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LIQUID MEMBRANE ION-SELECTIVE ELECTRODES FOR POTENTIOMETRIC DOSAGE OF SOME METAL IONS

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ABSTRACT

Four electrodes with liquid membrane, Cu^{2+} selective and Ni^{2+} selective, not described previously in the literature, were prepared and characterized. From these electrodes, 1 and 2 are based on simple complexes of Cu(II) and Ni(II) with 2,3-dithio-6-nitro-benzoquinoxaline-5,10-dione (dtnbqd), as ligand belonging to the dithiol class. Electrodes 3 and 4 are based on the corresponding mixed complexes in which the ammonia molecule acts as the second ligand and 2,3-dithio-6-nitro-benzoquinoxaline-5,10-dione as the first ligand.

KEYWORDS *copper, nickel, liquid-membrane electrodes, potentiometry, selectivity.*

RESUMO

Foram preparados e caracterizados quatro eletrodos novos com membrana líquida seletivos para Cu^{++} e Ni^{++}. Os eletrodos 1 e 2 foram baseados em complexos simples de Cu(II) e Ni(II) com 2,3-ditio-6-nitro-benzoquinoxalina-5,10-diona (dtnbqd), um ligante da classe do ditiol. Os eletrodos 3 e 4 foram baseados nos complexos mistos correspondentes, onde uma molécula de amonia age como o segundo ligante e 2,3-ditio-6-nitro-benzoquinoxalina-5,10-diona age como o primeiro ligante.

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INTRODUCTION

During the past years, ion-selective electrodes for a large series of cations and anions and their use in solving various analytical problems, in industrial processes, the automated control of environmental pollution, biochemistry etc., have been described in the literature[1-6].

This study is a continuation of our previous work described in earlier papers[7-12] and presents the possibility of obtaining Cu^{2+} and Ni^{2+} selective electrodes with a liquid membrane. These electrodes are based on complex combinations of Cu(II) and Ni(II), extractable in organic solvents, non-miscible in water.

The response of these electrodes to the concentration of Cu^{2+} (Ni^{2+}) in solution has been formally attributed to a process of exchange of Cu^{2+} (Ni^{2+}) ions between the analyzed aqueous solution and the solution of the membrane in nitrobenzene.

Considering this thermodynamic hypothesis, the expression of the membrane potential was derived:

$$E = E^{o} + RT/2F \ln a_{M^{2+}} \qquad (1)$$

where $a_{M^{2+}}$ is the activity of the Cu^{2+} or Ni^{2+} ions in aqueous solution. The possibility of using simple and mixed complexes of Cu(II) and Ni(II) for obtaining selective membranes for the copper or nickel ions has thus been proved.

EXPERIMENTAL

Materials. Analytical grade $CuSO_4$, $Ni(NO_3)_2$ and nitrobenzene with a purity of better than 99% were supplied by Merck. Water used was doubly distilled and deionized. The simple and mixed complexes used as ion selective membranes were synthesized according to a procedure previously described[13-15] and characterized by elemental analysis, UV/VIS spectroscopy, IR spectroscopy and ESR.

Equipment. The electrode used for the determinations has been made according to a procedure previously described by Pleniceanu et al[12].

Construction of the electrode. The body of the electrode is made of a 75 mm long teflon tube (1) (Fig. 1) with an inside diameter of 6 mm at the lower end, where it is closed with a 15 mm long graphite rod (2). This is impregnated with the solution of the active substance (10^{-3} M) in nitrobenzene. The internal reference solution (3) is made up of nitrobenzene in which the complex combination is dissolved. The graphite rod plays both the role of mechanical support for the liquid membrane and electrical support, taking over the electrical potential of the membrane when this one is in contact with the aqueous phase.

The internal reference electrode has been eliminated by introducing a 115 mm long stainless-steel wire (4) having a diameter of 1.5 mm. The wire was introduced inside the graphite rod and makes contact with the connection terminal (6) of the measuring instrument.

