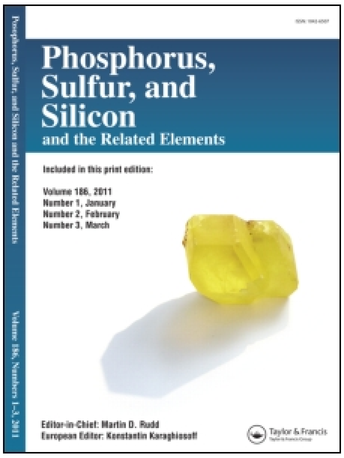

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Nitrocellulose Membrane, Modified by RC(S)NHP(X)(O*i*Pr)$_2$ (X = S, R = PhNH; X = O, R = PhNH, Ph), for Sorption Extraction of Cobalt Cations

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NITROCELLULOSE MEMBRANE, MODIFIED BY $RC(S)NHP(X)(O\textit{i}Pr)_2$ (X = S, R = PhNH; X = O, R = PhNH, Ph), FOR SORPTION EXTRACTION OF COBALT CATIONS

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The complexation and extraction properties of $RC(S)NHP(X)(OiPr)_2$ [X = S, R = PhNH (HL^I); X = O, R = PhNH (HL^{II}), Ph (HL^{III})] towards cobalt cations were studied. The nitrocellulose membrane was used as a carrier for HL^{I-III}. The maximal degree of extraction of cobalt cations from an aqueous solution is observed at pH = 7.8–8.4. It was established that complexes formed are kept in a water solution on a surface of the carrier and washed away in 96% aqueous ethanol. The membrane modified by HL^I allows extraction and concentration of Co(II) selectively, while the modification by HL^{III} leads to the selective extraction of Co(III).

Keywords Cobalt; complex; membrane extraction; thioamide; thiourea

INTRODUCTION

The ways to analyze objects of the ecological control with sorption extraction and concentration of components from solutions with their subsequent definition by atomic absorption, atomic emision, mass-spectrometry, and also electrochemical definition of metal ions is of interest.[1–7] In previous works,[1,2] we presented the methods of definition of the Ni(II), Zn(II), and Cd(II) cations by the preliminary concentration on the chelating sorbent and their subsequent determination by the flame-atomic absorption technique. The influence of pH and the volume of solution and eluent, and the speed of the solution and eluent injection were studied. The degree of extraction *R* is more than 95%. The limits of the Zn(II) and Cd(II) cations are 17.2 and 15.0 ng/mL, respectively. The technique and test-scale is developed for the definition of Zn(II) with limits of detection of 0.011 and 0.018 ng/mL.[3]

The approach to the analysis of platinum-containing materials has been discussed, including high-temperature dissolution of tests in acids under action of microwave radiation, the sorption concentration of the noble metals on complexing sorbents, and their definition by various physical methods (mass-, atomic-absorption, atomic-emision spectrometry).[4]

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In other works,[5,6] the techniques of inversion-voltammetric definitions of the Cu(II) ions are presented. The opportunity of definition of Cu(II) at ≥ 0.007 μg/L at 40-fold exess of arsenic has been shown.[5] The minimal determined concentration of copper at $I = 1 \times 10^{-3}$ A, $t = 10$ sec. is 5×10^{-7} mol/L.[6] On the basis of voltammetric study of the electrochemical behavior of Pd(II) and Pt(IV) on a background of 1 M HCl + 0.1 M ethelenediamine hydrochloride on the carbon electrode, the optimum conditions of the simultaneous definitions of 0.2–3 mg Pd(II) and Pt(IV) were established.[7]

In this article, we present the technique of the sorption extraction and concentration of Co(II) and Co(III) on the nitrocellulose membrane modified by complexing agents RC(S)NHP(X)(O*i*Pr)$_2$ [X = S, R = PhNH (**HL^{I}**); X = O, R = PhNH (**HL^{II}**); Ph (**HL^{III}**)] (Chart 1).

