Erzincan Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
2024, 17(2), 460-473
ISSN: 1307-9085, e-ISSN: 2149-4584
Araştırma Makalesi

Erzincan University
Journal of Science and Technology
2024, 17(2), 460-473
DOI: 10.18185/erzifbed.1478285
Research Article

# All-Solid-State PVC-Membrane Cu(II)-Selective Potentiometric Microsensor Based on a Novel Calix[4]arene Derivative

Cigdem CAY[1], Murat YOLCU[1*], Serkan SAYIN[2]

[1] Department of Chemistry, Faculty of Arts&Science, Giresun University, Giresun, Türkiye

[2] Department of Environmental Engineering, Faculty of Engineering, Giresun University, Giresun, Türkiye

**Received:** 04/05/2024, **Revised:** 28/06/2024, **Accepted:** 01/07/2024, **Published:** 31/08/2024

**Abstract**

In this study, 25,27-dihydroxy-26,28-bis(ethoxycarbonylbutyoxy)-5,11,17,23-p-tert-butylcalix[4]arene was used as an ionophore for the preparation of a novel all-solid-state type microsensor to make a selective potentiometric response towards Cu(II) ions. The optimum membrane composition of the microsensor was determined as 2% (w/w) ionophore, 67% (w/w) bis (2-ethylhexyl) sebacate (DOS), 30% (w/w) polyvinylchloride (PVC), and 1%(w/w) potassium tetrakis 4-chlorophenyl borate (KTpClPB). All-solid-state PVC-membrane Cu(II)-selective microsensor exhibited a highly selective Nernstian response of 31.3±2.1 mV slope ($R^2$= 0.997) with a short response time (<15 s) over the concentration range of $10^{-5}$ to $10^{-1}$ mol $L^{-1}$ of Cu(II) ions for 8 weeks with no significant difference in potentials. The microsensor was effectively performed in the pH range of 5.0–8.0, with a low detection limit of $7.67\times10^{-6}$ mol $L^{-1}$, and a temperature range of 15−40 °C. The prepared microsensor was successfully used both as an indicator electrode in the potentiometric titration of Cu(II) ions with EDTA and also in the determination of the Cu(II) content of environmental water samples. When the potentiometric results were compared with ICP-OES, they were found to be in good agreement with ICP-OES results at a 95% confidence level.

**Keywords:** Calixarene, all-solid-state, ion-selective sensor, copper, PVC membrane

# Yeni Tip Kaliks[4]aren Temelli Bütünüyle Katı-Hal PVC-Membran Cu(II)-Seçici Potansiyometrik Mikrosensör

**Öz**

Bu çalışmada, 25,27-dihidroksi-26,28-bis(etoksikarbonilbutyoksi)-5,11,17,23-p-tert-butilkaliks[4]aren bileşiği Cu(II) iyonlarına karşı seçici bir potansiyometrik yanıt elde etmek için bütünüyle katı hal kontak yeni tip mikrosensör hazırlanmasında iyonofor olarak kullanılmıştır. Mikrosensörün optimum membran bileşimi %2 (a/a) iyonofor, %67 (a/a) bis (2-etilheksil) sebakat (DOS), %30 (a/a) polivinilklorür (PVC) ve %67 (a/a) bis (2-etilheksil) sebakat (DOS) olarak belirlenmiştir. Bütünüyle katı-hal PVC-membran Cu(II)-seçici mikrosensör, 8 hafta boyunca potansiyellerde önemli bir fark olmadan Cu(II) iyonlarına $10^{-5}$ - $10^{-1}$mol $L^{-1}$ konsantrasyon aralığında kısa yanıt süresi (<15 s) ve 31,3±2,1 mV eğim ile ($R^2$= 0,997) oldukça seçici bir Nernst yanıtı sergilemiştir. Mikrosensör, $7.67\times10^{-6}$ mol $L^{-1}$ gibi düşük tayin sınırı, 15−40 °C sıcaklık ve pH 5,0–8,0 aralığında etkili bir performans sergilemiştir. Hazırlanan mikrosensör hem Cu(II) iyonlarının EDTA ile potansiyometrik titrasyonunda indikatör elektrot olarak hem de çevresel su örneklerinin Cu(II) içeriğinin belirlenmesinde başarıyla kullanılmıştır. Elde edilen potansiyometrik sonuçlar ICP-OES ile karşılaştırıldığında %95 güven düzeyinde iyi uyum içerisinde olduğu görülmüştür.

**Anahtar Kelimeler:** Kaliksaren, katı hal kontak, iyon seçici sensör, bakır, PVC membran

---

Corresponding Author: tmuratyolcu@yahoo.com
Cigdem CAY, https://orcid.org/0000-0001-7585-6119
Murat YOLCU, https://orcid.org/0000-0003-3477-3792
Serkan SAYIN, https://orcid.org/0000-0003-0518-3208

## 1. Introduction

Potentiometry based on ion-selective electrodes (ISEs), which are one of the electroanalytical methods that have attracted the increasing attention of researchers for a long time due to their advantages such as rapid response, broad dynamic range, low detection limit, procedure, cost-effectiveness, simple instrumentation, preparation, and reasonable selectivity [1, 2]. Potentiometry-based sensors are preferred in many different fields such as determining the qualitative and quantitative analyses of various inorganic and organic ions, medical drug analyses, industrial analyses, environmental monitoring and routine laboratory analyses [3]. Chemical or ion sensors are widely used in sample analysis because they provide rapid results and are suitable for all minimum concentrations and on-line monitoring without requiring any sample pre-treatment [4-6]. Calixarenes, considered third-generation supramolecules, have been used as receptors to identify various ions due to their remarkable ability to construct host-guest type complexes [7, 8]. Besides, their easy synthesis and tailor made functionalization have attracted an intense interest of chemists. In this sense, so far calixarenes have been successfully used effective ionophores for many kinds of guest such as metal cations, anions and neutral molecules [9-11]. Additionally, calixarenes have electron-rich internal cavities and can form complexes with metal ions of compatible sizes through dipole-dipole interaction. Electrochemical techniques have gained much attention recently established the use of calixarenes for heavy metal identification in the field of electroanalysis in the late 80s, especially for the development of ion-selective electrodes. The use of calixarenes in electrodes was expanded to various electrodes using various electroanalytical techniques in the following years. Calixarene derivatives have unique properties in material chemistry [4, 12].