In order to prevent evaporation of the internal solution and, as a consequence, any change of concentration in the membrane, the electrode is equipped with a screwed teflon stopper (5) at the top through which the stainless-steel wire

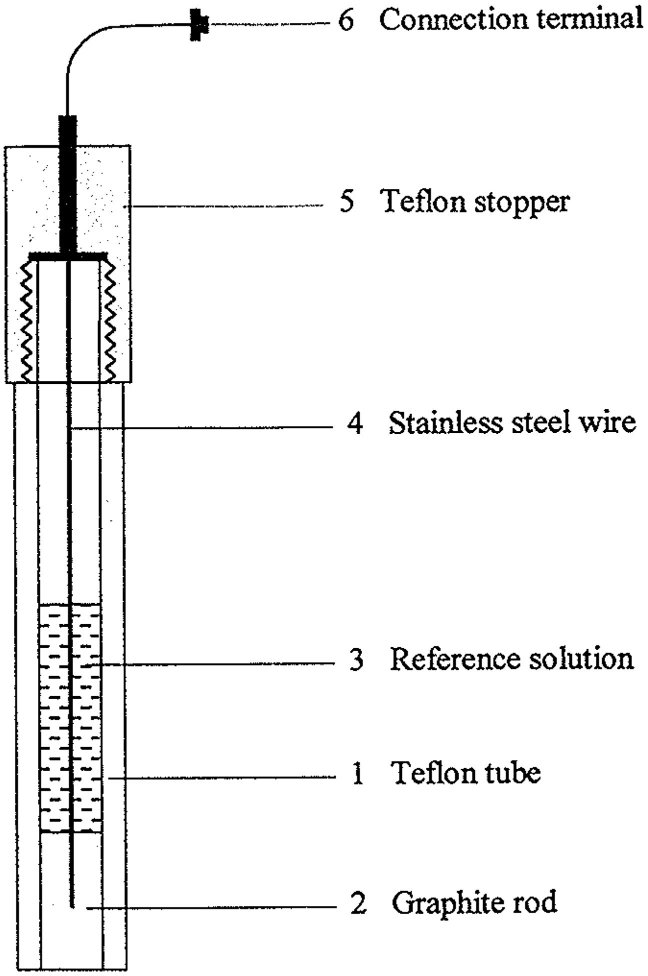
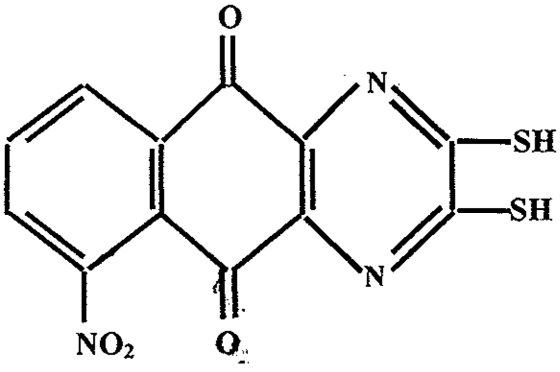


Fig.1 Schematic representation of the electrode.

penetrates, the system being perfectly air tight. The teflon stopper is detachable and allows the filling of the electrode with the organic solution (3).

Electrodes employed. Four new Cu^{2+} and Ni^{2+} selective electrodes with a liquid membrane have been obtained and characterised. Among these, electrodes 1 and 2 are based on simple complexes of Cu(II) and Ni(II) with a ligand of the dithiol class, 2,3-dithio-6-nitro-benzoquinoxaline-5,10-dione, which has the formula shown below:



Electrodes 3 and 4 are based on the corresponding mixed complex combinations with an ammonia molecule, which is present in the structure as a second ligand, along with the ligand belonging to the dithiol class. The formula of the simple and mixed complex combinations of Cu(II) and Ni(II) whose solutions in nitrobenzene constitute the membrane on a graphite rod for the electrodes under consideration are as follows:

Electrode 1: $[(n\text{-}C_4H_9)_4N]_2[Cu(dtnbqd)_2]$;
Electrode 2: $[(n\text{-}C_4H_9)_4N]_2[Ni(dtnbqd)_2]$
Electrode 3: $[Cu(NH_3)_2(dtnbqd)]$;
Electrode 4: $[Ni(NH_3)_2(dtnbqd)]$.