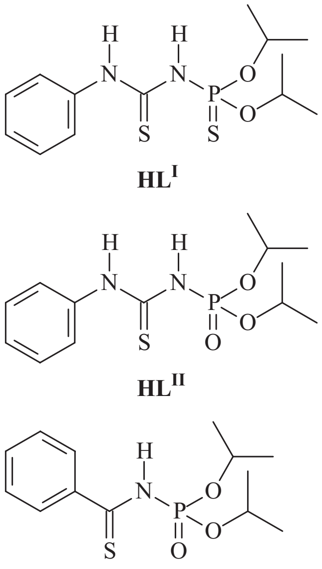

Chart 1

RESULTS AND DISCUSSION

Earlier it was established that Co(II) with RC(S)NHP(X)(O*i*Pr)$_2$ ligands forms complexes of the type [**CoL$_2$**].[8,9] The degree of oxidation of the central cation in solutions was not estimated. In the present research, it is shown that depending on the nature of the donor atoms and the substituent at the C=S group, the cobalt ion can be in degrees of oxidation +2 or +3 in solutions. For this purpose, electronic spectra and electroreduction of cobalt complexes with **HL$^{I–III}$** have been investigated.

The X-ray data testify to formation of the unique complex form of the structure [**CoL$^{I}_{2}$**] containing a tetrahedral complex core.[9] The degree of oxidation of the central atom was confirmed by the cyclic voltammetry. The two-electronic irreversible peak at −1.17 V belongs to the electroreduction of the coordinated Co^{2+} to Co^{0} (Figure 1).[10,11]

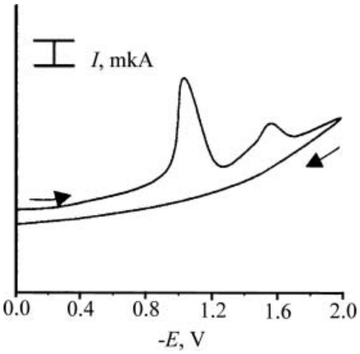

Figure 1 Cyclic voltammogram of [$\mathbf{CoL_2^{I}}$].

The reaction of Co(II) with $\mathbf{HL^{II}}$ leads to the formation of the mixture of complexes [$\mathbf{Co^{2+}L_2^{II}}$] and [$\mathbf{Co^{3+}L_3^{II}}$]. The cyclic voltammogram shows a pair of one-electron cathode-anode peaks at -0.83 and -0.62 V, corresponding to the reversible reduction of Co^{3+} to Co^{2+},[10,11] and one two-electron cathode peak at -1.15 V for the reduction of Co^{2+} to Co^0 (Figure 2).[10,11]

The phosphorylated thioamide $\mathbf{HL^{III}}$ forms three stable complexs [$\mathbf{Co^{2+}L_2^{III}}$], [$\mathbf{Co^{2+}(HL^{III})_2L_2^{III}}$], and [$\mathbf{Co^{3+}L_3^{III}}$].[8]

According to the cyclic voltammetry, the degree of oxidation of cobalt in [$\mathbf{Co(HL^{III})_2L_2^{III}}$] (Figure 3, curve 2) and [$\mathbf{CoL_3^{III}}$] (Figure 3, curve 3) is +2 and +3, respectively. The electrochemical reduction of [$\mathbf{CoL_3^{III}}$] is possible to present as follows:

$$\left[\mathbf{Co}^{3+}\mathbf{L}_3^{\mathbf{III}}\right] + \mathrm{e} \rightarrow \{\mathbf{Co}^{3} + \mathbf{L}_3^{\mathbf{III}}\}^- \quad (\mathrm{E_k} = -0.8\,\mathrm{V})$$

$$\left\{\mathbf{Co}^{3+}\mathbf{L}_3^{\mathbf{III}}\right\}^- \rightarrow \left[\mathbf{Co}^{2+}\mathbf{L}_2^{\mathbf{III}}\right] + \mathbf{L}^-$$

$$\left[\mathbf{Co}^{2+}\mathbf{L}_2^{\mathbf{III}}\right] + 2\mathrm{e} \rightarrow \mathrm{Co}^0 + 2\mathbf{L}^- \qquad (\mathrm{E_k} = -1.05\,\mathrm{V})$$

The cyclic voltammogram of [$\mathbf{CoL_2^{III}}$] (Figure 3, curve 1) contains a pair of one-electron cathode-anode peaks corresponding to the reversible reduction of Co^{3+} to Co^{2+} and one two-electron cathode peak for the reduction of Co^{2+} to Co^0. The first reversible peak is explained by the partial oxidation of [$\mathbf{CoL_2^{III}}$] to [$\mathbf{CoL_3^{III}}$] through the formation of