Copper is an element that is quite common in nature, both in metallic form and in various ores and minerals. It can also be found as both complex and solid particles in various types of water, such as groundwater, surface water, seawater, and drinking water [13]. Foods such as seafood and offal, mushrooms, grains and nuts can be listed to meet the need for copper in the human diet. Besides, in addition to these nutrients, a large portion of copper (about 25%) is provided to the human body from drinking water. Copper is a micronutrient essential for the proper functioning of living organisms, but in excess amounts it is toxic and hazardous to health. At the same time, the copper element takes part in many physiological processes, is involved in the synthesis of neuropeptides, has an immunological function and is a cofactor of many redox enzymes. While copper deficiency causes disorders in the functioning of the circulatory system and central nervous system, its excess can cause dysfunctions in the functioning of the internal organs and digestive system, as well as many side effects such as dizziness, nausea, muscle and abdominal pain [14, 15].

Due to the toxic effects of copper element on human and environmental health, it is very important to determine it in different samples. Different analytical methods can be used to determine Cu(II) ion concentration levels, such as inductively coupled plasma optical emission spectroscopy, inductively coupled plasma mass spectroscopy, high-performance liquid chromatography, atomic absorption spectrometry, and anodic stripping voltammetry [16-18]. Listed analytical methods; It cannot be preferred in routine analyzes due to its high costs, requiring sample pre-treatment and trained personnel, and high energy and time consumption [19-21].

In the present study, a novel potentiometric Cu(II)-selective microsensor, that is an all-solid-state PVC-membrane type, was designed using calix[4]arene derivative as an ionophore. The performance characteristics such as limit of detection, linearity, slope with standard deviation, response time, selectivity, repeatability, reproducibility, pH, temperature ranges of the microsensor were investigated in detail. The microsensor was successfully used for Cu(II) contents of some environmental water samples. The potentiometric results were compared with ICP-OES and it was seen that the results were in good harmony with the ICP-OES results at a confidence level of 95%.

## 2. Experimental

### 2.1. Chemicals

Tetrahydrofuran (THF), high molecular weight polyvinylchloride (PVC), o-nitrophenyl octyl ether (NPOE), bis(2-ethylhexyl) sebacate (DOS), dibutyl sebacate (DBS), potassium tetrakis (4-chlorophenyl) borate (KTpClPB), disodium ethylenediaminetetraacetate dihydrate (EDTA-$Na_2$), graphite, solvents, and all other salts were purchased from Sigma-Aldrich and used without further purification. Ultrapure SU 2227 as an epoxy resin and Desmodur RFE as a hardener were obtained from Victor and Bayer AG, respectively.

### 2.2. Apparatus

Potential measurements were made using a computer-programmed and multi-channel potentiometric system. A silver/silver chloride electrode (Basi-MF-2079-RE-5B) was used as a reference electrode for potential measurements. Shimadzu (Model AUX220) analytical scale was used in weighing operations. The pH values of the solutions were adjusted by using a Jenway 3040 model Ion Analyser. Deionized water was obtained from Sartorius Stedim (Arium*611UV) deionized water (18.6 MΩ) deionization system. Shimadzu (Model AUX220) analytical scale was used in weighing operations. Metformin molecules were removal from the polymer using a Memmer (GmbH + Co. KG D.91126 Typ: WNB 14) shaker. Weighing operations were performed using an analytical balance from Shimadzu (model AUX220). a Hitachi SU 1510 model instrument was used for Scanning Electron Microscopy (SEM) analysis. Spectro Blue II model instrument was used Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) analysis. All solutions were prepared using ultra-pure water from a Milli-Q (Millipore Corp.).

### 2.3. Synthesis of the Calixarene-based ionophore

The calixarene-based ionophore (25,27-dihydroxy-26,28-bis(ethoxycarbonylbutyoxy)-5,11,17,23-*p-tert*-butylcalix[4]arene (**2**)) shown in Figure 1 was synthesized according to the literature procedures [11].

Yield; 44%, mp: 177-180 °C. $^1$H-NMR (400 MHz, $CDCl_3$): δ(ppm) 7.49 (s, 2H, -OH), 7.04 (s, 4H, ArH), 6.80 (s, 4H, ArH), 4.26 (d, 4H, $J = 12.8$ Hz, Ar-$CH_2$-Ar), 4.15 (q, 4H, $J = 7.2$ Hz, -$OCH_2$), 3.99 (t, 4H, $J = 5.6$ Hz, -$OCH_2$), 3.30 (d, 4H, $J = 12.8$ Hz, Ar-$CH_2$-Ar), 2.48 (t, 4H, $J = 6.8$ Hz, -$CH_2$), 2.06-2.0 (m, 8H, -$CH_2$-), 1.28 (s, 18H, $Bu^t$), 1.26 (t, 6H, $J = 6.8$ Hz, -$CH_3$), 0.97 (s, 18H, $Bu^t$); $^{13}$C-NMR (100 MHz, $CDCl_3$): δ(ppm) 173.65 (C=O), 150.94, 150.10, 147.00, 141.58, 132.85, 127.97, 125.69, 125.26, 76.07, 60.49, 34.16, 34.03, 31.93, 31.26, 29.60, 21.75, 14.45.