RESULTS

Response of the electrodes to the concentration of Cu^{2+} (Ni^{2+}) ions. Table 1 illustrates the variation of electromotive force obtained with the four ion-selective electrodes at 25 °C and an ionic strength $\mu = 0.4$ (obtained with KNO_3 which does not influence the electrode potential), depending on the concentration of Cu^{2+} and Ni^{2+} ions.

Table 1

The values of the electromotive force of the Cu^{2+} and Ni^{2+} selective electrodes vs. the saturated calomel electrode (SCE) at 25 °C, $\mu = 0.4$ (KNO_3) and pH = 4 – 4.2

Electrode 1		Electrode 2		Electrode 3		Electrode 4	
Conc. of Cu^{2+} ions (M)	E (mV)	Conc. of Ni^{2+} ions (M)	E (mV)	Conc. of Cu^{2+} ions (M)	E (mV)	Conc. of Ni^{2+} ions (M)	E (mV)
10^{-1}	330.5	10^{-1}	302	10^{-1}	420	10^{-1}	410
10^{-2}	301.5	10^{-2}	273	10^{-2}	391	10^{-2}	381
10^{-3}	272.5	10^{-3}	244	10^{-3}	362	10^{-3}	352
10^{-4}	243.5	10^{-4}	215	10^{-4}	333	10^{-4}	323
10^{-5}	214.5	10^{-5}	186	10^{-5}	304	10^{-5}	294
10^{-6}	206.5	10^{-6}	171	10^{-6}	275	10^{-6}	265
10^{-}	-	10^{-7}	-	10^{-7}	263	10^{-7}	251

The influence of pH on the response of the Cu^{2+} (Ni^{2+})-selective electrodes was also studied. For very acidic solutions a part of the 2,3-dithio-6-nitro-benzoquinoxaline-5,10-dione in the mixed complexes is transformed into free dithiol and the electrode potential measured in acid solution are greater. The electrode potential measurements in alkaline solutions have smaller values, because some of the Cu^{2+} (Ni^{2+}) cations are precipitated as hydroxide in alkaline medium.

The pH of the aqueous solution of Cu^{2+} (Ni^{2+}) was set at the desired value by means of Kolthoff and Vleeschhouwer buffer solutions. The pH measurements were made with a MV 85 pH-meter, using a glass electrode and a saturated calomel electrode. Variation of pH between 2.5 and 6.35 for Cu^{2+} and 2 and 8.6 for Ni^{2+} does not affect the membrane potential. As a consequence the linear portion of the E-pH curves is a function of the Cu^{2+} (Ni^{2+}) concentration in the aqueous phase (Fig. 2, Fig. 3). All the direct measurements of the potential were carried out in solutions of $CuSO_4$, and $Ni(NO_3)_2$ respectively at pH 4 and 4.2, obtained with a CH_3COOH 0.2 M + CH_3COONa 0.2 M buffer solution (82 ml CH_3COOH 0.2 M + 18 ml CH_3COONa 0.2 M for pH = 4; 73.5 ml CH_3COOH 0.2 M + 26.5 ml CH_3COONa 0.2 M for pH = 4.2).

Selectivity of the electrodes. The selectivity constants for the cations indicated in Table 2 were estimated by Srinivasan and Rechnitz's method[16] and checked by Eisenman's procedure[17].

From Table 2 it can be observed that the newly developed electrodes have a cationic response $\Delta E/\Delta \log c$ of 29 mV at 25 °C. This value corresponds to a Nernstian slope of RT/2F. The Nernstian response is obeyed in the concentration range 10^{-1}-10^{-5} M for electrodes 1 and 2 based on the simple complexes, respectively 10^{-1}-10^{-6} M for electrodes 3 and 4, based on the corresponding mixed complexes. Consequently the Cu^{2+} (Ni^{2+}) selective electrodes can be used within these concentration ranges for potentiometric determination of copper and nickel.

