Determination of Copper in Black, Red Pepper and the Waste Water Samples by a Highly Selective Sensitive Cu(II) Microelectrode Based on a New Hexadentates Schiff's Base

Parviz Norouzi,*[*] Mohammad Reza Ganjali, Farnoush Faridbod, and Masoud Salavati-Niasari[†]

Center of Excellence in Electrochemistry (CEE), Faculty of Chemistry, University of Tehran, Tehran, Iran
[*]E-mail: norouzi@khayam.ut.ac.ir
[†]Department of Chemistry, Kashan University, Kashan, Iran

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A Cu^{2+} ion-selective membrane microelectrode has been fabricated from poly vinyl chloride (PVC) matrix membrane containing a new symmetrical hexadentate Schiff's base 2-{1-(E)-2-((Z)-2-{(E)-2-[(Z)-1-(2-hydroxyphenyl)ethylidene] hydrazono}-1-methylpropylidene)hydrazono]ethyl}phenol (HDNOS) as a neutral carrier, Potassium tetrakis(4-chlorophenyl) borate (KTpClPB) as an anionic excluder and *o*-nitrophenyloctyl ether (NPOE) as a plasticizing solvent mediator. The microelectrode displays linear potential response in the concentration range of 1.0×10^{-5}-1.0×10^{-11} M of Cu^{2+}. The microelectrode exhibits a nice Nernstian slope of 25.9 ± 0.3 mV decade^{-1} in the pH range of 3.1-8.1. The sensor has a relatively short response time in whole concentration ranges (~5 s). The detection limit of proposed sensor is 5.0×10^{-12} M (320 pg/L), and it can be used over a period of eight weeks. The practical utility of the sensor has been demonstrated by using it as an indicator electrode in the potentiometric titration of Cu^{2+} with EDTA. The proposed membrane electrode was used for the direct determining of Cu^{2+} content in black and red pepper, and in waste water samples.

Key Words : Copper, Ion-selective microelectrode, PVC membrane, 2-{1-(E)-2-((Z)-2-{(E)-2-[(Z)-1-(2-Hydroxyphenyl)ethylidene]hydrazono}-1-methyl propylidene)hydra zono]ethyl}phenol (HDNOS)

Introduction

Due to the vital importance of copper in biological,[1] environmental and industrial systems[2] and the urgent need for a highly selective and sensitive copper sensor for potentiometric determination of copper in these systems, a number of potentiometric sensors based on different ionophores such as 6-methyl-4-(1-phenylmethylidene)amino-3-thioxo-1,2,4-triazin-5-one, macrocyclic poly ether, 2-(1'-(4'-(1'-hydroxy-2''-naphthyl)methyleneamino)butyliminomethyl)-1-naphthol, diphenylisocyanate bis(acetylacetone) ethylenedinnine (DIBAE), as a new hexadentates Schiffs base, 1-hydroxy-2-(prop-2'-enyl)-4-(prop-2'-enyloxy)-9,10-anthraquinone, a new thiophene-derivative Schiff's base, mixed aza-thioether crowns containing a 1,10-phenanthroline, ortho-xylylene bis(dithiocarbamates), macrocyclic diamide have been reported.[3-16] These sensors have one, or two and in some cases all of following problems; a) relatively high detection limit, b) relatively narrow dynamic range, and c) suffer serious interfering ions such as Ni^{2+}, Co^{2+}, Pb^{2+} ions.

In this work, we wish to present a highly selective and sensitive Cu^{2+} membrane microsensor based on HDNOS as an excellent ion carrier for the sub-ppt level monitoring of Cu^{2+} ions in various real samples.

Experimental Section

Reagents. Potassium tetrakis(4-chlorophenyl) borate (KTpClPB), PVC of high relative molecular weight, *o*-nitrophenyloctyl ether (NPOE), nitrobenzene (NB), acetophenon (AP), dibutylphthalate (DBP), tetrahydrofuran (THF), chloride and nitrate salts of cations were of the highest purity available (from Merck and Aldrich) and were used without further purification. All aqueous solutions were prepared with deionized distilled water. The pH of all solutions was adjusted with the use of dilute nitric acid and sodium hydroxide.