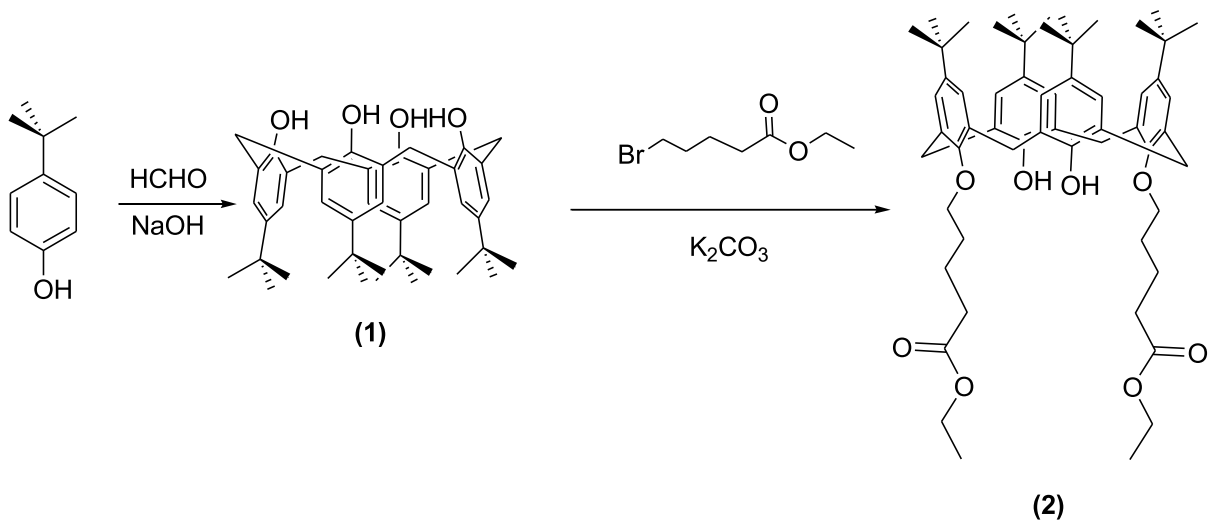

**Figure 1.** Synthesis scheme of 25,27- dihydroxy -26,28-bis(ethoxycarbonylbutyl-4-yl-oxy)-5,11,17,23-*p-ter*-butylcalix[4]arene

## 2.4. Fabrication of Cu(II)-Selective Microsensor

The Cu(II)-selective microsensor used in the study was produced according to the procedures described in our previous studies [22]. The microsensor was generally manufactured in two steps. In the first stage, a mixture of solid contacts consisting of 50% (w/w) graphite, 35% (w/w) epoxy and 15% (w/w) hardener in THF was prepared. Then a copper wire with a length of 10 mm and a radius of approximately 0.2 mm was dipped into the prepared solid contact mixture several times until a coating thickness of approximately 0.5 mm was obtained, and then the copper wire was left at room temperature for one day. In the second stage, ion selective membrane cocktail consisting of 2-4% (w/w) ionophore (dispersed in the cocktail), 28-30% (w/w) PVC, 1% (w/w) KTpClPB, and 67-69% (w/w) plasticizer (NPOE, DOS or DBS) was prepared in 2.5 mL THF. The surface of the solid contacts obtained in the first step was coated with this cocktail three or four times and then covered with an ion-selective membrane. The microsensor was left to dry for one day under laboratory conditions. Finally, the dried membrane sensor was soaked in $10^{-2}$ mol.L$^{-1}$ $Cu(NO_3)_2$ solution for at least 12 hours for conditioning purposes before use in measurements.

## 3. Results and Discussions

In order to test the potentiometric properties of the Cu(II)-selective microsensor; parameters such as calibration curve, linear working range, detection limit, repeatability, pH range, response time, selectivity and ratio of membrane components were studied. For this purpose, different PVC-membrane mixtures were prepared and their potentiometric properties were tested according to IUPAC recommendations [23].

### 3.1. Membrane Composition

Ionophore, plasticizer and polymer types and amounts are important parameters that affect the performance of the potentiometric sensor. Therefore, the effects of the ion-selective membrane composition, which significantly affects the sensitivity and selectivity of the sensor, the nature and amount of the plasticizer, and the amount of the lipophilic additive (KTpClPB), on the potential performances of Cu(II)-selective microsensor were investigated in detail. The results are shown in Table 1. Plasticizers containing NPOE, DOS and DBS, which are common PVC membrane solvents, were also examined. Membrane No-I prepared based on DOS plasticizer exhibited better potentiometric properties in terms of linear range and detection limit compared to other.

**Table 1.** Potentiometric performance characteristics of Cu(II)-selective microsensor

| No | Composition of Membrane (% w/w) | | | | | | Potentiometric Properties | | |
|---|---|---|---|---|---|---|---|---|---|
| | PVC | NPOE | DOS | DBS | KTClPB | Ionophore | Slope (mV/decade) | Linear range ($mol.L^{-1}$) | Detection limit ($mol.L^{-1}$) |
| I | 30 | 67 | - | - | 1 | 2 | 26.9±1.8 | $10^{-5}$-$10^{-1}$ | $5.7x10^{-5}$ |
| II | 30 | - | 67 | - | 1 | 2 | 31.3±2.1 | $10^{-5}$-$10^{-1}$ | $7.6x10^{-6}$ |
| III | 30 | - | - | 67 | 1 | 2 | 27.4±1.7 | $10^{-5}$-$10^{-1}$ | $6.3x10^{-5}$ |
| IV | 28 | 67 | - | - | 1 | 4 | 27.3±1.6 | $10^{-5}$-$10^{-1}$ | $8.5x10^{-5}$ |
| V | 28 | - | 67 | - | 1 | 4 | 26.5±2.2 | $10^{-6}$-$10^{-1}$ | $3.4x10^{-6}$ |
| VI | 28 | - | - | 67 | 1 | 4 | 25.9±1.0 | $10^{-5}$-$10^{-1}$ | $6.6x10^{-5}$ |
| VII | 27 | 69 | - | - | - | 2 | 25.7±2.8 | $10^{-5}$-$10^{-1}$ | $4.5x10^{-5}$ |
| VIII | 27 | - | 69 | - | - | 2 | 29.4±2.0 | $10^{-5}$-$10^{-1}$ | $2.4x10^{-6}$ |
| IX | 27 | - | - | 69 | - | 2 | 27.2±1.2 | $10^{-5}$-$10^{-1}$ | $3.9x10^{-5}$ |

The potentiometric response of the prepared microsensor was monitored as a function of Cu(II) concentration in the range $10^{-8}$ to $10^{-1}$ $mol.L^{-1}$. The dynamic potentiometric response of the sensor and calibration curve are shown in Figure 2 and 3, respectively. As can be seen from Figures, the microsensor shows a super-Nernstian behavior with a slope of 31.3±2.1 mV mV/decade ($R^2$= 0.997) over a linear concentration range of $10^{-5}$–$10^{-1}$ $mol.L^{-1}$, a lower detection limit of $7.67x10^{-6}$ $mol.L^{-1}$ and a short response time ($t_{95}$) of <15 s.

