Improving the Response of Copper(II) Selective PVC Membrane Electrode by Modification of N2S2 Donor Ligand

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Abstract

S,S'-bis(2-aminophenyl)ethanebis(thioate), (APhET), is reported as N2S2 ligand which form chelate with copper of high stability as compared to the other metals. Two modification of APhET, simpler 1,2-di-(*o*-aminophenylthio)ethane (DAPhTE), and the complex one 1,2-di-(*o*-salicylaldiminophenylthio)ethane (SAPhTE), were examined as the active material for copper(II) ion selective PVC membrane electrodes, and observed results are correlated. The obtained results with DAPhTE based electrodes show that only coordination abilities of ligand are insufficient for preparing the efficient membrane material. On the other hand, the results that are achieved with electrodes based on SAPhTE actuate interaction of ligand with polymer membrane matrix and necessity of ionophore immobilization in membrane.

Optimized SAPhTE based membrane electrode has a linear range down to 10^{-6} mol L^{-1}, with slope of 27.0 mV per decade, very rapid response time (under 5 seconds) and detection limit of 5.1×10^{-7} mol L^{-1}. Such electrode is suitable for determination of copper(II) in analytical measurements by direct potentiometry and in potentiometric titrations, within pH between 2 and 7. The electrode is selective for copper(II) ions over a large number of metal ions, with the exception on Hg^{2+} ion when is present in concentrations above 2×10^{-5} mol L^{-1}.

Keywords: copper(II), PVC membrane; selective electrode; ionophore; 1,2-di-(*o*-aminophenylthio)ethane; 1,2-di-(*o*-salicylaldiminophenylthio)ethane

1. Introduction

Various instrumental techniques and methods such as plasma mass spectrometry[1], flame photometry[2], voltammetry[3], UV-Vis spectrometry[4], atomic absorption spectrometry[5], chromatography[6], and gravimetric detection, are developed for the copper(II) quantification. However, these techniques are long-time, expensive, and require sample pretreatment and specialized persons for manipulation.

On the other hand, because of simplicity, wide dynamic range and fast response of the ion-selective electrodes (ISEs) the analytical procedures that overcome the above-described obstructions are provided.

In comparison with the other types of ISEs, (e.g. glass-, single crystal-, or precipitate- based electrode materials), the modern solvent polymer membrane based devices represent a generic approach to chemical sensing. Bühlmann et al. summarized the ionophores for Cu^{2+} sensors in 1998,[7] as recent Cu^{2+} solvent membranes based on ionophores.[8–34]

An important requirement for preparation of an ion selective sensor is that membrane electroactive material should have high lipophilicity and strong affinity for a target metal ion and poor affinity to the others.[29] It is well known that coordination abilities of ligands, containing sulfur or/and nitrogen atoms, are very selective to the transition metal ions.[20,21,28,32] Recently, we have presented copper(II) membrane electrodes with S,S'-bis(2-aminophenyl)ethanebis(thioate) (APhET) as a sensing material.[34] Continuing our work, as two potential copper (II) ionophores, we have chosen 1,2-di-(*o*-aminophenylthio)ethane

(DAPhTE) and its derivate 1,2-di-(*o*-salicylaldiminophenylthio)ethane (SAPhTE), because they have the same molecular frame as APhET. They were incorporated in poly(vinyl chloride) (PVC) membranes in order to enable determination of copper(II) ion. The results of this research are presented in this paper.

2. Experimental

2. 1. Reagents

All reagents used in these investigations were of analytical grade. Thiosemicarbazid, metallic potassium, absolute ethanol, salicylaldehyde, 2-aminothiophenol, sodium tetraphenylborate (NaTPB), poly(vinyl chloride) (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), dioctyl phthalate (DOP), tetrahydrofuran (THF), EDTA were purchased from Fluka (Buchs, Switzerland). Benzil, dibromethane were obtained from Sigma Aldrich (St. Louis, USA). Copper and potassium nitrates, acetic acid, ethanol, acetone, sodium hydroxide and hydrochloric acid were provided from Kemika (Zagreb, Croatia). For the purpose of cation determination, the cation nitrate salts were

used without any purification, while for determination of specific anion interferences potassium and sodium salts were used. Common stock solutions were used for the preparation of 0.1 and 0.01 mol L^{-1} solutions. All aqueous solutions were prepared using double distilled water.