Synthesis of the ionophore HDNOS. Step one: the synthesis of butane-2,3-dihydrazone: To a boiling solution of 11.63 g of aqueous hydrazine (0.24 M) in 100 mL of methanol, were added 75 mL of biacetyl (0.12 mol, 10.33 g), over a period of 120 minutes. Refluxing was continued for an additional 60 minutes. Then 200 mL of water were added and the methanol was removed by distillation. After cooling the resulting aqueous solution in an ice-bath, white crystals of the product were formed. These were filtered, washed with a little water, recrystalized from 100 mL of hot methanol, and dried in vacuum, m.p 158-159 °C (reported 158 °C); Yield ~54%. Anal. Cacd. For $C_4H_{10}N_4$: C, 42.09; H, 8.83; N, 49.08. Found: C, 42.16; H, 8.71; N, 49.74. IR (KBr, cm^{-1}): 3330, 3180 (νN-H); 1580 (νC=N), 1615 (νNH_2).

Step two: the Schiff-base ligand (Figure 1) was prepared according to literature through the well-known, as follows: 2,3-butanedihydrazone (1.14 g, 0.01 mol) was dissolved in 50 mL ethanol and then transferred into a 250 mL three-necked flask. Under reflux 2.72 g (0.02 mol) of 2-hydroxyacetophenone in 80 mL of ethanol was added dropwise to the flask. The stirred mixture was kept reacting for 3 h under

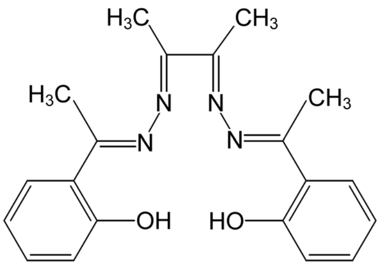

Figure 1. Structure of the ionophore HDNOS.

reflux, and then cooled to room temperature. The solid product was filtered, and the product was recrystallized from chloroform. Yield ~68%. Anal. Calcd. for $C_{20}H_{22}N_4O_2$: C, 68.55; H, 6.33; N, 15.99. Found: C, 68.41; H, 6.26; N, 9.24%. IR (KBr, cm^{-1}): 3443 ($\upsilon_{O\text{-}H}$); 1608, 1575 ($\upsilon_{C=N}$).

Electrode preparation. For the PVC membrane preparation, the dipping method was applied.[17] According to this method, 25 mg of powdered PVC, 69 mg of NPOE, 2 mg of additive KTpClPB and 4 mg of HDNOS were dissolved in 3 mL of THF and mixed well. The resulting mixture was transferred into a glass dish with a 2 cm diameter. The solvent was slowly evaporated until a relative oily concentrated was obtained. The gold electrode was prepared by sealing the gold micro-wire (Goodfellow Metals Ltd., UK) into a soft glass capillary. The capillary was then cut perpendicularly to its length to expose the gold wire. Electrical contact was made using silver epoxy (Johnson Matthey Ltd., UK). In the beginning of each experiment, the electrode surface was polished for 1 min with the aid of extra fine carborundum paper and then for 10 min with 0.3 mm alumina, sonicated in distilled water and dried in air. The polished gold electrode was dipped into the membrane solution mentioned above and the solvent was evaporated. A membrane was formed on the gold surface and the electrode was allowed to set overnight. The electrode was finally conditioned for 48 h by soaking in a 1.0×10^{-3} M of $CuCl_2$.

Apparatus. Potentials were measured by a Corning ion analyzer Model 250-pH/mV meter. The pH of the sample solutions was monitored simultaneously by a conventional glass pH electrode.

