

# A Copper(II) Ion-Selective Potentiometric Sensor Based on *N,N',N'',N'''*-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane in PVC Matrix

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## Abstract

The simple PVC-based membrane containing *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (*tpmc*) as an ionophore and dibutyl phthalate as a plasticizer, directly coated on a glassy carbon electrode was examined as a new sensor for  $\text{Cu}^{2+}$  ions. The potential response was linear within the concentration range of  $1.0 \times 10^{-1}$ – $1.0 \times 10^{-6}$  M with a Nernstian slope of 28.8 mV/decade and detection limit of  $7.0 \times 10^{-7}$  M. The electrode was used in aqueous solutions over a wide pH range (1.3–6). The sensor exhibited excellent selectivity for  $\text{Cu}^{2+}$  ion over a number of cations and was successfully used in its determination in real samples.

**Keywords:** Cu(II) potentiometric sensors, Coated glassy carbon rod, Ionophore, *N,N',N'',N'''*-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, Waste waters

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## 1. Introduction

The great importance of copper in biological [1–5], environmental [6] and industrial systems [7] has attracted considerable interest. Due to its remarkable properties copper is a strategic metal especially for cleaning energy products as the next industrial revolution [6]. Therefore, determination of copper ion in various materials such as water, biological, environmental, medical and industrial samples in the presence of other cations plays a significant role in a wide range of chemical and biological processes.

A variety of copper ion-selective electrodes (ISEs) has been constructed for potentiometric monitoring of  $\text{Cu}^{2+}$  ions. Beside well established all-solid-state  $\text{CuS}/\text{Ag}_2\text{S}$  electrodes, ISEs based on neutral carrier ligands are attracting increasing attention. Macrocyclic polythiaethers [8–10], noncyclic ionophores with dithiocarbamate groups and their derivatives [11–13], as well as dialkyldithiophosphates [14] as different ionophores have been used for a construction of ion-selective Cu(II) electrodes. Macrocycles, however, with nitrogen-ions exhibit increased affinity towards transition metal ions [15] and number of examinations of such macrocycles have shown their stronger response to  $\text{Cu}^{2+}$  ions in comparison to other transition metals [16]. A several ion-selective electrodes based on aza macrocycles have also been reported [17–20]. In view of macrocyclic ligands, *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (*tpmc*) derived from *cyclam*

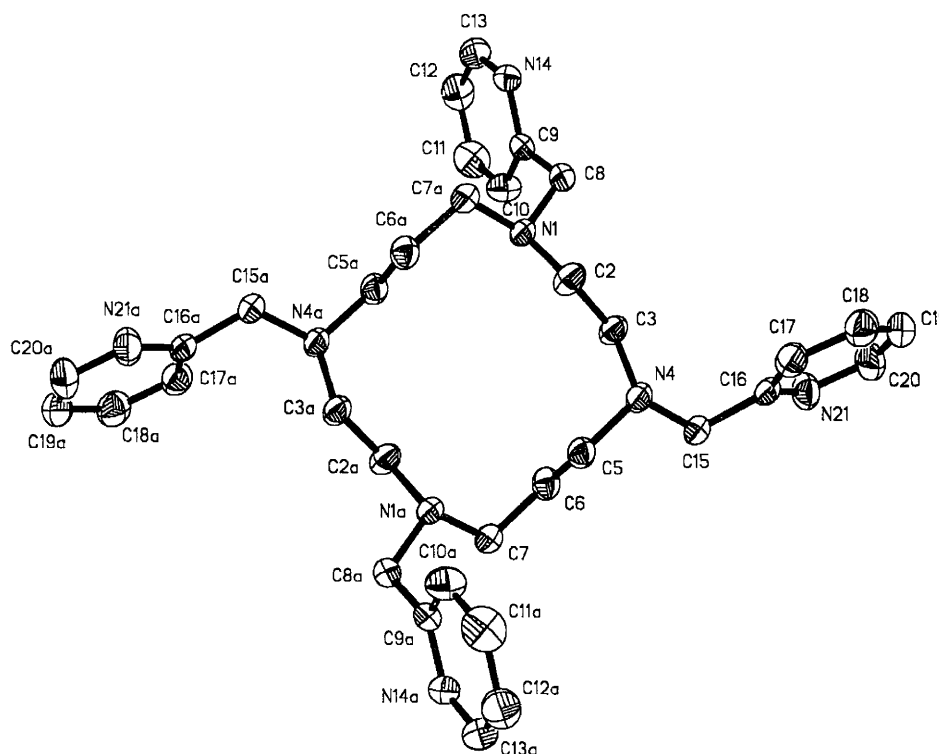
is especially suitable to achieve stable dinuclear complexes [21] (Scheme 1). A number of dinuclear Cu(II) complexes with the *tpmc* is known, in which the macrocycle exhibits the *chair* or the *boat* coordination mode. While the *chair* coordination is rarely obtained [21], when two simple anions, as additional ligands occupy apical positions, the latter one is favorable especially in presence of some bidentate ligand [22–24], which forms a bridge between the two copper atoms.

