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SPECTROPHOTOMETRIC METHOD FOR DETERMINATION OF COPPER (II) MICROQUANTITIES IN A BANANA, MUSHROOMS AND PEA

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Abstract. By spectrophotometric method was studied the complex formation of copper (II) with 1-phenyl-2-(2-hydroxy-4-nitrophenylhydrazo)butadione-1,3 in the presence of CPCl, CPBr and CTMABr. The optimal conditions for their formation, were determined and spectrophotometric characteristics were calculated. The effect of foreign ions on the complex formation was studied. The method was also studied for the photometric determination of copper in the banana, mushroom and pea.

Keywords: *copper(II), photometric determination, banana, mushroom, pea*.

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1. Introduction

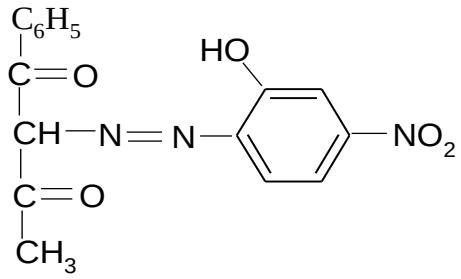
From the literature it is known that the photometric method is advantageous for the determination of trace amounts of copper (II) in objects of complex composition (Aliyeva *et al.*, 2011; Krishna *et al.*, 2009; Reddi *et al.*, 2000). Azo derivatives of β-diketones are highly selective reagents for photometric determination of copper (II) (Chiragov, 2003; Espandi *et al.*, 2012; Gadzhieva *et al.*, 2007; Singh *et al.*, 2007).

It is also known that in the complexation of cationic surfactants with acidic chromoric reagents, the degree of protonation of the reagents decreases and the complexation shifts into a more acidic medium (Amelin *et al.*, 1989; Gordon, 1979; Pilipenko & Tananayko, 1983; Savvin *et al.*, 1991).

For this reason, the synthesis of organic reagents of benzoylacetoneazo-derivatives and the use of their complexationwith Cu (II) in the presence of cation-surface active substances (CSAS) such as cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr), cetyltrimethylammonium bromide (CTMABr).

2. Experimental part

The reagent used was previously synthesized and its composition and structure were established by the method of elemental analysis, IR, NMR spectroscopy (Kopylovich *et al.*, 2011). The purity of the synthesized compound was verified by paper chromatography. The structural formula of the reagent:



Solutions and reagents

1-phenyl-2-(2-hydroxy-4-nitrophenylhydrazo) butadiene-1,3 is well soluble in ethanol. A $1 \cdot 10^{-3}$M ethanol reagent solution, a $1 \cdot 10^{-3}$ M water – ethanol solution of CPCl, CPBr, and CTMABr were used. A solution of copper (II) ($1 \cdot 10^{-3}$M) was prepared from metallic copper (99,9%) according to the method (Korostelev, 1964). To create the necessary acidity, fixonalHCl (pH 1-2) and ammonium acetate solutions (pH 3-11) were used.

Equipment

The pH of the solutions was controlled using a PHS-25 ionomer with a glass electrode. Optical density was measured on a Lambda 40 spectrophotometer (Perkin Elmer) and a KFK-2 photocalorimeter (l = 1 sm).

3. Results discussion

The chemical and analytical properties of the copper (II) complex with R are improved by complexation in the presence of a cationic surfactant. Fig. 1 shows the absorption spectra of the reagent, binary and mixed-ligand complexes.

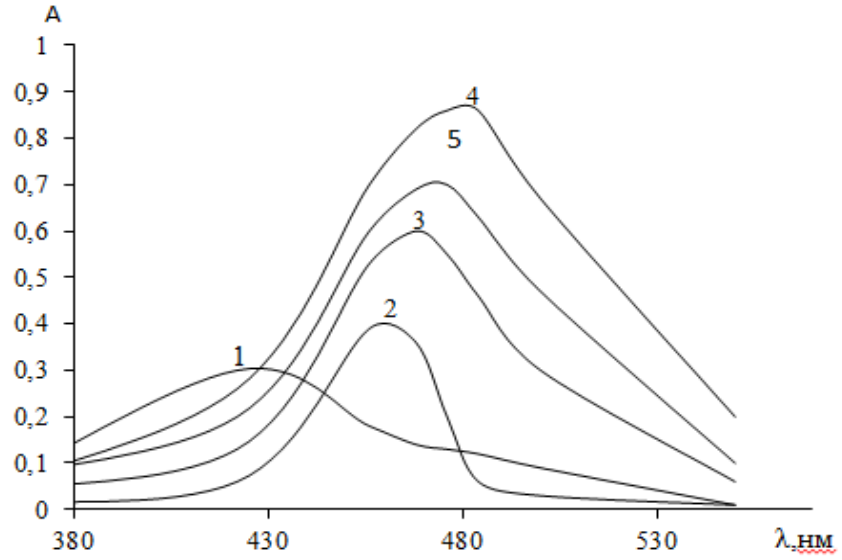


Figure 1. The absorption spectra of the reagent solution and its complexes with copper (II) in the presence and absence of CPCl, CPBr and CTMABr at the optimum pH value of the respective systems. 1.R, 2.CuR, 3.CuR - CPCl, 4.CuR - CPBr, 5.CuR - CTMABr