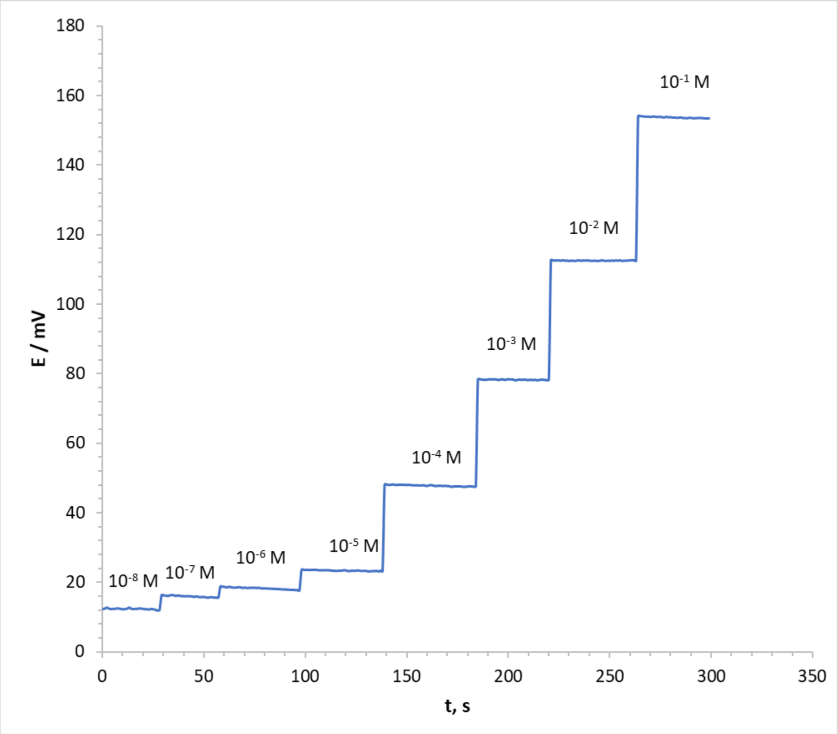

**Figure 2.** Dynamic potentiometric response of the Cu(II)-selective microsensor

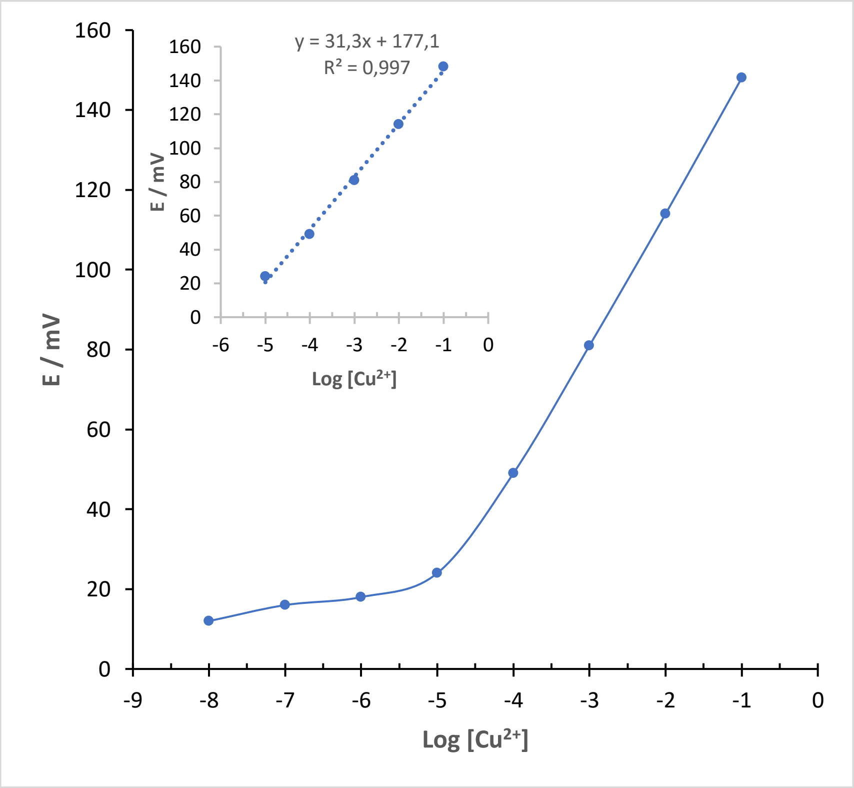

**Figure 3.** Calibration curves of the Cu(II)-selective microsensor

### 3.2. The Repeatability and Lifetime

In order to demonstrate the repeatability of the Cu(II)-selective microsensor, potential measurements were conducted in the Cu(II) solutions in the concentration range of $10^{-5}$–$10^{-1}$ mol.L$^{-1}$. The obtained real-time potential measurements depending on time are shown in Figure 4. As can be seen from Figure 4, the response of the sensor is highly repeatible in the concentration range of $10^{-5}$–$10^{-1}$ mol.L$^{-1}$ ( the average values ± standard deviations are 21.63±1.69, 49.53±1.73, 81.17±1.44, 112.89±1.25, 148.61±1.14). The potentiometric measurements in Figure 4 shows that the newly developed microsensor had good potentiometric repeatability and stability. The proposed sensor can also be used for 8 weeks without any significant drift in potential.

