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New Coated Graphite Potentiometric Sensor for Selective Determination of Copper (II) Ions

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Abstract

A highly selective copper (II) coated graphite sensor was prepared by 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix 5) as a supramolecule ionophore into plasticized polyvinyl chloride (PVC) membrane. The best response characteristic was observed using the membrane composition of PVC = 30.0 mg, dioctyl sebacate (DOS) = 63.5 mg, palmitic acid (PA) = 3.0 mg and kryptofix 5 = 3.5 mg. The sensor exhibits a nernstian slope (30.0±0.2 mV/decade) in a wide linear concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with detection limit of 8.7×10^{-6} M. The electrode has a fast response time of 15 s with a satisfactory reproducibility and relatively long life time of about 16 weeks without significant drift in potential. The sensor operates in the wide pH range of 2.0-10.0. This sensor reveals a good selectivity towards Cu^{2+} ion over a wide range of alkali, transition and heavy metal cations. The electrode was used as an indicator electrode for potentiometric titration of Cu^{2+} using EDTA solutions. The proposed sensor was applied for the direct determination of Cu^{2+} cation and the results were compared with those obtained from atomic absorption spectrometric analysis and were found in good agreement. Also this sensor was successfully used for determination of copper (II) in real samples.

Keywords: *Coated graphite sensor, Copper (II) cation, Potentiometry, Kryptofix 5.*

Introduction

Copper is an essential trace element that is vital to the health of all living things (humans, plants, animals and microorganisms). In humans, copper is essential to the proper functioning of organs and metabolic processes. The human body has complex homeostatic mechanisms which attempt to ensure a constant supply of available copper, while eliminating excess copper whenever this occurs. However, like

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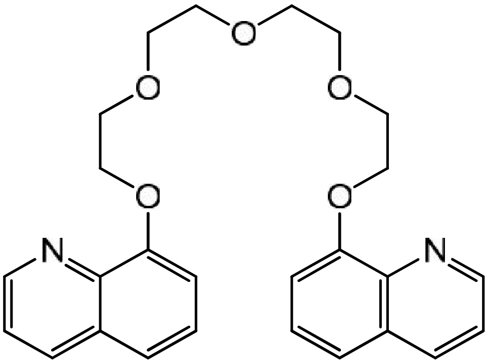
all essential elements and nutrients, too much or too little nutritional ingestion of copper can result in a corresponding condition of copper excess or deficiency in the body, each of which has its own unique set of adverse health effects. Copper excess is a subject of much current research. Distinctions have emerged from studies that copper excess factors are different in normal populations versus those with increased susceptibility to adverse effects and those with rare genetic diseases. This has led to statements from health organizations that could be confusing to the uninformed. [1-5]. Some conditions previously linked to copper deficiency include osteoporosis, osteoarthritis, rheumatoid arthritis, cardiovascular disease, colon cancer and chronic conditions involving bone, connective tissue, heart and blood vessels [6-9]. The determination of copper, therefore, is important and some instrumental methods such as UV-Vis spectrophotometry [10,11], stripping voltammetry [12,13], atomic absorption spectrometry [14,15] and Chromatography [16,17] are used for the determination of copper at low concentration level. These methods require sample pretreatment, are time consuming and not very useful for routine analysis of large number of environmental samples.

Ion-selective electrodes (ISEs) possess many advantages over traditional methods of analysis and provide accurate, reproducible, fast and regular selective determination of various ionic species. In addition, ion-selective sensors allow non-destructive, on-line monitoring of particular ions in a small volume of sample without any pretreatment. Because of these merits, the use of ISEs is increasing day by day in medicinal, environmental, agricultural and industrial fields [18-21].

Ionophore, also called the “ion carrier,” is the most important component of any polymeric membrane sensor with respect to sensitivity and selectivity, because the molecular-level phenomenon that is sensed by the ISE is the binding between the ionophore and target ion. The different selectivities of an ISE toward other ions, hence, may be considered to originate from the difference in binding strengths between any chosen ionophore, to be used in the sensor, and various ions. Supramolecules such as schiff bases, calixarenes, crown compounds and their derivatives are the excellent choice as sensing materials in the construction of potentiometric ion selective sensors because of their ability to complex selectively to a particular ion [22]. Further, it is reported that the introduction of other constituents into the flexible crown ring may enhance their selectivity towards a particular charged species. Therefore, in this study, 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix 5) (Scheme 1), a pod and with five donor oxygen atoms, has been tried as electroactive material for the fabrication of copper (II) selective sensor.