According to the experimental data given in Table 2, by comparison with the electrodes based on simple complexes, the Cu^{2+} (Ni^{2+}) selective electrodes based on mixed complexes have a wider range of linear response and a better selectivity for the interfering ions.

Dynamic response and reproducibility of electrodes. The response characteristics of the Cu^{2+} (Ni^{2+}) selective electrodes were estimated using solutions of $CuSO_4$ and $Ni(NO_3)_2$ having different concentrations, (usually 10 times higher) and by recording the values of the potentials as a function of time. The response times of the electrodes in dilute solutions (10^{-4}-10^{-6} M) were of about 2 minutes, whereas for more concentrated solutions (10^{-1}-10^{-3} M), the electrode potential reached an equilibrium value in about 20 seconds.

The reproducibility of the potential measurements was checked during a period of 3-5 weeks for the concentration range 10^{-1}-10^{-5} M $CuSO_4$ ($Ni(NO_3)_2$) in case of electrodes 1 and 2, respectively, 10^{-1}-10^{-6} M for electrodes 3 and 4 ($\mu = 0.4$).

Table 2

The characteristics of Cu^{2+} (Ni^{2+}) selective electrodes (based on simple and mixed complexes) at 25 °C, a constant ionic strength $\mu = 0.4$ (KNO_3) and pH = 4–4.2

Electrode M^{2+} -selective	$\Delta E/\Delta \log c$ (mV)	Range of linear response (M)	Constants of selectivity for the cations:			
			Cu^{2+}	Ni^{2+}	Fe^{2+}	Co^{2+}
1	29	10^{-1}-10^{-5}	-	$8 \cdot 10^{-4}$	$5.55 \cdot 10^{-4}$	$3.12 \cdot 10^{-3}$
2	29	10^{-1}-10^{-5}	$1.07 \cdot 10^{-3}$	-	$6.03 \cdot 10^{-4}$	$3.02 \cdot 10^{-3}$
3	29	10^{-1}-10^{-6}	-	$2.89 \cdot 10^{-4}$	$1.89 \cdot 10^{-4}$	$6.5 \cdot 10^{-4}$
4	29	10^{-1}-10^{-6}	$4.48 \cdot 10^{-4}$	-	$1.19 \cdot 10^{-4}$	$9.05 \cdot 10^{-4}$

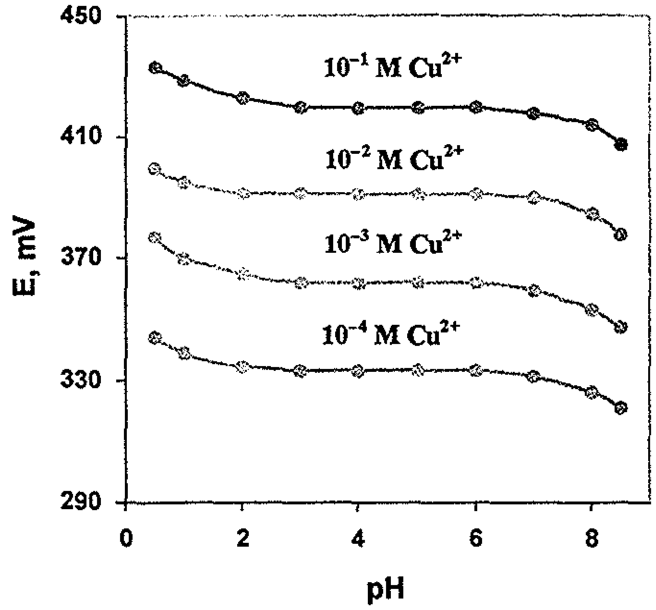


Fig.2 The effect of pH on the response of the Cu^{2+} selective electrode with $[Cu(NH_3)_2(dtnbqd)]$.