2. 2. Synthesis of Ligands

In general, DAPhTE was prepared by earlier reported method.[35] Alcoholic solution of dibromethane was added dropwise in the alcoholic solution of diamine and refluxed. Ligand SAPhTE was synthesized as reported earlier,[36,37] by adding alcoholic solution of the DAPhTE (one molecular proportion) to alcoholic solution of salicylaldehyde (two molecular proportions) in the presence of acetic acid.

2. 3. Electrode Preparation

Membrane components, PVC, plasticizer, ionophore and NaTPB as anionic excluder, were dissolved in minimal amount of THF, mechanically mixed and poured into Teflon moulds. THF was left to evaporate for 48 hours at the room temperature. A membrane was cut and glued on a PVC tube. The tube was filled up with an internal filling solution (1.0 × 10^{-5} mol L^{-1} Cu^{2+} in 0.1 mol L^{-1} KCl). The electrode was finally conditioned for 24 hours by wetting in 1 × 10^{-5} mol L^{-1} copper(II) solution. Membranes of various compositions were prepared and researched (see Table 1).

2. 4. Apparatus and Potential Measurements

All potentiometric measurements were carried out by means of the cell assembly showed on Figure 2.

A saturated calomel electrode (SCE) was used as an internal reference electrode. External reference electrode (RE$_1$) was double junction Ag/AgCl (KCl, 3 mol L^{-1}) (Mettler Toledo InLab 301 electrode), and internal (RE$_2$) was saturated calomel electrode (»Iskra« Kranj, Slovenia). The potentiometric measurements were carried out by means of Mettler Toledo SevenEasy pH meter, which
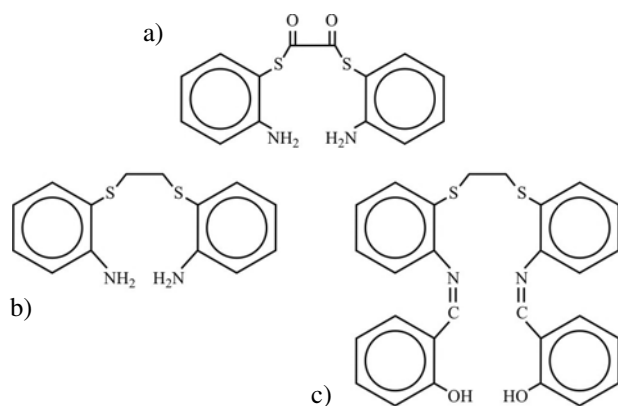
Figure 1. Structure of a) S,S'-bis(2-aminophenyl)ethanebis(thioate) (APhET); b) 1,2-di-(*o*-aminophenylthio)ethane (DAPhTE); c) 1,2-di-(*o*-salicylaldiminophenylthio)ethane (SAPhTE).

Table 1. Composition of PVC based Cu^{2+}-selective membranes containing DAPhTE and SAPhTE as electroactive material (in mg)

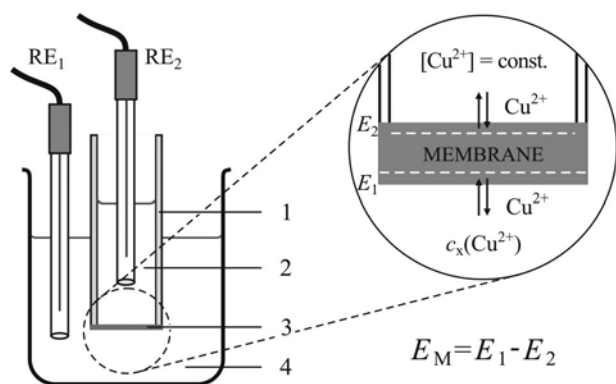| Electrode | Ionophore | | Plasticizer | | PVC | NaTPB |
	DAPhTE	SAPhTE	DOP	NPOE		
DAPhTE-1	2	–	132	–	66	2
DAPhTE-2	4	–	132	–	66	2
DAPhTE-3	2	–	–	132	66	2
DAPhTE-4	4	–	–	132	66	2
SAPhTE-1	–	2	132	–	66	2
SAPhTE-2	–	4	132	–	66	2
SAPhTE-3	–	6	132	–	66	2
SAPhTE-4	–	2	–	132	66	2
SAPhTE-5	–	4	–	132	66	2
SAPhTE-6	–	6	–	132	66	2

Figure 2. Cell assembly used in potentiometric measurements of copper(II) membrane electrode potential (E_M): 1 – PVC tube; 2 – internal reference solution; 3 – membrane; 4 – analyte solution.

