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Iodide selective membrane electrode based on copper (II)-bis-N-phenilsalicylidenaminato complex

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Abstract

An iodide ion-selective PVC membrane sensor based on copper (II)-bis-N-phenilsalicylidenaminato complex as a novel sensing material is successfully developed. The electrode showed a good selectivity for iodide ion with respect to common inorganic anions. The sensor exhibited a good linear response with slope of -58.6 ± 0.4 mV per decade over the concentration range of 5.0×10^{-6} to 1.0×10^{-1} mol L⁻¹, and a detection limit of 3.0×10^{-6} mol L⁻¹ of I⁻ ion. The electrode response was independent of pH in the range of 3.0 - 10.0. The proposed sensor was applied as an indicator electrode in potentiometric titration of I⁻ with Ag⁺ ion, and to determine the iodide in sodium chloride salt.

Keywords: Potentiometry, Iodide ion-selective electrode, PVC membrane, copper(II)-bis-N-phenilsalicylidenaminato complex

1. Introduction

Iodine is an indispensable microelement to human. Iodine is toxic and its vapors irritate the eyes and lungs. The maximum allowable concentration [1] in air when working with iodine is just 1.0 mg m⁻³. Iodine plays a key role in many biological activities such as, brain functions, cell growth, neurological activities, metabolism and thyroid functions. Iodide ions also present in the composition of various drugs. Due to vital importance of iodide in environment, medicines and industry, determination of iodide is very important in clinical and chemical analysis [2-4].

Several analytical methods have been reported for its determination at low concentration levels including gas chromatography [5], chemiluminescence [6], stripping voltammetry [7], flow injection analysis [8] and inductively coupled plasma atomic emission mass spectrometry [9]. Some of these methods are time consuming and some are very expensive. On the other hand potentiometric methods by ion selective sensors are inexpensive, simple and fast with high selectivity and wide linear range for direct determination of various species in biological and industrial analysis. In view of such advantages, efforts have been made to make selective sensors for different anions.

The first investigations relating to the ion selective electrodes were done at the beginning of 1990 [10]. The first iodide selective electrode was prepared by Pungor and Hollos [11,12] in 1961 using silver iodide and Paraffin as the membrane. They used this electrode for the

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determination of sulfur dioxide, by passing SO_2 gas through iodide solution, and the iodide formed was determined with this electrode. In recent decade some PVC membrane electrodes with complex carriers have been developed [13-16] with Nernstian slope. Many sensing agents have been described for the preparation of iodide-selective electrodes including Mn(II) porphyrinato [17], urea derivatives [18], Co(II) and Ni(II) cyclam derivatives [19], Hg(II) bis (benzoin)-semiethylene diamine complex [20] and salophen complex of Co(II) [21]. Some sensors have narrow working concentration range [18], and some suffer serious interference from lipophilic anions like SCN^- , CN^- and sal^- [18,19]. Recently copper(II) of N,N''-bis(salicylidene)-1,2-bis(p-aminophenoxy) ethane complex [22] and Cd(II) N,N'-bis(salicylidene)-1,4-diaminobutane [23] have also been used as ionophores in the construction of iodide selective electrode. In this study we have synthesized copper (II)-bis-N-phenilsalicyldenaminato complex and studied this as ionophore in the preparation of polymeric membrane sensor for low level determination of iodide ion.

2. Experimental

2.1. Reagents

Reagent-grade dibutyl phthalate (DBP), hexadecyltrimethyl ammonium bromide (HTAB), tetrahydrofuran (THF), and high relative molecular weight (PVC) were purchased from Aldrich and used as received. Sodium salts of all anions used (all from Merck) were of the highest purity available and used without any further purification. All the solutions were prepared in doubly distilled water.

2.2. Synthesis of bis(N-phenyl-salicydenaminato)copper(II)

The Schiff base ligand was synthesized similarly by following reported procedures [24,25]. Thus, treatment of an equimolar amount of salicylaldehyde (10 mmol) and aniline (10 mmol) in methanol (20 ml) at room temperature for 30 min gave rise to yellow micro crystals, yield 80%. The micro crystals were filtered off and re-crystallization has been performed in diethyl ether solution at room temperature.

