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IMPROVING THE DETERMINATION OF Cu(II) IONS WITH 1-(5-BENZYLTHIAZOL-2-YL)AZONAPHTHALEN-2-OL USING MICELLAR SOLUTIONS OF TRITON X-100

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In this paper the possibility of Cu(II) ions analysis with 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol in the presence of Triton X-100 as a non-ionic surfactant was checked. The sensitivity of the complexation reaction directly depends on the concentrations of the surfactant. The critical micelle concentrations of aqueous solutions of TX-100 in the presence of KCl were determined by means of maximum bubble pressure method. The influence of media acidity on the absorbance of the azo dye complex with Cu(II) ions in micellar solutions was examined. It was established that the absorption of the solution is higher after the addition of TX-100 and KCl. Optimal conditions (time of reaction, concentration of the surfactant and the electrolyte, pH value) for spectrophotometric determination of Cu(II) with the azo dye in micellar aqueous solutions were found.

Key words: thiazolylazonaphthol dyes, Triton X-100, copper(II), micellar solution, spectrophotometry.

Nowadays attention is paid to the use of non-ionic surfactant micelles for preconcentration and separation in analytical chemistry and separation sciences. Micelles have been accepted as a microscopic medium which provides a new basis for the development of new determination techniques of such analytes as metal ions or organic compounds by means of micelle-mediated extraction [1].

In analytical chemistry the main use of surfactants is in spectrophotometry and fluorimetry, particularly in the development of new methods of metal-ions determination. Usually, metal-chelate complexes formed in the micellar systems are more stable than those formed in the absence of micelles [2]. Micelles are responsible for many of the practical applications of detergents, among which very important is the enhancement of the solubility of organic compounds in water, owing to their incorporation in the micelle, where they experience an altered micro-environment. Furthermore, micelle systems are convenient to use because they are optically transparent, stable and relatively non-toxic [3].

This beneficial effects show the advantage of such surfactant systems in the development of new spectrophotometric methods for determining micro amounts of metal ions [4].

In spectrophotometric methods complexing agents such as thiazolylazo dyes have been successfully employed in metal ions determinations [5]. These compounds have attracted much attention not only by virtue that they are sensitive chromogenic reagents for spectrophotometric, liquid chromatography and extraction-photometric (including solid phase, liquid-liquid and cloud point extraction) determinations of many metal ions, but also because of their fastness of colour formation and low price [6]. The significant drawback for most of these compounds and their complexes is that they are only partly soluble or insoluble in water depending on the pH. However, surfactants have been conveniently used to enable the measurement in an aqueous medium [7]. The compounds that are widely used include 1-(2'-thiazolylazo)-2-naphthol (TAN) due to its ability to form azo-metal chelates with various cations. A number of applications have been proposed regarding the determination of transition metals such as copper, silver, chromium, nickel, zinc etc. using TAN [8–12].

Table 1

Methods of transition metal ions determination with thiazolylazo dyes in the presence of non-ionic surfactants

Metallic species	Chelating agent	Surfactant	Limit of detection, $\mu g\ L^{-1}$	Sample
Cr	TAN	Triton X-114	7.5 Cr(III), 3.5 Cr(VI)	Lake sediments
Mn	TAN	Triton X-114	0.28	Tap, river, sea and reservoir water
Co, Ni	TAN	Triton X-114	0.24 Co, 0.44 Ni	Tap, river and sea water
Zn, Fe	TAN	Triton X-114	1.51 Zn, 6.45 Fe	Human serum and urine
Ni	TAN	Triton X-114	5	Peach and apple leaves
Ag	TAN	OP-7	-	Mineral water
Pb, Cd	TAN	Triton X-114	4.5 Pb, 0.75 Cd	Supply, mineral, lake and river water
Hg	TAR	Triton X-114	14.5	River, lake and tap water, dental waste water, chrome plating industry effluent, textile industry effluent
Pd	4-(2-benzothiazolylazo)	CTAB	0.6	Water, synthetic alloys, Pd-charcoal, platting effluents, catalyst and soil
Pb, Cd	7-(6-methoxy-2-benzothiazolylazo)-8-hydroxyquinoline	Triton X-114	3.9 Pb, 0.19 Cd	Honey samples
V	TAC	Triton X-100	0.05	Red and white wine, tea and tomato
Rh, Pd, Pt	MBT	Triton X-100	0.001 Rh, 0.005 Pd, 0.006 Pt	Tablets
Cu	Sulfathiazolylazo resorsin	Triton X-100	0.64	Stream, waste, rain and tap water

