



Poly(vinyl) chloride membrane copper-selective electrode based on 1-phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione

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ABSTRACT

1-Phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione (H_2L) was used as an effective ionophore for copper-selective poly(vinyl) chloride (PVC) membrane electrodes. Optimization of the composition of the membrane and of the conditions of the analysis was performed, and under the optimized conditions the electrode has a detection limit of 6.30×10^{-7} M Cu(II) at pH 4.0 with response time 10 s and displays a linear EMF versus $\log[Cu^{2+}]$ response over the concentration range 2.0×10^{-6} to 5.0×10^{-3} M Cu(II) with a Nernstian slope of 28.80 ± 0.11 mV/decade over the pH range of 3.0–8.0. The sensor is stable for 9 weeks and exhibits good selectivity with respect to alkali, alkali earth and transition metal ions (e.g. Na^+ , K^+ , Ba^{2+} , Ca^{2+} , Zn^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} , Fe^{2+} , Al^{3+}) in the 3.0–8.0 pH range. It was successfully applied for the direct determination of copper(II) in zinc, aluminum and nickel based alloys, in soils polluted by oil, and as an indicator electrode for potentiometric titration of copper ions with EDTA.

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1. Introduction

Copper is one of the most widely spread heavy metals, hence its determination in environmental and industrial objects is of tremendous interest. Small quantities of copper are essential for living beings whereas it is highly toxic in a high concentration [1]. On the other hand, copper is an important material and extensively used for industrial, agricultural and domestic purposes due to its high electrical conductivity, chemical stability, plasticity, and capacity to form alloys with many metals [2]. Therefore, the copper content in many industrial [2], biological [3], medical [4], geochemical [5], and environmental [6,7] objects must be controlled on a daily basis and as a result, a development of novel methods for low-cost, simple, rapid, remote, and on-line detection and determination of copper in samples of different origin is of big interest.

Various analytical techniques have been proposed for determination of copper including spectrophotometric methods [8–14], atomic absorption spectrometry (AAS) [15,16], cold vapour AAS or flame AAS with electrothermal atomization [17,18], inductively coupled plasma emission spectrometry [19,20], gravimetry [21,22], chromatography [23,24], and anodic stripping voltam-

metry [25,26]. Most of the mentioned methods usually have sufficiently low detection limit and high selectivity, but also in many cases possess drawbacks such as high cost of equipment and expensive materials, time-consuming and complicated operation. Thus, these methods are generally unsuitable for simple, low cost and remote determination of copper, especially in field and domestic conditions.

At the same time, ion-selective electrodes (ISEs) provide convenient and fast procedures for determination of metal or nonmetal ions. In particular, a potentiometric detection based on ISEs offers advantages such as simple instrumentation, speed and ease of the sample preparation and measurements, relatively fast response, wide dynamic range, reasonable selectivity and low cost of materials. These characteristics have led to a number of already commercialized sensors for many ionic species, and the list of available electrodes has grown substantially over the last few years [27]. But the key component of such membrane ISE devices is the selective complexing agent (carrier, ionophore) that enables the specific recognition of an analyte in the presence of other interfering ions.

A wide range of organic reagents has been used as ion carriers for construction of copper selective electrodes (Table 1) [28–64], but most of these sensors have one or more of the following disadvantages: relatively low selectivity [28,31–36,39–44,46,50,56,59–64]; large response time [28,35,44,46,51,53,56,57,59]; high detection limits [35,36,40,53]; low sensitivity [34,60]; narrow working concentration range [30,32,34,60,61]; complicated procedure and high

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Table 1
Analytical parameters for some reported copper-selective PVC-membrane sensors.^a

