

Extraction in the Ni(II)—Organic Ligand—Polymethine Dye—Organic Solvent System and its Application for the Spectrophotometric Determination of Nickel

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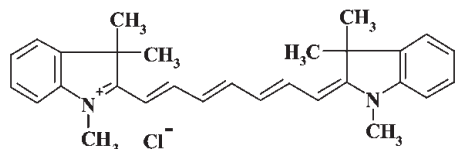
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Complex formation and extraction of Ni(II) with 1,3,3-trimethyl-2-[7-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)-hepta-1,3,5-trienyl]-3*H*-indolium chloride polymethine dye reagent and 1-nitroso-2-naphthol as organic ligand have been studied. The optimum conditions have been found: pH 7.2–9.5, $c(\text{dye reagent}) = 1.25 \times 10^{-4} \text{ mol dm}^{-3}$, $c(1\text{-nitroso-2-naphthol in toluene}) = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$. The Beer's law is obeyed for nickel(II) concentration up to 5.0 mg dm^{-3} . The effect of various foreign ions was examined. The new, simple, rapid, and sensitive (the molar absorptivity is $6.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) procedure of Ni(II) determination has been suggested.

Nickel is widely used in industry. Moreover, nickel is a biologically consequential microelement. Several spectrophotometric reagents were reported for the spectrophotometric determination of nickel [1–3]. Each of described reagents has advantages and disadvantages. Comparison of existing methods for the spectrophotometric determination of nickel is shown in Table 1.

The aim of this work was the investigation of the extraction in the nickel—organic ligand—polymethine dye—organic solvent system and its application for the spectrophotometric determination of Ni(II). The 1,3,3-trimethyl-2-[7-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)-hepta-1,3,5-trienyl]-3*H*-indolium chloride (DITC) reagent



has been investigated. The dye reagent was synthesized by Professor I. L. Mushkalo (the Institute of

Organic Chemistry, Kiev). The acid-base and spectrophotometric properties of this dye reagent were studied [4, 5].

EXPERIMENTAL

All chemicals used were of analytical reagent grade. Derivatives of benzene (toluene, benzene, *p*-xylene, ethylbenzene, and butylbenzene) for UV spectroscopy have been tested as extractants. Distilled water was used throughout the experiment. A 0.01 mol dm^{-3} stock solution of nickel(II) was prepared by dissolving precise amount of nickel sulfate in water. The concentration of Ni(II) was standardized complexometrically. The working solution containing $4 \times 10^{-4} \text{ mol dm}^{-3}$ of Ni(II) was prepared by dilution of the stock solution prior to use. A $1 \times 10^{-3} \text{ mol dm}^{-3}$ aqueous solution of DITC reagent was prepared by dissolving precise amount of its chloride salts recrystallized from methanol. The acidity of aqueous medium was set by the addition of $\text{CH}_3\text{COOH}-\text{NH}_4\text{OH}$ (0.1 mol dm^{-3}) buffer solutions. The solutions of ligands containing required concentration of 1-nitroso-2-naphthol or 2-nitroso-1-naphthol were prepared by dissolution in organic solvent. An SF-18 scanning spectrophotometer was used for the recording of the absorbance spectra

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Table 1. Comparison of Existing Methods for the Spectrophotometric Determination of Nickel

Reagent [Ref.]	Aqueous phase	Organic phase	λ/nm	$\varepsilon \times 10^{-4}$
				$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
Dimethylglyoxime [1]	1 % NH_4OH	Diethyl ether	553	0.16
α -Furyldioxime [2]	pH 7.5–9.0	CCl_4	436	1.82
α -Benzenedioxime [2]	pH 8.8–11.4	Chloroform	450	
Rhodamine 6G and 8-hydroxyquinoline [3]	pH 8	Benzene	560	
This paper (Table 2)	pH 7.2–9.5	Toluene	750	3.7
		Benzene	750	6.3

with glass cells of 3 mm path length. The pH values of solutions were measured by pH-meter pH-121 (Gomel) with glass electrode.

