SPECTROPHOTOMETRIC STUDY of the Complex FORMATION OF COPPER (II) WITH 1-Phenyl-2-[2-Hydroxy-3-sulfo-5-nitrophenylazo] 1,3-butadiene IN the presence OF CATION SURFACTANTS.

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ABSTRACT
Based on benzoylacetone synthesized 1-phenyl-2-[2-hydroxy-3-sulfo-5-nitrophenylazo] 1,3-butadiene (PHSNPAB). Studied complex formation of copper (II) with 1-phenyl-2-[2-hydroxy-3-sulfo-5-nitrophenylazo] 1,3-butadiene (PHSNPAB) in the presence and absence of the third component such as cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTMABr). Single ligand complexes are formed at pH = 3, λ = 444nm, and mixed ligand complexes at pH = 2 λ = 456, 454, and 461 nm, respectively (CPCl, and CPBr, CTMABr). Identified the relations of the reacting components in homogeneous composition of Cu-R (1: 2) and mixed ligand Cu-R-CPCl (1: 2: 2), Cu-R-CPBr (1: 2: 2) and Cu-R-CTMABr (1 2: 1) complexes, which concentration interval subordinated to Beer's law. The influence of external ions and masking substances on complex formation was studied. Method for the photometric determination of copper in the rocks was established.

Keywords
Synthesis, complex formation, CPCl, CPBr, CTMABr, stability constant.

Academic Discipline And Sub-Disciplines
Chemistry and analytical chemistry

SUBJECT CLASSIFICATION
Analytical chemistry; Inorganic Chemistry; Organic Chemistry; General chemistry

TYPE (METHOD/APPROACH)
Types of research: experiments; Approach: quantitative research

1. Introduction
Azo compounds are important, well-known and commonly used compounds in textile, paper industries and as dyeing agent in food and cosmetic industries. Azo compounds possess important analytic features, by providing a strong chromophore label-the quantity of which is determined by a colorimetric, spectrophotometric or spectrofluorometric methods. Additionally, azo compounds as have been reported show various biological activities, including antibacterial, antifungal, pesticides, antiviral and anti-inflammatory activities [1-5].

It is known from literature that, azo derivatives of benzoylacetone are widely used in photometric determination of elements [6-8]. Therefore, the study of analytical capabilities of azo derivative of benzoylacetone-1-phenyl-2-[2-hydroxy-3-sulfo-5-nitrophenylazo] butadiene-1,3 (PHSNPAB) and application for photometric define of copper in itself represents analytical interests.

The purpose of the following work is the development of photometric determination method for identifying copper (II) with PHSNPAB in the presence and in the absence of the third component.

2. Experimental part
PHSNPAB synthesized as a result of azocoupling reaction of diazotized 2-amino-4-nitro-6-sulphophenol-1 with benzoylacetone in a weakly alkaline medium [9], and its composition and structure were established by IR and NMR-spectroscopy.
Obtained reagent is water-soluble. In work used 1·10⁻³ M water solution of PHSNPAB, 1·10⁻³ M water solution of CPCl, CPBr, CTMABr and 1·10⁻³ M solution of copper (II) which were prepared from metallic copper (99.9%) on the base of methodology [10].

In order to create the necessary pH, used fix anal HCl (pH 1-2) and ammonium acetate buffer solution (pH 3-11). The pH of the solution was monitored by using an ionomer PHS-25 with a glass electrode. Absorbance of solutions was measured on a spectrophotometer Lambda 40 (Perkin Elmer) and CPK-2 photocolorimeter in a cuvette with 1 cm layer thickness.

3. RESULTS AND ITS DISCUSSION

The investigated complex compounds are formed immediately after mixing solutions. The ratio of the reactants in the complexes was found by method of isomolar series, the relative yield of Starika-Barbanel, equilibrium shift [11]. All methods showed that the ratio of Cu (II)-R in binary complexes is 1: 2, and in mixed-ligand complexes Cu (II)-R-CPCl = 1: 2: 2, Cu (II)-R-CPBr = 1 : 2: 2, Cu(II)-R-CTMABr = 1: 2: 1. The molar absorption coefficients of complexes were calculated from the saturation curves [11]. Established concentration ranges where Beer's law is observed (Table 1).