Scheme 1. Structure of ionophore 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix 5).

Experimental

Materials

All reagents were of analytical grade and used without further purification. High molecular weight polyvinyl chloride (PVC) and graphite powder were from Fluka. Sodium tetraphenylborate (NaTPB), palmitic acid (PA), dibutyl phthalate (DBP), dioctyl sebacate (DOS), dioctyl phthalate (DOP), nitrobenzene (NB), tetrahydrofuran (THF), nitric acid, sodium hydroxide, EDTA, 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix 5) and nitrate salts were from Merck. All solutions were prepared with double distillated deionized water.

Apparatus and EMF measurements

The potential measurements were carried out with a digital potentiometer Model PTR-79 (Zag Chemi, Iran) having ± 0.01 mV accuracy and an Ag/AgCl elelectrode (Azar electrode, Iran) was used as a reference electrode. Flame atomic absorption spectrometric (FAAS) measurements were performed on a 990-PG instrument equipped with an air-acetylene flame and a copper-hollow cathode lamp. The pH of the solutions was measured by a conventional glass pH electrode. All measurements were carried out at 25 °C with a cell type:

$$\mathrm{Ag/AgCl;\ KCl(satd.)}\ \|\ \mathrm{Cu^{2+}\ sample\ solution}\ |\ \mathrm{ion\ selective\ membrane}\ |\ \mathrm{graphite\ bar}$$

The potential readings were made after the potential reached to a constant value. The performance of the electrode was investigated by measuring the potential of Cu^{2+} solutions over the range of 1.0×10^{-8} to 1.0×10^{-1} M. The data were plotted as observed potential vs the logarithm of copper (II) cation concentration. Potentiometric selectivity coefficient (K_{ij}^{pot}) was determined by separate solution method (SSM).

Preparation of membrane and electrode construction

The electrode was prepared from a graphite bar (4 mm diameter and 50 mm long) from battery.

The graphite bars were polished and put in a concentrated HNO_3 solution overnight to clean the surface of the electrodes. Then, the bars were rinsed with THF and once again polished and washed with distilled water and allowed to dry. A mixture of PVC (as matrix), DOS (as plasticizer), palmitic acid (for increasing the electrical and mechanical conduction of coated membrane) and kryptofix 5 (as an electroactive material) to give a total mass of 100 mg, was dissolved in 2 ml of THF. The resulting clear solution was evaporated slowly at ambient temperature until an oily concentrated mixture was obtained. The graphite bar was then repeatedly dipped (three times, a few seconds between dips) into the mixture. A membrane was formed on the graphite surface as sensing layer which was allowed to set overnight at room temperature. The coated electrode was conditioned in a 1.0×10^{-3} M copper (II) nitrate solution for 24 h. The coating solutions were stable for several days and could be used for construction of new membranes.

Results and discussion

Effect of membrane composition on the sensor response and calibration curve

It is well known that some important features of the PVC-based membranes, such as the nature and amount of the ionophore, the properties of the plasticizer, the plasticizer/ PVC ratio and especially the nature of the additives used, significantly influence the sensitivity and selectivity of the ion selective sensors [23-26]. Thus, different aspects of preparation of membranes based on kryptofix 5 were investigated and the results are given in Table 1.

Table 1. Optimization of the Cu^{2+} selective membrane ingredients.

