

## Mixed Complex Combinations with a New Schiff Base used as Membranes Ion-Selective for Copper and Nickel Ions; Analytical Applications

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**Summary:** Four electrodes with liquid membrane, Cu<sup>2+</sup>-selective and Ni<sup>2+</sup>-selective, not previously described in the literature, were prepared and characterized. Electrodes 1 and 2 are based on mixed complexes of Cu(II) and Ni(II) with isonicotinoylhydrazon-2-aldehydepyrrole (INH2AP = HL<sup>1</sup>) as ligand and electrodes 3 and 4 are based on the mixed complexes with isonicotinoylhydrazon-2-hydroxy-1-naphthaldehyde (INH2HNA = H<sub>2</sub>L<sup>2</sup>). Cu<sup>2+</sup>-selective and Ni<sup>2+</sup>-selective electrodes have been used to determine the copper and nickel ions in aqueous solutions, by both direct potentiometric and potentiometric titration with EDTA. They have also been used for determining the Cu<sup>2+</sup> and Ni<sup>2+</sup> ions in industrial waters by direct potentiometry. The analytical results obtained have been checked by the standard addition method and by comparison with determinations through atomic absorption spectrometry.

### Introduction

Many analytical techniques, such as atomic absorption spectrometry and electro-analytical methods are used in environmental monitoring. Even if the sensitivity and precision of both methods are comparable, the big advantages of the electro-analytical techniques over the AAS are the cost effectiveness and the possibility that sampling and analysis take place on-site.

The literature [1-6] has highlighted the achievement of new 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. This study is a continuation of our previous work described in earlier papers [7-12] and presents the possibility of obtaining Cu<sup>2+</sup> and Ni<sup>2+</sup>-selective electrodes with liquid membrane. These electrodes are based on complex combinations of Cu (II) and Ni (II), extractable in water non-miscible organic solvent. The response of these electrodes to the concentration of Cu<sup>2+</sup> and Ni<sup>2+</sup> in solution has been formally attributed to a process of exchange of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions between the analyzed aqueous solution and the solution of membrane in nitrobenzene. Considering this thermodynamic hypothesis, the expression of the membrane potential was derived:

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

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

### Results and Discussion

#### *Response of Electrodes to the Concentration of Cu<sup>2+</sup> and Ni<sup>2+</sup> Ions*

In Table-1 it is illustrated that the variations of electromotive force obtained with the four ion-selective electrodes at 25°C and ionic strength  $\mu = 0.4$  (obtained with KNO<sub>3</sub> which does not influence the electrode potential), depending on the concentration of Cu<sup>2+</sup> and Ni<sup>2+</sup> ions. The influence of pH on the response of the Cu<sup>2+</sup> and Ni<sup>2+</sup>-selective electrodes was also studied. The pH of the aqueous solution of Cu<sup>2+</sup> and Ni<sup>2+</sup> was set at the desired value by means of Kolthoff and Vleeschouwer [13] buffer solutions. The pH measurements were made with a Jenway 3305 pH-meter, using a glass electrode and a saturated calomel electrode. The variation of pH between 5.2-9.3 for Cu<sup>2+</sup> and 5-9.5 for Ni<sup>2+</sup> does not affect the membrane potential. As a consequence the linear portion of the E-pH curves is a function of the Cu<sup>2+</sup> and Ni<sup>2+</sup> concentration in the aqueous phase

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(Figs. 1 and 2.). All the direct measurements of the potential were carried out in solutions of  $\text{CuSO}_4$  and  $\text{Ni}(\text{NO}_3)_2$ , respectively, at pH 6 and 6.5, achieved with a  $\text{CH}_3\text{COOH}$  0.2 M +  $\text{CH}_3\text{COONa}$  0.2 M buffer solution.

#### Selectivity of the Electrodes

The selectivity constants for the cations indicated in Table-2 were estimated by Srinivasan and Rechnitz's method [14] and checked by

Table-1: The values of the electromotive force of the  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ -selective electrodes vs. saturated calomel electrode (SCE) at  $25^\circ\text{C}$ ,  $\mu = 0.4$  ( $\text{KNO}_3$ ) and pH = 6 (6.5).