The copper(II) complex was synthesized in a similar manner using a method described elsewhere [26,27]. Thus, 2.5 mmol (0.499 g) of copper(II) acetate monohydrate was slowly added to a methanol solution (50 mL) of the Schiff base (5 mmol) and the resulting solution was stirred for 1h at room temperature. The resulting brown precipitates were collected by filtration, washed with 10 ml of methanol and recrystallized from dichloromethane/acetone (1:1 v/v). Yield 46%. Anal. Calc. for $\text{C}_{26}\text{H}_{20}\text{CuN}_2\text{O}_2$: C, 68.48; H, 4.42; N, 6.14. Found: C, 68.61; H, 4.29; N, 6.12. IR (KBr, cm^{-1}): $\nu_{\text{C=N}}$ = 1608, $\nu_{\text{C-O}}$ = 1329. Electronic spectra in CHCl_3 : d-d, 666 nm ($\epsilon = 243 \text{ M}^{-1}.\text{cm}^{-1}$). The structure of Cu(II) complex is shown in Fig. 1.

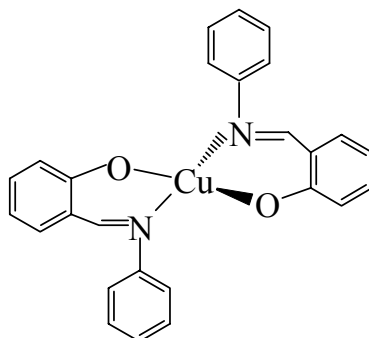


Fig. 1 Structure of copper (II)-bis-N-phenilsalicyldenaminato complex

2.3. Apparatus

The potentiometric measurements were accomplished by use of a digital pH/mV meter metrohm model 691. All emf measurements were carried out with the following assembly: Ag/AgCl/internal solution (1.0×10^{-2} mol L⁻¹ NaI) /PVC membrane / test solution / KCl (satd.) /AgCl /Ag. Activities were calculated according to the Debye-Huckel procedure [28].

2.4. Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 5 mg of ionophore, 3 mg cationic additive HTAB and 63 mg of plasticizer DBP. Then the mixture was dissolved in 5 ml of dry THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (4 mm i.d) was dipped into the mixture for approximately 10 s so that a non-transparent membrane of approximately 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for approximately 24 h. The tube was then filled with an internal solution 1.0×10^{-2} mol L⁻¹ NaI. The electrode was finally conditioned for 12 h by soaking in a 1.0×10^{-2} mol L⁻¹ NaI solution. An Ag/AgCl electrode was used as an internal reference electrode.

3. Results and discussion

In preliminary experiments, copper (II)-bis-N-phenilsalicylidenaminato complex was used as an ion carrier in construction of ion-selective electrodes for some common anions (Fig 2A and 2B). The membrane sensor displayed remarkable selectivity for iodide ions over other anions. The preferential response toward iodide is believed to be associated with the coordination of iodide with the central metal of the carrier.

3.1. The effect of membrane composition, internal solution and pH on the potential response

It is well known that the sensitivity, linear dynamic range, and selectivity of the ISEs depend not only on the nature of the carrier used, but also significantly on the membrane composition and the properties of the additives [29-31]. Thus the influence of the membrane composition, nature, and amount of plasticizer, and lipophilic additives on the potential response of the membrane was investigated, and the results are shown in Table 1. As it is seen, the best response was obtained with the membrane composed of the following ingredients: %31 PVC, %62 DBP, %4 complex and %3 additives.

Table 1
Optimization of membrane ingredients

Electrode number	Composition of the membrane (wt. %)				Slope (mV/decade)
	PVC	Plasticizer	Ionophore	HTAB	
1	31	68	1	0	-4.4 ± 1.2
2	31	67	2	0	-12.3 ± 0.9
3	31	66	3	0	-23.1 ± 0.7
4	31	65	4	0	-36.8 ± 0.6
5	31	64	5	0	-32.4 ± 0.6
6	31	64	4	1	-46.5 ± 0.5
7	31	63	4	2	-54.5 ± 0.5
8	31	62	4	3	-58.6 ± 0.4
9	31	61	4	4	-55.4 ± 0.4
10	31	61	5	3	-51.3 ± 0.6

