

Andriy Tupys, Oleksandr Tymoshuk and Petro Rydchuk

SPECTROPHOTOMETRIC INVESTIGATION OF Cu(II) IONS INTERACTION WITH 1-(5-BENZYLTHIAZOL-2-YL)AZONAPHTHALEN-2-OL

*Ivan Franko National University of Lviv,
6 Kyryla and Mefodiya St., 79005 Lviv, Ukraine; andriytupys@ukr.net*

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Abstract. The creation of Cu²⁺ ions chelate complex with 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol has been investigated using spectrophotometric methods. The optimal conditions for the complexation reaction and for extraction into the organic phase were found. The extraction-photometric method of copper microquantities determination was developed.

Keywords: spectrophotometry, extraction, copper, thiazolylazonaphthol dyes.

1. Introduction

Copper is one of the elements that is known from ancient times. Nowadays the industrial production of copper takes the second place after aluminum one. This is due to the application of copper in the production of cables, electrical conductive installations, heat exchangers, *etc.* It is the basic component of brass, bronze, copper-nickel and other alloys, which are characterized by good corrosion resistance in air, high electrical conductivity, ductility and sufficient strength. Copper catalysts are applied in some organic syntheses (the hydrogenation of fatty acids, the oxidation of propylene to acrolein, *etc.*).

Although copper is not a toxic element, its content in natural, waste and boiler water is regulated by specialized metrological agencies. That is why the necessity of copper determination in natural, biological and industrial objects has a great significance in analytical chemistry.

On controlling analytically the content of copper both classic chemical methods and physical ones are used and they demand perfect instrumental equipment which allows determination of copper in the presence of many

other elements with high sensibility. Spectrophotometry has recommended itself as a simple and cheap analytical method lately which is especially important for the laboratories in such developing countries as Ukraine.

Thiazolylazonaphthol dyes are the representatives of a very promising class of organic compounds and they can be applied for the control of copper content in various objects [1-4]. During the last decade they were investigated thoroughly for their further application as optical recording materials and future medicine against cancer. They are successfully used for the sensitive determination of such elements as Zn [7], Cd [8], Mn [9], Fe [10], Co [11], Ni [12], Cu [13], Hg [14], Pd [15] and even Tm [16].

Previously the interaction of cadmium(II), zinc(II), cobalt(II) and palladium(II) ions with 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (benzylthiazol or BnTAN), a new synthesized representative of thiazolylazonaphthol dyes, were investigated [17, 18] and the methods of their determination with sufficiently good precision were proposed. Literature data show that such reagent can be applied for the quantitative determination of copper(II) ions content.

The purpose of this work is the investigation of benzylthiazol interaction with copper(II) ions and setting the optimal conditions for the chelate complex compound creation. On solving this specific problem the development of copper determination method in environmental objects with high sensitivity and good selectivity will be possible. Another task is to determine copper(II) in a wide range of the acidity values and in the presence of other transition metal ions. This will allow to analyze the content of copper either in model solutions or in real objects such as various bronze or even coinage alloys.

2. Experimental

2.1. Equipment

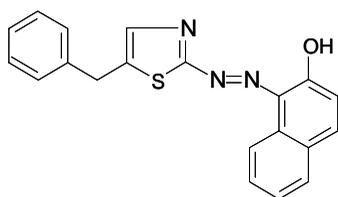
The measurements and control of the media acidity were carried out on pH-meter model pH-150 M equipped with a combined glass electrode, Gomelsky Plant of Measuring Devices, Belarus.

The measurements of absorbance were carried out on the computerized spectrophotometer ULAB 108 UV/VIS with 1.0 cm glass and quartz cells in the wavelengths range of 300–700 nm with the step of 2 nm and on the CPC-3 spectrophotometer with 1–5 cm cells. As the blank solution the distilled water or the appropriate solvent that resembles the extract were used.

2.2. Materials

The needed pH values were obtained by adding the solutions of HCl and NaOH (pH = 1.0–3.0); CH₃COOH and NaOH (pH = 3.5–7.0), NH₃·H₂O and HCl (pH = 7.0–10.0), HCl and NaOH (pH > 10.0) depending on the task of the experiment. Stock solutions of the transition metals (Cu, Cd and other) were prepared by dissolving their soluble salts in distilled water and adding the small amount of the acid which is similar to the salts anion to prevent the hydrolysis of the metals.

