STUDY OF COMPLEX FORMATION OF Ni (II) WITH 4- (2´, 3´, 4´-TRIHYDROXYPHENYL) -3-SULPHO-5-NITROPHENYLAZO BENZENE IN THE PRESENCE OF CATIONIC SURFACE ACTIVE SUBSTANCES

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Abstract. The effect of the third components of cationic surfactants - chloridecetylpyridinium (CPCl), cetylpyridinium bromide (CPBr), cetyltrimethylammonium bromide (CPMABr) for complexation of nickel (II) with 4- (2´, 3´, 4´-trihydroxyphenyl) -3-sulfo-5-nitrophenylazo benzene (R). Same- (NiR) and mixed-ligand complex compounds (Ni (II) -RCPCl, Ni (II) -RCPBr and Ni (II) -RCPMABr) are formed at pH 6, 3, 3 and 4, respectively. All complexes are formed immediately after mixing the solutions of the components and differ in stability. The ratio of the reacting components in the composition of same- (1: 1) and mixed-ligand (1: 1: 1) complexes are established. The interval of obedience to Beer's law is determined. The coefficients of the calibration curve equation are determined by the method of least squares. Complexation of nickel (II) is expressed by linear dependence of $A = f (c)$ is. Stability constants of same- (NiR) and mixed-ligand complexes (Ni (II) -RCPCl, Ni (II) -RCPBr and Ni (II) -RCPMABr) are calculated. Under optimal conditions of complexation, Ni-R was titrated with a solution of third components (CPCl, CPBr and CPMABr) by conductometric method. The influence of foreign ions on complexation of nickel (II) with R in the absence and in the presence of third components was studied.

1. Introduction

Compared to other transition metals, nickel is moderately toxic element and still at low concentration causes a general toxic effect on the human body, causing diseases of the nasopharynx and lungs, malignant tumors and dermatological discs. It was assumed that nickel is necessary for plants and some domestic animals (Shabani *et al.,* 2008; Kumar *et al.,* 2004; Sarma *et al.,* 2008; Mardanova *et al.,* 2018). Nickel-containing wastewater is harmful after penetration into water. This fact explained the importance of monitoring the concentration of nickel in food. Atomic absorption spectrometry of a flame and graphite furnace and spectrophotometric methods provide accurate and fast determination of nickel in plants and food (Li *et al.,* 2002; Maharramov *et al.,* 2015; Hu *et al.,* 2003; Bai *et al.,* 2010; Barman & Barua, 2009; Li & Zhai, 2014; Ranganath *et al.,* 2015; Macit et al., 2000). However, very often a direct definition cannot be applied due to the low concentration of analyzed or matrix interferences.

In the presented work, the complexation of nickel (II) with 4- (2´, 3´, 4´

trihydroxyphenyl) -3-sulfo-5-nitrophenylazo benzene (R) in the presence ofcationic surfactants - cetylpyridinium chloride (CPCl), bromide cetylpyridinium (CPBr), cetyltrimethylammonium bromide (CPMABr) was investigated by photometric method.

2. Experimental part

*Solutions and reagents***:** The reagent was synthesized according to the method (Igumenov *et al.*, 1982; Busev, 1972), its composition and structure established by the methods of elemental analysis and IR spectroscopy.
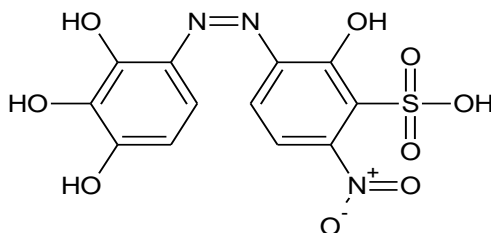
We used $1 \cdot 10^{-3}$ M ethanol solution of the reagent and water-ethanol solutions (3: 7) of the third components, which were prepared by dissolving their exact weighed portions. A solution of nickel (II) ion was prepared from $NiSO_4 \cdot 7H_2O$ by dissolving an accurately weighed portion in water. Acetate-ammonia buffer solutions were used to create the required acidity. All reagents used are of analytical grade at least.