Approximately 9% of all analytical techniques combined with micelle-mediated extraction are used in UV/Vis spectrophotometry. And about 9 % of them involve Triton X-100 as a non-ionic surfactant and 71 % use its analogue – Triton X-114. In Table 1 we report some methods proposed for metal preconcentration and determination using thiazolylazo dyes as complexing reagents in the presence of some surfactants such as Triton X-100 [13, 14].

In this work we will try to improve a previously developed method of toxic transition metal ions determination with a new thiazolylazonaphthol dye similar to TAN using micellar solutions of a non-ionic surfactant Triton X-100.

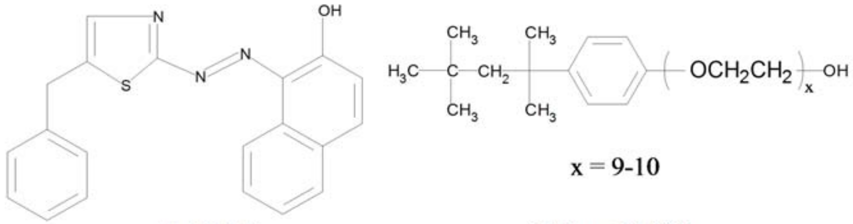
Experimental

A Jasco model V-670 UV-VIS spectrophotometer was used for spectral measurements in quartz cuvettes with the thickness of the absorbing layer of 1.0 cm. Acidity of the solution was controlled with a pH-meter model CPC-501 with a glass indicative electrode (hydromet ERH-13) using diluted solutions of NaOH and HCl. The solutions were heated in a Zalmed model SML-48/250 dryer. Double distilled water was used throughout the experiment.

A stock solution of copper(II) ($1.00 \cdot 10^{-3}$ mol L^{-1}) was prepared by dissolving $Cu(NO_3)_2{\cdot}3H_2O$ in water after adding a small amount of HNO_3 solution to prevent hydrolysis. Working solution of Cu^{2+} was prepared by diluting the stock solution. A $1.00 \cdot 10^{-3}$ mol L^{-1} alcoholic solution of 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (BnTAN) was prepared by the dissolution of an exact amount of the previously purified sample in pure ethanol. BnTAN was purified by double recrystallization from acetone and ethanol followed by filtration and vacuum distillation. Toluene and buffer solution with pH 7.00 (Na_2HPO_4/KH_2PO_4) were used during the preparation of solutions. All the chemicals used were of Analytical Reagent grade or the best quality available and they were supplied by Chempur® (Poland), CertiPUR® (Germany) and Scintran® (England).

Results and Discussions

A new analytical reagent 1-(5-benzylthiazol-2-yl)azonaphthalen-2-ol (BnTAN, Fig. 1) representing thiazolylazonaphthol dyes was investigated at first. This substance is a red powder barely soluble in water but soluble in ethanol, toluene, chloroform, DMF and other organic solvents. Previously it was recommended for the extraction-photometric determination of some transition metals such as zinc, cadmium, copper and other [15]. We wondered if it could be possible to determine ions of these metals directly in the water solution by modifying the organic reagent using a non-ionic surfactant, for example Triton X-100 (TX-100) which is widely used nowadays in various applications.



BnTAN **Triton X-100**

Fig. 1. Structural formulas of the reagent BnTAN and the surfactant Triton X-100.

So the solution of a surfactant was poured to the BnTAN aqueous solution with Cu^{2+} ions. According to Fig. 2, absorption spectra of the azo dye itself (λ_{max} = 490 nm) and its complex with Cu(II) (λ_{max} = 590 nm) have completely different absorption maxima. But the addition of TX-100 to the solution of a complex makes the absorption band almost twice bigger (from $\Delta A_{590} \sim 0.16$ to $\Delta A_{590} \sim 0.27$) and its shape becomes more sharp. In this case such phenomenon deserved detailed further investigations.