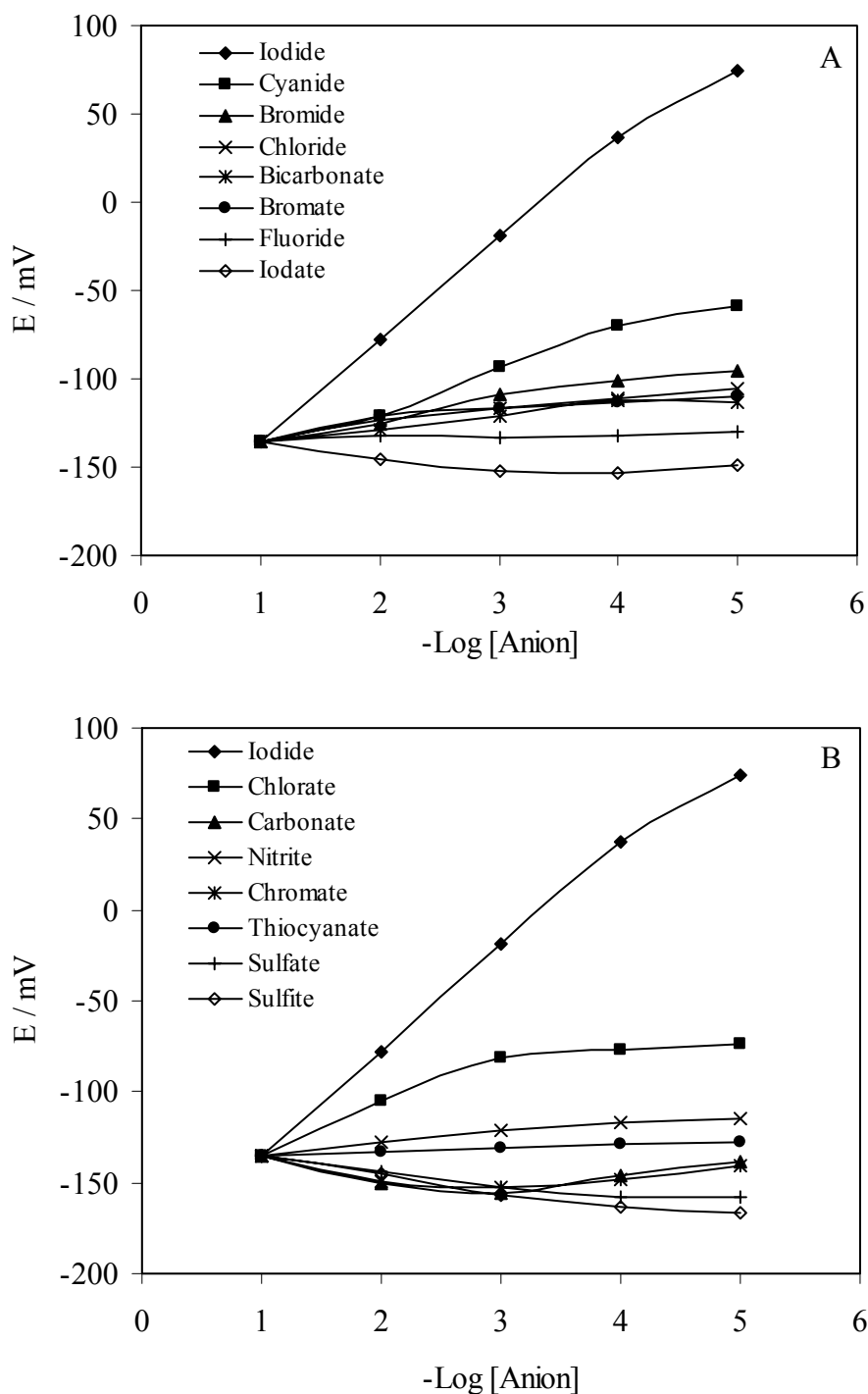


Fig. 2 Potential responses of various ion-selective electrodes based on copper (II)-bis-N-phenylsalicylidenaminato ionophore

The potentiometric response of the membranes was greatly improved in the presence of lipophilic cationic additives. It is known that, lipophilic salt, not only reduce the membrane resistance, but also enhance the response behavior and selectivity, and reduce interferences [32,33]. The presence of lipophilic ionic sites is beneficial for both neutral carrier and charged carrier-based ion selective electrodes [34,35]. The response of the blank membranes containing additives but no carrier at all was far from Nernstian.

The concentration of the internal solution (NaI) in the electrode was changed from 1.0×10^{-2} to 1.0×10^{-4} mol L⁻¹ and the emf versus I⁻ concentration plots were obtained. It was found that the variation of the concentration of the initial NaI solution did not cause any significant

difference in the slope of the resulting plots. However, a $1.0 \times 10^{-2} \text{ mol L}^{-1}$ concentration of internal reference solution showed a smooth Nernstian function of the polymeric membrane system and therefore, selected as concentration of internal solution.