General Procedure

The extraction was carried out in the graduated test tubes at room temperature. 0.5 cm^3 of $4 \times 10^{-4} \text{ M-Ni(II)}$ solution, 1 cm^3 of buffer solution, and 0.5 cm^3 of $1 \times 10^{-3} \text{ M-DITC}$ were introduced into the test tubes and the solution was brought to a final volume of 5 cm^3 . Next, Ni(II) was extracted by 5 cm^3 of the organic solvent containing required concentration of ligand for 1 min. After the extraction, the organic phase was separated, centrifuged, and the absorbance was measured against that of the blank, with cells of 3 mm path length. The blank test was prepared in the same conditions without addition of nickel.

Method

The weight of sample (multivitamin tablet) was put into the silica beaker and dissolved in 40 cm^3 of water, filtered and transferred to separation funnel. 1 cm^3 of 0.01 M-NaF (for masking), 5 cm^3 of buffer solution with pH 8.0, and 1 cm^3 of $1 \times 10^{-3} \text{ M-DITC}$ were added. After the addition of each reagent, the solution was mixed thoroughly. Next, 5 cm^3 of $1.25 \times 10^{-3} \text{ M-(1-nitroso-2-naphthol in toluene)}$ was added and the mixture was extracted for 1 min. The organic phase was separated, and the absorbance was measured at 750 nm, with cells of 3 mm path length. The calibration plot was constructed under the same conditions.

RESULTS AND DISCUSSION

In order to find optimum conditions for the complexation and extraction of Ni(II) with DITC reagent, the nature and concentration of ligand, the concentration of DITC, the influence of medium acidity, and the nature of extractant affecting the absorbance of coloured extracts were investigated.

As follows from Fig. 1 the optimum concentration of ligand is $(0.5\text{--}2.0) \times 10^{-3} \text{ mol dm}^{-3}$ for 1-nitroso-2-naphthol and $(0.6\text{--}2.0) \times 10^{-3} \text{ mol dm}^{-3}$

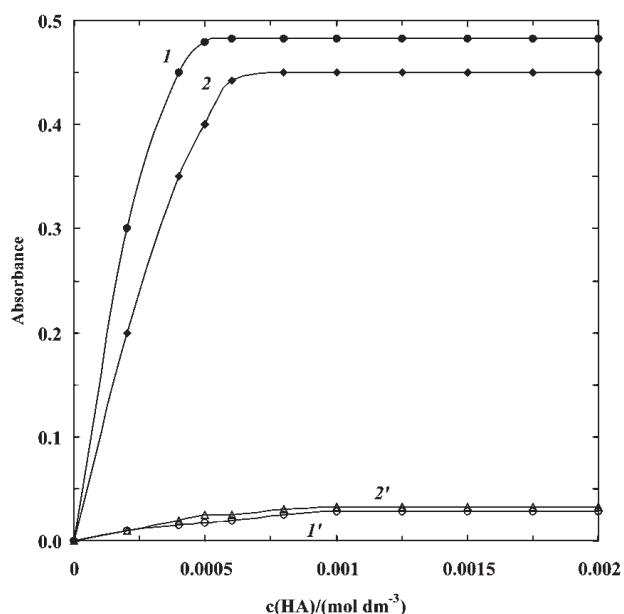


Fig. 1. Influence of the concentration of 1-nitroso-2-naphthol (I, I') and 2-nitroso-1-naphthol (2, 2') on the extraction of Ni(II) ion associates with DITC. $4 \times 10^{-5} \text{ M-Ni(II)}$; $1 \times 10^{-4} \text{ M-DITC}$; pH 8.0; I', 2' – blank tests.

for 2-nitroso-1-naphthol. Due to the higher value of the molar absorptivity, the 1-nitroso-2-naphthol was used as ligand for further experiments. Some theoretical aspects of the complexation were discussed [6]. The appropriate pH for the complexation and extraction can be predicted from the distribution diagram of Ni(II), DITC, and ligand species (Fig. 2). The extraction of nickel is the highest when the medium acidity ranges from pH 7.2 to pH 9.5 for 1-nitroso-2-naphthol (Fig. 3). In this case, Ni^{2+} , R^+ , and L^- predominate in an aqueous solution. The influence of the DITC concentration on the extraction of the Ni(II) was studied in the range from 1×10^{-6} to $3 \times 10^{-4} \text{ mol dm}^{-3}$ (Fig. 4). The optimum concentration of DITC is $(0.7\text{--}2.0) \times 10^{-4} \text{ mol dm}^{-3}$. The absorption spectra of the nickel(II) ion associate were recorded during the extraction by various solvents and the main analytical characteristics were calculated (Table 2). The best extractants were the aromatic hydrocarbons (benzene and toluene) with very high extractability