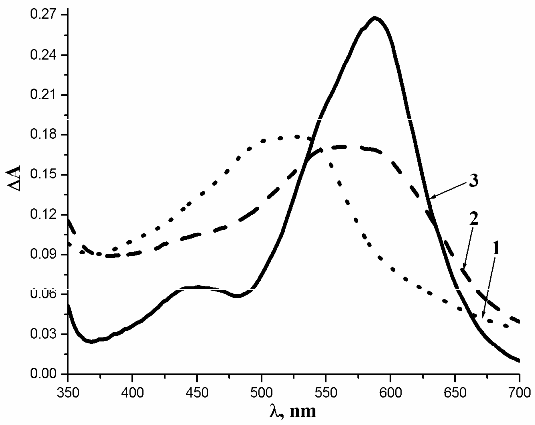


Fig. 2. Absorption spectra of BnTAN aqueous solutions in the absence (1) and presence of Cu^{2+} ions before (2) and after adding the solution of TX-100 (3);
[BnTAN] = $1.5 \cdot 10^{-5}$ M, [Cu^{2+}] = $7.5 \cdot 10^{-5}$ M, [TX-100] = $1.83 \cdot 10^{-3}$ M, V(buf.) = 0.1 ml, pH = 5.0, T = 22 ± 1 °C, l = 1.0 cm, blank: H_2O.

In analytical techniques we need to know how much surfactant is required for increasing the spectral properties of the analyzed complex. According to the reviewed literature data authors usually take an aliquot of a 10% solution of TX-100 and add it to the reagent and the analyte. Of course, for the analysis of a great amount of samples this will require a lot of surfactant. Solutions of BnTAN complex with Cu(II) with various concentration of TX-100 were prepared to determine the sufficient amount of a surfactant. Experiments show that increasing the concentration of TX-100 to a value of approximately $1.0 \cdot 10^{-3}$ M provides a rapid change in the absorptive properties of BnTAN-Cu(II) solution (Fig. 3) and even more concentrated solutions improve the sensitivity of the complexation reaction too but not so drastically. Such bend on the dependence curve of the solution absorbance on the TX-100 amount can be explained by reaching the critical micelle concentration (cmc) of the surfactant in water solution.

That's why we needed to determine the critical micelle concentration of TX-100 aqueous solution. Besides it is well known that the ionic strength of the solution has a direct influence on the micellar properties of the surfactant. So such main physico-chemical parameters as cmc, surface tension, surface excess concentration and molecular area were determined for Triton X-100 aqueous solutions in the presence of electrolyte KCl using maximum bubble pressure method (Table 2).

According to the official information of the TX-100 producer the critical micelle concentration of a clear TX-100 solution is equal to 0.22–0.24 mM. Our results have shown that a TX-100 solution without KCl had a cmc value of 0.507 mM. So in all further experiments a constant excess concentration of TX-100 will be supplied to reach this cmc in the solution.

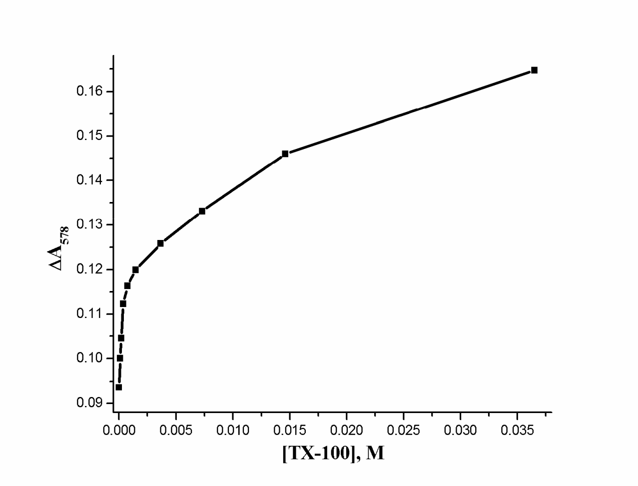


Fig. 3. Dependence of the absorbance of BnTAN aqueous solutions with Cu^{2+} ions on the concentration of added TX-100; [BnTAN] = $1.0 \cdot 10^{-5}$ M, [Cu^{2+}] = $2.0 \cdot 10^{-5}$ M, V(buf.) = 0.25 ml, pH = 7.0 ± 0.1, T = 22 ± 1 °C, l = 1.0 cm, blank: H_2O.