Membrane No.	Membrane mass composition (mg)				Slope (mV/decade)	Linear range (M)
	PVC	Ionophore (Kryptofix 5)	Additive	Plasticizer		
1	30	7.0	—	63.0 (DOS)	17.9±2.7	10^{-3}-10^{-1}
2	30	—	7.0 (PA)	63.0 (DOS)	14.2±2.0	10^{-3}-10^{-1}
3	30	4.0	3.0 (PA)	63.0 (DOP)	30.6±0.5	10^{-4}-10^{-2}
4	30	4.0	3.0 (PA)	63.0 (NB)	16.1±2.0	10^{-3}-10^{-1}
5	30	5.0	4.0 (PA)	61.0 (DBP)	26.7±0.3	10^{-3}-10^{-1}
6	30	5.0	3.0 (PA)	62.0 (DBP)	24.8±0.1	10^{-3}-10^{-1}
7	30	3.5	3.0 (PA)	63.5 (DOS)	30.0±0.2	10^{-5}-10^{-1}
8	30	5.5	4.5 (NaTPB)	60.0 (DBP)	31.5±2.2	10^{-3}-10^{-1}
9	30	5.0	5.0 (NaTPB)	60.0 (NB)	18.3±1.9	10^{-3}-10^{-1}
10	30	5.0	5.0 (NaTPB)	60.0 (DOP)	22.0±0.1	10^{-3}-10^{-1}
11	30	5.0	4.0 (NaTPB)	61.0 (DOP)	22.9±1.7	10^{-5}-10^{-1}
12	30	4.0	4.0 (NaTPB)	62.0 (DOS)	28.1±0.8	10^{-5}-10^{-2}
13	30	5.0	3.0 (NaTPB)	62.0 (DOS)	26.6±0.2	10^{-4}-10^{-1}
14	30	4.0	4.0 (NaTPB)	62.0 (DBP)	25.3±0.3	10^{-6}-10^{-3}
15	30	7.0	5.0 (NaTPB)	60.0 (DOS)	27.8±1.1	10^{-3}-10^{-1}
16	30	4.0	4.0 (graphite powder)	62.0 (DOS)	26.0±0.7	10^{-3}-10^{-1}
17	30	5.0	2.0 (graphite powder)	63.0 (DBP)	21.0±0.8	10^{-3}-10^{-1}

Ionophores for use in sensors should have rapid exchange kinetics and adequate complex formation constants in the membrane. Also, they should be well soluble in the membrane matrix and have a sufficient lipophilicity to prevent leaching from the membrane into the sample solution. In addition, the selectivity of the neutral carrier-based ISEs is known to be governing by stability constant of the neutral carrier-ion complex and its partition constant between the membrane and sample solution [27]. As is shown in Table 1, 3.5 mg of kryptofix 5 was chosen as the optimum amount of the ionophore in the PVC-membrane (membrane No. 7). In the absence of kryptofix 5, a non-Nernstian slope (14.2 mV/decade) was observed.

Solvent polymeric membrane ion selective electrodes are usually based on a matrix of the solvent mediator/PVC ratio of about 2. Polymeric films with such a plasticizer/PVC ratio will result in optimum physical properties and high enough mobility of their constituents. In this study, a plasticizer/PVC ratio of about 2 was found to be the most suitable. It is reported that the selectivity and working concentration range of membrane sensors are affected by the nature and amount of the plasticizer used. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ionophore molecules and the state of ligands [28]. As is obvious from Table 1, among the four different plasticizers used, DOS (63.5 mg) resulted in the best sensitivity (membrane No. 7).

The presence of lipophilic anions in cation selective membrane electrodes is advantageous for decreasing the ohmic resistance and anion interference, and for enhancing the response behavior, selectivity and sensitivity of the membrane electrodes. In addition, lipophilic anions induce permselectivity of the PVC membrane electrodes [29]. The potential response of the Cu^{2+}-ISE containing a lipophilic anion additive was investigated to examine the effect of the additive content (Table 1). The results revealed that the potential response of the electrode in the absence of additives led to weak sensitivity with a diminished slope of 17.9 mV/decade over a linear range from 1.0×10^{-3} to 1.0×10^{-1} M. The sensitivity was greatly improved by increasing the amount of lipophilic anion, which led to the best performance with a Nernstian slope. As is shown in Table 1, it is evident that the nature and amount of additive influence the performance of the membrane sensor. Thus, the addition of 3.0 mg palmitic acid (membrane No. 7) significantly increased the sensitivity of the response of the Cu^{2+} sensor.

