.5 cm) while making use of expansion of glass with heat. The open end of the glass tube was connected to a slight vacuum and the other end to a carbon rod

immersed in a solution of Schiff base-Fe (III) complex in nitrobenzene. The vacuum was disconnected after 5-10 min. The electrode was removed from the solution and any excess solution poured off. After filling the internal filling solution containing $1.0 \times 10^{-3}$ M iodine-, thiocyanate- or perchlorate and $1.0 \times 10^{-3}$ M sodium chloride and contacting with an AgCl-coated Ag wire, the electrode was instantly ready for use.

The following electrochemical cell was established with the prepared anion-selective electrode:

SCE / sample solution / liquid-membrane / internal filling solution / AgCl , Ag

A PVC membrane electrode based on trensal−Fe (III) complexes was prepared; it did not produce good results during examinations of its performance.

## 3. RESULTS and DISCUSSION

In our previous study, preparation of a nitrate-selective liquid membrane electrode based on the tris (2,2′,2′′-salicylidene-imino)triethylamine-iron (III) complex has been reported [25]. When we evaluated the selectivity coefficients of this electrode against various anions, it was seen that nitrate-electrode has exhibited significant selectivity towards $SCN^-$, $I^-$ and $ClO_4^-$ anions. Based upon this fact, this study was carried out in order to determine whether this electrode could be employed as a selective electrode for these anions. For this purpose the potentiometric response of the prepared liquid-membrane electrode was individually investigated against the iodine, thiocyanate and perchlorate ions.

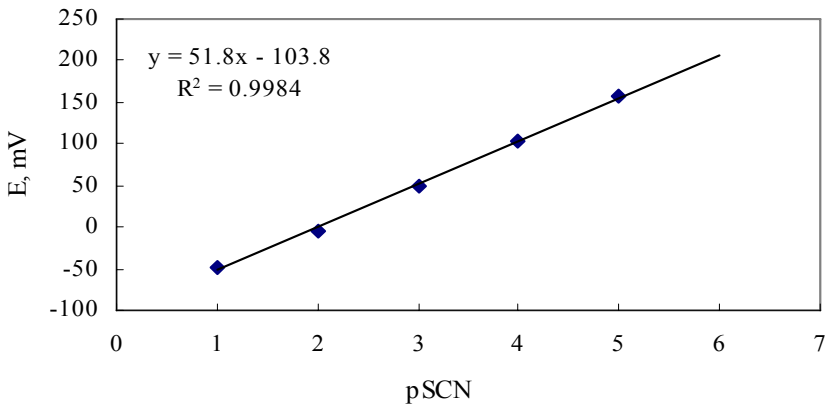


**Figure 2.** The calibration curve of the thiocyanate-selective electrode.

Appropriate aliquots of stock solutions of anions were introduced to the cell, and the corresponding potentials were determined. For a fixed ionic strength, all of the measurements were made in a 0.3 M ammonium sulfate solution. The pH values of these solutions were adjusted to 4.0 using formic acid / formate buffer. The potential readings were plotted against – log of anions concentrations (Figure 2–4).