Ionophore	Detection limit (M)	Linear range (M)	Response time (s)	Slope (mV/decade)	Selectivity coefficient $\geq 10^{-3}$	Ref.
Tetraethylthiuram disulfide	1.0×10^{-8}	1×10^{-8} to 1×10^{-1}	27	30	Na ⁺ , Mn ²⁺ , Pb ²⁺	[28]
13,14-Benzo-1,5-tetrathiacyclopentadecane		1×10^{-6} to 1×10^{-1}	10	29		[29]
Dithizone		1×10^{-5} to 1×10^{-3}				[30]
o-Xylylene-bis(methyloctadecyl-dithiocarbamate)		1×10^{-6} to 1×10^{-1}		29	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺	[31]
Calixdithiocarbamoylarene		1×10^{-4} to 1×10^{-2}		30	K ⁺ , Ca ²⁺ , Pb ²⁺ , Cd ²⁺	[32]
2,2'-[1,2-Ethanediy-bis(nitriloethylidene)]-bis(1-naphthalene)	3.1×10^{-6}	5×10^{-6} to 5×10^{-2}	5	29.8	Na ⁺ , Ni ²⁺ , Hg ²⁺	[33]
3,4,10,11-Tetraphenyl-1,2,5,8,9,12,13-octaaza-cyclotetra-deca-7,14-dithione-2,4,9,11-tetraene	1.6×10^{-6}	1×10^{-5} to 1×10^{-2}	2	27	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Ba ²⁺ , Zn ²⁺ , Cd ²⁺ , Hg ²⁺ , Pb ²⁺ , Fe ³⁺ , Al ³⁺	[34]
1,15-Diaza-3,4;12,13-dibenzo-5,8,11,18,21-pentaocyclotriicosane-2,14-dione	1.2×10^{-5}	1×10^{-5} to 1×10^{-1}	20	30.0	Na ⁺ , K ⁺ , Cs ⁺ , Sr ²⁺	[35]
Aza-thioether crown containing a 1,10-phenanthroline	8.0×10^{-6}	1×10^{-5} to 1×10^{-1}	15	29.4	Ag ⁺ , La ³⁺	[36]
2'-Picolyl sym-dibenzo-16-crown-5 ether	1.0×10^{-6}	1×10^{-5} to 1×10^{-1}		42		[37]
Bis-thiophenylpropanediamine	2.0×10^{-8}	6×10^{-8} to 1×10^{-1}	5	29.3	Zn ²⁺ , Hg ²⁺	[38]
Bis-2-thiophenyl propanediamine	3.0×10^{-8}	1×10^{-8} to 1×10^{-1}	5	29	Ni ²⁺ , Pb ²⁺ , Co ²⁺	[39]
2,2'-Dithiodianiline	6.0×10^{-6}	7×10^{-7} to 5×10^{-2}	10	30.0	Pd ²⁺ , Cd ²⁺ , Hg ²⁺ , Ni ²⁺ , Pb ²⁺ , Fe ³⁺	[40]
Copper(II)-salicylaniline Schiff's base + cyanocopolymer matrice		2.5×10^{-7} to 1×10^{-2}	13	28	Li ⁺ , Na ⁺ , K ⁺ , Cs ⁺ , Ag ⁺ , Ca ²⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Cd ²⁺ , Mn ²⁺	[41]
1,3-Dithiane,2-(4-methoxyphenyl)	1.0×10^{-6}	3×10^{-6} to 5×10^{-2}	5	29	K ⁺ , Cs ⁺ , Mg ²⁺ , Ca ²⁺ , Sr ²⁺ , Ag ⁺ , Mn ²⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Cd ²⁺ , Hg ²⁺	[42]
Diphenylisocyanate-bis(acetylaceton)ethylenedi-imine	6.0×10^{-7}	1×10^{-6} to 1×10^{-1}	15	29.8	Ni ²⁺ , Zn ²⁺ , Cd ²⁺	[43]
1-Hydroxy-2-(prop-2'-enyl)-4-(prop-2'-enyloxy)-9,10-antraquinone	5.0×10^{-8}	8×10^{-8} to 5×10^{-2}	20	29.1	Tl ⁺ , Ag ⁺ , K ⁺ , Co ²⁺ , Ni ²⁺ , Zn ²⁺ , Pb ²⁺ , Cd ²⁺	[44]
3,6,9,14-Tetrathiabicyclo[9.2.1]tetradeca-11,13-diene	3.2×10^{-7}	6.3×10^{-7} to 2.5×10^{-1}	10	28.0	Ag ⁺	[45]
2-Quinoyl-2-phenylglyoxal-2-oxime(phenylglyoxal-alpha-monoxime)	5.0×10^{-7}	1×10^{-6} to 1×10^{-1}	10–50	28.2	K ⁺ , Al ³⁺ , Fe ³⁺	[46]
Hydrotris(3-isopropylpyrazolyl)methane	2.0×10^{-6}	1×10^{-6} to 1×10^{-2}	10	29	Co ²⁺ , Ni ²⁺	[47]
2-(1-(4'-(1''-Hydroxy-2''-naphthyl)methyleneamino)butyliminomethyl)-1-naphthol	8.0×10^{-7}	1×10^{-6} to 1×10^{-1}	5	29.0	Tl ⁺	[48]
2,2'-[4,4'-Diphenyl-methane bis(nitrilomethylidene)]-bisphenol	3.0×10^{-6}	8×10^{-6} to 1×10^{-1}	15	29.5	Pb ²⁺	[49]
1,3-Dithiane,2-(4-methoxy phenyl) Schiff base	1.0×10^{-6}	3×10^{-6} to 5×10^{-2}	15	29.5	Na ⁺ , Ag ⁺ , Pb ²⁺	[50]
(2,3-diaminopyridine + o-vanilin) N,N'-ethylene bis(p-tert-butylsalicylaldiminato)	3.0×10^{-6}	5×10^{-6} to 1×10^{-1}	30	29.6	Ag ⁺ , Hg ²⁺	[51]
N,N'-ethylene bis(p-tert-butylsalicylaldiminato)	1.5×10^{-6}	4×10^{-6} to 1×10^{-1}		29.5	Pb ²⁺	[52]
Thiosemicarbazone	6.0×10^{-6}	6×10^{-6} to 1×10^{-1}	10–50	29.2	Hg ²⁺ , Pb ²⁺	[53]
2,2'-[1,2-Ethandiy-bis(nitrilomethylidene)]-bis[para-cresole]	3.1×10^{-6}	1×10^{-5} to 1×10^{-1}	10	29.7	Ni ²⁺ , Co ²⁺	[54]
6-Methyl-4-(1-phenylmethylidene)amino-3-thio-1,2,4-triazin-5-one	4.8×10^{-7}	1×10^{-6} to 1×10^{-1}	10	29.2	Ca ²⁺ , Sr ²⁺	[55]
N,N,N',N'-tetracyclohexyl-3-thioglutaric diamide	2.0×10^{-9}	1×10^{-7} to 1×10^{-6}	60	33.5	Ag ⁺ , Zn ²⁺ , Cd ²⁺ , Pb ²⁺	[56]
4-Amino-6-methyl-1,2,4-triazin-5-one-3-thione	6.2×10^{-7}	1×10^{-6} to 1×10^{-1}	20	29.3	Hg ²⁺ , Fe ³⁺	[57]
2-Mercaptobenzoxazole	2.0×10^{-6}	5×10^{-6} to 1.6×10^{-2}		29.2	Ni ²⁺ , Pb ²⁺	[58]
1,8-Bis(2-hydroxynaphthalaldiminato)3,6-dioxaoctane	1.0×10^{-6}	3.3×10^{-6} to 1.0	10–15	29.0	Na ⁺ , K ⁺ , Ag ⁺ , Ca ²⁺ , Co ²⁺ , Fe ³⁺ , Al ³⁺	[59]
2-{1-(E)-2-((Z)-2-((E)-2-((Z)-1-(2-Hydroxyphenyl)ethylidene)hydrazono)-1-methyl propylidene)hydra zono ethyl} phenol	5.0×10^{-12}	1×10^{-11} to 1×10^{-5}	5	25.9	Ni ²⁺ , Zn ²⁺ , Pb ²⁺ , Cd ²⁺	[60]
2,2'-[1,9-Nonanediyl bis(nitriloethylidene)]-bis(1-naphthol)	8.0×10^{-7}	1×10^{-6} to 5×10^{-3}	10	29.0	Pb ²⁺ , Zn ²⁺ , Fe ³⁺	[61]
2-(2-Mercaptophenylnitrilomethylidene)-phenol	5.0×10^{-6}	7×10^{-6} to 2.6×10^{-2}	10	28.3	Li ⁺ , Ca ²⁺ , Zn ²⁺ , Cd ²⁺ , Pb ²⁺ , Ce ³⁺ , Hg ²⁺ , Ag ⁺ , Fe ³⁺ , Al ³⁺ , La ³⁺	[62]
1,2,5,6,8,11-Hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene	8.1×10^{-8}	2×10^{-7} to 1.0×10^{-1}	5	29.5	K ⁺ , Tl ⁺ , Zn ²⁺ , Sr ²⁺ , Mg ²⁺ , Co ²⁺ , Cd ²⁺ , Mn ²⁺ , Cr ³⁺	[63]
Schiff Base (phenylalanine + salicylaldehyde)		1.9×10^{-6} to 1.0×10^{-1}	12	30	Mg ²⁺ , Sr ²⁺ , Ni ²⁺ , Co ²⁺ , Zn ²⁺ , Cd ²⁺ , Mn ²⁺ , Hg ²⁺ , Fe ³⁺ , Al ³⁺ , Cr ³⁺	[64]
1-Phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione	6.30×10^{-7}	2.0×10^{-6} to 5.0×10^{-3}	10	28.8	Fe ³⁺	This work