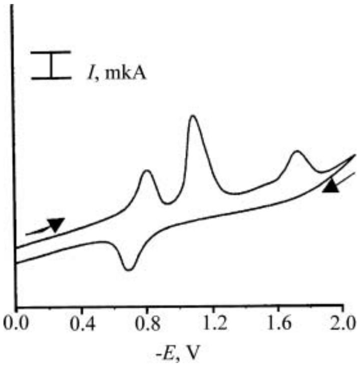

Figure 2 Cyclic voltammogram of [$\mathbf{CoL_2^{II}}$].

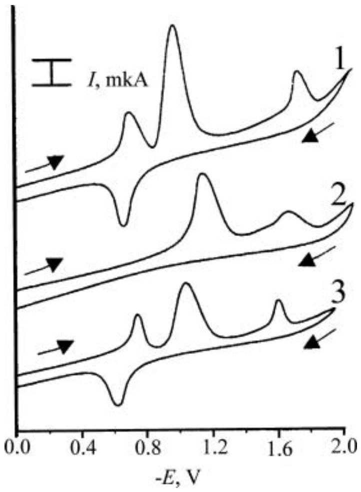

Figure 3 Cyclic voltammograms of $[\mathbf{CoL_2^{III}}]$ (curve 1), $[\mathbf{Co(HL^{III})_2L_2^{III}}]$ (curve 2), and $[\mathbf{CoL_3^{III}}]$ (curve 3).

the unstable low-spin Co(II) complex of the structure $[\mathbf{Co(ROH)_2L_2^{III}}]$ (R = H, alkyl) in the aqueous alcohol media.[8]

Complexation of cobalt cations by the thioureas $\mathbf{HL^{I}}$ and $\mathbf{HL^{II}}$, fixed on the polymeric carrier on the basis of cellulose nitrate, was studied. By the method of atomic absorption, it was established that the maximal extraction of cobalt cations from water solutions by the complexation with immobilized ligands occurs at pH $\sim$ $pK_{\mathbf{HL}}$ (Table I). Dependence of the extraction on sorption time is presented in Figure 4.

Difference in the time of extraction of cobalt is caused by the distinction in lability of the salts used for the preparation of model water solutions. The high lability of $Co(NO_3)_2$ causes small time of extraction of Co^{2+} (5 min), and the inertness of $[Co(NH_3)_6]Cl_3$ leads to the increase in time of extraction of Co^{3+} up to 15 min under the same experimental conditions. Data of the extraction and concentration are presented in Table II. The values of distribution of cobalt cations are higher than at liquid extraction.[12,13]

In studying the properties of the modified polymeric carrier, it was revealed that complexes formed in water are kept at the surface of the carrier and washed away in a solution of 96% ethanol, and the nitrocellulose matrix is not destroyed.

According to the cyclic voltammetry, it was established that the modification of the membrane by $\mathbf{HL^{I}}$ allows for extracting and concentrating of Co^{2+} selectively (Figure 5, curve 1). The cyclic voltammogram of the ethanolic solution of $[\mathbf{CoL^{I}_2}]$ is completely similar to the voltammogram of the isolated complex (Figure 1). Using $\mathbf{HL^{II}}$ as the modifying agent leads to the selective extraction of Co^{3+} (Figure 5, curve 2).

Table I Data of $pK_{\mathbf{HL}}$, pH, and the degree of extraction *R* for the thioureas $\mathbf{HL^{I}}$ and $\mathbf{HL^{II}}$

	$pK_{\mathbf{HL}}$	pH	*R*, %
$\mathbf{HL^{I}}$	8.28 ± 0.03	8.1–8.4	45
$\mathbf{HL^{II}}$	8.07 ± 0.03	7.8–8.2	50

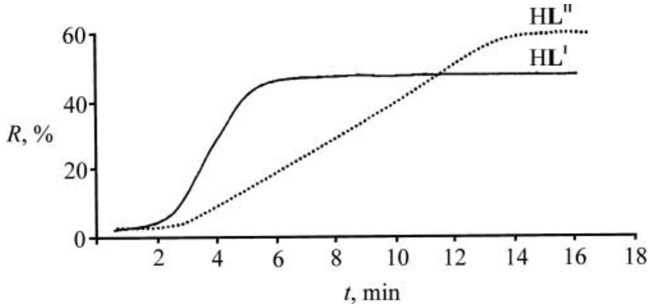

Figure 4 Degree of extraction of cobalt cations from the water solution.