Apparatus: The absorbances of the solutions was measured on a Lamda 40 spectrophotometer (Perkin Elmer) and a KFK-2 photocolorimeter in a cuvette with a layer thickness of 1 cm. The acidity of the buffer solutions was measured on a PHS-25 ion meter adjusted with standard buffer solutions. The specific electrical conductivity of the solutions was measured on a KEL-1M2 conductometer.

3. Results and discussions

We found that R (in ethyl alcohol) at pH 6 has an absorption band with a maximum (λ= 495 nm). Under these conditions, it forms a complex with nickel (II) (absorption maximum at 525 nm). The study of the obtained complex in the presence of cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr), cetyltrimethylammonium bromide (CPMABr) in a wide pH range showed that under the influence of the third component, a mixed-ligand complex of Ni (II) R-CPCl with a maximum light absorption λ = 548 nm , Ni (II) R-CPBr λ = 544 nm and for Ni (II) R-CTMABr λ = 552 nm are formed. The color of the reagent and complexes depends on the pH of the medium, therefore, the absorption spectra during complexation were studied against the background of the control experiment R-CPCl, R-CPBr and R-CTMABr. Under the influence of third components, a bathochromic effect is observed in all the resulting mixed-ligand complexes (Fig. 1).
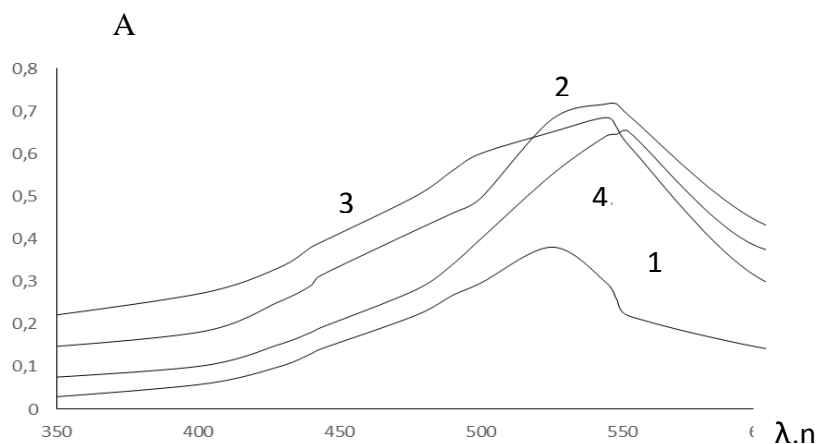
Figure 1. Absorption spectra of solutions of complexes with nickel (II)
1 –Ni (II) R, 2- Ni (II) R-CPCl, 3- Ni (II) R-CPMABr 4- Ni (II) R-CPMABr
$CNi = 4 \times 10^{-5} M$; $CR = 1 \times 10^{-4} M$

The study of the dependence of the absorbances on the pH of the solution showed that when interacting with cetylpyridinium chloride, cetylpyridinium bromide, cetyltrimethylammonium bromide, the optimal conditions of complexation shift into an acidic medium at pH 3, 3, 4 in complexes, respectively (Fig. 2).
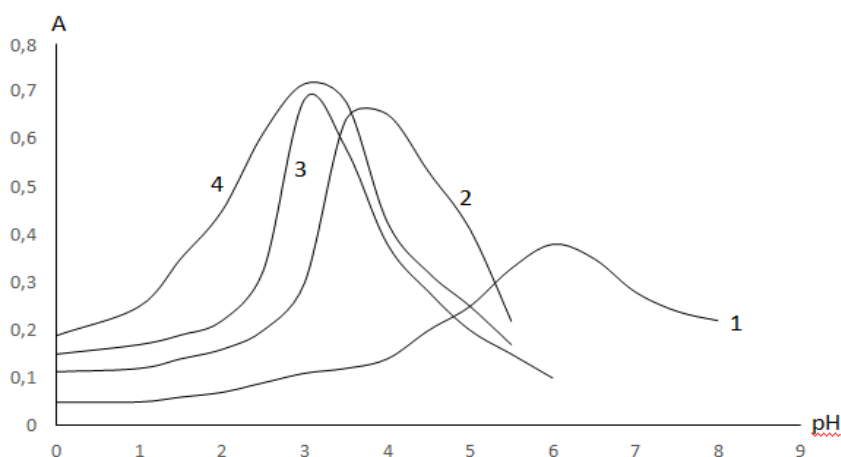

