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Nickel (II)-Selective PVC Membrane Potentiometric Electrode Using 1,4,8,12-Tetraazacyclopentadecane as Ionophore

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ABSTRACT

A potentiometric sensor based on 1,4,8,12-tetraazacyclopentadecane (ionophore) for the determination of Ni^{2+} ion has been developed. The optimum membrane contained 2.5% ionophore, 31.0% poly vinylchloride (PVC), 65.0% dibutyl phthalate (DBP) as a solvent mediator, and 0.5% potassium tetrakis p-chlorophenyl borate (KTPClPB), as a counter ion. The all solid-state contact PVC membrane Ni^{2+} -selective potentiometric membrane electrode exhibited high sensitivity and short response time. This sensor demonstrated a working concentration range of 1.0×10^{-1} – 1.0×10^{-5} mol L^{-1} , with a Nernstian behavior and a response time of 6–7 s. The detection limit of the Ni^{2+} -selective membrane electrode was about 2.8×10^{-5} mol L^{-1} . The PVC membrane Ni^{2+} -selective electrode demonstrated with a correlation coefficient $r^2=0.9563$ and usable within the pH range of 4–9, and the lifetime of the sensor was 5 weeks.

Keywords: Potentiometric sensor, PVC membrane, Nickel-selective

INTRODUCTION

Nickel is an element and can be found at low level in nature. Although it is essential to living organisms in small doses, it can be quite dangerous when the maximum tolerable amounts are exceeded [1-3]. Several methods such as flame photometry, atomic absorption spectrometry electro thermal atomization (AAS-ETA), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and atomic absorption spectrometry (AAS) can be used for determination of nickel. These methods generally require infrastructure backup and sample pretreatment; thus, are not very convenient for regular analysis of environmental samples [4-7]. Therefore, it is quite important to develop selective, portable and inexpensive diagnostic tools to determine nickel.

Potentiometric sensors have found widespread use for the direct determination of ionic species [1,8-14]. All solid-state contact PVC membrane sensors are simple, inexpensive, durable, capable of reliable response in a wide concentration range for a variety of both organic and inorganic ions and suitable for measurements in small volumes of sample or for the desired in vivo applications of ISEs that biomedical researchers have long awaited.

In this work, we developed an all solid-state contact PVC membrane Ni^{2+} selective potentiometric membrane electrode (ISE) based on 1,4,8,12-tetraazacyclopentadecane (Figure 1) as a suitable ionophore for Ni^{2+} determination [4-7]. The potentiometric performance of all solid-state contact PVC membrane nickel-selective potentiometric electrode (selectivity constant, liner working interval, response time, detection limit, repeatability, lifetime, and time dependent potential decay) was determined using computer controlled potentiometric measurement system in static conditions.

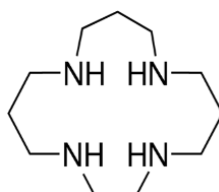


Figure 1: Structure of 1,4,8,12-tetraazacyclopentadecane

MATERIALS AND METHODS

Material

All of the reagents were used in this study were analytical reagent grade and double distilled deionized water. High molecular mass polyvinylchloride (PVC), dibütül ftalat (DBF), [Bis(2-etilhekzil)]sebakat (BEHS), o-nitrophenyloctylether (o-NPOE), potassium tetrakis (p-chlorophenyl) borate (KTPCIPB), tetrahydrofuran (THF) and graphite were obtained from Fluka. Epoxy resins (Macroplast Su 2227) and hardener (Desmodur RFE) was obtained from Henkel and Bayer respectively. Ni²⁺-selective ionophore (1,4,8,12- tetraazacyclopentadecane) was obtained from Merck.

Deionize water was obtained by means of a DI 800 Model deionize water system.

Ni²⁺ stock solution (1.0×10^{-1} mol L⁻¹) was prepared by using distilled deionize water. The stock solution was diluted gradually from 1.0×10^{-1} to 1.0×10^{-5} mol L⁻¹. All of the other used reagents were of analytical reagent grade. To increase the quality of water, deionize water was distilled twice throughout the study.