Table 2

Physico-chemical parameters of Triton X-100 aqueous solutions in the presence of electrolyte KCl

Electrolyte concentration [KCl], M	Critical micelle concentration $cmc \cdot 10^4$, M	Surface tension σ_{cmc}, $mN \cdot m^{-1}$	Surface excess concentration $\Gamma^{\sigma} \cdot 10^6$, $mol \cdot m^{-2}$	Area per molecule $S \cdot 10^{18}$, m^2
0	5.07	34.66	5.19	0.32
0.001	8.48	34.25	4.65	0.36
0.01	7.48	31.14	4.80	0.35
0.1	7.21	33.10	0.33	0.33

Another important task was to check the influence of media acidity on the absorbance of the azo dye complex with Cu^{2+} ions. It was studied over the pH range of 1.0–13.0. The respective spectra of solutions show that the change of pH from 1 to 5 follows decreasing of the absorbance band at $\lambda_{max.1} = 490$ nm and on the other hand increasing of the absorbance band at $\lambda_{max.2} = 596$ nm. So the colour of solutions changed from red to blue. At higher acidity values the complex decomposes because the absorbance maximum decreases and it is slowly shifted to the area of shorter wavelengths (Fig. 4).

Previously Cu(II) could not be determined in aqueous solutions because of bad solubility of its complex with BnTAN in water and the dependence of this complex formation on pH was less informative (Fig. 5). The addition of TX-100 forced the complex to dissolve in surfactant micelles. And in this case Cu(II) can be easily determined in water now by adding the appropriate amount of TX-100. Furthermore, it was noticed that the presence of the other strong electrolyte (KCl, for example) has improved spectral characteristics even more.

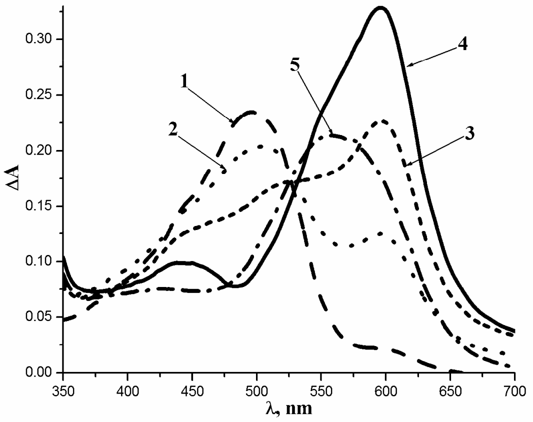


Fig. 4. Absorption spectra of BnTAN aqueous solutions in the presence of Cu^{2+} ions at various pH after the addition of TX-100 solution;
[BnTAN] = $1.5 \cdot 10^{-5}$ M, [Cu^{2+}] = $7.5 \cdot 10^{-5}$ M,[TX-100] = $1.83 \cdot 10^{-3}$ M, [KCl] = 1.0 M, V(buf.) = 0.1 ml, pH = 1.0 (1), 2.0 (2), 2.5 (3), 5.0 (4), 10.0 (5), $T = 22 \pm 1$ °C, $l = 1.0$ cm, blank: H_2O.