We embarked on the present study to develop ion selective Cu(II) electrode based on *tpmc* ligand as an ionophore in PVC matrix with a simple construction by using a simple procedure. In order to obtain further insight into the potentiometric response properties of the electrode, the potentiometric sensor obtained was successfully applied as an indicator electrode for the end point determination in the potentiometric titration of copper ions against EDTA. Furthermore, the determination of  $\text{Cu}^{2+}$  concentration in wastewater from Copper Mining and Smelting Complex Bor were evaluated.

## 2. Experimental

### 2.1. Reagents

- 1,4,8,11-tetraazacyclotetradecane (*cyclam*) was used from Aldrich Chemical Co.



Scheme 1. Crystal structure of the ionophore *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane, used as the electroactive material in the proposed Cu(II)-*tpmc* ionophore based ISE [25].

- 2) *N,N',N'',N'''*-tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (*tpmc*) (Scheme 1) was prepared by the modified procedure described in literature [26].
- 3) dibutyl phthalate (DBP) was used as received from Fluka.
- 4) poly(vinyl chloride), PVC, was used as Pevicon made by Fostatbolaget, Sweden.
- 5) sodium tetraphenylborate (NaTPB) and
- 6) tetrahydrofuran (THF) were of the highest purity available from Merck, except THF, which was distilled before use.
- 7) Reagent grade nitrate salts of all cations used from Merck, Fluka and Aldrich, were of the highest purity available and used without further purification.
- 8) Reagent grade nitrate salts of all cations used from Merck, Fluka and Aldrich, were of the highest purity available and used without further purification.
- 9) All other reagents used were of analytical reagent grade.
- 10) Doubly distilled deionized water (DDW) was used throughout.

**Preparation of ionophore:** To a mixed aqueous solution of 2-picolylchloride hydrochloride (3.8 g, 30 mmol) and an aqueous suspension of cyclam (1 g, 5 mmol) a solution of NaOH (2.4 g, 60 mmol) was added dropwise. The reaction mixture was stirred continuously for 72 hours, during which time most of the expected precipitate was separated while the color of the solution changed from pink to yellow. The

solution was allowed to stand in a refrigerator (5 °C) overnight. The solid was filtered and dried under vacuum over CaCl<sub>2</sub>. Re-crystallization was done from a hot ethanol. After a few days of slow evaporation shining colorless prisms of suitable size were collected, filtered off and dried over CaCl<sub>2</sub>. Yield: 1.95 g, 69.71%. Anal. Calcd. for (C<sub>34</sub>H<sub>44</sub>N<sub>8</sub>) (%): C, 72.30; H, 7.85; N, 19.84. Found: C, 72.48; H, 7.89; N, 19.68. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) = 1.75 (q, 4H, CCH<sub>2</sub>C); 2.53 (t, 8H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 2.66 (s, 8H, NCH<sub>2</sub>CH<sub>2</sub>NCH<sub>2</sub>); 3.57 (s, 8H, NCH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N); 7.07–8.48 (m, 16H, C<sub>5</sub>H<sub>4</sub>N). <sup>13</sup>C NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) = 161, 151, 134, 122, 121 (C<sub>5</sub> H<sub>4</sub>N); 62.10 (NCH<sub>2</sub>C<sub>5</sub>H<sub>4</sub>N); 52.11 (NCH<sub>2</sub>CH<sub>2</sub>N); 51.21 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N); 23.81 (CCH<sub>2</sub>C).