^a When the parameter was not indicated in the corresponding paper, a blank space is left in this table.

cost of the carrier synthesis [35,37,45,61]. In fact, the described sensors, although being prepared independently, have rather similar parameters (e.g. compare the slopes of potentiometric responses), however, none of them has all excellent analytical parameters (selectivity, sensitivity, response, low detection limits and long life time) and the cost is also important for such devices. Therefore, we decided to prepare a new inexpensive electrode with better parameters at least for some of the above mentioned points.

Previously, it was shown that azoderivatives of β -diketones (ADB) have a rich tautomeric potential (Scheme 1) and can be used for the classical spectrophotometric determination of copper(II) [65–70]. It was concluded that when azoderivatives of unsymmetric β -diketones are used, the number of ADB tautomers increases along with selectivity of copper analysis [65–81]. For this reason, in this work we tested an unsymmetric ADB, i.e. 1-phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione (H_2L), in a PVC matrix as an ionophore to prepare a Cu-selective membrane electrode.

2. Experimental

2.1. Materials and instrumentation

All the chemicals [analytical grade dibutyl phthalate (DBP), benzyl acetate (BA), acetophenone (AP), *o*-nitrophenyl octylether (NPOE), sodium tetraphenylborate (NaTPB), oleic acid (OA), tetrahydrofuran (THF) and high-molecular-weight polyvinyl chloride (PVC)] were obtained from commercial sources (Aldrich) and used as received. The water used for all preparations and analyses was bidistilled and deionized. Ammonium hydroxide (0.1 M), acetic acid (0.1 M), potassium hydroxide (0.1 M) and hydrochloric acid were used for pH control; the concentrated acids (HCl 33%, w/w, HNO₃ 65%, w/w) were used for dissolution of samples. The acidity of the solutions was measured using a CG825 pH-meter with an ESL-43-07 glass electrode adjusted by standard buffer solutions and an EVL-1M3.1 silver–silver chloride reference electrode. A 177 DMM (Keithley) microvoltmeter was used for the potential measurement at 25.0 ± 0.1 °C. The reference electrode was a METROHM (6.0702.100) double-junction, saturated calomel electrode with KCl as the bridging solution. A starting 1.00×10^{-1} M solution of copper(II) was prepared by dissolving $Cu(NO_3)_2 \times 2.5H_2O$ in distilled water.

2.2. Synthesis of H_2L

H_2L was synthesized according to the Japp–Klingemann reaction [82] between the diazonium salt of 2-hydroxyaniline and benzoylacetone.

2.2.1. Diazotization

0.0250 mol of 2-hydroxyaniline was dissolved in 50.00 mL of water upon addition of 1.000 g of crystalline NaOH. The solution was cooled in an ice bath to 0 °C, and 0.025 mol of NaNO₂ was added with subsequent addition of 5.00 mL HCl in portions of 0.20 mL for 1 h under vigorous stirring. During the reaction the temperature of the mixture must not exceed +5 °C.

2.2.2. Azocoupling

1.000 g of NaOH was added to a mixture of 0.0250 mol of benzoylacetone with 50.00 mL of water–ethanol (1:1, v/v). The solution was cooled in an ice bath, and a suspension of 2-hydroxyaniline diazonium (prepared according to the procedure of Section 2.2.1) was added in two equal portions under vigorous stirring for 1 h. On the next day, the formed precipitate of 1-phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione (H_2L) was filtered off, washed with water, recrystallized from ethanol and dried in air.

The characterization of H_2L was undertaken by elemental analysis, IR, ¹H and ¹³C NMR spectroscopies.

Yield, 72% (based on benzoylacetone), black powder, soluble in methanol, ethanol, acetone, dichloromethane, chloroform, tetrahydrofuran and insoluble in water. Anal. Calcd for C₁₆H₁₄N₂O₃ (*M* = 282.29): C, 68.07; H, 5.00; N, 9.92. Found: C, 67.45; H, 4.97; N, 9.78%. IR, cm⁻¹: 3485 ν (OH), 3360 ν (NH), 1645 ν (C=O), 1619 ν (C=O...H), 1597 ν (C=N), 756 ν (Ar). ¹H NMR of a mixture of enol-azo and hydrazo tautomers (300.13 MHz, DMSO-d₆). Enol-azo, δ : CH₃ signals were overlapped with the solvent peak, 6.91–7.81 (5H, C₆H₅ and 4H, C₆H₄), 10.56 (s, 1H, HO–Ar), 12.57 (s, 1H, HO–enol). Hydrazo, δ : CH₃ signals were overlapped with the solvent peak, 6.91–7.81 (5H, C₆H₅ and 4H, C₆H₄), 10.56 (s, 1H, HO–Ar), 14.53 (s, 1H, NH). ¹³C{¹H} NMR (100.61 MHz, DMSO-d₆). Enol-azo, δ : 30.14 (CH₃), 114.6 (C–N), 115.8 (C_{Ar–N=N}), 120.1, 125.9, 127.8 and 129.4 (C_{Ar–H}), 130.0, 131.8 and 132.8 (C_{Ar–H}), 146.4 (C_{Ar–OH}), 191.8 (C=O), 197.0 (C=O). Hydrazo, δ : 30.14 (CH₃), 114.6 (C_{Ar–N=N}), 115.8, 120.1, 125.9, and 127.8 (C_{Ar–H}), 129.4, 130.0, and 131.8 (C_{Ar–H}), 132.8 (C–N), 146.4 (C_{Ar–OH}), 191.8 and 197.0 (C=O).