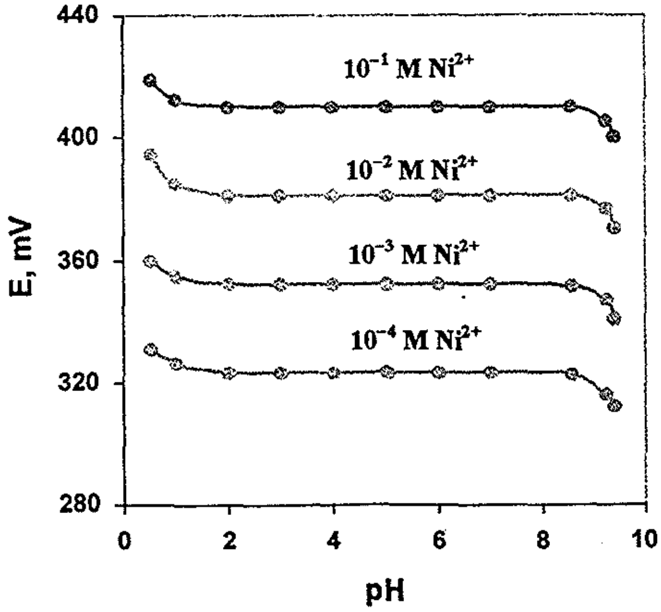


Fig.3 The effect of pH on the response of the Ni^{2+} selective electrode with $[Ni(NH_3)_2(dtnbqd)]$.

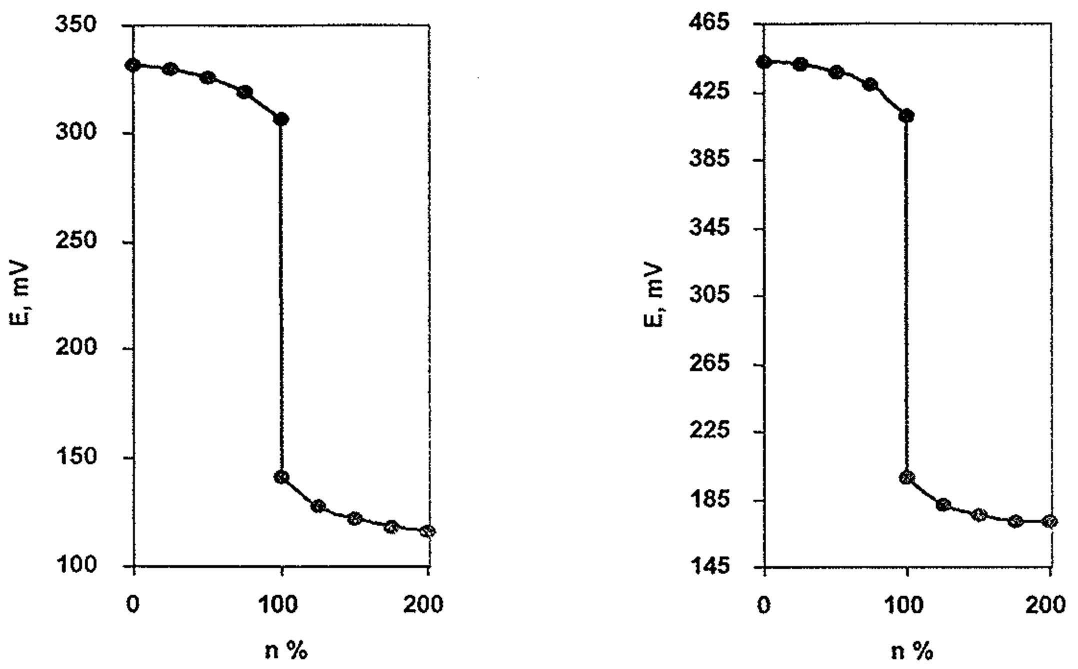


Fig. 4.1

Fig. 4.2

Fig.4 The potentiometric titration curves of Cu^{2+} ions with EDTA, obtained by using the Cu^{2+} selective electrodes based on simple complex, with a membrane of $[(n\text{-}C_4H_9)_4N]_2[Cu(dtnbqd)_2]$ (Fig. 4.1), and mixed complex, with a membrane of $[Cu(NH_3)_2(dtnbqd)]$, (Fig. 4.2).

