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New liquid-membrane electrodes used for potential determination of copper and nickel

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Summary — This paper presents the experimental and theoretical data regarding the design and characterization of four liquid-membrane electrodes, which have not been mentioned in the specialized literature so far. The membranes are solutions of the active substances in nitrobenzene on a graphite rod and are simple and mixed complex combinations of Cu(II) and Ni(II) ions with an organic ligand of the dithiol class. Cu^{2+}-selective and Ni^{2+}-selective electrodes have been used to determine the copper and nickel ions in aqueous solutions, by both direct potentiometry and potentiometric titration with EDTA. They have also been used for determining the Cu^{2+} and Ni^{2+} ions in industrial waters by direct potentiometry. The analytical results obtained have been checked by the standard additions method and by comparison with determinations through atomic absorption spectrometry.

liquid membrane electrode / potentiometry / copper / nickel

Résumé — Électrodes à membranes liquides, utilisées pour déterminer le potentiel du cuivre et du nickel. Cet article expose les travaux novateurs d'élaboration et de caractérisation de quatre électrodes à membranes liquides. Les substances actives sont en solution dans le nitrobenzène (les électrodes étant en partie constituées d'une barre de graphite), et sont des combinaisons simples de complexes de Cu(II) et de Ni(II), avec des ligands de la famille des dithiols. Des électrodes spécifiques du Cu^{2+} et du Ni^{2+} ont été utilisées pour déterminer les ions cuivre et nickel en solutions aqueuses, par des méthodes de potentiométrie directe et par titrage potentiométrique avec l'EDTA. Ces électrodes ont aussi servi à évaluer, par potentiométrie directe, le Cu^{2+} et le Ni^{2+} contenus dans les solutions rejetées par les industriels. Les résultats analytiques obtenus ont été contrôlés par des méthodes standards de titrage par addition et de détermination par la spectrométrie d'absorption.

électrode à membrane liquide / potentiométrie / cuivre / nickel

Introduction

In the last few years the literature has recorded the design of new ion-selective electrodes for copper and nickel metal ions. Thus, in a series of previous papers [1–9], we have presented the possibility of obtaining Cu^{2+}- and Ni^{2+}-selective electrodes with liquid membranes on the basis of complex combinations of copper and nickel, which have the property of being extracted in nitrobenzene, an organic solvent immiscible water.

The reponse of these ion-selective electrodes to the concentration of Cu^{2+} (Ni^{2+}) ions in solution has formally been attributed to a process of exchange of these metal ions between the analyzed aqueous solution and the solution of membrane in nitrobenzene. The system is considered to be in equilibrium when the electrochemical potentials of the Cu^{2+} (Ni^{2+}) metal ions are equal in the two phases, while the presence of the copper (nickel) in the aqueous phase does not affect the activity of these ions in the organic phase, which constitutes the membrane of the electrodes.

On the basis of this hypothesis, the expression for the membrane potential has been deduced thermodynamically:

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

where $a_{M^{2+}}$ represents the activity of the Cu^{2+} (Ni^{2+}) ions in an aqueous solution. The above-mentioned hypothesis does not explain the functioning mechanism of the electrodes, which have a Nernstian form, as shown by the expression (1). These electrodes have been successfully used in potentiometric methods of determining copper and nickel.

Experimental section

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), which is impregnated with the solution of the active

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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, using the electrical potential of the membrane when the latter is in contact with the aqueous phase.

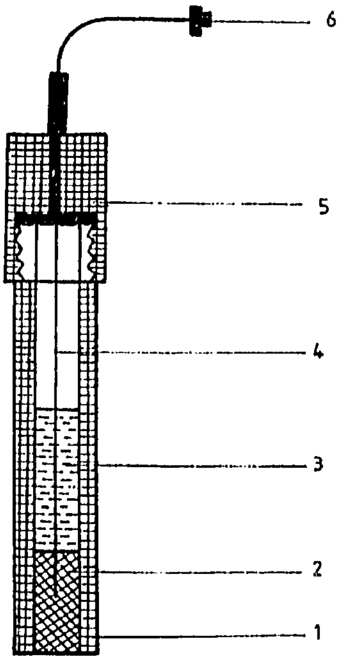


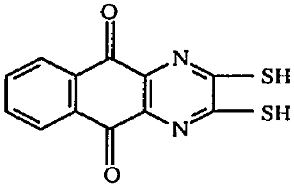
Fig 1. Schematic drawing of the electrode.