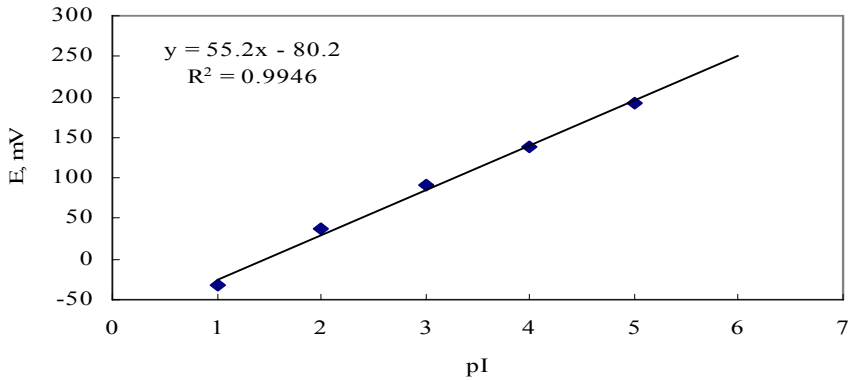


**Figure 3.** The calibration curve of the iodide-selective electrode.

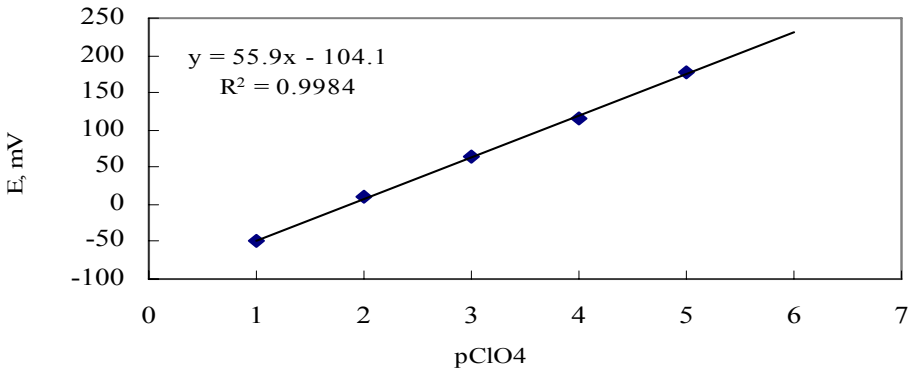


**Figure 4.** The calibration curve of the perchlorate-selective electrode.

### 3.1. Slopes, Working Ranges and Detection Limits of the Electrodes

Slopes, working range and detection limit of the iodide-, thiocyanate- and perchlorate selective electrodes were investigated and results are summarized in Table 1.

The calibration curve, prepared by the use of standard solutions, of the proposed $SCN^-$ electrode was given in Figure 2. As can be seen from the curves, the electrode exhibits a linear response

over the thiocyanate concentration range $1.0 \times 10^{-1}$ –1.0 x $10^{-5}$ mol $L^{-1}$ with a slope of 51.8 (±1.4) mV / pSCN. By considering the literature, this linear range is almost the same or better than the many other reported solid membrane, liquid membrane or the covered wire electrodes [9-13, 29-31]. Also there are many studies, in which detection limit is decrease down to $10^{-6}$ M, in the literature [9,13]. The slope of the electrode is less small than the Nernstian value, which is not an exceptional behavior, and is generally observed with a membrane electrode. Furthermore, in practice, slopes of between 55 and 59 mV $decade^{-1}$ at 25 °C are referred to as Nernstian for analytical purposes [18,19,32]. The limit of detection, as determined from the IUPAC recommendation, was found as $2.52 \times 10^{-6}$ M.

**Table 1.** The response properties of the liquid membrane electrodes based on tris (2,2′,2′′-salicylideneimino) triethylamine-iron (III)

| Electrode | Slope (mV/pX) | Working range, (mol/L) | Detection limit, (mol/L) |
|---|---|---|---|
| Thiocyanate | 51.8(±1.4) | $10^{-1} – 10^{-5}$ | $2.52\times 10^{-6}$ |
| Iodide | 55.2(±3.6) | $10^{-1} – 10^{-4}$ | $1.23\times 10^{-5}$ |
| Perchlorate | 55.9(±1.0) | $10^{-1} – 10^{-5}$ | $1.18\times 10^{-6}$ |

An example of calibration curves prepared for iodide ions was given in Figure 3. As can be seen from the Figure 3, response of the electrodes was linear changed with the range from $1.0 \times 10^{-1}$ to $1.0\times 10^{-4}$ M iodide concentration. In a study, which was made in 1993 (by Ruan R. et al), a PVC membrane electrode based on Schiff bases-metal complex as the ionophore is described which demonstrates selectivity toward the iodide ion. It has a linear response to iodide from $1.0 \times 10^{-1}$ to $1.0 \times 10^{-6}$ M with a slope of 55.2 mV. But, most of the electrodes are solid membrane and there is no previous study in the literature about preparing iodide selective liquid membrane electrode. Although the electrode has a limited working range, its slope (55.2 (±3.6) mV/pI) is very close to Nernstian value. The detection limit of the electrode was $1.23 \times 10^{-5}$ M.