## 2.2. Electrode Preparation

The PVC membrane contained 4–9% (w/w) ionophore, 34–39% PVC and 57–60% dibutyl phthalate. A total of 0.270 g of these reagents was mixed with 2.5 mL THF. A glassy carbon (GC) stick (Ø = 5 mm) (Sigardur-Sigri Electrographite, GmbH, Germany), sealed into the end of a glass and soldered onto a shielded cable, was directly coated by dipping it several times in the slurry mixture until a bead was formed coating the GC. This bead on the GC was allowed to dry in air over night and put into a 0.01 M copper(II) nitrate solution for about 1.5 h in order the Cu(II) cations to be captured in the ionophore cavities before use. This coated GC was finally used as Cu(II)-ISE.

### 2.3. Real Samples Preparation

Samples taken from electrolytic process and industrial waste water samples before and after process of cementation were obtained from Copper Mining and Smelting Complex Bor. Samples were handled according to standard procedures [27]. Iron in wastewater samples in a 10 mL aliquots was removed by precipitation with  $\text{NH}_4\text{OH}$  (1:1), while other ions and compounds ( $\text{As}^{3+}$ ,  $\text{Cl}^-$ ,  $\text{P}_4\text{O}_{10}$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cd}^{2+}$ ,  $\text{Na}^+$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ) present in the samples were not interfering. pH was adjusted by 0.1 M  $\text{HNO}_3$ , and solutions were heated for boiling on a hot plate for 10 min to decompose the metal complexes. Sample taken from electrolytic process was treated by 1 M  $\text{HNO}_3$  and heated for metal complexes decomposition, with ought previous preparation. The solution was quantitatively transferred to 100 mL volumetric flask and completed to the mark with DDW water.

### 3.4. Apparatus and Electrochemical Measurements

Elemental analyses were carried out on Elemental Vario EL III microanalysers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were ran on a Varian Gemini 2000 spectrometer operating in the Fourier transform mode (200 and 50 MHz) in  $\text{CDCl}_3$  at room temperature.

The potentials were measured in the series of standard  $\text{Cu}(\text{NO}_3)_2$  solutions within the range of  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  M and their ionic strength was adjusted with ammonium nitrate solution while the pH of all standard solutions was 5. The potential measurements were carried out at  $25^\circ\text{C}$  using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

$\text{SCE} \parallel \text{test/sample solution} \parallel \text{PVC membrane} \parallel \text{GC}$

All potentiometric and pH measurements were made on pH-211 Hanna Instruments, and SCE (model HI5412) was the product of the same factory. Activities were calculated by the Debye–Hückel procedure [28].

Possible influence of THF used to dissolve all components for construction of PVC matrix, on GC electrode used as sensor carrier was examined by cyclic voltammetry in 0.1 M  $\text{HClO}_4$  solution. The examined electrodes were polished GC or polished GC previously kept for a few minutes in THF solution. The polished GC electrode was prepared by abrasion with emery paper of decreasing grain size followed by polishing with alumina of 1  $\mu\text{m}$  particle size. The final cleaning of the electrodes was performed in DDW in an ultrasonic bath.

The experiments were performed at room temperature in the solution purged with purified nitrogen prior to each experiment. The counter electrode was a Pt wire while a SCE was used as a reference one. The electronic equipment consisted of a PAR Model 273 potentiostat and Philips Model 8033 X-Y recorder.

## 3. Results and Discussion

Our intention was to develop an ion selective  $\text{Cu}(\text{II})$  electrode based on a *tpmc* ionophore, immobilized in a PVC matrix using a simple construction procedure for performing  $\text{Cu}(\text{II})$  determinations in a wide variety of media. Besides, the development of reliable miniaturized sensor arrays for remote applications could be potential advances of the proposed  $\text{Cu}(\text{II})$ -*tpmc* ionophore based ISE.

### 3.1. Optimization of the Proposed $\text{Cu}(\text{II})$ -*tpmc* Ionophore Based ISE

Glassy carbon was applied as sensor carrier as well as a conductor and electron transmitter instead of Pt or Cu wire. It was found that THF used to dissolve all components for construction of PVC matrix oxidize GC. The cyclic voltammogram of polished GC electrode in 0.1 M  $\text{HClO}_4$  shows characteristic shape with redox peak at  $\sim 0.4$  V vs. SCE corresponding to quinoin type functional groups on GC surface as well as the double layer charge i.e., capacitance usual for polished GC [29]. After the treatment with THF cyclic voltammogram of the electrode reveals the features of the activated–oxidized GC with increased double layer charge as the consequence of increased roughness and increased fraction of functional groups [29] what is followed by promoted electron-transfer kinetics [30]. Most probably, this chemical oxidation of GC produced more active centers on the surface, which led to greater improvement of potentiometric response of electrode. We assume that those functional groups act as a mediator layer by which internal reference solution could be omitted.