APPARATUS

Potentiometric measurements were conducted at room temperature ($20 \pm 1^\circ\text{C}$) by using a home-made multi-channel potentiometric system controlled by a computer. The potential values as steady-state responses of the PVC membrane Ni²⁺-selective electrode were performed for different concentrations of standard solutions of Ni²⁺ respectively. A micro-sized solid silver/silver chloride electrode (obtained from Isedo medical instruments, Turkey) was used as reference electrode with the Ni²⁺-selective membrane electrode throughout the measurements. Investigation of the potentiometric characteristics of the prepared Ni²⁺-selective membrane electrode was done by measuring the potential differences between two points which is the cause of electrical currents were taken in the following cell assembly:

Micro-sized solid silver/silver chloride reference electrode/test solution/Ni²⁺-selective membrane electrode/all solid-state contact material/Cu wire.

Method

The potentiometric all solid-state contact Ni²⁺-selective membrane electrodes was prepared as described previously [15]. The graphite was bound in epoxy resin mixture in the all solid-state contact of the electrode and a hardener in THF solvent was added in the proportion of 1.0:0.5 w/w. The 1.0:1.0 w/w ratio of powdered graphite to epoxy resin was used. Following obtaining the appropriate viscosity, a plastic covered copper wire was dipped into the mixture for several times to acquire solid-state contact uniformly coated and allowed to stand overnight in an oven at 40°C.

The Ni²⁺-selective membrane solution comprised ionophore (2.5%, w/w), plasticizer (65.0%, w/w), KTPCIPB (0.5%, w/w) and PVC (31.0%, w/w) was dissolved in 5.0 ml of THF. The solid-state contact was dipped into the Ni²⁺-selective membrane solution at least three times. The coated membrane was then left to dry in the air for at least 3 hr. Lastly, before use the prepared all solid-state contact PVC membrane Ni²⁺-selective electrode, it was soaked in a 0.01 mol L⁻¹ of Ni²⁺ standard solution for at least 3 hr.

RESULTS AND DISCUSSION

Potentiometric performance of the pvc membrane Ni²⁺-selective membrane electrode

It is well known that the sensitivity, limit of detection, selectivity, dynamic range, response time obtained for a given sensor depend significantly on the composition of the sensor. Potentiometric performance of the PVC membrane Ni²⁺-selective membrane electrode was evaluated to optimize membrane composition.

By performing the optimum conditions that was determined, calibration curve of the PVC membrane Ni²⁺-selective membrane electrode was obtained over Ni²⁺ concentration range of 10^{-1} to 10^{-5} mol L⁻¹. The response of the PVC membrane Ni²⁺-selective membrane electrode was highly reproducible as shown in Figure 2. The PVC membrane Ni²⁺-selective electrode exhibited a linear response, the graph of the linear response was defined by the equation of $y = -33.06x + 2667.9$ with a correlation coefficient $r^2 = 0.9563$. The PVC membrane Ni²⁺-selective membrane electrode reached to a steady-state rapidly and its detection limit was 2.87×10^{-5} mol L⁻¹.

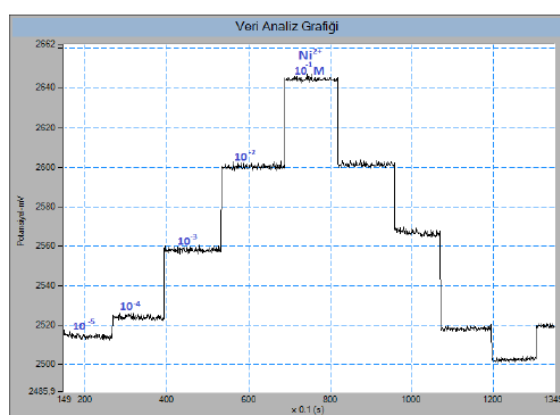


Figure 2: The potentiometric response to exhibits of Ni²⁺-selective membrane electrode against 1×10^{-1} - 5×10^{-5} mol L⁻¹ nickel concentration change

The response time of Ni²⁺-selective membrane electrode

The response time (t95%) was described by IUPAC as the time period for the presented potential of electrode to reach equilibrium with the sensible part of the membrane [16]. The Nickel concentration was rapidly increased from 10⁻⁵ to 10⁻¹ mol L⁻¹ and the t95% values were measured. The obtained response time was constantly less than 6 s.

The PH dependence of Ni²⁺-selective membrane electrode

The pH dependence of the electrode response was determined by using a solution with pH ranging from 2 to 12. The pH was adjusted with hydrochloric acid and sodium hydroxide. The Ni²⁺-selective membrane electrode showed a potential change against the nickel concentration of 10⁻³ mol L⁻¹ in acidic and basic mediums. The potential remained unaffected over a pH range 4–10.