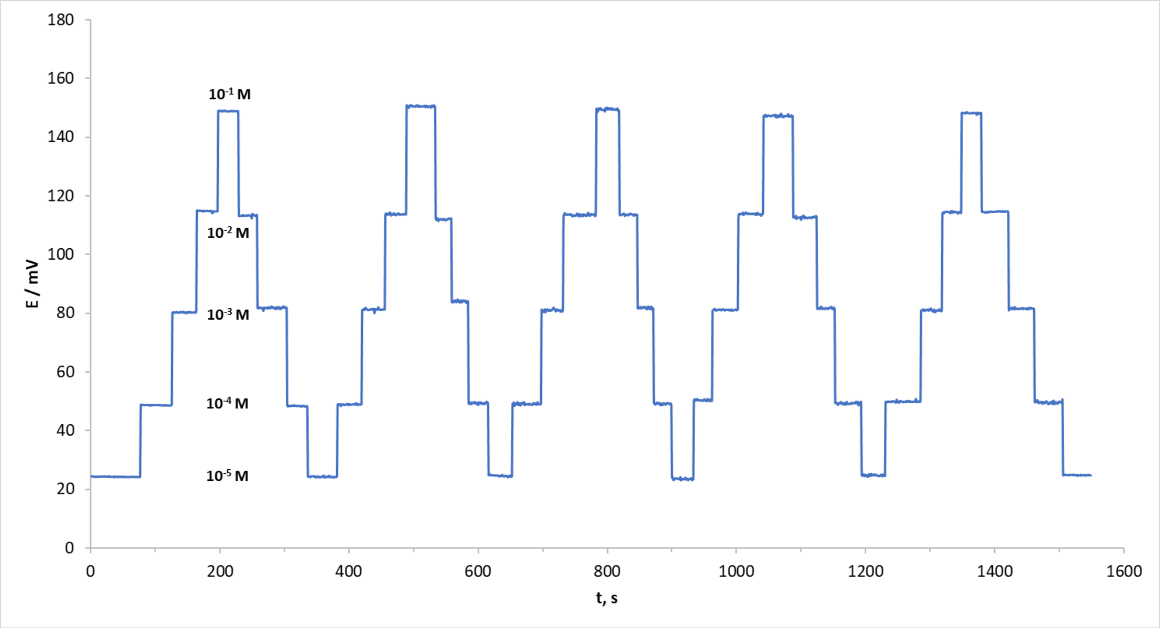

**Figure 4.** Repeatability measurements of the Cu(II)-selective microsensor

Measurements were performed to determine the lifetime of the Cu(II)-selective microsensor on certain days for 70 days in the range of $10^{-5}$ to $10^{-1}$ mol.L$^{-1}$ $Cu^{2+}$ and the changes in the slope values were examined. The obtained slope values are shown in Figure 5. It is seen that the stability of the microsensor deteriorates significantly after 60 days. The lifetime of the microsensor was calculated to be around 8 weeks as a result.

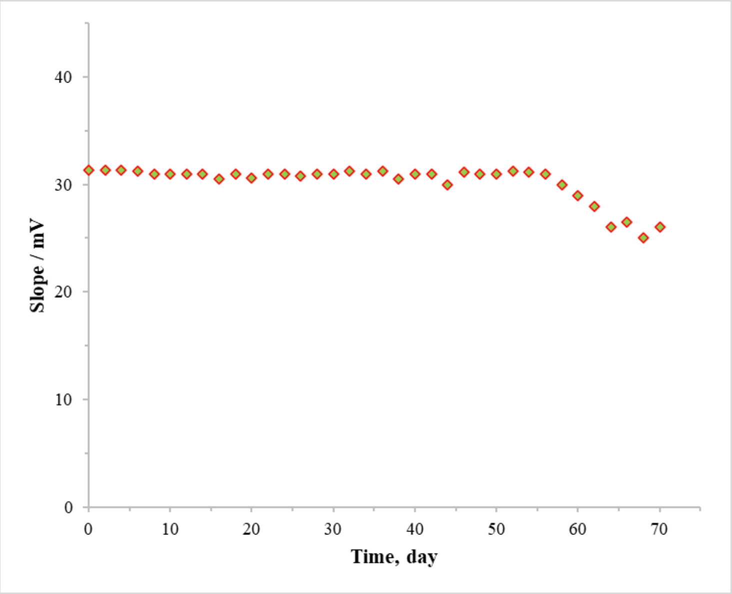

**Figure 5.** The lifetime graph of the Cu(II)-selective sensor

### 3.3. Selectivity

The most important property that affects the performance of an ion-selective electrode is selectivity and determines whether the sensor can be used in sample solution containing other ions. The selectivity coefficients of the Cu(II)-selective microsensor were calculated using the seperate solution method (SSM) [23]. The logarithmic selectivity coefficients obtained for Cu(II) ions compared to other cations ($X^{n+}$) are summarized in Table 2. The prepared microsensor was tested against cationic species commonly encountered in samples and exhibited high selectivity for Cu(II) ions.

**Table 2.** Selectivity coefficients for Cu(II)-selective microsensor

| Interferent | Log $K^{\mathrm{pot}}_{\mathrm{Cu^{2+},\,X^{n+}}}$ | Interferent | Log $K^{\mathrm{pot}}_{\mathrm{Cu^{2+},\,X^{n+}}}$ |
|---|---|---|---|
| $Li^+$ | -3.83 | $Na^+$ | -3.34 |
| $K^+$ | -2.38 | $Ca^{2+}$ | -3.17 |
| $Mg^{2+}$ | -3.14 | $Mn^{2+}$ | -2.70 |
| $Zn^{2+}$ | -2.89 | $Ni^{2+}$ | -2.75 |
| $Cd^{2+}$ | -2.62 | $Co^{2+}$ | -2.68 |
| $Cr^{3+}$ | -2.80 | $Pb^{2+}$ | -2.01 |

### 3.4. Effect of pH

One of the parameters that affects the properties of the microsensor is pH. To examine the effect of pH on the sensor response, the sensor potentials were measured over the pH range 2.0–10.0 (adjusted with $HNO_3$ and NaOH) for $10^{-3}$ and $10^{-2}$ mol.L$^{-1}$ Cu(II) solution. The results obtained are given in Figure 6. As can be seen from Figure 6, the potential of the microsensor remained unchanged between pH 5.0–8.0. The potential value varies significantly between pH 2.0 and

5.0. The change of potential in this range can be explained as the response of the sensor to hydronium ions in the membrane phase. When pH was increased above 8, an increase in potential was observed due to the formation of hydroxide complexes of Cu(II) in the basic solution.