Electrode 1		Electrode 2		Electrode 3		Electrode 4	
$\text{Cu}^{2+}$ , M	E(mV)	$\text{Ni}^{2+}$ , M	E(mV)	$\text{Cu}^{2+}$ , M	E(mV)	$\text{Ni}^{2+}$ , M	E(mV)
$10^{-1}$	390	$10^{-1}$	410	$10^{-1}$	430	$10^{-1}$	450
$10^{-2}$	361	$10^{-2}$	381	$10^{-2}$	401	$10^{-2}$	421
$10^{-3}$	332	$10^{-3}$	352	$10^{-3}$	372	$10^{-3}$	392
$10^{-4}$	303	$10^{-4}$	323	$10^{-4}$	343	$10^{-4}$	363
$10^{-5}$	274	$10^{-5}$	294	$10^{-5}$	314	$10^{-5}$	334
$10^{-6}$	246	$10^{-6}$	271	$10^{-6}$	286	$10^{-6}$	305
$10^{-7}$	233	$10^{-7}$	257	$10^{-7}$	273	$10^{-7}$	290

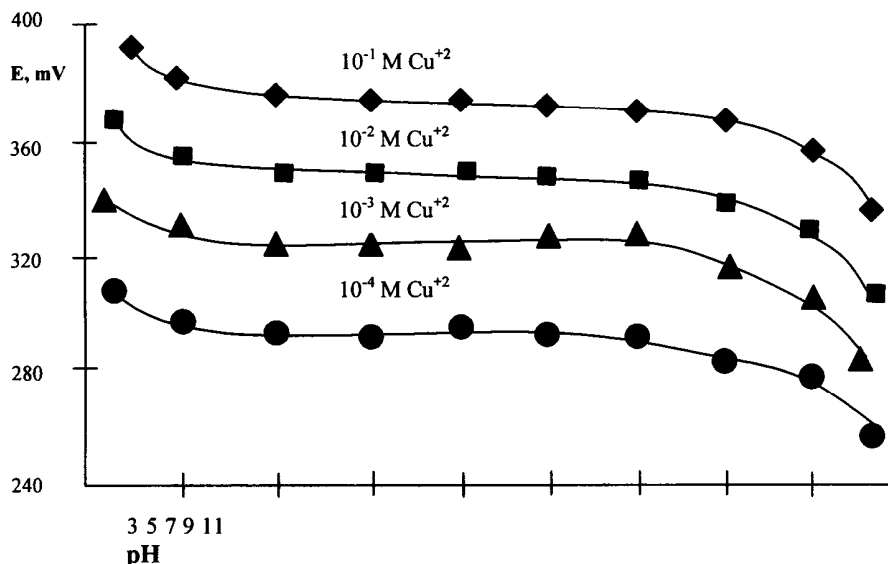


Fig. 1: The influence of pH on the response of the ion-selective electrode  $[\text{Cu}(\text{HL}^1)_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ .

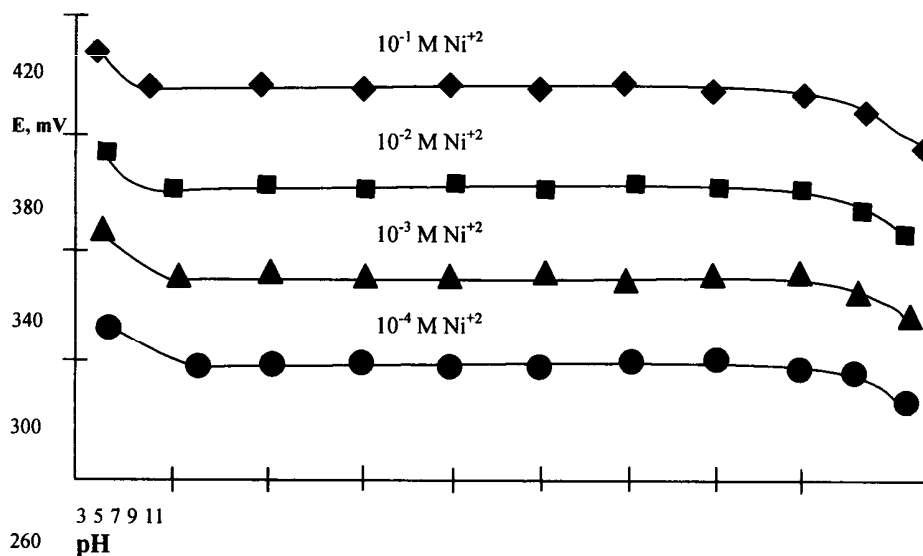


Fig. 2: The influence of pH on the response of the ion-selective electrode  $[\text{Ni}(\text{HL}^1)_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$ .