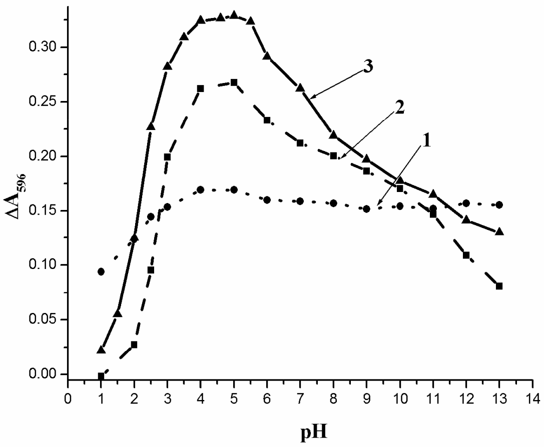


Fig. 5. Dependence of the absorbance of BnTAN aqueous solutions with Cu^{2+} ions on the media pH before (1) and after adding the solution of TX-100 (2) and KCl (3);
[BnTAN] = $1.5 \cdot 10^{-5}$ M, [Cu^{2+}] = $7.5 \cdot 10^{-5}$ M, [TX-100] = $1.83 \cdot 10^{-3}$ M, [KCl] = 1.0 M, V(buf.) = 0.1 ml, $T = 22 \pm 1$ °C, $l = 1.0$ cm, blank: H_2O.

Then the influence of the amount of added electrolyte on the absorbance of the complex had to be examined. It was found that high concentrations of potassium chloride usually contribute the determination of Cu(II) with BnTAN. Probably, it is connected with the influence of an electrolyte on the micellar properties of the surfactant. The minimal required concentration of KCl for the determination of Cu(II) is 1.0 M (Fig. 6).

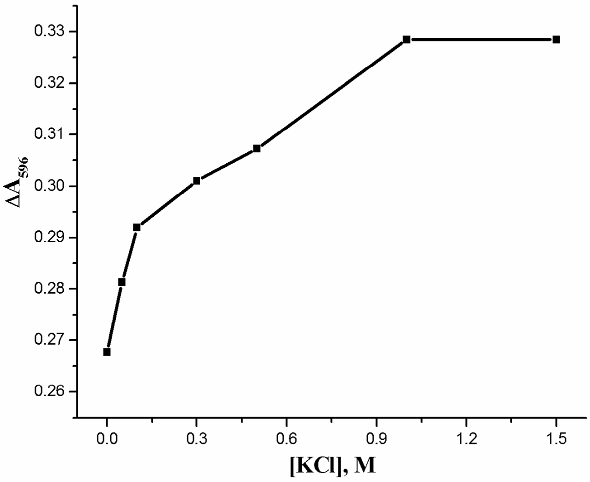


Fig. 6. Dependence of the absorbance of BnTAN aqueous solutions with Cu^{2+} on the ionic strength of the solution expressed as the concentration of potassium chloride; [BnTAN] = $1.5\cdot10^{-5}$ M, [Cu^{2+}] = $7.5\cdot10^{-5}$ M, [TX-100] = $1.83\cdot10^{-3}$ M, V(buf.) = 0.25 ml, pH = 5.0, $T = 22 \pm 1$ °C, $l = 1.0$ cm, blank: H_2O.

Also we analyzed thermal properties of obtained solutions with different concentrations of KCl for future perspective application in the cloud point extraction. By heating the micellar solutions the cloud point temperature (the Krafft point) was detected when solutions became cloudy. When the concentration of KCl was big (1.0 M) cloud point has been reached faster (at 49 °C). Other solutions ([KCl] $\leq$ 0.5 M) changed their optical properties at higher temperatures ($t \geq 54$ °C). Such results correspond well with the literature data. So the possibility of a preconcentration of Cu(II) with BnTAN at the cloud point using TX-100 and KCl as an electrolyte should be investigated next.

Nevertheless, the application of a strong electrolyte in micellar systems of Cu(II) chelate complex with the azo dye has one considerable drawback. It was noticed that solutions of Cu(II) complex with BnTAN containing KCl in the pH range from 2 to 7 become completely colorless one day after their preparation.

The stability of the complex was checked during first 5 hours after its preparation in the absence and presence of TX-100 and KCl (Fig. 7). It is obvious that the addition of an electrolyte causes the reduction of the solution absorbance (from $\Delta A_{596} \sim 0.32$ at the beginning to $\Delta A_{596} \sim 0.07$ after 5 hours). However, during first 5 minutes complex stays relatively stable (less than 0.5 % decrease of absorbance at $\lambda_{max} = 596$ nm) and can be examined in quantitative analysis.