The internal reference electrode has been eliminated by introducing a 115 mm long stainless-steel wire (4) with a diameter of 1.5 mm inside the graphite rod which 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 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 Cu^{2+}- and Ni^{2+}-selective electrodes with a liquid membrane have been obtained and characterized. Of these the electrodes 1 and 2 are based on simple complex combinations of Cu(II) and Ni(II) with a ligand of the dithiol class, 2,3-dimercaptobenzoquinoxaline-5,10-dione (2,3-dtbq-5,10-dione) as shown in (2) below, while electrodes 3 and 4 are based on the corresponding mixed complex combinations with the formula:



(2)

An ammonia molecule is present in the structure as a second ligand. The formulation 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 realized electrodes are as follows:

Electrode 1: $[(n\text{-}C_4H_9)_4N]_2[Cu(2,3\text{-dtbq-}5,10\text{-dione})_2]$
Electrode 2: $[(n\text{-}C_4H_9)_4N]_2[Ni(2,3\text{-dtbq-}5,10\text{-dione})_2]$
Electrode 3: $[Cu(NH_3)_2(2,3\text{-dtbq-}5,10\text{-dione})]$
Electrode 4: $[Ni(NH_3)_2(2,3\text{-dtbq-}5,10\text{-dione})]$

Results

Response of electrodes to the concentration of Cu^{2+} (Ni^{2+}) ions

In figures 2–5, we present the variation of the electromotive force obtained with the four ion-selective electrodes at 25 °C and an ionic strength $\mu = 0.4$ (provided with KNO_3 which does not influence the electrode potential), as a function of $-\log [M^{2+}]$.

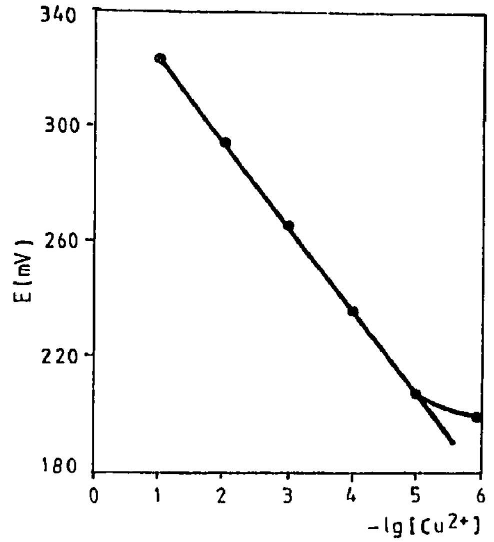


Fig 2. The variation of the electromotive force of the Cu^{2+}-selective electrode 1 vs the saturated calomel electrode (SCE) as a function of $-\log [Cu^{2+}]$, at 25 °C and $\mu = 0.4$ (KNO_3).

Influence of pH

The influence of pH on the response of the Cu^{2+}- and Ni^{2+}-selective electrodes was studied. It was found that unlike other types of electrodes, in the case of the liquid ion-selective membrane electrodes, the membranes modify their composition when the aqueous solution is too acid or too alkaline. The pH values of the samples of aqueous solution of Cu^{2+} (Ni^{2+}) were controlled with buffer solutions, according to Kolthoff and Vleeschhouwer [10], while the determinations of pH were made with a pH-meter (MV 85), using a glass electrode and a saturated calomel electrode.

We deduced experimentally that in the range 2.5–6.35 for Cu^{2+} and 2–8.6 for Ni^{2+} the pH variation

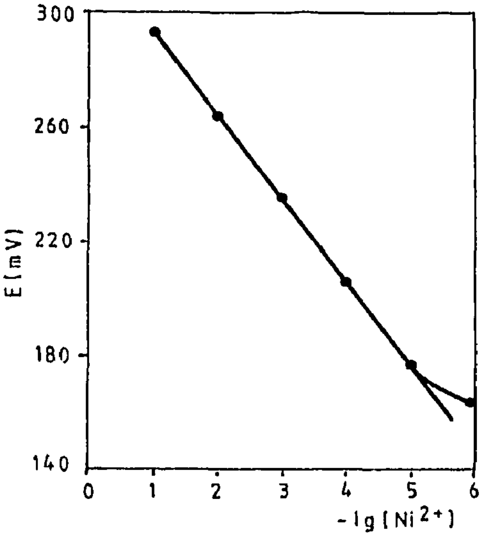


Fig 3. The variation of the electromotive force of the Ni^{2+}-selective electrode 2 vs the saturated calomel electrode (SCE) as a function of $-\log [Ni^{2+}]$, at 25 °C and $\mu = 0.4$ (KNO_3).