Table-2: The characteristics of Cu<sup>2+</sup> and Ni<sup>2+</sup>-selective electrodes (based on mixed complexes) at 25°C, a constant ionic strength  $\mu = 0.4$  (KNO<sub>3</sub>) and pH = 6 (6.5).

Electrode M <sup>2+</sup> -selective	$\Delta E/\Delta \log c$ (mV)	Range of linear response (M)	Constants of selectivity to the cations:			
			Sn <sup>2+</sup>	Pb <sup>2+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>
1.	29	10 <sup>-1</sup> -10 <sup>-6</sup>	4.1·10 <sup>-4</sup>	4.9·10 <sup>-4</sup>	3.15·10 <sup>-4</sup>	4.75·10 <sup>-4</sup>
2.	29	10 <sup>-1</sup> -10 <sup>-6</sup>	3·10 <sup>-4</sup>	4.1·10 <sup>-4</sup>	2.4·10 <sup>-4</sup>	3.9·10 <sup>-4</sup>
3.	29	10 <sup>-1</sup> -10 <sup>-6</sup>	2·10 <sup>-4</sup>	3.5·10 <sup>-4</sup>	1.5·10 <sup>-4</sup>	3.0·10 <sup>-4</sup>
4.	29	10 <sup>-1</sup> -10 <sup>-6</sup>	1.3·10 <sup>-4</sup>	1.8·10 <sup>-4</sup>	0.9·10 <sup>-4</sup>	2.2·10 <sup>-4</sup>

Eisenman's procedure [15]. From Table-2 it can be observed that the achieved 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 10<sup>-1</sup>-10<sup>-6</sup> M for all electrodes based on the mixed complexes. By consequence the Cu<sup>2+</sup> and Ni<sup>2+</sup>-selective electrodes can be used within this concentration ranges for potentiometric determination of copper and nickel. For Cu<sup>2+</sup>-selective electrodes 1 and 3, the interference of Ni<sup>2+</sup> ions is avoided by adding dimethylglyoxime as masking agent, while for Ni<sup>2+</sup>-selective electrodes 2 and 4,  $\alpha$ -nitroso- $\beta$ -naphthole reagent can be used to avoid the interference of Cu<sup>2+</sup> ions, in analyzed aqueous solutions. According to the experimental data given in Table-2, the Cu<sup>2+</sup> and Ni<sup>2+</sup>-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<sup>2+</sup> and Ni<sup>2+</sup>-selective electrodes were estimated using solutions of CuSO<sub>4</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> with 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<sup>-4</sup> - 10<sup>-6</sup> M) were of about 2 minutes, whereas for more concentrated solutions (10<sup>-1</sup>-10<sup>-3</sup> 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<sup>-1</sup> - 10<sup>-6</sup> M CuSO<sub>4</sub> and Ni(NO<sub>3</sub>)<sub>2</sub> for all four electrodes ( $\mu = 0.4$ ).

#### Analytical Applications; Determination of Copper and Nickel by Direct Potentiometry in Industrial Waters

The Cu<sup>2+</sup> and Ni<sup>2+</sup>-selective electrodes have been used to determine the Cu<sup>2+</sup> and Ni<sup>2+</sup> ions in aqueous solution both by direct potentiometry and by potentiometric titration with EDTA. For the direct potentiometric determination, a calibration curve is used. This has been obtained by the variation of the electrode potential of the Cu<sup>2+</sup> and Ni<sup>2+</sup>-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<sub>3</sub>) and pH 6(6.5). The lower M<sup>2+</sup> concentration limit, which can be determined by direct potentiometry, is of 10<sup>-6</sup> M with electrodes 1, 2, 3 and 4. The electrodes were also tested for potentiometric titration with EDTA by using 10<sup>-3</sup> M titrated solutions of CuSO<sub>4</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>. This titration was based on well-defined titration curves and a potential change of 197.5 and 201.5 mV for electrodes 1 and 2 was observed (Fig. 3.). In the case of electrodes 3 and 4 much larger changes of 211 and 215 mV were obtained (Fig. 4.).