ANALYTICAL APPLICATIONS

The Cu^{2+} (Ni^{2+}) selective electrodes have been used to determine the Cu^{2+} (Ni^{2+}) ions in aqueous solution both by direct potentiometry and by potentiometric titration with EDTA.

For the direct potentiometric determination, a calibration curve was used. This has been obtained by the variation of the electrode potential of the Cu^{2+} (Ni^{2+}) selective electrodes 1, 2, 3, 4, as a function of $-\log[M^{2+}]$, versus the saturated calomel electrode (SCE) as external reference electrode. The experimental data are shown in Table 1, and are obtained at 25 °C, $\mu = 0.4$ (KNO_3) and pH 4 (4.2). The lower M^{2+}

concentration limit, that can be determined by direct potentiometry is of 10^{-5} M with electrodes 1 and 2 and of 10^{-6} M with electrodes 3 and 4.

The electrodes were also tested for potentiometric titration with EDTA by using 10^{-3} M titrated solutions of $CuSO_4$ ($Ni(NO_3)_2$). These titrations were based on well-defined titration curves and a potential change of 162.5 and 160 mV for electrodes 1 and 2 was observed (Fig. 4). In the case of electrodes 3 and 4 much larger changes of 213.5 and 202 mV were obtained (Fig. 5).

Determination of copper and nickel by direct potentiometry in industrial waters. Samples of water originating from a water treatment station were analyzed; the concentration of copper and nickel has been determined for every sample by atomic absorption spectrometry (AAS). The content of copper was determined by direct potentiometry using the Cu^{2+} selective electrode No. 3, based on $[Cu(NH_3)_2(dtnbqd)]$.

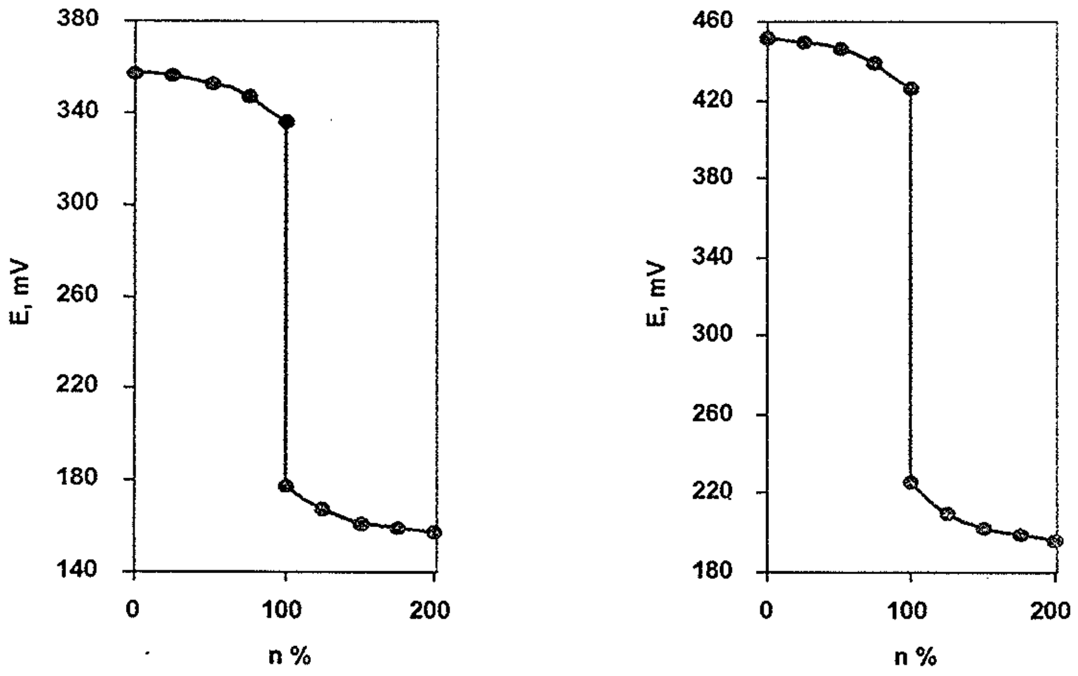


Fig.5 The potentiometric titration curves of Ni^{2+} ions with EDTA, obtained by using the Ni^{2+} selective electrodes based on simple complex, with a membrane of $[(n\text{-}C_4H_9)_4N]_2[Ni(dtnbqd)_2]$ (Fig. 5.1), and mixed complex, with a membrane of $[Ni(NH_3)_2(dtnbqd)]$, (Fig. 5.2).