The influence of the pH of the test solution ($1.0 \times 10^{-2} \text{ mol L}^{-1}$ of Γ) on the potential responses of the membrane sensor was tested in the pH range 2.0 to 12.4 (by using concentrated HCl or NaOH). The potential remains constant in the pH range 3.0 to 10.0. At higher alkaline media, the potential changed sharply, most probably due to the response of the sensor to hydroxide ions. In acidic media (pH < 3.0), the drift in the potential may be due to the instability of the ionophore (complex of the Cu(II) with the ligand) due to the nitrogen sites protonation.

3.2. Response characteristics of the electrode

Dynamic response time is an important factor for any ion selective electrode. In this study, the practical response time was recorded by changing solution with low to high iodide concentrations ($1.0 \times 10^{-5} \text{ mol L}^{-1}$ to $1.0 \times 10^{-1} \text{ mol L}^{-1}$). In whole the concentration range, the electrode reaches the equilibrium response in a very short time (approximately 9-25 s). To evaluate the reversibility of the electrode, a similar procedure at the opposite direction was adopted. This time measurements were performed in the sequence of high-to-low sample concentration and results showed that the potentiometric response of the sensor was reversible, although the time needed to reach equilibrium values were some what longer than that of the low-to-high order of sample concentration. The potentiometric response of the prepared iodide selective electrode was investigated against the iodide concentration. For this purpose, appropriate aliquots of a stock solution of iodide were introduced to the cell, and the corresponding potential was determined. The potential readings were plotted against $-\log [I^-]$.

The electrode potential response was linear over the concentration range of 5.0×10^{-6} to $1.0 \times 10^{-1} \text{ mol L}^{-1}$ of iodide. The calibration curve slope was $-58.6 \pm 0.4 \text{ mV decade}^{-1}$ and the detection limit, calculated as recommended by the IUPAC, was $3.0 \times 10^{-6} \text{ mol L}^{-1}$. The calibration plot is shown in Fig 3. The stability and reproducibility of the electrode was also tested. The standard deviation of 20 replicate measurements at three concentrations of 1.0×10^{-2} , 1.0×10^{-3} and $1.0 \times 10^{-4} \text{ mol L}^{-1}$ were ± 0.3 , ± 0.5 and $\pm 0.8 \text{ mV}$, respectively.

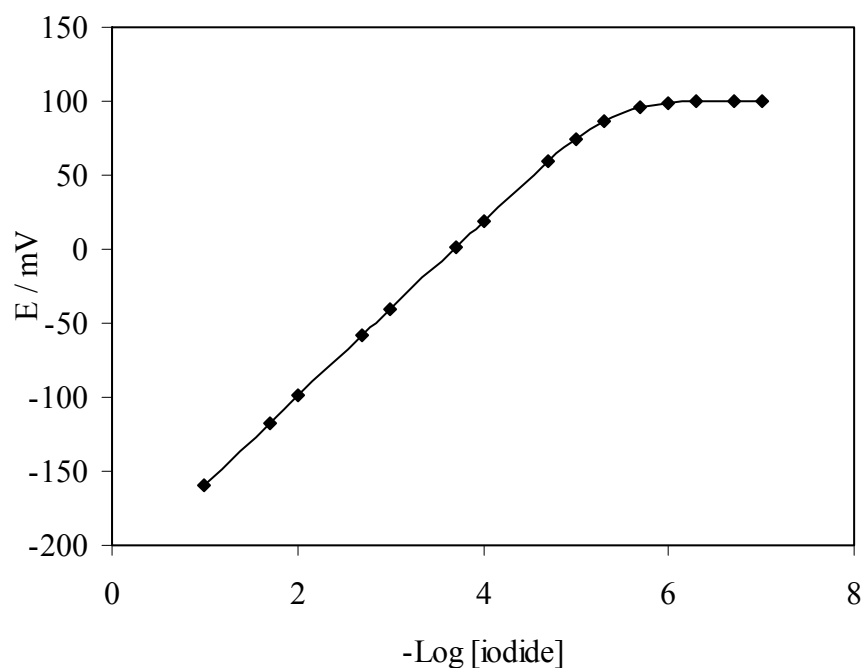


Fig. 3 Calibration curve of the iodide electrode based on copper(II)bis-N-phenilsalicylidenaminato ionophore