The characteristics of the ion-selective membranes, namely the response time, lifetime and selectivity are dependent on the ratio of the electroactive phase and the binder materials. Thus, several membrane compositions were investigated as shown in Table 1. The sensitivity of the electrode's response increases with increasing ionophore *tpmc* content until a value of 7% is reached. Further addition of ionophore will, however, results in diminished response of the electrode, most probably due to some inhomogeneities and possible super-saturation of the membrane [12]. As ion exchanger, NaTPB was added in 1% of total mass in order to improve the electrode performances, but potentiometric response totally disappeared. It is likely that this is due to the fact that borate blocked the active sites of the reagent and significantly decreased its reactivity. Since PVC as membrane matrix usually contains ionic impurities with cation-exchanger properties, neutral carrier-based cation-selective membranes are usually functional without the incorporation of anionic sites [31]. The membrane having a composition of 7:57:36 (*tpmc*:DBP:PVC) gave the best response characteristics (Table 1).

The response time of the electrode depends on the time of electrode conditioning prior to the application. The best response time of 10–50 s for standard solutions from  $1.0 \times$

Table 1. Composition and characteristics of Cu(II) ISE's based on *tpmc* ionophore.

No	Composition (w/w)%				Slope (mV/dec)	Working concentration range (mol/dm <sup>3</sup> )
	PVC	DBP	<i>tpmc</i>	NaTFB		
1	39	57	4	–	35 ± 3	5 × 10 <sup>−1</sup> –1 × 10 <sup>−5</sup>
2	35	60	5	–	33 ± 3	1 × 10 <sup>−2</sup> –1 × 10 <sup>−5</sup>
3	38	57	5	–	30 ± 3	1 × 10 <sup>−1</sup> –1 × 10 <sup>−6</sup>
4	37	57	6	–	29 ± 3	1 × 10 <sup>−1</sup> –1 × 10 <sup>−6</sup>
5	36	57	7	–	28 ± 3	1 × 10 <sup>−1</sup> –1 × 10 <sup>−6</sup>
6	35	57	7	1	5 ± 3	1 × 10 <sup>−2</sup> –1 × 10 <sup>−5</sup>
7	34	57	9	–	31 ± 3	1 × 10 <sup>−2</sup> –1 × 10 <sup>−5</sup>

10<sup>−1</sup> to 1.0 × 10<sup>−7</sup> M is achieved when electrode has been immersed in 0.01 M Cu(NO<sub>3</sub>)<sub>2</sub> conditioning solution for 1.5 h prior to the application.

Optimized electrode has linear working range of 1.0 × 10<sup>−1</sup>–1.0 × 10<sup>−6</sup> M with a Nernstian slope of 28.8 mV/decade of activity and detection limit is 7.0 × 10<sup>−7</sup> M. The calibration curve of this electrode is given in Figure 1. The lifetime of this electrode is about two months and after this period sensitivity will start to decrease.

The pH dependence of the sensor was examined by determining the potentials at 1.0 × 10<sup>−1</sup>, 1.0 × 10<sup>−2</sup>, 1.0 × 10<sup>−3</sup> and 1.0 × 10<sup>−5</sup> M Cu<sup>2+</sup> ions over a pH range of 0.7–8.5. The pH was adjusted with HNO<sub>3</sub> and NaOH solutions. The potentials developed (Figure 2) were independent of pH in the range of 1.3–6.0. The same range should be taken as the working pH range of the *tpmc* based Cu(II) sensor. It was observed that above pH 6.0 the potential starts to increase until reaching pH 7.5 in opposite to expectations and after that value decreases slowly because of the formation of copper(II) hydroxide in the solution at higher pH. At pH lower than 1.3 the potential drastically increases, possibly due to the electrode's response towards hydrogen ions.