All reagents and organic solvents used for the extractive investigations were of “chemically pure” and “particularly clean” qualifications. Stock and working solutions were prepared using distilled water. The stock solution of 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol was prepared by dissolving the exact amount of this reagent in ethanol (96 %). The working solutions of BnTAN were prepared by diluting the stock solution aliquot in ethanol. The structural formula of the reagent is:



(1)

2.3. Evaluation of the Purity of Organic Reagent

Before preparing the stock solution of benzylthiazol at the beginning this reagent was recrystallized from the ethanol. After that the degree of BnTAN purity was checked chromatographically with a mass spectrometric detection. As it can be seen from Fig. 1, there is only one maximum on the chromatogram with high value of analytical signal which means that there is one substance

with a respective molar weight of $M_r = 344.2$ and that is BnTAN. Besides using the computer processing of the chromatogram the content of pure benzylthiazol in the substance was calculated and it is 93.19 %.

2.4. Investigation of the Cu(II)

Interaction with BnTAN in Aqueous Solution

Volumes of BnTAN ($1.00 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$), Cu²⁺ ($1.00 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$) and universal buffer (or UBS; $0.5 \text{ mol} \cdot \text{l}^{-1}$ solution of CH₃COOH, H₃PO₄ and H₃BO₃) solutions were poured into a 25.0 ml flask and the distilled water was added to a total volume of ~20–22 ml. Then pH was adjusted in the range of 2.0–12.0 by means of NaOH solutions (0.1, 1.0 and $4.0 \text{ mol} \cdot \text{l}^{-1}$). For pH = 1.0 the solution was prepared in the same way but pH was adjusted by means of HCl solution ($6.0 \text{ mol} \cdot \text{l}^{-1}$). After that the distilled water was added to complete the volume in the flask and the absorption spectra were measured with distilled water as a blank solution.

2.5. Investigation of the Cu(II)

Interaction with BnTAN in Organic Solvents

Volumes of BnTAN ($1.00 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$), Cu²⁺ ($1.00 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$) and universal buffer solutions were poured into a 25.0 ml flask and the distilled water was added to a total volume of ~20–22 ml; then pH was adjusted by means of NaOH or HCl diluted solution. After that the distilled water was added to complete the volume in the flask and the solution was transferred to a 50–100 ml separatory funnel. Then 10.0 ml of organic solvent (toluene, carbon tetrachloride, etc.) were added to the solution and the obtained mixture was shaken during ~5 min. The organic extract was poured into a dry 25.0 ml flask, then the second part of 10.0 solvent was added to the solution and the extraction was repeated. After pouring the extract the pure solvent was added to the flask to complete the volume. The anhydrous Na₂SO₄ has always been applied for drying the extract and then the absorption of the solution was measured with solvent as a blank. The sequence of the procedure steps used in the study of the interaction between benzylthiazol and Cu(II) was generalized in Fig. 2.

Method of copper(II) determination using BnTAN

The aliquot of the analyzed solution was selected considering the final concentration of Cu(II) after the dilution of $2.0 \cdot 10^{-6} - 4.0 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; it was transferred to a 25.0 ml flask, then 1.3 ml of BnTAN solution with the concentration of $1.00 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ and 0.25 ml $0.5 \text{ mol} \cdot \text{l}^{-1}$ of universal buffer are added. Then the acidity of the

medium was adjusted to the value of pH = 5 by means of NaOH solution. After that the distilled water was added to complete the volume in the flask and the prepared solution was transferred into a separatory funnel with 10.0 ml of CCl₄. The complex was extracted during 5 min and the extract was poured into a dry flask (25.0 ml). Then the

procedure was repeated for the second part of organic solvent. The pure solvent was added to complete the volume in the flask with the extract and it was drained by the anhydrous sodium sulfate. The absorbance of the solution was measured at 590 nm with a pure solvent (carbon tetrachloride) as a blank solution.

