

A novel polymeric membrane electrode for the potentiometric analysis of Cu^{2+} in drinking water

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Abstract

Based on a novel ionophore, an ion-selective electrode has been developed for the determination of Cu^{2+} in drinking water. Its selectivity behavior is characterized and its lower detection limit optimized for measurements with different electrolyte backgrounds. The lower detection limit was $2 \times 10^{-9} \text{ M Cu}^{2+}$ for samples with low ionic background and $1 \times 10^{-7} \text{ M Cu}^{2+}$ with ionic background typically found in drinking water. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

Based on recent improvements of the lower detection limits [1–4] and selectivities [3,5], ion-selective electrodes (ISEs) with liquid [3–6] or solid internal contact [7–9] have become attractive tools for trace metal analyses. For example, detection limits in the subnanomolar (i.e. in the low ppt) range have been reported, among others, for Pb^{2+} [1,10], Cd^{2+} [11], and Ag^+ [12]. For practical purposes, the detection limit of the applied method should be 10 times lower than the legally allowed value. In the case of Pb^{2+} , it has been demonstrated that the performance of ISEs satisfies this requirement [10]. The values obtained with various drinking water samples have been validated by ICP-MS measurements [10].

The goal of the present contribution is to develop an ISE for monitoring Cu^{2+} in drinking water. Although Cu is an

essential element with a recommended daily intake of ca. 2 mg and is toxic only at high doses of $>15 \text{ mg day}^{-1}$, because of taste and corrosion effects, the allowed limit of Cu^{2+} is set to 1.3 mg L^{-1} ($2.05 \times 10^{-5} \text{ M}$) in the USA [13] similar to that in Canada (1.0 mg L^{-1} , [14]) and the European Union (2 mg L^{-1} [15]). The required lower detection limit of a Cu^{2+} -ISE is, therefore, ca. $2 \times 10^{-6} \text{ M}$. Compared with the above-mentioned performance of ISEs, this does not seem too demanding. Since, however, it must be achieved in the presence of relatively high concentrations of interfering cations, zero-current ion fluxes at this concentration are expected to influence the response function [12].

A series of Cu^{2+} -ISEs have been described in the literature [16–22]. The reported selectivities and lower detection limit of the ISE based on tetrabutyl thiuram disulfide in a PVC membrane without added lipophilic anionic sites [18] would be sufficient for determining Cu^{2+} concentrations in drinking water. However, during preliminary tests with added anionic sites, we have observed that these membranes blacken within 1 day indicating a chemical decomposition of the ionophore. Although no selectivity data are available for alkali and alka-

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line earth metal ions, diphenylthiocarbazone also seemed to be a promising Cu^{2+} ionophore [19]. However, its relatively low lipophilicity gave ISE membranes of short lifetime. The lower detection limit of a lariat crown ether-based Cu^{2+} -ISE is $>10^{-5}$ M and, thus, insufficient [21]. Again, no selectivity values are reported for alkali and alkaline earth metal ions, but the crown ether is likely not to discriminate these ions. Calixazacrown ether-based ISEs have an insufficient lower detection limit too [20] and no selectivity data are given for alkaline earth metal ions, the most important interfering species with potentiometric measurements in drinking water. The corresponding data are also missing for the ISEs based on hydrotris(3-isopropylpyrazolyl)methane [22]. As an additional problem in several cases, the selectivities were only determined with the matched potential method [21,22], and, therefore, are characteristic of the ISE's performance only under the particular conditions applied [23,24].

Commercially available solid-state Cu^{2+} -ISEs based on jalpait (coprecipitated $\text{CuS}/\text{Ag}_2\text{S}$) membranes have been applied already more than 30 years ago for determining Cu^{2+} in drinking water [25] and seawater [26]. Problems due to impurities in this sensing membrane [27] have been reduced quite recently by careful membrane preparation and the use of rotating electrodes [28]. Thus, a lower detection limit in the nanomolar range has been achieved [28].

In this work, we describe a polymeric membrane ISE based on a novel ionophore. Its selectivity behavior is characterized and the internal solution and the membrane composition is optimized in view of obtaining an optimal lower detection limit for monitoring Cu^{2+} in drinking water samples.