3.3. Determination of the potentiometric selectivity coefficients

One of the most important characteristics of any ion-selective sensors is its response to the primary ion in the presence of other ions in the solution, which is expressed in terms of the potentiometric selectivity coefficients ($K_{I,A}^{-n}$), describing the preference by the membrane for an interfering ion (A^{n-}) relative to I^- , were determined by the fixed interference method (FIM) [36]. The selectivity coefficient for an anion was evaluated by the mixed solution method with a fixed concentration of interference, and varying amounts of I^- concentrations. Potentiometric selectivity coefficient data of the sensor for several anions relative I^- are shown in Table 2.

Table 2

Logarithm of the Selectivity coefficients of various interfering ions

Anion	$\log(K_{I,A}^{-n})$	Anion	$\log(K_{I,A}^{-n})$
SO_3^{2-}	-2.80	CrO_4^{2-}	-2.64
SCN^-	-3.58	HCO_3^-	-3.75
CO_3^{2-}	-3.11	SO_4^{2-}	-4.03
NO_2^-	-3.44	IO_3^-	-3.67
F^-	-3.56	ClO_4^-	-2.47
CN^-	-2.18	Cl^-	-3.40
BrO_3^-	-3.50	Br^-	-2.68
NO_3^-	-3.50	OH^-	-3.80

The selectivity coefficients clearly show that the electrode is selective to iodide over a number of other inorganic anions. The selectivity pattern of the electrode for several anions are $CN^- > ClO_4^- > CrO_4^{2-} > Br^- > SO_3^{2-} > CO_3^{2-} > Cl^- > NO_2^- > NO_3^- = BrO_3^- > F^- > SCN^- > IO_3^- > HCO_3^- > OH^- > SO_4^{2-}$. The electrode demonstrates a significant deviation in selectivity from the Hofmeister series [37, 38]. The reason that the selectivity coefficients do not comply with the Hofmeister series can be due to specific interaction of the anions with the metal center in the carrier (CuL) used in this study, i.e. chemical recognition of the anions, and specially of iodide, by the complex.

Table 3 lists slope, linear range, detection limit, response time, pH range and selectivity coefficients of some of other iodide-selective electrodes against proposed iodide-selective electrode for comparative purposes [17-23]. As can be seen, pH range for proposed electrode is wider than other iodide-selective electrodes and the selectivity coefficients obtained for the proposed electrode are superior to those reported iodide-selective electrodes listed in Table 3.

Table 3

Analytical performance of several iodide selective electrodes

Ref.	Slope (mV/decade)	Linear range (M)	Detection Limit (M)	Res. time (s)	pH range	$\log K_{A,B}$				
						SO_4^{2-}	SCN^-	NO_2^-	ClO_4^-	NO_3^-
[17]	59.4	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	N.R.	8	2.0-8.0	5.0	1.95	4.62	2.05	5.0
[18]	57.7	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	2.3×10^{-6}	10	0.8-7.0	-	1.05	3.13	1.42	2.27
[19]	58.6	$4.0 \times 10^{-5} - 1.0 \times 10^{-1}$	1.6×10^{-5}	3	7.0	3.9	-	2.5	-	1.6
[20]	58	$5.0 \times 10^{-7} - 5.0 \times 10^{-4}$	N.R.	N.R.*	8.0-10.0	-	1.9	2.5	2.3	4.5
[21]	58.9	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	3.0×10^{-7}	15	3.1-9.8	4.52	3.3	4.64	3.6	4.2
[22]	58.8	$8.2 \times 10^{-7} - 1.0 \times 10^{-1}$	5.3×10^{-7}	3	2.0-5.0	2.28	0.73	1.29	1.04	2.26
[23]	59.2	$5.3 \times 10^{-7} - 1.0 \times 10^{-2}$	N.R.	11	2.5-9.0	4.24	2.2	3.8	3.15	4.5
This work	58.6	$5.0 \times 10^{-6} - 1.0 \times 10^{-1}$	3.0×10^{-6}	9-25	3.0-10.0	4.40	3.58	3.44	2.0	3.60

* N.R.: Not reported

3.4. Analytical applications

The proposed membrane iodide electrode was successfully used as an indicator electrode in potentiometric titration of iodide ion solution ($7.6 \times 10^{-4} \text{ mol L}^{-1}$) with AgNO_3 solution ($1.0 \times 10^{-2} \text{ mol L}^{-1}$). The result of titration is shown in Fig 4, indicating that the amount of I^- can be determined with the electrode. The new iodide-selective electrode was satisfactorily applied to the determination of iodide in water samples. The analyses were performed by direct potentiometry using the standard addition technique. The results are summarized in Table 4. Good recoveries obtained by the method reveal the capability of the method for determination of iodide ion in water samples.