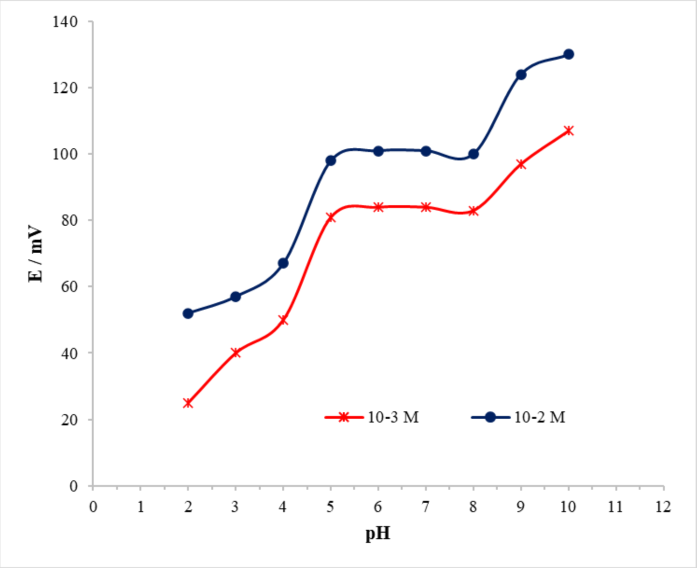

**Figure 6.** pH-mV graphic of the Cu(II)-selective microsensor

### 3.5. Temperature Effect

Temperature is among the other important features of ion-selective electrodes. For this purpose, in order to determine the optimum temperature range of the Cu(II)-selective microsensor, it was changed from 5 °C to 70 °C in $10^{-2}$ mol.L$^{-1}$ Cu$^{2+}$ solution and the potential values obtained against temperature are shown in Figure 7.

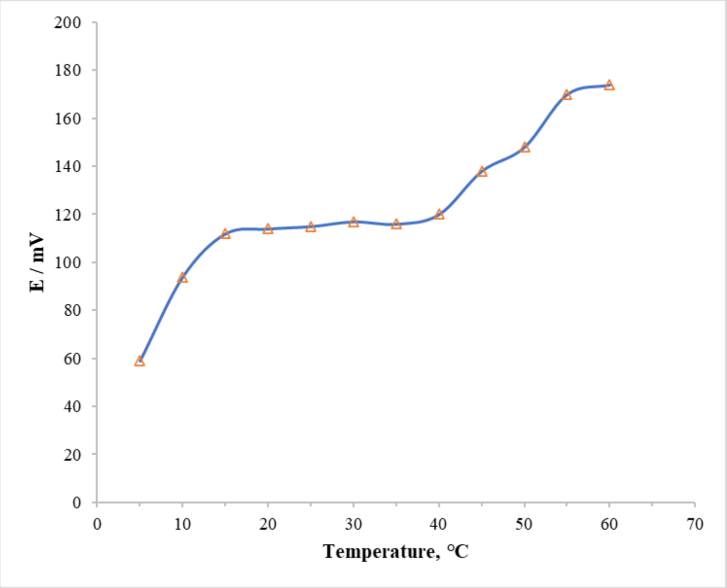

**Figure 7.** Temperature effect on the Cu(II)-selective microsensor performance

It is seen that there is no significant change in the potential values of the Cu(II)-selective microsensor at approximately 15-40 °C. It has been determined that the sensor is affected by temperatures above 40 °C and is also deformed. As a result, it can be said that the optimum temperature range of the sensor is 15-40 °C.

## 3.6. Analytical Applications

### 3.6.1. Potentiometric Titration

It has been observed that Cu(II)-selective microsensor prepared in optimum membrane composition works well under laboratory conditions. To display the applicability of the proposed microsensor in the real samples, the sensor was used as an indicator electrode in the potentiometric titration of 10 mL of $10^{-3}$ M $Cu(NO_3)_2$ with $10^{-3}$ M EDTA solution (pH=5.5). A typical titration curve is shown in Figure 8. As seen from Figure, the end point of titration (9.5±0.3 mL) can be accurately determined by the sensor.