2.3. Electrode preparation

28–34 mg PVC powder, 0–65 mg plasticizer [dibutyl phthalate (DBP), benzyl acetate (BA), *o*-nitrophenyl octylether (NPOE) or acetophenone (AP)], 3–7 mg anionic additives [sodium tetraphenylborate (NaTPB) or oleic acid (OA)] and 0–5 mg ionophore (H_2L) were dissolved in 3 mL tetrahydrofuran (THF), and stirred vigorously for 5 min. The resulting mixture was transferred into a glass dish of 2 cm diameter. After evaporation of solvent (ca. 24 h), the formed transparent membrane of ca. 0.5 mm thickness was removed carefully from the glass plate, then a 5 mm diameter piece was cut out and glued with commercial liquid PVC to one end of a PVC tube with the same diameter. After 24 h the electrode was filled with an internal filling solution [1.00×10^{-3} M $Cu(NO_3)_2 \times 2.5H_2O$ in 3 M KCl], preconditioned for 24 h in a 1.00×10^{-2} M solution of $Cu(NO_3)_2 \times 2.5H_2O$ before use and stored in the same solution when not in use.

2.4. EMF measurements

All EMF measurements were carried out using the following assembly:

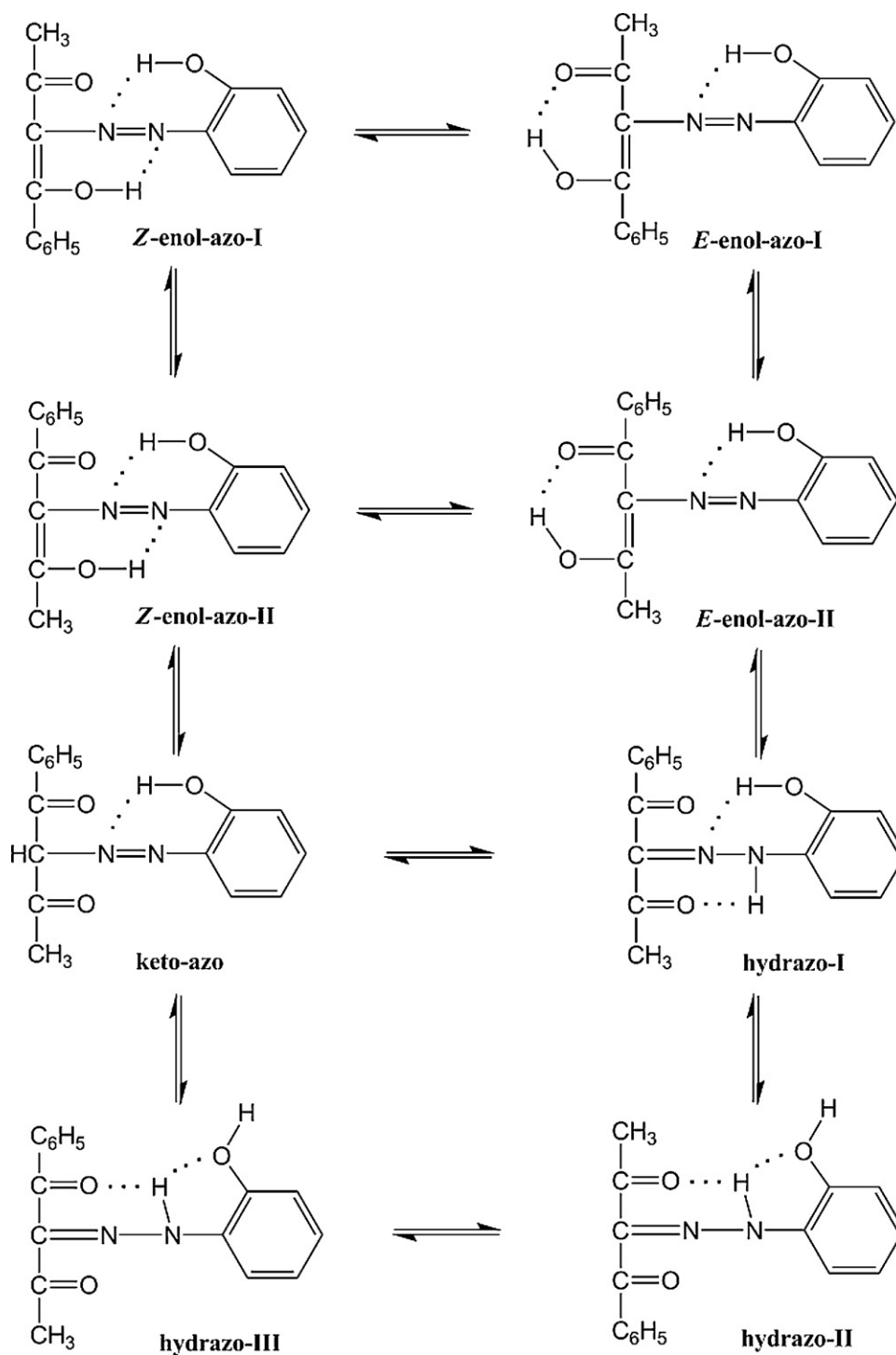
Ag–AgCl|KCl (3 M)|internal solution, 1.00×10^{-3} M $Cu(NO_3)_2 \times 2.5H_2O$ |PVC membrane|test solution|Hg–Hg₂Cl₂, KCl (saturated).

All the EMF observations were made with a 177 DMM (Keithley) microvoltmeter. The performance of the electrodes was studied by measuring the EMFs of copper nitrate solutions within concentration range 10^{-1} to 10^{-7} M. Each solution was stirred and the potential reading was recorded when it became stable, and then plotted as logarithmic function of Cu(II) cation activity. The activities of metal ions were based on the activity coefficient γ , data calculated from the modified form of the Debye–Hückel equation [83]:

$$\log \gamma = \left[\frac{-0.511Z^2\mu^{1/2}}{1 + 1.5\mu^{1/2}} \right] + 0.2\mu,$$

where μ is the ionic strength and *Z* is the valency. All measurements were carried out at 25 ± 0.1 °C.