Table 3

Results of Cu^{2+} (Ni^{2+}) ion determinations in industrial waters

Sample No.	Cu^{2+} (mg L^{-1})		Ni^{2+} (mg L^{-1})	
	Potentiometrically, with the Cu^{2+}-selective electrode No.3	By AAS	Potentiometrically, with the Ni^{2+}-selective electrode No.4	By AAS
1	1.01	1.06	0.15	0.20
2	1.79	1.80	0.21	0.25
3	0.80	0.79	0.09	0.13
4	1.01	1.10	0.18	0.20
5	1.59	1.65	0.23	0.28
6	3.57	3.70	0.11	0.16
7	3.18	3.27	0.29	0.35
8	2.84	2.91	0.33	0.35
9	2.01	2.10	0.42	0.46
10	1.27	1.35	0.19	0.20

Table 4

Results of Cu^{2+} ions determination in industrial waters using the method of standard additions

Sample No.	Cu^{2+} (mg L^{-1})			
	Initial Cu^{2+} (AAS method)	Cu^{2+} added	Theoretical total of Cu^{2+}	Experimental Cu^{2+}, with electrode No.3
1	0.79	1.00	1.79	1.75
2	1.06	1.00	2.06	2.00
3	1.65	1.00	2.65	2.60
4	2.91	0.50	3.41	3.36
5	3.70	0.50	4.20	4.16

Table 5

Results of Ni^{2+} ions determination in industrial waters using the method of standard additions

Sample No.	Ni^{2+}(mg L^{-1})			
	Initial Ni^{2+} (AAS method)	Ni^{2+} added	Theoretical total of Ni^{2+}	Experimental Ni^{2+}, with electrode No.4
1	0.20	2.00	2.20	2.17
2	0.25	1.50	1.75	1.70
3	0.28	1.50	1.78	1.73
4	0.35	1.75	2.10	2.06
5	0.46	1.50	1.96	1.92

In the same way, the content of nickel was determined by using the Ni^{2+} selective electrode No. 4, based on $[Ni(NH_3)_2(dtnbqd)]$.

The results of the experimental determinations are given in Table 3, representing the average values of the 6 measurements. It can be observed that the results obtained with the Cu^{2+} selective electrode No. 3 and the Ni^{2+} selective electrode No. 4 are in agreement with those obtained by AAS. To certify the advantages of using the potentiometric method with the mentioned Cu^{2+} and Ni^{2+} selective electrodes, the experimental data were checked by using the method of standard additions. The results given in Table 4 and Table 5 indicate a good agreement of the AAS and direct potentiometric methods. Also, they suggest that the use of the Cu^{2+} (Ni^{2+}) selective electrodes based on mixed complexes for the determination of cooper (nickel) ions in industrial waters is very appropriate

CONCLUSIONS

Four electrodes with liquid membrane, Cu^{2+} and Ni^{2+} ion-selective electrodes were prepared and characterized. The following characteristics were studied:

- the electrodes response to Cu^{2+} (Ni^{2+}) ion concentration;
- the influence of pH on the response of the Cu^{2+} (Ni^{2+}) selective electrodes;
- the selectivity of the electrodes;
- the dynamic response and reproducibility of the electrodes;

The analytical applications of these electrodes have also been studied by using the direct potentiometric and potentiometric titration methods.

The ion selective electrodes based on mixed complexes have been used for the determination of copper and nickel ions in industrial waters.

The electrodes with mixed complex membranes have a better selectivity for interfering ions and a much larger potential rise on the titration curve. For this reason, they are of practical interest for copper and nickel ion determinations in solutions that are more dilute and in industrial waters.

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