Thus, the best response was observed with the membrane composed of the following ingredients: 30.0 mg PVC, 63.5 mg DOS, 3.5 mg kryptofix 5 and 3.0 mg palmitic acid (membrane No. 7). The characteristic properties of this optimized coated membrane were studied and the calibration curve for Cu^{2+} cation is shown in Figure 1. Over the concentration range from 1.0×10^{-5} to 1.0×10^{-1} M of the cation, the electrode potential response was linear with the logarithm of copper cation concentration. The slope of the calibration curve was found to be: 30.0±0.2 mV/decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.7×10^{-6} M.

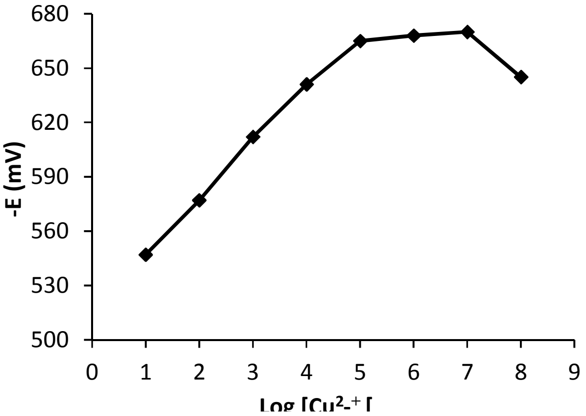


Figure 1. Calibration curve of the Cu^{2+} selective sensor based on kryptofix 5.

pH effect on potential response

The influence of pH on the potential response of the optimized sensor was tested over a pH range of 1.0-12.0 (concentrated NaOH or HNO_3 solutions were employed for the pH adjustment) and the result is shown in Figure 2. As it is seen, the pH effect of the test solutions (1.0×10^{-3} M and 1.0×10^{-2} M) on the potential response of the copper sensor was found to remain constant in the pH range of 2.0-10.0. The observed drift at higher pH values could be due to the formation of some hydroxyl complexes of Cu (II) in the solution. At the lower pH values, the potentials decreased. This is due to the existence of nitrogen donor atoms in the structure of the ionophore which can be easily protonated, indicating that the sensor responds to hydrogen ions.

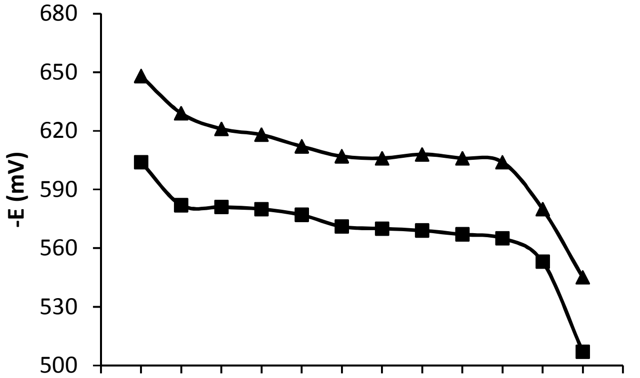


Figure 2. Effect of pH on potential response of the Cu^{2+} selective sensor using (■) 1.0×10^{-2} M and (▲) 1.0×10^{-3} M of Cu^{2+} solutions.

Static and dynamic response times

Static and dynamic response times are important factors for the assessment of the analytical applicability of ion selective sensors.

In the present study, the static response time was recorded (for sensor No. 7) by plotting the potential response vs. time, at 1.0×10^{-3} M and 1.0×10^{-2} M of Cu^{2+} ion solutions (Figure 3). As shown in this figure, throughout the entire concentration range, the sensor reached equilibrium in a short period of time (15 s) and potentials stay constant for about 2 min. This behavior can be due to the fast exchange kinetics of the complexation-decomplexation of Cu (II) cations with the ion carrier at the test solution-membrane interface.