was connected to a computer. The potential build up across the membrane electrode was measured using the following electrochemical cell assembly: Hg/Hg$_2$Cl$_2$ (saturated) (RE$_2$)|internal solution (1.0×10^{-5} mol L^{-1} Cu^{2+} in 0.1 mol L^{-1} KCl) | PVC membrane | test solution | Ag/AgCl (KCl, 3 mol L^{-1} (RE$_1$). The potential was recorded after addition of standard metal salt solution in magnetically stirred 0.1 mol L^{-1} KNO$_3$. The investigated concentration of copper(II) ions in the sample solution was from 1×10^{-8} mol L^{-1} to 5×10^{-2} mol L^{-1}. Detection limits were estimated according to IUPAC[38], from the cross point of the lines fitted to the linear segments of potential vs. log a_i curve, were a_i denotes single ion activity of the primary ion.

3. Results and Discussion

3. 1. Effect of N2S2 Donor Ligands Modification and Membrane Composition

Continuing our previous work,[34] we have firstly intended to test DAPhTE as an ionophore for the membrane electrode which is selective on copper(II), because it has the simplest form of APhET's molecular frame (see Figure 1). As APhET tend to form high selective 1:1 complex with copper(II) ion by coordination with both nitrogen and sulfur atoms[39] the electrode response to copper(II) ion may be consequence of the following complex reaction at the membrane surface:

$$APhET_{membrane} + Cu^{2+}(aq) \rightleftarrows [CuAPhET]^{2+}_{membrane}$$
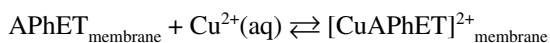
where APhET stays as a neutral carrier. Neutral carrier based cation-selective electrodes require lipophilic ionic sites (NaTPB in our case) with the charge which is opposite to that of the primary ion for obtaining a Nernstian response.

The membranes with different amount of ionophores and with different plasticizers, DOP ($\varepsilon = 7$) and o-NPOE ($\varepsilon = 24$), were prepared. The potential response of those electrodes was investigated as a function of copper(II) ions concentration in the range from 1×10^{-8} to 5×10^{-2} mol L^{-1}.

The results obtained with membrane electrodes based on 2 mg and 4 mg of DAPhTE are presented on Figure 3.
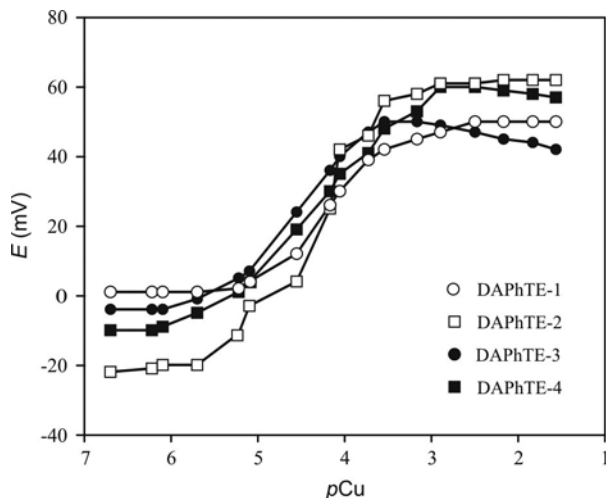

Figure 3. Potentiometric response of copper(II) membrane electrodes based on DAPhTE; influence of different plasticizers (DOP and o-NPOE) and various content of DAPhTE (2 and 4 mg).

It can be seen that all prepared electrodes were insensitive to the concentration of copper(II) ions over 5×10^{-4} mol L^{-1}. During measurements, these electrodes were also suffering from the long time response and unstable potential. Such behavior is probably caused by weak interaction of ionophore with a membrane bulk, provoking io-
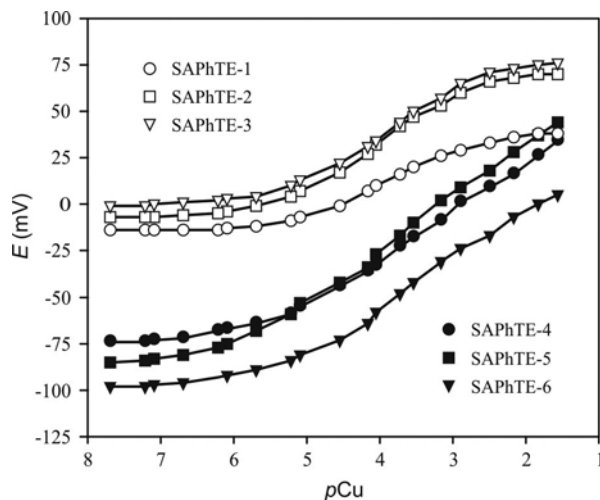