However, the voltammograms of [$\mathbf{CoL_3^{II}}$] (Figure 3, curve 3) and the complex transferred into the ethanolic solution from the nitrocellulose membrane are considerably different. This can be caused by the structure of complex, in the form of which the Co^{3+} cation is extracted from the water solution of $[Co(NH_3)_6]Cl_3$. Ammoniac complexes of Co(III) are destroyed by the sulfur-containing compounds.[14] Presence of the "hard" oxygen donor atom in the ligand structure also provides the advantage of $\mathbf{HL^{II}}$ coordination towards the "hard" Co(III) cation. Influence of the phenyl substituent also brings the contribution to the stabilization of the complex. We suppose that in this case, the Co(III) cation is extracted from the water solution in the form of heteroligand complex, irreversibly reduced on a mercury-film electrode.

The data obtained were used for the creation of methods for the selective electrochemical detection of Co^{2+} and Co^{3+} in the model solutions with the preliminary extraction and accumulation of cations in the form of the corresponding complexes on the nitrocellulose membrane. Dependence of the degree of extraction of Co^{2+} and Co^{3+} (*R*) on the nature of the ligand is presented in Figure 6.

In summary, it was established that the thiourea $\mathbf{HL^{I}}$ is appropriate for the extraction of Co(II), while the thioamide $\mathbf{HL^{III}}$ is selective towards Co(III). Phosphorylated thiourea $\mathbf{HL^{II}}$ forms an inseparable mixture of complexes with Co(II) and Co(III). Thus, the selectivity of the cobalt cation extraction depends on the nature of the donor atom X and the substituent at the C=S group of the chelating backbone RC(S)NHP(X).

The ligands have been used as modifying agents of the nitrocellulose membrane, and it was established that complexing forms are kept on a surface of the carrier and washed away in 96% aqueous EtOH and the matrix is not destroyed.

Table II Data of the extraction degree *R* and coefficient of concentration *S* of cobalt cations ($C_{HL} = 3 \times 10^{-3}$ mol/L, $t_{ex.} = 5$–15 min, $n = 2$ – number of extraction)

	$pH_{ex.}$	*R*, %	*S*	C, mol/L
$\mathbf{HL^{I}}$	8.28 ± 0.03	8.1–8.4	45	3×10^{-7}–5×10^{-4}
$\mathbf{HL^{II}}$	8.07 ± 0.03	7.8–8.2	50	8×10^{-8}–5×10^{-4}

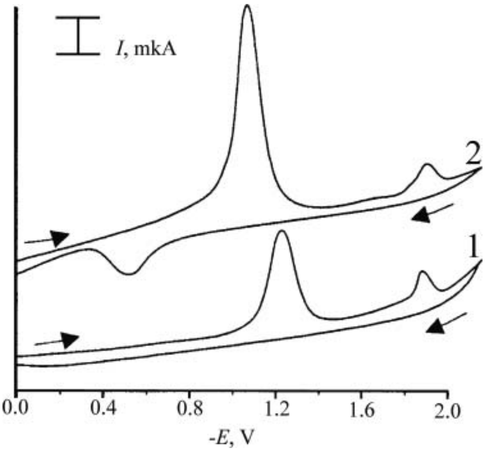

Figure 5 Cyclic voltammograms of cobalt complexes with $\mathbf{HL^{I}}$ and $\mathbf{HL^{II}}$ transferred into ethanolic solution from the nitrocellulose membrane.