Samples of water originating from a water cleaning 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<sup>2+</sup>-selective electrode No. 3, based on [Cu(HL<sup>2</sup>)Cl(H<sub>2</sub>O)<sub>2</sub>].

In the same way, the content of nickel was determined by using the Ni<sup>2+</sup>-selective electrode

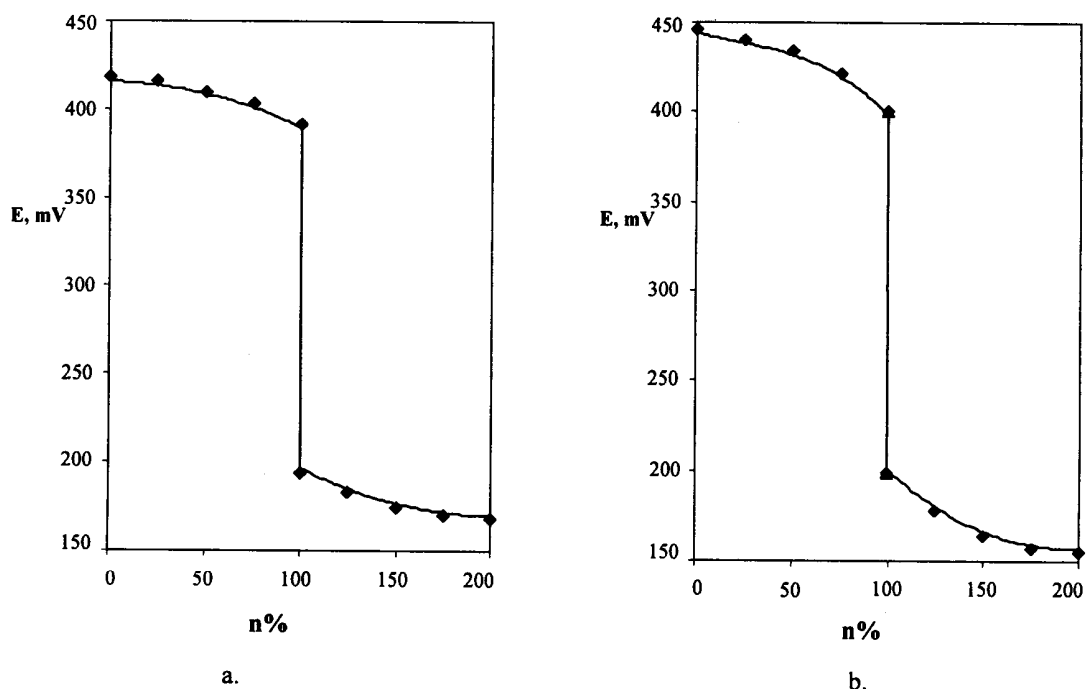


Fig. 3: The potentiometric titration curves of  $\text{Cu}^{2+}$  (a) and  $\text{Ni}^{2+}$  (b) ions with EDTA, obtained by using the ion-selective electrodes based on mixed complex with  $\text{HL}^1$ .