EMF measurements. All emf measurements were carried out with the following assembly; Hg_2Cl_2, KC1 (satd.) | sample solution | PVC membrane | gold surface

Results and Discussion

At first, the interaction between HDNOS and common cations was tested. To the best of our knowledge, there is no report on the stability of HDNOS complex with common metal ions. Thus, the HDNOS complexation with a number of cations was conductometrically investigated in an acetonitrile solution, at 25 ± 0.05 °C, in order to obtain a clue about the stability and selectivity of the resulting complexes. The stability constants of the HDNOS-M^{n+} complexes were calculated as described in detailes elsewhere.[18,19] The formation constants of the studied complexes are given in Table 1. The results in Table 1 shows the formation of a relatively strong 1 : 1 complex between HDNOS and Cu^{2+} ion.

Table 1. Formation constants of M^{n+}-HDNOS Complexes in acetonitrile solution in 25 ± 0.05 °C

Cation	Formation Constant log K_f
Li^+	< 2.0
Na^+	< 2.0
K^+	< 2.0
Mg^{2+}	< 2.0
Ca^{2+}	< 2.0
Cu^{2+}	5.31 ± 0.09
Zn^{2+}	2.74 ± 0.03
Co^{2+}	2.89 ± 0.09
Ni^{2+}	2.93 ± 0.12

Due to the exictance of the two nitrogen (as intermediate dodnor atom) and two oxygen atoms as (hard donor atom) makes it as sutiable ion carrier in construction of transition metal ion sensors especially for intermediate ones (copper, nickel, cobalt, and zinc ions). The obtained results that showed in Table 1 revealed that among the transitional metal ions tested, the copper ion has the most intraction with six donor atoms of the ionophore. And maybe used as a sutiable ionophore in construction of Cu^{2+} ion selective microelectrode.

Thus, in the next experiment, due to the specific interaction of copper ion and HDNOS, the neutral ion-carrier HDNOS was applied in the construction of PVC-based membrane microsensors for copper ion and a wide variety of metal ions, including alkali, alkaline earth, transition and heavy metal ions (in the same conditions). Except for the Cu^{2+}, for all other cations, the slope of the corresponding potential-pM plot is much lower than the expected Nernstian slopes of 60, 30 and 20 mV per decade for the univalent, bivalent and trivalent cations, respectively. However, Cu^{2+}, with the most sensitive response among all the tested cations, seems to be suitable determined by the membrane electrode based on the HDNOS.

Because the sensitivity and selectivity of any given membrane microelectrode is significantly related to the composition of the ion selective membrane and the nature of the solvent mediators and additives used,[20-28] we decided to study such effects on the behavior of the proposed microelectrode. The effect of the nature and amount of the plasticizer, the amount of PVC and the additive on the potential response of the proposed Cu^{2+} microelectrode were investigated. The obtained results are provided in Table 2.

Evidently, NPOE is a more effective solvent mediator than DBP in the preparation of the Cu^{2+} ion-selective electrode. This is due to the ability of NPOE as a polar solvent for extraction of Cu^{2+} ion with a very high charge density. It should be noted that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex.

The data given in Table 2 reveal that the presence of anionic additive in the construction of cationic sensors has a

Table 2. Optimization of membrane ingredients of the Cu^{2+} ion-selective microelectrode based on HDNOS

No.	PVC %	Plasticizer %	Ionophore %	Additive %	Slope
A	25	70,DBP	3	2	17.1 ± 0.2
B	25	69,DBP	4	2	18.6 ± 0.9
C	25	68,DBP	5	2	18.1 ± 0.3
D	25	69,AP	4	2	20.3 ± 0.3
E	25	69,NB	4	2	24.7 ± 0.6
F	25	69,NPOE	4	2	25.7 ± 0.3
G	25	73,NPOE	–	2	3.2 ± 0.2
H	30	64,NPOE	4	2	20.1 ± 0.3
I	20	74,NPOE	4	2	23.2 ± 0.2

beneficial influence on the performance characteristics of the membrane electrode. The presence of anionic additives can reduce the ohmic resistance and improve the response behavior and selectivity of the membrane electrodes.[29,30] Nevertheless, the best performance was obtained with a membrane composition of 25% PVC, 69% NPOE, 4% HDNOS, and 2% KTpClPB (No. F).