The dynamic response was evaluated by sequential fast stepwise addition under stirring of 1.00×10^{-1} M Cu^{2+} solution to 1.0×10^{-6} M copper(II) nitrate solution until 1.0×10^{-5} to 1.0×10^{-2} M concentration. Every time after addition of the following portion of the copper solution the time until the potential stabilization was fixed. Then the experiment was done in reverse direction by fast stepwise sequential dilutions with water starting from 1.0×10^{-2} M copper(II) nitrate solution.



Scheme 1. Possible tautomeric equilibria in H_2L .

The electrodes' stability and reproducibility were estimated by comparing the slopes obtained from periodic re-calibration within 1 mV/decade.

2.5. Determination of copper(II) in zinc-based alloys

A 0.100 g portion of the sample (A 292-2 containing Al 7.500, Mg 0.020, Fe 0.0075, Cu 1.000, Si 0.100, Pb 0.013, Cd 0.010, Sn 0.010% and the rest of Zn, or A 292-3 containing Al 8.200, Mg 0.045,

Fe 0.0065, Cu 0.800, Si 0.08, Pb 0.010, Cd 0.040, Sn 0.003%, and the rest of Zn) was dissolved in a mixture of 10.00 mL of H_2O , 1.00 mL of HCl (33%), and 3–4 drops of HNO_3 (65%) in a chemical beaker at $50^\circ C$. The solution was transferred into a 50.00 mL volumetric flask, neutralized by 0.1 M KOH to pH 4 and diluted to the mark with water. An aliquot portion of the solution was placed into a 25.00 mL volumetric flask and diluted to the mark with deionized water. Then, the EMF of the solution was measured using the equipment described above.

2.6. Determination of copper(II) in aluminum-based alloys

A 0.100 g portion of the sample (A 241-4 containing Si 2.000, Mn 0.070, Fe 0.300, Cu 0.700, Zn 5.900, Mg 0.160% and the rest of Al, or A 241-5x containing Si 1.400, Mn 0.200, Fe 0.600, Cu 1.300, Zn 5.000, Mg 0.450% and the rest of Al) was dissolved and analyzed analogously as described above for the zinc-based alloys.

2.7. Determination of copper(II) in nickel-based alloys

A 0.500 g portion of the sample (M 115-1 containing Cr 8.100, Co 1.450, Fe 0.050, Si 0.500, Mg 0.030, Mn 0.350, Cu 0.250, Pb 0.001, Bi 0.004, Sb 0.001, P 0.005, Al 0.250, C 0.050, Ti 0.005, Zr 0.150, As 0.0010%, and the rest of Ni, or M 115-2 containing Cr 9.200, Co 0.870, Fe 0.035, Si 0.250, Mg 0.050, Mn 0.250, Cu 0.180, Pb 0.003, Bi 0.002, Sb 0.002, P 0.003, Al 0.150, C 0.250, Ti 0.050, Zr 0.050, As 0.0025%, and the rest of Ni) was dissolved in a mixture of 10.00 mL of H₂O, 12.00 mL of HCl (33%) and 4.00 mL of HNO₃ (65%) in a chemical beaker at 70 °C. The solution was then analyzed as described above for the zinc-based alloys.

2.8. Determination of copper(II) in soils polluted by oil

A sample of soils polluted by oil (Surakhany region of Azerbaijan) was analyzed using the spectrophotometric method. A portion (2.000 g) of a sample was placed in a glassy carbon casserole and dissolved in a mixture of HF (35%, 38.00 mL), HCl (33%, 24.00 mL), and HNO₃ (65%, 8.00 mL). The obtained paste was treated with 12.00–16.00 mL of conc. HNO₃ at 60–70 °C to distil off HF. The obtained residue was dissolved in distilled water, filtered off and diluted to 50.00 mL with water.

3. Results and discussion

3.1. Optimization of electrode membrane composition

A number of characteristics (see Section 1) are required for a sensor to be considered as a suitable one for the ion determination. Those features, as well as the membrane composition and the additives employed, have been taken into account when H₂L was studied as an ionophore [28–64]. Since the sensitivity and selectivity of any membrane electrode is significantly related with the composition of the ion selective membrane and the used mediators [plasticizer (DBP, NPOE, BA, AP) and lipophilic additives (NaTPB, OA)], we decided to study the influence of these factors (the nature and amount of plasticizer, the amount of PVC and the lipophilic additive and ionophore) on the behaviour (the potential response) of the proposed electrode.

The performance characteristics of several differently prepared membranes are listed in Table 2. Since the nature of the plasticizer influences the dielectric constant, detection limits, sensitivity and selectivity of the membrane, as well as the mobility of the ionophore molecules and its complex [28–64], four plasticizers of different polarity including DBP ($\epsilon_T = 6.42$), NPOE ($\epsilon_T = 24.0$), BA ($\epsilon_T = 5.0$), and AP ($\epsilon_T = 17.3$) were used. The results (Table 2) show that DBP (61.00% DBP, 6.00% OA, 30% PVC, and 3% ionophore H₂L, run 10) gives the best sensitivity (the Nernstian slope of 28.80 mV/decade within the copper concentration 2.0×10^{-6} to 5.0×10^{-3} M) of the four studied plasticizers (Fig. 1), most probably due to the better solubility of H₂L in it.

The potentiometric response of the membranes was greatly improved in the presence of lipophilic anionic additives, NaTPB and OA. It is known that lipophilic salts not only reduce the ohmic resistance of the membrane, but also enhance the response and selectivity, reduce the interference caused by other anions and also may accelerate the exchange on the sample-membrane interface

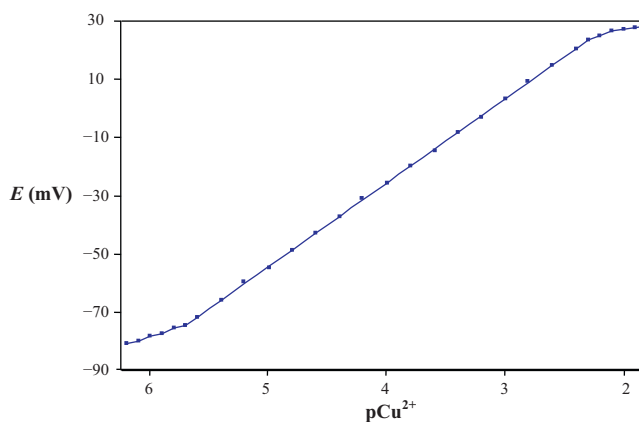


Fig. 1. Potentiometric response of the optimized [61.00% DBP, 6.00% OA, 30% PVC, and 3% ionophore (H₂L)] H₂L-based copper ion-selective electrode of run 10 (Table 2) at pH 4 (maintained by 1×10^{-1} M ammonium hydroxyde/acetic acid buffer).