As can be seen from the calibration graph, $ClO_4^-$-selective electrode exhibits a linear response over the range $1.0 \times 10^{-1}$ to $1.0 \times 10^{-5}$ M of perchlorate with a slope of 55.9 (±1.0) mV/p$ClO_4$

(Figure 4). The working range of this electrode is better than the other perchlorate-selective liquid membrane electrode mentioned in the literature [14,33]. For example, in a study reported by Jean et al [14], a liquid membrane electrode based on a berberine-perchlorate ion-pair complex has a working range from $1.0 \times 10^{-1}$ – $1.0 \times 10^{-4}$ M. Also, in the literature research we seen that there are a few studies about the preparing of the liquid membrane electrodes sensitive to perchlorate and most of the studies are solid membrane electrodes such as PVC membrane, epoxy polymer, coated wire electrode etc [6,10,15]. The lower limit of this kind of electrodes is below $10^{-6}$ M in some studies and its parallel to ours [6,33]. Detection limit of the electrode was calculated as $1.18 \times 10^{-6}$ M.

### 3.2. Response Times and the Lifetimes of the Electrodes

The response times of the electrodes depend slightly on the concentration change. If the concentration of thiocyanate changed from $10^{-6}$ to $10^{-5}$ M, the response time was about 20-25 s, but at concentrations higher than $10^{-5}$ M, the response time was shorter than 5-10 s. These periods are shorter than those of the thiocyanate-selective electrodes, which give a linear response in a similar concentration range [10,30]. This shows that the thiocyanate-selective electrode, which we prepared, is superior to most of the thiocyanate-selective electrodes mentioned in the literature as regards to the response time.

Recording its potentials at an optimum pH value and plotting its calibration curve each day determined the lifetime of the electrode. It was observed that there was no significant change in the slope of the electrode on the following day. Since a saturated solution of the trensal-Fe (III) complex in nitrobenzene can be stored for a long time without any decomposition (approximately for a month), the electrode was prepared by using this solution as a fresh organic phase, and the calibration curve was plotted every day. The parameters such as the slope, working range and response time, of an electrode prepared in this way were found to be reproducible. Plotting the calibration curve of the electrode every day using the same ionophore solution checked the slope of the electrode. According to our observations, we can claim that the lifetime of the electrode is quite long, as long as the pores of the graphite rod are not clogged (at least one month) [11,30].

### 3.3. The Selectivity Coefficients of the Electrodes

The selectivity coefficients for the each electrode were determined by the mixed solution method for three anion-selective electrodes. The resulting values were given in Table 2. The selectivity coefficients of the iodide-, thiocyanate- and perchlorate-selective electrodes ($k_{I,X}$ $k_{SCN,X}$ $k_{ClO4,X}$) were calculated by the mixed-solution method [25,28]. From the potential measurements of the solutions prepared with a fixed iodine-, thiocyanate- and perchlorate concentration ($1.0 \times 10^{-3}$ M) and varying concentration of the interference ion. In this work, interference studies were made for $F^-$, $Cl^-$, $Br^-$, $I^-$, $SCN^-$, $CH_3COO^-$, $NO_3^-$ , $NO_2^-$, $HSO_3^-$, $H_2PO_4^-$ , and $ClO_4^-$ monovalent ions.