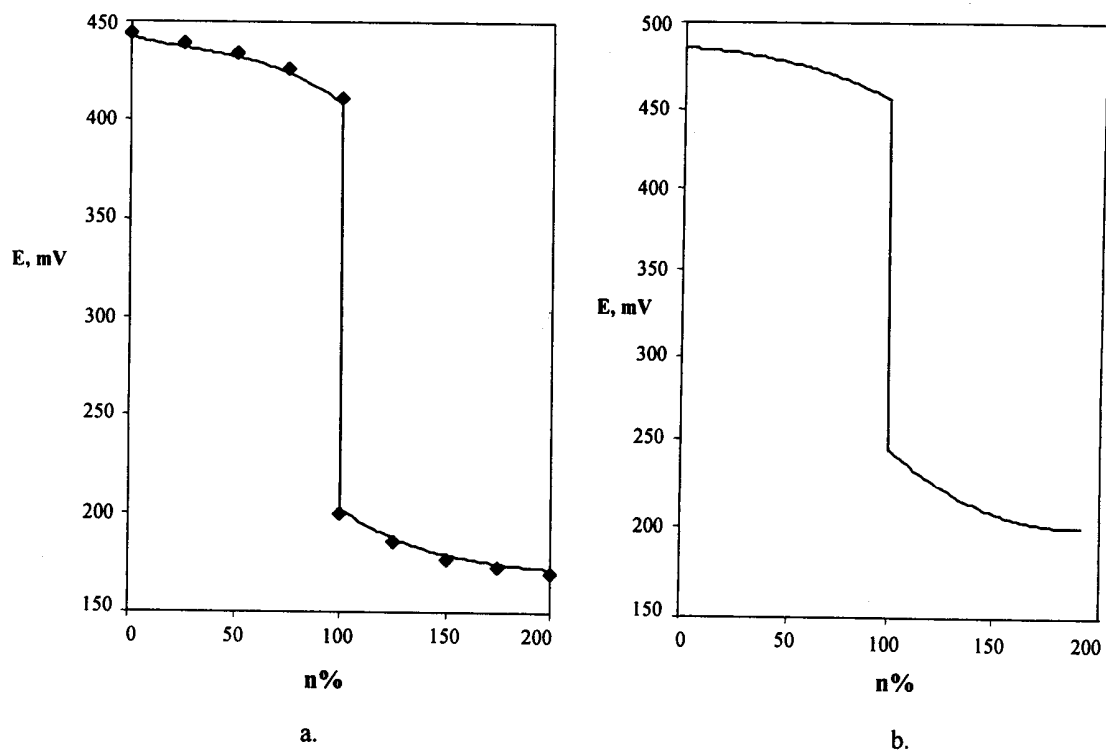
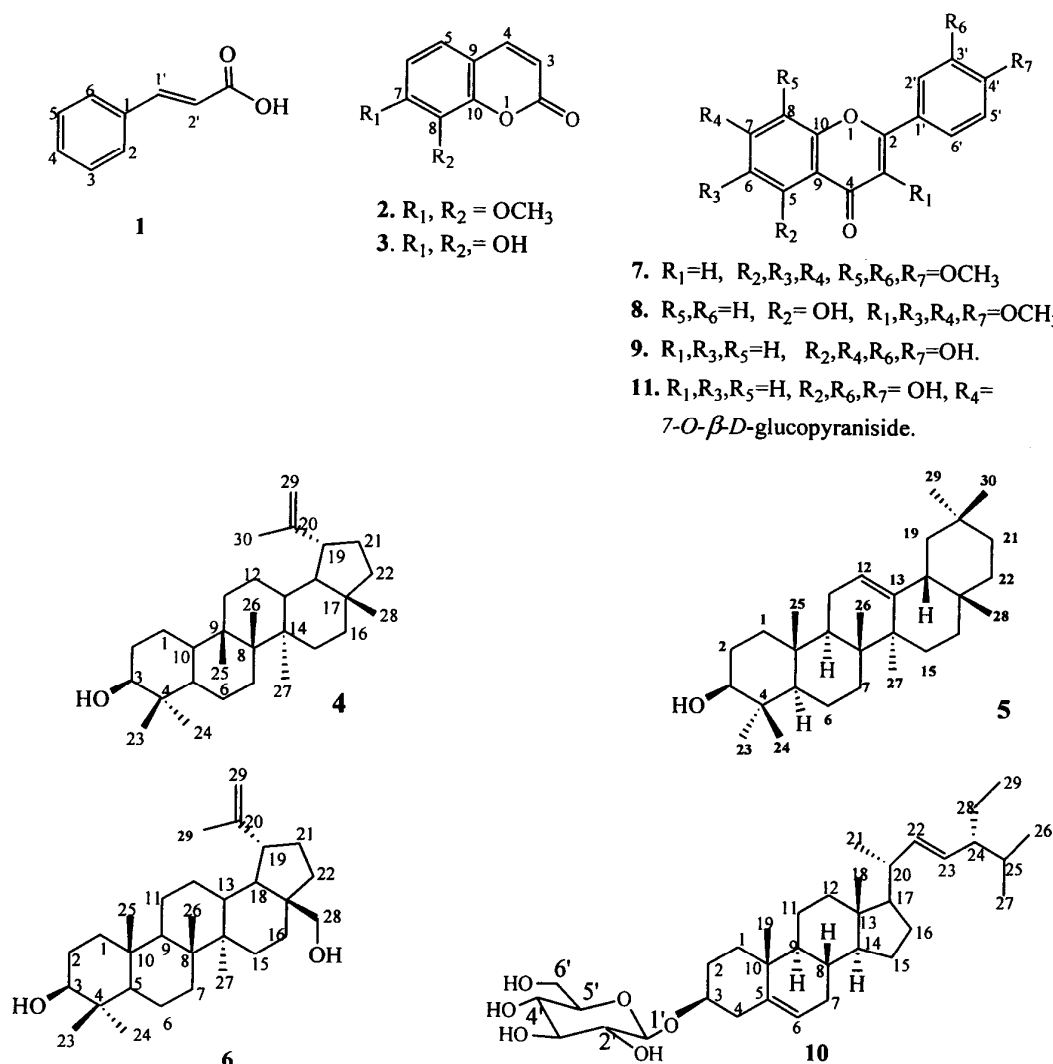