The potential response of the proposed microsensor is depicted in Figure 2. Figure 2 presents that the Cu^{2+} microsensor exhibits a Nernstian response to the concentration of Cu^{2+} ions in the range of 1.0×10^{-5}-1.0×10^{-11} M .

The microelectrode lifetime, which is a measure of microelectrode durability, was also studied in 12 weeks period. During this period, the microelectrode was used for 2 hours per day and 5 days per week. After each usage, it was washed completely. After 8 weeks, only relatively slight changes in the microelectrode slope and the detection limit from 25.7 ± 0.3 mV/decade and 5.0×10^{-12} M to 18.8 ± 0.7 mV/decade and 4.0×10^{-10} M of Cu^{2+} activity were observed, respectively. The results of this study are shown in Table 3.

In this study, the matched potential method (MPM) and separation solution method (SSM)[31,32] was used for the selectivity coefficients determination of the microelectrode.

According to MPM method, the specified activity (concentration) of the primary ion (A) (A = 1.0×10^{-11}-1.0×10^{-8} M of Cu^{2+}) is added to a reference solution (1.0×10^{-11} M of Cu^{2+}) and, afterwards, the potential is measured. In a separation experiment, the interfering ions (B) (B = 1.0×10^{-3}-1.0×10^{-2} M) are successively added to an identical reference solution until the measured potential matches that obtained before by adding the primary ions. The matched potential method selectivity coefficient, K_{MPM}, is then given by the resulting primary ion to the interfering ion activity (concentration) ratio. The selectivity coefficient, $K_{A,B}^{Pot}$, is determined as;

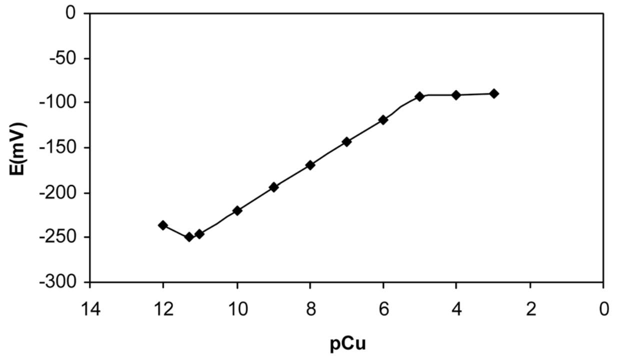

Figure 2. Calibration curve of Cu^{2+} ion-selective microelectrode sensor based on HDNOS (membrane F).

Table 3. Lifetime and stability of the Cu^{2+} ion-selective microelectrode based on HDNOS (membrane F)

Week	Slope	Detection Limit
1	25.7 ± 0.3	5.0×10^{-12}
2	25.6 ± 0.4	5.5×10^{-12}
3	23.8 ± 0.2	5.0×10^{-12}
4	25.3 ± 0.5	6.0×10^{-12}
5	25.6 ± 0.8	6.0×10^{-12}
6	25.1 ± 0.3	7.0×10^{-12}
7	25.0 ± 0.6	7.0×10^{-12}
8	25.2 ± 0.8	7.5×10^{-12}
9	24.1 ± 0.2	9.0×10^{-12}
10	23.0 ± 0.4	2.5×10^{-11}
11	20.9 ± 0.3	7.0×10^{-11}
12	18.8 ± 0.7	4.0×10^{-10}

$$K_{A,B}^{Pot} = a_A/a_B \tag{1}$$

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.