**Table 2.** Potentiometric selectivity coefficient for various anions with the thiocyanate-, perchlorate- and iodide-selective liquid membrane electrodes.

| $X^-$ | $k_{SCN,X}$ | $k_{I,X}$ | $k_{ClO4,X}$ |
|---|---|---|---|
| $F^-$ | $1.1 \times 10^{-2}$ | $2.9 \times 10^{-2}$ | $1.0 \times 10^{-2}$ |
| $Cl^-$ | $6.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | $8.2 \times 10^{-3}$ |
| $Br^-$ | $5.9 \times 10^{-2}$ | $4.0 \times 10^{-3}$ | $7.5 \times 10^{-3}$ |
| $I^-$ | $2.1 \times 10^{-1}$ | ----- | $2.1 \times 10^{-1}$ |
| $AcO^-$ | $5.0 \times 10^{-3}$ | $3.4 \times 10^{-2}$ | $1.4 \times 10^{-2}$ |
| $NO_3^-$ | $1.1 \times 10^{-2}$ | $1.7 \times 10^{-1}$ | $6.7 \times 10^{-2}$ |
| $HSO_3^-$ | $5.0 \times 10^{-3}$ | $9.0 \times 10^{-3}$ | $9.2 \times 10^{-2}$ |
| $H_2PO_4^-$ | $4.0 \times 10^{-3}$ | $3.0 \times 10^{-3}$ | $9.0 \times 10^{-3}$ |
| $SCN^-$ | ----- | $2.3 \times 10^{-1}$ | $1.4 \times 10^{-1}$ |
| $ClO_4^-$ | 2.33 | 11.3 | ------ |

In the literature, we generally encountered the selectivity coefficient values against the chloride, bromide, nitrate, perchlorate and thiocyanate anions for iodide-selective electrode. That's why the comparison was made for only these anions. The selectivity of the new developed electrode against the chloride and bromide anions is closely to the values given in the literature with a little difference [7, 23]. The selectivity of the electrode against nitrate, perchlorate and thiocyanate ions is better than the other studies mentioned in the literature and this is expectional situation. But, for the Beckmann 39606 model commercial electrode, $k_{I,SCN}$ was given as $10^4$. $k_{I,SCN}$ value

of the electrode prepared in this study is 0.23. Therefore, it can be said that, the iodide-selective electrode, which we prepared, is superior to the Beckman electrode.

Although the resulting values are not as good as commercially available electrodes, our proposed perchlorate-selective electrode can be used as an alternative electrode for given working ranges. Because, most of the perchlorate-selective electrodes reported in the literature have the same selectivity towards the investigated ions. Even in some studies, the selectivity coefficient value given for the thiocyanate ion is higher than the determined values for the proposed perchlorate-selective electrode [10,14].

### 3.4. Applicability of the Electrodes

In this stage of this study, whether the use of thiocyanate- and iodide-selective liquid membrane electrodes developed as an indicator electrode in the determination of silver ions by potentiometric titration was investigated. For this purpose, 30.0 mL 0.0100 M $AgNO_3$ solution was titrated with the 0.1000 M NaSCN and 0.1000 M KI. A sharp end-point was obtained for each electrode. Figure 4 shows an example of the titration of $Ag^+$ with NaSCN. Then the same concentration $AgNO_3$ solution was titrated according to Mohr method.

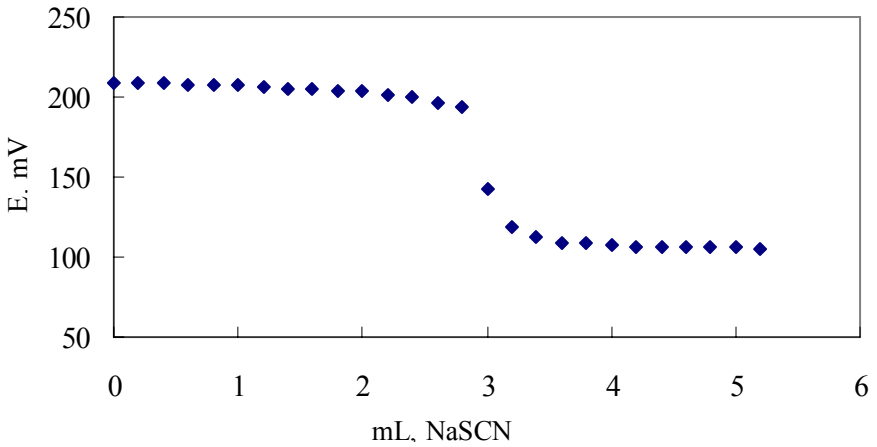


**Figure 5.** The titration of 30 mL 0.0100 M $AgNO_3$ with 0.100 M NaSCN by using thiocyanate-selective electrode based on tris (2, 2′,2″-salicylidene-imino) triethylamine-iron (III).

