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Photometric Definition of Copper (II) in Alloys on the Basis of Zinc

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Abstract: It has been synthesized 1-(2-tenoil)-4-threefluor-2 [-2-hydroxy-5-sulfonaphthalineazo] bythadione-1,3 (R) on the basis of 2-tenoilthreefluorasetone . It has been studied a stability of complexes of some metals with this reagent by the potentiometric and conductometric titrations methods. The basic spectrofotometric characteristics of reaction of copper with the synthesized reagent have been established. Influence foreign ions and masking substances on complex formation have been researched. The technique of photometric definition of copper (II) in alloys on basis of zinc has been developed.

Keywords: 1-(2-tenoil)-4-threefluor-2 [-2-hydroxy-5-sulfonaphthalineazo] bythadione-1,3; the potentiometric and conductometric titrations; photometric definition of copper (II).

Çinko Esaslı Alaşımlarda Fotometrik Yönlemle Bakır (II)Tayini

Özet: Bu çalışmada 2-tenoilthreefluorasetone esasında 1-(2-tenoil)-4-triflor-2 [-2-hidroxi-5-sulfonaftalineazo] bütadion-1,3 (R) sentezlenmiştir. Sentezlenen maddenin bazı metallerle komplekslei potansiyometrik ve kondüktometrik titrleme yöntemiyle incelenmiştir. Bu maddenin bakırla tepkimesinin spektrofotometrik özellikleri belirlenmiştir. Yabancı iyonların ve maskeleyici maddelerin kompleks oluşumuna etkisi araştırılmıştır. Çinko esaslı alaşımlarda fotometrik yönlemle bakır(II) tayini tekniği geliştirilmiştir.

Anahtar kelimeler: 1-(2-tenoil)-4-triflor-2 [-2-hidroxi-5-sulfonaftalineazo] bütadion-1,3; potansiyometrik ve kondüktometrik titrleme; fotometrik yönlemle bakır(II)tayini.

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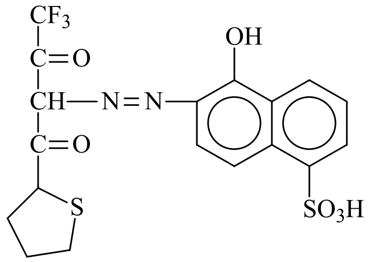
Introduction

Azoderivatives of β-diketons are high selective reagents for photometric definition of copper (II) in natural and industrial objects (Alieva et al. 2004, Gadjiyeva et al. 2006a, Gadjiyeva et al. 2006b), therefore synthesis of new azoderivatives of β-diketons and studying of their analytical opportunities are considered actual.

In the present work showed the synthesis of 1-(2-tenoil)-4-threefluor-2 [-2-hydroxy-5-sulfonaphthalineazo] bythadione-1,3 (R) on the basis of 2-tenoilthreefluorasetone and studied its complex formation with copper (II).

Material and Method

The compound (R) has been received by azoconnecting denitrifying of 2-amine-3-oxy-6-sulfonaphthaline with 2-Tenoilthreefluorasetone in weak alkali medium (Dedkov 1970), its structure and a structure are established by methods IR and PMR-spectroscopy. The structural formula of a reagent.



In work used salts of metals $FeCl_3•6H_2O$, $CuSO_4•6H_2O$, $UO_2SO_4•3H_2O$, $NiSO_4•7H_2O$, $CoSO_4•7H_2O$, $Cd(NO_3)_2•4H_2O$, $ZnSO_4$, $MnCl_2•4H_2O$, $MgSO_4•7H_2O$ with qualifications “chemical clean” and a water solution of reagent R. Ionic force of solutions supported a constant (μ=0,1) by introduction of calculated amount of KCl. A solution of copper (II) prepared from metallic copper (99,9 %) by a technique (Korostelev 1964). To creation of necessary values pH have applied fixonal HCl (pH1-2) and ammonia-acetate buffer solutions (pH 3-11). pH of solutions controlled by means of ion measuring instrument I-130 with a glass electrode. Optical density of solutions measured on spectrophotometer “Lambda -40”(Perkin Elmer) and photo colorimeter CFC-2 with thickness of an absorbing layer l =1 sm, specific electro conductivity on conductometer KEL-1M2.