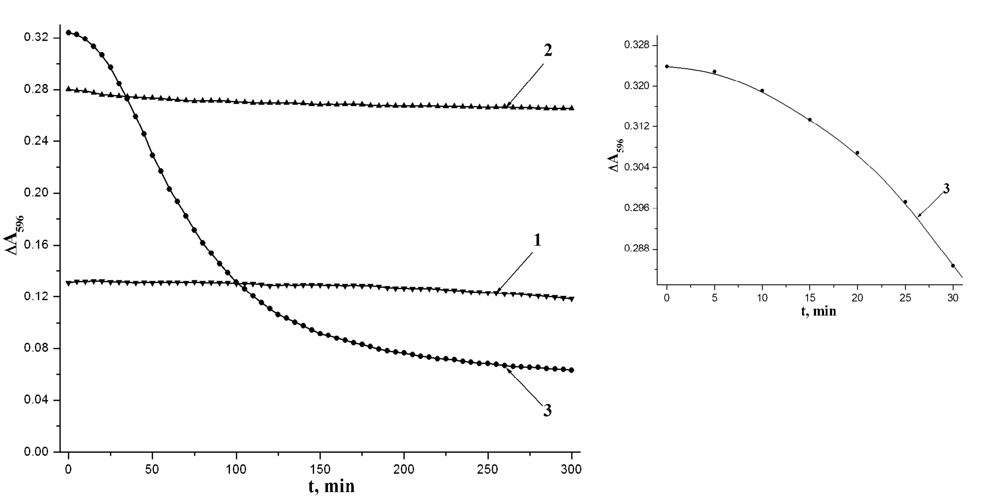


Fig. 7. Dependence of the absorbance of BnTAN aqueous solutions with Cu^{2+} before adding (1) and after adding TX-100 (2) and KCl (3) on the time after preparing the solution; [BnTAN] = $1.5 \cdot 10^{-5}$ M, [Cu^{2+}] = $7.5 \cdot 10^{-5}$ M, [TX-100] = $1.83 \cdot 10^{-3}$ M, [KCl] = 1.0 M, V(buf.) = 0.1 ml, $T = 22 \pm 1$ °C, $l = 1.0$ cm, blank: H_2O.

In this case we are to make a choice. If we want to obtain greater sensitivity of the complexation reaction the strong electrolyte should be used. But when the complex has to be analyzed in a long period of time the solution of potassium chloride must be forbidden.

Conclusions

In such way it was improved that surfactants are very useful in analytical reactions. The sensitivity of Cu(II) determination with BnTAN increases in almost 100 percent in the presence of Triton X-100. Because of good solubility of the complex in a micellar system the analysis can be carried out in aqueous solutions without toxic organic solvents. Such perspectives as the application of other surfactants (non-ionic or ionic) and cloud point extraction are of great significance.

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УДОСКОНАЛЕННЯ МЕТОДИКИ ВИЗНАЧЕННЯ ІОНІВ Cu(II) ІЗ 1-(5-БЕНЗИЛТІАЗОЛ-2-ІЛ)АЗОНАФТАЛЕН-2-ОЛОМ З ВИКОРИСТАННЯМ МІЦЕЛЯРНИХ РОЗЧИНІВ ТРИТОНУ Х-100

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Перевірено можливість аналізу іонів Cu(II) із 1-(5-бензилтіазол-2-іл)азонафтален-2-олом за наявності Тритону Х-100 як неіоногенної ПАР. Чутливість реакції комплексоутворення прямо залежить від концентрації ПАР. Визначено критичні концентрації міцелоутворення водних розчинів Тритону Х-100 за наявності KCl методом максимального тиску в бульбашці. Перевірено вплив кислотності середовища на оптичну густину комплексу азобарвника з іонами Cu(II) у міцелярних розчинах. З'ясовано, що поглинання розчину є вищим після додавання TX-100 і KCl. Знайдено оптимальні умови (час реакції, концентрація ПАР і електроліту, значення pH) для спектрофотометричного визначення Cu(II) з азобарвником у міцелярних водних розчинах.

Ключові слова: тіазолілазонафтолові барвники, Тритон Х-100, купрум(II), міцелярний розчин, спектрофотометрія.

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