Table 1. Main photometric characteristics of copper (II) complexes

| Complex | pH | $\lambda_{\text{max}}$ nm | $\varepsilon \times 10^3$ | $\lg \beta$ | Ratio of components | Linearity interval (mcg / ml) |
|---------|----|-------------------------|-------------------|-------------|-------------------|-----------------------------|
| CuR     | 3  | 444                     | 1,40              | 6,04±0,12   | 1:1               | 0,25-3,07                  |
| CuR-CPCl| 2  | 456                     | 2,3               | 11,24±0,12  | 1:2:2             | 0,12-2,56                  |
| CuR-CPBr| 2  | 454                     | 2,2               | 10,82±0,10  | 1:2:2             | 0,12-2,56                  |
| CuR-CTMABr| 2| 461                     | 2,5               | 12,04±0,09  | 1:2:1             | 0,12-2,56                  |

3.1. Absorption spectra.

The study of complex formation depending on the acidity of the medium, showed that the maximum output of the complex CuR observed at pH 3 ($\lambda_{\text{max}} = 444$nm), respectively. However, reagent in itself has a maximum absorbance at pH 2 ($\lambda_{\text{max}} = 461$ nm) (Figure 2).

Note: $[C_{Cu} = 1·10^{-3} \text{ M;} \ C_{R} = 1·10^{-3} \text{ M;} \ C_{X} = 1·10^{-3} \text{ M.} \ (X = \text{ CPCl, CPBr and CTMABr)}$

Figure 2 shows the absorption spectrum of the reagent.
In the presence of the third component—cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTMABr) optimum pH complex formation shifted to pH = 2 (CuR-CPCl), pH = 2 (CuR-CPBr) and pH = 2 (CuR-CTMABr). The absorption maximum of complexes (Figure 2.) is equal to: λ = 444nm (CuR), λ = 456nm (CuR-CPCl), λ = 454nm (CuR-CPBr), λ = 461nm (CuR-CTMABr) respectively. It is found that in the presence of the third component—cetylpyridinium chloride (CPCl), cetylpyridinium bromide (CPBr) and cetyltrimethylammonium bromide (CTMABr) ternary complexes are formed, which are observed to form a bathochromic shift in compare with the spectrum of the binary complex and the optimum pH in complex formation shifted to more acidic environment pH = 2 (CuR-CPCl), pH = 2 (CuR-CPBr) and pH = 2 (CuR-CTMABr).

The effect of external ions and masking substances on the photometric determination of copper (II) in the form of binary and mixed-ligand complexes was studied. Relative selectivity of systems is shown in Table 2.

| Ion or substance | R | R-CPCI | R-CPBr | R-CTMABr | N,N-Di-(2-carboxy-ethyl)-3,4-xylidine [13] |
|-----------------|---|-------|--------|----------|----------------------------------|
| Na              | * | *     | *      | *        | 1000                             |
| K               | * | *     | *      | *        | 1000                             |
| Ca              | * | *     | *      | *        | 250                              |
| Zn              | * | *     | *      | *        | 1000                             |
| Cd              | * | *     | *      | *        | 200                              |
| Mn              | * | *     | *      | *        | 1000                             |
| Ni              | 46| 118   | 115    | 115      | 500                              |
| Co              | 277| 364   | 340    | 345      | 500                              |
| Al              | * | *     | *      | *        | 750                              |
| Sm              | * | *     | *      | *        | 1                                |
| Fe(III)         | 9 | 60    | 55     | 55       | 5                                |
| Ga(III)         | 547| 647   | 610    | 600      | 0.01                             |
| In(III)         | 539| 645   | 620    | 620      |                                  |
| Bi(III)         | 33 | 124   | 110    | 110      |                                  |
| Sn(IV)          | 186| 280   | 255    | 250      |                                  |
| Hf(IV)          | 351| 460   | 430    | 415      |                                  |
Study of the effect of external ions and masking agents for photometric determination of copper (II) in the form of binary complexes and mixed-ligand showed that in the presence of cetylpyridinium chloride, cetylpyridinium bromide, and cetyltrimethylammonium bromide the selectivity of the reaction increases. The data on selectivity make it possible to apply the developed methodology for the photometric determination of copper (II) in the form of mixed-ligand complexes for the determination of trace amounts of its facilities in the complex.