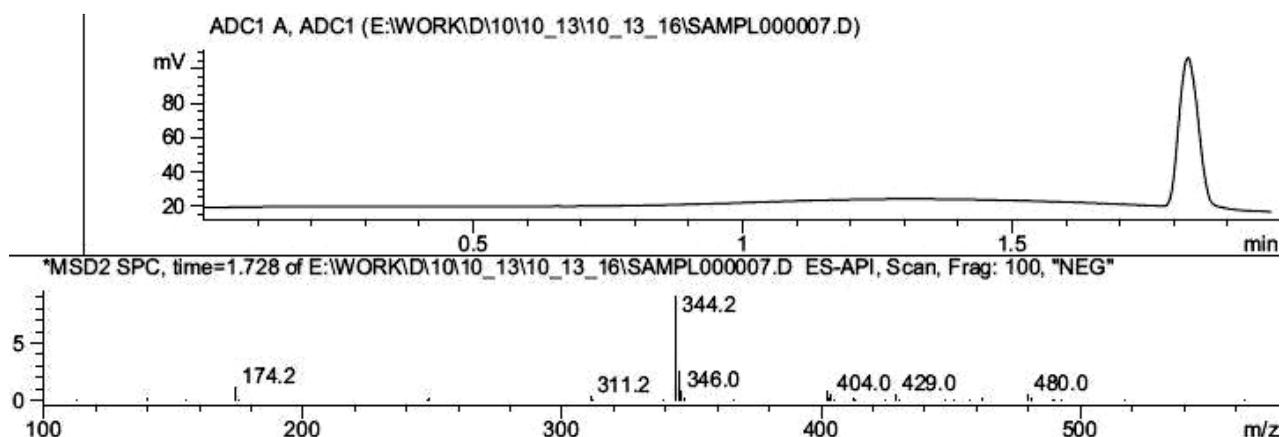


Fig. 1. The chromatogram of 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol with a mass spectrometric detection for the determination of the reagent purity

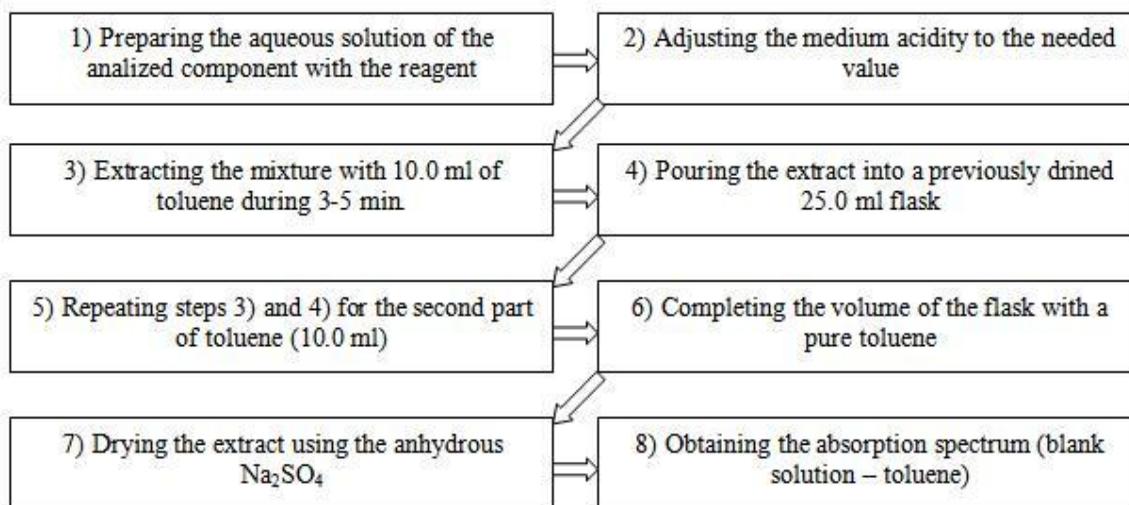


Fig. 2. The algorithm presenting the steps of the procedure used in the study of the interaction between benzylthiazol and Cu(II)

3. Results and Discussion

3.1. Investigation of the Cu(II) Interaction with BnTAN in Aqueous and Organic Solutions

1-(5-Benzylthiazol-2-yl)azonaphthalen-2-ol is a red organic substance. It is soluble in all organic solvents but

badly soluble in water. The molecular absorption spectrum of this compound is characterized by an absorbance maximum at the wavelength of 490 nm in the acidity range of pH = 1–10. For this reagent the Beer's law remains over a wide range of concentrations and the average effective value of molar absorption coefficient at 490 nm is $2.9 \cdot 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