The light absorption of the reagent is maximum at 422 nm, and its binary complex with copper (II) at 467 nm. The study of the complex in the presence of CSAS in a wide pH range showed that, under the influence of the third components, a bathochromic shift in the absorption spectrum is observed and the optical density of the solutions increases significantly. With the formation of mixed-ligand complexes, the output shifts to an acidic medium compared with the corresponding binary complex (Fig. 2). Based on this, it can be assumed that the modified forms of R with CSAS, i.e. associates have a greater analytical significance than R. In the presence of a CSAS, different-ligand complexes Cu-R-CPCl, Cu-R-CPBr, Cu-R-CTMABr are formed with a maximum absorption of 467 nm, 484 nm, 476 nm, respectively.

The study of the dependence of optical density on the pH of the solution showed that binary complexes are formed at pH 4, pH 2 (CPCl), pH 3 (CPBr, CTMABr).

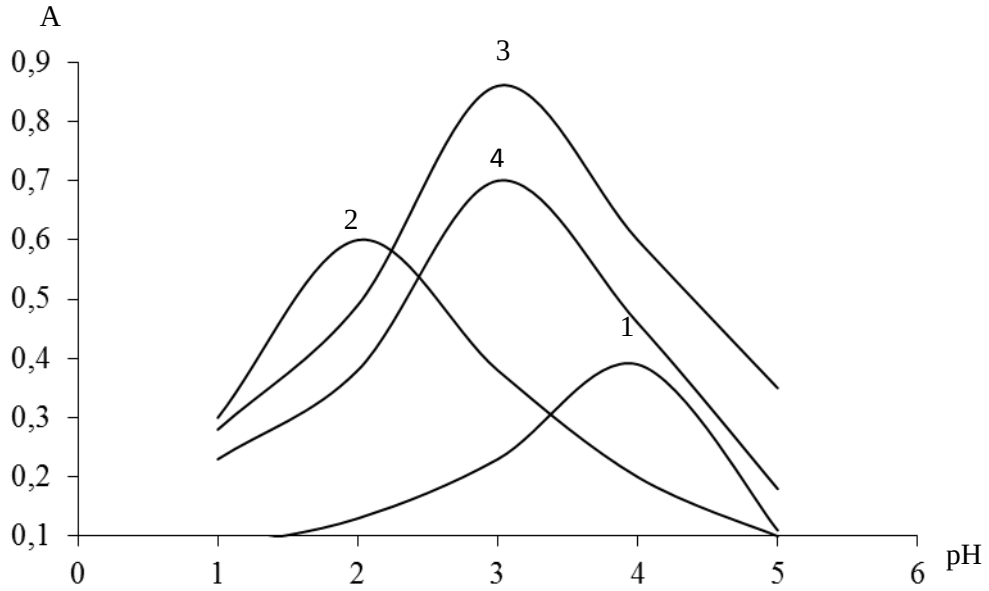


Figure 2. Dependence of the optical density of solutions of copper (II) complexes on at λ. 1.CuR, 2.CuR-CPCl, 3.CuR-CPBr, 4.CuR-CTMABr

The effect of the concentration of the reacting substances, temperature and time on the formation of binary and mixed-ligand complexes was studied. The output of the complex Cu(II) -R is maximum at a concentration of $8 \cdot 10^{-5}$ M reagent. The output of Cu (II)-R-CPCl, Cu (II)-R-CPBr and Cu (II)-R-CTMABr complexes is maximum at a concentration of $8 \cdot 10^{-5}$M, $4{,}8 \cdot 10^{-5}$M CPCl, $4 \cdot 10^{-5}$M CPBr and $3{,}2 \cdot 10^{-5}$M CTMABr.

Table 1. The main photometric characteristics of copper (II) complexes

Complexes	pH_{opt}	λ_{opt}	ε	lg	Ratio of thecomponents	Interval of subordination to the Beer's law, mcg/ml
Cu-R	4	456	9750	4,90±0,04	1:2	0,25-6,14
Cu-R-SPCl	2	467	15000	10,36±0,03	1:2:2	0,13-5,12
Cu-R-SPBr	3	484	21500	11,26±0,05	1:2:2	0,13-2,56
Cu-R-STMABr	3	476	17500	10,52±0,04	1:2:2	0,13-3,07

The ratio of the reacting components in the complexes was established by the methods of the relative yield of the Old Man-Barbanel, the equilibrium shift and the isomolar series. The molar absorption coefficients of the complexes were calculated from the saturation curves (Bulatov & Kalinkin, 1972). The concentration intervals are determined where Beer's law is observed (Table 1).