Figure 2. The dependence of the abrorbances of solutions of the complexes of Ni (II) on pH.
1 –Ni (II) R, 2- Ni (II) R-CPMABr, 3- Ni (II) R-CPBr, 3- Ni (II) R-CPCl.
$CNi = 4 \times 10^{-5} M$; $CR = 1 \times 10^{-4} M$

To select the optimal conditions, the influence of the concentration of reactants, temperature and the influence of time on the formation of a binary and mixed-ligand complexes was studied. The yield of the Ni (II) -R complex is maximum at a concentration of $8 \cdot 10^{-5}$ M R, Ni (II) R-CPCl at $8 \cdot 10^{-5}$ MR and $5.2 \cdot 10^{-5}$ M CPCl, Ni (II) R-CPBr at $8 \cdot 10^{-5}$ MR and $4.8 \cdot 10^{-5}$ M CPBr, Ni (II) R-CPMABr at $8 \cdot 10^{-5}$ M R and $4 \cdot 10^{-5}$ M CPMA Br. All complexes are formed immediately after mixing the solutions of the components and differ in stability.

The stability constants and the ratio of the components in the composition of the complexes were established by the methods of isomolar series, the Starick – Barbanel`s

relative yield method, and the method of equilibrium shift (Bulatov & Kalinkin, 1972).

Starick – Barbanel`s relative yield method allows accurate estimation of stoichiometric coefficients and can be applied to any stoichiometric reaction, regardless of the stability of the concentration of the interacting substances.The ratio of the components in the NiR complex is 1: 1. The study showed that the ratio of components in mixed-ligand complexes is 1: 1: 1.

Molar coefficients of light absorption, linearity interval of the graduated graphs for the determination of nickel (II), as well as other analytical characteristics of the reagents are given in Table 1.

Table 1. Spectrophotometric characteristics of nickel (II) complexes

Complex	pH	λ_{max}, nм	$\Delta\lambda$,nм	$\varepsilon \cdot 10^{-4}$, L/mol·sм	Me:R	Obedience to Beer`s law, mkg/mL	lgβ
Ni(II)R	6	525	29	0.950±0.04	1:1	0,12-2,32	9.24±0.04
Ni(II)R-CPCl	3	548	43	1,79±0.03	1:1:1	0,07-2,32	10,69 ±0,06
Ni(II)R-CPBr	3	544	42	1,71±0.02	1:1:1	0,07-2,32	10,24±0.06
Ni(II)R-CPMABr	4	552	33	1,63±0.03	1:1:1	0,07-2,32	10,02±0.04

The coefficients of the equation of the calibration curve were determined by the method of least squares (Batuner & Pozin, 1963). In the complexation of nickel (II), the dependence $A = f(c)$ is expressed by the following linear equations.

$A=(0,15\pm0,02)c+(4,8\pm0,12)10^{-2}$ NI(II)R
$A=(0,24\pm0,01)c+(3,2\pm0,10)10^{-2}$ Ni(II)R-CPCl
$A=(0,27\pm0,02)c+(6,9\pm0,09)10^{-2}$ Ni(II)R-CPBr
$A=(0,37\pm0,01)c+(7,2\pm0,08)10^{-2}$ Ni(II)R-CtMABr

As can be seen, with an increase in the slope angle (a) of the linear equations, the molar absorption coefficients of the complexes increase.

Under optimal conditions of complexation, Ni-R was titrated with a solution of third components (CPCl, CPBr, and CPMABr) by the conductometric method (Khudyakova & Kreshkov, 1976) (Table 2).