[28–64,84–92]. Thus, the influence of NaTPB and OA was studied and it was found that the best performance was also obtained with the above membrane composition [61.00% DBP, 6.00% OA, 30% PVC, and 3% ionophore (H₂L)] (Table 2, run 10). Probably, the higher potentiometric response of OA is caused by the good solubility of H₂L in it, while the mobility of Na ions from NaTPB decrease with the growth of the membrane viscosity. On the other hand, a good correlation between the membrane thickness and the PVC content of membrane is found, thus the detection limit of the sensor increases with decrease in the PVC content. However, if the membrane is too thin, it loses its mechanical strength and can be easily broken, as previously reported [45–48].

The concentration of the internal copper(II) solution within the electrode was varied from 1.0×10^{-4} to 1.0×10^{-2} M, and it was found that this variation does not cause any significant difference in the potentiometric response of the electrodes, except for the expected change in the intercept of the resulting Nernstian plots (28.80 mV/decade, Fig. 1). A 1.0×10^{-3} M concentration of the internal solution is quite appropriate for smooth functioning of the electrode system, thus we kept this concentration for further measurements.

3.2. Dynamic response and life time

For analytical applications, the dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by fast stepwise changing of the Cu²⁺ concentration from 1.0×10^{-6} to 1.0×10^{-2} M. The actual potential versus time (Fig. 2) shows that the dynamic response time was <10 s (thus mainly limited by diffusion, i.e. the rate of stirring) and then the potential remained unchanged at all studied concentrations. This short response time is most probably due to the fast exchange kinetics of complexation–decomplexation of Cu²⁺ ion with the H₂L ionophore on the tested solution–membrane interface [39]. A similar procedure in the opposite direction demonstrated the independence of the response time from the order of dilution. The durability tests show that the membrane electrode with the best characteristics (run 10 from Table 2) can be used for at least 9 weeks without any measurable response decay. After this time the Nernstian slope (the sensitivity) and detection limit of the sensor decrease and increase, respectively. It was established that the leaching of plasticizer, carrier, or ionic site from the polymeric film is the primary reason for the limit in the sensors' lifetime [28–64]; analogously, we suppose that these factors also influence the decay of our electrode.

Table 2
Membrane composition and corresponding potentiometric response in H₂L-based copper-selective electrodes.

Run	Composition, % (mass, w/w)								Detection limit (M)	Linear range (M)	Slope (mV/decade)
	H ₂ L	PVC	DBP	NPOE	BA	AP	NaTPB	OA			
1	3	30	62				5	7.13×10^{-6}	$7.4 \times 10^{-6} - 2.7 \times 10^{-3}$	17.87 ± 0.32	
2	3	30		62			5	2.55×10^{-5}	$3.3 \times 10^{-5} - 8.6 \times 10^{-4}$	4.70 ± 0.33	
3	3	30			62		5	1.48×10^{-5}	$2.8 \times 10^{-5} - 9.2 \times 10^{-4}$	8.14 ± 0.30	
4	3	30				62	5	2.72×10^{-5}	$3.6 \times 10^{-5} - 7.3 \times 10^{-4}$	6.68 ± 0.27	
5	3	30	62				5	6.11×10^{-6}	$6.3 \times 10^{-6} - 4.2 \times 10^{-3}$	24.65 ± 0.31	
6	3	30		62			5	2.59×10^{-5}	$3.6 \times 10^{-5} - 9.1 \times 10^{-4}$	3.80 ± 0.26	
7	3	30			62		5	7.23×10^{-6}	$8.3 \times 10^{-6} - 1.9 \times 10^{-3}$	15.57 ± 0.29	
8	3	30				62	5	3.35×10^{-5}	$3.4 \times 10^{-5} - 8.3 \times 10^{-4}$	4.02 ± 0.32	
9	3	30	63				4	9.96×10^{-7}	$4.2 \times 10^{-6} - 4.6 \times 10^{-3}$	27.14 ± 0.14	
10	3	30	61				6	6.30×10^{-7}	$2.0 \times 10^{-6} - 5.0 \times 10^{-3}$	28.80 ± 0.11	
11	3	28	64				5	1.15×10^{-6}	$5.7 \times 10^{-6} - 4.5 \times 10^{-3}$	26.75 ± 0.13	
12	3	32	60				5	5.85×10^{-7}	$3.0 \times 10^{-6} - 4.8 \times 10^{-3}$	27.90 ± 0.18	
13	3	34	58				5	3.83×10^{-6}	$5.9 \times 10^{-6} - 4.4 \times 10^{-3}$	26.10 ± 0.11	
14	2	30	61				7	6.95×10^{-6}	$7.2 \times 10^{-6} - 3.9 \times 10^{-3}$	23.64 ± 0.13	
15	4	30	61				3	8.91×10^{-7}	$3.3 \times 10^{-6} - 4.7 \times 10^{-3}$	27.58 ± 0.17	
16	5	30	60				5	4.30×10^{-6}	$6.0 \times 10^{-6} - 4.3 \times 10^{-3}$	25.46 ± 0.19	
17		30	65				5	2.56×10^{-5}	$3.7 \times 10^{-5} - 7.6 \times 10^{-4}$	3.28 ± 0.33	
18	5	30					5	7.25×10^{-5}	$7.4 \times 10^{-5} - 6.0 \times 10^{-4}$	1.97 ± 0.48	

3.3. Effect of pH

The effect of the pH on the sensor response was studied using two different concentrations (10^{-4} and 10^{-3} M) of Cu²⁺ ions. Studies were carried out over a pH range of 2–9. The addition of HCl and ammonium hydroxide/acetic acid buffer was done dropwise to adjust the pH. The potential remains constant over the 3.0–8.0 pH range, beyond which the potential changes considerably (Fig. 3). The observed drift at higher pH values could be due to the formation in solution of some hydroxo complexes of Cu²⁺ or even to Cu(OH)₂ precipitate [28–64,93]. The observed increase in potential at low pH values could be due to protonation of the L²⁻, HL⁻, H₂L or lipophilic additives. Since the potential remains constant over pH 3.0–8.0, this can be taken as the working pH range for the proposed electrode system; in particular, pH 4.0 was used for all the experiments in this work.