In alkaline media benzylthiazol forms with Cu²⁺ ions a violet chelate complex compound, just like with

Zn^{2+} and Cd^{2+} . Fig. 3 shows the spectrum of this substance with an absorption maximum at $\lambda = 590$ nm and this confirms that the complexation reaction is contrasting enough because the shift of absorption maximum is approximately 100 nm. Furthermore, in organic solvents the absorption band of the complex is less sloping. That is why it is helpful to use the extraction of this compound into organic phase which also allows concentrating it and then determining with higher sensitivity.

All possible organic solvents were checked as potential extractants for the Cu(II)-BnTAN complex removal from the aqueous solution. Fig. 4 illustrates that the highest value of the molar absorption coefficient was obtained in the medium of isoamyl alcohol. But it was decided that toluene should be used in further investigations because of the lowest value of optical density at the absorbance maximum of the free reagent after extraction.

For determination of the copper(II) analysis optimal conditions it is necessary to investigate how the yield of the substance depends on the acidity of the medium. Comparing the extractive abilities of various solvents at different pH values it is obvious that for most of them the complex is better extracted in alkaline solution but diethyl ether and chloroform are unsuitable for its removal from the aqueous alkaline phase (Fig. 5).

Speaking about the effect of pH on the creation of Cu(II)-BnTAN compound in details it is important to mention that in aqueous solution the complex compound can be created at pH = 2.5 and Fig. 6 indicates this fact. But the extraction does not pass completely at this acidity

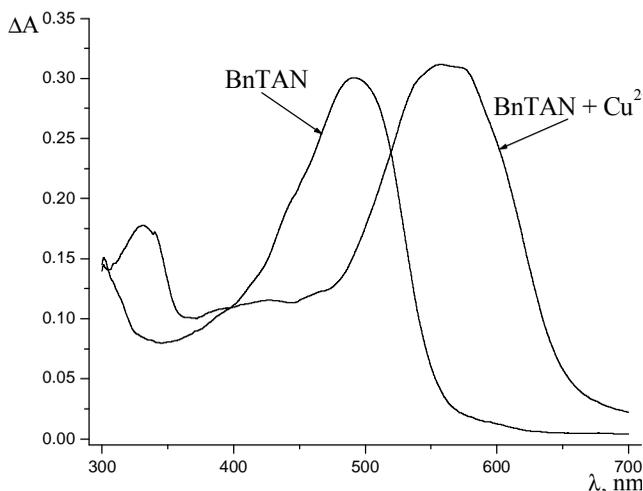


Fig. 3. Molecular absorbance spectra of 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol in toluene solutions in the absence and presence of Cu^{2+} ions; $C(BnTAN) = 2.32 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C(Cu^{2+}) = 1.16 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $C(NaOH) = 0.80 \text{ mol} \cdot \text{l}^{-1}$; $l = 1.0 \text{ cm}$

value and in this case it is better to extract the solutions starting from pH 5. The separation is more effective for alkaline solution with high pH values. That is why further investigations in the Cu(II)-BnTAN system were carried out at acidity limits of pH 5–13.

3.2. Establishing the Composition of the Cu(II)-BnTAN Complex

Classic spectrophotometric methods were used to establish the optimal correlation of reacting components with the highest yield of the complex which corresponds to its composition. The first one is the mole-ratio method (or “saturation method”) and it showed that while increasing the content of copper in the system at the constant concentration of an azodye the maximal optical density value was obtained at the correlation $C(Cu(II)):C(BnTAN) = 1:2$ (Fig. 7). It means that one metal ion interacts with two ligands of the organic reagent.

The alternative method of continuous variations (or Job’s method) confirmed that the molar fraction of the azodye in the complex is $\sim 67\%$ and respectively the molar fraction of copper(II) – 33% (Fig. 8). So copper actually is coordinated by two molecules of BnTAN. In analytical chemistry such correlation often indicates complexes with high stability constants. For similar complexes with a correlation of 1:1 such constants are smaller. The molar absorption coefficient of this structure is higher too because it includes two organic colored particles.