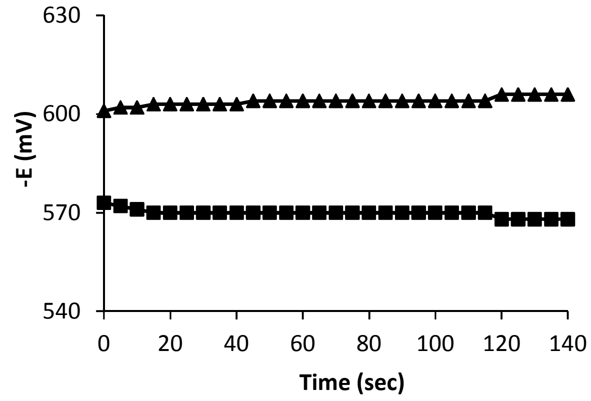


Figure 3. Static response time curve of the Cu^{2+} selective sensor for (■) 1.0×10^{-2} M and (▲) 1.0×10^{-3} M of Cu^{2+} solutions.

The dynamic response time has been recorded by changing solutions with different Cu^{2+} concentrations. The measurement sequence was from the lower (1.0×10^{-5} M) to the higher (1.0×10^{-1} M) concentration. The actual potential vs. time traces is depicted in Figure 4. As it is seen, the sensor reached the equilibrium response in a short time of about 15 s.

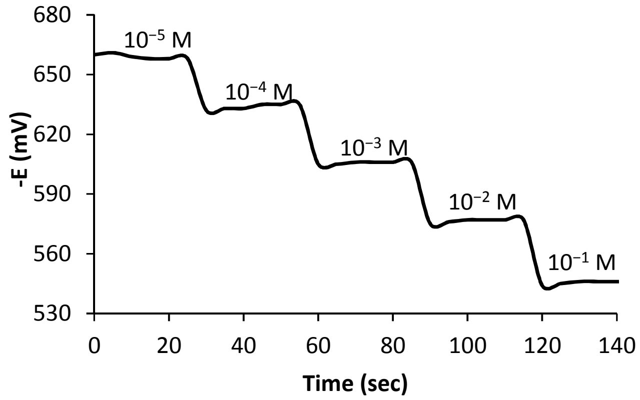


Figure 4. Dynamic response time of the Cu^{2+} selective sensor.

To evaluate the reversibility of the optimized sensor, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from (1.0×10^{-2} to 1.0×10^{-3} M) sample concentrations (Fig. 5). The results showed that, the potentiometric response of the sensor was reversible. The sensing behavior of the electrode remained unchanged when the potentials recorded either from low-to-high concentrations or vice versa.

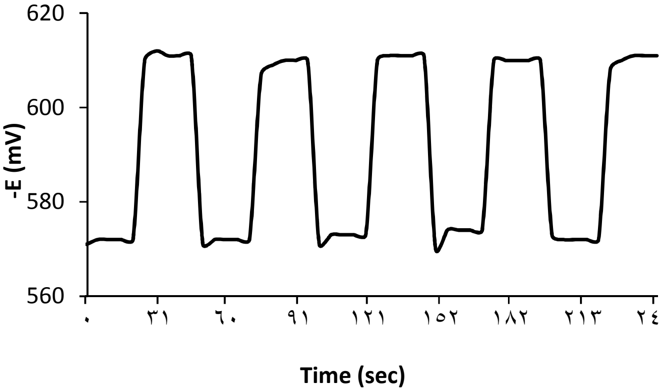


Figure 5. Response characteristics of the Cu^{2+} selective sensor for several high-to-low (1.0×10^{-2} to 1.0×10^{-3} M) sample cycles.

Selectivity

The potentiometric selectivity coefficient (K_{ij}^{pot}) of an electrode as one of the most important characteristics is defined by its relative response for the primary ion over other ions present in the solution. In this work, the potentiometric selectivity coefficient was determined by the separate solution method (SSM) [30,31]. In this method, the potential of a cell comprising an ion selective electrode and a reference electrode is measured with two separate solutions, one containing the ion *i* at the activity ai (but no *j*), the other one containing the ion j at the same activity $a_i = a_j$ (but no *i*). If the measured values are E_i and E_j, respectively, the value of K_{ij} pot is calculated from the equation:

$$\log K_{ij}^{pot} = \frac{E - E}{2.3 \quad R \ /z} + (1 - z_i/z_j) \log a_i$$

The resulting selectivity coefficient values thus obtained for the proposed Cu^{2+} sensor are given in Table 2. As can be seen, for all cation used (except for Li^+ and Co^{2+}), the selectivity coefficients are smaller than 0.01, which seem to indicate that the disturbance produced by these cations in the functioning of the Cu^{2+} sensor are negligible.