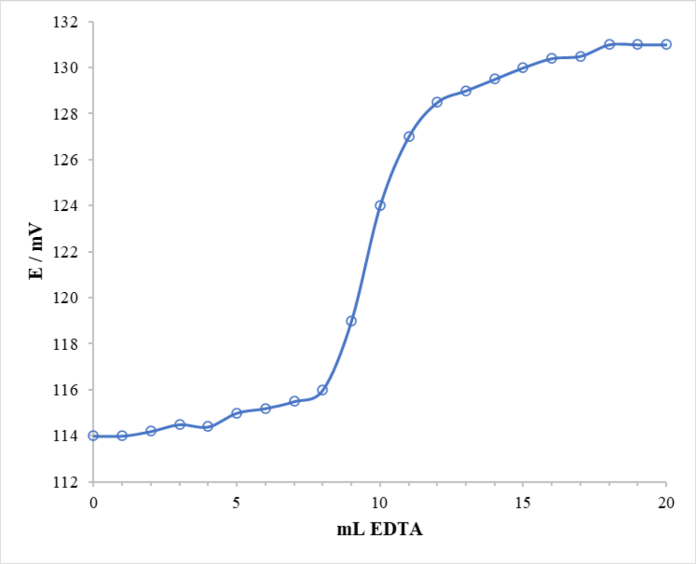

**Figure 8.** Titration curve of 10 mL $10^{-3}$ mol.L$^{-1}$ $Cu^{2+}$ with $10^{-3}$ mol.L$^{-1}$ EDTA

### 3.6.2. Real Sample Analysis

The prepared Cu(II)-selective microsensor was also applied to some environmental water samples (collected from Giresun Region on the north coast of Turkey) and for potentiometric determination of Cu(II) content in standard reference material (SRM) solution. The ICP-OES method was used as a reference method to evaluate the accuracy, precision and reliability of the results obtained in the accuracy of the potentiometric method. Before potential measurements, water samples were saturated (1:100) and the SRM solution was diluted (100:1). In order to analyze Cu(II) in these different real samples, the standard addition method was used and added $Cu^{2+}$ solutions at the different amounts as indicated in Table 3. Student's *t*-test and the relative error ($E_{ra}$) values were used for statistical processing of data. The calculated $t$ and $E_{ra}$ values are summarized in Table 3. As seen in Table 3, the developed Cu(II)–ISE displayed very high recovery rates in the analysis of Cu(II) in different real samples. The calculated *t* value (0.935) was less than the critical *t* value (3.182) at a 95% confidence level. Moreover, the $E_{ra}$ values were less than 15%. Thus, it can be concluded that the method applying the proposed microsensor is a satisfactory agreement compared with the ICP-MS method. As a result, it can be stated that the developed Cu(II)–selective sensor can be successfully used to determine Cu(II) ions in different real samples.

**Table 3.** Determination of $Cu^{2+}$ contents in water samples

| Sample | Concentration of $Cu^{2+}$ (ppm) * | | | |
|---|---|---|---|---|
| | Potentiometry | ICP-OES | $E_{ra}$ (%) | $t^{c}$ |
| Spring water | 0.018±0.005 | 0.016±0.001 | 12.5 | |
| River water | 0.146±0.034 | 0.132±0.005 | 10.6 | |
| Top water | 0.045±0.007 | 0.042±0.002 | 7.1 | 0.935 |
| Waste water | 0.623±0.092 | 0.594±0.012 | 4.9 | |
| SRM solution | 0.255±0.054 | 0.240±0.008 | 6.2 | |

[a] The average values of three determinations ± standard deviation.

[b] $E_{ra}$ is the relative error for the potentiometry versus ICP-OES.

[c] Calculated t value is 0.935 by a paired t test, the theoretical values of t is 3.182 (p=0.05).

### 3.6.3. Comparison of the Proposed Sensor with the other Cu(II)-selective Sensors

The comparison of the newly developed Cu(II)-selective microsensor with previously proposed Cu(II)-selective sensors or electrodes in the literature in terms of concentration range, detection limit, slope, pH operating range and response time parameters is summarized in Table 4.

**Table 4.** Comparation of the proposed sensor to the various reported Cu(II)-selective electrodes

| Referans | Linear Range, mol.L$^{-1}$ | Slope, mV/decade | Response Time, s | Detection Limit, mol.L$^{-1}$ | pH Range |
|---|---|---|---|---|---|
| [24] | $1.0x10^{-6}$-$1.0x10^{-1}$ | 29.60 | 8 | $8.75x10^{-7}$ | 5.0-9.0 |
| [25] | $1.0x10^{-5}$-$5.0x10^{-1}$ | 30.45 | - | $1.99x10^{-6}$ | 3.0-6.0 |
| [26] | $1.0x10^{-6}$-$1.0x10^{-1}$ | 28.50 | 20 | $4.0x10^{-7}$ | 4.0-7.0 |
| [27] | $1.0x10^{-5}$-$2.0x10^{-1}$ | 28.10 | 22 | $2.0x10^{-6}$ | 3.0-8.0 |
| [28] | $1.0x10^{-8}$-$1.0x10^{-1}$ | 29.50 | 15 | $5.0x10^{-6}$ | 3.5-6.5 |
| This work | $1.0x10^{-5}$-$1.0x10^{-1}$ | 31.30 | <15 | $7.6x10^{-6}$ | 5.0-8.0 |

As can be seen from the results in Table 4, it is concluded that the potentiometric properties of the fabricated sensor are comparable to previously reported electrodes in terms of the compared criteria. The concentration range and slope value are similar for all proposed sensors. The proposed Cu(II)-selective microsensor has a lower detection limit, a wider pH operating range, and relatively shorter response time compared to existing sensors in the literature. Thus, it can be clearly seen that the proposed Cu(II)-selective microsensor has some advantages over other previously developed Cu(II)-selective sensors or electrodes. The resulting Cu(II)-selective microsensor can be considered a good contribution to the list of Cu(II)-selective sensors available in the literature.

## 4. Conclusion

Calixarene derivatives have unique properties in material chemistry. For real application analysis, those with different functional moiety groups displayed excellent sensing behaviour towards heavy metal ions with good sensitivity, reproducibility, and repeatability. In addition, calixarene derivatives can be used directly as an ionophore in the construction of different chemical sensors, especially in that potentiometry-based ones. In the present work, a novel all-solid-state type PVC-membrane Cu(II)-selective microsensor has been developed a potentiometric sensor selective for Cu(II) ions using a calixarene derivative molecule as an ionophore. The produced Cu(II)-selective microsensor was successfully used as an indicator electrode for potentiometric titrations. The Cu(II)-selective micsensor was also successfully used for accurate, rapid, selective and reproducible determination of Cu(II) ions in environmental samples.

## Ethics in Publishing

There are no ethical issues regarding the publication of this study.

## Author Contributions

All authors contributed to the study’s conception and design. All authors read and approved the final manuscript. Cigdem Cay executed the experiments; Murat Yolcu carried out the manuscript writing, model validation and interpretation and corrections; Serkan Sayin synthesized the compound calixarene and interpretation and corrections.

## 5. References

[1] N. Dere, Z. Yolcu, M. Yolcu, A Novel Solid-State PVC-Membrane Potentiometric Dopamine-Selective Sensor Based on Molecular Imprinted Polymer, Acta Chim Slov, 69 (2022) 108-115.

[2] O. Özbek, Ö. Isildak, Potentiometric determination of copper(II) ions based on a porphyrin derivative, J Chin Chem Soc-Taip, 69 (2022) 1060-1069.

[3] M. Yolcu, N. Dere, A novel copper selective sensor based on ion imprinted 2-vinylpyridine polymer, Can J Chem, 96 (2018) 1027-1036.