These results were statistically analyzed at 95% confidence level in order to determine whether there was any significant difference between them. Due to the fact that the results are in good

accordance with each other it was concluded that these electrodes developed could be used as an indicator electrode in the potentiometric titration of silver ions.

## 4. CONCLUSIONS

- The results of this study show that the Schiff base-metal complexes (trensal- Fe(III)) may also use for preparing liquid membrane electrodes selective to thiocyanate, iodide and perchlorate anions.
- The proposed sensors are very easy to prepare, show high sensitivity, rapid response and wide dynamic range.
- Thiocyanate and iodide electrodes reported here have performance characteristics comparable to those of existing electrodes and are used as an indicator electrode in the potentiometric titration of silver ions.

## REFERENCES

**1.** Coetzee C.J. and Freiser H. Anion-responsive electrodes based on ion association extraction systems, Anal. Chem., 40(13), 2071, 1968

**2.** Coetzee C.J. and Freiser H., Liquid-liquid membrane electrodes based on ion association extraction systems, Anal. Chem., 41, 1128, 1969

**3.** Birch J.B. and Clarke D.E., An electrode selective to the dodecyl sulphate anion: Comments on the application of direct potentiometry to c.m.c. measurements, Anal. Chim. Acta, 61, 159, 1972.

**4.** Fogg A. G., Pathan A.S. and Burns D.T., A liquid-state perchlorate ion-selective electrode based on Brilliant green perchlorate, Anal. Chim. Acta, 73, 220, 1974.

**5.** Sharp M., A study of liquid-membrane perchlorate-selective electrodes made from an organic radical ion salt, Anal. Chim. Acta, 65, 405, 1973.

**6.** Liu J., Masuda Y., Sekido E., Perchlorate ion-selective coated-wire electrode based on a macrocyclic Schiff's base complex, Analyst, 115, 1089, 1990,

**7.** Yuan R., Chai Y.Q., Yu R.Q., Schiff base complex of cobalt (II) as neutral carriers for highly selective iodide electrodes, Anal. Chem., 65, 2572, 1993.

**8.** Amini M. K., Shahrokhian S., Tangestaninejad S., Thiocyanate-selective electrodes based on nickel and iron phtalocyanines, Anal. Chim. Acta, 402, 137, 1999.

**9.** Brown D.V., Chaniotakis N.A., Lee I.H, Ma S.C., Park S.B., Meyerhoff M.E., Nick R.J. and Groves J.T., Mn(III) - porphyrin-based thiocyanate-selective membrane electrodes: Characterization and application in flow injection determination of thiocyanate in saliva, Electroanalysis, I(6), 477, 1989.

**10.** Elmosalamy M.A.F., Moody G.J., Thomas J.D.R., Hassan S.S.M., Poly(vinyl chloride) matrix membrane electrodes responsive to thiocyanate, perchlorate and periodate, Anal. Lett., 20(10), 1541, 1987.

**11.** Florido A., Bachas L.G., Valiente M., Villaescusa I., Anion-selective electrodes based on a Gold(III)-triisobutylphosphine sulfide complex, Analyst, 119, 2421, 1994.

**12.** Bricker J., Daunert S., Bachas L.G., Valiente M., Selective electrodes for silver and anions based on polymeric membranes containing complexes of triisobutylphosphine sulfide with silver, Anal. Chem., 63(15), 585, 1991.

**13.** Li Z.Q., Wu Z.Y., Yuan R., Ying M., Shen G.L. and Yu R.Q., Thiocyanate-selective PVC membrane electrodes based on Mn(II) complex of *N,N*'-bis-(4-phenylazosalicylidene) *o*-phenylene diamine as a neutral carrier., *Electrochimica Acta,* 44(15), 2543, 1999.