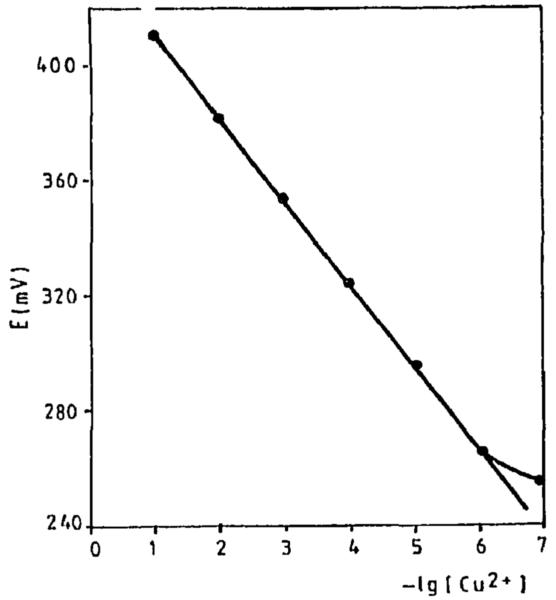


Fig 4. The variation of the electromotive force of the Cu^{2+}-selective electrode 3 vs the saturated calomel electrode (SCE) as a function of $-\log [Cu^{2+}]$, at 25 °C and $\mu = 0.4$ (KNO_3).

does not influence the membrane potential and that the linear portion of the curves E/pH is a function of the concentration of metal ions in the aqueous phase (fig 6 and 7).

The direct measurements of the potential were made in solutions of $CuSO_4$ and $Ni(NO_3)_2$ at pH 4 and 4.2, using a buffer solution of acetic acid/sodium acetate 0.2 M.

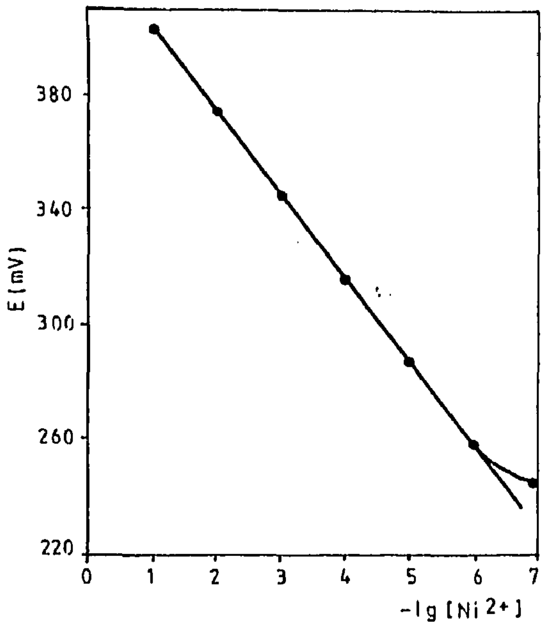


Fig 5. The variation of the electromotive force of the Ni^{2+}-selective electrode 4 vs the saturated calomel electrode (SCE) as a function of $-\log [Ni^{2+}]$, at 25 °C and $\mu = 0.4$ (KNO_3).