Fig. 4: The potentiometric titration curves of  $\text{Cu}^{2+}$  (a) and  $\text{Ni}^{2+}$  (b) ions with EDTA, obtained by using the ion-selective electrodes based on mixed complex with  $\text{H}_2\text{L}^2$ .

Fig. 1: Structure of compounds 1-11 isolated from *Daphne genkwa*.

10), 34.2 (C-7), 33.9 (C-22), 29.8 (C-21), 29.1 (C-16), 28.2 (C-23), 27.4 (C-2), 27.1 (C-15), 25.2 (C-12), 20.8 (C-11), 19.1 (C-30), 18.3 (C-6), 16.1 (C-25), 16.0 (C-26), 15.3 (C-24), 14.7 (C-27); HR-EI-MS,  $m/z$ : 442.3814 (calcd for  $\text{C}_{30}\text{H}_{50}\text{O}_2$ ; 442.3810), EI-MS (rel. int. %)  $m/z$ : 442  $[\text{M}]^+$  (14), 424 (100), 406 (14), 218 (22), 206 (28), 205 (11), 204 (7), 203 (6), 191 (7). The physical and spectral data showed complete agreement to those reported in the literature [15-16].

#### 5,6,7,8,3',4'-Hexamethoxyflavone (7)

Amorphous solid (9 mg), m.p. 113-114°C; UV ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) nm: 308 (3.9), 231 (3.06), 216 (4.11); IR (KBr)  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2930, 1711, 1615, 1580;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$ : 7.54 (1H, dd,  $J = 8.2, 2.2$  Hz, H-6'), 6.96 (1H, d,  $J = 8.2$  Hz, H-5'), 7.38 (1H, d,  $J = 2.2$  Hz, H-2'), 6.59 (1H, s, H-3), 3.92, 3.93, 3.94, 3.95 (12H, s, MeO-5, 6, 7, 8), 4.01, 4.08 (6H, s, MeO-3', 4');

The formulation of the mixed complex combinations of Cu(II) and Ni(II) whose solutions in nitrobenzene constitute the membrane on a graphite rod for the realized electrodes is as follows;

Electrode 1 :  $[\text{Cu}(\text{HL}^1)_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  ;

Electrode 2 :  $[\text{Ni}(\text{HL}^1)_2\text{Cl}_2] \cdot 2\text{H}_2\text{O}$  ;

Electrode 3 :  $[\text{Cu}(\text{HL}^2)\text{Cl}(\text{H}_2\text{O})_2]$  ;

Electrode 4 :  $[\text{Ni}(\text{HL}^2)\text{Cl}] \cdot 1/2\text{H}_2\text{O}$  ;

### Conclusions

Four electrodes with liquid membrane,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ -selective were prepared and characterized. The following characteristics were studied in this order: the electrodes response to  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ion concentration; the influence of pH on the response of the  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ - selective electrodes; the selectivity of the electrodes; the dynamic response and reproducibility of the electrodes; Also, the analytical applications of these electrodes have been taken into account 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 from industrial waters. For validation, all the samples were analysed by AAS technique and the results are in good agreement with those of direct potentiometric determinations. The electrodes with mixed complexes membranes have a better selectivity for interfering ions and a much larger potential rise on the titration curve. From this reason, they are of practical interest for copper and nickel ions determinations from solutions that are more dilute and from industrial waters, respectively.

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