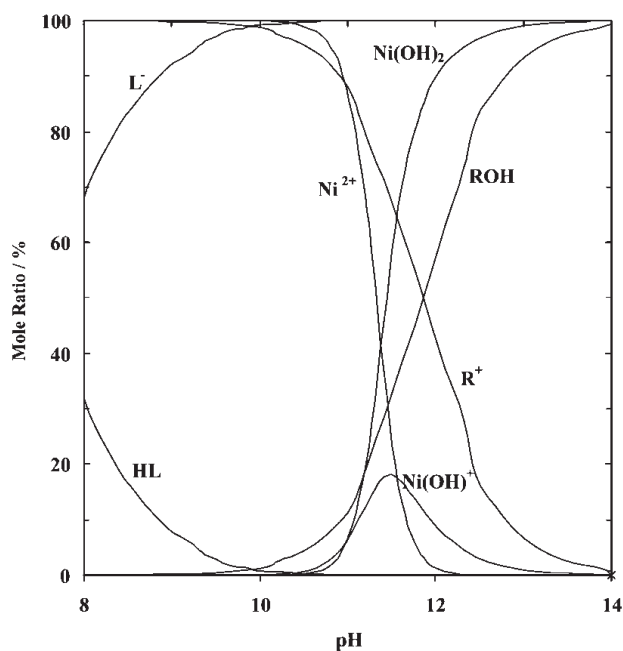


Fig. 2. Distribution diagram of Ni(II), DITC, and ligand species in an aqueous solution.

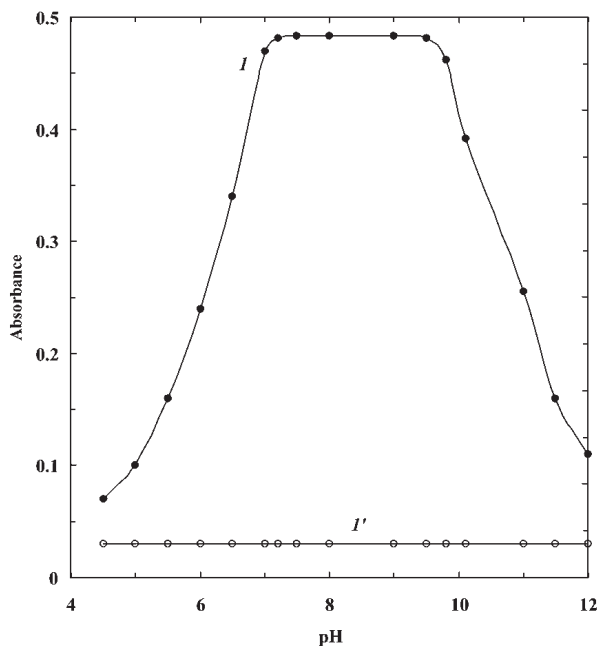


Fig. 3. Influence of the pH on the extraction of Ni(II) ion associates with DITC. 4×10^{-5} M-Ni(II); 1×10^{-4} M-DITC; 1×10^{-3} M-(1-nitroso-2-naphthol in toluene); I' – blank test.

of the ion associates and minimum extraction of the blank. Toluene was used as extractant due to its lower toxicity.