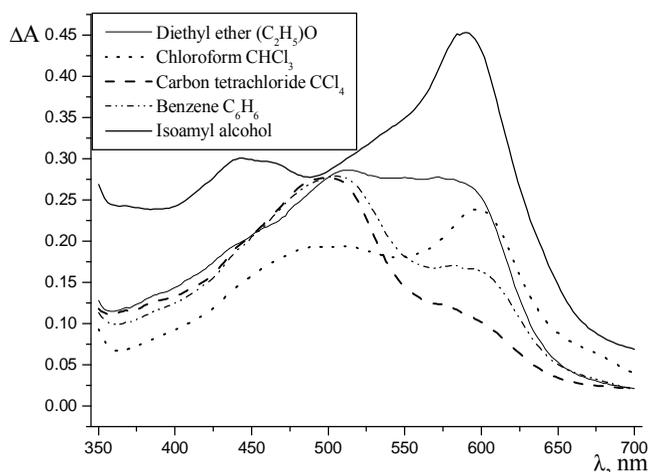


Fig. 4. Molecular absorbance spectra of BnTAN complex with Cu^{2+} ions extract in different solvents; $C(BnTAN) = 2.32 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C(Cu^{2+}) = 5.82 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C(NaOH) = 0.80 \text{ mol} \cdot \text{l}^{-1}$; $l = 1.0 \text{ cm}$

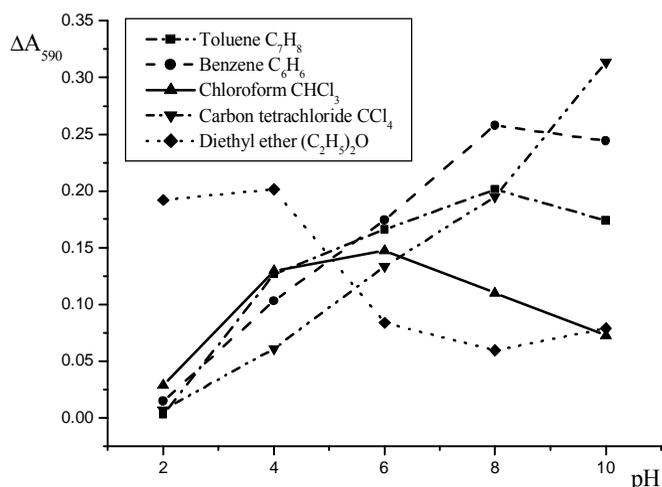


Fig. 5. Effect of the medium acidity on the maximum yield of Cu(II) with BnTAN complex in different solvents;
 $C(\text{BnTAN}) = 2.00 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$;
 $C(\text{Cu}^{2+}) = 1.00 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$;
 $C(\text{UBS}) = 5.0 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$; $l = 1.0 \text{ cm}$

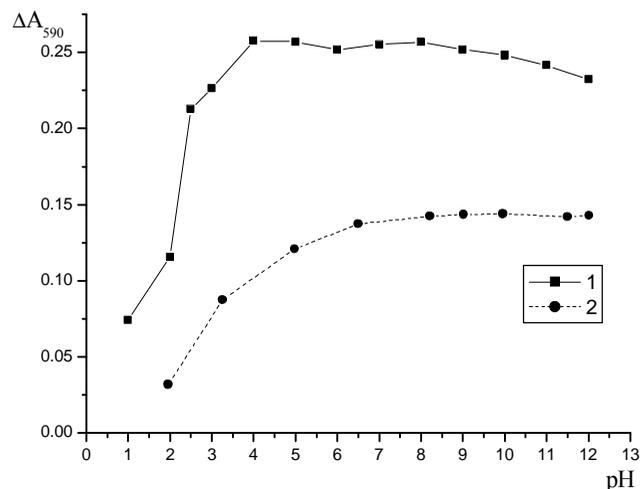


Fig. 6. Effect of the medium acidity on the maximum yield of Cu(II) with BnTAN complex in aqueous (1) and toluene (2) solutions; 1 – $C(\text{BnTAN}) = 2.00 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$;
 $C(\text{Cu}^{2+}) = 1.00 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $C(\text{UBS}) = 5.0 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$;
 $l = 1.0 \text{ cm}$; 2 – $C(\text{BnTAN}) = 1.16 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$;
 $C(\text{Cu}^{2+}) = 5.82 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C(\text{UBS}) = 5.0 \cdot 10^{-3} \text{ mol} \cdot \text{l}^{-1}$;
 $l = 1.0 \text{ cm}$