For definition of a constant dissosiation of reagent used pH-metric titration in the water medium. Volume of titrated $2•10^{-3}$ M of solutions-50 ml, titrant-$4•10^{-2}$ M KOH solution. For calculation of a constant dissociation of reagent applied algebraic method Shvarsenbakh.

$$K_1 = \frac{[H^+]\{a \cdot C_{H_2R} + [H^+] - [OH^-]\}}{(1-a) \cdot C_{H_2R} - [H^+] + [OH^-]};$$

$$K_2 = \frac{[H^+]\{(\underline{a}-1) \cdot C_{H_2R} + [H^+] - [OH^-]\}}{(2-\underline{a}) \cdot C_{H_2R} - [H^+] + [OH^-]}$$

$$-\lg K_{дис} = pH + \lg\frac{[HA]}{[A^-]}, \qquad -\lg K_{дис} = pK$$

Where C_{H_2R} - the common concentration (all particles) acids, which titrated; m-point of neutralization. The calculated constants dissociation of reagent: pK_1=4,93±0,02; pK_2=8,74±0,03.

In work has been shown, that azoderivatives of acetyl acetone most preferable owing to structure, stabilized due to intramolecular hydrogen connection, therefore we assume, that pK_1 characterizes breaking of ion of hydrogen from OH groups of phenyl, and pK_2-from hydrazone forms.

To definition of stepped constants of stability applied Bjerrum method (Bjerrum 1961).

$$[\mathrm{L}] = \frac{(2-a)\cdot c_{\mathrm{R}}}{[\mathrm{H}^{+}]\cdot K_{1} + 2[\mathrm{H}^{+}]^{2}\cdot K_{1}K_{2}}$$

$$\alpha_{\mathrm{L(H)}} = 1 + [\mathrm{H}^{+}]\cdot K_{1} + [\mathrm{H}^{+}]^{2}\cdot K_{1}K_{2}$$

$$\bar{\mathrm{n}} = \frac{c_{\mathrm{R}} - [\mathrm{L}]\cdot \alpha_{\mathrm{L(H)}}}{c_{\mathrm{Me}}}$$

Where C_R=2 •10-3; C_{Me}=1 •10^{-3}M; Me: R=1:2

K_1 and K_2 constants protonization of reagent; m-point of neutralization.

Results

Graphic dependences in coordinates $\bar{n}$ - pL are constructed. Return concentration of ligands (-lg L=pL) in points $\bar{n}$=0,5; $\bar{n}$=1,5 are equal to logarithms of constants of stability.

Titration of a mix of a reagent and salts of corresponding metals spent in the water medium at ratio Me:R=1:2 and temperature 25°C. The volume titrated solutions made 50sm^3 with the contents 2•10^{-3}M of R and 1•10^{-3}M of Me. As a titrant used the solution 4•10^{-2} M KOH. At calculation of constants of stability used the equation (Bjerrum 1961).

Constants of stability of complexes of some metals with R are resulted below:

	Fe(III)	Cu(II)	Ni (II)	Co (II)	Zn (II)	Mn(II)
lgK_1	9,37	8,49	8,26	8,17	8,13	8,06
lgβ_2	17,12	16,02	15,79	15,64	15,57	15,43

The received complex compounds also are investigated by a method conductometric titration of (Khudjakova and Kreshkovв 1976). 50 sm^3 of 1•10^{-3}M water solutions of the specified salts of metals titrated with 2 •10^{-2} M water solution R at T=298 K.

Disscussion

It has been established, that stability of complexes varies in following order: Fe> Cu> Ni> Co> Zn> Cd> Mn

Calculations of function of formation of investigated complexes have shown, that they change within the limits of 0 ≤$\bar{n}$≤ 2.With increase of ionic radius of ions of metals of value of constants of stability and specific electro conductivity decrease.

It has been established, that the reagent forms with ions of copper the colored compounds, suitable for its photometric definition. The exit of complex CuR is maximal at pH 4 (λ_{Max}=495 nanometer), the maximum light absorption of reagent is observed at λ=393 nanometer. Complexes of copper have maxima of absorption which move batochromicly relation to a maximum of absorption of a reagent. System CuR is formed quickly. The ratio of reacting components in a complex is established by methods of a relative exit of the Staric-Barbanel, shift of balance and izomolar series. Molar coefficient of absorption of a complex is calculated from curves of saturation (Dedkov and Koluzanova 1970). Intervals of concentration where law of Beer is observed are established.