In separation solution method (SSM) the concentrations of a cell comprising an ion-selective electrode and a reference electrode (ISE cell) are adjusted with each of two separate solutions, one containing the ion A of the activity a_A (but no B), the other containing the ion B (but no A) of the activity as high as required to achieve the same measured cell voltage. From any pair of activities a_A and a_B giving the same cell voltage, the value of K_{AB}^{Pot} may be calculated from the equation:

$$K_{AB}^{Pot} = a_A/a^{z_A/z_B} \tag{2}$$

The resulting selectivity coefficients values are summarized in Table 4. It is immediately obvious from these data that the proposed Cu^{2+} microelectrode is highly selective with respect to most cations. In the case of transition metal ions, the selectivity coefficients are in the order of 4.3×10^{-4} or smaller, which seems to indicate that the Cu^{2+} ions can be determined in the presence of other ions in the solution. In the case of alkali and alkalin earth metal ions, the selcetivity coefficient are very small (smaller than 3.0×10^{-6}).

The pH influence on the membrane microelectrode response to a 1.0×10^{-6} M Cu^{2+} solution was studied over a pH range of 2.0 to 10.0. The corresponding results are shown in Figure 3. In the pH range of 3.0 to 8.1, the potential does not alter with the pH change, which indicates

Table 4. Selectivity coefficients of various interfering cations for membrane F which are calculated by match potential method (MPM) and separation solution method (SSM)

Cation	MPM	SSM
Li^+	1.7×10^{-6}	4.9×10^{-6}
Na^+	1.9×10^{-6}	5.3×10^{-6}
K^+	1.8×10^{-6}	5.0×10^{-6}
Rb^+	1.2×10^{-6}	4.2×10^{-6}
Cs^+	1.0×10^{-6}	3.5×10^{-6}
Be^{2+}	1.0×10^{-6}	1.2×10^{-6}
Mg^{2+}	1.2×10^{-6}	1.5×10^{-6}
Ca^{2+}	2.5×10^{-6}	1.7×10^{-6}
Sr^{2+}	2.0×10^{-6}	1.5×10^{-6}
Ba^{2+}	1.6×10^{-6}	1.7×10^{-6}
Co^{2+}	4.3×10^{-6}	2.9×10^{-4}
Ni^{2+}	4.1×10^{-4}	2.7×10^{-4}
Zn^{2+}	1.7×10^{-4}	2.7×10^{-4}
Pb^{2+}	2.8×10^{-4}	3.9×10^{-4}
Cd^{2+}	1.9×10^{-4}	1.7×10^{-4}
Fe^{3+}	1.8×10^{-5}	1.5×10^{-5}

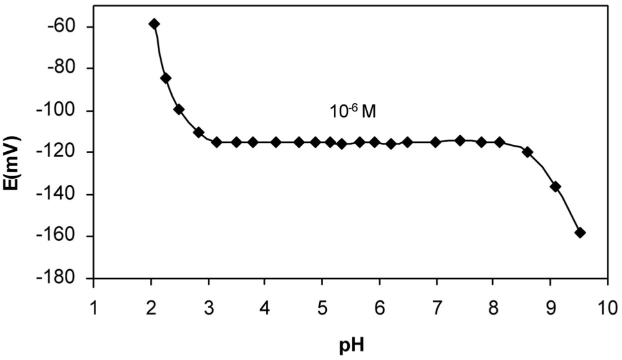

Figure 3. Effect of the pH of the test solution (1.0×10^{-6} M) on the potential response of the Cu^{2+} ion-selective microelectrode sensor based on HDNOS (membrane F).

the applicability of this microelectrode in the mentioned pH range. Beyond these limits, on the other hand, comparatively drastic drifts in the potential vs. pH behavior were observed. The observed drift at higher pH values of this range could be caused by the formation of the insoluble $Cu(OH)_2$ in the solution. In acidic solutions (pH values of less than the minimum of this range), the used ionophore could be protonated to some extent. This result leads to the improper function of the membrane electrode to the Cu^{2+} ion concentration.