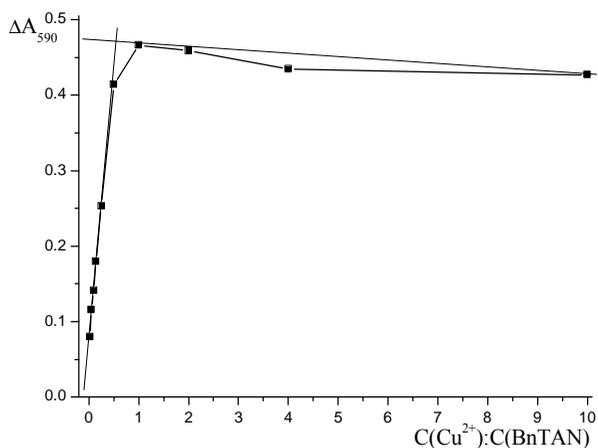


Fig. 7. Determination of the correlation between Cu^{2+} ions and BnTAN in the chelate complex using the mole-ratio method;
 $C(\text{BnTAN}) = 4.64 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$;
 $C(\text{NaOH}) = 0.80 \text{ mol} \cdot \text{l}^{-1}$; $l = 1.0 \text{ cm}$

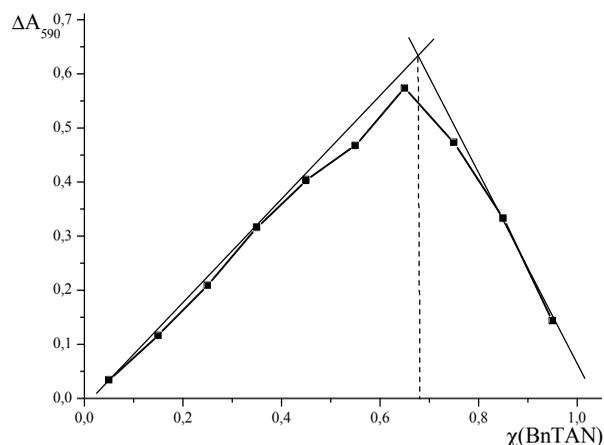
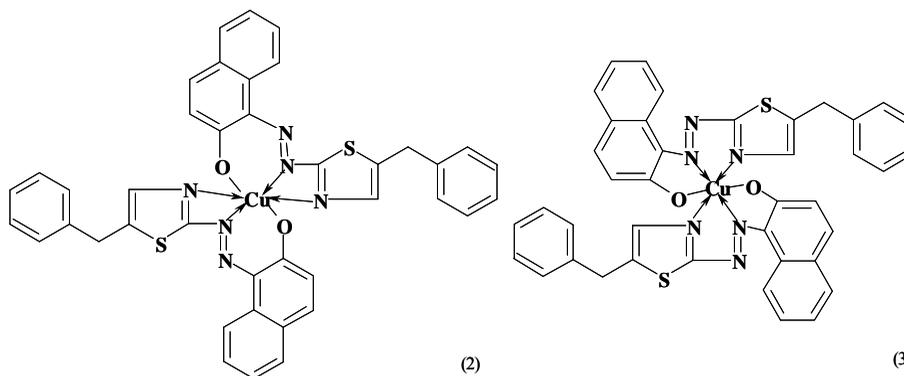


Fig. 8. Determination of the correlation between Cu^{2+} ions and BnTAN in the chelate complex using the method of continuous variations at $\text{pH} = 8$; $v_2 = 1.50 \cdot 10^{-6} \text{ mol}$;
 $C(\text{UBS}) = 1.0 \cdot 10^{-2} \text{ mol} \cdot \text{l}^{-1}$; $l = 1.0 \text{ cm}$

Basing on the isomolar curve the complex stability constant was calculated using a specialized computer program SpectroCalc-Complex (V. 1.08). The value of $\lg \beta = 6.07$ (or $\beta = 1.17 \cdot 10^6$) was obtained with a standard deviation of $s(A) = 3.272 \cdot 10^{-2}$.