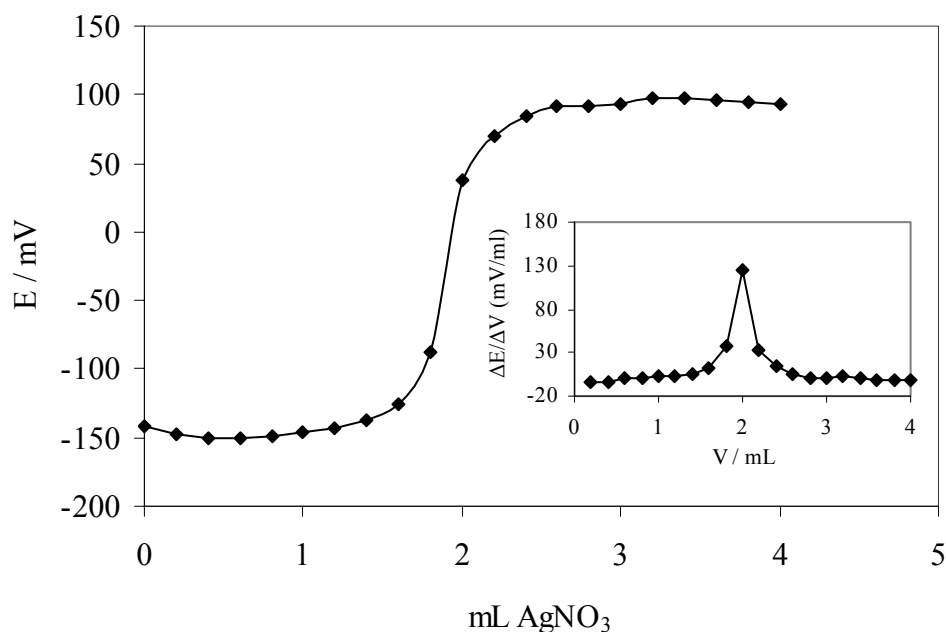


Fig. 4 Potentiometric titration curve of 25.0 mL $7.6 \times 10^{-4} \text{ mol L}^{-1}$ solution of I^- with $1.0 \times 10^{-2} \text{ mol L}^{-1}$ of AgNO_3 .

Table 4

Analytical results for iodide in water samples and by proposed sensor

Sample	Added I^- mol L^{-1}	Found I^- mol L^{-1}	Recovery %
Well water	0	5.01×10^{-6}	-
	2.00×10^{-5}	2.57×10^{-5}	103.6
	4.00×10^{-5}	4.32×10^{-5}	96.0
Tap water	0	-	-
	2.00×10^{-5}	2.04×10^{-5}	104.0
	4.00×10^{-5}	4.14×10^{-5}	103.5

In order to test the analytical utility of sensor it was used to determine iodide in POVIDONE (Ramin pharmaceutical laboratories) mouth wash sample. 10 ml of sample was oxidized with 10 mL of 5% H_2O_2 and 4.0 mL of NaOH . The mixture was heated, neutralized with H_2SO_4 to pH 6.9 and diluted with water. The obtained sample solution was analyzed by proposed membrane sensor. The result was shown in Table 5. The result is comparable with photometric method [39].

Table 5

Results of determination of iodide ion in mouthwash sample

Sample	Spectrophotometric Method	proposed sensor	Recovery %
POVIDONE	7.87×10^{-4} M	7.72×10^{-4} M	98.1

4. Conclusions

A copper organometallic complex performed well as an ionophore compound in the developed iodide selective electrode. The electrode showed better selectivity than most previous electrodes and was proved suitable for the determination of iodide in the presence of a much higher concentration of other anions. This electrode permits the direct measurement of iodide in the real samples without prior separation steps, thus considerably simplifying the determination procedure with respect to the other analytical methods used. With regard to sensitivity, that of the electrode described is similar to the sensitivity of the most sensitive iodide electrodes reported.

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