Table 2. Selectivity coefficients of various interfering ions for Cu^{2+} selective sensor.

Interference ion	**Selectivity coefficient ($K_{Cu,j}^{Pot}$)**
Ag^+	3.1×10^{-3}
K^+	5.6×10^{-3}
Li^+	2.6×10^{-2}
Sr^{2+}	9.5×10^{-3}
Pb^{2+}	7.8×10^{-4}
Ni^{2+}	9.3×10^{-3}
Zn^{2+}	5.5×10^{-4}
Cd^{2+}	4.3×10^{-3}
Co^{2+}	1.2×10^{-2}
Cr^{3+}	2.7×10^{-3}
Fe^{3+}	4.0×10^{-4}
Ce^{3+}	3.1×10^{-4}

Lifetime

The lifetime of the Cu^{2+} coated graphite sensor was tested over a period of 20 weeks. During this period, the electrode was in daily use over an extended period of time (1 h per day), and the results are provided in Table 3. According to Table 3, after 16 weeks a very slight gradual decrease in the slopes and linear concentration range was observed. This is caused by the leakage of the ionophore from the membrane to the solution.

Table 3. Lifetime of the Cu^{2+} selective sensor.

Week	Slope (mV/decade)	Linear concentration range (M)	Week	Slope (mV/decade)	Linear concentration range (M)
1	30.0±0.2	10^{-5}-10^{-1}	11	28.3±0.1	10^{-5}-10^{-1}
2	30.0±0.1	10^{-5}-10^{-1}	12	28.5±0.3	10^{-5}-10^{-1}
3	29.8±0.1	10^{-5}-10^{-1}	13	28.8±0.3	10^{-5}-10^{-1}
4	29.6±0.3	10^{-5}-10^{-1}	14	28.7±0.2	10^{-5}-10^{-1}
5	29.5±0.5	10^{-5}-10^{-1}	15	28.6±0.3	10^{-5}-10^{-1}
6	29.3±0.3	10^{-5}-10^{-1}	16	28.6±0.4	10^{-5}-10^{-1}
7	29.1±0.2	10^{-5}-10^{-1}	17	28.0±0.4	10^{-4}-10^{-1}
8	29.0±0.4	10^{-5}-10^{-1}	18	27.8±0.5	10^{-4}-10^{-1}
9	28.7±0.4	10^{-5}-10^{-1}	19	27.3±0.7	10^{-4}-10^{-1}
10	28.8±0.2	10^{-5}-10^{-1}	20	26.0±0.5	10^{-3}-10^{-1}

Analytical performance

The proposed Cu^{2+} sensor was found to work well under laboratory conditions. This electrode was used to determine the end-point in the potentiometric titration of Cu^{2+} with EDTA solutions. Two typical titration curves are shown in Fig. 6. In this process, 25 ml of 1.0×10^{-3} M and 25 ml of 1.0×10^{-4} M copper nitrate solutions were titrated with 1.0×10^{-2} M and 1.0×10^{-3} M EDTA solutions, respectively. As can be seen, the end points of titration are sharp and this titration method can determine the amount of copper ion accurately.

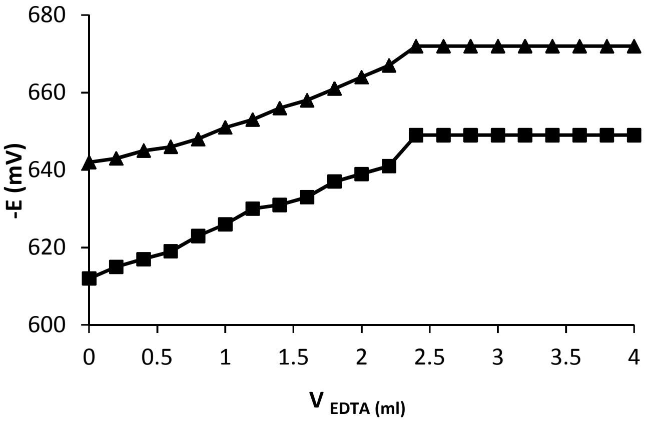


Figure 6. Potentiometric titration curves of 25 ml of Cu^{2+} (■1.0×10^{-3} M and ▲1.0×10^{-4} M) with 1.0×10^{-2} M and 1.0×10^{-3} M of EDTA solutions, respectively.