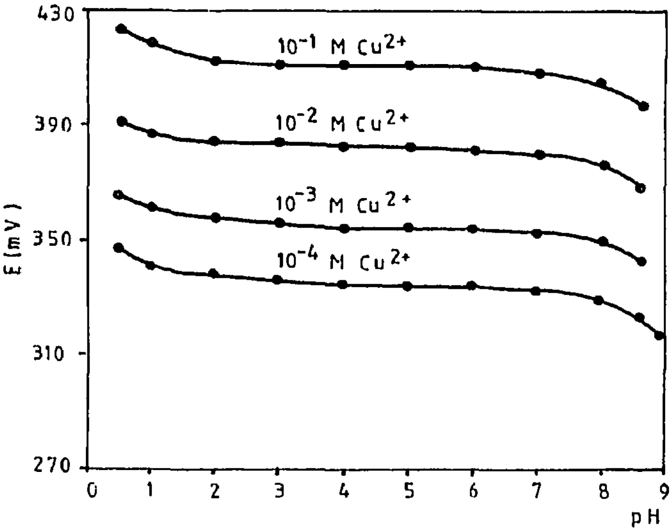


Fig 6. The influence of pH on the response of the Cu^{2+}-selective electrode with a membrane of $[Cu(NH_3)_2(2,3\text{-dtbq-}5,10\text{-dione})]$.

Selectivity of electrodes

The electrodes were tested for a series of cations which can participate in an ionic exchange equilibrium with the Cu^{2+} (Ni^{2+}) ions in the membrane. We found that a series of cations interfere only if they are present in concentrations approximately 1000 times higher than the concentrations of the ions of Cu^{2+} and Ni^{2+}, respectively. For these cations the selectivity constants have been determined using the Eisenman method [11] (table I).

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

Electrode M^+ selective	*$\Delta E/\Delta \log c$ (mV)*	*Range of linear response (M)*	*Selectivity constants to the cations*			
			Cu^{2+}	*Ni^{2+}*	*Fe^{2+}*	*Co^{2+}*
1	29	$10^{-1} - 10^{-5}$	–	1.09×10^{-3}	5.95×10^{-4}	3.52×10^{-3}
2	29	$10^{-1} - 10^{-5}$	1.37×10^{-3}	–	6.42×10^{-4}	3.56×10^{-3}
3	29	$10^{-1} - 10^{-6}$	–	3.39×10^{-4}	2.39×10^{-4}	1.14×10^{-3}
4	29	$10^{-1} - 10^{-6}$	4.98×10^{-4}	–	2.71×10^{-4}	9.58×10^{-4}

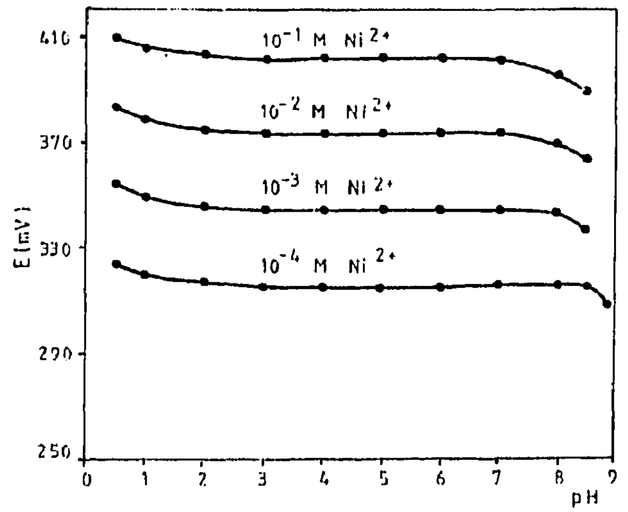


Fig 7. The influence of pH on the response of the Ni^{2+}-selective electrode with a membrane of $[Ni(NH_3)_2(2,3\text{-dtbq-}5,10\text{-dione})]$.

The experimental data shown in table I prove that, as compared to the electrodes based on simple complex combinations, the Cu^{2+}- and Ni^{2+}-selective electrodes based on mixed complexes, present an extension of the linear response range and a better selectivity as compared to the interfering ions. These results are in accordance with reality because the stability constants of the Cu^{2+} and Ni^{2+} complexes are of similar sizes.

Dynamic response and reproducibility of electrodes

The response characteristics of the Cu^{2+}- and Ni^{2+}-selective electrodes were evaluated by introducing the electrodes into solutions of different concentrations of $CuSO_4$ and $Ni(NO_3)_2$ and by recording the values of the potentials as a function of time.