3.4. Calibration curve and statistical data

The critical response characteristic for the electrode was determined according to IUPAC recommendations [94,95]. The response of the proposed sensor at varying concentration of the Cu(II) ion shows a linear response to this concentration in the range of 2.0×10^{-6} to 5.0×10^{-3} M at pH 4 (Fig. 1). The slope of calibration graph was calculated by the least-squares method [96]:

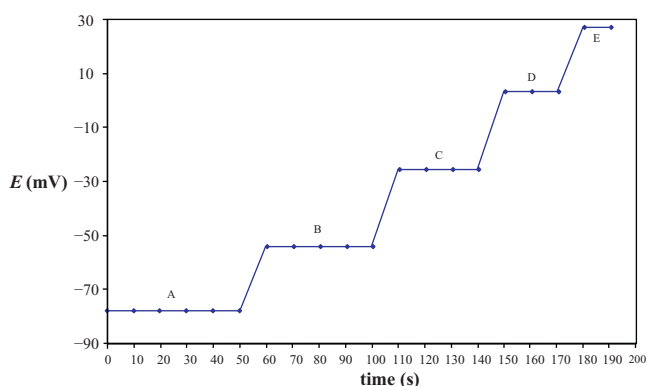


Fig. 2. Dynamic response of the optimized [61.00% DBP, 6.00% OA, 30% PVC, and 3% ionophore (H₂L)] H₂L membrane electrode of run 10 (Table 2) for step changes in concentration of Cu²⁺; (A) 1.0×10^{-6} M; (B) 1.0×10^{-5} M; (C) 1.0×10^{-4} M; (D) 1.0×10^{-3} M; (E) 1.0×10^{-2} M.

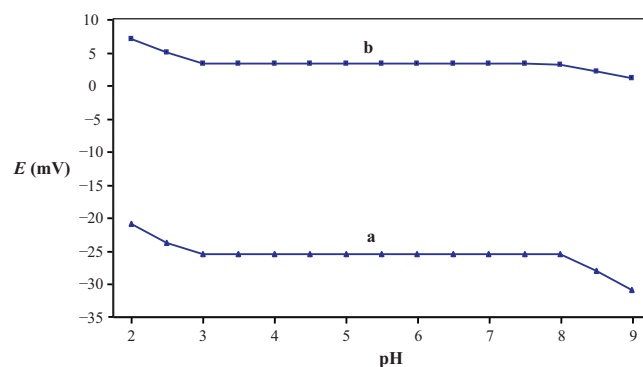


Fig. 3. Effect of pH of the test solution on the optimized [61.00% DBP, 6.00% OA, 30% PVC, and 3% ionophore (H₂L)] electrode (of run 10, Table 2) response for 1×10^{-4} (a) and 1×10^{-3} M (b) concentrations of Cu²⁺.

$E = (-28.80 \pm 0.11) \text{ pa} + (89.68 \pm 0.17)$ ($r = 0.999$, $n = 17$), where E is the EMF, pa is the antilogarithm of the activity of copper(II), n is the number of experiments with one electrode. The limit of detection as determined from the intersection of the two extrapolated segments of the calibration graph was 6.30×10^{-7} M. This slope was reproducible within 1 mV/decade error during 9 weeks indicating the high stability and reproducibility of the proposed membrane analytical system.

Table 3
Selectivity coefficients of various interfering ions (Mⁿ⁺).^a

M ⁿ⁺	K ^{MPPM}	K ^{MMSM}
Na ⁺	1.3×10^{-4}	1.5×10^{-4}
K ⁺	1.2×10^{-4}	1.5×10^{-4}
Ba ²⁺	1.4×10^{-4}	1.6×10^{-4}
Ca ²⁺	1.3×10^{-4}	1.5×10^{-4}
Zn ²⁺	2.2×10^{-4}	2.3×10^{-4}
Cd ²⁺	1.3×10^{-4}	1.4×10^{-4}
Co ²⁺	3.4×10^{-4}	3.9×10^{-4}
Mn ²⁺	2.1×10^{-4}	2.0×10^{-4}
Ni ²⁺	3.0×10^{-4}	3.1×10^{-4}
Fe ²⁺	1.3×10^{-4}	1.5×10^{-4}
Fe ³⁺	2.4×10^{-3}	2.9×10^{-3}
Al ³⁺	1.2×10^{-4}	1.3×10^{-4}

^a Measured by membrane electrode of run 10 (Table 2).

Table 4
Results of determination of copper(II) in zinc, aluminum and nickel based alloys, and soils polluted by oil ($n=5$, $P=0.95$).

Sample		Certified copper content (%)	Spectrophotometry [65–70] (%)	Cu-ISE (%)	RSD (%)
Zn-alloys	A 292-2	1.000	1.00 ± 0.02	1.000 ± 0.023	2.3
	A 292-3	0.800	0.79 ± 0.03	0.800 ± 0.027	3.4
Al-alloys	A 241-4	0.700	0.68 ± 0.03	0.700 ± 0.025	3.6
	A 241-5x	1.300	1.29 ± 0.02	1.300 ± 0.017	1.3
Ni-alloys	M 155-1	0.250	0.25 ± 0.01	0.250 ± 0.010	4.0
	M 155-2	0.180	0.18 ± 0.01	0.180 ± 0.008	4.4
Soils polluted by oil		–	$(6.77 \pm 0.01) \times 10^{-4}$	$(6.75 \pm 0.02) \times 10^{-4}$	3.6

3.5. Potentiometric selectivity

The most important characteristic of a membrane sensor is its response for the primary ion in the presence of other cations. The selectivity coefficients of the electrode towards different cationic species (M^{n+}) were evaluated by using both the matched potential method (MPM) [97–100] and the mixed solution method (MSM) [97,98], which are recommended by IUPAC [94,95,98]. According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution [97,98]. The selectivity coefficient, K^{MPM} , is determined as

$$K^{\text{MPM}} = \frac{\Delta A}{a_B} \quad (1)$$

where $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity and a'_A the activity of A in the presence of the interfering ion, a_B . The concentration of Cu^{2+} used as primary ion in this study was 1.0×10^{-4} M.