Analyzing the gathered data two hypothetical spatial structures of the complex were predicted.

According to them the copper(II) ion is connected with two molecules of benzylthiazol by means of ionic bond with oxygen atom and two dipolar bonds with nitrogen atoms. So metal creates either two six-membered cycles (2) or four five-membered cycles (3) with two ligands and this stabilizes the system.



To find out which mechanism is correct some additional investigations are required using such methods as X-ray diffraction and for this purpose the complex compound should be obtained in a crystalline state.

3.3. Development of the Method of Cu(II) Determination Using BnTAN

The linear plot of the “saturation curve” was used to obtain the calibration graph for the quantitative determination of copper(II) ions in different objects. It is obvious from Fig. 9 that the dependence remains linear within one order of concentrations. Such metrological characteristics as limits of linear dependence, parameters of the calibration curve and the limit of detection are written in Table 1. From them the conclusion can be made that the method of copper(II) determination is rather sensitive. Besides this method is perspective in case of copper selective determination in the presence of other metals because the acidity values range where Cu(II)

creates a complex compound with BnTAN is quite wide. Nevertheless such ions as Zn^{2+} and Cd^{2+} still somehow influence the determination of copper at pH 5 (Fig. 10) though they are not extracted well from the acid or neutral solutions but only from the alkaline ones. On the contrary other ions of transition and noble metals practically do not interfere in the quantitative determination of copper.

Table 1

Metrological characteristics of Cu(II) extraction-photometric determination using BnTAN
 $C(\text{BnTAN}) = 5.20 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$, pH 5, $V_{\text{CCl}_4} = 2 \cdot 10 \text{ ml}$,
 $\mu = 0.4$, $\lambda_{\text{max}} = 590 \text{ nm}$, $l = 1.0 \text{ cm}$

Limits of linear dependence, $\text{mol} \cdot \text{l}^{-1}$	$2.0 \cdot 10^{-6} - 4.0 \cdot 10^{-5}$
Calibration curve equation	$A = 0.021 + 0.070 \cdot 10^3 C_{\text{Cu(II)}}$
Correlation coefficient R	0.9975
Limit of detection C_{min} , $\text{mol} \cdot \text{l}^{-1}$	$1.7 \cdot 10^{-6}$

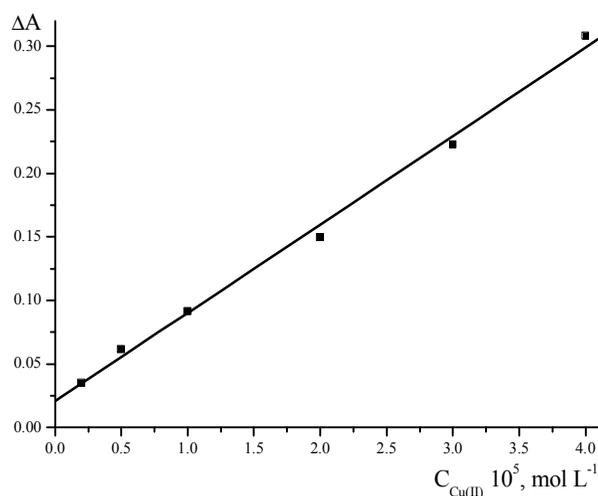


Fig. 9. The calibration curve for Cu(II) extraction-photometric determination using BnTAN; $C(\text{BnTAN}) = 5.20 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; pH 5; $V_{\text{CCl}_4} = 2 \cdot 10.0 \text{ ml}$; $\mu = 0.4$; $\lambda_{\text{max}} = 590 \text{ nm}$; $l = 1.0 \text{ cm}$