Calculation of the complexes stability constant. The stability constant of the same and mixed ligand complexes of copper(II) are calculated. To calculate the stability constant of the complex, we used the curve intersection method (Shevchenko, 1965).

The concentration of the complex was calculated from the expression

$$C_k = C_{Cu}\left(\frac{\Delta A_x}{\Delta A_n}\right)$$

$$\beta_n = \frac{C_k}{(C_{Cu} - C_k)(C_R - nC_k)^H}$$

where A_X and A_0 are the optical densities of the solutions of thecomplex at the current C_R value and at saturation, respectively. Then by equation

$$C_k = C_{CuR}\left(\frac{\Delta A_x}{\Delta A_n}\right)$$

$$\beta_n = \frac{C_k}{(C_{CuR} - C_k)(C_x - nC_k)^H}$$

When the molar ratio of the components of Cu:R=1:2; Cu:R:CPCl=1:2:2; Cu:R:CPBr=1:2:2; Cu:R:CTMABr=1:2:2; the stability constant was calculated. (x=CPCl; SPBr; CTMABr). According to the calculations, lgβ(CuR)=4,90±0,04; lgβ(Cu-R-CPCl)=10,36±0,03; lgβ(CuR-CPBr)=11,26±0,05; lgβ(CuR-CTMABr)=10,52±0,04.

The influence of foreign ions and masking substances on the photometric determination of copper (II) in the form of binary and mixed ligand complexes was studied. When comparing the selectivity of reagents known from literature for the determination of copper, it can be seen that the reagents we use in the presence of the third component are more selective (Table 2).

Table 2. Acceptable fold amounts of foreign substances with respect to copper (II) when it is defined as binary and mixed ligand complexes (5% error)

Ion or substance	CuR-CPCl	CuR-CPBr	CuR-CTMABr	N,N-di-(2-carboxy-ethyl) -3,4-xylidine (Neudachina *et al.*, 2005)
Na	*	*	*	1000
K	*	*	*	1000
Ca	*	*	*	250
Zn	*	*	*	1000
Cd	*	*	*	200
Mn	*	*	*	1000
Ni	143	140	140	500
Co	389	365	370	500
Al	*	*	*	750
Sm	*	*	*	1

Fe(III)	100	95	95	
Ga(III)	672	640	630	0,01
In(III)	670	645	650	
Bi(III)	149	135	140	
Sn(IV)	305	285	280	
Ti(IV)	545	515	520	
Mo(VI)	274	250	250	
W(VI)	440	405	405	
$C_2O_4^{2-}$	215	195	180	
EDTA	107	104	105	
Thiourea	163	154	150	
Citricacid	1195	1185	1080	
$Na_2HPO_4 \cdot 12H_2O$	815	785	810	
Wineacid	380	365	360	
F^-	380	375	370	

* Do not interfere.

4. Method of analysis

After drying, a portion of the sample of peas, mushrooms weighing 300 g, 400 g and 300 g of bananas 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 dish and treated three times with 4-5 ml of HCl at 60-70°C until the nitrogen oxides are completely distilled off. Next, the mixture is dissolved in distilled water, filtered in a flask with a capacity of 100 ml and diluted to the mark. An aliquot portion of the solution is transferred to a 25 ml volumetric flask, 2 ml of $1 \cdot 10^{-3}$ M reagent solution, 1 ml of 10^{-2} M SPBr solution are added, and the volume is made up to the mark with ammonium acetate buffer pH = 3. The optical density of the solution is measured on a KFK-2 device at λ = 490 nm against the background of the control experiment in a cell with a thickness of a light-absorbing layer l=1 sm.

The copper content is found from a previously constructed calibration curve. The results are presented in Table 3 and compared with the analysis 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 copper(II) with 1-phenyl-2-(2-hydroxy-4-nitrophenylhydrazo) butadiene-1,3 in the presence of SPBr is simple, express and gives reliable results.

Table 3. The results of the determination of copper(II) in food (n = 5, P = 0.95)

Analyzed object	Found Cu, % mass.	
	R+SPBr	AAS
Banana (Gro-Michel)	$(3,65 \pm 0,03) \cdot 10^{-4}$	$(3,70 \pm 0,03) \cdot 10^{-4}$
Mushrooms (Chanpinion)	$(2,15 \pm 0,02) \cdot 10^{-3}$	$(2,2 \pm 0,06) \cdot 10^{-3}$
Pea (Getman)	$(2,63 \pm 0,06) \cdot 10^{-3}$	$(2,68 \pm 0,03) \cdot 10^{-3}$

5. Conclusion

The complexation of copper(II) with 1-phenyl-2-(2-hydroxy-4-nitrophenylhydrazo) butadiene-1,3 was studied by photometric method in the presence

of CPCl, CPBr and CTMABr. The main spectrophotometric characteristics of the complexes were established.The results show that the copper (II) complex with 1-phenyl-2-(2-hydroxy-4-nitrophenylhydrazo) butadione-1,3 has the most extensive analytical capabilities. The developed techniques were applied to determine the copper in banana, mushroom and peas.

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