Figure 4. Potentiometric response of copper(II) membrane electrodes based on SAPhTE; influence of different plasticizers (DOP and o-NPOE) and varying content of SAPhTE (2, 4 and 6 mg)

nophore leaching into sample solution. The leaching rate into the sample must be kept as low as possible because necessity that an ionophore be highly lipophilic assures its compatibility with polymer membrane. Lipophilicity can be impaired to an ionophore by adding long alkyl chains or other bulky organic groups to the binding framework.[40]

Therefore, we examined SAPhTE as eventual ionophore, the ligand prepared by nucleophilic addition of salicylaldehyde to DAPhTE. The response of the electrodes prepared with different amount of SAPhTE, with DOP or *o*-NPOE as plasticizer, has been examined and data are shown in Figure 4.

Compared to DAPhTE, SAPhTE based membrane electrodes with DOP as plasticizer have lightly extended linear range. Nevertheless, those electrodes did not suffer from the long time response and unstable potential, which indicates on the rapid exchange kinetics due to conformational changes between SAPhTE and its copper complex. When *o*-NPOE was used as a plasticizer, linear range has been significantly improved similarly as in the case of APhET membrane electrodes.[34] This is probably consequence of the plasticizer polarity, which can be estimated from the interaction of charged species with the continuum of given dielectric constant. A plasticizer with high dielectric constant as *o*-NPOE enables divalent ion sensors and generation of free ions rather than ion-pairs, although dielectric constant of the membrane does not necessarily have to correspond exactly to the dielectric constant of the plasticizer.[41]

The response characteristics of the electrodes based on explored ligands are summarized in Table 2.

TE and NaTPB as anionic additive (1/2 mole ratio in respect to SAPhTE). This electrode exhibits the linear range down to 10^{-6} mol L^{-1} with slope of 27.0 mV per decade and detection limit of 5.1×10^{-7} mol L^{-1}.

A dynamic response and reversibility of the proposed SAPhTE membrane electrode at different concentrations of copper(II) ions was examined, and derived data are shown in Figure 5.

The time response was taken as the point when a differential quotient (dE/dt) of the potential-time curve became smaller than the value (dE/dt < 0.4 mV/min).[42] The ti-
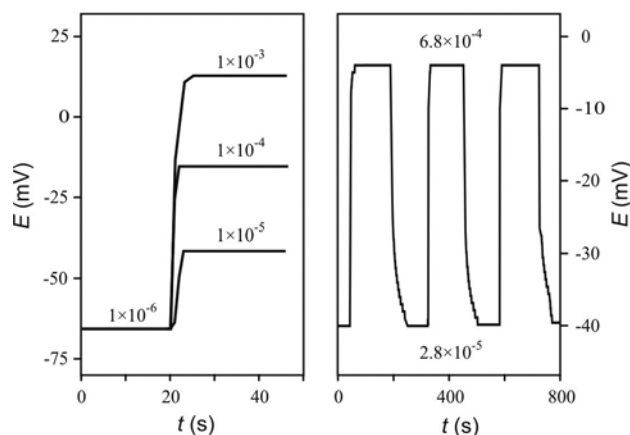

Figure 5. Dynamic potentiometric response and reversibility of the optimized SAPhTE based copper(II) membrane electrode (numbers besides lines in graphs are different concentration of copper(II) ions in mol L^{-1}).

Table 2. Effect of N2S2 ligands on the response of copper(II) membrane (66 mg of PVC, 132 mg of *o*-NPOE, 4 mg of ligand and 2 mg of NaTPB).

Ligand	DAPhTE	APhET	SAPhTE
Slope per decade	25.7	29.5 mV	27.0 mV
Linear range	$3 \times 10^{-6} – 3 \times 10^{-4}$ mol L^{-1}	$6 \times 10^{-6} – 5 \times 10^{-2}$ mol L^{-1}	$1 \times 10^{-6} – 5 \times 10^{-2}$ mol L^{-1}
Detection limit	2.3×10^{-6} mol L^{-1}	4.0×10^{-6} mol L^{-1}	5.1×10^{-7} mol L^{-1}
Response time	120 seconds	30 seconds	5 seconds

It can be seen that ligand replacement from simple DAPhTE to complex SAPhTE significantly improves linear range and response time of the membrane electrodes. Such behavior corresponds with assumption that beside the selective complexation of copper(II) ion, ionophore must be immobilized into the membrane by the organic groups linked on the ionophore binding framework.