The response times of the electrodes in diluted solutions ($10^{-4} - 10^{-6}$ M) were approximately 2 min, while in more concentrated solutions (10^{-1} – 10^{-3} M) the electrode potential reaches an equilibrium value in a few seconds. The four electrodes were tested over 3-5 weeks, noticing that the electrode potentials changed only by ±2 mV and ±3 mV, without modifying the electrode slope (29 mV/tenfold increase in concentration).

Analytical applications

The obtained Cu^{2+} and Ni^{2+}-selective electrodes were used for the determination of copper and nickel ions in aqueous solutions, by both direct potentiometry and potentiometric titration with EDTA.

For the direct potentiometric determination we used a calibration curve, which can be obtained through the variation of the electromotive force of the ion-selective electrodes 1, 2, 3 and 4 depending on $-\log[M^{2+}]$ compared with ESC at 25 °C and $\mu = 0.4$ (KNO_3) according to the data in figures 2-5. For this, we used titrated solutions of $CuSO_4$ and $Ni(NO_3)_2$, respectively, preferably 10^{-3} M.

The limit concentration of M^{2+} that can be determined by direct potentiometry is of the order 1×10^{-5} M with electrodes 1 and 2 and 1×10^{-6} M with electrodes 3 and 4. The electrodes have also been tested for the potentiometric titration with EDTA. For electrodes 1 and 2 based on simple complex combinations, we have obtained potential rises of 150/145 mV and potential rises higher than 201/196 mV for the electrodes based on mixed complex combinations (fig 8-9).

The same occurs with the Cu^{2+}- and Ni^{2+}-selective electrodes based on mixed complex combinations which have been used with good results for determining the copper and nickel ions in industrial waters.

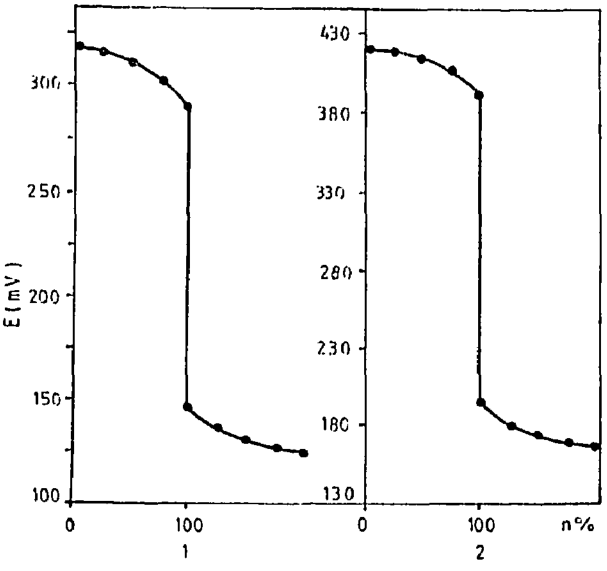


Fig 8. The curves of potentiometric titration of the Cu^{2+} ion with EDTA, by using Cu^{2+}-selective electrodes on the basis of a simple complex combination with a membrane of $[(n\text{-}C_4H_9)_4N]_2[Cu(2,3\text{-dtbq-}5,10\text{-dione})_2]$ (curve 1) and on the basis of a mixed complex combination, with a membrane of $[Cu(NH_3)_2(2,3\text{-dtbq-}5,10\text{-dione})]$ (curve 2).

Table II. The results of the determination of Cu^{2+} and Ni^{2+} ions in industrial waters.

Sample	*Cu^{2+} ($mg \cdot L^{-1}$)*		*Ni^{2+} ($mg \cdot L^{-1}$)*	
	Potentiometric with Cu^{2+}-selective electrode 3	*SAA method*	*Potentiometric with Ni^{2+}-selective electrode 4*	*SAA method*
1	0.80	0.83	0.57	0.61
2	1.78	1.80	0.11	0.15
3	1.42	1.46	0.16	0.20
4	1.57	1.60	0.22	0.27
5	1.00	1.03	0.19	0.23
6	2.10	2.15	0.24	0.27
7	1.25	1.31	0.27	0.31
8	1.10	1.16	0.13	0.17
9	0.55	0.60	0.32	0.35
10	0.85	0.89	0.41	0.45

Table III. The results of the determination of Cu^{2+} ions in industrial waters using the method of the standard additions.