The characteristics of *tpmc* based Cu(II) ISE in comparison with other reported coated wire ion-selective electro-

des and electrodes with internal solution are presented in Table 2. It can be seen that proposed electrode is quite comparable with others in all characteristics, but it has convincingly the largest pH working range, sometimes for more than 2 pH units. The most probable reason for this is lower affinity to protonation of *tpmc* ligand in comparison with those ligands applied for the synthesis of those sensors described in literature [13, 17, 32, 33]. Thus, applicability of Cu(II) ISE is extended to a remarkably acidic range of 1.5–2.5 with direct application in samples with low pH and this consists its main advantage.

### 3.2. Interference Study

Selectivity coefficients describing the preference by the membrane for an interfering ion relative to Cu<sup>2+</sup> were determined by the fixed interference method (FIM). The interfering ions concentration in solutions was 1 × 10<sup>−2</sup> M while for very interfering Ag<sup>+</sup> and Fe<sup>3+</sup> ions were 1 × 10<sup>−4</sup>. Data presented in Table 3 clearly indicate that the electrode is highly selective to Cu<sup>2+</sup> ion over various monovalent, divalent and trivalent cations and many common transition metals in a medium. It can be seen that the tolerance limits are of the order of 10<sup>−3</sup> or 10<sup>−4</sup>, which means that these ions have negligible impact on the function of the proposed Cu(II) sensor. Ions of Ag<sup>+</sup> and Fe<sup>3+</sup> strongly interfere; therefore removing them from the sample is desirable.

Cation binding to essentially all macrocycles is often described by the best-fit concept based on the relationship between binding cavity size and ionic radius [34]. Contrary to other cations (Ni<sup>2+</sup>, Co<sup>2+</sup>), which need an additional bidentate ligand (dithiocarbamate or  $\beta$ -diketones) forming a bridge between the two metal atoms only Cu(II) is capable to form very stable complex with *tpmc* without any other ligands, too [35]. In that respect, its structure has the advantage of being relatively less rigid and thus gives structurally well-defined moiety [22, 36], which delineates the preference of a certain ion. It seems to be a good explanation for sensor behavior and high selectivity of proposed electrode to copper(II) ions over other metal ions except Ag<sup>+</sup> and Fe<sup>2+</sup> cations.

Interference of anions which exhibit drastic redox, complexation or precipitation activities toward Cu<sup>2+</sup> cations were investigated to get a complete picture for determi-

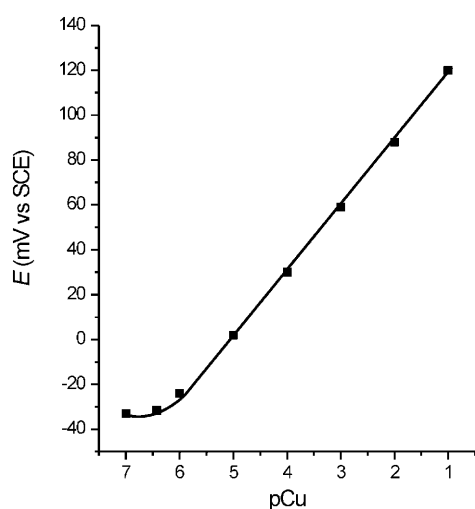


Fig. 1. Calibration curve of the proposed Cu(II)-*tpmc* ionophore based ISE in Cu<sup>2+</sup> solutions.

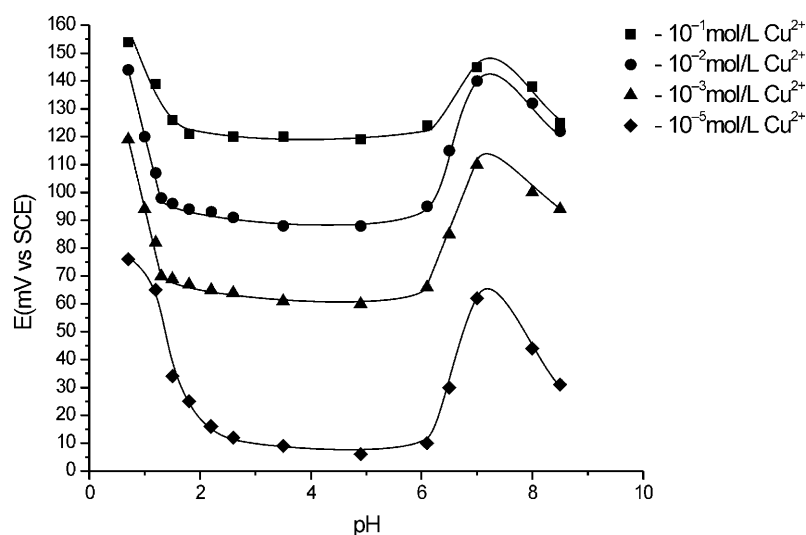


Fig. 2. Effect of pH on potentiometric response of the proposed Cu(II)-*tpmc* ionophore based ISE.