3. 2. Characterization of SAPhTE Based Electrode

The best performance of all explored electrodes have been obtained with the membrane electrode which contained 66 mg of PVC, 132 mg of *o*-NPOE, 4 mg of SAPh-

me response of the proposed SAPhTE electrode was under 5 seconds and it remained unchanged at varying concentration range. This indicates that the processes at an interface of aqueous and organic membrane phases genessing the membrane potential. In order to maintain the electrode lifetime the periodic calibration with standard solutions had to be performed. It was found that characteristics of the potentiometric response of membrane electrode remained unchanged after a period of 2 months. Over this period, the membrane electrodes were kept in dry and dark place. Before measurements the electrode was conditioned for 3 hours in 1×10^{-5} mol L^{-1} copper(II) solution.

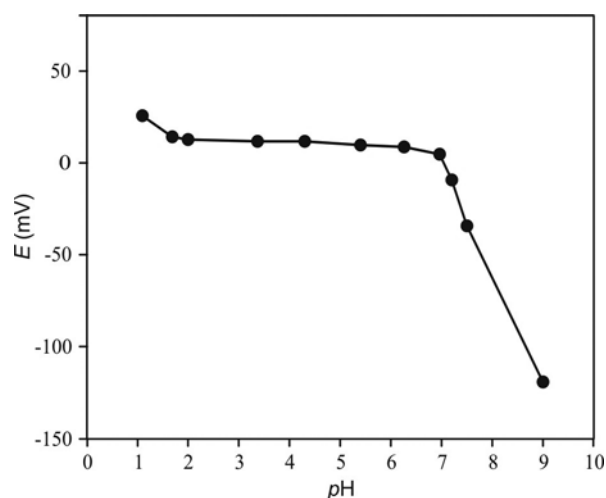Effect of pH on the potential response of membrane electrode was determined at the copper(II) ions concentra-

Figure 6. The effect of pH of the test solution on the potentiometric response of the optimized SAPhTE based copper(II) membrane electrode at 1×10^{-3} mol L^{-1} copper(II) ion.

tion of 1×10^{-3} mol L^{-1}. A pH range between 1 and 9 was controlled using HNO_3 and NaOH solutions.

As can be seen from Figure 6, a constant potential of membrane electrode was obtained when pH range was between 2 and 7. The electrode was affected when pH< 2, probably due to the interference from H^+. The potential drop in the alkaline media could be consequence of $Cu(OH)_2$ precipitation. Despite small solubility constant of $Cu(OH)_2$ (5×10^{-20}), high value of potential near pH 7 can be caused by metastable equilibrium condition of $Cu(OH)_2$ precipitation.[43]

Performance of the SAPhTE membrane electrode was also investigated in mixed ethanol-water medium. The membrane showed satisfactory response in the ethanol-water medium up to 20% of ethanol. The working range and the response remained almost the same except

Table 3. Selectivity coefficients for the optimized SAPhTE based copper(II) membrane electrode determined by MPM[*].

Interferent species B	$pK^{pot}_{Cu^{2+}, B}$
Pb^{2+}	−1.61
Zn^{2+}	−1.82
Mn^{2+}	−2.10
Cd^{2+}	−3.50
Fe^{2+}	−4.70
Co^{2+}	−4.70
Na^+	< −7
K^+	< −7
Ca^{2+}	< −7
Ni^{2+}	< −7
Ag^+	< −7

[*]MPM match potential method

for a slight change in slope (25 mV per decade) compared to those in aqueous media.

The selectivity coefficients for SAPhTE membrane electrode, obtained by match potential method (MPM, IUPAC[44]), are summarized in Table 3. The selectivity indicates that potentiometric measurements will not be disordered by no one of all these ions in the researched concentration range of copper(II) ion.

As some neutral ionophores containing nitrogen atoms exhibit serious interference to Hg^{2+} ions,[45,46] mixed run studies were carried out in order to have an estimate of tolerance level on Hg^{2+}. In these runs, the potentials of the sensor were determined as a function of copper(II) concentration in the presence of the fixed concentration of Hg^{2+} ions. It was found that quantities above 2×10^{-5} mol L^{-1} of Hg^{2+} ions caused significant divergence in the sensitivity of SAPhTE membrane electrode at low concentration of copper(II) potential.