Table 2. Results of conductometric titration of a Ni-R solution with a solution of the third components (CPCl, CPBr and CPMABr ($m \times 10^4$ $Ohm^{-1}cm^{-1}$)

V_{Ni}, mL / System	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0
R	1.80	1.77	1.75	1.73	1.72	1.70	1.69	1.68	1.68	1.68
R – CPCl	1.76	1.73	1.70	1.69	1.68	1.65	1.63	1.62	1.62	1.62
R – CPBr	1.70	1.64	1.58	1.50	1.45	1.40	1.38	1.38	1.38	1.38
R- CPMABr	1.62	1.58	1.50	1.45	1.40	1.35	1.33	1.32	1.32	1.32

The results show that the lower is the specific electrical conductivity, the greater is the stability of the complexes.

The effect of foreign ions on the complexation of nickel (II) with R in the absence and in the presence of third components has been studied. It was found that in the presence of third components, the selectivity of complexation reactions significantly increases (Table 3). These reagents are more selective for the spectrophotometric determination of nickel (II) in comparison with the reagents known from the literature (Mustafa *et al*., 2000).

Table 3. Permissible ratios of foreign ions to nickel (II) when it is determined in the form of same- and mixed-ligand complexes (error 5%)

Foreign ions	R	R- CPCl	R-CPBr	R- CPMABr	2-[(2-merkaptophenyl imino) metyl]phenol (Shabani et al., 2008)
Na(I)	*	*	*	*	300
K(I)	*	*	*	*	300
Mg(II)	124	414	414	248	250
Ca(II)	207	690	690	270	250
Ba(II)	472	2364	472	236	
Zn(II)	11	224	448	224	300
Cd(II)	215	1931	215	366	50
Co(II)	61	464	215	464	20
Cu(II)	**	110	110	22	20
Mn(II)	28	940	190	940	200
Al(III)	5	93	47	47	250
Fe(III)	10	193	193	193	20
Cr(III)	179	539	258	258	20
Pb(II)	71	142	142	71	
V(V)	35	176	88	88	
W(VI)	197	952	634	635	
Mo(VI)	331	828	828	372	
F^-	319	6379	6379	6379	
$C_2O_4^{2-}$	22	422	217	217	
HPO_4^{2-}	617	1234	617	1234	300
Lemon acid	116	231	462	462	
Wine acid	517	2506	2506	2506	
Thiourea	1310	1572	1310	262	

Note: *interferes** does not interfere

The developed technique was applied to determine nickel (II) in three varieties of apples.

Determination of nickel in three varieties of apples
Analysis technique. After drying, a weighed portion of a fruit sample weighing 200 g is placed in a graphite cup, burned in a muffle furnace at 550-750°C until the organic substances are completely decomposed. The resulting ash is dissolved in a

mixture of 15 ml of HCl and 5 ml of HNO_3 in a glassy carbon cup and treated three times with 4-5 ml of HCl at 60-70 °C until nitrogen oxides are completely distilled off. Then the mixture is dissolved in distilled water, filtered in a 100 ml flask and diluted to the mark. An aliquot of the solution is transferred into a 25 ml volumetric flask, 2 ml of 1×10^{-3} M reagent solution, 1 ml of 10^{-2} M solution of cetylpyridinium chloride (the volume is brought to the mark with an ammonium acetate buffer solution pH = 3). The absorbance of the solution is measured on device KFK-2 at $\lambda = 490$ nm against the background of a control experiment in a cuvette with a light-absorbing layer with thickness of l = 1 cm. The iron content is found according to a previously constructed calibration curve. The results are presented in Table 4 and compared with the analysis data of the atomic absorption method (AAS). The results of the proposed method and AAS are in good agreement with each other. Thus, the proposed method for the determination of nickel (II) with 1,3-diphenyl-2- (2-hydroxy-4-nitrophenylhydroso) propodione-1,3 in the presence of batophenontroline is simple, rapid and gives reliable results.

Table 4. Results of determination of nickel (II) in fruits (n = 5, P = 0.95)

Analyzed objects	Found Ni, % weight	
	R+ CPCl	AAS
Palmet	$(8,34\pm0,04)\times10^{-3}$	$(8,43\pm0,06)\times10^{-3}$
Simerenka	$(8,16\pm0,06)\times10^{-3}$	$(8,05\pm0,07)\times10^{-3}$
Fuji	$(8,02\pm0,06)\times10^{-3}$	$(7,87\pm0,05)\times10^{-3}$

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