**14.** Jain A.K., Jahan M. and Tyagi V., Construction and assessment of some perchlorate-selective liquid membrane electrodes, Anal.Chim. Acta, 231, 69, 1990.

**15.** Ganjali M.R., Yousefi M., Poursaberi T., Naji L., Niasari M.S. and Shamsipur M., Highly selective and sensitive perchlorate sensors based on some recently synthesized Ni (II)-hexaazacyclotetradecane complexes, Electroanalysis, 15(18), 1476, 2003.

**16.** Imato T., Jyo A. and Ishibashi N., Anion selective electrode based on oleophilic anion exchange resin membrane, Anal. Chem., 52(12), 1893, 1980.

**17.** Kataoka M. and Kambara T., A liquid membrane type perchlorate ion-selective electrode. J. Electroanal. Chem., 73, 279, 1976.

**18.** James H.J., Carmack G.P. and Freiser H., Coated wire ion-selective electrodes, Anal. Chem., 44(4), 856, 1972.

**19.** Hassan S.S.M. and Elsaied M.M., A new liquid-membrane electrode for selective determination of perchlorate, Talanta, 33(8), 679, 1986.

**20.** Yuan R., Song Y.Q., Chai Y.Q., Xia S.X., Zhang Q.Y., Yi B.M., Ying G., Shen L. and Yu R.Q., Design of Schiff base complexes of Co (II) for the preparation of iodide-selective polymeric membrane electrodes, Talanta , 48(3), 649, 1999.

**21.** Sun C., Zhao J. H., Sun Xy.Y., Zhang X. and Shen J., Fabrication of a multilayer film electrode containing porphyrin and its application as a potentiometric sensor of iodide ion, Talanta, 46(1), 15, 1998.

**22.** Zaamrani F.Z.E., Raurich J. G., Sastre A., Beyer L. and Florido A., PVC membranes based on silver (I) thiourea complexes., Anal. Chim. Acta, 402, 129, 1999.

**23.** Ying M., Yuan R., Zhang X.M., Song Y.Q., Li Z.Q., Shen G.L. and Yu R.Q., Highly selective iodide poly (vinyl chloride) membrane electrode based on a nickel (II) tetraazaannulene macrocyclic complex. Analyst, 122, 1143, 1997.

**24.** Li Z.Q., Yuan R., Ying M., Song Y.Q., Shen G.L. and Yu R.Q., Iodide-selective PVC membrane electrodes based on five transitional metal chelates of bis-furfural-semi-o-tolidine, Anal. Lett., 30, 1455, 1997.

**25.** Yılmaz N.A., Kenar A., Atakol O. and Kılıç E., A nitrate-selective electrode based on tris (2,2′,2″-salicylidene-imino) triethylamine, Anal. Sci., 17(11), 1269, 2001.

**26.** Perrin D.D. and Armarego W.L.F., Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, Oxford, 1991.

**27.** Elerman Y., Kabak M., Svoboda M., Fuess I.H. and Atakol O. Crystal structure of tris-(2,2′,2″)-triaminoethylamino-salicylidene iron(III) complex, J. Chem. Crystallogr., 25(5), 227, 1995.

**28.** Ruzicka J. and Tjell J.C., The liquid-state ion-sensitive electrode: Theory and experiments with N metal dithizonates, Anal Chim. Acta, 51, 1, 1970.

**29.** Jyo A., Egawa H., Effect of membrane matrices on performance of a thiocyanate ion-selective electrode based on the (5,10,15,20-tetraphenylporphyrinato)manganese(III) anion carrier. Anal. Sci., 8(6), 823, 1992.

**30.** Hassan S.S.M. and Elmosalamy M.A.F., Liquid membrane electrode for selective determination of thiocyanate, Analyst, 112, 1709, 1987.