The interference of anions has also been researched, as halides are known to cause interference in determination of copper(II) ion. No any interference was noticed at the examined anions: SO_4^{2-}, CH_3COO^-, salicylate, Br^-, Cl^-, phosphate, NO_3^- and SCN^-.

The analytical applicability of the electrode was further evaluated by potentiometric titration of copper(II) ions with EDTA. The amount of 30 ml of 1.3×10^{-3} mol L^{-1} Cu^{2+} solution was titrated against 1.0×10^{-2} mol L^{-1} EDTA. The obtained titration plot shown on Figure 7 is standard sigmoid shape and the end point corresponds to 1:1 stoichiometry of Cu-EDTA complex.
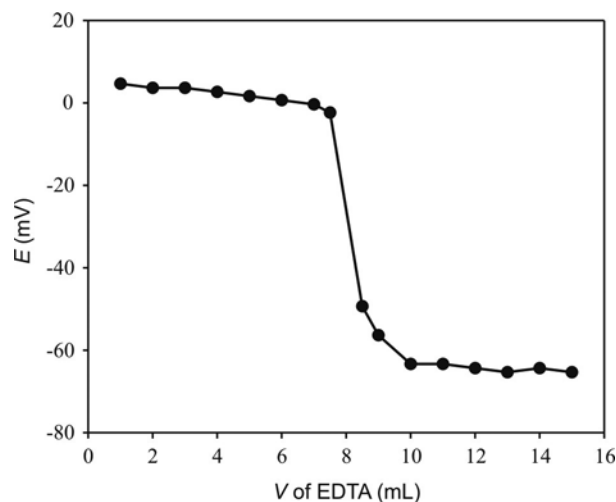

Figure 7. The potentiometric titration plot of 30 mL of 1.3×10^{-3} mol L^{-1} copper(II) against EDTA (0.01 mol L^{-1}) using the optimized SAPhTE based copper(II) membrane electrode at pH = 5.5.

This indicates that the an amount of copper(II) ions can be accurately determined from the resulting titration curve which provides a clearly noticeable ending point.

4. Conclusion

Two N2S2 ligands, DAPhTE and SAPhTE, were investigated as an active material in preparation of the copper(II) ion selective PVC membrane electrodes. Coordination abilities of DAPhTE as ligand were insufficient for preparing the efficient membrane material, because all DAPhTE based electrodes have been useless, probably because of the weak interaction of ionophore with a membrane bulk.

In order to improve slow response and unstable potential of DAPhTE electrodes, nucleophilic addition of salicylaldehyde has been performed resulting in another ligand, SAPhTE. Achieved results with electrodes based on SAPhTE actuate interaction of the ligand with the polymer membrane matrix and necessity of ionophore immobilization in the membrane.

Optimized SAPhTE electrode shows such performance which makes this electrode suitable for measuring of the concentration of copper(II) ions in wide variety of samples, without significant interactions from the other cationic or anionic species, with the exception of Hg^{2+}.

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Povzetek

S'-bis(2-aminofenil)etanebis(tioat), (APhET), v literaturi omenjajo kot N2S2 ligand, ki tvori stabilen kelat z bakrom. Preiskovali smo dve modifikaciji APhET, enostavnejši 1,2-di-(*o*-aminofeniltio)etan (DAPhTE), in kompleksnejši 1,2-di-(*o*-salicilaldiminofeniltio)etan (SAPhTE), kot aktivni substance v PVC membranskih elektrodah za določanje bakra (II). Rezultati, ki smo jih dobili z DAPhTE kažejo na to, da koordinacijske lastnosti liganda niso same po sebi dovolj za pripravo učinkovite membrane. Po drugi strani elektrode na podlagi SAPhTE ojačajo interakcijo liganda s polimerno matrico.

Membranska elektroda na podlagi SAPhTE izkazuje linearni odyiv do 10^{-6} molL^{-1}, z naklonom 27,0 mV na dekado, hiter odyiv (manj kot 5 s) in mejo detekcije $5,1 \times 10^{-7}$ molL^{-1}. Taka elektroda je primerna za določanje bakra(II) z neposredno potenciometrijo in v potenciometričnih titracijah, v območju pH med 2 in 7. Elektroda je selektivna za baker(II) glede na veliko število kovinskih ionov, z izjemo Hg^{2+}, če je prisoten v koncentracijah nad 2×10^{-5} molL^{-1}.