Table 1. The basic spectrofotometric characteristics of investigated reactions

Reagent	λ, nm	Cu:R	pH	ε·10^{-4}	Interval of submission to law Beer mkg/ml,
R	495	1:2	4	1,35±0,03	0,17-3,07

Influence of foreign cations is characterized by maximum permissible mass relations of element-copper, errors of definition did not exceed 5 % (Table 2). To definition of copper with R practically do not prevent alkaline and earth- alkaline metals Cd, Mn, Al, lots of Zn, Ca, In, Pb, V, Mo, W. Appreciable influence renders Fe. With a view of studying possible ways of increase of selectivity of definition of copper influence oxalate, citric and wine acids, urea, thiourea has been investigated, $Na_2HPO_4 \times 12H_2O$, NH_4F and EDTA.

The final solution can contain 1 ml of a solution of 10^{-4} M thiourea, 1 ml of a solution of a citric acid of 10^{-4} M and 1 ml of a solution of a wine acid of 10^{-4} M accordingly. Oxalate acid and EDTA can be present only at small amounts. Presence of significant amounts of urea, $Na_2HPO_4 \times 12H_2O$ and NH_4F is admissible.

Comparison of selectivity of reagents for definition of copper shows, that azoderivatives tenoilthreefluorasetone are more selective, than a pikramine -epsilon and pikramine M.

Table 2. Admissible ratio of extraneous substances and copper (II) at its definition in the form of Cu R (an error of 5 %)

Ion or substance	(R)	Pikramin – epsilon [9]	Pikramin M [10]
Na(I)	*		
K(I)	*		
Mg(II)	*		1:1000
Ca(II)	*		1:20
Ba(II)	*		
Zn(II)	1:1540		1:1500
Cd(II)	1:2980		1:1000
Mn(II)	*		
Ni(II)	1:100		1:50
Co(II)	1:100	1:500	1:100
Al(III)	1:2985		1:10
Fe(III)	1:10		
Ga(III)	1:240	1:60	
In(III)	1:380		
Zr(IV)	1:310	1:0,1	
Pb(II)	1:148		
V(V)	1:47	1:1	
Mo(VI)	1:165	1:3	
$C_2O_4^{2-}$	1:32		
EDTA	1:10		
UREA	*		
Thiourea	1:250		
Citric acid	1:705		
Wine acid	*		
$Na_2HPO_4 \cdot 12H_2O$	*	1:1182	
NH_4F	*	1:123	

Definition of copper in alloys on a zinc basis

0,1 g samples of alloys [A 95-4:0,18 Al; 0,025 Fe; 0,025 Pb; 0,010 Cd; 0,010 Cu; 0,010 Sb; 0,007 % Sn, rem. Zn; A 95-5:0,230 Al; 0,040 Fe; 0,040 Pb; 0,015 Cd; 0,015 Cu; 0,015 Sb; 0,010 % Sn, rem.Zn] dissolve in 10 ml of a mix of a water solution of 5 ml HCl and 1-2 of drops HNO_3 at 50°C, translate in a flask capacity of 50 ml and dilute with water up to a label.

The received solution (1 ml) is entered into a flask capacity of 25 ml, add 2мл $1 \cdot 10^{-3}$ M solution R, 1 ml $1 \cdot 10^{-1}$ M solution NH_4F and dilute up to a label with a buffer solution (pH 2). Optical density of solutions measure at λ =440 nanometers in λ =1 sm on KFK-2 concerning a solution of control experience (Table.3)

Table 3. Results of definition of copper in zinc alloys (n=3, p=0,95)

Standard sample	Found Cu, mkg/ml	Contents Cu on the passport, %	$\bar{x} \pm \frac{t \cdot S}{\sqrt{n}}$, %
A 95-4	0,80	0,010	0,010±0,003
A 95-5	1,20	0,015	0,015±0,002

Thus, on the basis of tenoilthreefluorasetone the new reagent is synthesized and the technique of photometric definition of copper in zinc alloys is developed.

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