3.2. The effect of pH and concentration of reactant.

The study of complex formation depending on pH (1-8) showed that the yield of binary Cu-R complex is maximal at pH = 3. In the presence of a third component - CPC, CPBr and CTMABr form intensely colored ternary compound CuR - CPC, CuR - CPBr and CuR - CTMABr, that have the maximum yield at pH = 2. The influence of reagents concentrations on the complex formation was studied. It was established that the yield of the complex Cu-R was maximum at $8 \times 10^{-6}$ M R, Cu(II)-R-CPCl $8 \times 10^{-5}$ M (R) and $4 \times 10^{-5}$ M(CPCI), Cu(II)-R- CPBr $8 \times 10^{-5}$ M (R) and $4,8 \times 10^{-5}$ M (CPBr), Cu(II)-R- CTMABr $8 \times 10^{-5}$ M (R) and $3,2 \times 10^{-5}$ M (CTMABr).

3.3. The calibration graph.

Prepared a series of solutions containing 0,25-3,07 mcg / ml (homo-ligand), 0,12-2,56 mcg / ml (mixed-ligand) Cu (II) complexes and their absorption measured at $\lambda_{opt}=490$ nm relative to a control experiment solution. Established concentration ranges where Beer’s law is observed and the molar absorption coefficients of the complexes from saturation curves (11) (Tabl 1). From Table 1 it is clear that using our proposed mixed-ligand complexes, it is possible to determine very small microgram amounts of copper.

3.4. Calculation of the stability constants of complexes.

Calculated stability constants one and mixed-ligand complexes of copper (II). In order to calculate the complex stability constants used method of intersection of curves [12].

The concentration of the complex was calculated from the expression

$$C_k = C_R \left( \frac{A_2 - A_0}{A_k} \right)$$

Where, $A_k$ and $A_0$ optical densities of solutions of complex at current value of $C_R$ and at saturation respectively. Then, according to the equation

$$C_k = C_R \left( \frac{A_2 - A_0}{A_k} \right)$$

At the molar ratio of the components Cu:R=1:2; Cu:R:CPCI=1:2:2; Cu:R:CPBr=1:2:2; Cu:R :CTMABr =1:2:1; calculated stability constant (x= CPC; CPBr; CTMABr). According to calculations $\lg \beta(Cu(II)R)=6,04 \pm 0,12$; $\lg \beta(Cu(II)RCPCl)=11,24 \pm 0,12$; $\lg \beta(Cu(II)R CPBr)=10,82 \pm 0,10$; $\lg \beta(Cu(II)RCTMABr)=12,04 \pm 0,09$.

3.5. Determination of copper(II) in the rocks.

For the analysis, was taken three different mountain-pyrite rock samples containing altered quartz diorite. The content of copper (II) in the samples was determined by the photometric and atomic absorption methods (Table. 3).
3.6. The progress of analysis.

5g of sample in a glassy carbon plate is dissolved in a mixture of 10 ml of 9 mL HF + HCl + 3 ml HNO₃. The resulting paste is treated with 5-6 ml of HNO₃ at 50-60°C till the complete distillation of HF. The resulting precipitate was dissolved in water, filtered to the flask 50 ml and diluted to the mark with water. By determining the copper (II) with photometric method aliquot part of the resulting solution is placed in 25 ml flask, added 2 ml of 1x10⁻³ M R solution, 1 mL 1x10⁻³ CTMABr solution and diluted with a solution till the mark pH 2. The absorption of the solutions was measured at 490 nm in a cuvette with l = 1 cm KFK-2 with respect to the blank test solution. The results of analysis are shown in Table 3.

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

| Samples | By photometric method found , % | By atomic - absorption method found % |
|---------|--------------------------------|-------------------------------------|
| 1       | 0.61±0.10                      | 0.600±0.006                         |
| 2       | 0.93±0.13                      | 0.937±0.003                         |
| 3       | 4.15±0.12                      | 4.17±0.004                          |

CONCLUSION

It has been studied a complexes formation of Cu(II) with 1-phenyl-2-[2-hydroxy-3-sulfo-5-nitrophenylazo] -1,3 butadiene in the presence sulfa-active substances by spectrophotometric method. Molar light absorption coefficients of complexes CuR, CuR – CPCI, CuR - CPBr and CuR - CTMABr equal 1400, 2300, 2200 and 2500. It was determined the stability constant of complexes. lgβ(Cu(II)R)=6.04±0.12; lgβ(Cu(II)-CPCI)=11.24±0.12; lgβ(Cu(II)R-CPBr)=10.82±0.10; lgβ(Cu(II)R-CTMABr)=12.04±0.09. Ber's law is obeyed observes in region 0.25-3.07 mcg/ml for CuR, 0.12-2.56 mcg/ml for CuR – CPCI, CuR - CPBr and CuR - CTMABr. The photometric determination of copper (II) has been developed on the mountain rock.

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