In the mixed solution method, the selectivity coefficient, K^{MSM} , was evaluated graphically from potential measurements on solutions containing a fixed concentration of Cu^{2+} ion (1.0×10^{-4} M) and varying amounts of interfering ions (M^{n+}) according to the equation

$$K^{\text{MSM}} a_M^{2/n} = a_{\text{Cu}} \left\{ \exp \frac{2(E_2 - E_1)F}{RT} \right\} - a_{\text{Cu}} \quad (2)$$

where E_1 and E_2 are the electrode potentials for the solution of Cu^{2+} ions alone and for the solution containing interfering ions and copper ions, respectively, and n is the charge of the interfering ion. According to Eq. (2), the K^{MSM} values for diverse cations can be evaluated from the slope of the linear graph of $a_{\text{Cu}} \left\{ \exp \frac{2(E_2 - E_1)F}{RT} \right\} - a_{\text{Cu}}$ versus $a_M^{2/n}$. The resulting values of the selectivity coefficients are summarized and compared in Table 3.

The selectivity coefficients obtained by both methods are usually rather similar for the mono-, bi- and trivalent interfering ions. Nevertheless, in the case of univalent interferences, the values

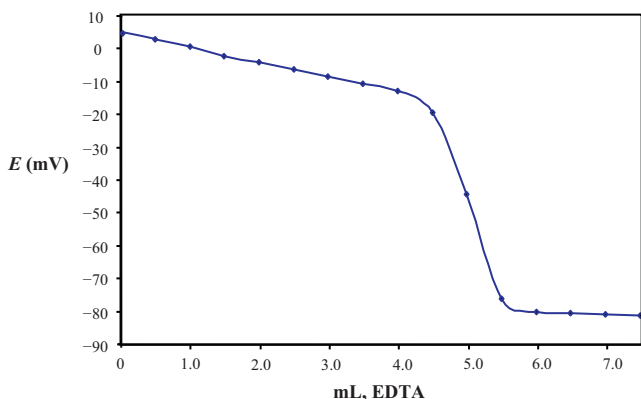


Fig. 4. Potentiometric titration curve of 50 mL of 1.0×10^{-3} M Cu^{2+} solution with 1.0×10^{-2} M EDTA (at pH 4), using the proposed sensor as an indicator electrode.

obtained by the MSM are significantly larger than those by the MPM. Such larger coefficients arise from the term $a^{2/n}$ in Eq. (2); the smaller the charge of the interfering ion, n , the larger the selectivity coefficient [35]. The selectivity coefficients are in the order of 10^{-4} to 10^{-3} for most of the interfering ions studied, what indicates that the disturbance produced by these metal ions in the operation of the Cu^{2+} ion-selective electrode is negligible. Among the studied interfering ions, Fe^{3+} has the highest selectivity coefficients, in the range $(2.4\text{--}2.9) \times 10^{-3}$, what may be connected with the higher charge and affinity of H_2L to this ion. The above results also clearly demonstrate that the electrode shows the best selectivity for the Cu^{2+} ion. The H_2L -based selective electrode has selectivity coefficients superior to those reported for other copper ion-selective electrodes, especially for interfering ions such as Zn^{2+} , Cd^{2+} , Co^{2+} , Mn^{2+} , Ni^{2+} , Al^{3+} and Fe^{2+} (Table 1) [28–64].

3.6. Analytical applications

Ion-selective electrodes are an ideal choice for both environmental and industrial measurements where simplicity, speed, low cost, possibility of automatization for rapid sampling, and selectivity in combination with accuracy are essential. The proposed Cu^{2+} ion-selective electrode was found to work well for determination of copper in samples of brass–zinc, aluminum and nickel based alloys, and soils polluted by oil (Table 4). In spite of the composite composition of the analyzed samples (See Section 2) the results obtained using H_2L -based electrode are in good agreement with the certified copper content and the results of the spectrophotometric method (Table 4).

In addition, the ISE was successfully applied to the titration of a Cu^{2+} ion solution with EDTA, and the resulting titration curve is shown in Fig. 4.

As shown, the amount of Cu^{2+} in solution can be accurately determined with the electrode. It is interesting to note that the resulting titration curve is unsymmetrical, as it was noticed before [101]. Before the titration end-point, the measured potential shows a usual logarithmic change with the amount (mL) of titrant added, while the potential response after the end-point remains almost constant, due to low concentration of free Cu^{2+} in solution.

Hence, on the basis of these results, we believe that this electrode can be applied for the determination of copper in other composite objects.

4. Conclusion

A copper-selective PVC membrane electrode was prepared with 1-phenyl-2-(2-hydroxyphenylhydrazo)butane-1,3-dione (H_2L) as a carrier and its composition (different plasticizers – DBP, NPOE, BA, AP; and different lipophilic additives – NaTBP and OA) was optimized. The membrane with the DBP plasticizer bearing the composition (% w/w) of 30:3:61:6 (PVC: H_2L :DBP:OA) gives the best performance. This electrode has a Nernstian response over a wide (2.0×10^{-6} to 5.0×10^{-3} M) copper concentration range, fast response time and good selectivity over a large number of metal ions. A comparison between all the characteristics of the pro-

posed potentiometric sensor and those of the previously known copper ion-selective electrodes (Table 1) [28–64] indicates that the current sensor shows better characteristics than several reported electrodes, i.e. being superior in terms of the detection limits, the response time and selectivity over other metal ions.

A procedure for the determination of copper(II) in zinc, aluminum and nickel based alloys, and soils polluted by oil was also developed. The membrane electrode was used as an indicator electrode for potentiometric titration of copper ions, and the developed method is selective, sensitive, reproducible, rapid, cheap and simple. For these reasons, it can be used in routine analysis and can be applied for the determination of copper in a diversity of objects – environmental, biological, medical and industrial samples without need for preconcentration or pretreatment steps and without significant interaction from other cationic species present in the samples.

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