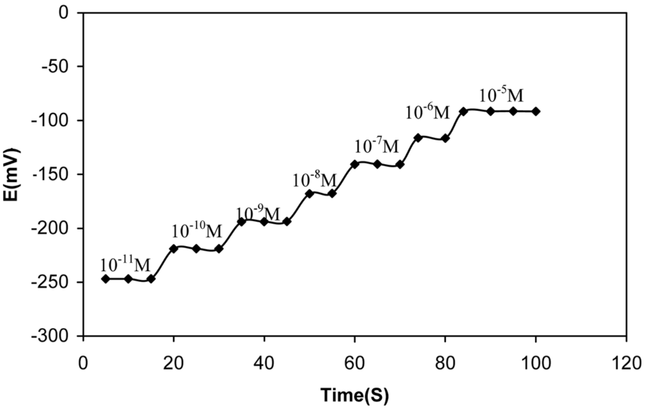

Figure 4. Response time of the ion-selective microelectrode based on HDNOS (membrane F) for step changes in concentration of Cu^{2+}.

The dynamic response time of the microelectrode, being another very important parameter in the evaluation of a microelectrode, was studied by varying the concentration of a solution from 1.0×10^{-11} M to 1.0×10^{-5} M and recording the times needed for the microelectrode to reach ± 1 mV of its equilibrium potential (Figure 4). The response time of the microelectrode was found to be about 5 seconds in the whole concentration range.

Table 5, compares the detection limit, linearity concentration range and major interfering ions of the proposed sensor with those reported for the previously reported Cu^{2+} sensors in the literature. As it is seen, the microelectrode, not only in the case of detection limit and response time but also in the case of the selectivity coefficients is superior to the previously reported Cu^{2+} ion-selective membrane electrodes.

Analytical Applications

The proposed Cu^{2+} microelectrode was found to work well under laboratory conditions. It was successfully applied to the determination of copper in two kinds of black and red pepper samples. A 1.0 mg sample of each pepper was taken in to a beaker and dissolved in concentrated nitric acid (5 mL) with heating. The solution was cooled, neutralized with a NaOH solution (pH was adjusted about 6.0), diluted and filtered. The filtrate was made to 25.0 mL with water in a calibrated flask. The concentration of each sample was measured by the copper microsensor, using the calibration method. The results obtained by the copper sensor and

Table 5. Comparision of the selectivity coefficieniont, detection limit, linear range, and response time of the best previously Cu^{2+} sensors with the proposed sensor (membrane no. F)

Reference	Detection limit	Linear range	Response time	$K_{MPM} > 10^{-4}$
7	5×10^{-8}	10^{-2} - 10^{8}	< 20 s	Tl^+, Ag^+, K^+, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}
10	8×10^{-6}	10^{-1} - 10^{-5}	< 15 s	Li^+, Na^+, K^+,Cs^+, Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}· Zn^{2+}· Pb^{2+}, Cd^{2+}, Fe^{3+}, Mg^{2+}, Be^{2+}
11	3×10^{-8}	10^{-1} - 10^{-8}	< 5 s	Ni^{2+}· Pb^{2+}, Co^{2+}
15	1.2×10^{-5}	10^{-1} - 10^{-5}	< 20 s	Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+}
This Work	5×10^{-12}	10^{-5} - 10^{-11}	< 5 s	none

Table 6. Determination of Cu^{2+} contents of red and black pepper by the Cu^{2+} ion-selective microelectrode based on HDNOS and Atomic Absorption

		Ion Selective Electrods (ppm)	Atomic Absorbtion (ppm)
Red Pepper	Sample 1	52.7 ± 0.5	50.9 ± 0.3
	Sample 2	50.3 ± 0.2	42.7 ± 0.9
Black Pepper	Sample 1	37.7 ± 0.5	35.8 ± 0.3
	Sample 2	19.5 ± 0.3	18.2 ± 0.7

Table 7. Determination of Cu^{2+} in waste water samples of acid-copper electroplating by the Cu^{2+} ion-selective microelectrode based on HDNOS and Atomic Absorption

	Ion Selective Electrods (ppm)	Atomic Absorbtion (ppm)
Sample 1	12.9 ± 0.3	12.2 ± 0.5
Sample 2	19.1 ± 0.6	18.5 ± 0.3
Sample 3	6.5 ± 0.6	13.6 ± 0.5

atomic absorption spectrometry are depicted in Table 6. As can be seen, there is a good correlation between the both methods.