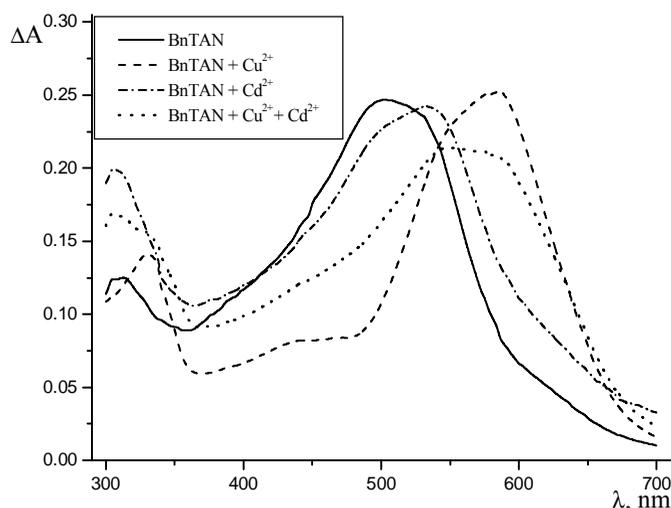


Fig. 10. Molecular absorbance spectra of 1-(5-benzylthiazol-2-yl)azobenzene-2-ol aqueous solutions in the absence and presence of Cu^{2+} and Cd^{2+} ions at pH 5; $C(\text{BnTAN}) = 2.00 \cdot 10^{-5} \text{ mol} \cdot \text{l}^{-1}$; $C(\text{Cu}^{2+}) = 1.00 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $C(\text{Cd}^{2+}) = 1.00 \cdot 10^{-4} \text{ mol} \cdot \text{l}^{-1}$; $l = 1.0 \text{ cm}$

Table 2

Results of Cu(II) ions extraction-photometric determination in model solutions
(C(BnTAN) = 5.20·10⁻⁵ mol·l⁻¹, V_{CCL₄} = 2·10 ml, μ = 0.4, l = 1.0 cm)

Added Cu(II)	Found Cu(II), μg	$\bar{X} \pm S \cdot t_{\alpha} / \sqrt{n}$, μg	S _r , %
39 μg Cu(II)	39.8	38.9 ± 4.5	4.7
	40.1		
	36.8		

The accuracy of the proposed extraction-photometric determination of Co(II) was confirmed on model solutions by the traditional “added – found” method. For this purpose the same amounts of copper(II) ions were poured into three solutions with the same volume and then a complex with 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol was extracted into toluene. The concentration of each extracted solution was found using a calibration curve. Results of the extraction-photometric determination of researched ions in model solutions are represented in Table 2.

The experimental results of the “added – found” method show that the proposed extraction-photometric determination of copper(II) ions as a complex compound with benzylthiazol gives accurate results and this analytical method is characterized by a good reproducibility.

The quantitative amount of copper(II) ions was determined according to the analytical method described in Subsection 2.5.

4. Conclusions

So the spectrophotometric properties of an interesting representative of thiazolylazonaphthol dyes benzylthiazol as a new analytical reagent for the copper(II) content determination were researched for the first time. The optimal conditions for the Cu(II) complexation reaction with BnTAN and the correlation of components in a complex compound were found. A simple, sensitive and quite selective method of extraction-photometric determination of copper using benzylthiazol was developed and it is characterized by a wide range of detected concentrations. This method of Cu(II) determination was successfully confirmed on model solutions which makes it possible to determine copper in natural, industrial and biological objects. That is why the proposed method can be implemented in different research laboratories for serial determinations of copper. Besides studying the coordination of Cu(II) with BnTAN gave interesting results too and because of that further investigations of this topic can be continued.

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СПЕКТРОФОТОМЕТРИЧНІ ДОСЛІДЖЕННЯ ВЗАЄМОДІЇ ЙОНІВ КУПРУМУ(II)

3-1-(5-БЕНЗИЛТІАЗОЛ-2-ІЛ)АЗОНАФТАЛЕН-2-ОЛОМ

Анотація. Спектрофотометричними методами було досліджено утворення хелатного комплексу йонів Cu²⁺ із 1-(5-бензилтіазол-2-іл)азонафтален-2-олом. Знайдено оптимальні умови для реакції комплексоутворення та екстракції в органічну фазу. Розроблено методіку екстракційно-фотометричного визначення мікрокількостей міді.

Ключові слова: спектрофотометрія, екстракція, мідь, тіазоліазонафтолові барвники.