Table 2. Response characteristics of the proposed Cu(II)-*tpmc* ionophore based ISE in comparison with similar electrodes described in literature. nm: not mentioned in the paper.

Response characteristics	Proposed electrode	[13] CWISE	[13] Sol-gel	[17] Inner ref. sol.	[32] CWISE	[33] CWISE
Slope (mV/decade)	28.8	29.2	28.1	29.9	28.2	28 ± 2
Linear range (M)	1.0 × 10 <sup>-1</sup> – 1.0 × 10 <sup>-6</sup>	1.0 × 10 <sup>-1</sup> – 1.0 × 10 <sup>-5</sup>	1.0 × 10 <sup>-1</sup> – 6.0 × 10 <sup>-6</sup>	1.0 × 10 <sup>-1</sup> – 1.12 × 10 <sup>-6</sup>	1.0 × 10 <sup>-1</sup> – 1.0 × 10 <sup>-6</sup>	1.0 × 10 <sup>-1</sup> – 1.0 × 10 <sup>-6</sup>
Detection limit (M)	7.0 × 10 <sup>-7</sup>	3.0 × 10 <sup>-6</sup>	6.0 × 10 <sup>-6</sup>	nm	5.0 × 10 <sup>-7</sup>	nm
Response time (s)	10–40	50	20–50	10 ± 2	10–50	15
Working pH range	1.3–6	4–7.5	4–7.5	2.1–6.2	3–6.5	1.5–6.7
Lifetime (months)	> 2	2	6	6	2	2

nation of Cu<sup>2+</sup> in real samples. The interfering ions concentration in solutions were 1 × 10<sup>-2</sup> M for Cl<sup>-</sup> and Br<sup>-</sup>, 10<sup>-4</sup> M for CNS<sup>-</sup>, ascorbates and [Fe(CN)<sub>6</sub>]<sup>3-</sup> while for other strongly interfering anions were 1 × 10<sup>-5</sup> M. It was found that S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, S<sup>2-</sup>, I<sup>-</sup> and [Fe(CN)<sub>6</sub>]<sup>4-</sup> strongly interfere even in concentrations of 10<sup>-5</sup> M and should, therefore, be removed from the sample for successful determination of Cu<sup>2+</sup>.

### 3.3. Analytical Applications

Applicability of the new Cu(II) ISEs based on *tpmc* ionophore in real samples is one of the primary require-

ments for its validation. Samples were taken from electrolytic process and industrial waste water samples before and after cementation process. The unknown concentration was estimated by direct potentiometry from the calibration curve of the proposed Cu(II)-*tpmc* ionophore based ISE. It is found that the copper contents obtained from five measurements are in satisfied agreement with those obtained by using reference atomic absorption spectrometry (AAS) (Table 4). Thus the electrode provides a good alternative for the determination of Cu<sup>2+</sup> in real samples.

The proposed electrode as the indicator electrode was also successfully applied in conjunction with SCE for the potentiometric titrations of Cu<sup>2+</sup> solution with a standard

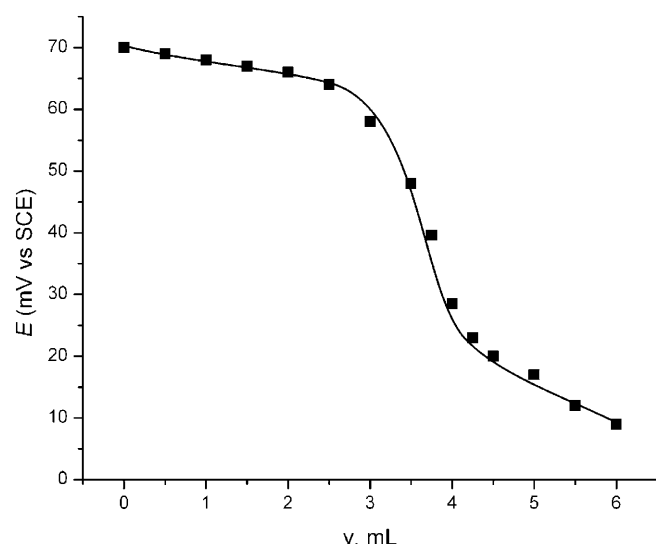
Table 3. Selectivity coefficients of the proposed Cu(II)-*tpmc* ionophore based ISE against various cations and anions.