The proposed sensor was also applied for the determination of copper ion contents in the wastewater samples of copper electroplating. 2.0 mL of each sample was taken and dissolved in distilled water in a 100 mL volumetric flask. To this solution 5.0 mL of sodium acetate/acetic acid buffer (pH of 5.0) was added to the flask and diluted to the mark with distilled water. The concentration of each sample was measured by the copper sensor, using the calibration method. The results obtained by the direct potentiometry and atomic absorption spectrometry are depicted in Table 7. As can be seen, there is a good correlation between the both methods.

Due to the high selectivity of the microsensors, the applicablity of the microelectrode was evaluated for the monitoring of the concentration of the copper ions in some binary mixtures and ternary mixtures. The results are summarized in Table 8. Table 8 showes the determination of the copper in a low concentration, in the presence of other ions with higher concentration, is posible. As can be seen from Table 8, the recovery of copper ion in the binary and ternary mixtures is in the range of 100.2-102.7%.

Table 8. Determination of Cu^{2+} ions in some binary and ternary mixtures by the Cu^{2+} ion-selective microelectrode based on HDNOS

Concentration of Cu^{2+}	Added Cations	Recovery%
1.0×10^{-10}	Na^+ 1×10^{-6}	100.2 ± 0.4
1.0×10^{-10}	K^+ 1×10^{-6}	100.7 ± 0.9
1.0×10^{-10}	Na^+, K^+ (1.0×10^{-6})	100.5 ± 0.03
1.0×10^{-10}	Ca^{2+}, Mg^{2+} (1.0×10^{-6})	100.9 ± 0.05
1.0×10^{-9}	Co^{2+} 1×10^{-6}	102.5 ± 0.03
1.0×10^{-9}	Ni^{2+} 1×10^{-6}	102.1 ± 0.07
1.0×10^{-9}	Zn^{2+} 1×10^{-6}	102.0 ± 0.05
1.0×10^{-9}	Zn^{2+}, Ni^{2+} (1.0×10^{-6})	102.7 ± 0.09
1.0×10^{-8}	Pb^{2+} 10^{-5}	102.3 ± 0.05
1.0×10^{-8}	Cd^{2+} 10^{-5}	101.9 ± 0.07
1.0×10^{-8}	Fe^{3+} 10^{-5}	100.8 ± 0.05
1.0×10^{-8}	Pb^{2+}, Fe^{3+} 10^{-5}	102.7 ± 0.09

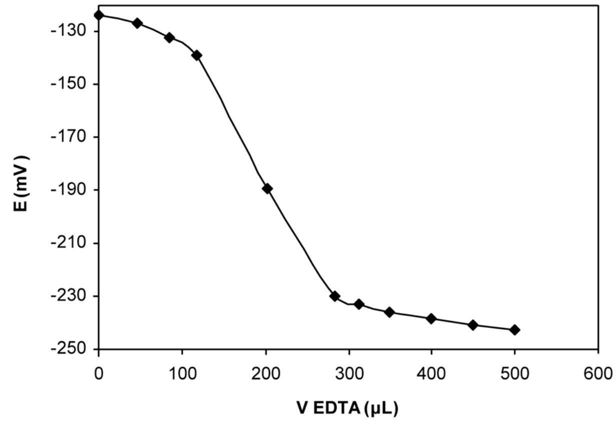

Figure 5. Potentiometric titration curve of 20.0 mL 1.0×10^{-6} M solution of Cu^{2+} with 1.0×10^{-4} M of EDTA.

This microelectrode was also applied as an indicator electrode for the titration of 20.0 mL of 1.0×10^{-6} M of Cu(II) solution with 1.0×10^{-4} M of standard EDTA (Figure 5). The amount of Cu^{2+} ions in solution could be determined with the microelectrode very well. The end point of the titration is sharp and the amount of Cu^{2+} ions in solution can be accurately determined with the electrode, and it was $(1.0 \pm 0.1) \times 10^{-6}$ M.

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