The reusability of Ni²⁺-selective membrane electrode

The all solid state-contact PVC membrane Ni²⁺-selective membrane electrode showed that exhibit to results can be fairly repeatedly. Figure 3 depicts the reusability of Ni²⁺-selective membrane electrode in 10⁻², 10⁻³, and 10⁻⁴ M Ni²⁺ concentrations.

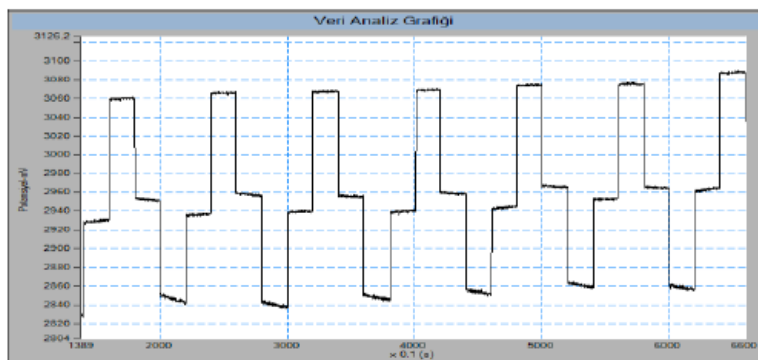


Figure 3: The reusability of Ni²⁺- selective membrane electrode

The potentiometric selectivity of Ni²⁺-selective membrane electrode

Ni²⁺-selective membrane electrode demonstrated a high potential disparity for Ni²⁺ as compared to the other metal ions which have electrode selectivity towards Ni²⁺ ions (Figure 4). The potentiometric selectivity coefficients of all solid-state copper sensor were assessed by the separate solutions method based on the IUPAC suggestion [17,18]. The selectivity coefficients calculated are given in Table 1.

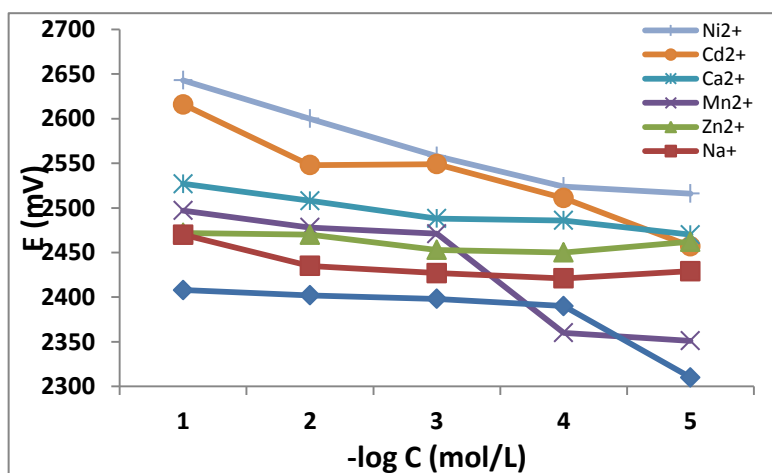


Figure 4: The potentiometric response to exhibits Ni²⁺-selective membrane electrode against interfering ions

Table 1: The selectivity coefficients of Ni²⁺-selective membrane electrode

Interfering	Na ⁺	K ⁺	Ca ²⁺	Cd ²⁺	Mn ²⁺	Zn ²⁺
(Log k ^{pot} _{Nickel,interfering})	-2.47	-2.54	-4.28	-3.541	-6.314	-4.836
(k ^{pot} _{Nickel,interfering})	3.38 × 10 ⁻³	2.88 × 10 ⁻³	5.24 × 10 ⁻⁵	2.87 × 10 ⁻⁴	4.85 × 10 ⁻⁷	1.46 × 10 ⁻⁵

The lifetime of Ni²⁺-selective membrane electrode

To investigate long term storage stability of Ni²⁺-selective membrane electrode, kept in dry at 4-6°C, the calibration curve was measured every day and the potentials were calculated. The sensor showed good storage stability for at least two month to standard Ni²⁺ concentration change.

CONCLUSION

All-solid-state Ni²⁺-selective potentiometric PVC membrane electrode based on 1,4,8,12-tetraazacyclotetradecane is developed for fast and simple analysis of nickel. The Ni²⁺-selective membrane electrode prepared with plasticizers and polyvinyl chlorate exhibited linear response over a wider concentration range with a Nernstian behavior, fast response time and selectivity over a large number of metal ions. Furthermore, Ni²⁺-selective membrane electrode could easily be prepared economically. The membrane is mechanically and chemically stable.

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