Interfering cation (M)	$K_{Cu,M}$ by FIM	Interfering cation (M)	$K_{Cu,M}$ by FIM	Interfering anion (A)	$K_{Cu,A}$ by FIM
Co <sup>2+</sup>	4.78 × 10 <sup>-4</sup>	Al <sup>3+</sup>	5.24 × 10 <sup>-4</sup>	Cl <sup>-</sup>	1.14 × 10 <sup>-2</sup>
Pb <sup>2+</sup>	3.09 × 10 <sup>-4</sup>	Hg <sup>2+</sup>	6.61 × 10 <sup>-3</sup>	Br <sup>-</sup>	6.3 × 10 <sup>-2</sup>
Zn <sup>2+</sup>	3.80 × 10 <sup>-4</sup>	Ag <sup>+</sup>	7.23	CNS <sup>-</sup>	0.17
Cd <sup>2+</sup>	3.63 × 10 <sup>-4</sup>	As <sup>3+</sup>	9.21 × 10 <sup>-4</sup>	[Fe(CN) <sub>6</sub> ] <sup>3-</sup>	0.68
Ni <sup>2+</sup>	2.29 × 10 <sup>-4</sup>	Fe <sup>3+</sup>	1.02	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1.81
Fe <sup>2+</sup>	1.05 × 10 <sup>-3</sup>	Mg <sup>2+</sup>	2.89 × 10 <sup>-4</sup>	[Fe(CN) <sub>6</sub> ] <sup>4-</sup>	Strong interference
Mn <sup>2+</sup>	8.49 × 10 <sup>-4</sup>			S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	3.98
Cr <sup>3+</sup>	7.94 × 10 <sup>-3</sup>			S <sup>2-</sup>	Strong interference
Na <sup>+</sup>	2.75 × 10 <sup>-4</sup>			I <sup>-</sup>	Strong interference
Ca <sup>2+</sup>	3.31 × 10 <sup>-4</sup>			ascorbates	0.58

Table 4. Determination of Cu(II) concentration in industrial samples by using the proposed Cu(II)-*tpmc* ionophore based ISE.

Samples	Cu(II) concentration [a] determined by proposed electrode (mol/L)	Cu(II) concentration [a] determined by AAS (mol/L)	RSD (%)
Cementation input	$4.43 \times 10^{-3} \pm 0.3$	$4.72 \times 10^{-3} \pm 0.1$	-6.14
Cementation output	$2.68 \times 10^{-3} \pm 0.3$	$2.51 \times 10^{-3} \pm 0.1$	6.77
Electrolytic bath	$3.74 \times 10^{-2} \pm 0.3$	$3.65 \times 10^{-2} \pm 0.1$	3.01

[a] Average and confidence interval of five separate measurements

Fig. 3. Potentiometric titration of 20 mL  $10^{-2}$  M  $\text{Cu}^{2+}$  solution with a primary 0.05 M EDTA solution by using the proposed Cu(II)-*tpmc* ionophore based ISE.

EDTA solution as the suitable titrant (Figure 3). The plot was of sigmoid shape and the inflexion point of the plot corresponds to 1:1 stoichiometry of copper–EDTA complex.

#### 4. Conclusions

The proposed Cu(II)-*tpmc* ISE, according to our knowledge, is the first one made by coated wire technique on GC rod. It is characterized by very simple preparation as well as construction and its performances are comparable with commercial Cu(II) ISEs. The working pH range is wider than of the other reported ionophore based potentiometric sensors. Additionally, the relatively long lifetime of this electrode (about two months) could not be negligible. In order to evaluate analytical applicability of the proposed electrode, it was successfully applied to the determination of Cu concentration in real samples of industrial wastewater, and it can be used as an alternative electrode in similar environmental and other samples.

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