[4] C.J. Mei, S.A.A. Ahmad, A review on the determination heavy metals ions using calixarene-based electrochemical sensors, Arab J Chem, 14 (2021).

[5] M.S. Engin, S. Sayin, S. Cay, E. Kir, T. Sardohan-Koseoglu, Preparation and characterisation of thiol functionalised-butylcalix[4]arene-embedded polymer inclusion membranes: performance and selectivity, Int J Environ an Ch, 99 (2019) 1103-1111.

[6] V.K. Gupta, S. Kumar, R. Singh, L.P. Singh, S.K. Shoora, B. Sethi, Cadmium (II) ion sensing through p-butyl calix[6]arene based potentiometric sensor, J Mol Liq, 195 (2014) 65-68.

[7] L.X. Chen, H.F. Ju, X.S. Zeng, X.W. He, Z.Z. Zhang, Silver ion-selective electrodes based on novel containing benzothiazolyl calix[4]arene, Anal Chim Acta, 437 (2001) 191-197.

[8] B. Sonmez, S. Sayin, E. E. Yalcinkaya, D. A. Seleci, H. B. Yildiz, D. O. Demirkol, S. Timur, Calixarene modified montmorillonite: a novel design for biosensing applications. RSC Adv., 2014, 4, 62895–62902

[9] H. E. K. Ertürün, A.D. Özel, S. Sayın, M. Yılmaz, E. Kılıç, Development of a pH sensing membrane electrode based on a new calix[4]arene derivative. Talanta132(2015)669–675.;

[10] S. Kucukkolbasi, S. Sayin, M. Yilmaz, Fabrication and Application of a New Modified Electrochemical Sensor Using Newly Synthesized Calixarene-Grafted Mwcnts for Simultaneous Determination of Cu(II) and Pb(II). Acta Chim. Slov. 2019, 66, 839–849.;

[11] S. Sayin, S. Cay, Novel An Efficient Fluorescent Probe Based on Calix[4]triazacrown-5 With Naphthalimide Group for Co2+, Cd2+ and Dopamine Detection. Journal of Fluorescence (2024) 34:729–741

[12] P. Kumar, All Solid State Nickel(II)-Selective Potentiometric Sensor Based on an Upper Rim Substituted Calixarene, Electroanal, 24 (2012) 2005-2012.

[13] C. Wardak, M. Grabarczyk, Analytical application of solid contact ion-selective electrodes for determination of copper and nitrate in various food products and drinking water, J Environ Sci Heal B, 51 (2016) 519-524.

[14] K. Pietrzak, C. Wardak, B. Cristóvao, Copper ion-selective electrodes based on newly synthesized salen-type Schiff bases and their complexes, Ionics, 28 (2022) 2423-2435.

[15] M. Bost, S. Houdart, M. Oberli, E. Kalonji, J.F. Huneau, I. Margaritis, Dietary copper and human health: Current evidence and unresolved issues, J Trace Elem Med Bio, 35 (2016) 107-115.

[16] C. Wardak, J. Lenik, Application of ionic liquid to the construction of Cu(II) ion-selective electrode with solid contact, Sensor Actuat B-Chem, 189 (2013) 52-59.

[17] V.K. Gupta, R. Prasad, A. Kumar, Preparation of ethambutol-copper(II) complex and fabrication of PVC based membrane potentiometric sensor for copper, Talanta, 60 (2003) 149-160.

[18] L.P. Singh, J.M. Bhatnagar, Copper(II) selective electrochemical sensor based on Schiff Base complexes, Talanta, 64 (2004) 313-319.

[19] C.D. Gutsche, K.C. Nam, Calixarenes .22. Synthesis, Properties, and Metal Complexation of Aminocalixarenes, J Am Chem Soc, 110 (1988) 6153-6162.

[20] K. Kurzatkowska, S. Sayin, M. Yilmaz, H. Radecka, J. Radecki, Calix[4]arene derivatives as dopamine hosts in electrochemical sensors, Sensor Actuat B-Chem, 218 (2015) 111-121.

[21] I. Bitter, A. Grün, G. Toth, B. Balazs, G. Horvath, L. Töke, Studies on CaIix(aza)crowus, II.I Synthesis of Novel Proximal Doubly Bridged CalixlrlJareaes by Intramolecular Ring Closure of syn l,3- and 1,2- ω- Chtoroalkylamides. Tetrahedron 54 (1998) 3857-3870.

[22] I. Isildak, M. Yolcu, O. Isildak, N. Demirel, G. Topal, H. Hosgoren, All-solid-state PVC membrane Ag-selective electrodes based on diaza-18-crown-6 compounds, Microchim Acta, 144 (2004) 177-181.

[23] P. R. Buck and E. Lindner, “Recommendations for Nomenclature of Ionselective Electrodes,” Pure and Applied Chemistry, 66-12 (1994) 2527-2536.

[24] O. Özbek, M.B. Gürdere, C. Berkel, Ö. Isildak, Electroanalytical Determination of Copper(II) Ions Using a Polymer Membrane Sensor, J Electrochem Sci Te, 14 (2023) 66-74.

[25] K. Udomphan, I. Sontawee, I. Dangsanga, 8-Hydroxyquinoline intercalated montmorillonite composite: characterization and application for copper ion determination as potentiometric electrode, J Solid State Electr, 27 (2023) 977-989.

[26] S. Kaur, J. Kaur, M. Rana, J. Sharma, I. Kaur, Salicylaldehyde based Schiff base: synthesis, characterisation and application for selective electrochemical detection of Cu in real samples, Int J Environ an Ch, (2023).

[27] M.A. Abu-Dalo, A.A. Salam, N.S. Nassory, Ion Imprinted Polymer Based Electrochemical Sensor for Environmental Monitoring of Copper(II), Int J Electrochem Sc, 10 (2015) 6780-6793.

[28] V.K. Gupta, L.P. Singh, R. Singh, N. Upadhyay, S.P. Kaur, B. Sethi, A novel copper (II) selective sensor based on Dimethyl 4, 4′ (o-phenylene) bis(3-thioallophanate) in PVC matrix, J Mol Liq, 174 (2012) 11-16.