The mole ratio of Ni(II), ligand, and dye reagent in the extracted coloured ion associate has been determined by various spectrophotometric methods. It was

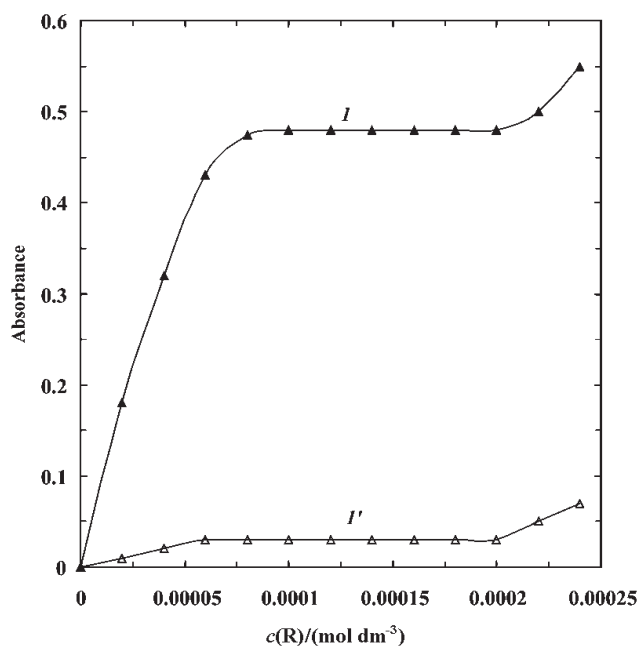
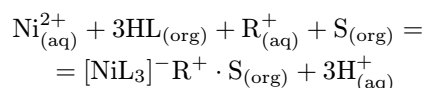


Fig. 4. Influence of the concentration of DITC on the extraction of Ni(II) ion associates. 4×10^{-5} M-Ni(II); pH 8.0; 1×10^{-3} M-(1-nitroso-2-naphthol in toluene); I' – blank test.

Table 2. Spectrophotometric Characteristics of the Extracted Nickel Ion Associates with DITC. 4×10^{-5} M-Ni(II), 1.6×10^{-4} M-DITC, pH 8.0, 1.25×10^{-3} M-(1-nitroso-2-naphthol)

Organic phase	λ/nm	$\epsilon \times 10^{-4}$
		$\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$
Toluene	750	3.7
Benzene	750	6.3
<i>p</i> -Xylene	748	3.2
Ethylbenzene	748	2.9
Butylbenzene	747	2.3

found that the $n(\text{Ni}) : n(\text{ligand}) : n(\text{DITC})$ ratio is 1 : 3 : 1. The extraction mechanism may be expressed as follows



where R^{+} is the cation of investigated reagent, L^{-} is the anion of ligand, S is toluene, (aq) is the aqueous phase, and (org) is the organic phase.

The stability constant calculated using the following equation

$$\beta = \frac{[\text{NiL}_3\text{R}] [\text{H}^{+}]^3}{[\text{Ni}^{2+}] [\text{HL}]^3 [\text{R}^{+}] [\text{S}]}$$

Table 3. Determination of Ni(II) in Multivitamin Tablets ($n = 5$, Average)

Sample	$m(\text{Ni})/\mu\text{g}$		Recovery
	This paper	AAS	%
1	5.1 ± 0.2	4.9	102
2	4.9 ± 0.2	5.0	98

The extraction constant is $(1.62 \pm 0.21) \times 10^4$. The stability constant is $\beta = 4.9 \times 10^7$.

Based on the obtained results, the new, simple, and sensitive extractive spectrophotometric procedure for Ni(II) determination has been suggested. In comparison with other spectrophotometric methods for the nickel determination, the suggested method is more sensitive (the molar absorptivity is $6.3 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The extraction equilibrium is established within 30 s and the absorbance of the extracts is stable for more than 6 h.

The absorbance of the coloured extracts obeys the Beer's law in the range $0.05\text{--}5.0 \text{ mg dm}^{-3}$. The limit of detection determined statistically from a blank test is 0.008 mg dm^{-3} . The effect of various foreign ions was examined. The determination of Ni(II) does not interfere with the 500—1000-fold of the alkaline elements, 100—200-fold of Co(II), Mn(II), Zn(II), Cr(III), Cd(II), Pb(II), Fe(III), and Al(III). Inter-

ference occurs with Au(III), Hg, Mo(VI), Mn(VII), Cr(VI), Sb(V), Tl(III), Re(VII), W(VI), and SCN^- , I^- . The accuracy of the determination was verified using the AAS method. Satisfactory results were obtained with relative standard deviation 5 % for 5 measurements. The method was used for the determination of nickel in the multivitamin tablet. The given results are shown in Table 3.

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