This sensor was also used to the direct determination of copper in doubly distilled water (DDW) spiked with 4.0 and 8.0 ppm copper (II). The results obtained were compared with those obtained from atomic absorption spectrometric (AAS) analysis and were found in good agreement (Table 4). Therefore, the designed sensor is preferable to AAS as an alternative method, because it is simple, rapid and relatively inexpensive.

Table 4. Determination of Cu^{2+} concentration in DDW samples spiked with 4.0 and 8.0 ppm copper (II) using the Cu^{2+} selective sensor and comparison with AAS.

Sample No.	AAS (ppm) (n = 3)	Cu^{2+} selective sensor (ppm) (n = 3)
1	4.2±0.1	4.4±0.3
2	8.1±0.3	8.3±0.5

Application in real samples

In addition, the Cu^{2+} selective sensor was successfully applied to the determination of copper (II) in neutral water samples and the results are shown in Table 5. It is obvious that the recovery of copper from different water samples is almost quantitative.

Table 5. Potentiometric determination of Cu^{2+} ion in different real water samples using the Cu^{2+} selective sensor.

Real water samples	**Added Cu^{2+} concentration (M)**	**Found Cu^{2+} concentration (M)**	**Recovery (%)**
Tap water (Ahvaz city, Iran)	1.0×10^{-4}	9.6×10^{-5}	96.0
River water (Dez river, Iran)	1.0×10^{-4}	9.5×10^{-5}	95.0
Persian Gulf water	3.0×10^{-4}	2.8×10^{-4}	93.3

Conclusion

Kryptofix 5 can be used as an excellent supramolecule ion carrier for construction of a PVC-based coated graphite ion selective sensor for determination of copper ions.

Table 6. Comparison of the characteristics of the proposed sensor with those of the previously reported Cu (II) sensors.

Ref. No.	Ionophore	Lifetime (week)	Slope (mV/decade)	pH range	Linear range (M)	Response time (s)
[32]	2,2'-dithiodianiline	4	30.0±1.0	1.0-3.0	7.0×10^{-7}-5.0×10^{-2}	10
[33]	bis[acetylacetonato]	12	29.3±0.2	2.6-6.0	2.0×10^{-6}-1.0×10^{-1}	9
[34]	4-phenyl-4-sulfide-11-(1-oxodecyl)-1,7-dithia-11-aza-4-phosphacyclotetradecane	7	30.7±1.7	3.9-6.4	3.0×10^{-6}-1.0×10^{-2}	—
[35]	1-phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione	9	28.8±0.1	3.0-8.0	2.0×10^{-6}-5.0×10^{-3}	10
[36]	dimethyl 4, 4′-(o-phenylene)bis(3-thioallophanate)	8	30.3	3.1-7.6	9.8×10^{-6}-1.0×10^{-1}	20
[This work]	1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (kryptofix 5)	16	30.0±0.2	2.0-10.0	1.0×10^{-5}-1.0×10^{-1}	15

The best composition of the proposed sensor was found to be PVC: DOS: PA: ionophore = 30.0:63.5:3.0:3.5 (w/w). It exhibits comparable performance to the reported Cu^{2+} selective sensors in many respects (Table 6), but shows significant superiority over them in terms of wide pH range (2.0-10.0) and long lifetime (16 weeks). The sensor responds to Cu^{2+} in a Nernstian fashion and displays good selectivity and detection limit. The proposed sensor can be used for copper determination both by direct potentiometry and potentiometric titration. It was also applied to determination of copper ions in real water samples.

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