Sample	*Cu^{2+} ($mg \cdot L^{-1}$)*			
	Initial Cu^{2+} (SAA)	*Addition of Cu^{2+}*	*Theoretical total*	*Experimental Cu^{2+} with electrode 3*
1	0.80	2.00	2.80	2.77
2	1.00	1.00	2.00	1.98
3	1.57	2.00	3.57	3.54
4	2.10	2.00	4.10	4.07
5	0.55	1.00	1.55	1.53

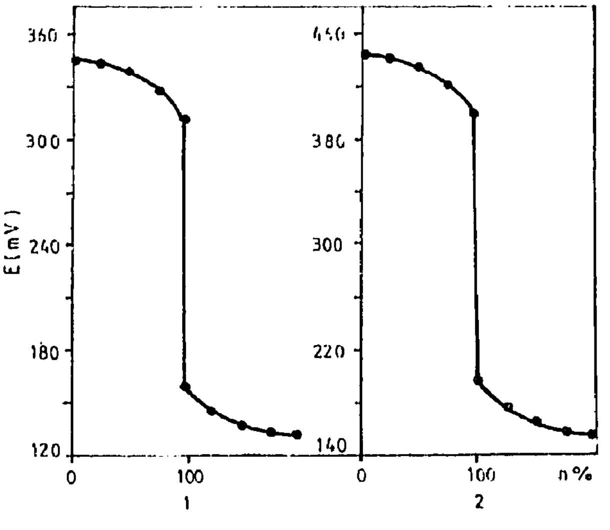


Fig 9. The curves of potentiometric titration of the Ni^{2+} ion with EDTA, by using Ni^{2+}-selective electrodes on the basis of a simple complex combination with a membrane of $[(n\text{-}C_4H_9)_4N]_2[Ni(2,3\text{-dtbq-}5,10\text{-dione})_2]$ (curve 1) and on the basis of a mixed complex combination, with a membrane of $[Cu(NH_3)_2(2,3\text{-dtbq-}5,10\text{-dione})]$ (curve 2).

The results of the experimental determinations are presented in table II. The values of concentration in Cu^{2+} and Ni^{2+} are expressed in $mg \cdot L^{-1}$ and were obtained potentiometrically with electrodes 3 and 4, respectively. We also present for comparison the values obtained through the atomic absorption spectrometry method (SAA), for both copper and nickel.

We observed that the values obtained from the samples of industrial water taken for analysis by the potentiometric method are in accordance with those obtained by the SAA method. These results are in accordance with the values of the selectivity constants of electrodes 3 and 4 compared with the ions of Ni^{2+} and Cu^{2+}, respectively (see table I above). To assert the advantage of using the potentiometric method with the electrodes 3 and 4, all the obtained experimental data have been checked by the method of the standard additions; these results are shown in tables III and IV.

The simple and mixed complex combinations necessary for the design of the four electrodes have been synthesized and then characterized through elemental analysis, UV/vis spectrometry, IR spectrometry and ESR [12–14].

Conclusions

Four selective electrodes have been obtained for Cu^{2+} and Ni^{2+} ions, of some simple and mixed complex combinations of copper and nickel with 2,3-dimercaptobenzoquinoxaline-5,10-dione with membranes made of solutions in nitrobenzene on a graphite rod. The study of these four electrodes has proved primary and secondary characteristics favorable for their practical utilization in potentiometric titrations and direct potentiometric determinations. We would like to emphasize the fact that the electrodes based on mixed complex combinations (3 and 4) have, in comparison with the electrodes based on simple complex combinations (1 and 2), an extension of the range of their

Table IV. The results of the determination of Ni^{2+} ions in industrial waters using the method of the standard additions.

Sample	*Ni^{2+} (mg·L^{-1})*			
	Initial Ni^{2+} (SAA)	*Addition of Ni^{2+}*	*Theoretical total*	*Experimental Ni^{2+} with electrode 4*
1	0.57	2.00	2.57	2.55
2	0.19	1.50	1.69	1.65
3	0.22	1.00	1.22	1.19
4	0.24	1.75	1.99	1.96
5	0.32	0.60	0.92	0.89

linear response, a better selectivity toward the interfering ions, and much higher potential rises of the titration curves. For this reason, they are adequate for the potentiometric determination of copper and nickel ions in dilute solutions (as low as 10^{-5} M) as well as for checking industrial waters.

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