EXPERIMENTAL

For the preparation of solutions, $Co(NO_3)_2$ and $[Co(NH_3)_6]Cl_3$ were used. The range of concentrations of the cobalt salts was 1×10^{-11}–1×10^{-2} mol/L. For the modifying agents, *N*-phenyl-*N′*-diisopropoxythiophosphorylthiourea PhNHC(S)NHP(S)(O*i*Pr)$_2$ ($\mathbf{HL^{I}}$), *N*-phenyl-*N′*-diisopropoxyphosphorylthiourea PhNHC(S)NHP(O)(O*i*Pr)$_2$ ($\mathbf{HL^{II}}$), and *N*-diisopropoxyphosphorylthiobenzamide PhC(S)NHP(O)(O*i*Pr) ($\mathbf{HL^{III}}$) were used.[8,9,15] The concentration of the reagents in the polymeric carrier was 1×10^{-3} mol/L. As a matrix for modification, a polymeric membrane on the basis of nitrate of cellulose of type «kolloksiline», containing about 11.5–12% nitrogroups, was used.

For pH-metric titration at 25 ± 0.05°C, the pH-150-M (Bjelorussia) device was used. Accuracy of the pH definition made to 0.01. As a display, the calibrated glass electrode was used as the indicator. The value of pH was calculated according to the equation $pH = pH_{exp.} - \Delta$ ($\Delta = -0.68 \pm 0.09$).

Electrochemical research was conducted on an SVA-1BM (Bulgaria) voltammetric system with a three-electrode cell at 25 ± 0.05°C under argon atmosphere. As a working electrode, the mercury-film electrode with a silver substrate with the hydrochloric bridge was used. The saturated silver-chloride electrode was used as the reference, and the auxiliary

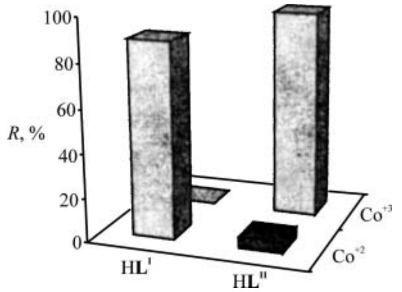

Figure 6 Degree of extraction of the Co(II) and Co(III) cations by the ligands $\mathbf{HL^{I}}$ and $\mathbf{HL^{II}}$.

electrode was a platinum wire. Cyclic voltammograms were recorded on a background of 0.1 M $LiClO_4$ in 96% aqueous isopropanol or ethanol. Speed of the linear development of potential was 200–500 mV/sec. The area of measurement of potentials was from -0.145 V to -2.0 V.

The number of electrons (n) participating in the electrochemical reaction was determined by comparison with height of the first lone-electronic wave of benzophenone in view of the amendment on distinction of molecular weights. Value of n was determined by the following equation:

$$n_{\mathrm{x}} = \left(I_{(\mathrm{lim})\mathrm{X}} \cdot n_{\mathrm{st.}} \cdot M_{\mathrm{st.}}^{1/6} \cdot C_{\mathrm{st.}}\right) / \left(I_{(\mathrm{lim.})\mathrm{st.}} \cdot n_{\mathrm{X}} \cdot M_{\mathrm{X}}^{1/6} \cdot C_{\mathrm{X}}\right)$$

where $I_{(\mathrm{lim.})\mathrm{X}}$ and $I_{(\mathrm{lim.})\mathrm{st.}}$ are limiting currents; M_{X} and $M_{\mathrm{st.}}$ are molecular weights; and C_{X} and $C_{\mathrm{st.}}$ are concentrations of the investigated compound (X) and standard compound (st.).

Modified Sorbent

The modified sorbent was made by dissolving nitrocelluloses (0.06 g) in a toluene (0.25 mL)/ethylacetate (1.75 mL) solution. The modifying compound, preliminarily dissolved in toluene (0.75 mL), was added. The mixture was stirred for 3–4 min and then transferred to a Petri dish ($d = 90$ mm). The matrix was dried, washed by deionized water, and separated from the dish.

Sorption Extraction

In static conditions, the determined cobalt cation was sorbated on a surface of the nitrocellulose membrane in the form of complexes with a modifying reagent. For this purpose, the modified membrane was placed in water solution (30 mL) of the metal salt with a concentration of 1×10^{-11}–1×10^{-2} mol/L (pH = 1.65–9.18) for 20–120 min. Then the membrane was taken out of the solution, and the remaining concentration of cobalt cations was measured by atomic absorption spectrophotometry on a Hitachi Z-6100 Polarized Zeeman Atomic Absorption Spectrophotometer (Hitachi, Japan) using the calibration curve described by the equation $A = 0.00523 + 199.47C_{\mathrm{M}}$.

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