2. Experimental

2.1. Reagents

Poly(vinyl chloride) (PVC), 2-nitrophenyl octyl ether (*o*-NPOE), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) and tetrahydrofuran (THF, puriss. p.a.) were Selectophore, tetraethylammonium nitrate (Et_4NNO_3), and the other salts were puriss. p.a., all from Fluka (CH-9471 Buchs, Switzerland); NaOH and HNO_3 solutions were Titrisol[®] from Merck (Darmstadt, Germany). Dicyclohexylamine and 3-thiaglutamic acid were also from Fluka. Aqueous solutions were prepared with freshly deionized water (specific resistance, $18 \text{ M}\Omega \text{ cm}$) from a NANOpure[®] reagent grade water system (Barnstead, CH-4009 Basel, Switzerland).

2.2. Synthesis of *N,N,N'*-tetracyclohexyl-3-thiaglutamic diamide (cf. Fig. 1)

To the stirred biphasic mixture of dicyclohexylamine (1.81 g, 10 mmol) dissolved in CH_2Cl_2 (20 ml) and 20% aqueous Na_2CO_3 (10 ml), 3-thiaglutamic acid dichloride

(0.95 g, 5 mmol; obtained according to Ref. [29]) in CH_2Cl_2 (10 ml) was added dropwise under ice-cooling ($5\text{--}10^\circ\text{C}$). After the reaction was completed (2 h, RT), the organic phase was separated, washed with dilute aq. HCl and water and dried (Na_2SO_4). The organic solvent was then removed under reduced pressure and the solid residue was recrystallized from EtOH to give white crystals (1.2 g, 55%; mp $205\text{--}207^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3): $\delta = 3.48$ (s, br, 6H, CH_2S and 2 CH), 2.95 br, 2.45 br, and 1–1.9 m (total of 42 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 58.8$ (CHN), 56.2 (CHN), 36.7 (CH_2S), 31.4, 29.9, 26.6, 25.9, 25.4, 25.3 (ring CH_2). IR (cm^{-1} , CHCl_3): 3000 (m), 2940 (s) 2850 (m), 1630 (s). MS (MALDI): 499 ($M+\text{Na}$)⁺, 477 ($M+\text{H}$)⁺, 296 ($M-N(\text{cyclohexyl})_2$)⁺. Elemental analysis, calc.: C, 70.54%; H, 10.15%; N, 5.77%; found: C, 70.36%; H, 10.08%; N, 5.77%.

2.3. ISE membranes and electrodes

Two kinds of membranes were used, one of conventional composition and a harder one with higher PVC content. The conventional membranes (Conv) contained ionophore (0.47 wt.%, 9.8 mmol/kg), NaTFPB (0.43 wt.%, 4.9 mmol/kg), *o*-NPOE (65.9 wt.%), and PVC (33.2 wt.%). The harder membranes contained ionophore (0.53 wt.%, 11.1 mmol/kg), NaTFPB (0.43 wt.%, 4.9 mmol/kg), *o*-NPOE (55.6 wt.%), and PVC (43.3 wt.%). The membrane components (totaling 260 mg) were dissolved in THF (2.0 ml) during ca. 2 h and poured into a glass ring (37 mm i.d.) fixed on a glass plate and covered with another glass plate. After overnight evaporation of the solvent at RT, disks of 5 mm in diameter were punched from the master membrane (thickness, ca. 200 μm) and glued with a PVC/THF slurry to a plasticized PVC tubing mechanically fixed onto a 1000 μl pipette tip. The inner filling solutions were Et_4NNO_3 and $\text{Cu}(\text{NO}_3)_2$ of different concentrations (see Table 1). The Ag/AgCl inner reference electrode in 10^{-2} M NaCl electrolyte was separated from the internal solutions by a diaphragm.

2.4. EMF measurements

Measurements were performed with a 16-channel electrode monitor (Lawson Labs Inc., Malvern, Pa. 19355,

Table 1
Internal solutions with 10^{-4} M $\text{Cu}(\text{NO}_3)_2$ and different concentrations of Et_4NNO_3 used in the different Cu^{2+} -ISEs

ISE	Et_4NNO_3 (M)	Cu^{2+} replaced by Et_4N^+ in the inner surface layer of the membrane (%)
Conv 1	1.9×10^{-4}	28.6
Conv 2	3.5×10^{-4}	46.0
Conv 3	1.7×10^{-3}	91.3
Conv 4	2.3×10^{-4}	33.5
Hard 1	3.5×10^{-4}	33.1
Hard 2	2.0×10^{-2}	99.9
Hard 3	1.7×10^{-3}	82.8

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