**31.** Rocheleau M.J. and Purdy W.C., The application of quaternary ammonium ionic polymers to electroanalysis: Part 1. Quaternary ammonium ionic polymer membranes for solid-state, ion-selective electrodes, Electroanalysis, 3, 929, 1991.

**32.** Jain A.K., Jahan M. and Tyagi V., Liquid membrane perchlorate-selective electrodes, Analyst, 112, 1355, 1987.

**33.** Bunaciu A.A., Ionescu M.S., Budişteanu N., Dinulescu A. and Coşofret,V.V., New $BF^{-}_{4}$ and $ClO^{-}_{4}$-selective membrane electrodes and their pharmaceutical applications, Talanta, 39(8) 1001, 1992.

**34.** Yuan R., Song Y.Q., Chai Y.Q., Xia S.X., Zhang Q.Y., Yi B.M., Ying G., Shen L. and Yu R.Q., Design of Schiff base complexes of Co (II) for the preparation of iodide-selective polymeric membrane electrode,. Talanta, 48(3), 649, 1999.

**35.** Sun C., Zhao J.H., Sun Xy Y., Zhang X., and Shen J., Fabrication of a multilayer film electrode containing porphyrin and its application as a potentiometric sensor of iodide ion, Talanta, 46(1), 15, 1998.

**36.** Zaamrani F.Z.E., Raurich J.G., Sastre A., Beyer L., and Florido A., PVC membranes based on silver (I) thiourea complexes, Anal. Chim. Acta, 402, 129, 1999.

**37.** Ying M., Yuan R., Zhang X.M., Song Y.Q., Li Z.Q., Shen G.L. and Yu R.Q., Highly selective iodide poly (vinyl chloride) membrane electrode based on a nickel (II) tetraazaannulene macrocyclic complex. Analyst, 122, 1143, 1997.

**38.** Li Z.Q., Yuan R., Ying M., Song Y.Q., Shen G.L. and Yu R.Q., Iodide-selective PVC membrane electrodes based on five transitional metal chelates of bis-furfural-semi-o-tolidine, Anal. Lett., 30, 1455, 1997.

**39.** Yılmaz N.A., Kenar A., Atakol O. and Kılıç E., A nitrate-selective electrode based on tris (2,2′,2′′-salicylidene-imino)triethylamine, Anal. Sci., 17(11), 1269, 2001.

**40.** Perrin D.D. and Armarego W.L.F., "*Purification of Laboratory Chemicals"*, 3rd ed., Pergamon Press, Oxford, 1991.

**41.** Elerman Y., Kabak M., Svoboda M., Fuess I.H. and Atakol O., Crystal structure of tris-(2,2′,2″)-triaminoethylamino-salicylidene iron(III) complex, J. Chem. Crystallogr., 25(5), 227, 1995.

**42.** Ruzicka J. and Tjell J.C., The liquid-state ion-sensitive electrode: Theory and experiments with N metal dithizonates, Anal Chim. Acta, 51, 1, 1970.

**43.** Jyo A. and Egawa H., Effect of membrane matrices on performance of a thiocyanate ion-selective electrode based on the (5,10,15,20-tetraphenylporphyrinato)manganese(III) anion carrier, Anal. Sci., 8(6), 823, 1992.

**44.** Hassan S.S.M. and Elmosalamy M.A.F., Liquid membrane electrode for selective determination of thiocyanate, Analyst, 112, 1709, 1987.

**45.** Rocheleau M.J. and Purdy W.C., The application of quaternary ammonium ionic polymers to electroanalysis: Part 1. Quaternary ammonium ionic polymer membranes for solid-state, ion-selective electrodes, Electroanalysis, 3, 929, 1991.

**46.** Jain A.K., Jahan M. and Tyagi V., Liquid membrane perchlorate-selective electrodes, Analyst, 112, 1355, 1987.

**47.** Bunaciu A., Ionescu M.S., Budişteanu N., Dinulescu A. and Coşofret V.V., New $BF^-_4$ and $ClO^-_4$-selective membrane electrodes and their pharmaceutical applications, Talanta, 39(8), 1001, 1992.